Graduate courses in Physics

Quantum Mechanics

applied to Atoms and Light

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Preface

This script represents a synthesis of several postgraduate courses given at the Institute of Physics of São Carlos (IFSC) of the University of São Paulo (USP). The courses are Quantum Mechanics (SFI5774), Atomic and Molecular Physics (SFI5814), Quantum Mechanics B (SFI5707), Interaction of Light and Matter (SFI5905), and Atomic Optics (SFI5887). The topics of the courses are, of course, closely intertwined. The purpose of this composite script is to emphasize the interconnection of topics and facilitate the understanding of how they are related. In part I we introduce the quantum mechanics, which represents the fundamental theory for the rest of the book. In the second part we focus on the structure of the atom. In the third and fourth part we study the properties of light, its interaction with individual atoms and atomic ensembles and how the interaction is influenced by cavities and surfaces. Finally, in part V we introduce the optics of matter wave.

The course is intended for masters and PhD students in physics. The script is a preliminary version continually being subject to corrections and modifications. Error notifications and suggestions for improvement are always welcome. The script incorporates exercises the solutions of which can be obtained from the author.

Information and announcements regarding the course will be published on the website:
http://www.ifsc.usp.br/strontium/ – > Teaching – > Semester

The student’s assessment will be based on written tests and a seminar on a special topic chosen by the student. In the seminar the student will present the chosen topic in 15 minutes. He will also deliver a 4-page scientific paper in digital form. Possible topics are:
- Observation of super- and subradiant spontaneous emission of two ions (Sec. ??),
- Squeezed states (Sec. 15.6),
- The Jaynes-Cummings model (Sec. 15.2),
- Quantum projection noise (Sec. 17.5.1),
- Quantum gates (Sec. 18.3),
- The method of quantum Monte-Carlo wavefunction simulation (Sec. 17.1.2),
- The quantum Zeno effect (Sec. 17.3.1),
- Bloch equations: derivation and interpretation (Sec. 14.2),
- The quantum jumps, its history and observation (Sec. 17.1.2),
- Schrödinger’s cat (Sec. 17.1.1),
- The Einstein-Podolski-Rosen hypothesis and its experimental falsification (Sec. 18.1.1),
- Elitzur and Vaidman bomb testing problem (Sec. 17.4.1),
- Topological phases and the Aharonov-Bohm effect (Sec. 17.6.1),
- Quantum non-demolition measurements (Sec. 17.6.2),
- Calculation of photoelectric effect from Fermi’s golden rule (Sec. 28.5.2.1),
- Quantum correlations and the experiments of Young and Hanbury-Brown-Twiss (Sec. 28.5.2.1),
- The Hartree-Fock method (Sec. 10.3.3),
- Temporal evolution of a free particle described by a Gaussian wave packet (Sec. 28.5.2.1),
- The WKB approximation (Sec. 5.3),
- Rydberg atoms (Sec. 8.4.4),
- The helium atom (Sec. 10.2),
- The quadratic and the dynamic Stark effect (Sec. 9.3),
- The blackbody radiation-induced Stark effect (Sec. 28.5.2.1),
- The method of combining atomic orbitals (LCAO) (Sec. 11.1.4),
- Ultracold molecules (Sec. ??),
- Efimov states (Sec. 28.5.2.1),
- Bose-Einstein condensation (Sec. 26.8.4).

The following literature is recommended for preparation and further reading:

Ph.W. Courteille, script on Optical spectroscopy: A practical course (2020)

Ph.W. Courteille, script on Electrodynamics: Electricity, magnetism, and radiation (2020)

Ph.W. Courteille, script on Quantum mechanics applied to atomic and molecular physics (2020)

W.R. Theis, Grundzüge der Quantentheorie, Teubner (1985)


Ch.C. Gerry and P.L. Knight, Introductory Quantum Optics, Cambridge University Press (2005)


C. Cohen-Tannoudji, B. Diu, F. Laloe, Quantum mechanics, vol. 1, Wiley Inter-science

D.J. Griffiths, Introduction to Quantum mechanics, Pearson Education Limited (2014)

L.I. Schiff, Quantum mechanics, McGraw-Hill Book Company (1968)


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Part I

Quantum Mechanics
Chapter 1

Antecedents of quantum mechanics

1.1 The discovery of the atom

The fundamental idea of quantum mechanics is the assumption of the existence of entities that, reaching a limit, can no longer be subdivided. Examples are the mass of a body, the speed of an electron orbiting an atom, or the intensity of a beam of light. This idea was first uttered by Leucippus 500 years a.c. and his student Democritus, who imagined matter being made of smallest particles which they called atoms. These atoms move freely, collide, combine, and separate: 'There is nothing more than atoms and free space.' The microscopic atoms would have the same characteristics as the macroscopic objects they form when they combine, for example, color and shape. The idea of the atom resurfaced and was refined in the course of the 18th century (see Tab. 1.1 below). Today, we know that the basic idea was good, but the reality is a little more complicated.

Table 1.1: Historical sketch of the quantization of matter

<table>
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<tr>
<th>Year</th>
<th>Inventor(s)</th>
<th>Event</th>
</tr>
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<td>500 a.c.</td>
<td>Democritus</td>
<td>invention of the atom</td>
</tr>
<tr>
<td>1800</td>
<td>Avogadro, Dalton</td>
<td>reinvention of the atom</td>
</tr>
<tr>
<td>1897</td>
<td>Thomson</td>
<td>charge transport, model of raisins in a cake</td>
</tr>
<tr>
<td>1909</td>
<td>Rutherford, Geiger, Marsden</td>
<td>α-scattering, charge localized in nuclei</td>
</tr>
<tr>
<td>1911</td>
<td>Rutherford</td>
<td>planetary model</td>
</tr>
<tr>
<td>1900</td>
<td>Bohr</td>
<td>quantized orbitals</td>
</tr>
<tr>
<td>1923</td>
<td>de Broglie</td>
<td>matter has characteristics of waves</td>
</tr>
<tr>
<td>1927</td>
<td>Davison, Germer, Stern</td>
<td>electron and atoms diffraction</td>
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</tbody>
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At the end of the 19th century, the physical world seemed simple: matter and light was all that existed. Matter was made up of atoms and light was a wave. Therefore, to describe a real system, it was enough to calculate the trajectories of its elementary particles, the propagation of light and the way they interact. We now know that life is not as simple, and that atoms are also waves and light also behaves like particles.

Frictions between the old notions and new observations appeared in the late 19th century, such as the ultraviolet divergence of black-body radiation. The pioneer of the new ideas was Max Planck who, in 1905, with a little help from Einstein quantized
CHAPTER 1. ANTECEDENTS OF QUANTUM MECHANICS

Figure 1.1: Particle-wave duality.

The electromagnetic field, and therefore the light, into small harmonic oscillators. This was the starting point for the development of a new theory called quantum mechanics. Soon, this theory was applied to explain the photoelectric effect. The second important step was initialized by Niels Bohr, who quantized the hydrogen atom in 1913 into discrete excitation levels.

Table 1.2: Historical sketch of the quantization of light

<table>
<thead>
<tr>
<th>Year</th>
<th>Inventor</th>
<th>Description</th>
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</thead>
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<td>1801</td>
<td>Young</td>
<td>light is diffracted like a wave</td>
</tr>
<tr>
<td>1860</td>
<td>Maxwell</td>
<td>unified theory of electrodynamics including light</td>
</tr>
<tr>
<td>1888</td>
<td>Hertz</td>
<td>detection of radio waves</td>
</tr>
<tr>
<td>∼ 1890</td>
<td>Planck</td>
<td>accurate measurements of the black-body radiation spectrum</td>
</tr>
<tr>
<td>1900</td>
<td>Planck</td>
<td>quantum hypothesis: $E = h\nu$</td>
</tr>
<tr>
<td>1905</td>
<td>Einstein</td>
<td>photoelectric effect, light behaves like a particle</td>
</tr>
</tbody>
</table>

1.1.1 Democrit’s model

'The principles of reality are atoms and emptiness while other things are mere opinions.' This is a quotation from the Greek philosopher Democritus 400 years before Christ and before Socrates. Together with his teacher Leucippus, he formed the first idea of indivisible particles: atoms.

Democritus’ work only survived as second-hand accounts, the major part of it having been written down by Aristotle, who also, defending the idea of the continuum, was the greatest critic of Democritus’ theory. Aristotle said that the reasoning that guided Democritus to affirm the existence of atoms was as follows. For a body to change its shape, it is necessary that its parts can move. This presupposes an emptiness (or vacuum) in which the matter moves. But if matter were divided infinitely into ever smaller parts, it would loose its consistency. Nothing could be formed because nothing could arise from the ever more infinitely deep dilution of matter into emptiness. Hence, he concluded that the division of matter can not be infinite, that is, there is an indivisible limit: the atom. 'There is only atoms and emptiness', he said.
Observing dust particles in a whirling motion within a ray of sunlight, Democritus was led to the idea that atoms would behave in the same way, randomly colliding, some crowding, others dispersing, others never yet joining with another atom.

The consistency of clusters of atoms, which makes something look solid, liquid, gaseous, or animated (which is the state of the soul) would then be determined by the shape of the atoms involved and their spatial arrangement. In this sense, water atoms are smooth and slippery; the atoms of steel have shapes with sharp edges that hold them solidly together; the atoms of salt, as their taste shows, are harsh and pointed; the atoms of air are small and little connected, penetrating all other materials; and the atoms of soul and fire are spherical and very delicate.

We know nowadays that Democritus’ first theory of the structure of matter was very close to the truth: There really are indivisible particles called atoms composed of a nucleus and an electronic shell, and the space between the atomic nuclei is, in fact, quite empty.

The atomic hypothesis came to be reborn in the modern age with the scientists Boyle, Clausius, Maxwell, and Boltzmann due to their successful explanations of the properties of gases based on the so-called kinetic theory, where they assumed a gas being constituted of identical molecules that collided elastically with each other and with the walls of the recipient containing them. The discovery of the atom through the laws of proportions in chemistry and the establishment of Avogadro’s number considerably strengthened the atomic hypothesis. The hypothesis was definitely consecrated with the various experiments that established the charge of the electron and
the mass ratio between electrons and protons.

By the beginning of the 19th century the atomic nature of matter had definitely been established, and the basic composition of the atoms was already relatively well known. It was known, through experiments, that electrons could be removed from neutral atoms thus creating positively charged ions and that only a certain number of electrons could be removed from each atom. This number proved to be dependent on the atomic species and was called the atomic number $Z$. This information was fundamental for establishing the basic composition of atoms. The question that arose at this point concerned the dimensions and configurations of the atomic system. How would loads and masses be distributed in this entity?

1.1.2 Thomson’s model and Rutherford’s experiment

The internal structure of a body can be studied by throwing beams of small particles against it. The detection of the angular distribution of the scattered particles gives access to the structure factor of the body. In crystallography we throw X-rays into super-complicated molecules to learn the architecture e.g. of proteins. And in medicine, X-rays reveal the internal structure of the human body. Obviously, the scattering technique is an extremely powerful tool, used in many areas of modern physics.

In a series of experiments done before 1911, Ernest Rutherford analyzed the internal structure of gold atoms using $\alpha$-particles, i.e., He$^{2+}$ atoms. The experiments carried out by Geiger, Marsden, and Rutherford consisted of observing the deflection of particles from a collimated beam when scattered by a thin metallic sheet (gold of thickness $\sim 1 \mu m$) carefully obtained by electroplating [see Fig. 1.4(c,d)].

![Figure 1.4: Comparison of Rutherford scattering by free electrons and electrons strongly bound to small nuclei. (a) Thomson’s ‘raisin-in-a-pudding’ type atom; (b) Rutherford’s ‘planetary’ atom. (c) Rutherford scattering by a raisin pudding atom and (d) by a planetary atom.](image)

The atomic model proposed by Joseph John Thomson suggests a structure re-
sembling a *pudding with raisins*: the electrons would be homogeneously distributed within an extended nucleus (size 0.1 nm) of positive charge thus compensating for the negative charge of the electrons. The α-particles would penetrate the gold nucleus, perceived as almost homogeneous, but would suffer multiple deflections due to collisions with the disordered electrons within the nucleus. Since electrons are very light, the angle of deflection \( \theta \) would be small, even after many collisions. For this model we expect a Gaussian dependence of the particles' deflection angle given by the *scattering cross section* [see Fig. 1.4(a-b)],

\[
\frac{d\sigma}{d\Omega} \propto e^{-\theta^2/\theta_0^2},
\]

where \( \theta_0 \) is a small angle.

However, the measurements performed on this *Rutherford scattering* showed different results:

- For a fixed scattering angle, the amount of particles scattered into a solid angle element \( d\Omega \) is proportional to the thickness of the metal foil.

- For a given fixed angle and a given metal sheet the amount of scattered particles in \( d\Omega \) varies inversely with \( E_{\text{kin}}^2 \), where \( E_{\text{kin}} \) is the kinetic energy of the α-particles.

- For a given energy and a given metal sheet, the number of particles scattered into \( d\Omega \) is proportional to \( (\sin \frac{\theta}{2})^{-4} \).

- For a given energy and sheet thickness, the number of particles scattered into \( d\Omega \) in a given direction is proportional to \( Z_{tg}^2 \), where \( Z_{tg} \) is the atomic number of the element that constitutes the sheet.

The extremely rare deflection of α-particles and their angular distribution can be understood by the assumption that the positive charge is concentrated in a very small volume (\( \sim 1 \) fm, that is 10000 times less than the size of the atom itself). This volume is called the atomic nucleus, hence the denomination of *nuclear model*. Since most of the particles pass through the gold sheet without hindrance, there must be a large gap between the nuclei. The electrons, which move within a large (in comparison with the diameter of the nucleus) empty space (the vacuum) around the nucleus, shield the positive nuclear charge, so that the atom appears outwardly neutral.

![Figure 1.5](image_url)

**Figure 1.5:** (a) Trajectory of an α-particle. (b) Illustration of the scattering cross section.
We now derive Rutherford’s scattering formula from the hypothesis of a point-like nucleus. Due to the repulsive action of the Coulomb force,

\[ F = \frac{Z_\alpha Z_{tg} e^2}{4\pi \varepsilon_0 r^2}, \]

we have for the trajectory of the \(\alpha\)-particle \((Z_\alpha = 2)\) a hyperbola [see Fig. 1.5(a)]. The large half-axis of the hyperbola can be determined from the following ansatz,

\[ E_{\text{kin}} = \frac{Z_\alpha Z_{tg} e^2}{4\pi \varepsilon_0} \frac{1}{2a}, \]

where \(2a\) is the minimum distance of the particle \(\alpha\), when it collides with the nucleus in a central collision \(^1\). The distance \(a\) depends on the kinetic energy and can also be used for non-central collisions. The collision parameter \(b\) is the minimum distance of the \(\alpha\)-particle to the nucleus, if it continued to fly in a straight line. In fact the \(\alpha\)-particle will be deflected by an angle \(\theta\). From the geometry of the hyperbola, as \(2\phi + \theta = 180^\circ\), we obtain the following equation:

\[ \tan \phi = \frac{b}{a} = \tan \left(90^\circ - \frac{\theta}{2}\right) = \cot \frac{\theta}{2}, \]

and therefore

\[ \cot \frac{\theta}{2} = \frac{b}{a} = \frac{8\pi \varepsilon_0 E_{\text{kin}}}{Z_\alpha Z_{tg} e^2 b}, \]

replacing \(a\) with the formula (1.3). Taking the derivative of this latter formula, we obtain a relation between the width \(db\) of the hollow cone and the pertinent width \(d\theta\) of the deflection angle \(\theta\),

\[ -\frac{1}{2\sin^2 \frac{\theta}{2}} d\theta = \frac{8\pi \varepsilon_0 E_{\text{kin}}}{Z_\alpha Z_{tg} e^2} db. \]

Let \(n_{tg} = \frac{N_{tg}}{V}\) be the density of the particles in the target \((N_{tg} \text{ atoms per volume } V)\) and \(x\) the film thickness. Then \(\sigma = \frac{A}{N_{tg}} = \frac{V/x}{N_{tg}} = \frac{1}{n_{tg} x}\) is the average cross-section per atom sensed by the \(\alpha\)-particle on its way through the film. The probability \(P(\theta)\ d\theta\) for the \(\alpha\)-particle of being within a ring at distance \(b\) from the nucleus (whose area is \(2\pi bdb\)) and being scattered into the angle \(\theta\) is then given by,

\[ P(\theta)\ d\theta = \frac{2\pi bdb}{\sigma} = n_{tg} x 2\pi bdb. \]

These particles, i.e., \(dN\) of the \(N\) particles, are deflected into the hollow cone with the probability,

\[ \frac{dN}{N} = P(\theta)\ d\theta = n_{tg} x 2\pi \frac{Z_\alpha Z_{tg} e^2}{8\pi \varepsilon_0 E_{\text{kin}}} \cot \frac{\theta}{2} \cdot \frac{Z_\alpha Z_{tg} e^2}{8\pi \varepsilon_0 E_{\text{kin}}} \cdot \frac{1}{2\sin^2 \frac{\theta}{2}} d\theta \]

\[ = n_{tg} x \frac{Z_\alpha^2 Z_{tg} e^4}{64\pi \varepsilon_0^2 E_{\text{kin}}^2} \cdot \frac{\cos \frac{\theta}{2}}{\sin^3 \frac{\theta}{2}} d\theta, \]

\(^1\)In a central collision, when the \(\alpha\)-particle reaches the minimum distance \(2a\), its initial kinetic energy, \(E_{\text{kin}}\), is fully converted into potential energy.
where we replaced the parameters \( b \) and \( db \) with the expressions (1.5) and (1.6). The solid angle of the cone can be expressed by,

\[
d\Omega = 2\pi \sin \theta d\theta = 4\pi \sin \frac{\theta}{2} \cos \frac{\theta}{2} d\theta .
\]

Thus, the number \( dN \) of particles scattered to the solid angle \( d\Omega \) remains,

\[
\frac{dN}{N} = n_{\text{tg}} x Z^{2} Z_{\text{tg}}^{2} e^{4} \frac{1}{256\pi^{2} \varepsilon_{0}^{2} E_{\text{kin}}^{2}} \sin^{4} \frac{\theta}{2} d\Omega .
\]

That is Rutherford’s scattering formula. Often, the formula is expressed with the differential cross section \( \frac{d\sigma}{d\Omega} \). We get,

\[
\frac{dN}{N} = \frac{d\sigma}{\sigma} = n_{\text{tg}} x d\sigma ,
\]

and therefore

\[
\frac{d\sigma}{d\Omega} = \frac{dN}{N n_{\text{tg}} x d\Omega} = \left( \frac{Z_{\alpha} Z_{\text{tg}} e^{2}}{4\pi \varepsilon_{0} \cdot 4 E_{\text{kin}}} \right)^{2} \frac{1}{\sin^{4} \frac{\theta}{2}} .
\]

Here, we have to make some comments:

- The angle \( \theta = 0 \) is not defined, since there exists a minimum deflection angle \( \theta_{\text{min}} \). This angle is reached, when the \( \alpha \)-particle moves at the distance \( b = b_{\text{max}} \) from the atom, that is, at the edge of the circular area of the cross section. For a greater collision parameter \( b \), the \( \alpha \)-particle traverses the field of the next neighboring atom, and the deflection angle increases again. We have:

\[
\sigma = \frac{A}{N_{\text{tg}}} = \pi b_{\text{max}}^{2} \quad \text{and} \quad \frac{\theta_{\text{min}}}{2} \simeq \tan \frac{\theta_{\text{min}}}{2} = \frac{Z_{\alpha} Z_{\text{tg}} e^{2}}{8\pi \varepsilon_{0} E_{\text{kin}} \cdot b_{\text{max}}} ,
\]

simply by inverting the formula (1.5). For very large impact parameters, that is, when the \( \alpha \)-particle passes the atom outside its electronic layer, the electrons of the atom shield the charge of the nucleus, an effect called screening.

- For very high energies, the distribution of the nuclear charge over a finite volume influences the scattering, calling for corrections in the Rutherford formula. Moreover, at short internuclear distances, nuclear forces appear additionally to the electromagnetic interaction.

- The integral over the probability distribution \( P(\theta)d\theta \) is normalized,

\[
\int_{\theta_{\text{min}}}^{\pi} P(\theta)d\theta = 1 .
\]

Similarly, we have for the surface integrals,

\[
\int_{\theta \geq \theta_{\text{min}}} \frac{d\sigma}{d\Omega} d\Omega = \sigma .
\]
Rutherford derived the formula (1.12) describing the scattering of $\alpha$-particles within classical physics. A derivation from the laws governing quantum mechanics using the *Born approximation* shows that Rutherford’s formula describes scattering correctly in first order, and that purely quantum effects present only minor corrections. We will review the Rutherford scattering in Excs. 1.1.6.1 and 1.1.6.2 and discuss the screening effect in Exc. 1.1.6.3.

### 1.1.3 Emission of radiation in the planetary model

The *planetary model* proposed by Rutherford suggests electrons spinning around a positively charged nucleus in circular orbits \(^2\). This motion of electrons should obey the laws of Maxwell’s electrodynamic theory. Let us now calculate some consequences of this picture.

We now treat the atom as a rotor where the negative particle, the electron, orbits the positive particle. The dipole moment is,

$$p_0 = -er .$$

We calculate in the Exc. 1.1.6.4 the power emitted by the acceleration $a = \omega^2 r$ of the electron on its circular trajectory,

$$P = \frac{\mu_0 \omega^4 P_0^2}{12 \pi c} .$$

The initial energy of the electron spinning around the nucleus (for a hydrogen atom $Z = 1$),

$$E = \frac{p^2}{2m_e} - \frac{e^2}{4\pi \varepsilon_0 r} = \frac{m_e \omega^2 r^2}{2} - \frac{e^2}{4\pi \varepsilon_0 r} ,$$

is dissipated by radiation of the power (1.17), i.e.,

$$-P = \frac{dE}{dt} = m_e \omega^2 r \frac{dr}{dt} + \frac{e^2}{4\pi \varepsilon_0 r^2} \frac{dr}{dt} = 2m_e \omega^2 r \frac{dr}{dt} .$$

\(^2\)This type of model had already been proposed by Jean Perrin in 1901 and by Hantaro Nagaoka in 1903, around the same time when Thompson developed his model. The planetary model was later on rescued by John William Nicholson in 1911.
The latter equation supposes an equilibrium between the centrifugal force and the Coulomb force,
\[ m_e \omega^2 r = \frac{e^2}{4\pi\varepsilon_0 r^2}, \tag{1.20} \]
allowing to link the revolution frequency \( \omega \) to the instantaneous radius of the orbit \( r(t) \). Resolving the Eq. (1.19) by \( \dot{r} \) and replacing the power by the relation (1.17) and the frequency \( \omega \) by the relation (1.20), we obtain,
\[ \frac{dr}{dt} = -\frac{P}{2m_e \omega^2 r} = -\frac{\mu_0 \omega^2 e^2}{24\pi m_e c} r = -\frac{e^4}{96\pi^2 \varepsilon_0^2 m_e^2 c^3 r^2}. \tag{1.21} \]
Integration of this equation gives,
\[ t - t_0 = -\frac{32\pi^2 \varepsilon_0^2 m_e^2 c^3}{e^4} \left[ r^3 - r^3(t_0) \right]. \tag{1.22} \]
Now inserting \( t_0 = 0 \) and assuming \( r(t_0) = a_B \), the time \( \tau \) within which the loss of energy due to radiation emission decreases the radius of the electronic orbit to \( r = 0 \), is,
\[ t = \tau = \frac{32\pi^2 \varepsilon_0^2 m_e^2 c^3 a_B^3}{e^4}. \tag{1.23} \]
Insertion of the numerical values gives the decay time \( \tau \sim 10^{-10} \) s. This is the effect called radiation collapse of the classical atomic model.

### 1.1.4 Zeeman effect in the planetary model

The orbital motion of the electron generates a ring current \( I = e/T = e\omega/2\pi \), which produces an orbital magnetic moment which, as shown in Exc. 1.1.6.5, can be calculated following the laws of electromagnetism,
\[ \vec{\mu}_\ell = IA\hat{n} = \frac{e\omega}{2\pi} \pi r^2 \hat{n}, \tag{1.24} \]
where \( A = \pi r^2 \) is the area of the trajectory. Introducing the angular momentum \( \mathbf{L} = m_e \omega r^2 \hat{n} \) we get in vector notation,
\[ \vec{\mu}_\ell = \frac{e}{2m_e} \mathbf{L}. \tag{1.25} \]

We now imagine this atom in the presence of a magnetic field \( \mathbf{B} \) oriented in the direction that we will call \( z \). This results in a precession of the magnetic moment around the field (similar to the precession of a spinning top in the presence of a gravitational field) governed by the equation,
\[ \frac{d\mathbf{L}}{dt} = \vec{\mu}_\ell \times \mathbf{B} = \frac{e}{2m_e} \mathbf{L} \times \mathbf{B} = -\Omega_L \times \mathbf{L}, \]
with \( \Omega_L = \frac{e}{2m_e} \mathbf{B} \) representing the precession frequency and being called Larmor frequency. It is evident that the presence of the magnetic field considerably alters the state of the atom, even producing profound modifications in the frequency of the
orbit of the electron $\omega_0$ and therefore in the energetic state of the atom. This change is called Zeeman effect.

The Zeeman effect can be calculated by imagining that the field has an arbitrary direction with respect to $\mathbf{L}$. In this case, the equation describing the electronic motion as resulting from an equilibrium between the centrifugal force and the Coulomb force needs to be complemented by a Lorentz force,

$$m_e \ddot{\mathbf{r}} + m_e \omega_0^2 \mathbf{r} = \mathbf{F}_L = -e \mathbf{v} \times \mathbf{B}.$$  

(1.26)

where $m_e \ddot{\mathbf{r}}$ is the centrifugal force due to the circular motion of the electron and $m_e \omega_0^2 \mathbf{r}$ the centripetal force due to the Coulomb attraction exerted by the nucleus. Assuming the direction of the magnetic field given by $\mathbf{B} = B \mathbf{e}_z$ with $B = 2m_e\Omega_L/e$, the equations of motion can be decomposed into,

$$\ddot{x} + \omega_0^2 x + 2\Omega_L \dot{y} = 0$$  

(1.27)

$$\ddot{y} + \omega_0^2 y - 2\Omega_L \dot{x} = 0$$

$$\ddot{z} + \omega_0^2 z = 0 .$$

The $z$-direction is not influenced. With the ansatz $x = a e^{i\omega t}$ and $y = b e^{i\omega t}$ we obtain the system of equations,

$$a(\omega_0^2 - \omega^2) + 2i\Omega_L \omega b = 0$$  

(1.28)

$$b(\omega_0^2 - \omega^2) - 2i\Omega_L \omega a = 0 ,$$

which has a non-trivial solution for $a$ and $b$ only when the determinant of the coefficients of $a$ and $b$ vanishes:

$$0 = \begin{vmatrix} \omega_0^2 - \omega^2 & 2i\Omega_L \omega \\ -2i\Omega_L \omega & \omega_0^2 - \omega^2 \end{vmatrix} = \omega^4 - (2\omega_0^2 + 4\Omega_L^2)\omega^2 + \omega_0^4 .$$  

(1.29)

We get,

$$\omega = \omega_{1,2} = \sqrt{\omega_0^2 + 2\Omega_L^2 \pm 2\Omega_L \sqrt{\omega_0^4 + \Omega_L^2}} = \omega_0 \pm \Omega_L + \frac{1}{2} \frac{\Omega_L^2}{\omega_0} + ... ,$$  

(1.30)

or, as $\Omega_L \ll \omega$, we get $\omega_{1,2} = \omega_0 \mp \Omega_L$. The result is a splitting of the energy levels proportional to the magnetic field,

$$\Delta E = 2h\Omega_L = \frac{hc}{m_e} B = 2\mu_B B ,$$  

(1.31)

where the abbreviation $\mu_B = e\hbar / 2m_e \simeq 9.27 \cdot 10^{-24}$ JT$^{-1}$ is called the magneton Bohr.

Although the classical derivation shows quantitative deviations from experimental observations, it is quite interesting, as it illustrates several aspects which have a quantum mechanical equivalence.

**Example 1 (Stern-Gerlach experiment):** Among several historical experiments carried out to unravel the atomic structure, one of the most important is
the experiment carried out by Otto Stern and Walter Gerlach in 1922 to measure the magnetic moment of atoms. The results of this experiment once again demonstrated the need for new concepts to explain the observations. Using Bohr’s quantization rule, \( L = n\hbar \), within the formula (1.25) we get,

\[
\vec{\mu} = -\mu_B \frac{L}{\hbar}.
\]

In the presence of a magnetic field the dipole undergoes an interaction \( W = -\vec{\mu} \cdot \mathbf{B} \), and therefore a feels a force,

\[
F = -\vec{\mu} \cdot \nabla \mathbf{B}.
\]

By subjecting beams of atoms to the gradient of a magnetic field and detecting this force, Stern and Gerlach were able to measure the magnetic moment produced by the rotation of the electrons around the atomic nuclei.

1.1.5 Bohr’s theory and its limitations

The classical model of the planetary atom provides a mechanical illustration of the microscopic world but fails to quantitatively explain experimental observations such as the discrete nature of atomic spectra.

The radiation emitted by hydrogen atoms is characterized by discrete, spectrally very thin lines. The observed lines are grouped in series named after Lyman, Ballmer and others,

\[
\frac{1}{\lambda} = R_H \frac{\mu}{m_e} \left( \frac{1}{m^2} - \frac{1}{n^2} \right),
\]

where \( m \) and \( n \) are integers. \( R_H = (1/4\pi e)^2(m_e e^4/4\pi\hbar^3 c) \) is the Rydberg constant and \( \mu = m_e m_{\text{at}}/(m_e + m_{\text{at}}) \) the reduced mass.

The discrete nature of spectral lines and the problem of the radiation collapse led Niels Bohr to formulate the following postulates:

1. There are specific stationary orbits, where electrons do not emit energy.

2. Each emission or absorption of radiation energy by electrons comes with a transition between stationary orbits. The radiation emitted during this transition is homogeneous.

3. The laws of mechanics can describe the dynamic equilibrium of electrons in stationary states, but fails to describe the transition of electrons between stationary orbits.

Thus, Bohr’s model predicts the quantization of energy levels, known as first quantization of quantum mechanics. The radii of the possible orbits can be calculated from the postulate that the orbital angular momentum be quantized in units of \( \hbar \), that is, the electrons form stationary de Broglie waves along the orbits.

A generalization of Bohr’s theory was provided by Arnold Johannes Wilhelm Sommerfeld. Assuming elliptical orbits for the electrons he managed to explain some features of the fine structure, provided the motion of the electron was treated relativistically. The basic premises were 1. stable orbits when the Coulomb attraction is balanced by the centrifugal force, 2. quantization of phase space \( \int r_dq = n_q\hbar \), and 3. quantization of angular momentum \( \int Ld\theta = n\hbar \).
In the picture proposed by Bohr, the radiative decay happens as an abrupt transition of an electron between an outer (more energetic) orbit and an inner (less energetic) orbit. Since the energies of stationary orbits are very well defined, the emitted radiation is mono-energetic, i.e., the spectrum consists of discrete characteristic lines.

We note here that the picture of an abrupt transition of electrons between discrete states, called the \textit{quantum jump}, did not receive Schrödinger’s blessing. He rather imagined for electrons, within his theory of quantum wave mechanics, wave-shaped orbitals instead of planetary trajectories, thus avoiding the problem of radiation due to charge deceleration and the quantum jump concept. According to him, during a transition between electronic orbits, the energy is transformed into radiation \textit{gradually}.\footnote{We note here, that quantum jumps were observed much later!}

1.1.6 Exercises

1.1.6.1 \textbf{Ex: Analysis of Rutherford scattering}

a. What conclusions can be drawn from the observation that Rutherford’s formula describes well the scattering of charged particles traveling through matter over a wide range of parameters?

b. Why do we see a deviation from Rutherford’s formula for large energies?

c. The scattering of protons with energy $E$ crossing a thin film of thorium is well described up to energies of $E = 4.3$ MeV by Rutherford’s formula. Estimate for this case the range of nuclear forces.

d. For small scattering angles $\theta$ we observe large deviations from Rutherford’s formula. Explain why?

e. Assume the thorium atoms of item (c) to form a periodic crystal with the lattice constant $d = 10a_B$. At which minimum angle $\theta$ Rutherford’s formula loses its validity.

1.1.6.2 \textbf{Ex: Rutherford scattering}

a. A beam of $\alpha$-particles with energy $E_{\text{kin}} = 3$ MeV and flux $I = 5 \cdot 10^3$ s$^{-1}$ impinges on a thick gold film $x = 1 \mu$m. Using Rutherford’s formula, calculate how many particles are scattered in $\Delta t = 10$ minutes in the range of angles $10^\circ \leq \theta \leq 30^\circ$.

b. Now, the gold film is replaced with an aluminum film of the same thickness. How many $\alpha$-particles are scattered under equal circumstances?

1.1.6.3 \textbf{Ex: Screening of electrons}

Consider thin layer of charge $-Z_{tg}e$ with radius $R$. This screening causes a scattering angle,

$$\tan \frac{\theta}{2} = \frac{D}{2b} \sqrt{1 - \frac{(b/R)^2}{1 + D/2R}},$$

with $D \equiv \frac{Z_{tg}e^2}{m_2v^2/2}$ for $b < R$. Verify how the screening changes the differential cross section $\frac{d\sigma}{d\Omega}$.
1.1.6.4  Ex: Radiation of an oscillating dipole

Calculate the angular distribution of the power radiated by an oscillating electric or magnetic dipole from expressions for the emitted electric and magnetic fields found in literature.

1.1.6.5  Ex: Magnetic moments

a. Derive from the expression \( \vec{\mu} = \frac{1}{2} \int_{\mathbb{R}^3} \mathbf{r} \times \mathbf{j}(\mathbf{r}') d^3 r' \) of classical electrodynamics and an appropriate parametrization of the current density \( \mathbf{j} \) the relation between the magnetic dipole moment \( \vec{\mu} \) due to the orbiting electron and the angular momentum \( \mathbf{L} \).

b. The length of the angular momentum vector being given by \( |\mathbf{L}| = \hbar \), calculate the magnetic moment for an electron and for a proton.

1.1.6.6  Ex: Bohr’s atom

In 1913, Niels Bohr presented his atomic model adapting Rutherford’s model to the quantization ideas proposed by Max Planck.

a. Impose the quantization rule for the angular momentum \( (\mathbf{L} = n\hbar) \) of an electron orbiting an atom of atomic number \( Z \) to find an expression for the radii of the allowed orbits.

b. According to Bohr’s model, the transition between different orbits is accompanied by the emission (or absorption) of a photon. Determine the energy of a photon emitted during a transition between the first excited state and the ground state of a hydrogen atom.

c. Consider an electron trapped in an infinite one-dimensional box potential of width \( a \). Determine an expression for the electronic energy levels.

d. What should be the width \( a \) of this potential, in terms of the Bohr radius, so ensure that a photon emitted during a transition between the first excited state and the ground state equals that obtained in item (b)?

1.1.6.7  Ex: The hydrogen atom

The hydrogen atom can be seen as a point-like proton and an electron distributed over space with charge density \( \rho = A e^{-2r/a_B} \) around the proton that is in the center. Here, \( A \) is a constant and \( r \) is the distance from the center.

a. Calculate \( A \) considering the fact that the atom is electrically neutral.

b. Calculate the amplitude of the electric field at a radius \( r = a_B \).

1.2  The discovery of the photon

The concept of the nature of light has a variable history. Newton proposed around \( \sim 1650 \) a corpuscular model to explain Snellius’ law on the refraction of a light beam penetrating a crystal. Around the same time Huygens found a wave-based interpretation. The two models predicted different speeds of light within the dense medium. Newton found, that the speed of light is greater in the medium than outside, while
Huygens found the opposite. In the late 1800’s the wave nature of light was established through observations of interference effects confirming Huygens’ hypothesis. At that time, the world appeared to be simple: Light was a wave and matter was composed of particles. However, some observations made were incompatible with this simplistic ideas, for example, the spectrum of blackbody radiation, the Compton effect, the specific heat of the solid, the radiation pressure, and the photoelectric effect. All these observations are readily understood by assuming a corpuscular nature of the light.

Nowadays, knowing the theory of quantum mechanics, we know that both ideas have their range of validity and that the electromagnetic radiation is dual: In general, propagation and interference effects are best described by waves. However, when interacting with matter, light tends to localize into small particles called photons.

### 1.2.1 Radiation in a conductive cavity

In the age of lasers a classical treatment of the emission and absorption of light may seem an atavism. However, even with coherent and monochromatic radiation sources, the most commonly used physical picture is that of a classical optical field interacting with an atom or a molecule whose energetic structure is treated quantum mechanically. And even the atomic or molecular dipole is often treated like a classical oscillator. The exposition of such a dipole to simple boundary conditions prepares the analogous development of a quantum oscillator and provides a direct path to quantization of the radiation field.

Even if we rarely do experiments by throwing light into a small hole in a metallic box, the electromagnetic fields obtained by solving Maxwell’s equation are particularly simple for boundary conditions, where the fields disappear on the inner surfaces of the box. Before discussing the physics of radiation in a perfectly conducting cavity, we have to introduce some basic relations between electromagnetic amplitudes, stored energy, and intensity.

The electric field of a plane wave oscillating with frequency $\omega$ and propagating through vacuum in the direction of propagation defined by the wave vector,

$$ k = \frac{2\pi}{\lambda} \hat{k}, \quad (1.33) $$

can be written,

$$ E = E_0 e^{i(k \cdot r - \omega t)}, \quad (1.34) $$

where $E_0 = E_0 \hat{e}$ consists of an amplitude $E_0$ and a polarization $\hat{e}$. Since the field $E_0$ is transverse to the direction of propagation, the polarization has two components perpendicular to $k$. The magnetic induction field associated with the wave is,

$$ B_0 = \frac{1}{c} E_0. \quad (1.35) $$

For a propagating wave $E$ and $B$ are in phase, while for a standing wave they are out of phase.

---

5Note, until today there remain doubts about the correct value of the momentum of light in dielectric media [422].

6The corpuscular hypothesis is now called the second quantization of quantum theory or quantization of the electromagnetic field.
1.2. THE DISCOVERY OF THE PHOTON

For a given cavity mode we can express the standing wave in this mode as,

\[ E = E_0(r)e^{-i\omega t}. \]  

(1.36)

The energy of the electromagnetic field of a standing wave, averaged over one oscillation of the frequency \( \omega \) is,

\[ \bar{U} = \frac{1}{2} \int \left( \frac{\varepsilon_0}{2} |E|^2 + \frac{1}{2\mu_0} |B|^2 \right) dV. \]  

(1.37)

Now, the energy density of the oscillating electromagnetic field is given by,

\[ \bar{u} = \frac{d\bar{U}}{dV} = \frac{1}{4} \left( \varepsilon_0 |E|^2 + \frac{1}{\mu_0} |B|^2 \right). \]  

(1.38)

From the equation (1.35) we can see that the contributions of the electric and magnetic fields are equal. Therefore,

\[ \bar{U} = \frac{1}{2} \int \varepsilon_0 |E|^2 dV \quad \text{and} \quad \bar{u} = \frac{1}{2} \varepsilon_0 |E|^2. \]  

(1.39)

Another important quantity is the flux of electromagnetic energy through a surface. The Poynting vector describing this flux is defined by,

\[ \mathbf{I} = \frac{1}{\mu_0} \mathbf{E} \times \mathbf{B}. \]  

(1.40)

Again using the equation (1.35), we find the value averaged over a time period,

\[ \bar{I} = \frac{1}{2} \varepsilon_0 c |E|^2. \]  

(1.41)

This quantity, called intensity, describes the fact that the flux is a density of energy multiplied with the velocity of propagation in vacuum,

\[ \bar{u}c = \frac{1}{2} \varepsilon_0 c |E|^2 = \bar{I}. \]  

(1.42)

The intensity can also be written,

\[ \bar{I} = \frac{1}{2} \sqrt{\varepsilon_0 / \mu_0} |E|^2. \]  

(1.43)

where the factor \( \sqrt{\mu_0 / \varepsilon_0} \) is called impedance of free space, because it has the unit of a resistance and the last equation has the same form as the power dissipated in a resistor,

\[ W = \frac{1}{2} \frac{V^2}{R}. \]  

(1.44)

1.2.2 Black body radiation

We now want to calculate the energy density inside the cavity before using the result to describe the interaction between light and a sample of two-level atoms located inside
the cavity. The basic idea is to say that the electrons inside the conducting surface of the cavity oscillate because of thermal motion. The oscillation generates a dipolar radiation leading to stationary waves developing within the cavity. As the walls of the cavity are conducting, the electric field \( \mathbf{E} \) must disappear inside the wall and on its surfaces. The task is now twofold: first count the number of possible standing waves, which satisfy the boundary conditions as a function of frequency; second, determine the energy for each wave and then calculate the spectral distribution of the energy within the cavity.

The equations describing the radiated energy in free space are,

\[
\nabla^2 \mathbf{E} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad \text{and} \quad \nabla \cdot \mathbf{E} = 0. \tag{1.45}
\]

The stationary waves solutions separate into terms oscillating in time and in space.

![Figure 1.7: (a) Cavity in position space showing the thermal motion of the electrons inside the walls. (b and c) Density-of-states in a cavity in momentum space.](image)

Now, respecting the boundary conditions for a three-dimensional box of length \( L \), we have for the components of \( \mathbf{E} \),

\[
\mathbf{E}(\mathbf{r}, t) = e^{-i\omega t}[\hat{\mathbf{e}}_x \cos(k_x x) \sin(k_y y) \sin(k_z z) + \hat{\mathbf{e}}_y \sin(k_x x) \cos(k_y y) \sin(k_z z) + \hat{\mathbf{e}}_z \sin(k_x x) \sin(k_y y) \cos(k_z z)] \tag{1.46}
\]

with the components,

\[
k_x = \frac{\pi n_x}{L} \quad \text{for} \quad n_x = 0, 1, 2, ...
\]

and similar for \( k_y \) and \( k_z \). Note, that for each component \( E_{x,y,z} \) the transverse amplitudes disappear in 0 and \( L \). By inserting this solution into Helmholtz’s equation (1.45), we obtain,

\[
k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c^2}. \tag{1.48}
\]

The states \( k_{x,y,z} \) (enumerated by \( n_{x,y,z} \)) form a three-dimensional orthogonal lattice of points in space \( \mathbf{k} \) separated by a distance along the axes \( k_x, k_y, k_z \) of \( \frac{\pi}{L} \), as shown

\[\text{See script on } \textit{Electrodynamics} \ (2020).\]
1.2. THE DISCOVERY OF THE PHOTON

In principle, the number of states that can be placed within a sphere of radius \( k \) in the momentum space is,

\[
N = \int_{\text{sphere}} dn_x dn_y dn_z .
\]

(1.49)

However, the periodic boundary conditions for \( |k| \) limit the components \( k_x, k_y, k_z \) to positive values \( (n \geq 0) \), that is, the volume under consideration is limited to an octant. On the other hand, we must multiply the number of states by two because of the degeneracy of polarizations,

\[
4N = \int_0^n 4\pi n^2 dn = \left( \frac{L}{\pi} \right)^3 \int_0^k 4\pi k^2 dk = \frac{4L^3 k^3}{\pi^2} = \frac{4L^3 \omega^3}{3\pi^2 c^3} .
\]

(1.50)

With this, we obtain the mode density,

\[
\frac{N}{L^3} = \frac{\omega^3}{3\pi^2 c^3} .
\]

(1.51)

The spectral density of modes \( \rho \) can be given in several units,

\[
\int \rho(n) dn = \int \rho(k) dk = \int \rho(\omega) d\omega = \frac{N}{L^3} ,
\]

(1.52)

such that,

\[
\rho(n) = \frac{\pi n^2}{L^3} \quad \text{or} \quad \rho(k) = \frac{k^2}{\pi^2} \quad \text{or} \quad \rho(\omega) = \frac{\omega^2}{\pi^2 c^3} .
\]

(1.53)

The density of oscillating modes within the cavity grows like the square of the frequency. Now, the mean energy per mode in a sample of oscillators in thermal equilibrium is, following the equipartition law, equal to,

\[
\bar{E} = k_B T ,
\]

(1.54)

where \( k_B \) is the Boltzmann constant. We conclude that the spectral energy density \( u_{RJ}(\omega) \) in the cavity is,

\[
u_{RJ}(\omega) d\omega = k_B T \rho(\omega) d\omega = k_B T \frac{\omega^2}{\pi^2 c^3} d\omega .
\]

(1.55)

This law is known as the Rayleigh-Jeans law of black-body radiation. As seen in Fig. 1.8, this law suggests the physically impossible fact, called ultraviolet catastrophe, that the energy storage in the cavity grows without limits like the square of frequency.

1.2.3 Planck’s distribution of modes

We obtained the result (1.54) by multiplying the number of modes with the mean energy per mode. As there is no doubt about our method of counting the modes, the
CHAPTER 1. ANTECEDENTS OF QUANTUM MECHANICS

problem with the ultraviolet catastrophe can only root in the use of the equipartition principle for assigning energy to the oscillators.

Planck’s idea to solve this problem was to first consider the probability distribution for exciting the modes (thermal states) for a sample of oscillators in thermal equilibrium at temperature \( T \). This probability distribution \( p \) comes from mechanical statistics and can be written in terms of the Boltzmann factor, \( e^{-E_n/k_B T} \), and the partition function \( q = \sum_{n=0}^{\infty} e^{-E_n/k_B T} \) as,

\[
p_n = \frac{e^{-E_n/k_B T}}{q}.
\]

Now Planck hypothesized that the energy be quantized, that is, it must be assigned in discrete portions, proportional to the frequency, such that,

\[
E_n = n\hbar \omega,
\]

where \( n = 0, 1, 2, \ldots \) and the proportionality constant \( \hbar \) is called Planck’s constant. With the abbreviation \( Z \equiv e^{-\hbar \omega/k_B T} \) and using the rule \( \sum_{n=0}^{\infty} Z^n = (1 - Z)^{-1} \), we find the average number,

\[
\bar{n} = \sum_n n p_n = (1 - Z) \sum_n n Z^n = (1 - Z) Z \frac{\partial}{\partial Z} \sum_n Z^n = \frac{Z}{1 - Z} = \frac{1}{e^{\hbar \omega/k_B T} - 1}.
\]

The probability of occupancy of state \( n \) is,

\[
p_n = (1 - Z) Z^n = \frac{\bar{n}^n}{(1 + \bar{n})^{1+n}},
\]

and the average energy is,

\[
\bar{E} = \sum_n E_n p_n = \sum_n n \hbar \omega e^{-n\hbar \omega/k_B T} = \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1},
\]

in contrast to the initial assumption (1.55).

Finally, we obtain Planck’s expression for the energy density inside the cavity by substituting \( \bar{e} \) for the factor \( k_B T \) in Rayleigh-Jeans’ law (1.54),

\[
\frac{u(\omega)d\omega}{\pi^2 c^3} = \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} d\omega.
\]
This result, drawn in Fig. 1.8, is much more satisfactory, because now the energy density has an upper bound, and coincides with the results of experiments. Note, that for high temperatures or low excitation energies, \( h\omega \ll k_B T \), Planck’s distribution converges to that of Rayleigh-Jeans’, \( u(\omega) \rightarrow u_{RJ}(\omega) \).

Note that the form of the expression for the energy depends on the parametrization and must be derived respecting \( u(\omega) d\omega = u(\lambda) d\lambda \), etc.. Often the blackbody radiation is expressed in terms of the *spectral radiance*,

\[
L(\omega) \equiv \frac{c}{4\pi} u(\omega),
\]

which can be understood as the (isotropic) energy flux into all directions of space.

Solve the Excs. 1.2.10.1 to 1.2.10.6.

### 1.2.4 The corpuscular nature of the photon

#### 1.2.4.1 The photoelectric effect

Light incident on a metallic surface can expel electrons. For this to occur, the light must have a *minimum frequency*. If the frequency is below this value, there is no point in increasing the light intensity: the electrons won’t be expelled. The main experimental observations are: 1. Electrons are ejected without apparent delay, i.e. it is not necessary (and it doesn’t help) to accumulate a certain amount of energy. 2. Higher light intensities increase the number of electrons, but not their kinetic energy after expulsion. 3. Red light does not eject electrons, even at high intensities. 4. Weak ultraviolet light only ejects few electrons, but with high kinetic energy.

These observations challenge the classical electromagnetic model according to which the Lorentz acceleration of the electrons should be proportional to the field amplitude. The observations were explained by Einstein’s theory of the *photoelectric effect*, which assumes the light to be quantized (unlike Planck, who preferred to quantize the process of light absorption),

\[
E = h\nu.
\]

Assuming a fixed exit work \( A \) for the extraction of an electron, we can measure the constant \( h \):

\[
h\nu = A + \frac{mv^2}{2} = A + eV \quad \rightarrow \quad h = \frac{eV}{\nu - \nu_g}.
\]

The energy of the fastest electrons is measured through the decelerating voltage by varying \( \nu \) and \( I \). We will discuss the photoelectric effect quantitatively later in the Exc. 5.4.6.7.

#### 1.2.4.2 Bremsstrahlung and the Franck-Hertz experiment

*Bremsstrahlung* is, in a way, the inverse process of the photoelectric effect. Here, electrons are accelerated toward a cathode. Finding a target they are rapidly decelerated, a process in which they emit a continuous spectrum of X-rays (in addition to characteristic lines attributed to electronic transitions in the target atoms). For any given kinetic energy the spectra have a red threshold corresponding to photons that receive the entire energy of the electron.
In the *Franck-Hertz experiment* free electrons produced in a plasma are accelerated by a strong electric field. Having traveled a sufficiently long distance they have acquired enough kinetic energy to excite electronic transitions in the atoms of the plasma. When an excitation occurs, the electron suddenly loses all its energy and must be accelerated again, starting from rest, before it can excite another atom.

### 1.2.4.3 Radiative pressure and Compton scattering

When light is scattered from a particle, it transfers momentum to it called *photonic recoil*. This effect, known as *radiation pressure*, occurs for example in *Compton scattering*.

X-rays scattered by the electrons of a carbon target are red-shifted by an amount, which increases with the scattering angle. This is the *Compton effect*. The data are understood assuming a corpuscular nature of light and applying the laws of conservation of energy and momentum to the collision processes between photons and electrons. The scattered photon sees its energy reduced and therefore its wavelength increased.

In a material where there are free electrons, this effect will occur at all photon energies. In other materials, it is only observed with high energy photons. For high energy photons, exceeding the atomic binding energy, the electrons can be considered free such that, in the scattering process, the photon is able to eject the electron from its atom. The photon receives the remaining energy and is deviated, such that the overall momentum of the system is conserved. The loss of energy for the photon results in a spectral shift to the red during its passage through the material.

Photons of visible light, on the other hand, do not have enough energy to eject bound electrons. In this case, the mass in the Compton formula must be replaced by the atomic mass, such that the spectral displacement becomes much smaller. This limit, which involves bound electrons, is that of Thomson and Rayleigh scattering.

The relevance of this effect lies in the fact that it shows that light exhibits properties commonly attributed to corpuscles, since Thomson’s scattering model, based on the classical theory of charged particles accelerated by electromagnetic fields, can not explain any spectral shift.

### 1.2.5 Einstein’s transitions rates

Bohr’s atom model explained for the first time how light interacts with matter: Atoms have discrete excitation levels. They absorb and emit energy packets $\hbar \omega$. Unfortunately, Bohr’s model can not predict transition rates. Here, Einstein helped out by developing a useful theory (see Fig. 1.9).

![Figure 1.9: Bohr model and Einstein rate diagram.](image-url)
We consider a two-level atom or a sample of atoms within a conducting cavity. We have \( N_1 \) atoms in the lower energy state \( E_1 \) and \( N_2 \) in the upper state \( E_2 \). Light interacts with these atoms through stimulated resonant absorption and emission. The rates, \( B_{12}(\omega) \) and \( B_{21}(\omega) \) are proportional to the energy spectral density \( u(\omega) \) of the cavity modes. The central idea of Einstein is to postulate that atoms in the higher state can emit light spontaneously at a rate \( A_{21} \), which depends only on the density of modes of the cavity, i.e. the volume of the cavity, but not the energy of the field of radiation. With the Einstein coefficients we can formulate valid rate equations in situations, where the spectral distribution of the radiation is wider than the spectral width of the atomic transition and where the spectral distribution of the light flux from the source, \( \bar{I}(\omega) \), is weak compared to the saturation intensity of the atomic transition. Even if modern light sources generally have very narrow and intense spectral emission bands, Einstein’s coefficients are often used in the spectroscopic literature to characterize the light-matter interaction with atoms and molecules.

The Einstein rate equations describe the energy flux between atoms and the optical modes of the cavity,

\[
\frac{dN_1}{dt} = - \frac{dN_2}{dt} = - R_{1\rightarrow 2} + R_{2\rightarrow 1} + S_{2\rightarrow 1} \\
= -N_1 B_{12}(\omega) + N_2 B_{21}(\omega) + N_2 A_{21} .
\]

\( R_{1\rightarrow 2} \) is the absorption rate, \( R_{2\rightarrow 1} \) the stimulated emission rate and \( S_{2\rightarrow 1} \) the spontaneous emission rate. The assumption of a third type of transition, called spontaneous emission, is necessary, if \( B_{12} = B_{21} \) but \( N_1 > N_2 \) in thermal equilibrium. In thermal equilibrium we have the condition of stationarity, \( \frac{dN_1}{dt} = - \frac{dN_2}{dt} = 0 \) for a given energy density value \( u(\omega) = u_{th}(\omega) \), such that,

\[
u_{th}(\omega) = \frac{A_{21}}{\left(\frac{N_1}{N_2}\right) B_{12} - B_{21}} .
\]

The Boltzmann distribution law controlling the distribution of the number of atoms in the lower and upper states is given by,

\[
\frac{N_1}{N_2} = \frac{g_1}{g_2} e^{-(E_1-E_2)/k_B T} ,
\]

where \( g_{1,2} \) are the degeneracies of the lower and upper states and \( E_2 - E_1 = \hbar \omega_0 \). We find,

\[
u_{th}(\omega) = \frac{A_{21}}{\left(\frac{g_1}{g_2} e^{\hbar \omega_0/k_B T}\right) B_{12} - B_{21}} .
\]

But this result must be consistent with the Planck’s distribution (1.61). Therefore, by comparing this equation with the equation (1.68), it must be,

\[
\frac{g_1 B_{12}}{g_2 B_{21}} = 1 .
\]

and also,

\[
\frac{A_{21}}{B_{21}} = \frac{\hbar \omega_0^3}{\pi^2 c^3} .
\]
This equation shows that, once we know one of the three transition rates, we can always calculate the others.

It is useful to compare the rate $A_{21}$ with $B_{21}$ from the equation (1.68) inserting the equation (1.69),

$$\frac{A_{21}}{B_{21} u_{th}(\omega)} = e^{\hbar \omega_0 / k_B T} - 1.$$  (1.71)

This expression shows that, when $\hbar (\omega_2 - \omega_1) \gg k_B T$, that is, for optical, UV, or X-ray frequencies, spontaneous emission dominates. But in low-frequency regimes, that is, IR, microwave, or radio waves, stimulated emission is more important. Note that even when stimulated emission dominates, spontaneous emission is always present and plays an important role, for example, in processes ultimately limiting the emission bandwidth of lasers.

### 1.2.6 Absorption spectrum for a single atom

Every light source has a certain spectral width. Conventional light sources, such as incandescent bulbs or plasmas have relatively broad emission bands compared to atomic or molecular absorbers, at least when the latter ones are studied in dilute gases. Even when we use pure spectral sources, such as a laser tuned to the peak of a resonance, the transition line always exhibits an intrinsic width associated with the interruption of the phase evolution of the excited state. Phase interruptions such as spontaneous or stimulated emission and collisions are common examples of line broadening mechanisms. The emission or absorption of radiation occurs within a frequency distribution centered about $\omega_0 \equiv \omega_2 - \omega_1$, and we must account for this spectral distribution in our calculation of the energy transfer.

The total power $P$ absorbed by a two-level atom with resonance frequency $\omega_0$ from a radiation field with the spectral intensity distribution $I(\omega)$ with the total intensity of the laser beam $\bar{I} = \int I(\omega) d\omega$ can be expressed as the integral,

$$P = \int \sigma(\omega) I(\omega) d\omega,$$  (1.72)

with the frequency-dependent optical cross section $^8$,

$$\sigma(\omega) = \frac{g_2}{g_1} \frac{\lambda^2}{2\pi} \frac{1}{(\omega - \omega_0)^2 + \frac{1}{4}\Gamma^2} = \frac{g_2}{g_1} \lambda^2 \frac{\Gamma}{4} \mathcal{L}_\Gamma(\omega - \omega_0).$$  (1.73)

where we defined the Lorentzian profile as,

$$\mathcal{L}_\beta(\Delta) \equiv \frac{\beta}{2\pi} \frac{1}{\Delta^2 + (\beta/2)^2} \quad \text{with} \quad \int_{-\infty}^{\infty} \mathcal{L}_\beta(\Delta)d\Delta = 1.$$  (1.74)

**Example 2 (Limiting cases)**: Let us analyze the two limiting cases when either one of the spectral distributions $I(\omega)$ or $\sigma(\omega)$ is much narrower than the other.

For a narrow laser, we may assume a $\delta$-peaked spectral intensity distribution,

$$I(\omega) = \bar{I} \delta(\omega - \omega_L).$$  (1.75)
When it drives a broad transition described by an optical cross section given by (1.73), the scattered power is,

\[ P = \bar{I}\sigma(\omega_L) . \]  
(1.76)

For a narrow transition, we may substitute the Lorentzian in (1.73) by a Dirac \(\delta\)-function,

\[ \sigma(\omega) \xrightarrow{\Gamma \to 0} \frac{g_2}{g_1} \frac{\lambda^2}{4} \frac{\Gamma}{\delta(\Delta)} . \]  
(1.77)

When it is driven by a broad laser, for which we assume a spectral intensity distribution,

\[ I(\omega) = \bar{I} \mathcal{L}_\beta(\omega - \omega_L) \quad \text{with} \quad \bar{I} = \int I(\omega) d\omega = \frac{I(\omega_L)}{\mathcal{L}_\beta(0)} = \frac{\pi \beta}{2} I(\omega_L) \]  
(1.78)

we obtain for the scattered power,

\[ P = \int \frac{g_2}{g_1} \frac{\lambda^2}{4} \frac{\Gamma}{\delta(\omega - \omega_0)} \bar{I} \mathcal{L}_\beta(\omega - \omega_L) d\omega = \frac{g_2}{g_1} \frac{\lambda^2}{4} \bar{I} \mathcal{L}_\beta(\omega_0 - \omega_L) . \]  
(1.79)

### 1.2.6.1 Broad laser driving a broad transition

Until now we assumed a fixed laser frequency \(\omega_L\) (with finite emission bandwidth) driving a fixed resonance frequency \(\omega_0\). What we call absorption spectrum is what we obtain when we tune either the laser frequency or when we (somehow) vary the resonance frequency, such that \(\Delta \equiv \omega_L - \omega_0\) is ramped. Assuming Lorentzian profiles with finite linewidths for both, \(\bar{I}\) and \(\sigma\), we get,

\[ P(\Delta) = P(\omega_L - \omega_0) = \int \sigma(\omega) I(\omega) d\omega = \int \frac{g_2}{g_1} \frac{\lambda^2}{4} \mathcal{L}_\Gamma(\omega - \omega_L) \bar{I} \mathcal{L}_\beta(\omega - \omega_0) d\omega \]

\[ = \frac{g_2}{g_1} \frac{\lambda^2}{4} \bar{I} \int \mathcal{L}_\Gamma(\omega' + \omega_0 - \omega_L) \mathcal{L}_\beta(\omega') d\omega' . \]  
(1.80)

That is, the absorption spectrum is obtained as a convolution of both profiles,

\[ P(\Delta) = \frac{g_2}{g_1} \frac{\lambda^2}{4} \bar{I} (\mathcal{L}_\Gamma * \mathcal{L}_\beta)(\Delta) . \]  
(1.81)

Figure 1.10: Absorption spectrum (blue) and spectral energy distribution of the source (red).

This result reproduces the two limiting cases discussed in the above example, since for narrow transitions, \(\Gamma \to 0\), that is \(\mathcal{L}_\Gamma \to \delta\), we recover the results (1.79), and for
narrow lasers, \( \beta \to 0 \), that is, \( L_\beta \to \delta \), we recover (1.76). Obviously, this formula holds for other line profiles e.g. when the resonance is broadened by some perturbations \(^9\).

### 1.2.6.2 Two-level atom in a blackbody radiation field

When considering a two-level atom interacting with a blackbody radiation field, we describe the spectral intensity distribution by (1.61),

\[
I(\omega) = \frac{\omega^2}{\pi^2 c^2} \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1}
\]

with

\[
\bar{I} = \int I(\omega) d\omega = \frac{\hbar}{\pi^2 c^2} \left( \frac{k_B T}{\hbar} \right)^4 \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2}{15 c^2 \hbar^3} (k_B T)^4.
\]

Since the width of the transition is negligibly small in comparison with the blackbody spectrum, \( \Gamma \to 0 \), we may evaluate the scattered power as,

\[
P = \int g_2 g_1 \lambda^2 \Gamma \left( \omega - \omega_0 \right) \frac{\omega^2}{\pi^2 c^2} \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1} d\omega
\]

(1.83)

\[
\Gamma \to 0 \implies \bar{g}_2 g_1 \lambda^2 \Gamma \left( \omega - \omega_0 \right) \frac{\omega^2}{\pi^2 c^2} \frac{\hbar \omega_0}{e^{\hbar \omega_0/k_B T} - 1}.
\]

### 1.2.7 Absorption in a gas

Let us now generalize the results to a gas of two-level atoms. As long as the transition linewidth is narrow [case (1.77)], the power is removed from the system only by spontaneous emission; absorption only converts radiation into atomic excitation which, subsequently, can be returned to the radiation field by stimulated emission. At steady-state the Einstein rate equation (1.65) reads,

\[
0 = -N_1 B_{12} u(\omega_0) + N_2 B_{21} u(\omega_0) + N_2 A_{21}.
\]

(1.84)

Using the result (1.69), we can write the amount of power removed from the system by spontaneous emission as,

\[
P = N_2 A_{21} \hbar \omega_0 = u(\omega_0) B_{12} (N_1 - \frac{g_1}{g_2} N_2) \hbar \omega_0.
\]

(1.85)

On the other hand, the power absorbed from the radiation field \( u(\omega_0) \), by atoms whose transition is described by the cross section (1.73), is given by,

\[
P = \int (N_1 - \frac{g_1}{g_2} N_2) \sigma(\omega) I(\omega) d\omega.
\]

(1.86)

Remembering \( I(\omega) = cu(\omega) \) and assuming a large radiation spectrum, \( I(\omega) \simeq I(\omega_0) \), a comparison of equations (1.85) and (1.86) yields,

\[
B_{12} = \frac{c}{\hbar \omega_0} \int \sigma(\omega) d\omega.
\]

(1.87)

\(^9\)Let us here remind the following identities holding for Lorentzian and Gaussian line profiles:

\[
(L_\gamma * L_\beta)(\Delta) = L_{\gamma + \beta}(\Delta) \quad \text{and} \quad (G_\Gamma * G_\beta)(\Delta) = G_{\sqrt{\gamma + \beta}^2}(\Delta).
\]
1.2. THE DISCOVERY OF THE PHOTON

1.2.7.1 Lambert-Beer law

The absorption probability distribution is convoluted with the spectral energy distribution of the light source, \( u(\omega) = d\bar{u}/d\omega \), which in turn is related to the energy density via, \( \bar{U} = V \bar{u} \), where \( V \) is the mode volume of the light field. Assuming that light propagates toward \( z \) and converting the time dependence into a spatial dependence, we have on one hand,

\[
P = -\frac{d\bar{U}}{dt} = -\frac{d\bar{u}}{dz} \Delta V = -c \frac{d\bar{u}}{dz} \Delta V .
\] (1.88)

On the other hand, assuming a narrow laser, \( I(\omega) = \bar{I} \delta(\omega - \omega_L) \), we get,

\[
P = \int (N_1 - \frac{g_1}{g_2} N_2) \sigma(\omega) I(\omega) d\omega = \bar{I} (N_1 - \frac{g_1}{g_2} N_2) \sigma(\omega_L) ,
\] (1.89)

Now comparing both results,

\[
\frac{d\bar{I}}{\bar{I}} = -\frac{N_1 - \frac{g_1}{g_2} N_2}{\Delta V} \sigma(\omega_L) dz \simeq -n \sigma(\omega_L) dz ,
\] (1.90)

The solution of this differential equation is,

\[
\bar{I} = \bar{I}_0 e^{-\sigma(\omega_L)nz} .
\] (1.91)

Here, \( z \) is the total distance, over which absorption takes place. The last equation is the Lambert-Beer law for light absorption. It is very useful for measuring atomic densities in gas cells or of atomic beams [403, 382, 623]. Solve the Excs. 1.2.10.8 to 1.2.10.10.

1.2.8 Saturation

Strong driving of a transition leads to its saturation and causes line broadening. To see this we go back to Einstein’s rate equations in steady-state (1.65) additionally simplifying by assuming \( g_1 = 1 = g_2 \), such that \( B_{12} = B_{21} \). Resolving these equations by \( N_1 \) and \( N_2 \) and using \( N_1 + N_2 = N \) and \( N_1 - N_2 = \Delta N \), we get,

\[
N_1 = N \frac{B_{21}u(\omega) + A_{21}}{2B_{21}u(\omega) + A_{21}} \quad \text{and} \quad N_2 = N \frac{B_{12}u(\omega)}{2B_{21}u(\omega) + A_{21}} .
\] (1.92)

For vanishing pump rate we expect, \( N_1 \xrightarrow{u \to 0} N \) and \( N_2 \xrightarrow{u \to 0} 0 \). In contrast, when the pump rate becomes much larger than the relaxation rates, \( N_1, N_2 \xrightarrow{u \to \infty} \frac{1}{2} \). This means that the absorption coefficient \( \alpha = \sigma(N_1 - N_2) \) goes to zero, and the medium becomes completely transparent,

\[
\Delta N = N \frac{A_{21}}{2B_{21}u(\omega) + A_{21}} = \frac{N}{1 + s(\omega)} .
\] (1.93)

The saturation parameter

\[
s(\omega) \equiv \frac{2B_{12}u(\omega)}{A_{21}}
\] (1.94)
represents the ratio of pumping rate to the relaxation rate. The pump rate due to a monochromatic wave with intensity $\bar{I}$ is obtained by comparing (1.85) with (1.89),

$$B_{12}u(\omega) = \frac{\sigma(\omega)\bar{I}}{\hbar \omega}.$$ \hspace{1cm} (1.95)

We obtain for the saturation parameter,

$$s(\omega) = \frac{2\sigma(\omega)\bar{I}}{\hbar \omega A_{21}}.$$ \hspace{1cm} (1.96)

According to (1.85) and (1.93) the power absorbed per unit volume on the transition by atoms with the populations $N_{1,2}$ in a radiation field with a broad spectral profile and spectral energy density $u(\omega)$ is,

$$P = \hbar \omega B_{12}u(\omega)\Delta N = \hbar \omega B_{12}u(\omega)\frac{N}{1 + s(\omega)}.$$ \hspace{1cm} (1.97)

With (1.94) this can be written as,

$$P = \hbar \omega \frac{A_{21}}{2} \frac{N}{1 + s(\omega)^{-1}}.$$ \hspace{1cm} (1.98)

Let us now remember that the absorption cross section (1.73) of a homogeneously broadened line is Lorentzian. This means that the saturation parameter itself becomes Lorentzian. We can assume that the relaxation rate $A_{21}$ is independent of $\omega$ within the frequency range of the line profile,

$$s(\omega) = s(\omega_0) \frac{(\Gamma/2)^2}{\Delta^2 + (\Gamma/2)^2}.$$ \hspace{1cm} (1.99)

Substituting this into (1.98) yields the frequency dependence of the absorbed radiation power per unit frequency interval $d\omega$,

$$P = \hbar \omega \frac{A_{21}}{2} \frac{N}{2} \frac{s(\omega_0)(\Gamma/2)^2}{(\omega - \omega_0)^2 + (\Gamma/2)^2[1 + s(\omega_0)]} = N\bar{I}\sigma(\omega_0) \frac{(\Gamma/2)^2}{\Delta^2 + (\gamma_s/2)^2},$$ \hspace{1cm} (1.100)

where we introduced the increased halfwidth of the Lorentzian profile,

$$\gamma_s \equiv \Gamma \sqrt{1 + s(\omega_0)}.$$ \hspace{1cm} (1.101)

Apparently, the halfwidth of the saturation-broadened line increases with the resonant saturation parameter $s(\omega_0)$. If according to (1.94) the induced transition rate at resonance equals the total relaxation rate $A_{21}/2$, the resonant saturation parameter becomes $s(\omega_0) = 1$, which increases the linewidth by a factor $\sqrt{2}$, compared to the unsaturated linewidth $\Gamma$ for weak radiation fields. Starting from (1.100) we can define a saturated absorption cross section,

$$\sigma_s(\omega) = \sigma_s(\omega_0) \frac{(\gamma_s/2)^2}{\Delta^2 + (\gamma_s/2)^2} = \sigma(\omega_0) \frac{(\Gamma/2)^2}{\Delta^2 + (\gamma_s/2)^2} = \sigma(\omega) \frac{1}{1 + s(\omega)},$$ \hspace{1cm} (1.102)
where the unsaturated absorption profile is,

\[ \sigma(\omega) = \sigma(\omega_0) \frac{(\gamma/2)^2}{\Delta^2 + (\gamma/2)^2}. \]  

(1.103)

This shows that the saturation decreases the absorption coefficient by the factor \(1 + s(\omega)\). At the line center, this factor has its maximum value \(1 + s(\omega_0)\), while it decreases to 1 for increasing \(|\Delta|\), see (1.101), see Fig. 1.11. This is the reason why the line broadens.

From (1.96) we see, that unity saturation, \(s(\omega_0) = 1\), corresponds to a light intensity of,

\[ \bar{I}_{\text{sat}} \equiv \frac{\hbar \omega}{2\sigma(\omega_0)} \Gamma = \frac{2\pi^2 c \hbar}{3\lambda^2} \Gamma. \]  

(1.104)

This intensity is called *saturation intensity*. Taking account of the degeneracies \(g_j\) of the levels the saturation intensity becomes \(^{10}\),

\[ I_{\text{sat}} = \frac{g_1}{g_2} \frac{2\pi^2 \hbar}{3\lambda_0^2} \Gamma. \]  

(1.105)

---

**Figure 1.11:** (code) Optical cross section at various saturation parameters.

Finally, we note that the resonant saturation parameter is basically a measure for the ratio between the stimulated population transfer rate, given by the the Rabi frequency \(\Omega\) and the spontaneous decay rate \(\Gamma\),

\[ s(\omega_0) = \frac{2\Omega^2}{\Gamma^2}. \]  

(1.106)

We thus obtain the important relationship between laser intensity and Rabi frequency,

\[ \Omega^2 = \sigma(\omega_0) \frac{\bar{I}}{\hbar \omega_0} \Gamma. \]  

(1.107)

\(^{10}\)Some authors define the saturation for \(s = 2\), as happens when \(\Omega = \Gamma\).
1.2.9 Specific heat of solids

The Debye model applies Planck’s law on the distribution of energy in electromagnetic radiation, which treats radiation as a gas of photons, to the energy distribution of atomic vibrations in a solid, treating them as a gas of phonons in a box (the box being the solid). Most of the steps of the calculation are identical, as both are examples of a massless bosonic gas with linear dispersion relation.

According to the equipartition theorem, every atom has 3 degrees of freedom due to its translational motion. Thus, in a crystal lattice with \( N \) atoms, we expect the total energy \( E = 3Nk_B T \) and the specific heat should be, following the Dulong-Petit law,

\[
C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk_B ,
\]

for all solids regardless of temperature.

It was observed, however, that the specific heat of solids decreases like \( C_V \propto T^3 \) as \( T \) approaches zero. It was Einstein’s idea to apply Planck’s formula by treating the \( N \) atoms as three-dimensional harmonic oscillators vibrating in a lattice. The discrete energies \( n\hbar\omega \) are identified with quasi-particles called phonons. The quantum nature of atoms does not matter, they just provide the medium supporting the phonons. Following the Bose-Einstein statistics, we must replace,

\[
k_B T \rightarrow \hbar\omega/(e^{\hbar\omega/k_B T} - 1) ,
\]

such that the derivative of the energy,

\[
C_V = \left( \frac{\partial}{\partial T} \frac{3Nk_B \hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right)_V = 3Nk_B \left( \frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} ,
\]

gives the specific heat. The disappearance of the specific heat at low temperatures,

\[
C_V \simeq \frac{3N(\hbar\omega)^2}{k_B T^2} e^{-\hbar\omega/(k_B T)} ,
\]

which is related to the finite localization energy of harmonic oscillators, does not describe experimental observations very well, and the model had to be refined by Debye, later on.

1.2.9.1 Debye model for the specific heat

While Einstein assumed monochromatic lattice vibrations, Debye’s approach was to allow a spectrum of vibrational frequencies. With the density of states,

\[
\rho(\nu) d\nu = \frac{4\pi V}{3} \nu^2 d\nu ,
\]

where \( v \) is the velocity of sound propagation, the formula is totally equivalent to the density-of-states for photons in a cavity. Assuming that there is an upper bound \( \nu_m \) for the vibrational frequencies, we normalize as \( 3N_0 = \int_0^{\nu_m} \rho(\nu) d\nu \). The energy now is \(^{11}\)

\[
E = \int_0^{\nu_m} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \frac{4\pi V}{3} \nu^3 d\nu = 9Nk_B \frac{T^4}{\theta^3} \int_0^{\theta/T} \frac{x^3 dx}{e^x - 1} .
\]

\(^{11}\)The fact that the electron gas also has a heat capacity is neglected.
The Debye temperature $\theta = h\nu_m/k_B$ is characteristic for the metal. The derivative is then,

$$C_V = 9Nk_B \left[ 4 \left( \frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3dx}{e^x - 1} - \frac{\theta}{T} e^{\theta/T} - 1 \right].$$ \hspace{1cm} (1.114)

At low temperatures this formula reproduces the Debye law,

$$C_V = \frac{12\pi^4}{5} Nk_B \left( T/\theta \right)^3.$$ \hspace{1cm} (1.115)

### 1.2.10 Exercises

#### 1.2.10.1 Ex: Resistance of vacuum

Show that $\sqrt{\mu_0/\varepsilon_0}$ has the dimension of a resistance and the value of 376.7 $\Omega$.

#### 1.2.10.2 Ex: The laws of Planck and Rayleigh-Jeans

Show that Planck’s law reproduces the Rayleigh-Jeans law in the low-frequency limit.

#### 1.2.10.3 Ex: The laws of Wien and Stefan-Boltzmann

a. Derive the parametrization of Planck’s law in terms of frequency $\nu$ and wavelength $\lambda$.

b. Derive the law of Stefan-Boltzmann according to which the total power radiated per unit surface area of a black body across all wavelengths (also known as the black-body radiant emittance) is given by $\sigma T^4$, where $\sigma \equiv \pi^2 k_B^4/60c^2\hbar^3$ is called the Stefan-Boltzmann constant.

c. Derive Wien’s displacement law according to which the maximum emission of a blackbody spectrum occurs at $\lambda_{\text{max}}T = 2.898 \times 10^{-3}$ Km in the wavelength parametrization and $\nu_{\text{max}}/T = 0.0588$ THz/K in the frequency parametrization. Determine the frequency of the maximum emission for the 2.7 K background radiation of the universe.

#### 1.2.10.4 Ex: Photons in a resonator

a. The light power emitted by a laser ($\lambda = 633$ nm) be $P = 1$ nW. How many photons does the laser emit per second? How many laser photons are in a mode volume of $L = 10$ cm length?

b. How many photons on average are inside an optical cavity having the same mode volume at ambient temperature, when there is no incident light?

#### 1.2.10.5 Ex: Number of modes in a cavity

a. How many modes do fit into a cubical box of 10 cm size for a frequency interval of 1000 Hz centered at a wavelength of 500 nm?

b. How many photons are in the box supposing it has a temperature of $T = 300$ K, respectively, $T = 6000$ K?
1.2.10.6  Ex: Number of photons emitted from lasers and blackbodies

a. Calculate the total number of photons per area per unit time emitted by a blackbody at temperature $T$.
b. The linewidth of a helium-neon laser is $\Delta \nu = 1000$ Hz. The operating wavelength is $\lambda = 632.8$ nm, the power is $P = 1$ mW, and the beam size $w_0 = 1$ mm. How many photons are emitted per second?
c. What would be the temperature of a blackbody radiator emitting the same number of photons from an equal area and over the same frequency interval as the laser?

1.2.10.7  Ex: Number of photons per radiation mode

Assume the isotropic emission of a pulsed flashlamp with spectral bandwidth $\Delta \lambda = 100$ nm around $\lambda = 400$ nm amounts to $P_0 = 100$ W peak power out of a volume of 1 cm$^3$. Calculate the spectral power density $u(\nu)$ and the spectral intensity $I(\nu)$ through a spherical surface $r = 2$ cm away from the center of the emitting sphere. How many photons per mode are contained in the radiation field?

1.2.10.8  Ex: Atoms in an optical cavity

a. Consider a closed optical cavity at $T = 600^\circ C$. The cavity has the shape of a $L = 1$ m-long and $d = 3$ cm-diameter tube. Calculate the total energy of the blackbody radiation inside the cavity.
b. Inside the cavity there is a gas with strontium atoms (1 fundamental level and 3 degenerate excited levels, $\lambda = 461$ nm). Using the expression (1.61), assuming thermal equilibrium, calculate the number of excited atoms for a partial pressure of the strontium gas of $10^{-3}$ mbar.
c. Calculate the optical density for a laser in resonance with the transition traversing the cavity along the symmetry axis.

1.2.10.9  Ex: Sodium atoms in an optical cavity

A sodium atom is placed in a cavity of volume $V = 1$ cm$^3$ with walls at the temperature $T$, producing a thermal radiation field with spectral energy density $\bar{u}(\nu)$. At what temperature $T$ are the spontaneous and induced transition probabilities equal

a. for the transition $3P \rightarrow 3S$ with the transition wavelength $\lambda = 589$ nm and the excited state lifetime $\tau_{3P} = 16$ ns;
b. for the hyperfine transition $3S (F = 3 \rightarrow F = 2)$ with the transition frequency $\nu = 1772$ MHz and the excited state lifetime $\tau_{3F} \simeq 1$ s?

1.2.10.10  Ex: Applying the Lambert-Beer law

The beam of a monochromatic laser passes through an absorbing atomic vapor with path length $L = 5$ cm. If the laser frequency is tuned to the center of an absorbing transition $|i\rangle \rightarrow |k\rangle$ with absorption cross section $\sigma_0 = 10^{-14}$ cm$^2$, the attenuation of the transmitted intensity is 10%. Calculate the atomic density $n_i$ in the absorbing level $|i\rangle$. 

Chapter 2

Foundations and mathematical tools

In the following, we will introduce step by step the formalism of quantum mechanics by gradually increasing the degree of abstraction. Applications of the formalism will be shown in consecutive chapters.

2.1 Basic notions

2.1.1 Dispersion relation and Schrödinger equation

A fundamental problem in physics is the issue of the propagation of physical entities. On one hand, we have the light, whose propagation in the vacuum is described by the dispersion relation \( \omega = ck \) or,

\[
\omega^2 - c^2k^2 = 0.
\] (2.1)

Since light is a wave, in the most general form, assuming the validity of the superposition principle, it can be described by a wave packet,

\[
A(r,t) = \int e^{i(k \cdot r - \omega t)} a(k) d^3k.
\]

It is easy to verify that the wave equation,

\[
\frac{\partial^2}{\partial t^2} A - c^2 \nabla^2 A = 0,
\] (2.2)

reproduces the dispersion relation.

On the other hand, we have slow massive particles possessing kinetic energy,

\[
E = \frac{p^2}{2m}.
\] (2.3)

With the hypothesis of de Broglie that even a massive particle has wave quality, we can try an ansatz \(^1\) of a wave equation satisfying the dispersion relation (2.3). From Planck’s formula, \( E = \hbar \omega \), and the formula of Louis de Broglie, \( p = \hbar k \), describing the particle by a wave packet \( \psi(r,t) = \int e^{i(k \cdot r - \omega t)} \varphi(k) d^3k \) not subject to external forces, it is easy to verify that the equation,

\[
\hbar \frac{\partial}{\partial t} \psi = \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi,
\] (2.4)

\(^1\)Trial, working hypothesis.
reproduces the dispersion relation. If the particle is subject to a potential, its total energy is \( E = p^2/2m + V(r,t) \). This dispersion relation corresponds to the famous Schrödinger equation,

\[
\hbar \frac{\partial}{\partial t} \psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r,t) \right) \psi . 
\] (2.5)

2.1.2 Relativistic particle waves

Despite the similarities between light particles and material particles, there are notable differences: The photon is a relativistic particle with no rest mass. How can we establish a relationship between such different objects?

To clarify this relationship we now consider particles that are similar to light in the sense that they have high velocities, that is, relativistic particles. From the relativistic principle of the equivalence of mass and energy, we obtain for a massive particle

\[
E^2 = m^2c^4 + c^2p^2 
\]
or,

\[
\omega^2 - c^2k^2 = \frac{m^2c^4}{\hbar^2} . 
\] (2.6)

This dispersion relation can be obtained from the differential equation,

\[
\frac{\partial^2}{\partial t^2} A - c^2 \nabla^2 A = -\frac{m^2c^4}{\hbar^2} A , 
\] (2.7)

inserting, for example, the already proposed wave packet \( A(r,t) = \int e^{i(k \cdot r - \omega t)} a(k) d^3k \), supposed not to be subject to external forces. The equation (2.7) is a wave equation called Klein-Gordon equation. For particles without rest mass, as in the case of photons, the equation is reduced to the wave equation of light (2.2).

Now, making the transition to non-relativistic velocities, \( v \ll c \), we can expand the dispersion relation,

\[
E = \sqrt{m^2c^4 + c^2m^2v^2} = mc^2 \left( 1 + \frac{v^2}{2c^2} + \ldots \right) \text{ or } \hbar \omega \simeq mc^2 + \frac{\hbar^2k^2}{2m} . 
\] (2.8)

In analogy with the Klein-Gordon equation we can derive the approximate dispersion relation (2.8) from a wave equation,

\[
\hbar \frac{\partial}{\partial t} A = \left( mc^2 - \frac{\hbar^2}{2m} \nabla^2 \right) A . 
\] (2.9)

With the transformation \( \psi = e^{-imc^2t/\hbar} A \), we rediscover the Schrödinger equation (2.4),

\[
\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \Delta \psi
\] (2.10)
as the non-relativistic limit of the Klein-Gordon equation.

It is interesting to note that in all cases discussed, obviously the dispersion relations and the differential equations can be interconverted by the substitutions,

\[
E \rightarrow \hbar \frac{\partial}{\partial t} \quad \text{and} \quad p \rightarrow -i\hbar \nabla . 
\] (2.11)

We will discuss this later in the context of Ehrenfest’s theorem in Secs. 2.1.6, 2.1.7, and 2.4.5.
2.1. BASIC NOTIONS

2.1.3 Born’s interpretation

The first part of this script is devoted to individual particles or systems of distinguishable massive particles, and we will only turn our attention to light and indistinguishable particles when discussing the (second) quantization of fields.

According to our current conviction, the complete reality (neglecting relativistic effects) on any system is contained in the Schrödinger equation (2.5). That statement does not make us smarter without having to explaining the meaning of the wavefunction \( \psi \). In an attempt to marry the concepts of particles and waves, Max Born proposed in 1926 the interpretation of the quantity

\[
\int_V |\psi(r, t)|^2 d^3r
\]  

(2.12)

as probability of finding the particle inside the volume \( V \).

If \( |\psi(r, t)|^2 \) has the meaning of a probability density or probability distribution, the square of the wavefunction must be integrable,

\[
\|\psi(r, t)\|^2 \equiv \int_{\mathbb{R}^3} |\psi(r, t)|^2 d^3r < \infty .
\]  

(2.13)

This allows us to proceed to a normalization of the wave function,

\[
\tilde{\psi}(r, t) \equiv \frac{\psi(r, t)}{\sqrt{\int_{\mathbb{R}^3} |\psi(r, t)|^2 d^3r}},
\]  

(2.14)

such that \( \|\tilde{\psi}(r, t)\| = 1 \).

2.1.4 Continuity equation

In quantum mechanics we associate the wavefunction that describes a quantum system to a probability wave. As the Schrödinger equation describes a time evolution, in order to be useful, the wavefunction must allow for probability flows. We define the probability density and the probability flow by,

\[
\rho(r, t) \equiv \psi^*(r, t)\psi(r, t) ,
\]  

(2.15)

\[
\mathbf{j}(r, t) \equiv \frac{\hbar}{2mi} [\psi^*(r, t)\nabla \psi(r, t) - \psi(r, t)\nabla \psi^*(r, t)] .
\]  

Starting from the Schrödinger equation we can easily derive the continuity equation (see Exc. 2.1.8.1),

\[
\dot{\rho}(r, t) + \nabla \cdot \mathbf{j}(r, t) = 0 ,
\]  

(2.16)

or in the integral form,

\[
-\frac{d}{dt} \int_V \rho d^3r = \int_V \nabla \cdot \mathbf{j} d^3r = \oint_{\partial V} \mathbf{j} \cdot d\mathbf{S} ,
\]  

(2.17)

using Gauß’ law. With \( I \equiv \int_S \mathbf{j} \cdot d\mathbf{S} \), the probability current which flows through the surface \( S \) delimiting the probability charge \( Q \equiv \int_V \rho(r, t) d^3r \), we obtain,

\[
-Q = I .
\]  

(2.18)

The continuity equation is obviously similar to that of electromagnetism.
2.1.5 Distributions in space and time

So far we only spoke of spatial distributions, $\psi(r, t)$. But we could also consider velocity or moment distributions. In classical mechanics, a particle has a well-defined position and velocity. Knowing the position and velocity, Newton’s equations allow predicting its coordinates at future times. Let us now investigate whether the Schrödinger equation allows this as well.

The more general solution of the Schrödinger equation can be written as a superposition of plane waves $e^{i(r \cdot k - \omega t)}$ with frequencies $\omega = p^2/(2\hbar m)$ and wave vectors $k = p/\hbar$. Each plane wave has an individual amplitude $\varphi(p)$, such that,

$$
\psi(r, t) = \frac{1}{\hbar^{3/2}} \int d^3p \varphi(p)e^{i(r \cdot k - \omega t)} = \int d^3p \frac{1}{\hbar^{3/2}} \varphi(p)e^{i(r \cdot p/h - p^2t/2mh)} ,
$$

with $h \equiv 2\pi\hbar$. At time $t = 0$, this expansion is nothing more than a Fourier transform,

$$
\psi(r, 0) = \frac{1}{\hbar^{3/2}} \int d^3p \varphi(p)e^{ir \cdot k} ,
$$

that we can reverse,

$$
\varphi(p) = \frac{1}{\hbar^{3/2}} \int d^3r \psi(r, 0)e^{-ir \cdot k} .
$$

In the absence of forces the momentum distribution becomes stationary. We can now use the momentum distribution $\varphi(p)$ as coefficients of the expansion of the temporal wavefunction $\psi(r, t)$, as shown above. Thus, the expansion represents a general solution of the time-dependent Schrödinger equation. The magnitude $|\varphi(p)|^2$ is the probability density in momentum space.

**Example 3 (Normalization of the wave function in momentum space):** It is easy to show that the probability density in momentum space is also normalized:

$$
\int |\varphi(p)|^2d^3p = \frac{4\pi^2}{\hbar^3} \int d^3p \int d^3r \psi^*(r)\psi(r)e^{ir \cdot k} = \frac{4\pi^2}{\hbar^3} \int d^3k \delta^3(r - r') = \int |\psi(r)|^2d^3r = 1 ,
$$

knowing that the Fourier transform of a plane wave is nothing more than the Dirac distribution.

Since the probability distributions $|\psi(r)|^2$ and $|\varphi(p)|^2$ are interconnected by Fourier transform, we already know that we can not localize both simultaneously. If one is well localized, the other is necessarily delocalized. Do the Exc. 2.1.8.2.  

---

2Localize: Restrict the distribution volume indefinitely.
2.1. BASIC NOTIONS

2.1.6 Eigenvalues

We have already seen that the position and momentum distributions of a particle are spread. We calculate the mean values of these distributions, denoted by \( \langle r \rangle \) and \( \langle p \rangle \), as first moments of the respective distributions:

\[
\langle r \rangle = \int d^3r |\psi(r,t)|^2 r \quad \text{and} \quad \langle p \rangle = \int d^3p |\varphi(p,t)|^2 p . \tag{2.22}
\]

Using the expansions (2.19) and (2.20), we can calculate,

\[
\langle p \rangle = \int \varphi^*(p) p \varphi(p) d^3p = \int \frac{1}{\hbar i} \int \psi^*(r) e^{ikr} d^3r p \varphi(p) d^3p = \int \frac{1}{\hbar i} \int \psi^*(r) \frac{\hbar}{i} \nabla \varphi(p) d^3p d^3r = \int \varphi^*(r) \frac{\hbar}{i} \nabla \psi(r) d^3r .
\]

This calculation shows that the expectation value, called eigenvalue, of the momentum can be expressed through an operator \( \hat{p} \equiv (\hbar/i) \nabla \) acting on the wavefunction.\(^3\)

More generally, we can compute the eigenvalue of a function in \( r \) and \( p \) via,

\[
\langle f(r,p) \rangle = \int d^3r \psi^*(r) f(r,\hat{p}) \psi(r) . \tag{2.23}
\]

However, it is important to note that the operators \( \hat{r} \) and \( \hat{p} \) do not necessarily commute.

**Example 4 (Non-commutation of space and momentum):** Considering a one-dimensional motion, we verify,

\[
\hat{p}_x \psi = \frac{\hbar}{i} \frac{d}{dx} \psi = \frac{\hbar}{i} \psi + \frac{\hbar}{i} \frac{d}{dx} \psi \neq \frac{\hbar}{i} \frac{d}{dx} \psi = x \hat{p}_x \psi .
\]

2.1.7 Temporal evolution of eigenvalues

We now consider the temporal evolution of the position of a particle. We will use in the following the partial integration rule \( \int_V \psi \nabla \xi = \oint_{\partial V} \psi \xi - \int_V \nabla \psi \xi = - \int_V (\nabla \psi) \xi \), assuming that at least one of the functions, \( \psi \) or \( \xi \), disappears at the edge of the volume, which can be guaranteed by choosing the volume large enough. To begin with, we will concentrate on the \( x \)-component of the position, the time derivative of which is computed using the continuity equation (2.16),

\[
\frac{d}{dt} \langle x \rangle = \int d^3r \frac{d}{dt} |\psi|^2 x = - \int d^3r x \nabla \cdot j = - \int d^3r \int_{-\infty}^0 \frac{d}{dt} x^+ j^+ + \int d^3r j \cdot \nabla x = \int d^3r j_x , \tag{2.24}
\]

\(^3\)From now on, the hat over a physical magnitude will denote quantum operators.

\(^4\)We note here that the rules \( \langle \psi | \hat{x} | \psi \rangle \leftrightarrow \langle \phi | - \frac{\hbar}{i} \nabla_p | \phi \rangle \) and \( \langle \psi | \frac{\hbar}{i} \nabla_x | \psi \rangle \leftrightarrow \langle \phi | \hat{p} | \phi \rangle \) from the Fourier transformation are useful for numerical simulations of the Schrödinger equation: Instead of calculating the spatial derivative \( \left( \frac{\hbar}{i} \nabla \right)^2 \) of the wavefunction, one makes a Fast Fourier Transform (FFT) to momentum space, multiplies with \( p \), and transforms back.
Generalizing to three dimensions, we can write,
\[
\frac{d}{dt} \langle m \mathbf{r} \rangle = m \int d^3 r \frac{\hbar}{2mi} [\psi^* \nabla \psi - \psi \nabla \psi^*] \tag{2.25}
\]
\[
= \frac{1}{2} \int d^3 r [\psi^* \hat{p} \psi + \psi \hat{p} \psi^*] = \int d^3 r \psi^* \hat{p} \psi = \langle \hat{p} \rangle ,
\]
since the eigenvalue of \( \hat{p} \) is a real quantity.

Now, we define the abbreviation:
\[
\hat{H} \equiv -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) ,
\tag{2.26}
\]
called the Hamilton operator or Hamiltonian and we calculate the second derivative of the position using the Schrödinger equation (2.5),
\[
\frac{d}{dt} \langle \hat{p} \rangle = \int d^3 r \left[ \left( \frac{i}{\hbar} \hat{H} \psi \right)^* \hat{p} \psi + \psi^* \hat{p} \frac{i}{\hbar} \hat{H} \psi \right] = \frac{i}{\hbar} \int d^3 r \psi^* (\hat{H} \hat{p} - \hat{p} \hat{H}) \psi = \frac{i}{\hbar} \langle [\hat{H}, \hat{p}] \rangle ,
\tag{2.27}
\]
introducing the commutator \([\hat{a}, \hat{b}] \equiv \hat{a} \hat{b} - \hat{b} \hat{a}\) as an abbreviation. After that,
\[
\frac{i}{\hbar} \langle [\hat{H}, \hat{p}] \rangle = \frac{i}{\hbar} \langle [\hat{V}, \hat{p}] \rangle = \frac{i}{\hbar} \int d^3 r \psi^* \left[ \frac{\hat{V} \hbar}{i} \nabla \psi - \frac{\hbar}{i} \nabla (V \psi) \right] = -\int d^3 r \psi^* \psi \nabla V = \langle \hat{F} \rangle .
\tag{2.28}
\]
In summary, we found a law,
\[
\langle \hat{F} \rangle = \frac{d^2}{dt^2} \langle m \mathbf{\hat{r}} \rangle ,
\tag{2.29}
\]
much like the Newton law, but instead of applying to localized particles, the law applies to the eigenvalues of probability distributions. Similar laws can be derived for angular momentum and energy conservation.

The observation made by Paul Ehrenfest, that in quantum mechanics the mean values follow the same laws of classical mechanics, is called Ehrenfest’s theorem.

2.1.8 Exercises

2.1.8.1 Ex: Conservation of probability

Demonstrate the conservation of local probability through the definitions of probability densities, \( \rho(\mathbf{r}, t) \), and probability current \( \mathbf{j}(\mathbf{r}, t) \).

2.1.8.2 Ex: Fourier theorem

The spatial distribution of a particle is given by a Gaussian function with the width \( \Delta x \). Calculate the momentum distribution and its width \( \Delta p \). Just consider one spatial dimension. Show that \( \Delta x \Delta p = \hbar \) using the rms definition for the widths.

2.2 Postulates of quantum mechanics

In this section we will introduce the fundamentals and main methods of quantum mechanics. We will learn what are observables and get to know the postulates which establish the foundation of quantum mechanics, as well as Heisenberg’s famous principle of uncertainty.
2.2. POSTULATES OF QUANTUM MECHANICS

2.2.1 Superposition principle (1. postulate)

A physical system can be found in several states. For example, a particle may be at rest or in motion, an atom may be excited or deexcited. In quantum mechanics, every possible state is described by a wavefunction $\psi$. Wavefunctions can be functions of various types of coordinates, for example, of position $\psi = \psi(r)$, of momentum $\psi = \psi(p)$, or of energy $\psi = \psi(E)$. The choice of the coordinates is called representation.

One peculiarity of quantum systems is that they may be in a superposition of states. That is, if $\psi_1, \psi_2, \ldots, \psi_k$ are possible states with amplitudes $c_k$, automatically the functions,

$$\psi = \sum_k c_k \psi_k \quad \text{or} \quad \psi = \int dk c(k) \phi(k) \quad (2.30)$$

are possible states as well. This is called superposition principle, and means, for example, that a particle may be simultaneously in several places or that an atom may be at the same time excited and deexcited.

There are systems that can only exist in a restricted number of states, such as the two-level atom. Others may exist in an infinite number of states or even in a continuous distribution of states.

2.2.2 Interpretation of the wave function (2. postulate)

A state function (or wavefunction) characterizes a system of which we may calculate various properties. The function can adopt complex values devoid of immediate physical interpretation. In fact, the wavefunction is above all a mathematical construct. On the other hand, the norm $|\psi|^2$ has the meaning of a probability of the system to be in the state $\psi$. This is the famous interpretation of Max Born of the wave function (see Sec. 2.1.3).

If $\psi_k$ with $k = 1, 2, \ldots$ are all possible states of a system, the interpretation as a probability requires,

$$\sum_k |\psi_k|^2 = 1 \quad (2.31)$$

Analogically, for a continuous distribution, for example, in spatial representation,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad (2.32)$$

That is, the probability needs normalization.

2.2.3 Dirac bra-ket notation and vector representation

In order to distinguish more easily the amplitudes (which are complex numbers) and the wavefunctions we will now use the Bra-Ket notation introduced by Paul Dirac. The functions are represented by kets,

$$|\psi\rangle = \sum_k c_k |k\rangle \quad (2.33)$$
The complex transpositions of these states are represented by bras,

$$\langle \psi | = | \psi \rangle \dagger = \sum_{k} c_{k}^{*} \langle k | .$$ (2.34)

But the notation has other advantages. For example, let us suppose that we know the three possible states of a system, $|1\rangle$, $|2\rangle$, and $|3\rangle$, which are linearly independent. Then we can define the states as vectors:

$$|1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} , \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} , \quad |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} .$$ (2.35)

These three states can be interpreted as the basis of a vector space representing the system. Now, each wavefunction can be expanded on this basis and expressed by a vector. An arbitrary ket state of this system will then be,

$$|\psi\rangle = \begin{pmatrix} c_{1} \\ c_{2} \\ c_{3} \end{pmatrix} .$$ (2.36)

The corresponding bra state will be,

$$\langle \psi | = (c_{1}^{*} \quad c_{2}^{*} \quad c_{3}^{*}) .$$ (2.37)

Now we can easily calculate the probability for a system to be in a state $|\psi\rangle$,

$$||\psi||^{2} = \langle \psi | \psi \rangle = (c_{1}^{*} \quad c_{2}^{*} \quad c_{3}^{*}) \cdot \begin{pmatrix} c_{1} \\ c_{2} \\ c_{3} \end{pmatrix} = |c_{1}|^{2} + |c_{2}|^{2} + |c_{3}|^{2} .$$ (2.38)

### 2.2.4 Observables (3. postulate)

The only way to get information about a system is to measure the values of characteristic quantities of the system, e.g. energy or linear momentum. In classical mechanics we have learned that a system can be completely characterized by a set of measurable physical quantities. For example, the motion of a rigid body of mass $m$ and inertial moment $I$ is defined by its position $r$, its moment $p$, and its angular momentum $L$. In quantum mechanics we describe observable physical quantities by operators acting on the Hilbert space of wavefunctions, $|\psi\rangle \mapsto \hat{p} |\psi\rangle$, where $\hat{p}$ would be the operator of the linear momentum. To better distinguish the observables, we decorate their symbols with a hat. We will see more ahead (see Sec. 2.3.5) that every quantum system is completely described by a complete set of observables.

To find the current values $a_{\psi}$ of any observable $\hat{A}$ in a specific situation given by a wave function $\psi$, we need to solve an equation of eigenvalues,

$$\hat{A}|\psi\rangle = a_{\psi} |\psi\rangle .$$ (2.39)

We can rewrite the equation as $a_{\psi} = \langle \psi | \hat{A} |\psi\rangle$. The values $a_{\psi}$ are real numbers, if the observable is a Hermitian operator, that is,

$$\hat{A} = \hat{A}^{\dagger} \implies a_{\psi} = a_{\psi}^{*} .$$ (2.40)
2.2. POSTULATES OF QUANTUM MECHANICS

We leave proof of this for the Exc. 2.2.9.1.

Thus, we postulate the substitution of the dynamic variable characterizing a classical system by abstract objects called operators. These operators can be understood as mathematical prescriptions, e.g., differential operators acting on a state of the system. The expectation value of any operator \( \hat{A} \) characterizing a system in a state \( |\psi\rangle \) is
\[
a_{\psi} \equiv \langle \hat{A} \rangle_\psi \equiv \langle \psi | \hat{A} | \psi \rangle / \langle \psi | \psi \rangle.
\]
Such operators are specific for a system, but independent of its state. The dynamical variables for a specific state are obtained as eigenvalues of the respective variable in that specific state. The temporal evolution of the operators or of the states is governed by equations of motion (see Sec. 2.4)\(^5\).

2.2.5 Representation of operators as matrices

In the same way as we already represented wavefunctions by vectors, we can also represent operators by matrices,
\[
\hat{A} \equiv \sum_{i,j} |i \rangle a_{ij} \langle j| = \begin{pmatrix} \vdots & \vdots \\ a_{ij} & \vdots \\ \vdots & \vdots \end{pmatrix} = \begin{pmatrix} \langle j | \hat{A} | i \rangle & \vdots \\ \vdots & \vdots \end{pmatrix}.
\]
(2.41)

To extract components from a matrix we do, \( \langle i | \hat{A} | j \rangle \), for example,
\[
\langle 1 | \hat{A} | 1 \rangle = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \cdot \hat{A} \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} = a_{11}.
\]
(2.42)

**Projectors** are particular operators defined by,
\[
\hat{P}_k \equiv |k\rangle \langle k| = \begin{pmatrix} 0 & \vdots & \vdots \\ \vdots & 1 & \vdots \\ \vdots & \vdots & 0 \\ 0 & \vdots & \vdots \end{pmatrix}.
\]
(2.43)

The eigenvalue of a projector, \( \langle \hat{P}_k \rangle = \langle \psi | \hat{P}_k | \psi \rangle = |\langle k | \psi \rangle|^2 \), is nothing more than the probability of finding a system, whose general state is \( |\psi\rangle \), in the particular state, since expanding as done in (2.33), we have,
\[
\langle \hat{P}_k \rangle = \sum_{m,n} c_m^* c_n \langle m | k \rangle \langle k | n \rangle = |c_k|^2.
\]
(2.44)

Using the matrix formalism we can define other interesting operators and verify their properties,
\[
|1\rangle \langle 1| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad |2\rangle \langle 2| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix},
\]
\[
|1\rangle \langle 2| = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad |2\rangle \langle 1| = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \hat{\sigma}^+.
\]
(2.45)

\(^5\)Note that there are theoretical attempts to generalize the concept of observables to non-Hermitian operators [45, 46] only displaying \(PT\)-symmetry.
The rising and lowering operators,
\[ \hat{\sigma}^\pm = \frac{1}{2}(\hat{\sigma}_x \pm i\hat{\sigma}_y) , \]  
are also called Pauli spin matrices, because they were introduced by Wolfgang Pauli.

The vector,
\[
\hat{\sigma} \equiv \begin{pmatrix}
\hat{\sigma}_x \\
\hat{\sigma}_y \\
\hat{\sigma}_z 
\end{pmatrix} = \begin{pmatrix}
\hat{\sigma}^+ + \hat{\sigma}^- \\
i(\hat{\sigma}^- - \hat{\sigma}^+) \\
[\hat{\sigma}^+ , \hat{\sigma}^-]
\end{pmatrix}
\]  
(2.47)
is called Pauli vector and the vector
\[
\vec{\rho} \equiv \begin{pmatrix}
\langle \hat{\sigma}_x \rangle \\
\langle \hat{\sigma}_y \rangle \\
\langle \hat{\sigma}_z \rangle
\end{pmatrix}
\]  
(2.48)
is called Bloch vector.\(^6\) The eigenvalue of the Bloch vector has a fixed length (see Exc. 2.2.9.2).

The representation of physical quantities by matrices allows the description of quantum superposition states. The purpose of Exc. 2.2.9.3 is to illustrate this at the example of a particle passing through a double slit.

2.2.6 Correspondence principle (4. postulate)

Operators do not necessarily commute. We have already seen in Sec. 2.1.6, that in one dimension the position and the momentum operators do not commute. We can generalize to three dimensions via,
\[ [\hat{p}_j, \hat{x}_k] = -i\hbar \delta_{jk} \quad \text{and} \quad [\hat{p}_j, \hat{p}_k] = 0 = [\hat{x}_j, \hat{x}_k] , \]  
(2.49)
which is easily verified by replacing the operators with \( \hat{x}_k = x_k \) and \( \hat{p}_k = \frac{\hbar}{i} \nabla \) and allowing the commutators to act on a wavefunction \( \psi(x) \).

Conversely, quantum mechanics follows from classical mechanics with the prescription \(^8\), \( A(q_k, p_k, t) \rightarrow \hat{A}(\hat{q}_k, \hat{p}_k, t) = \hat{A} \). Letting the smallest amount of energy possible go to zero, \( \hbar \rightarrow 0 \), the commutator disappears, the energy spectrum becomes continuous, and we recover classical mechanics.

2.2.7 Schrödinger equation and quantum measurements (5. postulate)

The time evolution is given by the Schrödinger equation,
\[ i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle . \]  
(2.50)

\(^6\)The Bloch vector is widely used in describing the interaction of a two-level system with a light field.

\(^7\)Schrödinger invented the wave mechanics when he derived his wave equation from the dispersion relation for massive particles. Heisenberg invented a mechanics (detailed in later sections), which he called mechanics of matrices. Later, he showed the formal equivalence of both theories.

\(^8\)Considering the Weyl order.
A closed system, disconnected from the rest of the world (we will now call the rest of the world reservoir) is not subject to dissipation, i.e., it does not lose energy to the reservoir. Such a system is always described by a hermitian Hamiltonian. Unfortunately, this system also does not allow information leakage, that is, we cannot measure the system. This is reflected in the fact that the Schrödinger equation does not allow to describe the process of a quantum measurement. This is because before the measurement, the system can be in several states or even in a superposition of states, while after the measurement we know exactly the state. This amounts to a reduction of entropy, which is not allowed in a closed system.

The famous postulate of state reduction or projection of the wavefunction formulated by John von Neumann describes the quantum measurement process as a sequence of two distinct steps. In a first step, the measuring apparatus projects the measured operator $\hat{A}$ on an eigenvector basis. That is, if the measurement is compatible with the operator $\hat{1}$, we obtain a distribution of probability amplitudes of the results,

$$\hat{A} \rightarrow \langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \langle \psi | \hat{A} | \sum_k c_k | k \rangle = \sum_k a_k c_k \langle \psi | k \rangle = \sum_k a_k | c_k |^2 ,$$

(2.51)

with $\langle \psi | \psi \rangle = \sum_k | a_k |^2 = 1$. Therefore, we can understand $| \langle k | \psi \rangle |^2$ as the probability of the system to be in the eigenstate $| k \rangle$.

Figure 2.1: Superposition.

In a second step, the observing scientist will read the measuring device and note the result, which will necessarily be one of the possible $a_k$,

$$\langle \hat{A} \rangle \rightarrow a_k .$$

(2.52)

---

9 For simplicity, we only consider pure state, here.

10 To understand the meaning of compatible, we must establish a more complete theory of measurement including the reservoir in the quantum description.

11 Alternatively, $\hat{A} \rightarrow \sum_k | k \rangle \langle \hat{A} | k \rangle \langle k |$. 
If the state is stationary, it will never change any more. That is, each subsequent measurement will yield the same result. The Ex. 2.2.9.4 illustrates the process of quantum measurement at the example of a measurement of the excitation energy of a two-level atom.

### 2.2.8 Stationary Schrödinger equation

The general form of the Schrödinger equation in one dimension is,

\[
\hat{H}\Psi(t, x) = \frac{i\hbar}{\partial t}\Psi(t, x) ,
\]

with \(\hat{H} \equiv \frac{\hat{p}^2}{2m} + V(x, t)\) and \(\hat{p} \equiv -i\hbar \frac{\partial}{\partial x}\). If the potential is independent of time, \(V(x, t) = V(x)\), we can do the following ansatz, \(\Psi(x, t) \equiv \psi(x)f(t)\). Insertion into the Schrödinger equation yields,

\[
\frac{1}{\psi(x)} \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi(x) = \frac{i\hbar}{f(t)} \frac{d}{dt}f(t) = \text{const.} \equiv E .
\]  

The solution of the right-hand side of the equation is \(i\hbar(\ln f - \ln f_0) = E(t - t_0)\). Hence,

\[
f(t) = f(0)e^{-iE(t-t_0)/\hbar}.
\]  

Obviously, \(|\Psi(x, t)|^2 = |\psi(x)|^2\).

Now, we can see that the stationary Schrödinger equation,

\[
\hat{H}\psi(x) = E\psi(x) ,
\]

is nothing more than an eigenvalue equation. This means that the Schrödinger wave mechanics is equivalent to the mechanics of the Heisenberg matrices. The Excs. 2.2.9.5 and 2.2.9.6 are first simple calculations of the eigenvalues and eigenvectors of a two-level system.

### 2.2.9 Exercises

#### 2.2.9.1 Ex: Reality of eigenvalues

Show that the eigenvalues of an observable are real.

#### 2.2.9.2 Ex: Normalization of the Bloch vector

Calculate the eigenvalue of the length of the Pauli vector and the length of the Bloch vector (2.47).

#### 2.2.9.3 Ex: Quantum superposition

Discuss how matrices can describe the creation of superposition states at the example of a particle passing through a double slit. Identify the slits with the states \(\langle 1| = (1 \ 0)\) and \(\langle 2| = (0 \ 1)\) and construct an observable for the position of the particle. How this observable must behave in the classical limit?
2.2.9.4 **Ex: Quantum measurement**

Explain the idea of quantum measurement at the example of a measurement of the excitation energy of a two-level atom.

2.2.9.5 **Ex: Two-level atom**

Consider a two-level atom. The Hamiltonian is given by,

\[
\hat{H} = \begin{pmatrix} 0 & 0 \\ 0 & \hbar \omega_0 \end{pmatrix}.
\]

Using the stationary Schrödinger equation, calculate the eigenvalues and eigenvectors.

2.2.9.6 **Ex: The ammonium molecule**

Consider the two states \(|1\rangle\) and \(|2\rangle\) of the ammonium molecule outlined in the figure. Suppose they are orthormal, \(\langle i|j \rangle = \delta_{ij}\), and that only these two states are accessible to the system, so that we can describe it using the basis formed by \(|1\rangle\) and \(|2\rangle\). On this basis the Hamiltonian \(\hat{H}\) of the system is given by,

\[
\hat{H} = \begin{pmatrix} E_0 & -E_1 \\ -E_1 & E_0 \end{pmatrix}.
\]

a. If the system is initially in state \(|1\rangle\), will it remain in that state at a later time? How about if the initial state is \(|2\rangle\)?

b. Obtain the eigenvalues \(E_I\) and \(E_{II}\) and the respective eigenvectors \(|I\rangle\) and \(|II\rangle\) of \(\hat{H}\), expressing them in terms of \(|1\rangle\) and \(|2\rangle\).

c. What is the probability of measuring an energy \(E_I\) in the following state,

\[|\psi\rangle = \frac{1}{\sqrt{5}}|1\rangle - \frac{2}{\sqrt{5}}|2\rangle\]

b. Based on the above result, we can predict at least one possible electromagnetic radiation emission frequency for an ammonia sample. What is this frequency?

Figure 2.2: The two states of the ammonium molecule.

2.3 **Abstract formalism of quantum mechanics**

The formal development of quantum mechanics will be the subject of this section. We will learn how to find a complete set of observables characterizing a system, discuss the role of symmetries in quantum mechanics and show how to switch between several representations of the same system.
2.3.1 Lie algebra

The quantum mechanical operators form a Lie algebra \( \mathcal{L}^2 \). This means that \( \mathcal{L}^2 \) is at the same time a complex and linear vector space with respect to addition and scalar multiplication and a non-commutative ring with scalar internal product. In particular, \( \mathcal{L}^2 \) is unitary, normalized, and complete and acts on a Hilbert space of quantum states,

\[
\hat{A}^\dagger \hat{B} |\psi\rangle = \hat{A} (\hat{B} |\psi\rangle).
\]

\[
(\hat{A} + \hat{B}) |\psi\rangle = \hat{A} |\psi\rangle + \hat{B} |\psi\rangle,
\]

\[
(\alpha \hat{A}) |\psi\rangle = \alpha (\hat{A} |\psi\rangle),
\]

\[
(\hat{A}\hat{B}) |\psi\rangle = \hat{A}(\hat{B} |\psi\rangle).
\]

The properties of the Hilbert space are,

\[
\hat{A} |\psi + \varphi\rangle = \hat{A} |\psi\rangle + \hat{A} |\varphi\rangle,
\]

\[
\hat{A} |a\psi\rangle = a \hat{A} |\psi\rangle.
\]

For a Hermitian operator, \( \hat{A} = \hat{A}^\dagger \), we have \( \langle \psi | \hat{A} |\psi\rangle = \langle \hat{A} \psi |\psi\rangle \) or \( \langle \hat{A} \rangle \equiv \langle \psi | \hat{A} |\psi\rangle = \langle \hat{A} \rangle^\ast \), using the Dirac bra-ket notation,

\[
\langle \psi | \dagger \equiv |\psi\rangle.
\]

There are identity and nullity operators,

\[
\hat{1} |\psi\rangle = |\psi\rangle \quad \text{and} \quad \hat{0} |\psi\rangle = 0.
\]

We define the (anti-)commutator as,

\[
[\hat{A}, \hat{B}]_\mp = \hat{A}\hat{B} \pm \hat{B}\hat{A},
\]

which can be \( \neq 0 \). The sum of two hermitian operators is hermitian, but the product is not, since,

\[
(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger = \hat{A} + \hat{B} \quad \text{but} \quad (\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger = \hat{B}\hat{A} \neq \hat{A}\hat{B}.
\]

On the other hand, the following relations of hermitian operators are always hermitian,

\[
\hat{A}\hat{B} + \hat{B}\hat{A} \quad \text{and} \quad i(\hat{A}\hat{B} - \hat{B}\hat{A}.
\]

We define the scalar product as,

\[
\langle \psi | \varphi \rangle.
\]

Two states are called orthogonal, if \( \langle \psi | \varphi \rangle = 0 \). The norm is written as,

\[
|\psi|^2 = \langle \psi | \psi \rangle,
\]

the deviation is,

\[
\Delta A \equiv \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}.
\]

A unitary operator is defined by \( \hat{A}^{-1} = \hat{A}^\dagger \).
2.3.2 Complete bases

If it is impossible to find a set of amplitudes \( c_n \),

\[
\{c_n\} \text{ such that } \sum_n c_n |n\rangle = 0 ,
\]

(2.67)

the functions are called \textit{linearly independent}. A set of linearly independent functions may form a \textit{basis}. The space opened by a set of linearly independent functions is called \textit{Hilbert space}.

An operator \( \hat{A} \) is completely characterized by its \textit{eigenvalues} and \textit{eigenfunctions}. If a set of eigenfunctions \( |n\rangle \) is \textit{complete}, every allowed state of the system can be expanded in these eigenfunctions,

\[
|\psi\rangle = \sum_n c_n |n\rangle \quad \text{and} \quad \hat{A}|n\rangle = a_n |n\rangle .
\]

(2.68)

To calculate properties of a specific system, we often want to find a matrix representation for the operator \( \hat{A} \). For this, we solve the stationary Schrödinger equation, that is, we calculate the eigenvalues and \textit{eigenvectors}. When all eigenvalues are different, \( a_n \neq a_m \), we know that the corresponding eigenvectors are orthogonal, \( \langle n|m\rangle = 0 \),

\[
\hat{A}|n\rangle = a_n |n\rangle , \quad \hat{A}|m\rangle = a_n |m\rangle , \quad \forall\{n, m\} a_n \neq a_m \quad (2.69)
\]

\[
\implies \forall\{n, m\} \langle n|m\rangle = \delta_{m,n} .
\]

Exc. 2.3.9.1 asks for demonstrating this.

Frequently, for example, in the case of a particle confined to a potential, there exist discrete eigenvalues (for \( E < 0 \)) simultaneously with continuous eigenvalues (for \( E > 0 \)). Assuming \( \langle m|m'\rangle = \delta_{m,m'} \), \( \langle m|k\rangle = 0 \) and \( \langle k|k'\rangle = \delta^{(3)}(k - k') \), with a complete base,

\[
\sum_m |m\rangle\langle m| + \int d^3k |k\rangle\langle k| = \mathbb{1} ,
\]

(2.70)

an arbitrary vector can be expanded on an orthogonal basis,

\[
|\psi\rangle = \sum_m |m\rangle\langle m|\psi\rangle + \int d^3k |k\rangle\langle k|\psi\rangle .
\]

(2.71)

This also applies to observables,

\[
\hat{A} = \sum_{m,n} |m\rangle\langle m|\hat{A}|n\rangle\langle n| + \int d^3kd^3l |k\rangle\langle k|\hat{A}|l\rangle\langle l| ,
\]

(2.72)

and functions of observables,

\[
f(\hat{A}) = \sum_{m,n} |m\rangle f(\langle m|\hat{A}|n\rangle)\langle n| + \int d^3kd^3l |k\rangle f(\langle k|\hat{A}|l\rangle)\langle l| .
\]

(2.73)
2.3.3 Degeneracy

The eigenvectors form a natural basis for the Hilbert space. However, a problem arises in the case of degeneracy, that is, when some eigenvalues are equal, $a_n = a_m$. In this case, the eigenvectors that correspond to degenerate eigenvalues are not completely defined, and we have to construct a basis verifying that all constructed eigenvectors are orthogonal. For this, there exists the method of orthogonalization by Schmidt, which works like this: We assume that we have already solved the eigenvalue equation, that is, we found a degenerate eigenvalue, $\hat{A}|a_k\rangle = a|a_k\rangle$ for every $k = 1, \ldots, g_k$, where $g_k$ is the degree of degeneracy, and that we also found a complete basis of eigenvalues $|a_m\rangle$, but which is not orthogonal, that is, $\exists \{m, n\}$ with $\langle a_n | a_m \rangle \neq 0$. The task is to build another basis $|b_m\rangle$ satisfying $\langle b_n | b_m \rangle = \delta_{n,m}$.

The first vector of the orthogonal base can be chosen freely, e.g.,

$$|b_1\rangle \equiv |a_1\rangle . \quad (2.74)$$

Since the basis $\{|a_k\rangle\}$ is assumed to be complete, the second vector is necessarily a linear combination of vectors $|a_k\rangle$, that is, $|b_2\rangle = |a_2\rangle + \lambda |b_1\rangle$. With the condition $\langle b_1 | b_2 \rangle = 0 = \langle b_1 | a_2 \rangle + \lambda \langle b_1 | b_1 \rangle$, we determine the parameter $\lambda$, and obtain for the second vector,

$$|b_2\rangle \equiv |a_2\rangle - |a_1\rangle \frac{\langle b_1 | a_2 \rangle}{\langle b_1 | b_1 \rangle} . \quad (2.75)$$

In the same way, we can derive for a third vector, $|b_3\rangle = |a_3\rangle + \mu |b_1\rangle + \nu |b_2\rangle$, the conditions, $\langle b_1 | a_3 \rangle = 0 = \langle b_1 | a_3 \rangle + \mu \langle b_1 | b_1 \rangle$ and $\langle b_2 | b_3 \rangle = 0 = \langle b_2 | a_3 \rangle + \nu \langle b_2 | b_2 \rangle$, and obtain,

$$|b_3\rangle \equiv |a_3\rangle - |a_1\rangle \frac{\langle b_1 | a_3 \rangle}{\langle b_1 | b_1 \rangle} - |b_2\rangle \frac{\langle b_2 | a_3 \rangle}{\langle b_2 | b_2 \rangle} . \quad (2.76)$$

An overall way of writing this down is,

$$|b_k\rangle \equiv \left( 1 - \frac{|b_1\rangle \langle b_1|}{\langle b_1 | b_1 \rangle} - \frac{|b_2\rangle \langle b_2|}{\langle b_2 | b_2 \rangle} - \ldots - \frac{|b_{k-1}\rangle \langle b_{k-1}|}{\langle b_{k-1} | b_{k-1} \rangle} \right) |a_k\rangle . \quad (2.77)$$

In the Exc. 2.3.9.2 we practice the orthogonalization of a set of three linearly independent but non-orthogonal vectors, and in the Exc. 2.3.9.3 we find an orthogonal basis for a partially degenerate three-level system.

2.3.4 Bases as unitary operators

One way to formulate the eigenvalue problem is as follows: Let $|n\rangle$ be an orthonormal basis with the respective eigenvalues $a_n$ of an operator $\hat{A}$:

$$\hat{A}|n\rangle = a_n |n\rangle \quad \text{with} \quad \langle n | m \rangle = \delta_{mn} . \quad (2.78)$$

We construct the matrices,

$$U \equiv \begin{pmatrix} |1\rangle & |2\rangle & \cdots \end{pmatrix} \quad \text{and} \quad \hat{E} \equiv \begin{pmatrix} a_1 & 0 & \cdots \\ 0 & a_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} . \quad (2.79)$$
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With the definition of $U^\dagger$ we have,

$$
U^\dagger = \begin{pmatrix}
\langle 1 | \\
\langle 2 | \\
\vdots
\end{pmatrix}
$$

and

$$
U^\dagger U = \begin{pmatrix}
\langle 1|1 \rangle & \langle 1|2 \rangle & \cdots \\
\langle 2|1 \rangle & \langle 2|2 \rangle & \cdots \\
\vdots & \vdots & \ddots
\end{pmatrix} = \hat{1}.
$$

(2.80)

Therefore,

$$
U^\dagger U = \hat{1} \implies U^\dagger U U^{-1} = \hat{1} U^{-1} \implies U^\dagger = U^{-1} \quad \text{(2.81)}
$$

Also,

$$
\hat{A} |n\rangle = \hat{E} |n\rangle \quad \text{and} \quad \hat{A} U = U \hat{E}.
$$

(2.82)

That is, by knowing the unitary matrix (or transformation matrix) $U$, we can solve the eigenvalue problem simply by $\hat{E} = U^{-1} \hat{A} U$.

Note, that this does not apply to a non-orthonormal basis. In this case, we need to do a Schmidt orthogonalization and use the condition $\det \hat{U} = 1$. We apply the technique detailed in this section to solve Excs. 2.3.9.4 and 2.3.9.5.

2.3.5 Complete set of commuting operators

Even for simple systems, we can ask various types of questions (measurements). Considering, for example, a particle flying freely in space, we can gather its position or its velocity. Let $a$ be the result of a measurement of the observable $\hat{A}$, that is, $a = \langle \psi_a | \hat{A} | \psi_a \rangle$. Due to the measurement we know that the system is in the state $| \psi_a \rangle$. Immediately after this first measurement we perform another measurement of another observable $\hat{B}$ giving $\langle \psi_a | \hat{B} | \psi_a \rangle$. The result of this measurement can only yield an eigenstate, $b = \langle \psi_a | \hat{B} | \psi_a \rangle$, if the operators commute, $[\hat{A}, \hat{B}] = 0$. That is, if two operators $\hat{A}$ and $\hat{B}$ commute, and if $|\psi\rangle$ is an eigenvector of $\hat{A}$, then $|\psi\rangle$ is also an eigenvector of $\hat{A}$ with the same eigenvalue:

$$
[\hat{A}, \hat{B}] = 0, \quad a = \langle \psi | \hat{A} | \psi \rangle \quad \implies \hat{A} (\hat{B}|\psi\rangle) = a (\hat{B}|\psi\rangle) \quad \text{and} \quad \langle \psi | \hat{B} | \psi \rangle \in \mathbb{R}.
$$

(2.83)

In addition, we observe that if two operators commute, the orthonormal basis constructed for one of the operators is also orthonormal for the other. That is, if two operators $\hat{A}$ and $\hat{B}$ commute and if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two eigenvectors of $\hat{A}$ with different eigenvalues, then the matrix element $\langle \psi_1 | \hat{B} | \psi_2 \rangle$ is equal to zero:

$$
[\hat{A}, \hat{B}] = 0, \quad a_1 = \langle \psi_1 | \hat{A} | \psi_1 \rangle \neq \langle \psi_2 | \hat{A} | \psi_2 \rangle = a_2 \quad \implies \langle \psi_1 | \hat{B} | \psi_2 \rangle = 0.
$$

(2.84)

Finally, we affirm that, if two operators $\hat{A}$ and $\hat{B}$ commute, we can construct an orthonormal basis $\{|\psi_{a,b}\rangle\}$ with common eigenvectors of $\hat{A}$ and $\hat{B}$:

$$
[\hat{A}, \hat{B}] = 0 \implies \exists \{|\psi_{a,b}\rangle\} \quad \text{tal que} \quad \hat{A} |\psi_{a,b}\rangle = a |\psi_{a,b}\rangle \quad \text{and} \quad \hat{B} |\psi_{a,b}\rangle = b |\psi_{a,b}\rangle.
$$

(2.85)
The statements (2.83) to (2.85) are verified in Exc. 2.3.9.6.

The fact that commuting operators have a common system of eigenvectors authorizing sharp eigenvalues can be used to construct and characterize a state.

**Example 5 (Measuring momenta in orthogonal directions):** For example, the obvious solutions of the eigenvalue equations,

\[
\hat{p}_x |\psi_{p_x}\rangle = \frac{\hbar}{i} \frac{d}{dx} |\psi_{p_x}\rangle = p_x |\psi_{p_x}\rangle \quad \text{and} \quad \hat{p}_y |\psi_{p_y}\rangle = \frac{\hbar}{i} \frac{d}{dy} |\psi_{p_y}\rangle = p_y |\psi_{p_y}\rangle
\]

are the plane waves \( e^{ip_x x/\hbar} \) and \( e^{ip_y y/\hbar} \). Therefore, the total state of the particle can be described by,

\[
|\psi_{p_x, p_y, p_z}\rangle = |\psi_{p_x}\rangle |\psi_{p_y}\rangle = e^{(i/\hbar)(p_x x + p_y y)} f(z) .
\]

However, these eigenfunctions are infinitely degenerate, since the linear momentum in \( z \)-direction is not specified. A third operator \( \hat{p}_z |\psi\rangle = p_z |\psi\rangle \) commutes with the others,

\[
[\hat{p}_k, \hat{p}_m] = 0 .
\]

Hence,

\[
|\psi_{p_x, p_y, p_z}\rangle = e^{(i/\hbar)(p_x x + p_y y + p_z z)} ,
\]

is a possible state of the system.

On the other hand, choosing \( \hat{p}_z^2 = -\hbar^2 \frac{\partial^2}{\partial z^2} \) as the third operator, giving the eigenvalues \( p_z^2 \), the state would have been,

\[
|\psi_{p_x, p_y, p_z^2}\rangle = e^{(i/\hbar)(p_x x + p_y y)} \cos \frac{p_z z}{\hbar} \quad \text{or} \quad |\psi_{p_x, p_y, p_z^2}\rangle = e^{(i/\hbar)(p_x x + p_y y)} \sin \frac{p_z z}{\hbar} .
\]

Therefore, there are two solutions with the same eigenvalues, \( p_x, p_y, p_z^2 \). To lift this degeneracy, we need to introduce yet another observable. This observable can be, for example, the *parity* \( \hat{P} \), that is, the behavior of the wave function upon mirroring \( z \rightarrow -z \) in the \( x-y \) plane. The fact that the set of operators \( p_x, p_y, p_z \) on one hand and \( p_x, p_y, p_z^2, \hat{P} \) on the other are equivalent, shows that the required number of observables for a complete characterization depends on their judicious choice.

Also, the number needed for a complete set of commuting operators (CSCO) depends on the number of degrees of freedom and the symmetry of the system. In the case of the free particle in one dimension it is enough to consider one observable only, for example, \( \hat{x} \) or \( \hat{p} \). In three dimensions, we already need at least three commuting observables. In Exc. 2.3.9.7 we will try to find a CSCO for a matrix with partially degenerate eigenvalues.

### 2.3.6 Uncertainty relation

We have already learned that observables that do not commute cannot be measured with arbitrary precision. This principle can be quantified as follows: If \( \hat{A} \) and \( \hat{B} \) are two observables, then,

\[
\Delta \hat{A} \Delta \hat{B} \geq \frac{1}{2} |[\hat{A}, \hat{B}]| .
\]

(2.87)
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This is Heisenberg’s famous uncertainty principle. For example, $[\hat{p}, \hat{x}] = -i\hbar$, and hence, $\Delta p \Delta x \geq \hbar/2$. We will see later (see Sec. 3.3.1), that $[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$ such that $\Delta l_x\Delta l_y \geq \hbar\langle l_z \rangle/2$. More difficult to show, since time has no simple quantum operator, is $\Delta E \Delta t \geq \hbar/2$. In the Exc. 2.3.9.8 we will show the Schwartz inequality, and in the Exc. 2.3.9.9 we ask for a formal derivation of Heisenberg’s uncertainty principle.

2.3.7 Representations

2.3.7.1 Spatial representation

A Hilbert space can be discrete or, as in the case of the momentum of a free particle, continuous. In this latter case, the eigenvalues are continuously distributed, since the equation,

$$-i\hbar \nabla_r \psi(r) = p\psi(r), \quad (2.88)$$

has solutions for each value of $E$. The eigenfunctions are $\psi(r) = ae^{ip \cdot r/\hbar}$. Eq. (2.88) clearly has the form of an eigenvalue equation, for which we have already introduced the Heisenberg matrix formalism. The question now is how these descriptions combine.

Observables that do not commute correspond to expansions on different bases and generate alternative representations. For example, we can represent quantum mechanics in position space or linear momentum space. If $|r\rangle$ is a basis of the space of the particles’ state,

$$\hat{r}|r\rangle = r|r\rangle, \quad \langle r'|r\rangle = \delta^3(r' - r), \quad \int_{\mathbb{R}^3} |r\rangle\langle r|d^3r = 1, \quad (2.89)$$

we can expand the position operator on a position basis as,

$$\hat{r} = \int_{\mathbb{R}^3} r|r\rangle\langle r|d^3r, \quad (2.90)$$

and any state vector as,

$$|\psi(t)\rangle = \int_{\mathbb{R}^3} |r\rangle\psi(t, r)d^3r. \quad (2.91)$$

The quantities $\langle r|\psi(t)\rangle = \psi(t, r)$ Schrödinger wave functions. We can also say that the wavefunctions are the coordinates of the state in the particular base $|r\rangle$. Consequently,

$$\langle r|\hat{f}|r'\rangle = r\delta^3(r - r') \quad (2.92)$$

and

$$\langle r|f(\hat{r})|r'\rangle = f(r)\delta^3(r - r'). \quad (2.93)$$

It is also true that,

$$\langle r|\hat{A}|\psi(t)\rangle = \int_{\mathbb{R}^3} A(r, r')\psi(t, r')d^3r', \quad (2.93)$$

where the quantity $A(r, r') \equiv \langle r|\hat{A}|r'\rangle$ is called kernel of the operator. The transition from Heisenberg’s abstract mechanics to Schrödinger’s wave mechanics is done by the substitutions $|\psi(t)\rangle \rightarrow \psi(t, r)$ and $\hat{A} \rightarrow A(r, r')$. 


2.3.7.2 Momentum representation

The uncertainty relation is symmetric in \( \hat{r} \) and \( \hat{p} \). Nothing prevents us from choosing as a basis,

\[ \hat{p}|p\rangle = p|p\rangle \quad , \quad \langle p'|p\rangle = \delta^3(p' - p) \quad , \quad \int_{\mathbb{R}^3} |p\rangle\langle p| d^3p = \mathbf{\hat{1}} , \]  

(2.94)
in which we can expand the momentum operator on a momentum basis as,

\[ \hat{p} = \int_{\mathbb{R}^3} p|p\rangle\langle p| d^3p , \]  

(2.95)
with the wavefunctions,

\[ |\psi(t)\rangle = \int_{\mathbb{R}^3} |p\rangle \varphi(p, t) d^3p , \]  

(2.96)
where \( \langle p|\psi(t)\rangle = \varphi(t, p) \). The formulas are analogous to the ones in the spatial representation. In particular, in the momentum representation the position operator is \( \hat{r} = \hbar \nabla \hat{p} \).

The representations follow from one another by Fourier transformation. Since

\[ -\hbar \nabla \varphi(r)|p\rangle = p\varphi(r)|p\rangle , \]  

we know,

\[ \langle r|p\rangle = \frac{1}{\hbar^{3/2}} \exp\left(\frac{i}{\hbar} r \cdot p \right) , \]  

(2.97)
where the prefactor \( \hbar^{-3/2} \) is introduced to take account of the unit of the states. \( \psi \) and \( \varphi \) are different representations of the same quantum state related by,

\[ \langle r|\psi(t)\rangle = \int_{\mathbb{R}^3} \langle r'|p\rangle \langle p|\psi(t)\rangle d^3p = \frac{1}{\hbar^{3/2}} \int_{\mathbb{R}^3} e^{ir \cdot p/\hbar} \varphi(p, t) d^3p = \varphi(r, t) \]  

(2.98)
\[ \langle p|\psi(t)\rangle = \int_{\mathbb{R}^3} \langle p|r\rangle \langle r|\psi(t)\rangle d^3r = \frac{1}{\hbar^{3/2}} \int_{\mathbb{R}^3} e^{-ir \cdot p/\hbar} \varphi(r, t) d^3r = \varphi(p, t) . \]

Normalization ensures that \( \psi = \mathcal{F}^{-1}\mathcal{F}\psi \) with the relation,

\[ \delta(x) = \lim_{t \to \infty} \frac{1}{2\pi} \int_{-t}^{t} e^{ikx} dk . \]  

(2.99)
Using the wavevector \( \hbar \mathbf{k} = p \) we can also write,

\[ \psi(r) = \frac{1}{(2\pi \hbar)^{3/2}} \int_{\mathbb{R}^3} e^{i\mathbf{r} \cdot \mathbf{k}} \tilde{\varphi}(\mathbf{k}) d^3k \quad \text{and} \quad \tilde{\varphi}(\mathbf{k}) = \frac{1}{(2\pi \hbar)^{3/2}} \int_{\mathbb{R}^3} e^{-i\mathbf{r} \cdot \mathbf{k}} \psi(r) d^3r , \]  

(2.100)
defining the function \( \tilde{\varphi}(\mathbf{k}) \equiv \hbar^{3/2} \varphi(p) \). Applying the Fourier transform to functions of operator we can calculate,

\[ \langle r|G(\mathbf{p})|r'\rangle = \int d^3p \langle r|G(\mathbf{p})|p\rangle \langle p|r'\rangle = \int d^3p G(\mathbf{p}) \langle r|p\rangle \langle p|r'\rangle \]  

(2.101)
\[ = \frac{1}{\hbar^{3/2}} \int d^3p G(\mathbf{p}) e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} = \frac{1}{\hbar^{3}} (\mathcal{F}G)(\mathbf{r} - \mathbf{r}') . \]

\[ ^{12}\text{Note that the units of the wavefunctions are defined by normalization: } \langle r'|r\rangle = \delta^3(r - r') . \]

Introducing the parenthesis \([...]\) to extract the unit of a physical quantity, we find, \( [\mathbf{r}] = [\psi(\mathbf{r})] = [r^{-3/2}] \) and \( [p] = [\varphi(p)] = [p^{-3/2}] \). We do not assign a unit to the abstract state \( |\psi\rangle \), that is, \( ||\psi|| = 1 \).
In Exc. 2.3.9.10 we will show $\langle r | \hat{p} | \psi \rangle = (\hbar/i) \nabla_r \langle r | \psi \rangle$, thus justifying that we can understand an operator as a rule to determine what happens to a function. For example, the rule $\hat{p}_x$ asks for a derivation of the wavefunction by $x$.

### 2.3.8 Spanning a Hilbert space with several degrees of freedom

All systems analyzed up to this point were characterized by a single degree of freedom (e.g., energy, momentum, or angular momentum), which could have a continuous or discrete spectrum. Even when we treated systems exhibiting various degrees of freedom (motion of a particle in 3D space, electron orbitals in the hydrogen atom), we always found a way to separate the degrees of freedom into orthogonal Hilbert spaces, which allowed us to treat the dynamics of the degrees of freedom separately. In this chapter, we will establish the theoretical foundations allowing us to analyze systems, where degrees of freedom can not be separated because they are entangled or interact. In particular, we will consider the system of two spins and the coupling of angular momenta in general.

#### 2.3.8.1 Projection and internal sum

A **projector** is an operator which *reduces* the domain of an operator, originally acting on a Hilbert space $\mathcal{H}$ to the **subspace** defined by the projector. We consider an operator $\hat{A}$ with the matrix representation,

$$
\hat{A} \equiv \sum_{i,j} |i\rangle A_{ij} \langle j| = \begin{pmatrix} \vdots & \cdots & \cdots \\ \vdots & A_{ij} & \cdots \\ \vdots & \cdots & \vdots \end{pmatrix},
$$

acting on wavefunctions $|\psi\rangle \in \mathcal{H}$ which can be expanded on a basis $|i\rangle$ of $\mathcal{H}$. Now, we consider a subspace $\mathcal{R} \subset \mathcal{H}$ defined by the base $|k\rangle$. Then the projector $\hat{P}_\mathcal{R}$ can be represented by,

$$
\hat{P}_\mathcal{R} \equiv \sum_k |k\rangle \langle k| = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.
$$

Applied to the operator $\hat{A}$,

$$
\hat{A}_\mathcal{R} \equiv \hat{P}_\mathcal{R} \hat{A} = \hat{P}_\mathcal{R} \hat{A} \hat{P}_\mathcal{R} = \sum_{k,l} |k\rangle A_{kl} \langle l| = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \cdots & A_{kl} & 0 \\ 0 & \cdots & \cdots & 0 \end{pmatrix}.
$$
Applied to a state $|i\rangle$,

$$
|\psi\rangle_\mathcal{R} = \hat{P}_\mathcal{R}|\psi\rangle = \sum_k c_k |k\rangle = \begin{pmatrix} 0 \\ \vdots \\ c_k \\ 0 \end{pmatrix}.
$$

(2.105)

We study an example in the 2.3.9.11

Consequently, we can understand the Hilbert space as the sum of its subspaces,

$$
\hat{A} = \bigoplus \hat{A}_\mathcal{R} \quad \text{and} \quad \bigoplus \hat{P}_\mathcal{R} = \mathbb{I}.
$$

(2.106)

The dimensions of the subspaces are additive,

$$
\dim \hat{A} = \sum \dim \hat{A}_\mathcal{R}.
$$

**Example 6 (Projection for a three-level atom):** The Hamiltonian of a three-level atom with excitation of two transitions is given by,

$$
\hat{H} = \begin{pmatrix}
\omega_1 & \Omega_{12} & 0 \\
\Omega_{12} & \omega_2 & \Omega_{23} \\
0 & \Omega_{23} & \omega_3
\end{pmatrix}.
$$

The projector,

$$
\hat{P} = \begin{pmatrix} 1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{pmatrix}
$$

reduces the Hamiltonian to a two-level transition,

$$
\hat{H}_\mathcal{R} = \begin{pmatrix}
\omega_1 & \Omega_{12} & 0 \\
\Omega_{12} & \omega_2 & 0 \\
0 & 0 & 0
\end{pmatrix}.
$$

Obviously, the concatenation (2.106) only serves to increase the Hilbert space of a given degree of freedom described by a given observable, e.g., when we add one more level of energy to the spectrum of an atom described by a Hamiltonian. If, in contrast, we want to add another degree of freedom, we need the external sum or external product discussed below.

### 2.3.8.2 External product

We have previously worked with systems exhibiting more than one degree of freedom and therefore having to be characterized by more than one observable with its spectrum of eigenstates. One example are the electronic orbitals of the hydrogen atom $|n\ell m\rangle$, which need three quantum numbers to be labeled unambiguously. Obviously, each quantum number increases the dimensionality of the Hilbert space. Another
example is the system $|\alpha\beta\rangle$ of two particles with spin $\frac{1}{2}$, each spin being defined on its respective space,

$$|\alpha\rangle = \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = (\alpha_i)_i \in \mathcal{H}_A \quad \text{and} \quad |\beta\rangle = \begin{pmatrix} \beta_1 \\ \beta_2 \end{pmatrix} = (\beta_k)_k \in \mathcal{H}_B .$$

(2.107)

The combined state is,

$$|\alpha\beta\rangle \in \mathcal{H}_A \otimes \mathcal{H}_B \quad \text{with dim } \mathcal{H}_A \otimes \mathcal{H}_B = \text{dim } \mathcal{H}_A \text{ dim } \mathcal{H}_B .$$

(2.108)

The symbol $\otimes$ denotes the external tensorial product of two vectors (states). Now, in order to represent the multidimensional space $\mathcal{H}_A \otimes \mathcal{H}_B$ by a matrix, we use the fact that it is isomorphic to the space $\mathcal{H}_I \otimes \mathcal{H}_A \otimes \mathcal{H}_B$, that is, we proceed to a reorganization of the quantum numbers identifying,

$$|\gamma\rangle \equiv |\alpha\rangle |\beta\rangle = |\alpha\rangle \otimes |\beta\rangle = |\alpha\beta\rangle = \begin{pmatrix} \alpha_1 \beta_1 \\ \alpha_1 \beta_2 \\ \alpha_2 \beta_1 \\ \alpha_2 \beta_2 \end{pmatrix} = (\gamma_m)_m \in \mathcal{H}_A \otimes \mathcal{H}_B ,$$

(2.109)

where $m = 1, 2, 3, 4$ is identified with $(i, k) = (1, 1), (1, 2), (2, 1), (2, 2)$. The new vector is element of the 4-dimensional vector space $\mathcal{H}_A \otimes \mathcal{H}_B$. If $\{|\alpha\rangle_i\}$ and $\{|\beta\rangle_k\}$ are bases in their respective spaces $\mathcal{H}_A$ and $\mathcal{H}_B$, then $\{|\gamma\rangle_m\}$ is a basis of the product space $\mathcal{H}_A \otimes \mathcal{H}_B$.

Figure 2.3: Illustration of the isomorphism between $\mathcal{H}_A \otimes \mathcal{H}_B$ and $\mathcal{H}_I \otimes \mathcal{H}_A \otimes \mathcal{H}_B$.

For observables we proceed in the same way: The external product of two commutators spans a Hilbert product space with the dimension corresponding to product of the dimensions of the sub-spaces. Assuming that,

$$\hat{A} \equiv \sum_{i,j} |i\rangle A_{ij} \langle j| \quad \text{and} \quad \hat{B} \equiv \sum_{k,l} |k\rangle B_{kl} \langle l| .$$

(2.110)

then

$$\hat{A} \otimes \hat{B} \equiv \sum_{(ik)(jl)} |ik\rangle A_{ij} B_{kl} \langle jl| ,$$

such that

$$\dim \hat{A} \otimes \hat{B} = \dim \hat{A} \dim \hat{B} .$$

For example, $|i\rangle \langle j| \otimes |k\rangle \langle l| = |ik\rangle \langle jl|$. For two two-dimensional operators $\hat{A}$ and $\hat{B}$, the external product is defined by,

$$\hat{A} \otimes \hat{B} = \begin{pmatrix} A_{11}B_{11} & A_{11}B_{12} & A_{12}B_{11} & A_{12}B_{12} \\ A_{11}B_{21} & A_{11}B_{22} & A_{12}B_{21} & A_{12}B_{22} \\ A_{21}B_{11} & A_{21}B_{12} & A_{22}B_{11} & A_{22}B_{12} \\ A_{21}B_{21} & A_{21}B_{22} & A_{22}B_{21} & A_{22}B_{22} \end{pmatrix} ,$$

(2.112)
and can be decomposed as,

\[
\hat{A} \otimes \hat{B} = (\hat{A} \otimes \mathbb{I})(\mathbb{I} \otimes \hat{B}) = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}.
\]

(2.113)

The concept (2.111) can be generalized to more degrees of freedom like,

\[
\hat{A} \otimes \hat{B} \otimes \hat{C} = \sum_{(ikm)(jln)} |ikm\rangle A_{ij} B_{kl} C_{mn} \langle jln| ,
\]

(2.114)

Obviously, the external product is associative \((\hat{A} \otimes \hat{B}) \otimes \hat{C} = \hat{A} \otimes (\hat{B} \otimes \hat{C})\), but does not commute, even though the operators acting on different spaces do commute, \([\hat{A}, \hat{B}] = 0\). Nevertheless, we can reverse the order of the product of two operators using,

\[
\hat{A} \otimes \hat{B} = \hat{S}(\hat{B} \otimes \hat{A})\hat{S} \quad \text{with} \quad \hat{S} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.
\]

(2.115)

We note, that it is important to distinguish from what space the vector came from. In our notation, the vector before the symbol of the tensorial product \((\otimes)\) is belongs to the space \(\mathcal{H}_A\), and the one after the \(\otimes\) belongs to the space \(\mathcal{H}_B\). With the definition (2.110) we can verify that the operators only act on their respective states:

\[
(\mathbf{A} \otimes \mathbf{B})(|\alpha\rangle \otimes |\beta\rangle) = \mathbf{A}|\alpha\rangle \otimes \mathbf{B}|\beta\rangle.
\]

(2.116)

**Example 7 (External product):** We can check the relationship (2.116) by the definitions (2.109) and (2.112) of the external product,

\[
\left[ \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \otimes \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \right] \left[ \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} \otimes \begin{pmatrix} \beta_1 \\ \beta_2 \end{pmatrix} \right] = \begin{pmatrix} A_{11} B_{11} + A_{12} B_{12} \\ A_{21} B_{11} + A_{22} B_{12} \end{pmatrix} \begin{pmatrix} \alpha_1 \beta_1 \\ \alpha_2 \beta_2 \end{pmatrix} = \begin{pmatrix} (A_{11} \alpha_1 + A_{12} \alpha_2)(B_{11} \beta_1 + B_{12} \beta_2) \\ (A_{21} \alpha_1 + A_{22} \alpha_2)(B_{21} \beta_1 + B_{22} \beta_2) \end{pmatrix} = \begin{pmatrix} A_{11} A_{12} & A_{11} A_{22} \\ A_{21} A_{12} & A_{21} A_{22} \end{pmatrix} \begin{pmatrix} \alpha_1 \beta_1 \\ \alpha_2 \beta_2 \end{pmatrix}.
\]

(2.117)
2.3. DIRECT EXTERNAL SUM

Using the nomenclature (2.110) we define the external direct sum by,

\[ \hat{A} \oplus \hat{B} \equiv \sum_{(ik)(jl)} |ik\rangle (A_{ij} + B_{kl}) \langle jl| , \tag{2.118} \]

that is,

\[ \hat{A} \oplus \hat{B} = \begin{pmatrix} A_{11} + B_{11} & A_{11} + B_{12} & A_{12} + B_{11} & A_{12} + B_{12} \\ A_{11} + B_{21} & A_{11} + B_{22} & A_{12} + B_{21} & A_{12} + B_{22} \\ A_{21} + B_{11} & A_{21} + B_{12} & A_{22} + B_{11} & A_{22} + B_{12} \\ A_{21} + B_{21} & A_{21} + B_{22} & A_{22} + B_{21} & A_{22} + B_{22} \end{pmatrix} . \tag{2.119} \]

It can be decomposed as,

\[ \hat{A} \oplus \hat{B} = \hat{A} \oplus \hat{O} + \hat{O} \oplus \hat{B} = \hat{A} \otimes \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \otimes \hat{A} . \tag{2.120} \]

Again, using the definition (2.115) of the unitary operator \( \hat{S} \), we can reverse the order of the operator by,

\[ \hat{A} \oplus \hat{B} = \hat{S}(\hat{B} \oplus \hat{A}) \hat{S} . \tag{2.121} \]

**Example 8** (Direct external sum of two diagonal Hamiltonians): As an example we consider a two-level atom excited by radiation and trapped in an external harmonic potential. We assume that the degrees of freedom do not interact. As the Hamiltonian of the HO is diagonal, the total Hamiltonian is organized into a diagonal matrix of quadratic subspaces,

\[ \hat{H} = \hbar \omega (n + \frac{1}{2}) \oplus \begin{pmatrix} 0 & \hbar \Omega \\ \hbar \Omega & \hbar \Delta \end{pmatrix} = \begin{pmatrix} \hbar \omega & \hbar \omega + \hbar \Omega & 0 & 0 & \cdots \\ \hbar \omega & \hbar \omega + \hbar \Omega & 0 & 0 & \cdots \\ 0 & 0 & \frac{3}{2} \hbar \omega & \frac{3}{2} \hbar \omega + \hbar \Omega & \cdots \\ 0 & 0 & \frac{3}{2} \hbar \omega + \hbar \Omega & \frac{3}{2} \hbar \omega + \hbar \Delta & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix} . \]

It acts on the product state \( |n\rangle |i\rangle \), where the first ket denotes the vibrational level and the second ket the electronic excitation of the atom.

Other examples are studied in 2.3.9.12 and 2.3.9.13.

2.3.8.4 Trace

The **trace** of an operator over a subspace reduces its domain to the remaining dimensions (the \(-\)symbol is a place holder for the dimension over which we do NOT want to trace):

\[ \text{Tr}_B \hat{A} \otimes \hat{B} = \sum_{(ik)(jl)(-m)} \langle \cdot m | ik \rangle A_{ij} B_{kl} \langle jl| \cdot m = \sum_{(ik)(jl)(-m)} |i\rangle A_{ij} B_{kl} \langle j| \delta_{km} \delta_{lm} \]

\[ = \sum_{(i)(j)(m)} |i\rangle A_{ij} B_{mm} \langle j| = \hat{A} \sum_m B_{mm} = \hat{A} \text{Tr}_B \hat{B} . \tag{2.122} \]
For example, $\text{Tr}_\rho \hat{A} \otimes \hat{\rho} = \hat{A}$. See the Excs. 2.3.9.14 and 2.3.9.15.

It can be shown,

$$\text{Tr}\hat{A}\hat{B} = \text{Tr}\hat{B}\hat{A} \ . \quad (2.123)$$

### 2.3.9 Exercises

#### 2.3.9.1 Ex: Orthogonality

Show that two eigenvectors of a Hermitian operator associated with two different eigenvalues are orthogonal.

#### 2.3.9.2 Ex: Orthonormalization

Orthonormalize the base $\langle a_1 \rangle = (1 \quad -1 \quad 0)$, $\langle a_2 \rangle = (0 \quad 1 \quad 0)$, $\langle a_3 \rangle = (0 \quad 1 \quad 1)$.

#### 2.3.9.3 Ex: Orthonormal base

Construct an orthonormal basis for the following operator describing a partially degenerate three-level system,

$$\hat{A} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} .$$

#### 2.3.9.4 Ex: Eigenvalue equation

Calculate the unitary matrix $U$ transforming the Hamiltonian $\hat{H} = \begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix}$ into a diagonal matrix $E = U^\dagger \hat{H} U$.

#### 2.3.9.5 Ex: Eigenvalues and eigenvectors

Find the eigenvalues and -vectors of the operator $\hat{A} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$ and construct the unitary matrix which transforms this operator into a diagonal matrix.

#### 2.3.9.6 Ex: Commuting operators

a. Show that if two operators $\hat{A}$ and $\hat{B}$ commute and if $|\psi\rangle$ is an eigenvector of $\hat{A}$, $\hat{B}|\psi\rangle$ also is an eigenvector of $\hat{A}$ with the same eigenvalue.
b. Show that if two operators $\hat{A}$ and $\hat{B}$ commute and if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two eigenvector of $\hat{A}$ with different eigenvalues, the matrix element $\langle \psi_1 | \hat{B} | \psi_2 \rangle$ is equal to zero.
c. Show that if two operators $\hat{A}$ and $\hat{B}$ commute, we can construct an orthonormal basis of eigenvectors common to $\hat{A}$ and $\hat{B}$. 
2.3.9.7  **Ex: Eigenvalues**

a. Find the eigenvalues and eigenvectors of the operator \( \hat{A} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & \mu & 0 \\ 1 & 0 & 1 \end{pmatrix} \) for \( 0 < \mu < 2 \).

b. Write down the unitary matrix \( U \) satisfying the eigenvalue equation: \( \hat{A}U = UE_A \), where \( E_A \) is the matrix that has all eigenvalues of \( \hat{A} \) in its diagonal.

c. Now consider the case \( \mu = 0 \). Find a complete set of commuting operators (CSCO). That is, calculate the components of a second operator \( \hat{B} \) which commutes with \( \hat{A} \) as a function of its eigenvalues \( \lambda_1, \lambda_2, \) and \( \lambda_3 \), and verify \( [\hat{A}, \hat{B}] = 0 \). Find the most general form of operator \( \hat{B} \).

2.3.9.8  **Ex: Schwartz inequality**

Demonstrate the Schwartz inequality \( |\langle u|v \rangle|^2 \leq \langle u|u \rangle \langle v|v \rangle \).

2.3.9.9  **Ex: Heisenberg’s uncertainty principle**

Develop the formal derivation of Heisenberg’s uncertainty principle.

2.3.9.10  **Ex: Fourier transform**

Show that \( \langle \mathbf{r} | \hat{P} | \psi \rangle = \frac{\hbar}{i} \nabla \langle \mathbf{r} | \psi \rangle \) reproduces the Schrödinger equation in position representation.

2.3.9.11  **Ex: Projection of the motion of a particle**

Project the Hamiltonian of the motion of a free particle onto the plane \( x-y \) at the position \( z = z_0 \).

2.3.9.12  **Ex: Complete system of commuting operators**

Construct the Hilbert space of two independent two-level systems.

2.3.9.13  **Ex: Liouville equation**

Show that \( \left( \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \right) \otimes \hat{A} + \left( \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \right) \otimes \hat{B} = \hat{A} \oplus \hat{B} \).

2.3.9.14  **Ex: Liouville equation**

Show at the example of a two-level system that the von Neumann equation, \( \dot{\hat{\rho}} = \mathcal{L}\hat{\rho} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] \), can be written, \( \dot{\hat{\rho}} = -\frac{i}{\hbar} (\hat{H} \otimes I - I \otimes \hat{H}) \hat{\rho} \), using the definition of the external product.

2.3.9.15  **Ex: Unitary transformation of singlet states**

Consider two spins \( a \) and \( b \) that do not interact. Applying to each spin the same transformation to another base, show that the singlet state has in each base the following form: \( |\psi \rangle = \frac{1}{\sqrt{2}} (|\uparrow\rangle_a |\downarrow\rangle_b - |\downarrow\rangle_a |\uparrow\rangle_b) \).
2.4 Time evolutions

2.4.1 Unitary transformations

The best we can do to characterize a system is, obviously, to measure all its observables. However, neither the state functions nor the observables are fixed unambiguously, since defining a unitary operator, $\hat{U} = \hat{U}^\dagger$, we can do,

$$\langle \psi | \hat{A} | \psi \rangle = \langle \psi | \hat{U}^\dagger \hat{A} \hat{U}^\dagger \hat{U} | \psi \rangle = \langle \hat{U} \psi | \hat{A} \hat{U}^\dagger | \hat{U} \psi \rangle .$$  \hspace{1cm} (2.124)

That is, exchanging $| \psi \rangle$ by $\hat{U} | \psi \rangle$ and at the same time $\hat{A}$ by $\hat{U} \hat{A} \hat{U}^\dagger$, we obtain quantities describing the same physical reality, since the eigenvalues are unchanged. This allows us to choose the best mathematical representation for a specific problem. As an example, we will apply the temporal unitary transformation to solve the dynamics of a coupled two-level system in Exc. 2.4.6.1.

2.4.2 Schrödinger picture

Important examples of how the same system can be represented in different ways (related by unitary transformations) are the Heisenberg, Schrödinger, and interaction pictures.

The Schrödinger picture, denoted by the subscript $S$, is defined by the choice of a Hamiltonian,

$$\hat{H}_S = \hat{H}(t, \hat{p}_S, \hat{r}_S) \quad \text{with} \quad \frac{d}{dt} \hat{p}_S = \frac{d}{dt} \hat{r}_S = 0 .$$  \hspace{1cm} (2.125)

That is, the observables of the system $\hat{A}_S(t, \hat{p}_S, \hat{r}_S)$ can only depend explicitly on time, but not via the operators $\hat{p}_S$ and $\hat{r}_S$, which are stationary,

$$\frac{d}{dt} \hat{A}_S = \frac{\partial \hat{A}_S}{\partial t} + \hat{p}_S \frac{\partial \hat{A}_S}{\partial \hat{p}_S} + \hat{r}_S \frac{\partial \hat{A}_S}{\partial \hat{r}_S} .$$  \hspace{1cm} (2.126)

This is,

$$\frac{d}{dt} \hat{A}_S(t) = \frac{\partial \hat{A}_S}{\partial t} \hat{A}_S(t) .$$  \hspace{1cm} (2.127)

In this case, the formal solution of the Schrödinger equation,

$$\frac{i\hbar}{d} \frac{d}{dt} |\psi_S(t)\rangle = \hat{H}_S |\psi_S(t)\rangle ,$$  \hspace{1cm} (2.128)

can be written,

$$|\psi_S(t)\rangle = e^{-(i/\hbar)\hat{H}_S t}|\psi_S(0)\rangle \equiv \hat{U}(t)|\psi_S(0)\rangle .$$  \hspace{1cm} (2.129)

Apparently, the temporal dynamics is completely within the wave functions.

Example 9 (The time evolution operator): Generalizing to an arbitrary initial time $t_0$ we write the temporal translation operator,

$$U(t, t_0) |\psi(t_0)\rangle = |\psi(t)\rangle .$$  \hspace{1cm} (2.130)
By the expression (2.129) we find immediately, with \( t_0 < t_1 < t_2 \),
\[ U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0) \quad \text{and} \quad U(t_0, t) = U^\dagger(t, t_0) = U^{-1}(t, t_0) = U(t, t_0)^{-1}. \]
The conjugate operator of time evolution acts on the vector 'bra',
\[ \langle \psi(t) \rangle = \langle \psi(t_0) | U^\dagger(t, t_0). \]

### 2.4.3 Heisenberg picture

As unitary transformations do not change the physics, the system described by,
\[ |\psi_S(t)\rangle \rightarrow \hat{U}(t)^\dagger |\psi_S(t)\rangle \equiv |\psi_H\rangle \quad \text{and} \quad \hat{A}_S(t) \rightarrow \hat{U}(t)^\dagger \hat{A}_S(t) \hat{U}(t) \equiv \hat{A}_H(t) \]
with the transformation defined by equation (2.129), is equivalent. The subscript \( H \) means the Heisenberg picture. In particular, we obviously have,
\[ \hat{H}_S = \hat{H}_H \equiv \hat{H}. \]

Thus, the matrix element of the operator \( \hat{A}_S \) in Schrödinger’s picture with the time-dependent base \( \{|\psi_S(t)\rangle\} \) is equal to the matrix element of the operator \( \hat{A}_H = U^\dagger \hat{A}_S U \) in Heisenberg’s picture with the time-independent base \( \{|\psi_H\rangle\} \). In this picture the wavefunctions are independent of time,
\[ \frac{d}{dt} |\psi_H\rangle = \frac{d}{dt} |\psi_S(0)\rangle = 0, \]
but the operators depend \( im- \) and explicitly \( on \) time,
\[ \frac{d}{dt} \hat{A}_H(t) = \frac{d}{dt} \left( \hat{U}(t)^\dagger \hat{A}_S(t) \hat{U}(t) \right) = \frac{d\hat{U}^\dagger}{dt} \hat{A}_S(t) \hat{U}(t) + \hat{U}(t)^\dagger \frac{d\hat{A}_S(t)}{dt} \hat{U}(t) \]
\[ = \frac{i}{\hbar} \hat{H}^\dagger \hat{U}(t)^\dagger \hat{A}_S \hat{U}(t) + \hat{U}(t)^\dagger \hat{A}_S \frac{-i}{\hbar} \hat{H} \hat{U}(t) + \hat{U}(t)^\dagger \frac{\partial \hat{A}_S(t)}{\partial t} \hat{U}(t). \]
That is,
\[ \frac{d}{dt} \hat{A}_H(t) = \frac{i}{\hbar} [\hat{H}, \hat{A}_H(t)] + \frac{\partial \hat{A}_H(t)}{\partial t}. \]

This so-called Heisenberg equation, which describes the temporal evolution of an operator acting on time-independent states in the Heisenberg picture, is equivalent to the Schrödinger equation, which expresses the temporal evolution of a quantum state in Schrödinger’s picture.

According to equation (2.135), the rate of temporal variation of an operator in the Heisenberg representation is given by the commutator of that operator with the total Hamiltonian of the system. Note that if an operator representing a dynamic variable commutes with the Hamiltonian in the Schrödinger representation, it will also commute with the Hamiltonian in the Heisenberg representation and thus with the complete set of commutating observables,
\[ [\hat{H}, \hat{A}_S] = 0 \quad \iff \quad [\hat{H}, \hat{A}_H] = 0. \]
We will show this in the Exc. 2.4.6.2.
Example 10 (Position and momentum operators in the Heisenberg picture): We know that in Schrödinger’s picture (2.125), the operators \( \hat{\rho}_S \) and \( \hat{r}_S \) are stationary. Using this fact in derivation (2.134), we can show for example for the momentum operator,

\[
\frac{\partial}{\partial t} \hat{p}_S = 0 \quad \Rightarrow \quad \frac{\partial}{\partial t} \hat{p}_H = 0 \quad \Rightarrow \quad \frac{d}{dt} \hat{p}_H = \frac{i}{\hbar} [\hat{H}, \hat{p}_H].
\]

In the Exc. 2.4.6.3 we will use the Heisenberg picture to derive the equations of motion for a particle confined to a potential.

2.4.4 Interaction picture

The interaction picture deals with problems where the total Hamiltonian is composed of a time-independent part and a time-dependent part,

\[
\hat{H} = \hat{H}_0 + \hat{V}(t).
\]

(2.137)

Analogously to Eq. (2.129), we define a time evolution operator in terms of the time-independent part of the total Hamiltonian,

\[
| \psi_I(t) \rangle = e^{i\hat{H}_0 t/\hbar} | \psi_S(t) \rangle \quad \text{and} \quad A_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{A}_S e^{-i\hat{H}_0 t/\hbar}.
\]

(2.138)

Now we are interested in the temporal dependence of quantum states and operators in the interaction picture. Replacing the inverse function \( | \psi_S(t) \rangle = e^{-i\hat{H}_0 t/\hbar} | \psi_I(t) \rangle \) in the Schrödinger equation (2.128) we immediately see,

\[
\hat{V}(t) | \psi_I(t) \rangle = \frac{i}{\hbar} \frac{\partial}{\partial t} | \psi_I(t) \rangle.
\]

(2.139)

 Apparently, in the interaction picture, only the perturbative term in Hamiltonian controls the temporal evolution. Taking the time derivative of both sides of the equation (2.138) transforming an operator from the Schrödinger to the interaction picture results in,

\[
\frac{d \hat{A}_I}{dt} = \frac{i}{\hbar} [\hat{H}_0, \hat{A}_I] + \frac{\partial \hat{A}_I}{\partial t}.
\]

(2.140)

Therefore, we see that the time derivative can be expressed in the form of a commutator, resembling the Heisenberg equation (2.135), except that only the unperturbed term of the Hamiltonian appears in the argument of the commutation operator.

Example 11 (Schrieffer-Wolff transformation): The Schrieffer-Wolff transformation is a unitary transformation used to perturbatively diagonalize the system Hamiltonian to first order in the interaction. As such, the Schrieffer-Wolff transformation is an operator version of second-order perturbation theory. The Schrieffer-Wolff transformation is often used to project out the high energy excitations of a given quantum many-body Hamiltonian in order to obtain an effective low energy model. The Schrieffer-Wolff transformation thus provides
a controlled perturbative way to study the strong coupling regime of quantum-many body Hamiltonians.

Consider a quantum system evolving under the time-independent Hamiltonian operator $\hat{H}$ of the form $\hat{H} = \hat{H}_0 + V$, where $\hat{H}_0$ is a Hamiltonian with known eigenstates $|m\rangle$ and corresponding eigenvalues $E_m$, and where $V$ is a small perturbation. Moreover, it is assumed without loss of generality that $\hat{V}$ is purely off-diagonal in the eigenbasis of $\hat{H}_0$, i.e.,

$$\langle m|\hat{V}|m\rangle = 0 \quad (2.141)$$

for all $m$. Indeed, this situation can always be arranged by absorbing the diagonal elements of $\hat{V}$ into $\hat{H}_0$, thus modifying its eigenvalues to,

$$E'_m = E_m + \langle m|\hat{V}|m\rangle \quad (2.142)$$

The Schrieffer-Wolff transformation is a unitary transformation which expresses the Hamiltonian in a basis (the 'dressed' basis) where it is diagonal to first order in the perturbation $\hat{V}$. This unitary transformation is conventionally written as:

$$\hat{H}' = e^{iS} \hat{H} e^{-iS} \quad (2.143)$$

When $\hat{V}$ is small, the generator $S$ of the transformation will likewise be small. The transformation can then be expanded in $S$ using the Baker-Campbell-Haussdorf formula,

$$\hat{H}' = \hat{H} + [iS, \hat{H}] + \frac{1}{2} [iS, [iS, \hat{H}]] + \ldots \quad (2.144)$$

In terms of $\hat{H}_0$ and $\hat{V}$, the transformation becomes,

$$\hat{H}' = \hat{H}_0 + \hat{V} + [iS, \hat{H}_0] + [iS, \hat{V}] + \frac{1}{2} [iS, [iS, \hat{H}_0]] + \frac{1}{2} [iS, [iS, \hat{V}]] + \ldots \quad (2.145)$$

The Hamiltonian can be made diagonal to first order in $\hat{V}$ by choosing the generator $S$ such that,

$$[\hat{H}_0, iS] = \hat{V} \quad (2.146)$$

This equation always has a definite solution under the assumption that $\hat{V}$ is off-diagonal in the eigenbasis of $\hat{H}_0$. Substituting this choice in the previous transformation yields:

$$\hat{H}' = \hat{H}_0 + \frac{1}{2} [iS, \hat{V}] + O(\hat{V}^3) \quad (2.147)$$

This expression is the standard form of the Schrieffer-Wolff transformation. Note that all the operators on the right-hand side are now expressed in a new basis 'dressed' by the interaction $\hat{V}$ to first order.

In the general case, the difficult step of the transformation is to find an explicit expression for the generator $S$. Once this is done, it is straightforward to compute the Schrieffer-Wolff Hamiltonian by computing the commutator $[S, \hat{V}]$. The Hamiltonian can then be projected on any subspace of interest to obtain an effective projected Hamiltonian for that subspace. In order for the transformation to be accurate, the eliminated subspaces must be energetically well separated from the subspace of interest, meaning that the strength of the interaction $\hat{V}$ must be much smaller than the energy difference between the subspaces. This is the same regime of validity as in standard second-order perturbation theory.
2.4.4.1 Hamiltonian in the transformed system

We have seen that the unitary transformation,

\[ |\psi_U\rangle = U^\dagger |\psi\rangle, \quad \hat{A}_U = U^\dagger \hat{A} U, \]

leaves the physics of a system unchanged. The question is now, how the Schrödinger equation,

\[ \hat{H} |\psi\rangle = i\hbar \frac{d}{dt} |\psi\rangle \]  

transforms into the new system, that is, what will the Hamiltonian \( \hat{H}' \) look like in the transformed equation,

\[ \hat{H}' |\psi_U\rangle = i\hbar \frac{d}{dt} |\psi_U\rangle. \]

We calculate,

\[ \frac{i\hbar}{\frac{d}{dt}} |\psi_U\rangle = i\hbar U^\dagger \frac{d}{dt} |\psi\rangle + i\hbar \hat{U}^\dagger |\psi\rangle = (U^\dagger \hat{H} + i\hbar \hat{U}^\dagger) |\psi\rangle \]

\[ = (U^\dagger \hat{H} + i\hbar \hat{U}^\dagger) U |\psi_U\rangle = (U^\dagger \hat{H} U + i\hbar \hat{U}^\dagger U) |\psi_U\rangle = \hat{H}' |\psi_U\rangle. \]

Hence,

\[ \hat{H}' = U^\dagger \hat{H} U + i\hbar \hat{U}^\dagger U. \]  

Example 12 (Interaction picture): The above derivation is general and holds for any unitary transformation. We will now apply it to transform the Hamiltonian \( \hat{H} = \hat{H}_0 + \hat{V}(t) \) into the interaction picture via the transformation \( U = e^{-\frac{i}{\hbar}\hat{H}_0 t}. \) From

\[ \hat{U}^\dagger = \frac{i}{\hbar} \hat{H}_0 e^{\frac{i}{\hbar} \hat{H}_0 t} = \frac{1}{\hbar} \hat{H}_0 U^\dagger \]  

we calculate,

\[ \hat{H}' = U^\dagger \hat{H} U + i\hbar \hat{U}^\dagger U = U^\dagger \left[ \hat{H}_0 + \hat{V}(t) \right] U + i\hbar \frac{1}{\hbar} \hat{H}_0 U^\dagger U \]

\[ = U^\dagger \left[ \hat{H}_0 + \hat{V}(t) \right] U - \hat{H}_0 = U^\dagger \hat{V}(t) U, \]

which confirms the validity of the Schrödinger equation (2.139) in the interaction picture, provided the Hamiltonian is taken to be the perturbation part \( \hat{V}(t) \), only. In the Heisenberg picture \( \hat{V}(t) = 0 \), such that,

\[ \hat{H}' = 0. \]  

2.4.5 Ehrenfest’s theorem

For linear operators satisfying \([\hat{A}, \hat{B}] = i\) we can give a generalization of the commutation relation:

\[ [\hat{A}, F(\hat{A}, \hat{B})] = i \frac{\delta F(\hat{A}, \hat{B})}{\delta \hat{B}}. \]
This can be verified by a Taylor expansion of \( F(\hat{A}, \hat{B}) \) by \( \hat{B} = 0 \), as will be shown in Exc. 2.4.6.4. An immediate consequence of \([\hat{p}, \hat{r}] = -i\hbar\) is,

\[
[\hat{p}, F(\hat{r})] = -i\hbar \frac{\delta F(\hat{r})}{\delta \hat{r}} .
\] (2.158)

The momentum observable is not singularly defined by the commutation relation, because each unitarily transformed operator satisfies the relation as well. We can expand a unitarily equivalent momentum as \( \hat{p} = U\hat{p}U^+ = e^{iF(\hat{r})}\hat{p}e^{-iF(\hat{r})} = p + i[\hat{F}(\hat{r}), p] + \frac{1}{2!}[\hat{F}(\hat{r}), [\hat{F}(\hat{r}), p]] + \ldots \) using the relation (2.202).

The observables in the Heisenberg picture follow the same equations of motion as the corresponding classical quantities. This correspondence principle is called Ehrenfest theorem. For example, when working with position and momentum variables \([\hat{x}, \hat{p}] = i\) and \(\hat{H} = \frac{\hbar^2}{2m}\hat{k}^2 + V(\hat{x})\), we obtain,

\[
[\hat{x}, \hat{H}] = i\hbar \frac{\delta \hat{H}}{\delta \hat{p}} \quad \text{and} \quad [\hat{p}, \hat{H}] = -i\hbar \frac{\delta \hat{H}}{\delta \hat{x}} ,
\] (2.159)

and using the Heisenberg equation (2.135),

\[
\dot{\hat{x}} = \frac{\delta \hat{H}}{\delta \hat{p}} \quad \text{and} \quad \dot{\hat{p}} = -\frac{\delta \hat{H}}{\delta \hat{x}} .
\] (2.160)

We will demonstrate this in Exc. 2.4.6.5 for the case of a harmonic potential.

In the Schrödinger picture the equation of motion for the eigenvalues of the observables takes the form,

\[
\frac{d}{dt} \langle \hat{A} \rangle = \langle \partial_t \psi | \hat{A} \hat{S} | \psi \rangle + \langle \psi | \partial_t \hat{A} \hat{S} | \psi \rangle = \frac{\partial}{\partial t} \langle \hat{A} \rangle + i\hbar \langle [\hat{H}, \hat{A}] \rangle .
\] (2.161)

The eigenvalues behave as Heisenberg observables in Eq. (2.134), that is, they follow the laws of Hamilton’s and Newton’s mechanics.

The important result now is that the equations that govern the eigenvalues of the observables are identical in the both pictures, since from the Heisenberg picture we obtain with Eq. (2.134),

\[
\frac{d}{dt} \langle \hat{A}_H \rangle = \frac{\partial}{\partial t} \langle \hat{A}_H \rangle + \frac{i}{\hbar} \langle [\hat{H}, \hat{A}_H] \rangle .
\]

### 2.4.6 Exercises

#### 2.4.6.1 Ex: Coupled two-level atom

Calculate the time evolution of an atom with two levels coupled by a light field using the Hamiltonian,

\[
\hat{H} = \begin{pmatrix} 0 & \frac{1}{2}\hbar\Omega \\ \frac{1}{2}\hbar\Omega & -\hbar\Delta \end{pmatrix} ,
\]

where \(\Delta = \omega - \omega_0\) is the detuning between the frequency of the light and the frequency of the transition and \(\Omega\) the Rabi frequency. **Help:** Determine the matrix of the eigenvalues \(\hat{E}\) and the unitary transformation \(U\) given by \(U^\dagger \hat{H} U = \hat{E}\) and use the
formal solution of the Schrödinger equation:  
\[ |\psi(t)\rangle = e^{-\frac{i\hat{H}t}{\hbar}}|\psi(0)\rangle = e^{-i\hat{U}t}\hat{U}e^{-i\hat{H}t/\hbar}|\psi(0)\rangle = U^\dagger e^{-i\hat{E}t/\hbar}|\psi(0)\rangle. \]

2.4.6.2 Ex: Commutator in Schrödinger’s and Heisenberg’s picture

Show that operators which commute with the Hamiltonian in the Schrödinger picture also do it in the Heisenberg picture. Use the rule \([\hat{A}, \hat{B}] = \hat{A}[\hat{H}, \hat{B}] + [\hat{H}, \hat{A}]\hat{B}\).

2.4.6.3 Ex: Motion in Heisenberg’s picture

Consider the Hamiltonian \(\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m}{2}\omega^2 \hat{x}^2\). Using the relation \([\hat{p}, \hat{x}] = -i\hbar\) calculate in the Heisenberg picture the equations of motion for the observables \(\hat{p}, \hat{x}\), and \(\hat{p}\hat{x}\).

2.4.6.4 Ex: Commutator of a function of operators

Prove the relationship (2.157).

2.4.6.5 Ex: Ehrenfest’s theorem

Compare the equations of Ehrenfest’s theorem with those of Hamilton-Jacobi for a classical particle subject to a time-independent potential. Discuss the classical limit, that is, when the Hamilton-Jacobi equations approach those of Ehrenfest.

2.5 Symmetries in quantum mechanics

We already saw in Sec. 2.3.4 that, beyond observables, there is another category of operators that does not correspond to measurable physical quantities, but is very useful in the quantum formalism. These are the unitary transformation. In this section we will encounter some interesting examples.

2.5.1 Translation and rotation

2.5.1.1 Temporal translation operator

The temporal evolution of a system is described by the Schrödinger equation whose formal solution can be written as follows,

\[ |\psi(t)\rangle = e^{-\frac{i\hat{H}t}{\hbar}}|\psi(0)\rangle. \] (2.162)

With this we can define an evolution operator or temporal translation,

\[ U_{tp}(\tau) \equiv e^{-\frac{i\hat{H}t}{\hbar}} \quad \text{tal que} \quad U_{tp}(\tau)|\psi(t)\rangle = |\psi(t + \tau)\rangle. \] (2.163)

The temporal evolution has already been discussed extensively in Sec. 2.4.

\[ \text{The MATLAB code for calculating time evolution (QM_Fundaments_Evolucao.m) can be found on the web page of this course.} \]
2.5. SYMMETRIES IN QUANTUM MECHANICS

2.5.1.2 Spatial translation operator

In this section we look for a unitary translation operator,

\[ \mathcal{T}_{tr} \mathbf{r} \equiv \mathbf{a} + \mathbf{r}. \]  \hspace{1cm} (2.164)

Before this, we need to derive the following calculation rule for commutators, which will be done in Exc. 2.5.5.1:

\[ e^{\hat{A}} \hat{B} e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!} [\hat{A}, [\hat{A}, \hat{B}]] + \ldots. \]  \hspace{1cm} (2.165)

Applying this formula to the two operators \( \hat{p} \) and \( \hat{r} \) related by the commutation rule (2.49), we obtain,

\[ e^{(i/\hbar) \mathbf{a} \cdot \hat{p}} e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} = \hat{r} + [(i/\hbar) \mathbf{a} \cdot \hat{p}, \hat{r}] + \frac{1}{2!} [(i/\hbar) \mathbf{a} \cdot \hat{p}, \mathbf{a}] \hat{r}^0 + \ldots = \hat{r} + \mathbf{a}. \]  \hspace{1cm} (2.166)

That is, the operator \( U_{tr}(\mathbf{a}) \equiv e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} \) (2.167)
performs a spatial translation of the position operator. The operator is unitary,

\[ U_{tr}(\mathbf{a})^{-1} = U_{tr}(\mathbf{a})^\dagger, \]  \hspace{1cm} (2.168)

and forms a group since \( U_{tr}(\mathbf{a}) U_{tr}(\mathbf{b}) = U_{tr}(\mathbf{a} + \mathbf{b}) \). Summarizing the impact of the translation on the operators of space,

\[ U_{tr}(\mathbf{a}) \hat{r} U_{tr}(\mathbf{a}) = \hat{r} + \mathbf{a}, \hspace{1cm} U_{tr}(\mathbf{a}) \hat{p} U_{tr}(\mathbf{a}) = \hat{p}, \]  \hspace{1cm} (2.169)

where the second relation is obvious.

To demonstrate how the translation acts on a state, let us calculate,

\[ \hat{r} e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} |\mathbf{r}\rangle = e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} (\hat{r} + \mathbf{a}) |\mathbf{r}\rangle = (\mathbf{r} + \mathbf{a}) e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} |\mathbf{r}\rangle. \]  \hspace{1cm} (2.170)

Hence,

\[ U_{tr}(\mathbf{a}) |\mathbf{r}\rangle = e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} |\mathbf{r}\rangle = |\mathbf{r} + \mathbf{a}\rangle. \]  \hspace{1cm} (2.171)

Finally, comparing the expansion of the translation operator

\[ e^{(-i/\hbar) \mathbf{a} \cdot \hat{p}} |\mathbf{r}\rangle = \left( 1 - \frac{i}{\hbar} \mathbf{a} \cdot \hat{p} - \frac{1}{\hbar^2} (\mathbf{a} \cdot \hat{p})^2 \frac{2!}{2!} + \ldots \right) |\mathbf{r}\rangle, \]  \hspace{1cm} (2.172)

with the Taylor expansion of the translated state,

\[ |\mathbf{r} + \mathbf{a}\rangle = \left( 1 + \mathbf{a} \cdot \nabla + \frac{(\mathbf{a} \cdot \nabla)^2}{2!} + \ldots \right) |\mathbf{r}\rangle. \]  \hspace{1cm} (2.173)

we obtain

\[ \hat{p} |\mathbf{r}\rangle = -\frac{\hbar}{i} \nabla |\mathbf{r}\rangle. \]  \hspace{1cm} (2.174)
2.5.1.3 Rotation operator

In this section we look for the unitary transformation corresponding to the rotation operator \([591]\),

\[
\mathcal{T}_{rt} \mathbf{r} \equiv e^{\vec{\alpha} \times \mathbf{r}}. \tag{2.175}
\]

We calculate,

\[
e^{\vec{\alpha} \times \mathbf{r}} = \sum_{n} \frac{(\vec{\alpha} \times \mathbf{r})^{n}}{n!} = \mathbf{r} + \vec{\alpha} \times \mathbf{r} + \frac{1}{2} \vec{\alpha} \times (\vec{\alpha} \times \mathbf{r}) + .. \tag{2.176}
\]

Therefore, the observable \(\hat{L}\) that is, we find,

\[
\text{with the Taylor expansion of the state,}
\]

\[
\text{The explicit form of } \hat{L}, \text{ where we define the angular momentum operator as we will see in Exc. 2.5.5.2. We define the unitary rotational transformation by,}
\]

\[
U_{rt}^{\dagger}(\vec{\alpha}) \hat{\mathbf{r}} U_{rt}(\vec{\alpha}) = e^{\vec{\alpha} \times \hat{\mathbf{r}}}, \quad U_{rt}(\vec{\alpha}) |\mathbf{r}\rangle = |e^{\vec{\alpha} \times \mathbf{r}}\rangle. \tag{2.177}
\]

To derive the explicit form of the rotation operator, we consider two rotations about the same axis \(\vec{\alpha} = \lambda_1 \hat{\mathbf{e}}_{\alpha} + \lambda_2 \hat{\mathbf{e}}_{\alpha}\), such that

\[
U_{rt}(\lambda_1 \hat{\mathbf{e}}_{\alpha}) U_{rt}(\lambda_2 \hat{\mathbf{e}}_{\alpha}) = U_{rt}(\lambda_1 \hat{\mathbf{e}}_{\alpha} + \lambda_2 \hat{\mathbf{e}}_{\alpha}). \tag{2.178}
\]

Calculating the derivative of this equation by \(\lambda_1 = 0\) and then setting \(\lambda_1 = 0\), we have,

\[
\begin{align*}
\frac{d U_{rt}(\lambda_1 \hat{\mathbf{e}}_{\alpha})}{d \lambda_1} \bigg|_{\lambda_1=0} U_{rt}(\lambda_2 \hat{\mathbf{e}}_{\alpha}) & = \frac{d U_{rt}(\lambda_1 \hat{\mathbf{e}}_{\alpha} + \lambda_2 \hat{\mathbf{e}}_{\alpha})}{d \lambda_1} \bigg|_{\lambda_1=0} \frac{d(\lambda_1 + \lambda_2)}{d \lambda_1} \bigg|_{\lambda_1=0} \\
\implies \frac{d \lambda_1 \hat{\mathbf{e}}_{\alpha}}{d \lambda_1} \bigg|_{\lambda_1=0} \cdot \nabla_{\vec{\alpha}} U_{rt}(\vec{\alpha}) |_{\vec{\alpha}=0} U_{rt}(\lambda_2 \hat{\mathbf{e}}_{\alpha}) & = \frac{d U_{rt}(\lambda_2 \hat{\mathbf{e}}_{\alpha})}{d \lambda_2} \bigg|_{\lambda_1=0} \\
\implies \hat{\mathbf{e}}_{\alpha} \cdot \frac{\mathbf{L}}{\hbar} U_{rt}(\lambda_2 \hat{\mathbf{e}}_{\alpha}) & = \frac{d U_{rt}(\lambda_2 \hat{\mathbf{e}}_{\alpha})}{d \lambda_2} \bigg|_{\lambda_1=0} \tag{2.179}
\end{align*}
\]

where we define the angular momentum operator \(\hat{\mathbf{L}} \equiv \hbar \nabla_{\vec{\alpha}} U_{rt}(\vec{\alpha}) |_{\vec{\alpha}=0}\). The solution of the last differential equation is, with \(\lambda_2 \hat{\mathbf{e}}_{\alpha} = \vec{\alpha} |_{\lambda_1=0}\),

\[
U_{rt}(\vec{\alpha}) = e^{(-i/\hbar) \mathbf{L} \cdot \vec{\alpha}}. \tag{2.180}
\]

The explicit form of \(\mathbf{L}\) follows from its action on a state \(|\mathbf{r}\rangle\). Comparing the expansion of the operator (2.180),

\[
U_{rt}(\alpha) |\mathbf{r}\rangle = (1 - \frac{i}{\hbar} \mathbf{L} \cdot \vec{\alpha} + ...) |\mathbf{r}\rangle \tag{2.181}
\]

with the Taylor expansion of the state,

\[
|e^{\vec{\alpha} \times \mathbf{r}}\rangle = |\mathbf{r} + \vec{\alpha} \times \mathbf{r} + ...\rangle = |\mathbf{r}\rangle + (\vec{\alpha} \times \mathbf{r}) \cdot \nabla_{\mathbf{r}} |\mathbf{r}\rangle + ... , \tag{2.182}
\]

we find,

\[
-\frac{i}{\hbar} \hat{\mathbf{L}} \cdot \vec{\alpha} |\mathbf{r}\rangle = (\vec{\alpha} \times \mathbf{r}) \cdot \nabla_{\mathbf{r}} |\mathbf{r}\rangle = \vec{\alpha} \cdot (\mathbf{r} \times \nabla_{\mathbf{r}} |\mathbf{r}\rangle) = \vec{\alpha} \cdot (-\frac{i}{\hbar} \hat{\mathbf{r}} \times \hat{\mathbf{p}}) |\mathbf{r}\rangle, \tag{2.183}
\]

that is,

\[
\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \tag{2.184}
\]

Therefore, the observable \(\hat{\mathbf{L}}\) is the orbital angular momentum of the particle producing the rotations.
2.5.2 Galilei and Lorentz boosts

The Galilei transform (or Galilei boost) is defined by,

\[ \mathcal{T}_v \mathbf{r} = \mathbf{r} + vt \quad \text{and} \quad \mathcal{T}_v \mathbf{p} = \mathbf{p} + mv. \]  

(Holds \( \mathcal{T}_v, \mathcal{T}_{v_2} = \mathcal{T}_{v_1 + v_2} \). We derive the expression for the operator of this transformation from its actions on the position and momentum states. For the position we have with (2.167),

\[ U_G(v)|\mathbf{r}\rangle \propto e^{(-i/\hbar)\mathbf{p} \cdot vt} |\mathbf{r}\rangle = |\mathbf{r} + vt\rangle. \]  

For the momentum we can proceed analogously,

\[ U_G(v)|\mathbf{p}\rangle \propto e^{(i/\hbar)\mathbf{r} \cdot vm} |\mathbf{p}\rangle = |\mathbf{p} + mv\rangle. \]

That is, by defining \( \mathbf{G} = \hat{\mathbf{p}}t - \hat{\mathbf{r}}m = i\hbar \nabla U_G(v)|_{\mathbf{v}=0} \), the unitary transformation

\[ U_G(v) = e^{(i/\hbar)\mathbf{r} \cdot \mathbf{G}} \]

meets the requirements (2.186) and (2.187). We just need to check,

\[ e^{(i/\hbar)\mathbf{v} \cdot \mathbf{r} m} |\mathbf{r}\rangle = e^{(i/\hbar)\mathbf{r} \cdot \mathbf{v} m} \int_{\mathbb{R}^3} |\mathbf{p}\rangle |\mathbf{p}|d^3p = \frac{1}{i\hbar^2}\int_{\mathbb{R}^3} |\mathbf{p}\rangle e^{-i/\hbar}\mathbf{r} \cdot (\mathbf{p} - \mathbf{v} m)d^3p = |\mathbf{r}\rangle \]

and analogously,

\[ e^{(-i/\hbar)\mathbf{v} \cdot \mathbf{p} t} |\mathbf{p}\rangle = e^{(i/\hbar)\mathbf{p} \cdot \mathbf{v} t} \int_{\mathbb{R}^3} |\mathbf{r}\rangle |\mathbf{r}|d^3p = \frac{1}{i\hbar^2}\int_{\mathbb{R}^3} |\mathbf{r}\rangle e^{(i/\hbar)\mathbf{p} \cdot (\mathbf{r} - \mathbf{p} t)}d^3p = |\mathbf{p}\rangle. \]

With the commutator of \( \hat{\mathbf{p}} \) and \( \hat{\mathbf{r}} \) we derive,

\[ [\mathbf{G} \cdot \mathbf{a}, \mathbf{G} \cdot \mathbf{b}] = 0, \]

and with that, using the Baker-Haussdorff formula (4.92), we verify,

\[ U_G(v_1)U_G(v_2) = e^{(-i/\hbar)(v_1 + v_2)\cdot \mathbf{G} - [v_1 \cdot \mathbf{G}, v_2 \cdot \mathbf{G}] / 2\hbar^2} = U_G(v_1 + v_2). \]

Obviously, for very high velocities, the Galilei-boost should be replaced by the Lorentz transform (or Lorentz boost) \[313\]. Here, we only note, that the additivity of velocities expressed by equation (2.191) does not hold for non-collinear relativistic velocities \[314\].

2.5.3 Gauge transformations

We learn in electrodynamics \[315\] that the motion of a particle carrying the charge \( q \) and interacting with an electrical potential \( \Phi(r, t) \) and a magnetic vector potential \( \mathbf{A}(r, t) \) is governed by the electric and the magnetic field,

\[ \mathcal{E}(r, t) = -\nabla \Phi - \partial_t \mathbf{A} \quad \text{and} \quad \mathbf{B}(r, t) = \nabla \times \mathbf{A}. \]  

\[14\]We need to keep in mind that, following Glauber’s rule, \( e^{A}e^{B} = e^{A+B+[A,B]/2} \) with \( A \equiv \mathbf{v} \cdot \hat{\mathbf{p}}t \) and \( B \equiv \mathbf{v} \cdot \hat{\mathbf{r}}m \). However, the commutator \( [\mathbf{v} \cdot \hat{\mathbf{p}}t, \mathbf{v} \cdot \hat{\mathbf{r}}m] = -i\hbar m v^2 \) is independent of \( \hat{\mathbf{p}} \) and \( \hat{\mathbf{r}} \), such that it only contributes an unimportant phase.

\[15\]See script on Electrodynamics (2020).

\[16\]See script on Electrodynamics (2020).
Also, we know that the fields are invariant under the substitution,
\[ \Phi \rightarrow \Phi' \equiv \Phi - \partial_t \chi \quad \text{and} \quad A \rightarrow A' \equiv A + \nabla \chi , \]
where \( \chi(r,t) \) is a scalar field called *gauge field*.

In quantum mechanics the *gauge transformation* defined by,
\[ U_{\text{cl}}(\chi) = e^{-iq\chi(r,t)/\hbar} \]
obviously keeps the Schrödinger equation invariant. Transforming operators and wave functions as,
\[ \hat{H} \rightarrow U_{\text{cl}} \hat{H} U_{\text{cl}}^{-1} \equiv \hat{H}_U \quad \text{and} \quad |\psi\rangle \rightarrow U_{\text{cl}} |\psi\rangle \equiv |\psi_U\rangle , \]
we calculate for the energy,
\[ \hat{H}_U |\psi_U\rangle = U_{\text{cl}} \hbar \frac{d}{dt} U_{\text{cl}}^{-1} |\psi_U\rangle = U_{\text{cl}} \hbar U_{\text{cl}}^{-1} \frac{d}{dt} |\psi_U\rangle + U_{\text{cl}} \hbar \left( \frac{-iq}{\hbar} U_{\text{cl}}^{-1} \frac{d\chi}{dt} \right) |\psi_U\rangle \]
\[ = i\hbar \left( \frac{d}{dt} - \frac{iq}{\hbar} \frac{d\chi}{dt} \right) |\psi_U\rangle , \]
and for the momentum,
\[ \hat{p}_U |\psi_U\rangle = U_{\text{cl}} (-i\hbar \nabla) U_{\text{cl}}^{-1} |\psi_U\rangle = U_{\text{cl}} (-i\hbar) U_{\text{cl}}^{-1} (\nabla |\psi_U\rangle) + U_{\text{cl}} (-i\hbar) \left( \frac{-iq}{\hbar} U_{\text{cl}}^{-1} \nabla \chi \right) |\psi_U\rangle \]
\[ = (-i\hbar) \left( \nabla - \frac{iq}{\hbar} (\nabla \chi) \right) |\psi_U\rangle , \]
This corresponds to the substitutions:\footnote{In quadrivectorial notation \( i\hbar \partial_\mu \rightarrow i\hbar \partial_\mu + q \partial_\mu \chi \).}
\[ U_{\text{cl}} \hbar \frac{d}{dt} U_{\text{cl}}^{-1} = i\hbar \frac{d}{dt} + q \frac{d\chi}{dt} \quad \text{and} \quad U_{\text{cl}} \hat{p} U_{\text{cl}}^{-1} = \hat{p} - q \nabla \chi . \]
This shows that the gauge transformation applies to the *minimal coupling* rule,
\[ \hat{H} = \hat{H}_{\text{kin}} + q\Phi \quad \text{and} \quad m\mathbf{v} = p - qA \]
confirming the rules (2.194). That is, the Hamiltonian of a particle carrying the charge \( q \) and interacting with an electric potential \( \Phi \) and a magnetic vector potential \( A \) is,
\[ \hat{H} = \frac{1}{2m} (p - qA - q\nabla \chi)^2 + q\Phi + q\partial_t \chi . \]

### 2.5.4 Noether’s theorem and conservation laws

The fundamental laws of physics are often expressed as symmetries. The knowledge of symmetries allows the characterization of a system and its behavior without the need to know its details. We can often deduce the differential equation of motion from the symmetries. The fundamental symmetries define the fundamental laws of physics. Following *Noether’s theorem* each symmetry corresponds to a conserved quantity, that is, a quantities that remains invariant for all time. The invariance of a
2.5. SYMMETRIES IN QUANTUM MECHANICS

system under symmetry transformation represents a conservation law. For example, the homogeneity of space corresponds to the conservation of linear momentum.

In quantum mechanics, a symmetry transformation is defined by,

\[ |\psi\rangle \rightarrow U|\psi\rangle \quad \text{and} \quad \hat{Q} \rightarrow U\hat{Q}U^\dagger. \] (2.202)

Therefore, to find a conservation law, i.e., an invariable observable (also called constant of motion), we must verify that the observable and the transformed wavefunctions simultaneously satisfy the same fundamental equations (that is, Schrödinger’s or Heisenberg’s equation) as the original observable and wavefunctions. For example, if the wavefunction \( |\psi\rangle \) satisfies the Schrödinger equation, the wave function \( U|\psi\rangle \) must do this too,

\[
\hat{H}U|\psi\rangle = \frac{i\hbar}{\partial t} U|\psi\rangle = i\hbar \frac{dU}{dt}|\psi\rangle + i\hbar U \frac{d}{dt}|\psi\rangle = i\hbar \frac{dU}{dt}|\psi\rangle + U \hat{H}|\psi\rangle.
\] (2.203)

Consequently, we obtain the relation,

\[
[H, U] = i\hbar \dot{U}.
\] (2.204)

As shown in (2.161) and (2.162), an operator that commutes with the Hamiltonian does not explicitly depend on time, that is, it is conserved.

2.5.4.1 Temporal homogeneity

Temporal homogeneity means invariance under translation in time, that is, under the unitary temporal transformation,

\[
U(\tau) \equiv |\psi(\tau)\rangle\langle\psi(0)| = e^{(i/\hbar)\hat{E}\tau}.
\] (2.205)

Since \( \frac{d}{dt} e^{(i/\hbar)\hat{E}\tau} = 0 \), this means \( e^{(i/\hbar)\hat{E}\tau}, \hat{H} \) = 0, which implies conservation of energy \( [\hat{E}, \hat{H}] = 0 \). This will be verified in the Exc. 2.5.5.3.

Example 13 (Homogeneity of time): We imagine the following mental experiment or Gedankenexperiment: We consider two attractive bodies that move away from each other until they reach the perihelia. At this point, before the bodies reapproach, we change the laws, for example, by modifying the force of attraction. As a consequence, when the bodies arrive at the initial point, the total energy is non-zero. Therefore, the conservation of energy indicates that the laws are invariant.

2.5.4.2 Temporal isotropy

The fundamental laws of classical physics and quantum mechanics are all symmetrical under time reversal. That is, they are remain invariant when we change the arrow of time, \( t \rightarrow -t \).
2.5.4.3 Spatial homogeneity

*Spatial homogeneity* means invariance under spatial translation, that is, under the unitary translational transformation,

$$ U_{tr}(a) \equiv \int |r + a \rangle \langle r| d^3r = e^{(-i/h) \hat{p} \cdot a} . \quad (2.206) $$

This is equivalent to momentum conservation $[\hat{p}, \hat{H}] = 0. \quad (18)$

**Example 14 (Homogeneity of space):** Ehrenfest’s theorem says $[\hat{p}, \hat{H}] = -i\hbar \frac{\partial \hat{H}}{\partial \hat{p}}$. Therefore, the commutator is not zero when there is a potential, $\hat{H} = \hat{p}^2/2m + V(\hat{r})$. This is obvious, because the potential introduces an energy inhomogeneity to a particle interacting with the potential. However, this does not mean that the space itself is inhomogeneous, because in order to verify the translational invariance of space, we must displace the entire system, that is, the particle together with the potential. For example, if the potential is generated by another particle we must consider the Hamiltonian $\hat{H} = \hat{p}_1^2/2m_1 + \hat{p}_2^2/2m_2 + V(\hat{r}_1 - \hat{r}_2)$.

2.5.4.4 Spatial isotropy

*Spatial isotropy* means invariance under rotation, that is, under rotational unitary transformation,

$$ U_{rt}(\phi) \equiv e^{(-i/h) \hat{L} \phi} . \quad (2.207) $$

This is equivalent to the conservation of angular momentum $[\hat{L}, \hat{H}] = 0$.

2.5.4.5 Parity conservation

Besides continuous symmetry transformations there exist discrete transformations. Discrete symmetries are important in elementary particle physics. The *parity conservation* means invariance to spatial reflection: $r \rightarrow -r$. A parity transformation is defined by the mirroring of the wavefunction through a point in space, for example $r = 0$,

$$ \hat{P}|\psi(r)\rangle \equiv |\psi(-r)\rangle . \quad (2.208) $$

with

$$ \hat{P}^2 = \hat{P} . \quad (2.209) $$

We talk about *even* parity when $\hat{P}|\psi(r)\rangle = |\psi(r)\rangle$ and *odd* parity when $\hat{P}|\psi(r)\rangle = -|\psi(r)\rangle$. See Exc. 2.5.5.4.

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18Imagine that the forces attracting two bodies to each other are not equal: Contrary to Newton’s third law, body A attracts body B, more than the body B attracts the body A. In that case after a while the two bodies have different momenta. With the unitary transformation $U_{tr}(a) = e^{-i\hat{p} \cdot a/h} \approx 1 - i\epsilon \hat{p} \cdot a/h + ...$ we have,

$$ U_{tr}H|\psi\rangle = U_{tr}E\psi|\psi\rangle = E\psi U|\psi\rangle = H|\psi(r + a)\rangle \Rightarrow H|\psi(r)\rangle . $$

Since, $[H, \hat{p}] = 0$, Heisenberg’s equation yields,

$$ \frac{\partial}{\partial t} \langle \psi|\hat{p} \cdot a|\psi\rangle = \frac{1}{i\hbar} \langle \psi|[\hat{p} \cdot a, \hat{H}]|\psi\rangle = 0 . $$
2.5.4.6 Invariance to the velocity of the inertial system

The *Galilei boost* asks for Galilei invariance regarding the transformation,

\[ U_G(v) \equiv \int \int |r + vt, p + mv\rangle \langle r, p|d^3rd^3p \, , \]  

that is, the independence of the inertial system on its velocity \( v \).

2.5.4.7 Charge conservation

Let us consider again the *gauge transform* \( (2.194) \). We know that the Lagrangian density in free space is given in terms of the potentials by,

\[ \mathcal{L}(x^{\mu}) = \frac{\varepsilon_0}{4} F^{\mu\nu} F_{\mu\nu} - A_\mu j^\mu = \frac{\varepsilon_0}{4} E^2 - \frac{1}{2\mu_0} B^2 - A_\mu j^\mu \]  

(2.211)

and the *action* is simply the fourth-dimensional integral,

\[ S = \int \mathcal{L}(x^{\mu})dVdt \, . \]  

(2.212)

From the Lagrangian formulation, Maxwell’s equations can be derived by requiring the action to be minimal, \( \delta S = 0 \), which yields the Euler-Lagrange equations. As the field equations do not change under gauge transformation, this implies that the action is also unchanged.

To find the relation with *charge conservation*, we simply have to compare the actions in different gauges. First, we express the Lagrangian transformed into the old gauge,

\[ \mathcal{L}'(x^{\mu}) = \frac{\varepsilon_0}{4} \{ \nabla[\Phi - \partial_t \chi^\mu] + \partial_\mu [A + \nabla \chi^\mu] \}^2 - \frac{1}{2\mu_0} \{ \nabla \times [A + \nabla \chi^\mu] \}^2 \]  

(2.213)

\[ = \mathcal{L} + (\partial_t \chi) \rho + \nabla \chi \cdot j \, . \]

With this result, we can calculate the difference between the actions under gauge transformation and recall, that they can not be different:

\[ 0 \overset{!}{=} S' - S = \int [(\partial_t \chi) \rho + \nabla \chi \cdot j]dVdt = - \int \chi [\partial_t \rho + \nabla \cdot j]dVdt \, , \]  

(2.214)

using partial integration \(^{19}\) and choosing volumes so large, that every charge is inside. This is the *continuity equation* derived from the gauge invariance of the action. The calculation really is nothing more than an application of Noether’s theorem from which we could have derived directly the continuity equation, \( \partial_\mu j^\mu = 0 \).

In summary, the conservation of charge means invariance with respect to gauge transformations,

\[ U_{cl}(\chi) \equiv e^{-i\mathcal{Q}(r,t)/\hbar} \, , \]  

(2.215)

\(^{19}\)Think about the argument, because \( \int \partial_t |\chi|dtdt = 0! \)
where $\chi$ is the gauge field. We note that $q$ and $\chi$ are conjugated observables. Therefore, if $[\chi, \hat{H}] = 0$, then the charge $q$ is a conserved quantity.

Transformations can be combined. For example, we believe that nowadays all laws are invariant with respect to CPT transformation, that is, a combination of charge conjugation, parity inversion, and $\theta$-transform.

### 2.5.5 Exercises

#### 2.5.5.1 Ex: Calculus with commutator

Derive the rule (2.165) via a Taylor expansion of the operator $\hat{G}(\tau) \equiv e^{\tau \hat{A}} \hat{B} e^{-\tau \hat{A}}$.

#### 2.5.5.2 Ex: Rotation operator

Derive the rule $e^{\vec{\alpha} \times \vec{r}} = \sum_n \frac{\vec{\alpha} \times \vec{r}}{n!} = \hat{e}_\alpha (\hat{e}_\alpha \cdot \vec{r}) + \hat{e}_\alpha \times \vec{r} \sin \alpha - \hat{e}_\alpha \times (\hat{e}_\alpha \times \vec{r}) \cos \alpha$.

#### 2.5.5.3 Ex: Constants of motion

Show at the example of energy conservation using the relation (2.204), that energy commutes with the Hamiltonian if $\dot{E} = 0$.

#### 2.5.5.4 Ex: Parity

Show that the eigenfunctions of the Hamiltonian $\hat{H} = -(\hbar/2m)(d^2/dx^2) + V(x)$ have well-defined parity, i.e., parity is a good quantum number in cases where the energy is an even function of position, $V(x) = V(-x)$. 
Chapter 3

Rotations / Central potentials

3.1 Particle in a central potential

Many potentials do not have Cartesian symmetry, but fortunately, many problems have some kind of symmetry, cylindrical, spherical or periodic. Those with cylindrical or spherical symmetry can be solved by separating the curvilinear coordinates, as we will show in the following. Particularly important are spherical potentials caused by central forces, for example, the Coulomb force between the proton and the electron in the hydrogen atom.

3.1.1 Transformation to relative coordinates

The hydrogen atom represents a two-body problem. We consider the two masses $m_{1,2}$ of a proton and an electron separated by a distance $r$ and interacting through a potential $V(r)$. The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla^2 r_1 + \frac{\hbar^2}{2m_2} \nabla^2 r_2 + V(r_1 - r_2),$$

(3.1)

where $r_{1,2}$ are the positions of the proton and the electron. With the ansatz $\Xi(t, r_1, r_2) = \Xi(r_1, r_2)e^{-iE_{tot}t/\hbar}$, the time-dependent Schrödinger equation

$$\hat{H}\Xi(t, r_1, r_2) = i\hbar \frac{d}{dt} \Xi(t, r_1, r_2),$$

(3.2)

becomes stationary,

$$\left[ -\frac{\hbar^2}{2m_1} \nabla^2 r_1 + \frac{\hbar^2}{2m_2} \nabla^2 r_2 + V(r_1 - r_2) \right] \Xi(r_1, r_2) = E_{tot}\Xi(r_1, r_2).$$

(3.3)

Now we transform into the center-of-mass system making for the total wavefunction the ansatz $\Xi(r_1, r_2) = e^{-iP \cdot R/\hbar}\Psi(r)$ with $R \equiv m_1 r_1 + m_2 r_2$ and $r \equiv r_1 - r_2$ and introducing the abbreviation $M = m_1 + m_2$. This corresponds to a product of a plane wave, describing the linear motion of the center of the masses, and a radial wave function, which describes the relative motion of the atom. The kinetic energy of one
mass is:
\[
\frac{-\hbar^2}{2m_1} \nabla^2 \Psi(r) e^{-i\mathbf{P}\cdot\mathbf{R}/\hbar} \\
= \frac{-\hbar^2}{2m_1} \left[ e^{-i\mathbf{P}\cdot\mathbf{R}/\hbar} \nabla^2 \Psi(r) \right. \\
+ 2\left. \left( \frac{-im_1\mathbf{P}}{\hbar M} \right) e^{-i\mathbf{P}\cdot\mathbf{R}/\hbar} \nabla \Psi(r) \right) \\
= e^{-i\mathbf{P}\cdot\mathbf{R}/\hbar} \left[ \frac{-\hbar^2}{2m_1} \nabla^2 \Psi(r) + \frac{i\hbar \mathbf{P}}{M} \nabla \Psi(r) - \frac{m_1 \mathbf{P}^2}{2M^2} \Psi(r) \right].
\]

Hence, for two atoms,
\[
E_{\text{tot}} \Xi(r_1, r_2) - V(r) \Xi(r_1, r_2) \\
= e^{-i\mathbf{P}\cdot\mathbf{R}/\hbar} \left[ \frac{-\hbar^2}{2m_1} \nabla^2 \Psi(r) + \frac{-\hbar^2}{2m_2} \nabla^2 \Psi(r) + \frac{i\hbar \mathbf{P}}{M} \left( \nabla r_1 + \nabla r_2 \right) \Psi(r) + \frac{\mathbf{P}^2}{2M} \Psi(r) \right].
\]

Using \( \nabla r_1 = -\nabla r_2 = \nabla r \), we see that the third term cancels, such that,
\[
\frac{\mathbf{P}^2}{2M} \Psi(r) + \frac{-\hbar^2}{2m_1} \nabla^2 \Psi(r) + \frac{-\hbar^2}{2m_2} \nabla^2 \Psi(r) + V(r) \Psi(r) = E_{\text{tot}} \Psi(r).
\]

Subtracting the energy of the center-of-mass motion with \( E = E_{\text{tot}} - \frac{\mathbf{P}^2}{2M} \) and introducing the abbreviation \( m^{-1} = m_1^{-1} + m_2^{-1} \), we finally get,
\[
\left[ \frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi(r) = E \Psi(r).
\]

### 3.1.2 Particle in a cylindrical potential

The equation (3.7) is three-dimensional because \( \Psi(r) \) is a scalar field and the momentum operator in Cartesian coordinates is given by,
\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.
\]

However, in some situations, the symmetry of the system allows to reduce dimensionality similarly to the cases of the box potential and the three-dimensional harmonic oscillator. Let us now discuss the cases of cylindrical and spherical symmetry.

Electrons in magnetic fields are subject to the Lorentz force, which keeps them in a rotating motion. We can rewrite the momentum operator in cylindrical coordinates,\( x = \rho \cos \varphi \), \( y = \rho \sin \varphi \), \( z = z \), as
\[
\nabla^2 = \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial z^2}.
\]

Now, with the assumption that the potential only depends on \( \rho \), we can try ansatz \( \Psi(r) = R(\rho)\xi(\varphi)\zeta(z) \),
\[
\frac{1}{R(\rho)} \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + V(\rho) \right) \right] R(\rho) - \frac{\hbar^2}{2m} \frac{1}{\zeta(z)} \frac{\partial^2}{\partial z^2} \zeta(z) - \frac{\hbar^2}{2m\rho^2} \frac{1}{\xi(\varphi)} \frac{\partial^2}{\partial \varphi^2} \xi(\varphi) = E.
\]
First, we separate the axial motion,

$$-\frac{\zeta''}{\zeta} = \text{const} \equiv \frac{2mE_z}{\hbar^2}, \quad (3.12)$$

the solution of this equation being a superposition of two plane waves counterpropagating along the axis $z$, $\zeta(z) = Ae^{ik_zz} + Be^{-ik_zz}$. Now, we separate the azimuthal motion,

$$\rho^2 \frac{\partial R^2(\rho)}{\partial \rho^2} + \rho \frac{\partial R(\rho)}{\partial \rho} + \frac{2m\rho^2}{\hbar^2} [E - V(\rho)] - \rho^2 k_z^2 = -\xi'' = \text{const} \equiv m^2_\varphi. \quad (3.13)$$

The solution of the right-hand part of the equation is $\xi(\varphi) = Ce^{im_\varphi\varphi} + De^{-im_\varphi\varphi}$. Finally, we have the radial equation,

$$\frac{1}{R(\rho)} \frac{\partial R(\rho)}{\partial \rho^2} + \frac{1}{\rho R(\rho)} \frac{\partial R(\rho)}{\partial \rho} - \frac{2m}{\hbar^2} [E - V(\rho)] - k_z^2 - \frac{m^2_\varphi}{\rho^2} = 0, \quad (3.14)$$

with the effective potential $V_{\text{eff}} = V(\rho) + \frac{\hbar^2 m^2_\varphi}{2m \rho^2}$. For a homogeneous potential, $V(\rho) = V_0$, the solution will be a superposition of Bessel functions.

**Example 15 (Rigid rotor in cylindrical coordinates):** To give an example, we disregard the potential, $V(\rho) = 0$, and we consider for the particle an orbit with constant radius, $\rho = \text{const}$ such that $R'(\rho) = 0$. In this case, we only need to treat the orbital motion described by the right part of Eq. (3.13). For the solution of this equation, $\xi(\varphi) = Ae^{im_\varphi\varphi}$, to be well-defined, we need $\xi(\varphi) = \xi(\varphi + 2\pi)$. This implies,

$$m_\varphi = 0, \pm 1, \pm 2, \ldots$$

and

$$E_\varphi = \frac{\hbar^2 m^2_\varphi}{2m \rho^2}.$$  

The allowed energies $E_{m_\varphi} = E_\varphi$ can be obtained by letting the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \varphi^2},$$

with the moment of inertia $I = m\rho^2$ actuate on the azimuthal wavefunction $\xi(\varphi)$. We now define the operator,

$$\hat{l}_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}.$$  

This operator acts on the wavefunction $\xi$ as follows,

$$\hat{l}_z \xi(\varphi) = \hbar m_\varphi \xi(\varphi).$$

It is easy to show that wavefunctions with different values $m_l$ are orthogonal.

Note: 1. The state $m_\varphi = 0$ has zero energy; that is, it has no zero-point energy.
2. The particle is delocalized within a ring of radius $r$: $\Delta l_z \Delta \sin \varphi \geq \frac{\hbar}{2} |\langle \cos \varphi \rangle|$.
3.1.3 Hamiltonian in spherical coordinates

We can rewrite the momentum operator in spherical coordinates,

\[ x = r \sin \vartheta \cos \phi, \quad y = r \sin \vartheta \sin \phi, \quad z = r \cos \vartheta, \]  
\[ (3.15) \]

as \(^1\),

\[ \nabla^2_r = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{\hbar^2} \]  
\[ \text{where} \quad \frac{L^2}{\hbar^2} \equiv \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \phi^2}, \]  
\[ (3.16) \]

is an abbreviation called Legendre operator. For an isotropic potential, \( V(r) = V(r) \), we can try the ansatz,

\[ \Psi(r) = R(r)Y(\vartheta, \phi) \]  
\[ (3.17) \]

to solve the Schrödinger equation (2.56),

\[ \frac{r^2}{R(r)} \left[ -\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + V(r) - E \right] R(r) = -\frac{1}{2m} \frac{\hat{L}^2 Y(\vartheta, \phi)}{Y(\vartheta, \phi)} = \text{const} \equiv -\frac{\hbar^2}{2m} \ell(\ell+1), \]  
\[ (3.18) \]

where we choose a separation constant, \( \ell(\ell+1) \), the significance of which we shall soon learn. Considering only the angular part,

\[ \hat{L}^2 Y(\vartheta, \phi) = \hbar^2 \ell(\ell+1)Y(\vartheta, \phi), \]  
\[ (3.19) \]

and making another separation ansatz,

\[ Y(\vartheta, \phi) = \Theta(\vartheta)\Phi(\phi), \]  
\[ (3.20) \]

we obtain,

\[ \sin^2 \vartheta \left( \frac{1}{\Theta(\vartheta)} \frac{\partial}{\partial \vartheta} \sin \vartheta \frac{\partial}{\partial \vartheta} \Theta(\vartheta) + \ell(\ell+1) \right) = -\frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial \phi^2} \Phi(\phi) = \text{const} \equiv m^2, \]  
\[ (3.21) \]

where we choose a separation constant, \( m^2 \). Introducing another abbreviation,

\[ \hat{L}_z \equiv \frac{\hbar}{i} \frac{\partial}{\partial \phi}, \]  
\[ (3.22) \]

the azimuthal equation takes the form

\[ \hat{L}_z \Phi(\phi) = \hbar m \Phi(\phi), \]  
\[ (3.23) \]

As in the case of the cylindrical potential, the solution of the azimuthal equation is, using the normalization,

\[ \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \]  
\[ (3.24) \]

with the magnetic quantum number \( m = 0, \pm 1, \pm 2, \ldots \)

\(^1\)We may also write: \( \mathbf{p}^2 = (\hat{e}_r \cdot \mathbf{p})^2 + (\hat{e}_r \times \mathbf{p})^2 = \mathbf{p}_r^2 + \frac{L^2}{r^2} \), where \( \mathbf{p}_r^2 \) is the radial part of the Laplace operator and \( \frac{L^2}{r^2} \) the angular part.
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The polar equation,

\[
\frac{1}{\Theta(\vartheta) \sin \vartheta} \frac{\partial}{\partial \vartheta} \sin \vartheta \frac{\partial}{\partial \vartheta} \Theta(\vartheta) + \ell(\ell + 1) = \frac{m^2}{\sin^2 \vartheta},
\]

(3.25)
is called Legendre’s differential equation and can be solved by a power series in \( \cos k \vartheta \).

For \( m = 0 \), the solutions are the Legendre polynomials, \( P_\ell(\cos \vartheta) \) with

\[
P_\ell(z) = \frac{1}{2\ell!} \frac{d^\ell}{dz^\ell} \left[ (z^2 - 1)^\ell \right].
\]

(3.26)
The first polynomials are,

\[
P_0(z) = 1 , \quad P_1(z) = z , \quad P_2(z) = \frac{1}{2} (3z^2 - 1) , \quad P_3(z) = \frac{1}{2} (5z^3 - 3z).
\]

(3.27)

For \( m > 0 \), the solutions are the associated polynomials,

\[
P_{\ell}^m(z) = (-1)^m (1 - z^2)^{m/2} \frac{d^m}{dz^m} P_\ell(z) = \frac{(-1)^m}{2^\ell \ell!} (1 - z^2)^{m/2} \frac{d^{\ell+m}}{dz^{\ell+m}} (z^2 - 1)^\ell
\]

\[
P_{\ell}^{-m}(z) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_{\ell}^m(z).
\]

(3.28)
The polar function must still be normalized,

\[
\Theta_{\ell m}(\vartheta) = P_{\ell}^{m}(\cos \vartheta) \sqrt{\frac{2\ell + 1}{2 \pi} \frac{(\ell - m)!}{(\ell + m)!}}.
\]

(3.29)
The functions \( Y_{\ell m}(\vartheta, \varphi) \) are the spherical harmonics. They form an orthonormal system,

\[
\int_0^\pi \int_0^{2\pi} Y_{\ell' m'}^*(\vartheta, \varphi) Y_{\ell m}(\vartheta, \varphi) \sin \vartheta d\vartheta d\varphi = \delta_{\ell' \ell} \delta_{m' m}.
\]

(3.30)

Finite solutions only exist when the angular momentum quantum number is \( \ell = 0, 1, .. \) and for \( |m| \leq \ell \).

The solutions of the angular part of the Schrödinger equation for the hydrogen atom are finally,

\[
Y_{\ell m}(\vartheta, \varphi) = \frac{1}{\sqrt{2\pi}} P_{\ell}^{m}(\cos \vartheta) \sqrt{\frac{2\ell + 1}{2 \pi} \frac{(\ell - m)!}{(\ell + m)!}} \ e^{im\varphi}.
\]

(3.31)
The spherical harmonics are simultaneously eigenfunctions of the operators \( \mathbf{L}^2 \), as can be seen from Eq. (3.19), and of the operator \( L_z \) according to Eq. (3.23). The quantities represented by the quantum operators \( \hat{H}, \hat{L}^2, \hat{L}_z \) are conserved in the hydrogen system. The conservation of the angular momentum is due to the spherical symmetry of the Coulomb potential.

We will verify the parity of the spherical harmonics in Exc. 3.1.5.1.
Figure 3.1: Angular wavefunctions. Shown are the Legendre polynomials $P^m_\ell(\cos \vartheta)$ for $\ell = 0, 1, 2, 3$ and $m = 0, \ldots, \ell$. Red: $m = 0$, green: $|m| = 1$, blue: $|m| = 2$, and magenta: $|m| = 3$.

### 3.1.4 Separation of radial motion

In Sec. 3.1.3 we derived, after having separated the motion of the center-of-mass (that is, of the heavy nucleus) and the angular coordinates, the radial equation (3.18) describing the radial component of the electronic motion,

$$\frac{1}{R(r)} \left[ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + V(r) - E \right] R(r) = -\frac{L^2}{2mr^2}, \quad (3.32)$$

Now, we make the substitution $R(r) = u(r)/r$ and the radial equation becomes,

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{L^2}{2mr^2} + V(r) \right] u(r) = Eu(r). \quad (3.33)$$

This equation is very similar to a one-dimensional Schrödinger equation, but there is an additional potential term called **centrifugal potential**, $V_c(r) \equiv \frac{L^2}{2mr^2}$. \quad (3.34)

For example, for the potential of an electron orbiting a proton, we have,

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2\ell(\ell + 1)}{2mr^2} - E \right] u_{E\ell}(r) = 0. \quad (3.35)$$
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Figure 3.2: (code) Sum of a Coulomb potential and centrifugal potential for $\ell = 0$ (lower curve), $\ell = 1$ (center curve), and $\ell = 2$ (upper curve).

We will discuss this equation intensely in the context of the hydrogen atom.

In Exc. 3.1.5.2 we derive the radial Gross-Pitaevskii equation for a Bose-Einstein condensate trapped in a spherical potential. In the Exc. 3.1.5.3 we will study particles inside a central potential of zero depth, in the Excs. 3.1.5.4 and 3.1.5.5 we consider 3D spherical box potentials and in Exc. 3.1.5.6 a spherical harmonic potential.

Example 16 (Rigid rotor in spherical coordinates): We continue the discussion of the rigid rotor, now in spherical coordinates. In the case that the orbit of the particle is fixed to a radius $R$, we can neglect the kinetic energy due to the radial motion and the potential, both being constant. In this case the radial Schrödinger equation is,

$$\left[ \frac{\hbar^2 \ell (\ell+1)}{2mr^2} \right] u_{E\ell} = E_{\ell} u_{E\ell}. $$

The energies of the rigid rotor are

$$E_{\ell} = \frac{\hbar^2 \ell (\ell+1)}{2I},$$

with the momentum of inertia $I = mR^2$.  

3.1.5 Exercises

3.1.5.1 Ex: Parity of the spherical harmonic functions

We consider the parity transformation $P$ with $(x, y, z) \xrightarrow{P} (-x, -y, -z)$. Use spherical coordinates to show that $Y_{\ell m} \xrightarrow{P} (-1)^\ell Y_{\ell m}$, and therefore that a spherical surface function has even parity when $\ell$ is even, and odd parity, when $\ell$ is odd.

3.1.5.2 Ex: Bose-Einstein condensate in an isotropic potential

The Gross-Pitaevskii equation describing the wavefunction of a Bose-Einstein condensate is,

$$i\hbar \frac{\partial \psi({\mathbf r})}{\partial t} = \left( -\frac{\hbar^2}{2m} \Delta + V_{trp}(r) + g|\psi({\mathbf r})|^2 \right) \psi({\mathbf r}),$$

where the factor $g$ depends on the force of the interatomic interaction and $V_{trp}$ is the potential trapping the atoms. For $V({\mathbf r}) = V(r)$ the wave function will have radial symmetry, $\psi({\mathbf r}) = \frac{\phi(r)}{r}$. Rewrite the Gross-Pitaevskii equation for the function $\phi$. 

3.1.5.3 Ex: Motion of a free particle in spherical coordinates

Obtain the eigenfunctions of a free particle as the limiting case of its motion in a central force field with \( V(r) \to 0 \). Compare the derived eigenfunctions – associated with the complete set of observables \( H, L^2, \text{ and } L_z \) – to those described by plane waves – associated with the motion characterized by the observables \( p_x, p_y, p_z \), and \( \hat{H} = \frac{P^2}{2m} \), which also constitute a complete set of observables.

3.1.5.4 Ex: Particle in a spherical box

Find the energy levels and wavefunctions of a particle confined in a spherical box described by potential energy, \( V(r) = 0 \) for \( r < a \) and \( V(r) = \infty \) for \( r \geq a \) considering the angular momentum \( \ell = 0 \).

3.1.5.5 Ex: Finite spherical 3D potential well

a. Derive the possible energy levels and associated wavefunctions for a particle trapped in a spherical 3D potential well of depth \( V_0 \) and radius \( a \). Note that this problem is analogous to Mie scattering of scalar waves.
b. Discuss the case of a well surrounded by infinitely high walls.

3.1.5.6 Ex: Particle in a spherical harmonic potential

A quantum particle of mass \( m \) is subject to a potential
\[
V = \frac{1}{2}m\omega^2(x^2 + y^2 + z^2).
\]
a. Obtain the energy levels of this particle. That is, determine the eigenvalues of
\[
-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi.
\]
b. Consider the fundamental level and the first two excited levels. Set up a table showing for each of these three levels the energy value, the degeneracy, and the respective states in terms of the quantum numbers.
c. Using
\[
\nabla^2\psi = \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{L^2}{r^2} \right] \psi
\]
and remembering \( \hat{L}^2Y_{\ell m}(\theta, \phi) = \hbar^2\ell(\ell + 1)Y_{\ell m} \), write down the differential equation of item (a) for the radial part of the wavefunction (it is not necessary to solve it). Identify in this equation the effective potential \( V_{\text{eff}}(r) \).
d. Solve the differential equation of the previous item for the case where \( \ell = 0 \) and determine the corresponding eigenvalue. To do this, allow for a solution of the type \( e^{-\alpha r^2} \) and determine \( \alpha \).

3.2 Quantum treatment of hydrogen

According to Rutherford’s and Bohr’s planetary atomic model we may imagine an atom as a very heavy nucleus having a positive electric charge surrounded by a very
light negatively charged charge electronic cloud. Since the nucleus is very small compared to the electronic cloud, we treat it as an entity with mass $M$ and charge $Ze$, where $Z$ is the number of protons and corresponds to the order of the element in the periodic system.

The canonical procedure for calculating all properties of an atom is to establish its Hamiltonian, that is, to determine the kinetic energies of all components and all interaction energies between them, and to solve the Schrödinger equation. For each component we write the kinetic energy,

$$ T_{ncl} = \frac{P^2}{2M} \quad \text{and} \quad T_{ele} = \sum_{i=1}^{Z} \frac{p_i^2}{2m}. \quad (3.36) $$

Here, $(R, P)$ are the nuclear coordinates and $(r_i, p_i)$ those of the electrons. The energies that corresponds to the interactions, that is, Coulombian attraction or repulsion, between the components of the atom are,

$$ V_{ncl-ele} = -\sum_{i=1}^{Z} \frac{Ze^2}{4\pi\varepsilon_0 |R - r_i|} \quad \text{and} \quad V_{ele-ele} = \sum_{i \neq j=1}^{Z} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|}. \quad (3.37) $$

There are also interactions due to the spin of the particles, which we will deal with later.

Obviously, the solution to this many-body problem is very complicated. For this reason, we will in this chapter, based on the Schrödinger equation, calculate the complete spectrum of the simplest possible atom, hydrogen. This atom consists of a proton and an electron, only.

Figure 3.3: The hydrogen model applies to other atoms having a single valence electron occupying a sufficiently large space, that it sees the nucleus together with rest of the electrons shielding the nucleus as a single positive charge.

### 3.2.1 Bohr’s model

Let us now turn our attention to the radial part of the Schrödinger equation describing a particle in a radial potential. We expect that the quantum solutions for the hydrogen atom are similar to the predictions of Bohr’s model. Following this model, the orbit is stable when the attraction force is equal to the centrifugal force. But in addition, Bohr postulated, that only certain energies are allowed. For the hydrogen atom he found,

$$ E_n = -\frac{1}{2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{r_n} = -\frac{Z^2\hbar^2}{2ma_B^2 n^2} = -\frac{Z^2e^2}{4\pi\varepsilon_0} \frac{1}{\frac{2a_B}{n^2} n^2} = -\frac{Z^2e^2}{n^2} 13.6 \text{ eV}, \quad (3.38) $$
with the *Bohr radius*

\[
a_B \equiv 4\pi\varepsilon_0 \frac{\hbar^2}{m e^2}.
\] (3.39)

With this equation he was able to explain the spectral observations. Electrons can only jump from one level to another, while emitting or absorbing a photon. The series observed in the hydrogen spectrum \((E_n - E_m)/\hbar\) are the Lyman \((m = 1)\), the Balmer \((m = 2)\), the Paschen \((m = 3)\) and the Brackett series \((m = 4)\).

![Figure 3.4: The hydrogen transitions.](image)

The discussion of the hydrogen atom within quantum mechanics can start from the radial Schrödinger equation (3.35) with the Coulomb attraction potential,

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2\ell(\ell + 1)}{2mr^2} - E \right] u_{\ell}(r) = 0.
\] (3.40)

In order to facilitate comparison with Bohr’s classical model, let us express the energy in terms of Bohr’s energy, \(E \equiv E_n = E_1/n^2\), and write the radius in units of \(a_B\), that is, \(\tilde{r} \equiv Zr/a_B\). This yields,

\[
\tilde{r} u''_{n,\ell}(\tilde{r}) + \left( -\frac{\ell(\ell + 1)}{\tilde{r}^2} + \frac{2}{\tilde{r}} - \frac{1}{n^2} \right) u_{n,\ell}(\tilde{r}) = 0.
\] (3.41)

To ensure that for large radii, \(r \to \infty\), the solution is finite, we need an asymptotic behavior like \(u_{n,\ell}(\tilde{r} \to \infty) = e^{-\tilde{r}/n}\). To ensure that for small radii, \(r \to 0\), the solution is finite, we need \(u_{n,\ell}(\tilde{r} \to 0) = \tilde{r}^{\ell+1}\). We derive the asymptotic solutions in Exc. 3.2.3.1. The resulting differential equation only has solutions for an integer and positive *main quantum number* \(n\) and when \(\ell = 0, 1, \ldots, n - 1\). That is, in the relation \(E = E_1/n^2\) the parameter \(n\) is integer and positive, such that energy levels remain degenerate in \(\ell\) and \(m\). This means that Bohr’s postulate of discrete (i.e. quantized) energy levels is valid (uff!)  

Substituting the ansatz,

\[
u_{n,\ell}(\tilde{r}) = D_{n\ell}\tilde{r}^{\ell+1}e^{-\tilde{r}/n}L(\tilde{r}) ,
\] (3.42)

it’s easy to show (see Exc. 3.2.3.2), that the differential equation (3.41) reduces to,

\[
\tilde{r}L''(\tilde{r}) + 2 \left[ (\ell + 1) - \frac{1}{n}\tilde{r} \right] L'(\tilde{r}) + 2 \left[ 1 - \frac{1}{n}(\ell + 1) \right] L(\tilde{r}) = 0.
\] (3.43)
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Figure 3.5: Level scheme.

Still with the abbreviation $\rho \equiv 2\tilde{r}/n = 2Zr/na_B$ the ansatz

$$u_{n\ell}(\rho) = D_{n\ell}\rho^{\ell+1}e^{-\rho/2}L(\rho),$$

leads to the differential equation \(^2\)

$$\rho L''(\rho) + [2(\ell + 1) - \rho] L'(\rho) + [n - \ell - 1]L(\rho) = 0.$$

The solutions of this differential equation, $L^{(2\ell+1)}_{n-\ell-1}(\tilde{r})$, are the Laguerre polynomials. These polynomials are listed in mathematical tables. Using the properties of these polynomials it is possible to show that the radial functions are orthogonal and can be normalized (see Exc. 3.2.3.3). Fig. 3.6 shows the curves for the lowest orbitals.

Finally, we can write the total solutions,

$$\psi_{n,\ell,m}(r,\theta,\phi) = \frac{u_{n,\ell}(r)}{r}Y_{\ell,m}(\theta,\phi) \quad \text{with} \quad E_n = -\frac{\hbar^2}{2ma_B^2} \frac{Z^2}{n^2},$$

where $n = 1, 2, 3, .., \ell = 0, 1, .., n - 1 \quad m = -\ell, -\ell + 1, .., \ell$. Of course, each energy level $n$ is,

$$\sum_{\ell=0}^{n-1}(2\ell + 1) = n^2.$$

\(^2\)Laguerre’s associated differential equation is,

$$\rho \partial^2_{\rho} L^{(\alpha)}(\rho) + (\alpha + 1 - \rho)\partial_{\rho} L^{(\alpha)}(\rho) + \nu L^{(\alpha)}(\rho) = 0.$$

The Laguerre polynomials are generated by

$$L^{(\alpha)}_{\nu}(\rho) = \frac{e^{\rho} \rho^{-\alpha}}{\alpha!} \frac{d^\nu}{d\rho^\nu} \left( e^{-\rho} \rho^{-\alpha} \right).$$
times degenerate.

Here is a list of the first wavefunctions of the hydrogen atom,

\[
\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_B} \right)^{3/2} e^{-\tilde{r}}
\]

\[
\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_B} \right)^{3/2} (2 - \tilde{r})e^{-\tilde{r}/2}
\]

\[
\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_B} \right)^{3/2} \tilde{r}e^{-\tilde{r}/2} \cos \theta
\]

\[
\psi_{21\pm 1} = \frac{1}{8\sqrt{2\pi}} \left( \frac{Z}{a_B} \right)^{3/2} \tilde{r}e^{-\tilde{r}/2} \sin \theta e^{\pm i\varphi}
\]

\[
\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_B} \right)^{3/2} (27 - 18\tilde{r} + 2\tilde{r}^2)e^{-\tilde{r}}
\]

\[
\psi_{31\pm 1} = \frac{\sqrt{2}}{81\sqrt{3\pi}} \left( \frac{Z}{a_B} \right)^{3/2} (6 - \tilde{r})\tilde{r}e^{-\tilde{r}/3} \sin \theta e^{\pm i\varphi}
\]

\[
\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a_B} \right)^{3/2} \tilde{r}^2 e^{-\tilde{r}/3} (3\cos^2 \theta - 1)
\]

where we use the abbreviation \( \tilde{r} \equiv Zr/a_B \). Using these wavefunctions we can now
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calculate important eigenvalues such as, for example,

\[ \langle 1 \rangle_{n\ell m} = 1 \]
\[ \langle \hat{r} \rangle_{n\ell m} = n^2 \left[ \frac{1}{2} \left( 1 - \frac{\ell(\ell + 1)}{n^2} \right) \right] \]
\[ \langle \hat{r}^2 \rangle_{n\ell m} = n^4 \left[ \frac{3}{2} \left( 1 - \frac{\ell(\ell + 1)}{n^2} - \frac{1}{3} \right) \right] \]
\[ \langle \hat{r}^3 \rangle_{n\ell m} = n^6 \left[ \frac{35}{8} - \frac{35}{8n^2} \frac{15}{4n^2} (\ell + 2)(\ell - 1) + \frac{3}{8n^4} (\ell + 2)(\ell + 1)\ell(\ell - 1) \right] \]
\[ \langle \hat{r}^4 \rangle_{n\ell m} = n^8 \left[ \frac{63}{8} + \frac{35}{8n^2} (2\ell^2 + 2\ell - 3) + \frac{5}{8n^4} 5\ell(\ell + 1)(3\ell^2 + 3\ell - 10) + \frac{12}{n^8} \right] \]
\[ \langle \frac{1}{\hat{r}} \rangle_{n\ell m} = \frac{1}{n^2} \]
\[ \langle \frac{1}{\hat{r}^2} \rangle_{n\ell m} = \frac{1}{n^3(\ell + \frac{1}{2})} \]
\[ \langle \frac{1}{\hat{r}^3} \rangle_{n\ell m} = \frac{n}{n^4\ell(\ell + \frac{1}{2})(\ell + 1)} \]
\[ \langle \frac{1}{\hat{r}^4} \rangle_{n\ell m} = \frac{3n^2 - \frac{1}{2} \ell(\ell + 1)}{n^5(\ell + \frac{3}{2})(\ell + 1)(\ell + \frac{1}{2})\ell(\ell - \frac{1}{2})} . \]

These results will become important later. In Exc. 3.2.3.4 we will calculate the eigenvalue \( \langle r \rangle \) for several orbitals \( |\Psi_{n\ell m}\rangle \).

3.2.2 The virial theorem

Originally derived for classical mechanics, the virial theorem also holds for quantum mechanics, as shown for the first time by Vladimir Aleksandrovich Fock. We evaluate the commutator between the Hamiltonian

\[ \hat{H} = \hat{p}^2 / 2m + V(\hat{r}) , \]

and the product of the position operator \( \hat{r} \) with the momentum operator \( \hat{p} = -i\hbar \nabla \) of the particle:

\[ [\hat{H}, \hat{r} \cdot \hat{p}] = [\hat{H}, \hat{r}] \cdot \hat{p} + \hat{r} \cdot [\hat{H}, \hat{p}] = -i\hbar \frac{\hat{p}^2}{m} + i\hbar \hat{r} \cdot \nabla V , \]

using the theorems of Ehrenfest. Therefore, we find for the operator \( \hat{Q} = \hat{r} \cdot \hat{p} \) the commutator,

\[ \frac{i}{\hbar} [\hat{H}, \hat{Q}] = 2E_{\text{kin}} - \hat{r} \cdot \nabla V . \]

The left side of this equation is precisely \(-d\hat{Q}/dt\), following the Heisenberg equation of motion. The eigenvalue \( \langle d\hat{Q}/dt \rangle \) of the temporal derivative vanishes in steady state, therefore we obtain the virial theorem,

\[ 2\langle E_{\text{kin}} \rangle = \langle \hat{r} \cdot \nabla V \rangle . \]
Example 17 (Virial theorem applied to a central potential): For example, for a central potential $V(r) \propto r^s$ we obtain,

$$2\langle E_{\text{kin}} \rangle = \langle \hat{r} \cdot \hat{e}_r \frac{\partial V}{\partial r} \rangle = s\langle V \rangle.$$ 

In Exc. 3.2.3.5 we calculate the eigenvalues $\langle r^{-1} \rangle$ and $\langle p^2 \rangle$ and we verify the virial theorem. Finally, in Exc. 3.2.3.6 we calculate transition matrix elements between different orbitals.

### 3.2.3 Exercises

#### 3.2.3.1 Ex: Asymptotes of Laguerre’s polynomials

Derive the asymptotic solutions of equation (3.41).

#### 3.2.3.2 Ex: Laguerre equation

Show that the equation (3.41) transforms with the ansatz (3.42) into equation (3.43).

#### 3.2.3.3 Ex: Laguerre functions

Using the orthogonality relation of associated Laguerre polynomials,

$$\int_0^\infty \rho^\alpha e^{-\rho} L_n^{(\alpha)}(\rho) L_m^{(\alpha)}(\rho) d\rho = \frac{\Gamma(n + \alpha + 1)}{n!} \delta_{n,m},$$

$$\int_0^\infty \rho^\alpha e^{-\rho} L_n^{(\alpha)}(\rho) \rho^2 d\rho = \frac{(n + \alpha)!}{n!}(2n + \alpha + 1),$$

and the recursion formula,

$$nL_n^{(\alpha+1)}(\rho) = (n - \rho)L_n^{(\alpha+1)}(\rho) + (n + \alpha)L_{n-1}^{(\alpha)}(\rho),$$

$$\rho L_n^{(\alpha+1)}(\rho) = (n + \alpha)L_{n-1}^{(\alpha)}(\rho) - (n - \rho)L_n^{(\alpha)}(\rho),$$

a. calculate the normalization constant $D_{n,l}$ for a hydrogen-like atom with atomic number $Z$;

b. calculate the mean value $\langle r \rangle_{nlm} = n^2a_B Z \left[1 + \frac{1}{2} \left(1 - \frac{\ell(\ell + 1)}{n^2}\right)\right]$;

c. calculate the mean value $\langle \frac{1}{r} \rangle_{n\ell m} = \frac{Z}{n^2a_B}$.

#### 3.2.3.4 Ex: Orbital radii in Bohr’s model

Using the results of 3.2.3.3, obtain the expectation values $\langle r \rangle$ for the states $\Psi_{100}$, $\Psi_{210}$ and $\Psi_{320}$ of the hydrogen atom. Compare the results with those of Bohr’s model.
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3.2.3.5 Ex: The virial theorem and Bohr’s model

Calculate, for the state $\Psi_{320}$ of the hydrogen atom, the expectation values $\langle \frac{1}{r} \rangle$, $\langle L^2 \rangle$, and $\langle p^2 \rangle$.

From the results, obtain the expectation values for the kinetic and potential energies, $\langle T \rangle$ and $\langle V \rangle$, and show that, consistent with the virial theorem, $\langle T \rangle = -\frac{1}{2}\langle V \rangle$.

Compare the results with Bohr’s model.

3.2.3.6 Ex: Transition matrix elements

Using the following (non-normalized) wavefunctions of hydrogen, $\psi_{100}(r) = e^{-\tilde{r}}$, $\psi_{210}(r) = \tilde{r}e^{-\tilde{r}/2}\cos \theta$ e $\psi_{21\pm 1}(r) = \tilde{r}e^{-\tilde{r}/2}\sin \theta e^{\pm i\phi}$, calculate the matrix elements (a) $\langle \psi_{100}|\tilde{z}|\psi_{210} \rangle$, (b) $\langle \psi_{100}|\tilde{z}|\psi_{211} \rangle$, (c) $\langle \psi_{100}|\tilde{x} - i\tilde{y}|\psi_{210} \rangle$, and (d) $\langle \psi_{100}|\tilde{x} - i\tilde{y}|\psi_{211} \rangle$ using the formulae:

$$\int_0^\infty x^4 e^{-3x/2} dx = \frac{256}{81}, \quad \int_0^\pi \sin^3 x dx = \frac{4}{3},$$
$$\int_0^\pi \cos x \sin^2 x dx = 0, \quad \int_0^\pi \cos^2 x \sin x dx = \frac{2}{3}.$$

Try to interpret the results.

3.3 Angular momentum

3.3.1 The orbital angular momentum operator

The definition of orbital angular momentum is adopted from classical mechanics:

$$\hat{L} = \hat{r} \times \hat{p} = -i\hbar \hat{\nabla} = -i\hbar \begin{vmatrix} \hat{e}_x & \hat{e}_y & \hat{e}_z \\ \partial_x & \partial_y & \partial_z \\ x & y & z \end{vmatrix}.$$

(3.54)

To better understand the properties of the angular momentum operator in quantum mechanics we will derive in the Excs. 3.3.4.1 and 3.3.4.2 some of its properties.

Figure 3.7: Illustration of angular momentum in quantum mechanics.
3.3.1.1 Constants of motion

The preceding chapter dealt with the resolution of the radial and angular equations for the case of a radial potential. The radial equation allowed to calculate the eigenenergies of the Hamiltonian $\hat{H}$,

$$\hat{H} \psi = E_n \ell \psi .$$

(3.55)

We also found the common eigenvalues and eigenfunctions of operators $\hat{l}^2$ and $\hat{l}_z$ [see Eqs. (3.19) and (3.23)]. We now use the notation $|\ell, m\rangle$ for the eigenfunctions,

$$\hat{l}^2 |\ell, m\rangle = \hbar^2 (\ell + 1) |\ell, m\rangle \quad \text{and} \quad \hat{l}_z |\ell, m\rangle = \hbar m |\ell, m\rangle .$$

(3.56)

With this we have,

$$[\hat{H}, \hat{l}^2] |\psi\rangle = \hat{H} \hbar^2 (\ell + 1) |\psi\rangle - \hat{l}^2 E |\psi\rangle = 0 \quad \text{(3.57)}$$

and 

$$[\hat{H}, \hat{l}_z] |\psi\rangle = \hat{H} \hbar m |\psi\rangle - \hat{l}_z E |\psi\rangle = 0 .$$

Therefore, the operators $\hat{l}^2$ and $\hat{l}_z$ are constants of motion,

$$[\hat{H}, \hat{l}_z] = 0 = [\hat{H}, \hat{l}^2] .$$

(3.58)

Exc. 3.3.4.3 asks to show explicitly, at the example of an isotropic three-dimensional harmonic oscillator, that $\hat{l}^2$ and $\hat{l}_z$ are constants of motion.

3.3.2 SU(2) algebra of angular momentum and spin

So far, we have solved the angular eigenvalue equation in the spatial representation for an orbital angular momentum, $\hat{l} = \hat{r} \times \hat{p}$. But it is not clear, whether every angular momentum has this representation, which is derived from classical notions. In fact, we will see that the electron has an intrinsic spin with no orbiting charges. What we must show now is that for any spin $\hat{j}$ satisfying

$$\hat{j} \times \hat{j} = i \hbar \hat{j} ,$$

(3.59)

or $[\hat{j}_m, \hat{j}_n] = i \hbar \epsilon_{kmn} \hat{j}_k$ using the Levi-Civita symbol, we obtain a consistent algebra.

Since $\hat{j}^2$ and $\hat{j}_z$ commute (we show this from Eq. (3.59) in Exc. 3.3.4.4), they have common eigenfunctions $|j, m\rangle$. We can write the eigenvalues as,

$$\hat{j}^2 |j, m\rangle = \hbar^2 j(j + 1) |j, m\rangle \quad \text{and} \quad \hat{j}_z |j, m\rangle = \hbar m |j, m\rangle ,$$

(3.60)

where, for now, we only know that $m$ is real and $j \geq 0$. But since $\langle j, m |\hat{j}^2 |j, m\rangle \geq \langle j, m |\hat{j}_z^2 |j, m\rangle$, it is clear that $j(j + 1) \geq m^2$.

3.3.2.1 Creation and annihilation operator

Now we introduce the rising operator $\hat{j}_+$ and the lowering operator $\hat{j}_-$ via

$$\hat{j}_\pm = \hat{j}_x \pm i \hat{j}_y \quad \text{such that} \quad \hat{j}_- = \hat{j}_+^\dagger .$$

(3.61)
It is easy to check the following relationships
\[ [\hat{j}_z, \hat{j}_\pm] = \pm \hbar \hat{j}_\pm \quad \text{and} \quad [\hat{j}^2, \hat{j}_\pm] = 0 \quad \text{and} \quad \hat{j}_+ \hat{j}_- = \hat{j}^2 - \hat{j}_z^2 = \hbar \hat{j}_z. \quad (3.62) \]

With this we find
\[ \hat{j}_z \hat{j}_\pm |j, m\rangle = (|\hat{j}_z, \hat{j}_\pm\rangle + \hat{j}_\pm \hat{j}_z |j, m\rangle) = \hbar (m \pm 1) \hat{j}_\pm |j, m\rangle \]
and
\[ \hat{j}^2 |j, m\rangle = \hbar^2 j(j+1) \hat{j}_\pm |j, m\rangle. \]

That is, $\hat{j}_\pm |j, m\rangle$ is an eigenstate of $\hat{j}^2$ and $\hat{j}_z$ with the eigenvalues $j$ and $m \pm 1$, respectively, if $j_\pm |j, m\rangle \neq 0$. Hence,
\[ \hat{j}_+ |j, m\rangle \propto |j, m+1\rangle. \quad (3.64) \]

In order not to violate the condition $m^2 \leq j(j+1)$, we need to fix $\hat{j}_\pm |j, \pm j\rangle = 0$. Therefore, for a specified $j$, the $m$ can have only one of the $2j+1$ possible values $m = -j, -j+1, \ldots, j$. Since $2j+1$ is an integer, $j$ can only have values $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ Thus, the eigenvalue equation of the observables $\hat{j}^2, \hat{j}_z$ is solved since we could have chosen instead of $\hat{j}_z$ any one of the components of $\hat{j}$, knowing that the others do not commute with the chosen one.

All spin components $\hat{j}_z$ and the scalar $\hat{j}^2$ can only have discrete eigenvalues. The smallest unit is $\hbar/2$. With the normalization $\langle j, m | j', m' \rangle = \delta_{jj'} \delta_{mm'}$ we have,
\[ \langle j, m | \hat{j}_\pm | j, m \rangle = \langle j, m | (\hat{j}^2 - \hat{j}_z^2 = \hbar \hat{j}_z) | j, m \rangle = \hbar^2 [j(j+1) - m(m \pm 1)], \quad (3.65) \]
and
\[ \hat{j}_\pm | j, m \rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} | j, m \pm 1 \rangle. \quad (3.66) \]

In Exc. 3.3.4.5 we calculate the uncertainty of the angular momentum components, in Exc. 3.3.4.6 we write the operator $\hat{j}_x$ in a matrix form, and in Exc. 3.3.4.7 we calculate projections of the spin of the electron in different directions of the quantization axis.

### 3.3.3 The electron spin

Every angular momentum $\hat{\mathbf{l}}$ generates a magnetic dipole moment $\mu_\ell \propto \hat{\mathbf{l}}$, which interacts with external magnetic fields, $V(B) = \mu_\ell \cdot B$. Inhomogeneous magnetic fields exert forces on dipole moments, $\mathbf{F} = -\nabla (\mu_\ell \cdot B)$, which are detected by the Stern-Gerlach experiment. This experiment reveals not only the quantization of angular momentum, but also the presence of semi-integral values for the magnetic quantum number.

In 1925 Uhlenbeck and Goudsmit proposed that the electron could have an intrinsic angular momentum with the quantum number $s = 1/2$. This angular momentum, called spin, would not correspond to any orbiting mass or charge distribution within the classical radius of the electron of the type $\mathbf{l} = \mathbf{r} \times \mathbf{p}$. The spin is a purely quantum phenomenon because it disappears when $\hbar \to 0$. It is believed nowadays that the electron is actually point-like with no detectable deviation from Coulomb’s law at any distance. The spin of the electron does not follow from the Schrödinger equation, but can be included, ad hoc. On the other hand, it is interesting that it is a necessary
consequence of the stringent relativistic derivation of quantum mechanics by Paul Dirac.

To characterize the spin, we can use the whole SU(2) formalism of the quantum mechanics of angular momentum:

$$\hat{s} \times \hat{s} = i\hbar\hat{s},$$  \hspace{1cm} (3.67)

and

$$\hat{s}^2|\frac{1}{2}, \pm \frac{1}{2}\rangle = \hbar^2 \frac{3}{4}|\frac{1}{2}, \pm \frac{1}{2}\rangle, \hspace{0.5cm} \hat{s}_z|\frac{1}{2}, \pm \frac{1}{2}\rangle = \pm \frac{\hbar}{2}|\frac{1}{2}, \pm \frac{1}{2}\rangle, \hspace{1cm} (3.68)$$

and

$$\hat{s}_\pm = \hat{\sigma}_\pm = |\frac{1}{2}, \pm \frac{1}{2}\rangle\langle |\frac{1}{2}, \mp \frac{1}{2}|.$$  

The operators $\hat{\sigma}_\pm$ are the Pauli spin matrices.

### Exercises

#### 3.3.4.1 Ex: Properties of the angular orbital momentum

Show that $\hat{\mathbf{l}} \times \hat{\mathbf{l}} = i\hbar \hat{\mathbf{l}}$ and $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$.

#### 3.3.4.2 Ex: Levi-Civita tensor

Demonstrate $[l_k, r_m] = i\hbar r_n \varepsilon_{kmn}$ where the Levi-Civita tensor is defined by $\varepsilon_{kmn} = 1$ when $(kmn)$ is an even permutation of $(123)$, $\varepsilon_{kmn} = -1$ for an odd permutation, and $\varepsilon_{kmn} = 0$ when two of the indices are equal.

#### 3.3.4.3 Ex: Angular orbital momentum of a harmonic oscillator

Show for an isotropic three-dimensional harmonic oscillator: $[\hat{H}, \hat{l}_x^2] = [\hat{H}, \hat{l}_y^2] = 0$. Make explicit calculations, that is, show

$$\left[ \frac{p^2}{2m}, \hat{l}_z \right] = 0 = \left[ \frac{m}{2} \omega^2 r^2, \hat{l}_z \right] \quad \text{e} \quad \left[ \frac{p^2}{2m}, \hat{l}_x^2 \right] = 0 = \left[ \frac{m}{2} \omega^2 r^2, \hat{l}_y^2 \right].$$

#### 3.3.4.4 Ex: Commutation of the absolute value and the components of the orbital angular momentum

Show $[\hat{j}_z^2, \hat{j}_z] = 0$.

#### 3.3.4.5 Ex: Uncertainty of angular momentum components

Shows that if $\hat{j}_z$ is precise, then $\hat{j}_x$ and $\hat{j}_y$ are imprecise.

#### 3.3.4.6 Ex: Matrix representation of the components of the angular momentum

Calculate the matrix elements of $\hat{j}_x$ and $\hat{j}_z^2$ in the base where $\hat{j}_z$ is observable. Give the general formula and examples for $j = \frac{1}{2}$ and $j = 1$.  

3.3.4.7 Ex: Spin-1/2-particle in a magnetic field

Consider a spin-1/2-particle whose magnetic moment is $\vec{\mu} = \gamma \vec{S}$ (where $\gamma$ is a constant). We can describe the quantum state of this particle in terms of the space generated by the eigenvectors $|+\rangle$ and $|\rangle$ of the operator $\hat{S}_z$, which measures the spin projection in z-direction:

$$\hat{S}_z |+\rangle = \frac{\hbar}{2} |+\rangle, \quad \hat{S}_z |\rangle = -\frac{\hbar}{2} | \rangle.$$

Initially ($t = 0$) the particle is in the state $\psi(t = 0) = |+\rangle$ and is subject to a uniform magnetic field $\vec{B} = B\hat{e}_y$, so that:

$$\hat{H} = -\vec{\mu} \cdot \vec{B} = -\gamma B \hat{S}_y.$$

a. What are the possible measurements of the spin projection on the y-axis?

b. Find the eigenvectors of $\hat{S}_y$.

c. Get $|\psi(t)\rangle$ at $t > 0$ in terms of the eigenvectors $|+\rangle$ and $|\rangle$ defined above.

d. Obtain the mean expectation values of the observables $S_x$, $S_y$ and $S_z$ as a function of time.

3.4 Coupling of angular momenta

3.4.1 Singlet and triplet states with two electrons

In this section we first consider the spin states of two electrons, which can be combined into two groups with well-defined total spin. With this we can understand the energy spectrum of helium, which is very much dominated by Pauli’s principle and quantum statistics. The introduced concepts can be extended to atoms with many electrons.

Angular momentum is an important quantum number in the treatment of the internal structure of atoms. The two electrons in the helium electronic shell each contribute a spin of $S = \frac{1}{2}$, which couple to a total angular momentum. Let us consider, for simplicity, two free electrons. The state of the two-particle system is an element of the product space of the two Hilbert spaces in which the individual electrons are described. We will now apply the formalism of Sec. 2.3.8 explicitly to a pair of electrons. The states that the two electrons can occupy are:

$$|\gamma_1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \equiv |\uparrow\uparrow\rangle,$$

$$|\gamma_2\rangle = |\uparrow\downarrow\rangle, \quad |\gamma_3\rangle = |\downarrow\uparrow\rangle, \quad |\gamma_4\rangle = |\downarrow\downarrow\rangle.$$ (3.69)

The Pauli matrices act on the spin of the individual electrons $a$ and $b$. They can be
extended to the product Hilbert space as follows,
\[
\frac{\hbar}{2} \hat{\sigma}_x \otimes I_2 = \frac{\hbar}{2} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad \frac{\hbar}{2} I_2 \otimes \hat{\sigma}_x = \frac{\hbar}{2} \begin{pmatrix} \sigma_x & 0 \\ 0 & \sigma_x \end{pmatrix}
\] (3.70)
\[
\frac{\hbar}{2} \hat{\sigma}_y \otimes I_2 = \frac{\hbar}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \frac{\hbar}{2} I_2 \otimes \hat{\sigma}_y = \frac{\hbar}{2} \begin{pmatrix} \sigma_y & 0 \\ 0 & \sigma_y \end{pmatrix}
\]
\[
\frac{\hbar}{2} \hat{\sigma}_z \otimes I_2 = \frac{\hbar}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \frac{\hbar}{2} I_2 \otimes \hat{\sigma}_z = \frac{\hbar}{2} \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}
\]

With these operators we can now build other operators. We first consider the three components of the total angular momentum,
\[
\hat{S}_k = \frac{\hbar}{2} (\hat{\sigma}_k \otimes I_2 + I_2 \otimes \hat{\sigma}_k)
\] such that
\[
\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \frac{i\hbar}{2} \begin{pmatrix} 0 & -1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 \\ 0 & -1 & -1 & 0 \end{pmatrix}, \quad \hat{S}_z = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}
\] (3.71)

The operator for the square of the absolute value of the total angular momentum is calculated as follows:
\[
\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}
\] (3.72)

Now we look for the eigenvalues of the total angular momentum. The equation for the eigenvalues of \(S_z\),
\[
\hat{S}_z |\gamma_k\rangle = M_S |\gamma_k\rangle ,
\] is already diagonal in the introduced basis \(\{\gamma_k\}\) with the eigenvalues,
\[
M_S = \hbar, 0, 0, -\hbar
\] (3.73)

For \(\hat{S}^2\) the situation is more interesting: The states \(|\gamma_1\rangle\) and \(|\gamma_4\rangle\) are eigenstates of \(\hat{S}^2\) for the eigenvalue \(2\hbar^2\), but the states \(|\gamma_2\rangle\) and \(|\gamma_3\rangle\) are not eigenstates. On the other hand, we know that the linear combination of two eigenstates with the same eigenvalue is also a eigenstate. Therefore, the states
\[
|\gamma_a\rangle = \frac{1}{\sqrt{2}} (|\gamma_2\rangle - |\gamma_3\rangle) \quad \text{and} \quad |\gamma_s\rangle = \frac{1}{\sqrt{2}} (|\gamma_2\rangle + |\gamma_3\rangle)
\] (3.75)
are still eigenstates of \(\hat{S}_z\), but they also are eigenstates of \(\hat{S}^2\), since we can easily verify,
\[
\hat{S}^2 |\gamma_s\rangle = 2\hbar^2 |\gamma_s\rangle \quad \text{and} \quad \hat{S}^2 |\gamma_a\rangle = \hbar^2 |\gamma_a\rangle ,
\] (3.76)
using the matrices (3.71). In summary, for the eigenvalue \(\langle \hat{S}^2 \rangle = 2\hbar^2\) there exist the following three states:
\[
\begin{cases}
|\gamma_1\rangle & m_s = 1 \\
|\gamma_4\rangle & m_s = -1 \\
|\gamma_s\rangle & m_s = 0
\end{cases} \quad \text{triplet } , \quad S = 1
\] (3.77)
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For $\langle S^2 \rangle = 0$ there is only one state:

$$ |\gamma_a \rangle \quad m_a = 0 \quad \text{singlet} \ , \ S = 0 \ . \quad (3.78) $$

By exchanging the two electrons, the vectors $|\gamma_1 \rangle$ and $|\gamma_4 \rangle$ retain their shape, while the mixed vectors change their shape: $\gamma_2 \leftrightarrow \gamma_3$. Under particle exchange $|\gamma_a \rangle$ reverses its sign, that is, it is antisymmetric, while $|\gamma_1 \rangle$, $|\gamma_4 \rangle$ and $|\gamma_c \rangle$ conserve their signs, that is, they are symmetrical.

In summary, the triplet states have the quantum number of the total angular momentum (with the expected value for $\hat{S}^2$ of $\hbar^2 S(S + 1) = 2\hbar^2$), and they are symmetrical about the exchange of particles. The singlet state has the quantum number of the total angular momentum $S = 0$, and it is antisymmetric about the exchange of particles.

A similar treatment can be done with bosons, as will be discussed in Sec. 10.1.

3.4.2 Coupling two spins

We now consider a perturbation of the system which, for some reason, only affects the first spin. In the absence of the second atom we would have,

$$ \hat{H}_1 = \begin{pmatrix} 0 & \Omega \\ \Omega^* & 0 \end{pmatrix} \ . \quad (3.79) $$

Including the second atom,

$$ \hat{H} = \hat{H}_1 \otimes I = \begin{pmatrix} \Omega \\ \Omega^* \end{pmatrix} \begin{pmatrix} \Omega \\ \Omega^* \end{pmatrix} \ . \quad (3.80) $$

In this case, the perturbation Hamiltonian does not commute with the total angular momentum,

$$ [\hat{S}^2, \hat{H}] \neq 0 \ . \quad (3.81) $$

Another type of perturbation affects both spin symmetrically (e.g., Dicke superradiance with two atoms in the same radiative mode or two counterpropagating modes in a ring cavity). The interaction Hamiltonian is now the sum of the individual perturbations,

$$ \hat{H} = \hat{H}_1 \otimes I + I \otimes \hat{H}_1 = \begin{pmatrix} \Omega^* & \Omega \\ \Omega^* & \Omega \\ \Omega^* & \Omega \\ \Omega^* & \Omega \end{pmatrix} \ . \quad (3.82) $$

This Hamiltonian commutes with the total angular momentum,

$$ [\hat{S}^2, \hat{H}] = 0 \ . \quad (3.83) $$

$S$ now is a good quantum number. Singlet states do not couple with triplets. This is the idea behind Dicke’s superradiance. The absolute value of the total angular momentum is conserved. The quantum number $S$ is called Dicke cooperatividade [162].
Electrically charged orbiting particles produce a magnetic field. This field can influence the motion of other particles. In the same way, the spin of an electron can influence its own orbital motion. That is, angular momenta can couple and interact in a complicated way. Even to describe the behavior of an atom as simple as hydrogen in an external field, we need to construct the eigenstates of the total angular momentum resulting from a coupling of the electron’s intrinsic spin and its orbital motion.

On the other side, we have hitherto considered predominantly hydrogen and hydrogen-like atoms, that is, atoms with a nucleus and a single (valence) electron. But in fact atoms can have more than 100 electrons, which complicates the exact description. In atoms with many electrons, one of the most common coupling schemes is when the angular momenta of all electrons couple to a total angular momentum, \( \hat{L} = \sum_k \hat{l}_k \), which then couples to the total spin, \( \hat{S} = \sum_k \hat{s}_k \), to form the complete total angular momentum, \( \hat{J} = \hat{L} + \hat{S} \). We generally assign total momenta to capital letters.

Adopting an unbiased notation we study some properties of the total angular momentum, \( \hat{j} \equiv \hat{j}_1 + \hat{j}_2 \). In Exc. 3.4.5.1 we find that the addition of angular momenta produces a quantity which is also an angular momentum, but not the subtraction.

The angular momenta of two particles or two angular momenta of different origins in a single particle represent independent degrees of freedom, \([j_1, j_2] = 0\). Without interaction between angular momenta the Hilbert spaces are orthogonal:

\[
\mathcal{H}_1 \otimes \mathcal{H}_2 = \begin{pmatrix} \mathcal{H}_1 & 0 \\ 0 & \mathcal{H}_2 \end{pmatrix}.
\] (3.84)

The eigenfunctions act on a space of dimension, \( \dim \mathcal{H}_1 \cdot \dim \mathcal{H}_2 \):

\[
|j_1, m_{j1}; j_2, m_{j2}\rangle.
\] (3.85)

That is, there is a complete set of commuting operators \( \{\hat{j}^2_1, \hat{j}_{1z}, \hat{j}^2_2, \hat{j}_{2z}\} \). Therefore, we can specify quantum numbers \( j_1, j_2, m_{j1}, \) and \( m_{j2} \) simultaneously. On the other hand, the group \( \{\hat{j}^2, \hat{j}_{z}\} \) also represents a complete set of commuting operators, as shown in Exc. 3.4.5.2. It has the basis

\[
|(j_1, j_2)j, m_j\rangle.
\] (3.86)

To describe the two angular momenta simultaneously we must opt between the decoupled picture \( |j_1, m_{j1}; j_2, m_{j2}\rangle \) and the coupled picture \( |(j_1, j_2)j, m_j\rangle \). For now, the choice of the picture makes no difference, but we will see later that there may be an energy associated with the coupling. In this case, as we will show, that the choice of the coupled base is more natural, because the energy commutes like \( [\hat{H}, \hat{j}^2] = 0 = [\hat{H}, \hat{j}_z] \), but \( [\hat{H}, \hat{j}^2_1] \neq 0 \neq [\hat{H}, \hat{j}^2_2] \).

\[\text{That is, the Hamiltonian of the system does not contain terms of type } \hat{j}_1 \cdot \hat{j}_2, \text{ but may have terms proportional to } \hat{j}_1 + \hat{j}_2.\]
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Figure 3.8: Illustration of the coupling of two angular momenta.

3.4.3.1 Allowed values of total angular momentum

Since we do not specify an interaction energy between the spins or between spins and external fields, all states are energetically degenerate. In the decoupled image the degeneracy is easily calculated,

$$\# = \sum_{m_{j_1}=-j_1}^{j_1} \sum_{m_{j_2}=-j_2}^{j_2} 1 = (2j_1 + 1)(2j_2 + 1).$$

(3.87)

Now we need to find the possible values of \( j \) and \( m_j \) in the coupled picture. The values of \( m_j \) follow immediately from \( \hat{j}_1 + \hat{j}_2 = \hat{j} \).

$$m_j = m_{j_1} + m_{j_2}.$$  

(3.88)

With \( |m_{j_1}| \leq j_1 \) and \( |m_{j_2}| \leq j_2 \) the values of \( m_j \) are limited to

$$|m_j| \leq j_1 + j_2.$$  

(3.89)

We often know the two angular momenta \( j_1 \) and \( j_2 \) and all their projections in the decoupled base,

$$|m_{j_1}| \leq j_1 \quad \text{and} \quad |m_{j_2}| \leq j_2.$$  

(3.90)

To find the quantum numbers in the coupled base, we arrange the states ordering them by their total magnetic quantum number \( m_j \). We can, without losing generality, concentrate on the situation \( j_1 \geq j_2 \). The following table reproduces the possible combinations. The \( x \)-symbols represent Clebsch-Gordan coefficients:

<table>
<thead>
<tr>
<th>( m_{j_1} + m_{j_2} = j )</th>
<th>( j )</th>
<th>( j )</th>
<th>( j )</th>
<th>( j )</th>
<th>( j )</th>
<th>( j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j_1 )</td>
<td>( j_2 )</td>
<td>( j_1 - 1 )</td>
<td>( j_2 - 1 )</td>
<td>( j_1 - 2 )</td>
<td>( j_2 - 1 )</td>
<td>( j_1 - 2 )</td>
</tr>
<tr>
<td>( j_1 )</td>
<td>( j_2 + 1 )</td>
<td>( j_2 + 1 )</td>
<td>( j_2 + 1 )</td>
<td>( j_2 + 1 )</td>
<td>( j_2 + 1 )</td>
<td>( j_2 + 1 )</td>
</tr>
<tr>
<td>( j_1 - 1 )</td>
<td>( j_2 - 1 )</td>
<td>( j_1 - 2 )</td>
<td>( j_2 - 1 )</td>
<td>( j_1 - 2 )</td>
<td>( j_2 - 2 )</td>
<td>( j_1 - 2 )</td>
</tr>
</tbody>
</table>

The possible values for \( j \) are all those allowing for \( j \geq |m_j| = |m_{j_1} + m_{j_2}| \), that is,

$$|j_1 - j_2| \leq j \leq j_1 + j_2.$$  

(3.91)
Each value of \( j \) has the degeneracy \( 2j+1 \). Therefore, as will be verified in Exc. 3.4.5.3, the total degeneracy is,

\[
\sum_{j=|j_1-j_2|}^{j_1+j_2} 2j + 1 = (2j_1 + 1)(2j_2 + 1) \quad (3.92)
\]

Example 18 (Spin states in the presence of \( L \cdot S \) coupling): As an example we consider two electrons both having \( s_i = \frac{1}{2} \) and \( \ell_i = 1 \). As illustrated in Fig. 3.9, the coupling first gives \( S = s_1 + s_2 = 0,1 \) and \( L = \ell_1 + \ell_2 = 0,1,2 \). Then we determine the possible values of the total angular momentum \( J = L + S = 0,1,2 \) depending on the values of \( L \) and \( S \).

![Figure 3.9: Possible spin states of two electrons occupying the \((4p)^2\) orbital. Spin-orbit coupling \( L \cdot S \) leads to a splitting of the energy levels.](image)

### 3.4.4 Clebsch-Gordan coefficients

For now, we will only describe how to add two angular momenta, \( \hat{j}_1 \) and \( \hat{j}_2 \). Since they act on different degrees of freedom,

\[
[\hat{\alpha}_1 \cdot \hat{j}_1, \hat{\alpha}_2 \cdot \hat{j}_2] = 0 \quad (3.93)
\]

for arbitrary vectors \( \hat{\alpha}_k \). We have a system of common eigenvectors, \( |\eta, j_1, j_2, m_1, m_2\rangle \), where \( \eta \) are the eigenvalues of other observables commuting with \( \hat{j}_1 \) and \( \hat{j}_2 \). These eigenvectors give the values \( \hbar^2 j_1 (j_1 + 1) \) and \( \hbar^2 j_2 (j_2 + 1) \) for the observables \( \hat{j}_1^2 \) and \( \hat{j}_2^2 \), as well as \( \hbar m_1 \) and \( \hbar m_2 \) for the observables \( \hat{j}_z \). The number of states is \( (2j_1 + 1)(2j_2 + 1) \). Now we want to construct the eigenstates of the total angular momentum \( \hat{j} = \hat{j}_1 + \hat{j}_2 \). Since

\[
[\hat{j}, \hat{j}^2] = 0 = [\hat{j}, \hat{j}^2] \quad (3.94)
\]

there exist common eigenstates \( |j_1, j_2, j, m\rangle \) for the set of observables \( \hat{j}_1^2, \hat{j}_2^2, \hat{j}^2 \) and \( \hat{j}_z \). These eigenstates are linear combinations of the individual states,

\[
|\langle j_1, j_2\rangle j, m\rangle = \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2| (j_1, j_2) j, m \rangle \quad (3.95)
\]

\[
= \sum_{m_1, m_2} |j_1, j_2, m_1, m_2\rangle \left( \begin{array}{c} j_1 \\ m_1 \\ j_2 \\ m_2 \end{array} \right) .
\]
The matrix coefficient is called *Clebsch-Gordan coefficient*. The Clebsch-Gordans disappear when the conditions

\[|j_1 - j_2| \leq j \leq j_1 + j_2 \quad \text{and} \quad m = -j_1 - j_2, -j_1 - j_2 + 1, \ldots, j_1 + j_2 \quad (3.96)\]

are not satisfied.

The unitary transformation matrices between decoupled and coupled bases,

\[|j_1, j_2, m_1,j_2,m_2\rangle = U_{CGC} |j_1, m_1;j_2,m_2\rangle, \quad (3.97)\]

are listed in tables of the Clebsch-Gordan coefficients.

**Example 19 (Clebsch-Gordans for the coupling of two spins 1/2):** For example, for the system consisting of two 1/2 spins we have,

\[
\begin{pmatrix}
|\frac{1}{2},\frac{1}{2},1,1\rangle \\
|\frac{1}{2},\frac{1}{2},1,0\rangle \\
|\frac{1}{2},\frac{1}{2},0,0\rangle \\
|\frac{1}{2},\frac{1}{2},1,-1\rangle
\end{pmatrix}
= \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\
0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
|\frac{1}{2},\frac{1}{2},1,1,1\rangle \\
|\frac{1}{2},\frac{1}{2},1,1,0\rangle \\
|\frac{1}{2},\frac{1}{2},1,0,0\rangle \\
|\frac{1}{2},\frac{1}{2},1,0,1\rangle
\end{pmatrix}.
\]

In the Excs. 3.4.5.4 and 3.4.5.5 we write all possible states of two angular momenta in decoupled and coupled bases. In Excs. 3.4.5.6, 3.4.5.7, we derive the matrix representation of two spins in the decoupled and the coupled base. In 3.4.5.8, and 3.4.5.9 we practice the transformation between decoupled and coupled bases, and in Exc. 3.4.5.10 we verify a rule guaranteeing the unitarity of the Clebsch-Gordan transformation. Finally in 3.4.5.11, 3.4.5.12, and 3.4.5.13 we study \(L \cdot S\)-coupling.

### 3.4.4.1 Coupling of three angular moments

Three angular momenta can be coupled in three different configurations: First \(j_1\) with \(j_2\), then the total spin \((j_1,j_2)_{j_12}\) with the third one \(j_3\). We use the notation \(||(j_1,j_2)_{j_12},j_3|J\rangle\) or \(||(j_1,j_3)_{j_13},j_2|J\rangle\) or \(||(j_2,j_3)_{j_23},j_1|J\rangle\). The recoupling of three spins

\[
\begin{align*}
\hat{j}_1 + \hat{j}_2 &= \hat{j}_{12} \\
\hat{j}_3 &= \hat{j}_3 \\
\hat{j}_{13} + \hat{j}_2 &= \hat{J}
\end{align*}
\]

is described by \(\{6j\}\)-symbols, for example,

\[
||(j_1,j_2)_{j_12},j_3|J\rangle = \sum_{j_{13}}\{6j\}||(j_1,j_3)_{j_13},j_2|J\rangle. \quad (3.99)
\]

\(\text{The Clebsch-Gordans are related to the (3j) de Wigner symbols.}\)
3.4.4.2 Notation for atomic states with LS-coupling

In an atom, the spins of the electrons often couple to a total spin, \( S = \sum_k s_k \), and separately the orbital angular momenta to a total orbital angular momentum, \( L = \sum_k l_k \). These two total spins now couple to a total angular momentum, \( J = L + S \). When this LS-coupling happens, the following notation is used to characterize the electronic states in atoms:

\[
2S + 1 \langle L, J \rangle .
\]  
(3.100)

3.4.4.3 jj-coupling

There is also the case that for each electron its spin couples to its own orbital angular momentum, \( j_k = l_k + s_k \), before coupling to the total angular momenta of other electrons, \( J = \sum_k j_k \). This is called jj-coupling. In the case of two electrons the recoupling of the four involved spins

\[
\begin{align*}
l_1 + l_2 &= L \\
s_1 + s_2 &= S \\
\end{align*}
\]

\( j_1 + j_2 = J \)

is described by \( \{9j\} = \begin{pmatrix} l_1 & l_2 & L \\ s_1 & s_2 & S \\ j_1 & j_2 & J \end{pmatrix} \)-symbols,

\[
\langle (l_1, s_2)j_1, (l_2, s_2)j_2 | J \rangle = \sum_{L, S} \{9j\} \langle (l_1, l_2) L, (s_1, s_2) S | J \rangle .
\]  
(3.102)

3.4.5 Exercises

3.4.5.1 Ex: Addition/subtraction of angular momenta

Show that \( \hat{j}_1 + \hat{j}_2 \) is an angular momentum, but not \( \hat{j}_1 - \hat{j}_2 \).

3.4.5.2 Ex: CSCO for coupled angular momenta

Be \( \hat{j} = \hat{j}_1 + \hat{j}_2 \). Show that \( \{\hat{j}_1^2, \hat{j}_2^2, \hat{j}_z\} \) is a CSCO; that is, show that

a. \( \hat{j}_1^2 \) commutes with \( \hat{j}_2^2 \);

b. \( \hat{j}_2^2 \) does not commute with \( \hat{j}_1^z \) or \( \hat{j}_2^z \) and that we can not specify \( m_{j_1} \) or \( m_{j_2} \) together with \( j \).

3.4.5.3 Ex: Multiplicity of coupled angular momenta

Verify \# = (2j_1 + 1)(2j_2 + 1) within the coupled representation.

3.4.5.4 Ex: Possible states of two (de-)coupled angular momenta

Find all possible states with the angular momenta \( j_1 = 1 \) and \( j_2 = 1/2 \) in decoupled and coupled pictures.
3.4. COUPLING OF ANGULAR MOMENTA

3.4.5.5 Ex: Fine and hyperfine structure of the rubidium atom $^{85}$Rb

1. The rubidium atom $^{85}$Rb has one valence electron. In the first excited state this electron has the orbital angular momentum, $L = 1$. What are the possible states?

2. In the fundamental state of this atom the total electronic angular momentum $J$ couples with the spin of the nucleus, $I = 5/2$, to form the total angular momentum $F = J + I$. Determine the possible values for the angular momentum $F$ and the magnetic quantum number $m_F$.

3.4.5.6 Ex: Expansion of the hyperfine structure of the rubidium atom $^{87}$Rb

Determine for the states $S_{1/2}$ and $P_{3/2}$ of an atom with nuclear spin $I = 3/2$ and hyperfine coupling $\hat{J} \cdot \hat{I}$ how the eigenstates of the coupled base expand into the decoupled base. Do not consider external magnetic fields.

3.4.5.7 Ex: Transition amplitudes between Zeeman sub-states

a. We consider the atom of $^{87}$Rb having the nuclear angular momentum $I = 3/2$. What are the possible hyperfine states $F$ resulting from a coupling of $I$ with the total electronic angular state angular momentum of the ground state $^2S_{1/2}$? What are the possible Zeeman sub-states of $F$?

b. What are the possible hyperfine states $F'$ resulting from a coupling of $I$ with the total electronic angular momentum of the excited state $^2P_{3/2}$, $F' = 2$? What are the possible Zeeman sub-states of $F''$?

c. A transition between a ground hyperfine state and an excited hyperfine state can be described by a coupling of the total angular momentum $F$ with the angular momentum of the photon $\kappa$ forming the angular momentum of the excited state $F'$. To see this, we now consider the levels $F = 1$ and $F' = 2$. Expand the coupled angular momentum $|(F,\kappa)F',m_{F'}\rangle = |(1,1)2,m_{F'}\rangle$ on a decoupled basis for every possible value $m_{F'}$. Use the table in Fig. 3.10 to determine the Clebsch-Gordan coefficients.

Note: The Clebsch-Gordans only compare the oscillator strengths of transitions between Zeeman sub-states of a given set $(F,F')$. In order to compare the oscillator strengths to other transitions $(F,F')$ it is necessary to calculate $6j$-coefficients.

3.4.5.8 Ex: Gymnastics of angular momentum operators

Consider the problem of adding angular momenta $j_1 = 1$ and $j_2 = 1/2$:

a. What are the possible values of $m$ and $j$, in which $j^2|j,m\rangle = j(j+1)\hbar^2|j,m\rangle$ and $j_z|j,m\rangle = m\hbar|j,m\rangle$?

b. What are the degeneracy $g_{j_1,j_2}(m)$?

c. Find the base states $\{|j,m\rangle\}$, which are common to the operators $j_1^2$, $j_2^2$, $j$, $j_z$, expanded in the base $\{|j_1,m_1\rangle \otimes |j_2,m_2\rangle\}$ of the eigenstates of $j_1^2$, $j_2^2$, $j_{1z}$, $j_{2z}$.

3.4.5.9 Ex: (Un-)coupled bases of the spherical harmonics

Expand the triplet state $^3P_J$ of strontium in a decoupled basis and write down the transformation matrix between the bases.
3.4.5.10 Ex: Properties of Clebsch-Gordan coefficients

Given the momenta \( j_1 \) and \( j_2 \), and \( C_{m_1,m_2} \) denoting the Clebsch-Gordan coefficients, prove that \( \sum_{m_1,m_2} |C_{m_1,m_2}|^2 = 1 \).

3.4.5.11 Ex: Spin-orbit coupling

a. Show that the operator \( \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \) associated with the spin-orbit coupling, satisfies the relation \( \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}_z \hat{S}_z + (\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+)/2 \).

Obtain the matrix representation of the operator \( \mathbf{L} \cdot \mathbf{S} \), considering the bases:

b. \( \{ |m_L \rangle \otimes |m_S \rangle \} \) of the eigenstates which are common to the operators \( \hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z \);

c. \( \{|J,M\}\} \), which is associated with the operators \( \hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z \).

d. Give the explicit matrices for the case \( L = 1 \) and \( S = \frac{1}{2} \) in the representations (b) and (c) and verify that the two representations yield the same eigenvalue spectrum.

3.4.5.12 Ex: Expansion of the spin-orbit coupling

Consider the problem of adding the orbital angular momentum \( \ell \) and a spin \( \frac{1}{2} \). Obtain the \( 2\ell + 1 \) states \( |\ell + 1/2, m_j \rangle \), in addition to the \( 2\ell \) states \( |\ell - 1/2, m_j \rangle \) (which constitute a common basis for the operators \( \mathbf{l}^2, \mathbf{s}^2, l_z, s_z \)), expanded in the base \( |m_1,m_2\rangle \) of the eigenstates of the operators \( \mathbf{l}^2, \mathbf{s}^2, l_z, s_z \). You can simplify the procedure by deriving two recurrence relationships from which the desired states follow 5.

3.4.5.13 Ex: External product of two spins

Derive the matrix representation of the spin-orbit coupling operator \( \mathbf{L} \cdot \mathbf{S} \) for \( L = 1 \) and \( S = \frac{1}{2} \) from the definition of the outer product.

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5See Cohen-Tannoudji, Vol.2, Complement A.X.
3.4. COUPLING OF ANGULAR MOMENTA

Note: A square-root sign is to be understood over every coefficient, e.g., for \(-8/15\) read \(-\sqrt{8/15}\).

\[ Y_0^0 = \sqrt{\frac{3}{4\pi}} \cos \theta \]
\[ Y_1^0 = -\sqrt{\frac{3}{4\pi}} \sin \theta e^{i\phi} \]
\[ Y_0^1 = \sqrt{\frac{5}{4\pi}} \left(3 \cos^2 \theta - \frac{1}{2}\right) \]
\[ Y_1^1 = -\sqrt{\frac{5}{4\pi}} \sin \cos \theta e^{i\phi} \]
\[ Y_0^2 = \frac{1}{15} \sqrt{\frac{1}{2}} \sin^2 \theta e^{i\phi} \]

\[ 3/2 \times 1/2 \]

\[ d_{m,0} = \sum d_{m,m'}^l d_{m',0} = \sum \]

\[ Y_{-1}^{-1} = 0 \]
\[ Y_{-1}^{-1} = \sqrt{\frac{1}{2}} \]
\[ Y_{1}^{1} = \sqrt{\frac{1}{2}} \]
\[ Y_{1}^{1} = 0 \]

\[ Y_{-\ell}^{-m} = (-1)^m Y_{\ell}^{m} \]

\[ d_{m,0} = \sum d_{m,m'}^l d_{m',0} = \sum \]

\[ 2 \times 3/2 \]

\[ d_{3/2,3/2} = \frac{1 + \cos \theta}{2} \]
\[ d_{3/2,1/2} = -\frac{1 + \cos \theta}{2} \]
\[ d_{1/2,-1/2} = \frac{1 + \cos \theta}{2} \]
\[ d_{1/2,1/2} = -\frac{1 + \cos \theta}{2} \]

\[ 2 \times 1 \]

\[ d_{1/2,1/2} = \frac{1 + \cos \theta}{2} \]
\[ d_{1/2,-1/2} = -\frac{1 + \cos \theta}{2} \]

\[ d_{m,0} = \sum d_{m,m'}^l d_{m',0} = \sum \]

\[ 1 \times 1 \]

\[ d_{1/2,1/2} = \frac{1 + \cos \theta}{2} \]
\[ d_{1/2,-1/2} = -\frac{1 + \cos \theta}{2} \]

\[ 1 \times 1 \]

\[ d_{1/2,1/2} = \frac{1 + \cos \theta}{2} \]
\[ d_{1/2,-1/2} = -\frac{1 + \cos \theta}{2} \]

\[ 1 \times 1 \]

\[ d_{1/2,1/2} = \frac{1 + \cos \theta}{2} \]
\[ d_{1/2,-1/2} = -\frac{1 + \cos \theta}{2} \]

\[ Y_{-\ell}^{-m} = (-1)^m Y_{\ell}^{m} \]

\[ \langle j_1 j_2 m_1 m_2 j_1 j_2 J M \rangle = (-1)^{j_1 - j_2} (j_2 j_1 m_2 m_1 j_1 j_2 J M) \]

Figure 3.10: Clebsch-Gordan coefficients.
Chapter 4

Linear motion / Separable potentials

In this chapter we will analyze the translational and vibrational motion of a quantum particle. We will give special consideration to the rectangular potential and the harmonic oscillator.

4.1 Translational motion

In one dimension the Hamiltonian of a free particle is,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}.$$  \hfill (4.1)

Therefore, the general solution of the Schrödinger stationary equation,

$$\hat{H}\psi(x) = E\psi(x),$$  \hfill (4.2)

is,

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \text{with} \quad k = \sqrt{\frac{2mE}{\hbar^2}}.$$  \hfill (4.3)

Note that the $e^{ikx}$ functions are not quadratically integrable, since

$$\int_{-\infty}^{\infty} |e^{ikx}|^2 dx = \int_{-\infty}^{\infty} dx \to \infty.$$  

On the other side, they do not represent actual physical systems. In practice, we need to consider wave packets or specify a finite volume for the particle. Note also that the spectrum of eigenvalues is continuous. Do the Exc. 4.1.3.1.

4.1.1 Quadratic integrability

To allow for an interpretation as probability density we need to ask for quadratic integrability,

$$\int |\psi|^2 d^3r = 1.$$  \hfill (4.4)

This means that the wavefunction can not be infinite inside a finite volume. But it can be infinite within an infinitely small volume. Also, since the Schrödinger equation contains the second derivative by position, the wavefunction must be continuous and have a continuous derivative.
4.1.2 Separation of dimensions

Frequently, a 3D potential can be written in the way,

\[ V(x, y, z) = V_x(x) + V_y(y) + V_z(z) . \]  

(4.5)

This is the case, for example, for a rectangular well with \( V_x(x) = V_y(y) = V_z(z) = V_0/3 \) inside the well and \( V(x, y, z) = 0 \) outside. It also holds for a harmonic potential,

\[ V(r) = \frac{m \omega^2}{2} (\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) . \]  

(4.6)

In these cases, the following ansatz for the wavefunction is generally useful,

\[ \psi(r) = \psi_x(x) \psi_y(y) \psi_z(z) , \]  

(4.7)

since inserting the ansatz into the Schrödinger equation,

\[ \left[ -\hbar^2 \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} + V_x(x) + V_y(y) + V_z(z) \right] \psi_x(x) \psi_y(y) \psi_z(z) = E \psi_x(x) \psi_y(y) \psi_z(z) , \]  

(4.8)

the equation separates into three independent one-dimensional equations,

\[ -\hbar^2 \frac{d^2 \psi_x(x)}{dx^2} + V_x(x) = \text{const.} \equiv E_x , \]  

(4.9)

and the same for \( y \) and \( z \). Since, \( E = E_x + E_y + E_z \) may have the same value for different combinations of \( E_x, E_y, \) and \( E_z \), multidimensional systems are often degenerate.

4.1.3 Exercises

4.1.3.1 Ex: Trapped particle

Consider the problem of a particle of mass \( m \) forced to move in a single direction and completely confined to a box, with walls placed at the positions \( x = 0 \) and \( x = a \).

a. The particle be in the ground state, what is its energy and its wavefunction?

b. Suppose the particle has the following wavefunction:

\[ \psi_I(x) = \frac{1}{\sqrt{7a}} \left[ 2 \cos \left( \frac{\pi}{2a} (6x - a) \right) - 3i \sin \left( \frac{2\pi}{a} x \right) + \cos \left( \frac{\pi}{2a} (2x - a) \right) \right] , \]

what is the probability that a measurement of the energy and yields the result \( E = \frac{2\pi^2 \hbar^2}{ma^2} \)?

c. Considering again the state of item (a) (the ground state), what is the probability distribution for the momentum of this particle?

d. Still starting from the ground state, suppose we remove (instantaneously) the walls, leaving the particle free (\( \hat{H} = \hat{p}^2/2m \)). What is the energy of this free particle?

Formulae:

\[ \int_0^L e^{iBx} \sin \left( \frac{n\pi x}{L} \right) dx = \frac{n\pi L[1 - (-1)^n e^{iB L}]}{n^2\pi^2 - B^2 L^2} \quad \text{for} \quad n = 1, 2, 3, ... \]

\[ \int_{-\infty}^{\infty} \frac{x^2}{(1 - x^2)^2} \cos^2 \frac{\pi x}{2} dx = \frac{\pi^2}{4} \]
4.2 Rectangular Potential

4.2.1 Box potential

Let us now place the particle into a rectangular potential well, such that the Hamiltonian is,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad \text{with} \quad V(x) = \begin{cases} 0 & \text{for } x \in [0, L] \\ \infty & \text{for } x \notin [0, L] \end{cases} \quad (4.10)$$

As the potential barriers are high, the walls are hard, that is, the particle, even being a quantum particle, can not penetrate. The wavefunction and the possible energy values are,

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \text{and} \quad E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \quad . \quad (4.11)$$

The Exc. 4.2.5.1 asks to demonstrate the result (4.11) illustrated in Fig. 4.1.

Obviously the spectrum of eigenvalues is now discrete. They can be enumerated by an integer \( n \) called quantum number. Note that the energy levels are not equidistant.

**Example 20 (Localization energy):** There is a minimal energy \( E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \) which is called zero point energy or localization energy. This energy can be understood as a consequence of Heisenberg’s uncertainty principle. We can make the following gross estimation of the zero point energy. Obviously, the particle is localized with an uncertainty lower than \( \Delta x < L \). Hence, \( \Delta p > \hbar / \Delta x > \hbar / L \).

The average kinetic energy is,

$$\langle p^2 \rangle = \frac{\langle p \rangle^2 + \Delta p^2}{2m} = \frac{\Delta p^2}{2m} > \frac{\hbar^2}{2mL^2} \quad .$$

The fact that the numerical value is different from the value calculated by the formula (4.11) comes from the particular geometry of the box potential.

4.2.2 Multidimensional box potential

In a multidimensional well there can be degeneracy if the well exhibits symmetries. In the case of a 2D quadratic well \( L_x = L_y \), the eigenenergies are doubly degenerate, since \( E_{n_x,n_y} = E_{n_y,n_x} \). In the case of a 3D cubic well \( L_x = L_y = L_z \), the eigenenergies are 6-fold degenerate, because \( E_{n_x,n_y,n_z} = E_{n_y,n_x,n_z} = E_{n_z,n_x,n_y} = E_{n_z,n_y,n_x} = E_{n_y,n_z,n_x} = E_{n_z,n_y,n_x} \). The states and energies of the 2D well are calculated in Exc. 4.2.5.2.

4.2.3 Potentials with several sections of constant depths

To find the global wavefunction in potentials with several sections of constant depths, we solve Schrödinger’s equations separately for each section,

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_a \right) \psi_a(x) = E \psi_a(x) \quad . \quad (4.12)$$
The general solution for a section $a$ with potential energy $V_a$ is,

$$\psi_a(x) = A_a e^{i k_a x} + B_a e^{-i k_a x}, \quad (4.13)$$

where $k_a = \frac{1}{\hbar} \sqrt{2m(E - V_a)}$. If $E > V_a$, the wave is propagating. $k_a$ is the Broglie wavevector of the wave. If $E < V_a$, the wave is evanescent. That is, the wave decays within a distance $\kappa_a = -i k_a$.

If the particle is confined, that is, if $E < V(x \to \pm \infty)$, the possible energy levels are quantized and the spectrum is discrete.

For every transition between two sections $a = 1$ and $a = 2$ we require the boundary conditions,

$$\psi_1(x) = \psi_2(x) \quad \text{and} \quad \psi'_1(x) = \psi'_2(x). \quad (4.14)$$

Together with the normalization, $1 = \int_{-\infty}^{\infty} |\psi|^2 dx$, these conditions are sufficient to determine the wavefunction unambiguously.
4.2. Rectangular Potential

4.2.4 Potential well

Consider a particle with energy $E$ and a potential well of finite depth such that $V(x) = V_0 < 0$ for $-L/2 > x > L/2$ and $V(x) = 0$ otherwise, as illustrated on the left side of Fig. 4.3. The particle be confined, $E < 0$.

The wavevectors are

$$k_1 = k_3 = \frac{i}{\hbar} \sqrt{2mE} = i \frac{1}{\hbar} \sqrt{2m|E|} = i\kappa_1$$
and

$$k_2 = \frac{1}{\hbar} \sqrt{2m(E - V_0)}$$ (4.15)

with $\kappa_1 \in \mathbb{R}^+$. The boundary conditions yield,

$$A_1 e^{-ik_1L/2} + B_1 e^{ik_1L/2} = A_2 e^{-ik_2L/2} + B_2 e^{ik_2L/2}$$

(4.16)

$$-ik_1 A_1 e^{-ik_1L/2} + ik_1 B_1 e^{ik_1L/2} = -ik_2 A_2 e^{-ik_2L/2} + ik_2 B_2 e^{ik_2L/2}$$

$$A_2 e^{ik_2L/2} + B_2 e^{-ik_2L/2} = A_3 e^{ik_1L/2} + B_3 e^{-ik_1L/2}$$

$$ik_2 A_2 e^{ik_2L/2} - ik_2 B_2 e^{-ik_2L/2} = ik_1 A_3 e^{ik_1L/2} - ik_1 B_3 e^{-ik_1L/2}$$.

For confined particles, $E < 0$, the problem is totally symmetric. In addition, the wavefunction must disappear for $x \to \pm \infty$. Therefore, we can simplify,

$$A_1 = 0 = B_3$$ and $$A_3 = B_1$$ (4.17)

The first two equations (4.16) now give,

$$B_1 e^{ik_1L/2} = A_2 e^{-ik_2L/2} + B_2 e^{ik_2L/2} = \frac{k_2}{k_1} \left( -A_2 e^{-ik_2L/2} + B_2 e^{ik_2L/2} \right) .$$

(4.18)

We now consider the quotient $B_2/A_2$. Using the right part of equation (4.18),

$$\frac{B_2}{A_2} = \frac{e^{-ik_2L/2}(k_2 + k_1)}{e^{ik_2L/2}(k_2 - k_1)} = \frac{e^{-ik_2L}(k_2 + i\kappa_1)^2}{k_2^2 + \kappa_1^2} .$$

(4.19)

Since the amplitudes are real, the imaginary part of the quotient (4.19) should disappear, which is the case when,

$$0 = \text{Im} \ e^{-ik_2L}(k_2 + i\kappa_1)^2 = 2\kappa_1 k_2 \cos k_2 L + (\kappa_1^2 - k_2^2) \sin k_2 L$$

(4.20)

$$\Rightarrow \tan k_2 L = \frac{2\kappa_1 k_2}{-\kappa_1^2 + k_2^2} .$$
In order to construct graphically the values of the momenta \( k_2 \) of the particle associated with the allowed energy levels, we introduce a constant \( \beta \equiv \frac{\hbar}{(L\sqrt{2m|V_0|})} \).

Hence,

\[
\tan k_2L = \tan \frac{1}{\beta} \sqrt{1 - |E/V_0|} = \frac{2\sqrt{|E/V_0|}}{\frac{1}{1 - 2|E/V_0|}} = \frac{2\kappa_1k_2}{-\kappa_1^2 + k_2^2} .
\]

\[(4.21)\]

Apply the notions obtained in this section to solve Exc. 4.2.5.3.

4.2.5 Exercises

4.2.5.1 Ex: Particle in a box

Obtain the wavefunctions and associated energy levels of a particle confined in a box, where \( V(x) = 0 \) for \( 0 \leq x \leq l \) and \( V(x) = \infty \) outside.

4.2.5.2 Ex: Particle in a two-dimensional box

Obtain the wavefunctions and associated energy levels of a particle trapped in a two-dimensional box inside which the particle is confined to a rectangular surface with
4.3. POTENTIAL BARRIER

dimensions $L_1$ in $x$-direction and $L_2$ in $y$-direction, $V(x, y) = 0$ for $0 \leq x \leq L_1$ and $0 \leq y \leq L_2$ and $V(x, y) = \infty$ else.

4.2.5.3 Ex: Particle in a well

Obtain the energies of the bound states of a particle in the potential well in which $V(x) = \infty$ for $x < 0$, $V(x) = -V_0$ for $0 \leq x \leq L/2$ and $V(x) = 0$ to $x > L/2$.

Compare the obtained values with those of the symmetrical well discussed in Sec. 4.2.4 and the well with infinitely high walls discussed in Sec. 4.2.1.

4.3 Potential barrier

The linear momentum of a particle described by $\psi(x, t) = A e^{ikx}$ is,

$$\langle \psi | \hat{p} | \psi \rangle = \langle \psi | \frac{\hbar}{i} \frac{d}{dx} | \psi \rangle = \hbar k . \quad (4.23)$$

Therefore, this particle propagates towards $+\infty$. On the contrary, the particle $Be^{-ikx}$ propagates towards $-\infty$. Thus, the two solutions (4.13) of the Schrödinger equation (4.12) correspond to propagating particle waves. From here on we will use the letter $A$ ($B$) to denote the amplitudes of waves propagating in direction $\infty$ ($-\infty$).

In locations where the potential changes abruptly, the particle can be partially reflected.

4.3.1 $\mathcal{T}$-scattering matrix

As we have already shown in the previous section, we can write the transformation of the amplitudes due to a potential step at position $L$ as,

$$A_2 e^{ik_2 L} + B_2 e^{-ik_2 L} = A_1 e^{ik_1 L} + B_1 e^{-ik_1 L} \quad (4.24)$$

$$ik_2 A_2 e^{ik_2 L} - ik_2 B_2 e^{-ik_2 L} = ik_1 A_1 e^{ik_1 L} - ik_1 B_1 e^{-ik_1 L} .$$

We can summarize these two equations in a matrix formalism,

$$\begin{pmatrix} A_2 \\ B_2 \end{pmatrix} = \mathcal{T} \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} , \quad (4.25)$$

with the scattering matrix $\mathcal{T}$ for a particle with energy $E$ (see Fig. 4.2),

$$\mathcal{T} = \frac{1}{2} \begin{pmatrix} 1 + \frac{k_1}{k_2} & e^{i(k_1 - k_2)L} & -1 + \frac{k_1}{k_2} & e^{i(-k_1 - k_2)L} \\ 1 - \frac{k_1}{k_2} & e^{i(k_1 + k_2)L} & 1 + \frac{k_1}{k_2} & e^{i(-k_1 + k_2)L} \end{pmatrix} . \quad (4.26)$$

If there are more zones with different depths, we may concatenate the scattering matrices. Denoting by $\mathcal{T}_{m \rightarrow n}$ the scattering matrix describing a transition at position $L_{m,n}$ of a potential of the depth $V_m$ to another potential $V_n$, we write,

$$\mathcal{T} = \mathcal{T}_{2 \rightarrow 3} \mathcal{T}_{1 \rightarrow 2} . \quad (4.27)$$
4.3.2 \textit{S}-scattering matrix

Another common definition is the \textit{scattering matrix} $S$,

\[
\begin{pmatrix}
A_2 \\
B_1
\end{pmatrix} = S
\begin{pmatrix}
B_2 \\
A_1
\end{pmatrix}.
\] (4.28)

To see how the scattering matrices are interconnected, we start with

\[
\begin{pmatrix}
A_2 \\
B_2
\end{pmatrix} = T
\begin{pmatrix}
A_1 \\
B_1
\end{pmatrix} = \left( \frac{T_{11}A_1 + T_{12}B_1}{T_{21}A_1 + T_{22}B_1} \right),
\] (4.29)

Multiplying the first line with $T_{22}$ and the second with $-T_{12}$ and adding them,

\[
T_{22}A_2 - T_{12}B_2 = \left( \begin{array}{cc}
T_{11} & T_{12} \\
T_{21} & T_{22}
\end{array} \right) A_1.
\] (4.30)

This equation resolved by $A_2$ along with the second equation (4.29) resolved by $B_1$ give,

\[
\begin{pmatrix}
A_2 \\
B_1
\end{pmatrix} = S
\begin{pmatrix}
B_2 \\
A_1
\end{pmatrix} = \left( \frac{T_{12}/T_{22}}{1/T_{22}} \begin{array}{cc}
T_{11} & T_{12}/T_{22} \\
-T_{21}/T_{22}
\end{array} \right)
\begin{pmatrix}
B_2 \\
A_1
\end{pmatrix}.
\] (4.31)

The matrix $S$ describes the causality of scattering process more adequately: The amplitude $A_2$ in region (2) results from the superposition of a wave $B_2$ being reflected by the barrier and a wave $A_1$ being transmitted by the barrier. The amplitude $B_1$ in region (1) results from the superposition of a wave $A_1$ being reflected by the barrier and a wave $B_2$ being transmitted by the barrier. Therefore, the matrix $S$ is more appropriate for the description of the quantum reflection, as we will discuss in the next section. However, it has the disadvantage that it cannot be concatenated in the same way as the $T$ matrices.

Unlike the $T$ matrix the $S$ matrix is \textit{unitary}, since

\[
\det S = S_{11}S_{22} - S_{12}S_{21} = -\frac{T_{11}}{T_{22}} = -e^{2ik_1L}.
\] (4.32)

Also, it is possible to show,

\[
S^\dagger S = \begin{pmatrix}
S_{11}^* & S_{12}^* \\
S_{12}^* & S_{22}^*
\end{pmatrix}
\begin{pmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{pmatrix} = \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}.
\] (4.33)

4.3.3 \textit{Quantum reflection at a potential step}

The \textit{quantum reflection} is a non-classical property of the motion of a particle. An example is the \textit{reflection} of a quantum particle by an \textit{attractive} potential. To study this effect, we consider a plane wave $e^{ik_1x}$ propagating in region (1) ($E_1 > V_1$) encountering a potential step up or down at position $x = 0$ leading to another region (2). Using the $S$ matrix formalism introduced in the previous section,

\[
S = \frac{1}{k_1 + k_2}
\begin{pmatrix}
k_2 - k_1 & 2k_1 \\
k_2 & k_1 - k_2
\end{pmatrix},
\] (4.34)
we find that one part of the wave is reflected into the region (1), another is transmitted into the region (2),

\[
\begin{pmatrix} A_2 \\ B_1 \end{pmatrix} = S \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \left( T_{11} - T_{12} T_{21} / T_{22} \right) = \left( \frac{(1+k_1/k_2)^2-(1-k_1/k_2)^2}{2(1+k_1/k_2)} \right)
\]

\[
= \frac{1}{k_1 + k_2} \left( \frac{2k_1}{k_1 - k_2} \right).
\]

We use \( B_2 = 0 \), since no wave comes from the side of region (2), and \( A_1 = 1 \), because it simplifies the formulas and does not affect the generality of the results. The interesting results are:

- Even when \( E_2 < V_2 \), the particle enters the classically prohibited region: \( \psi_2(x) \propto e^{-\kappa_2 x} \) with \( \kappa_2 = \frac{1}{\hbar} \sqrt{2m(V_2 - E_2)} \), i.e. the transmission is non-zero, \( |A_2| > 0 \).
- Even with \( E_2 > V_2 \), the particle has a probability of being reflected at the step, \( |B_1| > 0 \).

**Example 21 (Contrast of a partially reflected wave):** Defining \( K_\pm \equiv \frac{1}{2} (\max \psi_1^2 \pm \min \psi_1^2) \), the contrast of the wavefunction in region (1) is given by \( K_- / K_+ \). Writing the function as \( \psi_1 = e^{ik_1x} + B_1 e^{-ik_1x} \) it is easy to show, that

\[
|B_1| = \frac{\sqrt{K_+ + K_-} - \sqrt{K_+ - K_-}}{\sqrt{K_+ + K_-} + \sqrt{K_+ - K_-}} \approx K_- / 2K_+.
\]

This formula can be understood as an analogue of Fresnel’s formula for matter waves \(^1\).

In Exc. 4.3.7.1 we calculate the behavior of a Broglie wave passing through a potential step and entering a classically forbidden region. In Exc. 4.3.7.2 we investigate a model describing the collision between attracting or repelling particles via a partial reflection at a potential step.

### 4.3.4 Continuity of probability flow

The continuity equation (2.16) requires that the **probability flux** be preserved in stationary situations,

\[
0 = \frac{dj}{dx} = \frac{d}{dx} \frac{\hbar}{2mi} \left[ \psi^\ast \left( \frac{d}{dx} \psi \right) - \left( \frac{d}{dx} \psi^\ast \right) \psi \right].
\]

Applying this to a potential step separating the regions \( n = 1, 2 \), we find,

\[
\begin{align*}
\dot{j}_n &= \frac{\hbar}{2mi} \left[ \psi^\ast \frac{d}{dx} \psi - \psi \frac{d}{dx} \psi^\ast \right] \\
&= \frac{\hbar}{2mi} \left[ (A_n e^{-ik_n x} + B_n e^{ik_n x})(tk_n A_n e^{ik_n x} - ik_n B_n e^{-ik_n x}) \\
&- (A_n e^{ik_n x} + B_n e^{-ik_n x})(-tk_n A_n e^{-ik_n x} + ik_n B_n e^{ik_n x}) \right] \\
&= \frac{\hbar k_n}{m} (|A_n|^2 - |B_n|^2).
\end{align*}
\]

\(^1\)In this sense light reflection at an optical interface (with typical losses of 4% for glass) can be interpreted as quantum reflection of light.
Hence, \( j_1 = j_2 \) implies \( k_1 |A_1|^2 - k_1 |B_1|^2 = k_2 |A_2|^2 - k_2 |B_2|^2 \). Assuming that the particle comes from side 1 and \( B_2 = 0 \), we have,

\[
1 = |B_1|^2 + \frac{k_2}{k_1} |A_2|^2 = R + T ,
\]

defining the *transmission* \( T \) and the *reflection* \( R \) as,

\[
T \equiv \frac{k_2}{k_1} |S_{12}|^2 = \frac{k_2}{k_1} |A_2|^2 \quad \text{and} \quad R \equiv |S_{22}|^2 = |B_1|^2.
\]

### 4.3.5 Tunneling and quantum reflection at a potential well

Particles thrown with a kinetic energy \( E \) against potential barriers can cross them even if \( V_0 > E \) or be reflected even when \( V_0 < E \), as illustrated in Fig. 4.5(a). This can be verified by considering a particle propagating from \( x = -\infty \) towards \( x = +\infty \) through a potential well located at \( x \in [0, a] \). We determine the concatenation \( T = T_{2 \rightarrow 3} T_{1 \rightarrow 2} \). Then we find the \( S \) matrix that corresponds to the \( T \) matrix and solve the problem in the same way as in the previous section. For example, we can calculate the transmission and reflection probabilities. The formula is derived in Exc. 4.3.7.3,

\[
R = 1 - T = \left( 1 + \frac{16E/V_0(1 - E/V_0)}{(e^{\kappa L} - e^{-\kappa L})^2} \right)^{-1}
\]

and sketched in Fig. 4.5(b).

![Figure 4.5](image-url)

**Figure 4.5**: (code) (a) Tunnel effect and quantum transmission and reflection at a potential barrier. (b) Coefficients of transmission and reflection (horizontal) through the shown potential barrier as a function of the energy normalized to the height of the barrier \( E/V_0 \). The dashed red curve corresponds to a low barrier, \( \beta \equiv \frac{1}{h} L \sqrt{2mV_0} = 3 \), the blue solid curve corresponds to a deep barrier \( \beta = 10 \).
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4.3.6 The delta-potential

In quantum mechanics the $\delta$-potential can be used to simulate situations, where a particle is free to move in two regions of space with a barrier in between. For example, an electron can move almost freely in a conducting material, but when two conducting surfaces are put close together, the interface between them acts as a barrier for the electron that can be approximated by a $\delta$-potential. The $\delta$-potential is a limiting case of the finite potential well when we decrease its width while maintained the product of its width and its depth constant. Here, for simplicity, we only consider a one-dimensional potential well, but the analysis can be expanded to more dimensions.

The time-independent Schrödinger equation for the wavefunction $\psi(x)$ of a particle in one dimension is,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2}(x) + \alpha \delta(x)\psi(x) = E\psi(x) \quad (4.42)$$

The potential is called a $\delta$-potential well if $\alpha$ is negative and a $\delta$-potential barrier if $\alpha$ is positive.

The potential splits the space in two parts ($x < 0$ and $x > 0$). In each of these parts the potential energy is zero, and the Schrödinger equation reduces to,

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi \quad (4.43)$$

This is a linear differential equation with constant coefficients, whose solutions are linear combinations of $e^{ikx}$ and $e^{-ikx}$, where the wavenumber $k$ is related to the energy by $k = \sqrt{\frac{2mE}{\hbar^2}}$. In general, due to the presence of the $\delta$-potential in the origin, the coefficients of the solution need not be the same in both half-spaces:

$$\psi(x) = \begin{cases} \psi_1(x) = A_1e^{-ikx} + B_1e^{ikx} & \text{for } x < 0 \\ \psi_2(x) = A_2e^{-ikx} + B_2e^{ikx} & \text{for } x > 0 \end{cases} \quad (4.44)$$

where, in the case of positive energies (real $k$), $e^{ikx}$ represents a wave traveling to the right, and $e^{-ikx}$ one traveling to the left. One obtains a relation between the coefficients by imposing that the wavefunction be continuous at the origin,

$$\psi(0) = \psi_1(0) = \psi_2(0) = A_1 + B_1 = A_2 + B_2 \quad (4.45)$$

A second relation can be found by studying the derivative of the wavefunction. Normally, we could also impose differentiability at the origin, but this is not possible because of the $\delta$-potential. However, if we integrate the Schrödinger equation around $x = 0$ over an interval $[-\epsilon, +\epsilon]$:

$$-\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} \psi''(x)dx + \int_{-\epsilon}^{+\epsilon} V(x)\psi(x)dx = E \int_{-\epsilon}^{+\epsilon} \psi(x)dx \quad (4.46)$$

In the limit $\epsilon \to 0$, the right-hand side of this equation vanishes; the left-hand side becomes,

$$-\frac{\hbar^2}{2m} [\psi_2'(0) - \psi_1'(0)] + \alpha \psi(0) \quad (4.47)$$
Substituting the definition of $\psi$ into this expression, we obtain,

$$-\frac{\hbar^2}{2m}ik(-A_1 + B_1 + A_2 - B_2) + \alpha(A_1 + B_1) = 0 \ . \ (4.48)$$

The boundary conditions thus give the following restrictions on the coefficients,

$$
\begin{align*}
A_1 + B_1 - A_2 - B_2 &= 0 \\
-A_1 + B_1 + A_2 - B_2 &= \frac{2m\alpha}{\hbar^2}k^2(A_1 + B_1)
\end{align*}
$$

(4.49)

![Figure 4.6](image)

Figure 4.6: (a) The $\delta$-potential (green) and the bound state wavefunction (blue). (b) Double $\delta$-potential (green).

### 4.3.6.1 Bound states

The graph of the bound state wavefunction solution to the $\delta$-function potential is continuous everywhere, but its derivative is not defined at $x = 0$.

In any one-dimensional attractive potential there will be a bound state. To find its energy, note that for $E < 0$, $k = i\sqrt{2m|E|}/\hbar = i\kappa$ is imaginary and the wavefunctions which were oscillating for positive energies in the calculation above, are now exponentially increasing or decreasing functions of $x$ (see above). Requiring that the wave functions do not diverge at infinity eliminates half of the terms: $A_1 = B_2 = 0$. The wavefunction is then,

$$
\psi(x) = \begin{cases}
\psi_1(x) = B_1e^{\kappa x} & \text{for } x < 0 \\
\psi_2(x) = A_2e^{-\kappa x} & \text{for } x > 0
\end{cases}
$$

(4.50)

From the boundary conditions and normalization conditions, it follows that,

$$A_2 = B_1 = \sqrt{\kappa} \quad \text{and} \quad \kappa = -\frac{m\alpha}{\hbar^2} ,
$$

(4.51)

from which follows that $\alpha$ must be negative, that is the bound state only exists for the well, and not for the barrier. The Fourier transform of this wavefunction is a Lorentzian function. The energy of the bound state is then,

$$E_b = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\alpha^2}{2\hbar^2} \ .
$$

(4.52)

The $\delta$-potential well and its wavefunction are exhibited in Fig. 4.6(a).
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4.3.6.2 Scattering

For positive energies, the particle is free to move in either half-space: \( x < 0 \) or \( x > 0 \), but it may be scattered at the delta function potential. The quantum case can be studied in the following situation: a particle incident on the barrier from the left side \( (B_1) \). It may be reflected \( (A_1) \) or transmitted \( (B_2) \). To find the amplitudes for reflection and transmission for incidence from the left, we put in the above equations \( B_1 = 1 \) (incoming particle), \( A_1 = r \) (reflection), \( A_2 = 0 \) (no incoming particle from the right), and \( B_2 = t \) (transmission), and solve for \( r \) and \( t \) even though we do not have any equations in \( t \). The result is,

\[
t = \frac{1}{1 - \frac{m\alpha}{\hbar^2 k}}, \quad r = \frac{1}{\frac{\hbar^2 k}{m\alpha} - 1}.
\]

(4.53)

Due to the mirror symmetry of the model, the amplitudes for incidence from the right are the same as those from the left. The result is that there is a non-zero probability,

\[
R = |r|^2 = \frac{1}{1 + \frac{\hbar^4 k^2}{m^2\alpha^2}} = \frac{1}{1 + \frac{2\hbar^2 E}{m\alpha^2}}.
\]

(4.54)

for the particle to be reflected. This does not depend on the sign of \( \lambda \), that is, a barrier has the same probability of reflecting the particle as a well. This is a significant difference from classical mechanics, where the reflection probability would be 1 for the barrier (the particle simply bounces back), and 0 for the well (the particle passes through the well undisturbed). The probability for transmission is,

\[
T = |t|^2 = 1 - R = \frac{1}{1 + \frac{\hbar^4 k^2}{m^2\alpha^2}} = \frac{1}{1 + \frac{m\alpha^2}{2\hbar^2 E}}.
\]

(4.55)

Figure 4.7: (code) Transmission (red) and reflection (blue) probability of a \( \delta \)-potential well. The energy \( E > 0 \) is in units of \( E_b = m\alpha^2/2\hbar^2 \).

An application example regards the interfaces between two conducting materials. In the bulk of the materials, the motion of the electrons is quasi-free and can be
described by the kinetic term in the above Hamiltonian with an effective mass $m$. Often, the surfaces of such materials are covered with oxide layers or are not ideal for other reasons. This thin, non-conducting layer may then be modeled by a local $\delta$-function potential. Electrons may then tunnel from one material to the other giving rise to a current.

**Example 22 (Double delta potential):** The $\delta$-function model is actually a one-dimensional version of the hydrogen atom. The model becomes particularly useful when applied to the hydrogen molecule ion, as shown in the following.

The double-well $\delta$-function models a diatomic hydrogen molecule by the corresponding Schrödinger equation:

$$ -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2}(x) + V(x)\psi(x) = E\psi(x), $$

where the potential is now:

$$ V(x) = -q\lambda [\delta(x + \frac{R}{2}) + \delta(x - \frac{R}{2})] $$

where $0 < R < \infty$ is the 'internuclear' distance with $\delta$-function (negative) peaks located at $x = \pm R/2$ (shown in brown in the diagram). Keeping in mind the relationship of this model with its three-dimensional molecular counterpart, we use atomic units and set $\hbar = m = 1$. Here $0 < \lambda < 1$ is a formally adjustable parameter. From the single well case, we can infer the 'ansatz' for the solution to be:

$$ \psi(x) = Ae^{-d|x + \frac{R}{2}|} + Be^{-d|x - \frac{R}{2}|}. $$

Matching of the wavefunction at the $\delta$-function peaks yields the determinant:

$$ \begin{vmatrix} q - d & qe^{-dR} \\ q\lambda e^{-dR} & q\lambda - d \end{vmatrix} = 0 \quad \text{where} \quad E = -\frac{d^2}{2}. $$

Thus, $d$ is found to be governed by the pseudo-quadratic equation:

$$ d_{\pm}(\lambda) = \frac{1}{2}q(\lambda + 1) \pm \frac{1}{2} \left\{ q^2 (1 + \lambda)^2 - 4\lambda q^2 [1 - e^{-2d_{\pm}(\lambda)R}] \right\}^{1/2}, $$

which has two solutions $d = d_{\pm}$. For the case of equal charges (symmetric homonuclear case), $\lambda = 1$ and the pseudo-quadratic reduces to:

$$ d_{\pm} = q[1 \pm e^{-d_{\pm}R}]. $$

The '+' case corresponds to a wave function symmetric about the midpoint (shown in red in the diagram) where $A = B$ and is called gerade. Correspondingly, the '-' case is the wavefunction that is anti-symmetric about the midpoint where $A = -B$ is called ungerade (shown in green in the diagram). They represent an approximation of the two lowest discrete energy states of the three-dimensional $H_2^+$ and are useful in its analysis. Analytical solutions for the energy eigenvalues for the case of symmetric charges are given by:

$$ d_{\pm} = q + W(\pm qRe^{-qR})/R, $$

where $W$ is the standard Lambert function. Note that the lowest energy corresponds to the symmetric solution $d_+$. In the case of unequal charges, and for that matter the three-dimensional molecular problem, the solutions are given by a generalization of the Lambert function (see section on generalization of...
4.3. POTENTIAL BARRIER

Lambert function and references herein).

One of the most interesting cases is when \( qR \leq 1 \), which results in \( d_\perp = 0 \). Thus, one has a non-trivial bound state solution with \( E = 0 \). For these specific parameters, there are many interesting properties that occur, one of which is the unusual effect that the transmission coefficient is unity at zero energy.

4.3.7 Exercises

4.3.7.1 Ex: Tunneling

A rubidium-87 atom moves in free space (region 0) with velocity \( v = 1 \) cm/s (see diagram). Suddenly it encounters a gap with depth \( V_1 = -k_B \cdot 1 \mu K \).

a. What is the particle’s Broglie wavelength in region 1?
b. Now the atom encounters a barrier of height \( V_2 = -V_1 \). What is the probability that the particle will enter region 2?
c. What is the probability of finding the particle inside region 2 up to a depth of \( x_2 = 10 \) nm?

![Figure 4.8: Particle in a potential landscape.](image)

4.3.7.2 Ex: Collisions

A collision between attractive or repulsive particles can be described by the Schrödinger equation as a one-dimensional scattering,

\[
-\frac{\hbar^2}{2m} \psi''(x) + \alpha \delta(x) \psi(x) = E \psi(x).
\]

The energy spectrum may be a discrete spectrum of bound states and a continuum of free states.

a. Calculate the transmission coefficient for the case of a particle with energy \( E \) thrown against the potential energy barrier \( V(x) = \alpha \delta(x) \). Does the result change for the case when \( V(x) = -\alpha \delta(x) \), with \( \alpha > 0 \)?
b. For this last potential, find the energy of the bound state and its corresponding wavefunction.

4.3.7.3 Ex: Energy barrier

Consider a particle with energy \( E \) thrown (in the direction \( \hat{e}_x \)) against a potential energy barrier of finite height and width, such that \( V(x) = 0 \) for \( x < 0 \) or \( x > L \) and \( V(x) = V_0 \) for \( 0 \leq x \leq L \).
4.3.7.4 **Ex: Wavepacket reflected at a potential barrier**

Simulate the reflection of a Gaussian wavepacket at a potential barrier for various kinetic energies using the Julia programming language.

4.3.7.5 **Ex: Infinite rectangular double-well potential**

Consider the rectangular double-well potential sketched in Fig. 4.9 and

a. calculate the energy levels according to the procedure taught in Sec. 4.3.5 and

b. prepare a numerical calculation of the wavefunctions, e.g. using the Fourier grid method introduced in Sec. 11.2.5, for $^{87}$Rb using the following dimensions of the potential: $V_0 = h \times 15$ MHz, $L = 40$ nm, and $b = 3$ nm.

4.4 **Harmonic oscillator**

Many systems oscillate. Common examples are vibrations of atoms bound in a molecule or in a crystalline lattice, of particles trapped in applied electric or magnetic fields, or light in an electromagnetic mode. Most periodic movements are approximately harmonic for small amplitude vibrations and can be treated in a way that we will detail now.

We start with the unidimensional *harmonic oscillator* (OH),

$$
\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) - E \right] \psi(x) = 0 \quad \text{where} \quad V(x) = \frac{m}{2} \omega^2 x^2.
$$

(4.56)
4.4.1 Factorization of the Hamiltonian and Fock states

Respecting the fact that the operators \( \hat{p} \) and \( \hat{x} \) do not commute, \( \frac{i}{\hbar} [\hat{p}, \hat{x}] = 1 \), we can rewrite the Hamiltonian of the harmonic oscillator in the following way,

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega^2 \hat{x}^2 = \hbar \omega \left[ \left( \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \sqrt{\frac{1}{2m\hbar \omega}} \hat{p} \right) \left( \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \sqrt{\frac{1}{2m\hbar \omega}} \hat{p} \right) + \frac{1}{2} \right]
\]

with the abbreviation \( \hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \sqrt{\frac{1}{2m\hbar \omega}} \hat{p} \) and its Hermitian transposition \( \hat{a}^\dagger \).

Now let’s try to find out the properties of the operators \( \hat{a}^\dagger \) and \( \hat{a} \). First of all, the commutator is,

\[
[\hat{a}, \hat{a}^\dagger] = \left[ \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \sqrt{\frac{1}{2m\hbar \omega}} \hat{p}, \sqrt{\frac{m\omega}{2\hbar}} \hat{x} - i \sqrt{\frac{1}{2m\hbar \omega}} \hat{p} \right] = \frac{i}{\hbar} [\hat{p}, \hat{x}] = 1 .
\]  

(4.58)

Knowing \( \hat{H} |\psi\rangle = E |\psi\rangle \) is it clear that \( \hat{a}^\dagger \hat{a} \) is an observable with the eigenvalue \( n \equiv \frac{E}{\hbar \omega} - \frac{1}{2}, \)

\[
\hat{a}^\dagger \hat{a} |\psi\rangle = (\frac{E}{\hbar \omega} - \frac{1}{2}) |\psi\rangle \equiv n |\psi\rangle \implies |\psi\rangle = |n\rangle .
\]  

(4.59)

Now, we show that the states \( \hat{a} |\psi\rangle \) are eigenstates of the operator defined as \( \hat{n} \equiv \hat{a}^\dagger \hat{a} \), since,

\[
\hat{a}^\dagger \hat{a} |\psi\rangle = (\hat{a}^\dagger (\hat{a}^\dagger + [\hat{a}, \hat{a}^\dagger]) \hat{a} |\psi\rangle = (\hat{a}^\dagger \hat{a} - \hat{a}) |\psi\rangle = \hat{a}(\hat{a}^\dagger \hat{a} - 1) |\psi\rangle = (n - 1) \hat{a} |\psi\rangle
\]

\[
\implies \hat{a} |\psi\rangle \propto |n - 1\rangle
\]

\[
\implies n = \langle n | \hat{a}^\dagger \hat{a} | n \rangle = C^2 \langle n - 1 | n - 1 \rangle
\]

\[
\implies C = \sqrt{n} .
\]  

(4.60)

We note that the quantum number of the new \( |n - 1\rangle \) is decreased by 1. Similarly, we show for the state \( \hat{a}^\dagger |\psi\rangle \),

\[
\hat{a}^\dagger \hat{a}^\dagger |\psi\rangle = \hat{a}^\dagger ((\hat{a}^\dagger + [\hat{a}, \hat{a}^\dagger]) \hat{a}) |\psi\rangle = \hat{a}^\dagger (1 + \hat{a}^\dagger \hat{a}) |\psi\rangle = (n + 1) \hat{a}^\dagger |\psi\rangle
\]

\[
\implies \hat{a}^\dagger |\psi\rangle \propto |n + 1\rangle
\]

\[
\implies n + 1 = \langle n | \hat{a}^\dagger \hat{a} + [\hat{a}, \hat{a}^\dagger] | n \rangle = C^2 \langle n + 1 | n + 1 \rangle
\]

\[
\implies C = \sqrt{n + 1} .
\]  

(4.61)

Therefore, this new state is also an eigenvector \( |n + 1\rangle \), with a quantum number increased by one unit. \( \hat{a}^\dagger \) and \( \hat{a} \) are creation and annihilation operators of an energy packet,

\[
\hat{a}^\dagger |n\rangle = \sqrt{n + 1} |n + 1\rangle \quad \text{and} \quad \hat{a} |n\rangle = \sqrt{n} |n - 1\rangle .
\]  

(4.62)

The matrix representation of the field operators is,

\[
\hat{a}^\dagger = \sum_n \sqrt{n + 1} |n + 1\rangle \langle n| \quad \text{and} \quad \hat{a} = \sum_n \sqrt{n} |n - 1\rangle \langle n| .
\]  

(4.63)
Now it is clear, that \( \hat{n} \) can be understood as a number operator \(^2\). The energy spectrum of the harmonic oscillator is equidistant,

\[
E_n = \hbar \omega (n + \frac{1}{2}) .
\] (4.64)

The state with \( n \) quanta can be created from the vacuum,

\[
|n\rangle = \frac{\hat{a}^\dagger |n - 1\rangle}{\sqrt{n!}} = \frac{\hat{a}^\dagger n \sqrt{n!}}{\sqrt{n!}} |0\rangle .
\] (4.65)

The state \(|n\rangle\) is called number state or Fock state.

### 4.4.1.1 Uncertainty in Fock states

We consider an OH of mass \( m \) and angular frequency \( \omega \) prepared in the stationary state \(|n\rangle\) which is an eigenstate of the Hamiltonian \( \hat{H} \) with eigenvalue \((n + \frac{1}{2})\hbar\omega\). Defining the characteristic size of the OH, \( a_{ho} = \sqrt{\hbar/m\omega} \), the annihilation and creation operators can be written,

\[
\hat{a} = \frac{1}{\sqrt{2}} \left( \frac{\hat{x}}{a_{ho}} + i \frac{\hbar}{a_{ho}} \hat{p} \right) \quad \text{and} \quad \hat{a}^\dagger = \frac{1}{\sqrt{2}} \left( \frac{\hat{x}}{a_{ho}} - i \frac{\hbar}{a_{ho}} \hat{p} \right) .
\] (4.66)

Therefore, the position and momentum operators are,

\[
\sqrt{2} \frac{1}{a_{ho}} \hat{x} = \hat{a} + \hat{a}^\dagger \quad \text{and} \quad \sqrt{2} i \frac{\hbar}{a_{ho}} \hat{p} = \hat{a} - \hat{a}^\dagger .
\] (4.67)

The mean squared deviations of the position \( \hat{x} \) and the momentum \( \hat{p} \) are,

\[
\Delta x^2 = \langle n|\hat{x}^2|n\rangle = \frac{a_{ho}^2}{2} \langle n|\hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a} + \hat{a}^\dagger \hat{a}^\dagger|n\rangle = \frac{a_{ho}^2}{2} \langle n|2\hat{n} + 1|n\rangle
\]

\[= \frac{a_{ho}^2}{2} (2n + 1) \] (4.68)

\[
\Delta p^2 = \langle n|\hat{p}^2|n\rangle = \frac{-\hbar^2}{2a_{ho}^2} \langle n|\hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} + \hat{a}^\dagger \hat{a}^\dagger|n\rangle = \frac{-\hbar^2}{2a_{ho}^2} \langle n| - 2\hat{n} - 1|n\rangle
\]

\[= \frac{\hbar^2}{2a_{ho}^2} (2n + 1) .
\]

From the results of the previous item we obtain the uncertainty relation \( \Delta x \Delta p \) for the OH in the state \(|n\rangle\),

\[
\Delta p \Delta x = \frac{\hbar}{2} (2n + 1) .
\] (4.69)

**Example 23 (Localization energy):** The non-vanishing energy of the fundamental state of the harmonic oscillator, \( E_0 = \hbar \omega/2 \), is an immediate consequence of the Heisenberg principle \( \Delta x \Delta p \geq \hbar \), because in analogy with Example 20 we calculate,

\[
\frac{\langle p^2 \rangle}{2m} = \Delta p^2 > \frac{\hbar^2}{2m \Delta x^2} > \frac{\hbar^2}{2ma_{ho}^2} = \frac{\hbar \omega}{2} .
\]

In the case of an electromagnetic field this energy is called vacuum fluctuation.

---

\(^2\) Also, we can define phase operators by \( \exp(\mp i\phi) = \sum_n |n \mp 1\rangle \langle n| \).
4.4. HARMONIC OSCILLATOR

4.4.2 Harmonic oscillator in spatial representation

To simplify the Schrödinger equation in spatial representation, we transform the differential equation into a recursion formula,

\[ \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega^2 x^2 \right] \psi(x) = \hbar \omega \left( n + \frac{1}{2} \right) \psi(x) , \]  

(4.70)

we use the scale \( \tilde{x} \equiv x/a_{ho} \), where \( a_{ho} = \sqrt{\hbar/m\omega} \) is the spatial extent of the ground state. Therefore,

\[
\frac{2}{\hbar \omega} \left[ -\frac{\hbar^2}{2m} \frac{d^2}{d(a_{ho}\tilde{x})^2} + \frac{m}{2} \omega^2 (a_{ho}\tilde{x})^2 \right] \tilde{\psi}(\tilde{x}) = \frac{2}{\hbar \omega} \left[ -\frac{\hbar \omega}{2} \frac{d^2}{d\tilde{x}^2} + \frac{\hbar \omega}{2} \tilde{x}^2 \right] \tilde{\psi}(\tilde{x})
= \left[ -\frac{d^2}{d\tilde{x}^2} + \tilde{x}^2 \right] \tilde{\psi}(\tilde{x}) = (2n + 1) \tilde{\psi}(\tilde{x}) .
\]

Now we start looking for asymptotic solutions. For \( \tilde{x} \to \pm\infty \), that is, when the particle enters the classically forbidden region, we can neglect the total energy of the particle,

\[
\left[ -\frac{d^2}{d\tilde{x}^2} + \tilde{x}^2 \right] \tilde{\psi}_\infty(\tilde{x}) \approx 0 .
\]

(4.71)

The solution of this equation is \( \tilde{\psi}_\infty(\tilde{x}) = C e^{-\tilde{x}^2/2} \), since

\[
\left[ -\frac{d^2}{d\tilde{x}^2} + \tilde{x}^2 \right] \tilde{e}^{\tilde{x}^2/2} = \frac{d}{d\tilde{x}} (-\tilde{x}) \tilde{e}^{\tilde{x}^2/2} + \tilde{x}^2 \tilde{e}^{-\tilde{x}^2/2}
= -\tilde{x}^2 \tilde{e}^{-\tilde{x}^2/2} + \tilde{e}^{-\tilde{x}^2/2} + \tilde{x}^2 \tilde{e}^{-\tilde{x}^2/2} = e^{-\tilde{x}^2/2} \approx 0 .
\]

(4.72)

This motivates the ansatz \( \tilde{\psi}(\tilde{x}) = e^{-\tilde{x}^2/2} H(\tilde{x}) \) for the complete differential equation (4.70),

\[
\left[ -\frac{d^2}{d\tilde{x}^2} + \tilde{x}^2 \right] e^{-\tilde{x}^2/2} H(\tilde{x}) = -e^{-\tilde{x}^2/2} \frac{d^2}{d\tilde{x}^2} H(\tilde{x}) - 2 \frac{d e^{-\tilde{x}^2/2}}{d\tilde{x}} \frac{dH(\tilde{x})}{d\tilde{x}} - \frac{d^2 e^{-\tilde{x}^2/2}}{d\tilde{x}^2} H(\tilde{x}) + \tilde{x}^2 e^{-\tilde{x}^2/2} H(\tilde{x})
= -e^{-\tilde{x}^2/2} \frac{d^2}{d\tilde{x}^2} H(\tilde{x}) - 2(-\tilde{x}) e^{-\tilde{x}^2/2} \frac{dH(\tilde{x})}{d\tilde{x}} + \left[ -\tilde{x}^2 e^{-\tilde{x}^2/2} + e^{-\tilde{x}^2/2} \right] H(\tilde{x}) + \tilde{x}^2 e^{-\tilde{x}^2/2} H(\tilde{x})
\equiv (2n + 1) e^{-\tilde{x}^2/2} H(\tilde{x}) .
\]

(4.73)

Thus, the functions \( H(\tilde{x}) \) must satisfy the differential equation,

\[ H''(\tilde{x}) = 2\tilde{x} H'(\tilde{x}) - 2n H(\tilde{x}) . \]

(4.74)

We can verify that the Hermite polynomials defined by,

\[ H_n(\tilde{x}) = (-1)^n \tilde{x}^n \frac{d^n}{d\tilde{x}^n} e^{-\tilde{x}^2} , \]

(4.75)

transform the differential equation into a recursion formula,

\[ H_{n+1}(\tilde{x}) = 2\tilde{x} H_n(\tilde{x}) - 2n H_{n-1}(\tilde{x}) , \]

(4.76)

which allows us to easily calculate the polynomials,

\[ H_0(\tilde{x}) = 1 , \quad H_1(\tilde{x}) = 2\tilde{x} , \quad H_2(\tilde{x}) = 4\tilde{x}^2 - 2 , \quad ... \]
In summary, the eigenfunction of a harmonic oscillator in the state of excitation \( n \) is,

\[
\langle x | n \rangle = \psi_n(x) = C_n e^{-x^2/2a_h^2} H_n(x/a_h),
\]

where the constant \( C_n \) is determined by the normalization condition (7.18), \( \langle \psi_m | \psi_n \rangle = \delta_{m,n}, \)

\[
C_n = \frac{1}{\sqrt{a_h \sqrt{2\pi n!}}}. \quad (4.79)
\]

The Hermite functions, \( H_n \), are found in mathematical tables, see 7.1.4. The spatial and momentum wavefunctions for the vibrational ground state are,

\[
\langle x | 0 \rangle = \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{a_h}} e^{-x^2/2a_h^2} \quad \text{and} \quad \langle p | 0 \rangle = \frac{1}{\sqrt{\pi}} \frac{1}{\sqrt{\hbar}} e^{-a_h p^2/2\hbar^2}. \quad (4.80)
\]

Here we will only show the graphical representation of \( \langle \psi \rangle \) in Fig. 4.10. The Exc. 4.4.6.1 asks to evaluate HO in a classically forbidden region and in Exc. 4.4.6.2 we will calculate the spectrum of a semi-harmonic HO.

Figure 4.10: (code) Wavefunctions and energies for a rectangular well.

### 4.4.3 Properties of the harmonic oscillator

We note that there are regions where \( \psi(\tilde{x}) \neq 0 \) even though \( V(x) > E \). This effect is purely quantum. Classically, we can not find a particle in regions where its energy is below the potential.

We also note that for high quantum numbers, \( n \to \infty \), we expect to recover the classical predictions, i.e.,

\[
\lim_{n \to \infty} |\psi(x)|^2 = P_E(x),
\]

where \( P_E \) is the probability density of finding the oscillating particle at position \( x \). The probability of finding the particle in a range \( dx \) close to the location \( x \) is easily
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calculated,
\[ E = \frac{m}{2}v^2 + \frac{m}{2}\omega^2x^2 \]  
\[ \Rightarrow P_E(x)dx = \frac{t(x + dx) - t(x)}{T} = \frac{dx}{vT} = \frac{1}{\sqrt{2E/m - \omega^2x^2}}. \]

We see that for high energy values the wavefunction approaches the classical expectation.

We already mentioned that there exist solutions only for certain energies \( E_n = \hbar\omega(2n + 1) \). Consequently, the energy levels are equidistant, \( E_{n+1} - E_n = \hbar\omega \), as if there were a box into which we add, one after the other, particles with the energy \( \hbar\omega \) until we have accumulated \( n \) portions of energy. These particles are called phonons in the case of vibrations of massive particles, and photons in the case of a radiation field.

The fact that the energy distribution is the same as the one proposed by Planck for the black-body radiation suggests the use of the harmonic oscillator to describe the second quantization.

4.4.4 Time evolution of the unperturbed harmonic oscillator

Here we study the temporal evolution of a population distribution in a harmonic oscillator. The formal solution of the Schrödinger equation is,
\[ |\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle. \]  
\[ \langle\psi(t)|\hat{A}|\psi(t)\rangle = \sum_{m,n} c_m^*c_ne^{i\omega t(m-n)}\langle m|\hat{A}|n\rangle. \]

Figure 4.11: Ladder of levels.
If the oscillator is initially in an eigenstate, $|\psi(0)\rangle = |k\rangle$, we obtain,

$$|\psi(t)\rangle = e^{-i\omega(t+1/2)}|k\rangle\quad\text{and}\quad \langle \psi(t)|\hat{A}|\psi(t)\rangle = \langle k|\hat{A}|k\rangle,$$

(4.87)

that is, the state remains stationary. Motion needs non-diagonal elements of $\hat{A}$.

Another observation is that the populations do not change, even in the case of an initial superposition, since,

$$P_k(t) = |\langle k|\psi(t)\rangle|^2 = |c_k|^2.$$

(4.88)

We conclude that

- movement of an observable $\hat{A}$ is possible, but only due to variations of the phase factors;
- to carry out transitions between the vibrational states is necessary to perturb the oscillator, e.g. by applying fields of electromagnetic radiation.

**Example 24 (Motion of a harmonic oscillator):** We now consider some specific examples. If the studied observable is the Hamiltonian and the initial state an arbitrary superposition, then

$$\langle \psi(t)|\hat{H}|\psi(t)\rangle = \hbar\omega \sum_{m,n} c_m^* c_n e^{i\omega t(m-n)} \langle m|\hat{n} + \frac{1}{2}|n\rangle = \hbar\omega \sum_n |c_n|^2 \left(n + \frac{1}{2}\right).$$

That is, the total energy of the oscillator is the sum of the energies of the states weighted with the populations of those states. In the case of the position operator,

$$\langle \psi(t)|\hat{x}|\psi(t)\rangle = \frac{\hbar \omega}{\sqrt{2}} \sum_{m,n} c_m^* c_n e^{i\omega t(m-n)} \langle m|\hat{a} + \hat{a}^\dagger|n\rangle$$

$$= \frac{\hbar \omega}{\sqrt{2}} \sum_n \left(c_{n-1}^* c_n e^{-i\omega t} \sqrt{n} + c_{n+1}^* c_n e^{i\omega t} \sqrt{n+1}\right)$$

$$\xrightarrow{m,n\to\infty} a_\hbar \sqrt{2} \sum_n \sqrt{n}|c_n|^2 \cos \omega t.$$

That is, the particle can only oscillate, if there are populations in consecutive states. If this is not the case, $\langle \psi(t)|\hat{x}|\psi(t)\rangle = 0$. The oscillation frequency is always $\omega$, independent of the energy of the particle. We will study this in Excs. 4.4.6.3, leaving the discussion of the temporal evolution of perturbed oscillators to later sections.

### 4.4.5 Multidimensional harmonic oscillator

The 3D harmonic potential is given by

$$V_{ho}(\mathbf{r}) = \frac{m}{2} \omega_x^2 x^2 + \frac{m}{2} \omega_y^2 y^2 + \frac{m}{2} \omega_z^2 z^2.$$

(4.89)

Making the ansatz

$$\psi(\mathbf{r}) = \psi_x(x)\psi_y(y)\psi_z(z),$$

(4.90)
we can separate the spatial directions and obtain a one-dimensional equation for each coordinate, such that the coordinates can be considered separately. Each function $\psi_k(x_k)$ is of the form (4.78) and the energies are,

$$E_k = \hbar \omega_k (n_k + \frac{1}{2}) ,$$

(4.91)

where $k = x, y, z$.

### 4.4.6 Exercises

#### 4.4.6.1 Ex: Ground state of a harmonic oscillator

Equating the ground state energy of quantum HO to that of its classical analog, obtain the maximum elongation $x_m$. Now, knowing that the ground state wavefunction is proportional to the Gaussian $\psi_0 \propto e^{-x^2/2x_m^2}$, obtain the expression for the probability of finding the HO outside the classical limits and estimate its value.

#### 4.4.6.2 Ex: Particle in a semi-harmonic well

Find the energy levels of a particle in a potential energy well of the form $V(x) = \infty$ for $x < 0$ and $V(x) = \frac{m \omega^2 x^2}{2}$ for $x > 0$. What is the parity of the allowed states?

#### 4.4.6.3 Ex: Vibration of a harmonic oscillator

Consider a HO of mass $m$ and angular frequency $\omega$. At time $t = 0$ the oscillator’s state is $|\psi(0)\rangle = \sum_n c_n |n\rangle$, where $|n\rangle$ are the stationary states of the HO with energy $(n + 1/2)\hbar \omega$.

a. What is the probability $P$ for measuring, at an arbitrary time $t > 0$, an energy of the HO higher than $2\hbar \omega$? For the case when $P = 0$, what are the non-zero coefficients $c_n$?

b. From now on, we assume that only $c_0$ and $c_1$ are nonzero. Write down the normalization condition for $|\psi(0)\rangle$ and the mean value $\langle \hat{H} \rangle$ of energy in terms of $c_0$ and $c_1$.

With the additional requirement $\langle \hat{H} \rangle = \hbar \omega$, calculate $|c_0|^2$ and $|c_1|^2$.

c. Given that the normalized state vector $|\psi(0)\rangle$ is defined to less than an overall phase factor, we determine this factor by choosing the real and positive coefficients $c_0$ and $c_1 = |c_1|e^{i\theta}$. Assuming $\langle \hat{H} \rangle = \hbar \omega$ and $\langle \hat{x} \rangle = \frac{1}{2} \sqrt{\hbar/m\omega}$, calculate $\theta$.

d. With $|\psi(0)\rangle$ determined (according to the previous item), write down $|\psi(t)\rangle$ for $t > 0$ and calculate the value $\theta$ at this time $t$. Deduce the average value $\langle \hat{x} \rangle(t)$ of the position at time $t$.

### 4.5 Superposition states of a harmonic oscillator

#### 4.5.1 Coherent states

##### 4.5.1.1 Glauber’s formula

A useful formula that we will use later is the Glauber formula (or Baker-Hausdorff formula),

$$e^{\hat{A}\hat{B}} = e^{\hat{A} + \hat{B} + [\hat{A}, \hat{B}]/2} ,$$

(4.92)
which holds when \( \hat{A} \) and \( \hat{B} \) commute with their commutator, i.e., \([\hat{A}, [\hat{A}, \hat{B}]] = [\hat{B}, [\hat{A}, \hat{B}]] = 0\).

**Example 25 (The Baker-Hausdorff formula):** In order to prove the Baker-Hausdorff formula, we consider the operator,

\[
\hat{G}(\tau) \equiv e^{\tau(\hat{A}+\hat{B})} e^{-\tau\hat{B}} e^{-\tau\hat{A}}.
\]

The derivative is,

\[
\hat{G}'(\tau) = (\hat{A} + \hat{B})e^{\tau(\hat{A}+\hat{B})} e^{-\tau\hat{B}} e^{-\tau\hat{A}} - e^{\tau(\hat{A}+\hat{B})} \hat{B}e^{-\tau\hat{B}} e^{-\tau\hat{A}} - e^{\tau(\hat{A}+\hat{B})} e^{-\tau\hat{B}} \hat{A}e^{-\tau\hat{A}}
= e^{\tau(\hat{A}+\hat{B})} \left[ \hat{A} e^{-\tau\hat{B}} - e^{-\tau\hat{B}} \hat{A} \right] e^{-\tau\hat{A}} = e^{\tau(\hat{A}+\hat{B})} \left[ \hat{A} - e^{-\tau\hat{B}} \hat{A} e^{-\tau\hat{B}} \right] e^{-\tau\hat{A}}
= e^{\tau(\hat{A}+\hat{B})} \left[ \hat{A} - (\hat{A} + [-\tau\hat{B}, \hat{A}] + \frac{1}{2}[\tau\hat{B}, [-\tau\hat{B}, \hat{A}]] + ...) \right] e^{-\tau\hat{B}} e^{-\tau\hat{A}},
\]

using the formula (2.165). If now \([\hat{A}, [\hat{A}, \hat{B}]] = 0 = [\hat{B}, [\hat{A}, \hat{B}]]\), then,

\[
\hat{G}'(\tau) = e^{\tau(\hat{A}+\hat{B})} \tau[\hat{B}, \hat{A}] e^{-\tau\hat{B}} e^{-\tau\hat{A}} = -\tau[\hat{A}, \hat{B}] e^{\tau(\hat{A}+\hat{B})} e^{-\tau\hat{B}} e^{-\tau\hat{A}} = -\tau[\hat{A}, \hat{B}] \hat{G}(\tau).
\]

The solution of this differential equation is,

\[ G(\tau) = e^{-(\tau^2/2)[\hat{A}, \hat{B}]} \hat{G}(0). \]

With \( \hat{G}(0) = 1 \) we obtain at the point \( \tau = 1 \),

\[ e^{\hat{A}+\hat{B}} e^{-\hat{B}} e^{-\hat{A}} = e^{-(1/2)[\hat{A}, \hat{B}]} . \]

### 4.5.1.2 Displacement operator

We now consider the so-called displacement operator \(^3\),

\[
\hat{D}(\alpha) \equiv e^{\alpha \hat{a}^\dagger - \alpha^* \hat{a}}, \quad (4.93)
\]

and try to discover its features.

\( \hat{D}(\alpha) \) is a unitary operator, since using Glauber’s formula (4.92) we get,

\[
\hat{D}^\dagger(\alpha) \hat{D}(\alpha) = e^{\alpha^* \hat{a} - \alpha \hat{a}^\dagger} e^{\alpha \hat{a}^\dagger - \alpha^* \hat{a}} = e^{\alpha^* \hat{a} - \alpha \hat{a}^\dagger + \alpha \hat{a}^\dagger - \alpha^* \hat{a} + [\alpha^* \hat{a} - \alpha \hat{a}^\dagger, \alpha \hat{a}^\dagger - \alpha^* \hat{a}]/2}
= e^{[\alpha^* \hat{a} - \alpha \hat{a}^\dagger, \alpha \hat{a}^\dagger - \alpha^* \hat{a}]/2} = e^{[\alpha^* \hat{a}, \alpha \hat{a}^\dagger]/2 + [-\alpha \hat{a}^\dagger, \alpha \hat{a}^\dagger]/2 + \alpha^* \hat{a} - \alpha \hat{a}^\dagger]/2 + [-\alpha \hat{a}^\dagger, \alpha^* \hat{a}]/2}
= e^{[\alpha \hat{a}^\dagger, \alpha \hat{a}]/2 + [\alpha] \hat{a}^\dagger, \hat{a}] / 2} = e^{0} = 1.
\]

We can rewrite the displacement operator like this:

\[
\hat{D}(\alpha) = e^{\alpha \hat{a}^\dagger - \alpha^* \hat{a}} = e^{\alpha \hat{a}^\dagger} e^{-[\alpha \hat{a}^\dagger, -\alpha^* \hat{a}]/2} = e^{\alpha \hat{a}^\dagger} e^{-\alpha^* \hat{a}} e^{[\alpha \hat{a}^\dagger, \hat{a}] / 2}
= e^{\alpha \hat{a}^\dagger} e^{-\alpha^* \hat{a}} e^{-[\alpha] \hat{a}^\dagger, \hat{a}] / 2}. \quad (4.95)
\]

\(^3\)The operator acts on the phase space spanned by the operators \( \hat{a} \) and \( \hat{a}^\dagger \), that is, \( \hat{z} \propto \text{Re} \hat{a} \) and \( \hat{p} \propto \text{Im} \hat{a} \).
4.5. **SUPERPOSITION STATES OF A HARMONIC OSCILLATOR**

The state resulting from the action of the operator $\hat{D}(\alpha)$ onto the estado fundamental of the HO is,

$$|\alpha\rangle \equiv \hat{D}(\alpha)|0\rangle = e^{-|\alpha|^2/2}e^{\alpha \hat{a}^\dagger - \alpha^* \hat{a}}|0\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{(\alpha \hat{a}^\dagger)^n}{n!}|n\rangle$$

(4.96)

$$= e^{-|\alpha|^2/2} \left(1 + \alpha \hat{a}^\dagger + \frac{(\alpha \hat{a}^\dagger)^2}{2!} + \ldots\right)|0\rangle = e^{-|\alpha|^2/2} \left(|0\rangle + \frac{\alpha}{1!} \sqrt{1}|1\rangle + \frac{\alpha^2}{2!} \sqrt{2!}|2\rangle + \ldots\right),$$

that is, the state $|\alpha\rangle$ is a superposition distributed according to the **Poisson distribution**,

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle.$$  

(4.97)

Applying the step-down operator $\hat{a}$ onto the state $|\alpha\rangle$, we find,

$$\hat{a}|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \hat{a}|n\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \sqrt{n}|n-1\rangle$$

(4.98)

that is,

$$\hat{a}|\alpha\rangle = \alpha |\alpha\rangle.$$  

(4.99)

We can also write,

$$\langle \alpha | \hat{a}^\dagger = (\hat{a}|\alpha\rangle)\dagger = (\alpha |\alpha\rangle)^\dagger = \langle \alpha | \alpha^* .$$

The state $|\alpha\rangle$ is called **coherent state** or **Glauber state**. We note that, in spite of its appearance, the equation (4.99) is not an eigenvalue equation, since $\hat{a}$ is not observable.

Using the formula (2.165), we verify immediately,

$$\hat{D}^\dagger(\alpha) \hat{a} \hat{D}(\alpha) = \hat{a} + \alpha, \quad \hat{D}^\dagger(\alpha) \hat{a}^\dagger \hat{D}(\alpha) = \hat{a}^\dagger + \alpha^*.$$  

(4.100)

Furthermore, the product of two displacement operators is, apart from a phase factor, another displacement operator satisfying,

$$\hat{D}(\alpha) \hat{D}(\beta) = e^{(\alpha \beta^* - \alpha^* \beta)/2} \hat{D}(\alpha + \beta),$$  

(4.101)

---

4We can also define a **Bargmann state** as the eigenstate corresponding to the step-up operator using the notation $\hat{a}^\dagger|\alpha\rangle = \alpha ||\alpha\rangle$.

5For the differential calculus with Glauber states it is practical to use the **Wirtinger derivative**, 

$$\hat{a}^\dagger - \alpha^* = \frac{\partial}{\partial \alpha^*} \quad \text{and} \quad \hat{a}^\dagger - \alpha = \frac{\partial}{\partial \alpha}. $$

With the bosonic operators we can construct the observables,

$$\hat{x} + i\hat{p} = \sqrt{2} \hat{a} \quad , \quad \frac{\partial}{\partial \alpha} - i\frac{\partial}{\partial \beta} = 2\partial_{\alpha^*} \quad , \quad \frac{\partial}{\partial \alpha} + i\frac{\partial}{\partial \beta} = 2\partial_{\alpha^*} .$$

In two dimensions [199], $d^2 \alpha = d(\text{Re} \alpha)d(\text{Im} \alpha) = dxdp$. 

as will be verified in Exc. 4.5.6.1. When acting on an eigenket, the phase factor \( e^{(\alpha \beta^* - \alpha^* \beta)/2} \) appears in each term of the resulting state, which makes it physically irrelevant.

### 4.5.1.3 Uncertainty in Glauber states

Consider a HO prepared in a state \( |\alpha\rangle \). The eigenvalues of the observables \( \hat{x} \equiv \frac{a_{ho}}{\sqrt{2}} (\hat{a}^\dagger + \hat{a}) \) and \( \hat{p} \equiv \frac{i\hbar}{a_{ho}\sqrt{2}} (\hat{a}^\dagger - \hat{a}) \) are,

\[
\frac{\sqrt{2}}{a_{ho}} \langle \alpha | \hat{x} | \alpha \rangle = \langle \alpha | \hat{a} + \hat{a}^\dagger | \alpha \rangle = \alpha + \alpha^* \quad \text{and} \quad \frac{\hbar a_{ho}}{\sqrt{2}} \langle \alpha | \hat{p} | \alpha \rangle = \langle \alpha | \hat{a} - \hat{a}^\dagger | \alpha \rangle = \alpha - \alpha^*.
\]

With this the eigenvalues of the quadratures become,

\[
\frac{2}{a_{ho}^2} \langle \alpha | \hat{x}^2 | \alpha \rangle = \langle \alpha | (\hat{a} + \hat{a}^\dagger)^2 | \alpha \rangle = \langle \alpha | \hat{a}\hat{a} + 1 + 2\hat{a}^\dagger \hat{a} + \hat{a}^\dagger\hat{a}^\dagger | \alpha \rangle = \alpha^2 + 1 + 2|\alpha|^2 + \alpha^* = 1 + \frac{2}{a_{ho}^2} \langle \alpha | \hat{x} | \alpha \rangle^2
\]

\[
\frac{-\hbar^2}{2a_{ho}^2} \langle \alpha | \hat{p}^2 | \alpha \rangle = \langle \alpha | (\hat{a} - \hat{a}^\dagger)^2 | \alpha \rangle = \langle \alpha | \hat{a}\hat{a} - 1 - 2\hat{a}^\dagger \hat{a} + \hat{a}^\dagger\hat{a}^\dagger | \alpha \rangle = \alpha^2 - 1 - 2|\alpha|^2 + \alpha^* = -1 + (\alpha - \alpha^*)^2 = -1 - \frac{2\hbar^2}{a_{ho}^2} \langle \alpha | \hat{p} | \alpha \rangle^2.
\]

The uncertainties defined in (2.66) become,

\[
\Delta x^2 = \langle \alpha | \hat{x}^2 | \alpha \rangle - \langle \alpha | \hat{x} | \alpha \rangle^2 = \frac{a_{ho}^2}{2}, \quad (4.104)
\]

\[
\Delta p^2 = \langle \alpha | \hat{p}^2 | \alpha \rangle - \langle \alpha | \hat{p} | \alpha \rangle^2 = \frac{\hbar^2}{2a_{ho}^2}. \quad (4.105)
\]

And finally, we find the Heisenberg relation,

\[
\Delta p \Delta x = \frac{\hbar}{2}. \quad (4.105)
\]

Comparing with the uncertainty relation (4.69) derived for Fock states, we conclude that the uncertainty is always smallest for Glauber states. In this sense, the Glauber states are the ones which are closest to classical states characterized by the absence of uncertainty.

### 4.5.1.4 Orthogonality of Glauber states

Glauber are not orthogonal, since,

\[
| \langle \alpha | \beta \rangle |^2 = e^{-|\alpha - \beta|^2}. \quad (4.106)
\]

We leave the demonstration for Exc. 4.5.6.2, but we note here already that for \( |\alpha - \beta| \gg 0 \) the states are approximately orthogonal. The reason for this is, that the respective population distributions through the Fock states, \( |\langle n | \alpha \rangle |^2 \) and \( |\langle n | \beta \rangle |^2 \), do not overlap and hence do not interfere. The state \( |\alpha\rangle + | - \alpha\rangle \) is sometimes called Schrödinger cat state. In Exc. 4.5.6.4 we will show why such states are very difficult to detect.
4.5.2 Kicking a harmonic oscillator

Let us now study the dynamics of a harmonic oscillator subject to a kick. By kicking we understand a translation in momentum space defined by the Galilei boost operator (2.187),

\[ U_G(\mathbf{k}) \equiv e^{i\mathbf{k}\cdot\hat{r}}, \]

where \( \mathbf{p} = \hbar \mathbf{k} \) is the gain in momentum due to the kick. A common situation where such a kick occurs is the photonic recoil that an atom receives upon absorption of a photon. Using the relationship (2.165) derived in Exc. 2.5.5.1 it is easy to verify the following expressions of the left-hand panel,

\[
\begin{align*}
    e^{i\mathbf{k}\cdot\hat{r}} |\mathbf{r}\rangle &= |\mathbf{r}\rangle \\
    e^{i\mathbf{k}\cdot\hat{p}} |\mathbf{p}\rangle &= |\mathbf{p} + \hbar \mathbf{k}\rangle \\
    e^{-i\mathbf{k}\cdot\hat{r}} e^{i\mathbf{k}\cdot\hat{p}} &= \hat{\mathbf{r}} \\
    e^{-i\mathbf{k}\cdot\hat{r}} \hat{p} e^{i\mathbf{k}\cdot\hat{p}} &= \hat{\mathbf{p}} + \hbar \mathbf{k} \\
    e^{-i\mathbf{k}\cdot\hat{r}} \frac{\hat{\mathbf{p}}^2}{2m} e^{i\mathbf{k}\cdot\hat{r}} &= \frac{(\hat{\mathbf{p}} + \hbar \mathbf{k})^2}{2m}
\end{align*}
\]

The rule imply \( [e^{i\mathbf{k}\cdot\hat{r}}, \hat{\mathbf{p}}] \neq 0 \neq [e^{i\mathbf{k}\cdot\hat{p}}, \hat{\mathbf{r}}] \). That is, we describe the kick by simply adding the corresponding momentum \( \hbar \mathbf{k} \) to the system and adjusting the kinetic energy accordingly. Of course the assumption of an infinitely fast transition is an idealization and the ultimate reason for the non-conservation of momentum and energy by the system. In real situations, such as in the case of photonic recoil, the dynamics should be described by a collision process which conserves momentum and energy.

The right-hand panel of Eq. (4.108) summarizes rules for calculating with the spatial displacement operator introduced in Sec. 2.5.1,

\[ U_{tr}(\mathbf{b}) \equiv e^{-i\mathbf{b}\cdot\hat{p}/\hbar}. \]

By analogy we find \( [e^{-i\mathbf{b}\cdot\hat{p}/\hbar}, \hat{\mathbf{r}}] \neq 0 \neq [e^{-i\mathbf{b}\cdot\hat{p}/\hbar}, \hat{\mathbf{r}}] \).

4.5.2.1 Transitions between vibrational states via momentum kick

Let us now restrict to one dimension and study, how the transformation operators \( U_G = e^{ikx} \) and \( U_{tr} = e^{-ibp/\hbar} \) couple the vibrational states of a harmonic oscillator. With the formalism developed in the last sections and with the abbreviation,

\[ \alpha \equiv ik\alpha_0/\sqrt{2}, \]

we find,

\[ e^{ikx} = e^{\frac{ik\alpha_0^2}{2} (\hat{a} + \hat{a}^\dagger)} = e^{\alpha\hat{a} + \alpha^*\hat{a}^\dagger} = D(\alpha), \]

which is nothing else than the displacement operator (4.96) generating coherent states, \( |\alpha\rangle = D(\alpha)|0\rangle \). That is, the momentum kick attempts to put the oscillator into a coherent state with the mean occupation number \( n = |\alpha|^2 = \frac{1}{2} k^2 a_{\alpha_0}^2 \). Note that the same effect is obtained setting,

\[ \alpha \equiv -b/(a_{\alpha_0}\sqrt{2}) \]
and applying the translation operator

\[ e^{-ib\hat{p}/\hbar} = e^{-b\hat{a}^\dagger - \alpha^* \hat{a}} = D(\alpha). \]  

(4.113)

Now,

\[ \langle n | e^{ik\hat{x}} | 0 \rangle = \langle n | \alpha \rangle = \langle n | e^{-|\alpha|^2/2} \sum_{m=0}^{\infty} \frac{\alpha^m}{\sqrt{m!}} | m \rangle \]

(4.114)

\[ = e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} = e^{-|k\hbar\omega|^2/4} \frac{(ik\hbar\omega)^n}{\sqrt{n!}}. \]

This formula tells us that for small \( \alpha \), transitions may only occur to the vibrational states \( |0\rangle \) and \( |1\rangle \), since,

\[ \langle n | e^{ik\hat{x}} | 0 \rangle \approx 0 \quad \sum_{n=0}^{\infty} |\langle n | e^{ik\hat{x}} | 0 \rangle|^2 = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{|\alpha|^2n}{n!} = 1. \]

(4.116)

For small momentum kicks we may approximate the transition matrix elements by,

\[ \langle m | e^{ik\hat{x}} | n \rangle \approx \langle m | 1 + ik\alpha_{\hbar\omega} \sqrt{2} (\hat{a} + \hat{a}^\dagger) | n \rangle \]

\[ = \delta_{m,n} + \frac{ik\alpha_{\hbar\omega}}{\sqrt{2}} (\sqrt{n}\delta_{m,n-1} + \sqrt{n+1}\delta_{m,n+1}), \]

(4.117)

such that,

\[ \sum_{m \neq n} |\langle m | e^{ik\hat{x}} | n \rangle|^2 \approx k^2 a_{\hbar\omega}^2 (n + \frac{1}{2}). \]

(4.118)

Figure 4.12: (code) Transition matrix element \( |\langle n | e^{ik\hat{x}} | 0 \rangle|^2 \) as a function of \( k\hbar\omega \). The curves are Poisson distributions of photon numbers in coherent states.
4.5. SUPERPOSITION STATES OF A HARMONIC OSCILLATOR

Formula (4.118) tell us that the probability for a transition between vibrational states depends on the parameter $ka_{ho}$, which we will discuss in the next section. For small $ka_{ho}$ it gets increasingly more difficult for the system to leave the original vibrational state $|n\rangle$ and to form a coherent state. After a momentum kick, the population is coherently distributed over several vibrational states in a way to fulfill momentum and energy conservation. Let us consider, for simplicity, an initial state $|0\rangle$. If the kick is weak or the trap strong (i.e. if $|\alpha| < 1$), the atom will stay in $|0\rangle$ with a high probability amplitude and go to $|1\rangle$ only with a small probability amplitude. We will derive in Exc. 4.5.6.5 the general expression for the transition matrix element for arbitrary values of the Lamb-Dicke parameter,

$$
\langle m | e^{ik \hat{x}} | n \rangle = e^{i|\alpha|^2 / 2} \sum_{k=0}^{n} \sqrt{\binom{n}{k} \binom{m}{k}} \langle n - k | \alpha \rangle \langle m - k | \alpha \rangle .
$$  \hspace{1cm} (4.119)

The formula satisfies,

$$
\sum_{m} |\langle m | e^{ik \hat{x}} | n \rangle|^2 = \sum_{m} \langle n | e^{ik \hat{x}} | m \rangle \langle m | e^{-ik \hat{x}} | n \rangle = \langle n | e^{ik \hat{x}} e^{-ik \hat{x}} | n \rangle = 1 .
$$  \hspace{1cm} (4.120)

Kicking a harmonic oscillator initially in state $|0\rangle$ we obtain for the expectation value of position and momentum,

$$
\langle \alpha | \hat{p} | \alpha \rangle = \langle 0 | D(\alpha)^\dagger \hat{p} D(\alpha) | 0 \rangle = \langle 0 | e^{ik \hat{x}} \hat{p} e^{-ik \hat{x}} | 0 \rangle = \langle 0 | \hat{p} | 0 \rangle + \hbar k
$$

$$
\langle \alpha | \hat{x} | \alpha \rangle = \langle 0 | \hat{x} | 0 \rangle
$$

4.5.2.2 Lamb-Dicke regime

We already introduced $|\alpha|$ as the amplitude of the coherent vibrational state created by kicking a harmonic oscillator. Defined as,

$$
\eta \equiv |\alpha| = \frac{1}{\sqrt{2}} ka_{ho}
$$

with $a_{ho} \equiv \sqrt{\frac{\hbar}{m\omega_{ho}}}$.

\hspace{1cm} (4.121)

the so-called Lamb-Dicke parameter measures degree of confinement of a particle in a harmonic trap with respect to the momentum shift. We say that we are in the Lamb-Dicke regime, when the particle is localized to a volume smaller than wavelength, $2\pi x_0 \ll \lambda$, corresponding to the momentum kick.

Figure 4.13: Illustration of the Lamb-Dicke parameter.
We can also rewrite the Lamb-Dicke parameter in terms of the trap’s secular frequency, $\omega_{ho}$, and the recoil-shift,

$$\eta = \sqrt{\frac{\omega_{rec}}{\omega_{ho}}} \quad \text{with} \quad \omega_{rec} = \frac{\hbar k^2}{2m}, \quad (4.122)$$

where we understand the recoil-energy $\hbar \omega_{rec}$ as the kinetic energy gained through the recoil acceleration. In this form the Lamb-Dicke parameter tells us that, in the Lamb-Dicke regime, the energy of the momentum kick is not sufficient to excite vibrational states,

$$(2n + 1)\frac{\hbar^2 k^2}{m} \ll \omega_{ho}. \quad (4.123)$$

That is, cold particles in low vibrational states $n$ can not accommodate the recoil shift within the vibrational spectrum of the trap. Consequently, the recoil cannot be transferred to the particle itself, but must be absorbed by the entire trap. This is the case of the strong binding regime in ion traps, which is analogous to the Mößbauer effect discussed in Sec. 16.3.3.

Finally, the Lamb-Dicke parameter can be rewritten in terms of the inverse Doppler modulation index,

$$\eta = \frac{k v_{max}}{2 \omega_{ho}} \quad \text{with} \quad \frac{m}{2} v_{max}^2 = \hbar \omega_{ho}. \quad (4.124)$$

Accelerated by the momentum kick, the atom will execute harmonic oscillations with frequency $\omega_{ho}$ and with the maximum velocity-excursions $v_{max}$. Hence, any quantity depending on the atomic velocity, e.g. the Doppler-shift, will be modulated. We will discuss this in Sec. 16.3.3, as well.

**Example 26 (Absorption of recoil by a molecular dimer):** To be able to discuss the validity of energy and momentum conservation in a kicked system, let us consider a molecule made of two atoms with masses $m_1$ and $m_2$. Then we kick atom 1 via the momentum shift operator $e^{ik\hat{x}_1}$ (e.g. during a photon absorption process with the associated recoil) and analyze the motional dynamics of the whole system. (We restrict ourselves to one dimension.)

The first step is to write down the Hamiltonian,

$$\hat{H} = -\frac{\hbar^2}{2m_1} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m_2} \frac{d^2}{dx_2^2} + \frac{\mu}{2} \omega_{ho}^2 (x_1 - x_2)^2,$$

We transform in the center-of-mass system via,

$$M \equiv m_1 + m_2 \quad \text{and} \quad \frac{1}{\mu} \equiv \frac{1}{m_1} + \frac{1}{m_2},$$

$$R = \frac{m_1 x_1 + m_2 x_2}{M} \quad \text{and} \quad r = x_1 - x_2.$$
Applying the separation ansatz $\psi(x_1, x_2) = \Theta(R) \phi(r)$ to the Schrödinger equation,
\[
\left[ -\frac{\hbar^2}{2m_1} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m_2} \frac{d^2}{dx_2^2} + \frac{\mu}{2} \omega_{ho}^2 (\hat{x}_1 - \hat{x}_2)^2 \right] \psi(x_1, x_2) = E_{tot} \psi(x_1, x_2),
\]
we calculate,
\[
\frac{d}{dx_{1,2}} = \frac{dR}{dx_{1,2}} \frac{d}{dR} + \frac{dr}{dx_{1,2}} \frac{d}{dr} = \frac{m_{1,2} dr}{M dR} \pm \frac{d}{dr}
\]
\[
\frac{d^2}{dx_{1,2}^2} = \frac{m_{1,2}^2 d^2}{M^2 dR^2} \pm 2 \frac{m_{1,2} d}{M dR} \frac{d}{dr} + \frac{d^2}{dr^2}
\]
\[
\frac{\hbar^2}{2m_1} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m_2} \frac{d^2}{dx_2^2} = -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} - \frac{\hbar^2}{2 \mu} \frac{d^2}{dr^2}.
\]

Hence, we get,
\[
-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} \Theta(R) = (E_{tot} - E) \Theta(R), \quad \left[ -\frac{\hbar^2}{2 \mu} \frac{d^2}{dr^2} + \frac{\mu}{2} \omega_{ho}^2 \hat{r}^2 \right] \phi(r) = E \phi(r).
\]

Now, we analyze the kick operator $e^{ik\hat{x}_1}$ with $\hat{x}_1 = \hat{R} - \frac{m_2}{M} \hat{\mathbf{r}}$. We find that, because of $[\hat{R}, \hat{r}] = 0$,
\[
e^{ik\hat{x}_1} = e^{ik\hat{R}} e^{-ik \frac{m_2}{M} \hat{\mathbf{r}}}.
\]

This means that the kick operator simultaneously acts on both: the center-of-mass receives a recoil accelerating it by an amount $p_{cm} = \hbar \eta$, and the vibrational relative motion receives a kick of an amount $p_{r} = \hbar \omega_{ho} M$ following the dynamics described in Sec. 4.5.2.

Obviously, the total system conserves momentum, which is imparted to the center-of-mass motion. Whether the kick also excites the relative motion depends on mass ratio. In the limit $m_1 \ll m_2$ we find $p_{r} = \hbar k$, while in the limit $m_1 \gg m_2$ we get $p_{r} \to 0$. In terms of the Lamb-Dicke parameter, we find,
\[
\eta = \frac{p_{r} \omega_{ho}}{\hbar} = \frac{km_2}{M \sqrt{2}} \sqrt{\frac{\hbar}{\mu \omega_{ho}}} = \frac{km_2}{m_1 + m_2} \sqrt{\frac{\hbar}{2 \omega_{ho}}} \left( \frac{1}{m_1} + \frac{1}{m_2} \right).
\]

Hence, in the limit $m_1 \ll m_2$ we expect a much larger Lamb-Dicke parameter than for $m_1 \gg m_2$.

### 4.5.3 Shaking a harmonic oscillator

As we mentioned below the formulae (4.108), the transformation in momentum space is not a realistic concept for a kick. In practice, a kick will always be the results of a collision, which is understood here as a scattering of a free (massive or massless) particle at our harmonically trapped particle. And the scattering process will take a finite amount of time, e.g. the duration of a radiative $\pi$-pulse required to excite an atomic transition.

As a first example let us consider a harmonic oscillator subject to periodic forcing,

\[
\hat{H}(t) = \hat{H}^{(0)} + \hat{H}^{(1)} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega_{ho}^2 \hat{x}^2 + \frac{\hbar \Omega}{2} (\hat{a} e^{i \nu t} + \hat{a}^\dagger e^{-i \nu t}),
\]  
\[
(4.125)
\]
and study its time evolution,

$$|\psi(t)\rangle = e^{-i\hat{H}t} \sum_n a_n |n\rangle \xrightarrow{a_n = \delta_{n,0}} e^{-i\hat{H}t} |0\rangle , \quad (4.126)$$

when the oscillator is initially in the state $|0\rangle$. We rewrite the time evolution propagator as,

$$e^{-i\hat{H}t} = e^{i\omega_{ho}t(\hat{n}+1/2)-(i\Omega t/2)(\hat{a}e^{i\nu t} + \hat{a}^\dagger e^{-i\nu t})} . \quad (4.127)$$

To simplify the propagator, we first have a closer look at the terms $\hat{a}e^{i\omega_{ho}t}$ and $\hat{a}^\dagger e^{-i\omega_{ho}t}$, which we evaluate through their action on the complete system of eigenfunctions,

$$e^{-i\hat{H}t} |\hat{a}e^{i\nu t}|n\rangle = e^{i\omega_{ho}t(\hat{n}+1/2)} e^{i\Delta t} e^{i\nu t} |n\rangle , \quad (4.128)$$

$$e^{-i\hat{H}t} |\hat{a}^\dagger e^{-i\nu t}|n\rangle = e^{i\omega_{ho}t(\hat{n}+1/2)} e^{-i\Delta t} e^{-i\nu t} |n\rangle . \quad (4.129)$$

Substituting these expression into the propagator (4.127) we get,

$$e^{-i\hat{H}t} = e^{-i\omega_{ho}t(\hat{n}+1/2)} e^{i\Delta t} e^{i\nu t} e^{i\omega_{ho}t(\hat{n}+1/2)} . \quad (4.130)$$

Now, making use of the relationship,

$$e^{-\hat{A}} \hat{B} e^{\hat{A}} = \sum_n \frac{e^{-\hat{A}} \hat{B} e^{\hat{A}} n}{n!} = \sum_n \frac{(e^{-\hat{A}} \hat{B} e^{\hat{A}})^n}{n!} = e^{-\hat{A}} \hat{B} e^{\hat{A}} , \quad (4.131)$$

which is easy to show by expansion of $e^{\hat{B}}$, we find $^6$,

$$e^{-i\hat{H}t} = e^{-i\omega_{ho}t(\hat{n}+1/2)} e^{-i\omega_{ho}t(\hat{n}+1/2)} e^{i\Delta t} e^{i\nu t} e^{-i\omega_{ho}t(\hat{n}+1/2)} . \quad (4.132)$$

In particular, for $\Delta = 0$,

$$\langle n | e^{-i\hat{H}t} |0\rangle = e^{-ni\omega_{ho}t} \langle n | e^{-i\omega_{ho}t(\hat{n}+1/2)} e^{i\nu t} e^{-i\omega_{ho}t(\hat{n}+1/2)} |0\rangle . \quad (4.133)$$

The dynamics is illustrated in Fig. 4.15. In Exc. 4.5.6.6 we will study how to generalize the problem to non-resonant excitation.

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$^6$Note, that this formula can not be simplified using the Baker-Hausdorff formula, because $[\hat{n}, [\hat{n}, \hat{a}]] \neq 0.$
4.5. **SUPERPOSITION STATES OF A HARMONIC OSCILLATOR**

![Figure 4.15: (code) (a) Populations of the vibrational states after a given interaction time. (b) Time evolution of the lowest populations.]

4.5.4 **Forcing a harmonic oscillator**

The transfer of momentum is the result of a (generally) constant force applied for a certain amount of time,

\[
hk = \int_{-\infty}^{\infty} mg \Theta_{[0, \Delta t]}(t) \, dt ,
\]

where \( g \) denotes the acceleration. That is, we expect that a harmonic oscillator,

\[
\hat{H}(t) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega_{ho}^2 x^2 - mg \hat{x} \Theta_{[0, \Delta t]}(t),
\]

forced for a period of time \( \Delta t \) should have suffered a kick.

4.5.4.1 **Displaced harmonic oscillator**

To begin with, we will derive the dynamics of a harmonic oscillator suddenly exposed to a homogeneous constant force \( F(t) = mg \Theta_{[0, \infty]}(t) \). It is easy to see, that the perturbed Hamiltonian can be cast into the form

\[
\hat{H}^{(1)}(t) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega_{ho}^2 \left( \hat{x} - \frac{g}{\omega_{ho}^2} \right)^2 - \frac{mg^2}{2\omega_{ho}^2},
\]

where the last constant term plays no role in the dynamics. Knowing the eigenvalues and -states of the unperturbed Hamiltonian, the obvious solution of the perturbed eigenvalue problem is,

\[
\hat{H}^{(1)}|\psi_n^{(1)}\rangle = E_n^{(1)}|\psi_n^{(1)}\rangle
\]

with 

\[
E_n^{(1)} = E_n - \frac{mg^2}{2\omega_{ho}^2}
\]

and 

\[
\langle x | \psi_n^{(1)}(x) = \psi_n(x - \frac{g}{\omega_{ho}^2}) = \langle x | n \rangle.
\]

\[\text{Note, that the transition from (4.135) to (4.137) can also be obtained by a redefinition of the field operators: } \hat{b} \equiv \hat{a} - \frac{mg_{ho}}{\hbar\omega_{ho}\sqrt{2}}, \text{ since,}
\]

\[
\hat{H} = \hbar\omega_{ho}(\hat{a}^\dagger \hat{a} + \frac{1}{2}) - \frac{mg_{ho}}{\sqrt{2}} (\hat{a} + \hat{a}^\dagger) = \hbar\omega_{ho}(\hat{b}^\dagger \hat{b} + \frac{1}{2}) - \frac{mg^2}{2\omega_{ho}^2}.
\]
Using the properties (2.167) and (2.169) we may write,
\[ \langle x - \frac{g}{\omega_{ho}} | n \rangle = \langle x | U^\dagger (\frac{g}{\omega_{ho}}) | n \rangle = \langle x | e^{-(i/h)(g/\omega_{ho})\hat{p}} | n \rangle , \] (4.138)
and using the representation (4.67) of the momentum operator by the field operators and introducing the abbreviation \( \beta \equiv \frac{g}{\omega_{ho} a_{ho} \sqrt{2}} \) we can rewrite,
\[ \langle x - \frac{g}{\omega_{ho}} | n \rangle = e^{-\beta (\hat{a} - \hat{a}^\dagger)} (x | n \rangle . \] (4.139)

The temporal evolution is given by the time-dependent Schrödinger equation. Since the jump is finite, the solution must be well behaved at time \( t = 0 \),
\[ \langle x | \psi_n^{(1)} (t) \rangle = \langle x | e^{-(i/h)\hat{H}^{(1)} t} | \psi_n^{(1)} (0) \rangle \]
\[ = \langle x | e^{-(i/h)\hat{H}^{(1)} t} e^{-\beta (\hat{a} - \hat{a}^\dagger)} | n \rangle \]
\[ = \langle x | e^{-(i/h)\hat{H}^{(1)} t} e^{-\beta (\hat{a} - \hat{a}^\dagger)} e^{(i/h)\hat{H}^{(1)} t} e^{-\beta (\hat{a} - \hat{a}^\dagger)} | n \rangle . \] (4.140)

To simplify the first three exponential functions, we use the relationship (4.128) and write the temporal solution,
\[ \psi_n^{(1)} (x, t) = e^{-\beta (\hat{a} e^{i\omega_{ho} t} - \hat{a}^\dagger} e^{-(i/h)\hat{H} t} \psi_n (x) \]
\[ = e^{-\beta (\hat{a} - \hat{a}^\dagger)} \cos \omega_{ho} t - i \beta (\hat{a} + \hat{a}^\dagger) \sin \omega_{ho} t e^{-(i/h)E_n^{(0)} t} \psi_n (x) . \] (4.141)

Using Glauber’s formula (4.92) we find,
\[ \psi_n^{(1)} (x, t) = e^{-i\beta (\hat{a} + \hat{a}^\dagger)} \sin \omega_{ho} t e^{-\beta (\hat{a} - \hat{a}^\dagger)} \cos \omega_{ho} t e^{i\beta^2 \sin \omega_{ho} t \cos \omega_{ho} t} e^{-(i/h)E_n^{(0)} t} \psi_n (x) \]
\[ = e^{-i(mg/\omega_{ho}) \tilde{\omega} \sin \omega_{ho} t} e^{-(i/h)(g/\omega_{ho}) \hat{p}} e^{i\beta^2 \sin \omega_{ho} t \cos \omega_{ho} t} e^{-(i/h)E_n^{(0)} t} \psi_n (x) \]
\[ = e^{-i\beta (\hat{a} + \hat{a}^\dagger)} \sin \omega_{ho} t e^{i\beta^2 \sin \omega_{ho} t \cos \omega_{ho} t} e^{-(i/h)E_n^{(0)} t} \psi_n (x - \frac{g}{\omega_{ho}} \cos \omega_{ho} t) . \] (4.142)

Finally,
\[ |\psi_n^{(1)} (x, t) |^2 = |\psi_n (x - \tilde{x}(t)) |^2 \text{ where } \tilde{x}(t) \equiv \frac{\frac{g}{\omega_{ho}} \cos \omega_{ho} t} . \] (4.143)

This means that the spatial distribution of \( \psi_n^{(1)} \) around \( \tilde{x}(t) \) is the same as of \( \psi_n \) around \( \tilde{x} = 0 \). The entire distribution oscillates without deformation. The momentum distribution follows from the Fourier transform,
\[ \phi_n^{(1)} (p, t) = \frac{1}{\sqrt{2\pi \hbar}} \int dx e^{-(i/h)px} \psi_n^{(1)} (x, t) \]
\[ = \frac{1}{\sqrt{2\pi \hbar}} \int du e^{-(i/h)pu} e^{-(i/h)um\omega_{ho} \frac{g}{\omega_{ho}} \sin \omega_{ho} t} e^{i\gamma (p, t)} \psi_n \]
\[ = e^{i\gamma (p, t)} \phi_n (p + m\omega_{ho} \frac{\frac{g}{\omega_{ho}} \sin \omega_{ho} t} , \]

where the abbreviation \( \gamma = \gamma^* \) contains all unitary transformations of (4.142), that do not depend on \( x \). We obtain,
\[ |\phi_n^{(1)} (p, t) |^2 = |\phi_n (p - \tilde{p}(t)) |^2 \text{ where } \tilde{p}(t) \equiv \frac{-m}{\omega_{ho} \sin \omega_{ho} t} \] . (4.145)
4.5.4.2 Discussion of the kick dynamics

For the acceleration of the harmonic oscillator to resemble a 'kick', the time during which the perturbation is active must be much smaller than a trap oscillation period, \( \omega_{ho} \Delta t \ll 1 \). In this case, we may expand the oscillatory motion (4.143) and (4.145),

\[
\bar{x} = \frac{g}{\omega_{ho}^2} \quad \text{and} \quad \bar{p} = -mg\Delta t \equiv -\hbar k ,
\]

which is consistent with the initial request (4.134). It is also clear that, for a given force \( mg \), the maximum momentum that can be transmitted is limited, \( \hbar k < mg/\omega_{ho} \).

As long as the kick-approximation \( \omega_{ho} \Delta t \ll 1 \) holds, we may simply describe the dynamics during the application of the force, via a time-dependent kick operator,

\[
e^{i\Delta t \hat{k}} = D(\alpha(t)) ,
\]

where the acquired momentum increases linearly with time according to \( k(t) = k_{\text{max}}(\min(t, \Delta t), 0) \). I.e. the populations of the vibrational states evolve like (4.114) into a coherent state with increasing amplitude \( |\alpha(t)|^2 \). At the end of the kick, on a much slower time-scale \( \omega_{ho}^{-1} \), the wavefunctions will start to oscillate all in phase, according to (4.143).

The time-dependence of the states \( |\alpha(t)\rangle \), as shown in Exc. 4.5.6.7 is given by \(^8\)

\[
|\alpha(t)\rangle = e^{-(i/\hbar)\hat{H}t}|\alpha(0)\rangle = \sum_n e^{-(i/\hbar)E_n t} e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} |n\rangle
\]

\[
= e^{-i\omega_{ho}t/2} \sum_n e^{-|\alpha|^2/2} \frac{(\alpha e^{-i\omega_{ho}t})^n}{\sqrt{n!}} |n\rangle = |\alpha(0)e^{-i\omega_{ho}t}\rangle .
\]

With (4.128) we find,

\[
\hat{x}(t) = e^{-(i/\hbar)\hat{H}t}\hat{x}(0)e^{(i/\hbar)\hat{H}t} = \hat{x}(0) \cos\omega_{ho}t + \frac{\hat{p}(0)}{m\omega_{ho}} \sin\omega_{ho}t \quad \text{and}
\]

\[
\hat{p}(t) = e^{-(i/\hbar)\hat{H}t}\hat{p}(0)e^{(i/\hbar)\hat{H}t} = m\omega_{ho}\hat{x}(0) \sin\omega_{ho}t + \hat{p}(0) \cos\omega_{ho}t ,
\]

or with (4.148),

\[
\langle\alpha(t)|\hat{x}|\alpha(t)\rangle = \langle\alpha(0)|\hat{x}|\alpha(0)\rangle \cos\omega_{ho}t + \frac{1}{m\omega_{ho}} \langle\alpha(0)|\hat{p}|\alpha(0)\rangle \sin\omega_{ho}t
\]

\[
\langle\alpha(t)|\hat{p}|\alpha(t)\rangle = m\omega_{ho}\langle\alpha(0)|\hat{x}|\alpha(0)\rangle \sin\omega_{ho}t + \langle\alpha(0)|\hat{p}|\alpha(0)\rangle \cos\omega_{ho}t .
\]

We note, that the position and momentum wavefunctions \( \langle x|n\rangle \) and \( \langle p|n\rangle \) of the excited vibrational states are complicated Hermite polynomials, but we don’t have to write them down explicitly to get to the last result.

The results are that the motion of the momentum-shifted oscillator written in the original basis of the unshifted oscillator is a harmonic oscillation,

\[
\langle x(t)|n\rangle = \psi_n(x - \frac{k}{m\omega_{ho}} \sin\omega_{ho}t) \quad \text{and} \quad \langle p(t)|n\rangle = \phi_n(p - \hbar k \cos\omega_{ho}t) .
\]

We will derive some further properties in 4.5.6.8.

\(^8\) Be careful: \( D(\alpha) \) is only a displacement operator for imaginary \( \alpha \).
4.5.4.3 Simulation of the displacement of a harmonic oscillator

The Hamiltonian of a harmonic oscillator subject to an external force can be cast into the form,

\[
\hat{H}(t) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m}{2} \omega_{ho}^2 x^2 + mgx = \hbar \omega_{ho} (\hat{a}^\dagger \hat{a} + \frac{1}{2}) + mg \sqrt{\frac{\hbar}{2}} (\hat{a} + \hat{a}^\dagger)
\]

\[
= \begin{pmatrix}
\ddots & \ddots & \ddots & \ddots & \cdots \\
\ddots & (n - \frac{1}{2}) \hbar \omega_{ho} & mg \frac{\hbar \omega_{ho}}{\sqrt{2}} \sqrt{n} & \ddots & \\
g(\sqrt{\frac{\hbar}{2}} \sqrt{n} & (n + \frac{1}{2}) \hbar \omega_{ho} & \ddots & \ddots \end{pmatrix}.
\]

(4.152)

The temporal evolution of the state is given by,

\[
|\psi(t)\rangle = e^{-(i/\hbar)\hat{H}t} |\psi(0)\rangle = e^{-(i/\hbar)\hat{H}t} \sum_n a_n |n\rangle \xrightarrow{a_n = \delta_{n,0}} e^{-(i/\hbar)\hat{H}t} |0\rangle,
\]

(4.153)

when the oscillator is initially in the state $|0\rangle$. Note, that without perturbation, $|\psi(t)\rangle = \sum_n e^{-i\omega_{ho}(n+1/2)t} a_n |n\rangle$.

Various quantities now are interesting to plot as a function of time. Firstly, we calculate the populations $|\langle n|\psi(t)\rangle|^2$ of the various states and the total energy from,

\[
\langle n|\psi(t)\rangle = \langle n|e^{-(i/\hbar)\hat{H}t} \sum_m a_m |m\rangle = \langle n|e^{-(i/\hbar)\hat{H}t}\sum_m a_m |m\rangle.
\]

(4.154)

Secondly, we get for the temporal evolution of the spatial wavefunction,

\[
\langle x|\psi(t)\rangle = \sum_n \langle x|n\rangle \langle n|\psi(t)\rangle = \sum_n \langle x|n\rangle \langle n|e^{-(i/\hbar)\hat{H}t}\sum_m a_m |m\rangle,
\]

(4.155)

where $|\langle x|n\rangle |\psi(t)\rangle|^2$ is the spatial representation of the wavefunction of the $n$-th eigenstate derived in (4.78),

\[
\langle x|n\rangle = e^{-x^2/2a_{ho}^2} H_n(x/a_{ho}) \sqrt{a_{ho} \sqrt{\pi} 2^n n!},
\]

(4.156)

weighed with instantaneous population (4.154) of this state. We thus obtain for the total wavefunction,

\[
\langle x|\psi(t)\rangle = \sum_n \frac{e^{-x^2/2a_{ho}^2} H_n(x/a_{ho})}{\sqrt{a_{ho} \sqrt{\pi} 2^n n!}} \langle n|e^{-(i/\hbar)\hat{H}t}|n\rangle.
\]

(4.157)
Furthermore, we may calculate the expectation values of the position and the momentum of the harmonic oscillator from the total wavefunction \(|\psi(t)\rangle\),

\[
\langle \psi(t)|\hat{x}|\psi(t)\rangle = \int \langle \psi(t)|\hat{x}|x\rangle \langle x|\psi(t)\rangle dx = \int x|\psi(x,t)|^2 dx
\]

(4.158)

\[
\langle \psi(t)|\hat{p}|\psi(t)\rangle = \int \langle \psi(t)|\hat{p}|p\rangle \langle p|\psi(t)\rangle dp = \int p|\phi(p,t)|^2 dx ,
\]

where \(\phi(p,t)\) is the Fourier transform of \(|\psi(x,t)\rangle\) according to (2.98). In practice, it is however easier to calculate them from the populations \(|n|\psi(t)\rangle\),

\[
\langle \psi(t)|\hat{x}|\psi(t)\rangle = \frac{a_n}{\sqrt{2}} \sum_n \langle \psi(t)|\hat{a} + \hat{a}^\dagger|n\rangle \langle n|\psi(t)\rangle
\]

\[
\langle \psi(t)|\hat{p}|\psi(t)\rangle = \frac{\hbar}{\sqrt{2}} \sum_n \langle \psi(t)|\hat{a} - \hat{a}^\dagger|n\rangle \langle n|\psi(t)\rangle
\]

(4.159)

4.5.5 Quantization of the electromagnetic field

The quantization of light (also called second quantization) triggered by Max Planck’s treatments of black-body radiation in 1905 resolved the problem of the ultraviolet divergence and explained the photoelectric effect. Twenty years later the quantization of the atom by Niels Bohr (also called first quantization) explained the internal structure of the atom.

The operator for the electric field of a laser mode is given by,

\[
\hat{E} = iE_m[\hat{a} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t} - \hat{a}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r} + i\omega t}],
\]

(4.160)

where \(E_m = \sqrt{\hbar \omega/2\varepsilon_0 V}\) and \(V\) is the mode volume. Exc. 4.5.6.9 asks to calculate the eigenvalues \(\langle \hat{E} \rangle\) and \(\Delta \hat{E}\).

It is sometimes convenient to represent the light field by its quadratures. With the definition \(\hat{a} \equiv \hat{x}_1 + i\hat{x}_2\), where \(\hat{x}_1, \hat{x}_2\) are non-commuting observables ([\(\hat{x}_1, \hat{x}_2\] = \(i/2\)), we can write the field as,

\[
\hat{E} = -2E_m[\hat{x}_1 \sin(\mathbf{k}\cdot\mathbf{r} - \omega t) + \hat{x}_2 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t)].
\]

(4.161)

Heisenberg’s uncertainty relations requires,

\[
\Delta x_1 \Delta x_2 \geq \frac{1}{4} .
\]

(4.162)

For coherent states, \(\Delta x_1 = \Delta x_2 = \frac{1}{2}\).

4.5.6 Exercises

4.5.6.1 Ex: Sum of displacements operators

Prove formula (4.101).
4.5.6.2 Ex: Harmonic oscillator and coherent states

a. Verify whether the Glauber states of a harmonic oscillator are orthogonal.
b. Show that $\langle |\alpha| |\hat{n}| |\alpha\rangle = |\alpha|^2$, $\langle |\alpha| |\hat{n}^2| |\alpha\rangle = |\alpha|^4 + |\alpha|^2$, and $\Delta \hat{n} = |\alpha|$.
c. What is the population of the state $|n\rangle$ of a harmonic oscillator in a Glauber state?

4.5.6.3 Ex: Annihilation operator acting on Fock and Glauber states

Explain why the annihilation operator $\hat{a}$ does not reduce the photon number of a Glauber state in contrast to a Fock state.

4.5.6.4 Ex: Schrödinger cat state

Calculate the probability of finding $n$ photons in Schrödinger’s cat state $|\psi\rangle = 2^{-1/2}(|\alpha\rangle \pm |\alpha\rangle)$.

4.5.6.5 Ex: Transition elements for arbitrary Lamb-Dicke parameters

Calculate the general expression for $\langle m| e^{ik\hat{x}} |n\rangle$ with the abbreviation $\alpha \equiv i k a \omega / \sqrt{2}$ for arbitrary values of the Lamb-Dicke parameter using the following results of the discussion of the displacement operator $D(\alpha) = e^{\alpha \hat{a}^\dagger - \alpha^* \hat{a}} = e^{-|\alpha|^2/2} e^{\alpha \hat{a}^\dagger} e^{-\alpha^* \hat{a}}$ for Glauber states. The relations

$$|n\rangle = \left( \hat{a}^\dagger \right)^n |0\rangle \quad \text{and} \quad \langle n| \alpha \rangle = e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}}$$

describe the relation between Fock and Glauber states. Furthermore,

$$D(-\alpha) = D^\dagger(\alpha) \quad \text{and} \quad D^\dagger(\alpha) \hat{a}^\dagger D(\alpha) = \hat{a}^\dagger + \alpha^* .$$

4.5.6.6 Ex: Resonantly excited harmonic oscillator

Write down the Hamiltonian of a harmonic oscillator subject to an oscillating homogeneous force, and numerically simulate the evolution of the vibrational states starting from the ground state.

4.5.6.7 Ex: Shifted harmonic oscillator

Consider a HO of mass $m$, angular frequency $\omega$, and electric charge $q$ immersed in a uniform electric field oriented parallel to the axis $\hat{e}_x$ of the oscillator.

a. Get the energies of the stationary states of the HO and show how to get the corresponding eigenstates.
b. Calculate the expectation values $\langle x \rangle$ and $\langle p \rangle$ for the displaced oscillator now using Glauber states (or arbitrary superpositions of states) and taking advantage of the formulas (4.67), (4.100), and (2.165).
c. Now, the electric field is suddenly turned off. Calculate the time evolution of the oscillator.
4.5.6.8  Ex: Spatial wavefunction of a particle in a coherent state

a. Derive the following relations for the harmonic oscillator having received a recoil momentum,

\[ \langle \psi_n^{(1)} | \hat{x} | \psi_n^{(1)} \rangle = 0 \quad \text{and} \quad \langle \psi_n^{(1)} | \hat{p} | \psi_n^{(1)} \rangle = \hbar k . \]

b. Calculate the temporal evolution of the oscillator after having received the recoil via,

\[ \langle x | e^{-i \hat{H} t / \hbar} e^{-i k \hat{x}} | n \rangle . \]

c. Calculate the spatial wavefunction of a particle in a coherent state

\[ \langle x | \alpha \rangle = \sum_n e^{-|\alpha|^2 / 2} \frac{n^n}{\sqrt{n!}} \langle x | n \rangle . \]

4.5.6.9  Ex: Glauber state

Calculate \( \langle \hat{E} \rangle \) and \( \Delta \hat{E} \).
Figure 4.16: (code) Evolution of a harmonic oscillator subject to time-dependent forcing. (a) Histogram of the final population of the vibrational states. (b) Time evolution of the vibrational state populations. (c) Time evolution of the applied force (black) and of the expectation values of position (red) and momentum (brown). (d) Spatial wavefunctions $|\langle n | \psi(x) \rangle |^2$ (Hermite polynomials) (blue) of the lowest vibrational states of the harmonic potential (black). The green Gaussian is the coherent sum of the spatial wavefunctions $\sum_n |\langle n | \psi(x) \rangle |^2$, and the cyan Gaussian the coherent sum of the momentum wavefunctions $\sum_n |\langle n | \psi(p) \rangle |^2$. The horizontal yellow line is the total energy of the system. You may also run a movie of the simulation clicking on (watch movie)! Furthermore, a presentation about the topic of recoil on trapped atoms is available at (watch talk)!

Figure 4.17: Illustration of the Glauber states. Here, $\hat{x}_1 \equiv \hat{a} + \hat{a}^\dagger$ and $\hat{x}_2 \equiv i(\hat{a} - \hat{a}^\dagger)$. 
Chapter 5

Approximation methods

Virtually every problem going beyond the potential well, the harmonic oscillator, or the hydrogen atom without spin and external fields is impossible to solve analytically. In this chapter we will talk about techniques to solve approximately problems in more realistic situations. There are a number of methods of which we will discuss the only following: 1. The stationary or time-dependent perturbation method is useful for evaluating small perturbations of the system, for example, caused by external electric or magnetic fields; 2. the variational method, which serves to find and improve trial wavefunctions, the initial shapes of which are generally motivated by the symmetries of the system; 3. the semi-classical WKB method; 4. and finally the method of self-consistent fields, which is an iterative method of solving the Schrödinger equation.

5.1 Stationary perturbations

5.1.1 Time-independent perturbation theory

We first introduce time-independent perturbation theory (TIPT) for multilevel systems. We separate the Hamiltonian into an unperturbed part,

\[ \hat{H}^{(0)} |\psi^{(0)}\rangle = E^{(0)} |\psi^{(0)}\rangle, \]

and perturbations, which are proportional to a small parameters \( \lambda \),

\[ \hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + .. . \]

The perturbed wavefunctions are,

\[ |\psi\rangle = |\psi^{(0)}\rangle + \lambda |\psi^{(1)}\rangle + \lambda^2 |\psi^{(2)}\rangle + .. . \]

and the energies

\[ E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + .. . \]

The contributions \( \propto \lambda^n \) are the corrections of order \( n \). The equation we need to solve now is,

\[ \hat{H} |\psi\rangle = E |\psi\rangle. \]
By inserting all the expansions above and segregating all orders of $\lambda^k$, we find the following system of equations,

\begin{align*}
\hat{H}^{(0)}|\psi^{(0)}\rangle &= E^{(0)}|\psi^{(0)}\rangle \\
(\hat{H}^{(0)} - E^{(0)})|\psi^{(1)}\rangle &= (E^{(1)} - \hat{H}^{(1)})|\psi^{(0)}\rangle \\
(\hat{H}^{(0)} - E^{(0)})|\psi^{(2)}\rangle &= (E^{(2)} - \hat{H}^{(2)})|\psi^{(0)}\rangle + (E^{(1)} - \hat{H}^{(1)})|\psi^{(1)}\rangle \\
&\ldots
\end{align*}

5.1.1.1 First order energy correction

We now consider eigenstates $|\psi^{(1)}_n\rangle$ of the perturbed system and expand the first-order correction of the wavefunction in a linear combination of unperturbed eigenvectors $|\psi^{(0)}_n\rangle \equiv |n\rangle$,

$$
|\psi^{(1)}_n\rangle = \sum_m |m\rangle \langle m| \psi^{(1)}_n\rangle .
$$

(5.7)

We insert this expansion into the second equation (5.6) and multiply with $\langle n|$,

$$
\langle n|(\hat{H}^{(0)} - E^{(0)}_n) \sum_m |m\rangle \langle m| \psi^{(1)}_n\rangle = 0 = \langle n|E^{(1)}_n - \hat{H}^{(1)}|n\rangle .
$$

(5.8)

We obtain for the first order correction of the energy of unperturbed states,

$$
E^{(1)}_n = \langle n|\hat{H}^{(1)}|n\rangle .
$$

(5.9)

As a first example we will calculate in Exc. 5.1.3.1 the first order correction for the energy of a slightly deformed one-dimensional box potential.

5.1.1.2 First order correction for the wavefunction

Now let us have a look at the first-order correction for the wavefunction again considering the second equation (5.6),

$$
\langle m|\hat{H}^{(0)} - E^{(0)}_n|\psi^{(1)}_n\rangle = \langle m|E^{(1)}_n - \hat{H}^{(1)}|n\rangle .
$$

(5.10)

When $n = m$, the left side of this equation disappears. Therefore, $E^{(1)}_n - \langle n|\hat{H}^{(1)}|n\rangle = 0$, and we can restrict to the terms $n \neq m$ discarding the terms in $E^{(1)}_n$,

$$
\langle m|\psi^{(1)}_n\rangle = \frac{E^{(1)}_n - \langle m|\hat{H}^{(1)}|n\rangle}{E^{(0)}_n - E^{(0)}_m} = \frac{\langle m|\hat{H}^{(1)}|n\rangle}{E^{(0)}_n - E^{(0)}_m} .
$$

(5.11)

We obtain for the first-order correction for the energy of the states,

$$
|\psi^{(1)}_n\rangle = \sum_m |m\rangle \langle m| \psi^{(1)}_n\rangle = \sum_{m \neq n} |m\rangle \frac{\langle m|\hat{H}^{(1)}|n\rangle}{E^{(0)}_n - E^{(0)}_m} .
$$

(5.12)

This procedure simulates the distortion of the state by blending it with other states. The perturbation induces virtual transitions to other states. The perturbation is large when the blended levels are close.
5.1. STATIONARY PERTURBATIONS

See Exc. 5.1.3.2. In Exc. 5.1.3.3 we calculate the first order correction due to the finite extension of the hydrogen nucleus. In Exc. 5.1.3.4 we treat the coupling of the energy levels of a two-level system as a first order perturbation, and compare the result with the exact solution. The Stark effect for an electron confined in a box can be discussed (see Exc. 5.1.3.5) in first order TIPT.

5.1.1.3 Second order correction for the energy

To calculate the second order correction for the energy we expand the second order correction,

\[ |\psi^{(2)}_n\rangle = \sum_m |m\rangle \langle m| \psi^{(2)}_n\rangle, \]  
\[ \tag{5.13} \]

import it into the third equation (5.6) and multiply with \( \langle n| \),

\[ \langle n| (\hat{H}^{(0)} - E^{(0)}_n) \sum_m |m\rangle \langle m| \psi^{(2)}_n\rangle = \langle n| (E^{(2)}_n - \hat{H}^{(2)})|n\rangle + \langle n| (E^{(1)}_n - \hat{H}^{(1)}) \sum_m |m\rangle \langle m| \psi^{(1)}_n\rangle. \]  
\[ \tag{5.14} \]

Now,

\[ \sum_m \langle m| \psi^{(2)}_n\rangle (E^{(0)}_n - E^{(0)}_m) \delta_{nm} = 0 = E^{(2)}_n - \langle n| \hat{H}^{(2)}|n\rangle + \sum_m \langle m| \psi^{(1)}_n\rangle \left( E^{(1)}_n \delta_{nm} - \langle n| \hat{H}^{(1)}|m\rangle \right). \]  
\[ \tag{5.15} \]

The left-hand side of this equation disappears. Also, on the right-hand side, for \( n \neq m \), the term \( E^{(1)}_n \delta_{nm} \) disappears, and for \( n = m \) the whole parenthesis disappears. Therefore, we can discard the term \( E^{(1)}_n \) and restrict the sum to terms with \( n \neq m \).

Inserting the coefficients \( \langle m| \psi^{(1)}_n\rangle \) calculated in (5.11), we finally obtain,

\[ E^{(2)}_n = \langle n| \hat{H}^{(2)}|n\rangle + \sum_{m \neq n} \frac{\langle n| \hat{H}^{(1)}|m\rangle \langle m| \hat{H}^{(1)}|n\rangle}{E^{(0)}_n - E^{(0)}_m}. \]  
\[ \tag{5.16} \]

The first term is similar to the first order correction; the eigenvalue of the second order perturbation calculated in the base of the unperturbed states. The second term describes the shift of the energies through possible temporary transitions to other states.

In Exc. 5.1.3.6 we treat a system of three coupled levels up to the second perturbative order. The Stark effect discussed in Exc. 5.1.3.7 needs the TIPT calculation up to the second order.

5.1.2 TIPT with degenerate states

Exact calculations show that the effect of a perturbation is larger – but finite – for degenerate states. On the other hand, from the above expressions for the corrections of both energies and wavefunctions, we would infer that these corrections can become very large for small perturbations or even diverge.

Fortunately, the fact that every linear combination of degenerate wavefunctions is an eigenfunction of the Hamiltonian as well gives us the freedom to choose the combination, which is most similar to the final form of the perturbed wavefunctions.
For example, considering a perturbation by a magnetic field it may be advantageous to expand the spherical functions $Y_{lm}$ on a basis of cylindrical coordinates. We will see in the following that we can solve both problems, the selection of the initial combination and the prevention of divergent denominators at once, without explicitly specifying the expansion.

We consider eigenstates $|n, \nu\rangle$ with the energy $E_{n}^{(0)}$ being $r$ times degenerate with respect to the quantum number $\nu$, where $\nu = 1, \ldots, r$. All states satisfy

$$\hat{H}^{(0)}|n, \nu\rangle = E_{n}^{(0)}|n, \nu\rangle . \quad (5.17)$$

We construct linear combinations that most resemble the perturbed states

$$|\psi_{n\mu}^{(0)}\rangle = \sum_{\nu=1}^{r} c_{\mu\nu} |n, \nu\rangle . \quad (5.18)$$

When the perturbation $\hat{H}^{(1)}$ is applied, we assume that the state $|\psi_{n\mu}^{(0)}\rangle$ is distorted towards the similar state $|\psi_{n\mu}\rangle$, and the energy changes from $E_{n}^{(0)}$ to $E_{n\mu}$. We now need the index $\mu$ to label the energy, since the degeneracy can be removed by the perturbation. As before, we write now,

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + .. \quad (5.19)$$

$$|\psi_{n\mu}\rangle = |\psi_{n\mu}^{(0)}\rangle + \lambda |\psi_{n\mu}^{(1)}\rangle + ..$$

$$E_{n\mu} = E_{n}^{(0)} + \lambda E_{n\mu}^{(1)} + .. .$$

The replacement of these expansions in $\hat{H}|\psi_{n\mu}\rangle = E_{n\mu}|\psi_{n\mu}\rangle$, and a collection of the terms in $\lambda$ up to first order gives,

$$\hat{H}^{(0)}|\psi_{n\mu}^{(0)}\rangle = E_{n}^{(0)}|\psi_{n\mu}^{(0)}\rangle$$

$$\left( E_{n}^{(0)} - \hat{H}^{(0)} \right) |\psi_{n\mu}^{(1)}\rangle = \left( E_{n\mu}^{(1)} - \hat{H}^{(1)} \right) |\psi_{n\mu}^{(0)}\rangle . \quad (5.20)$$

As before, we try to express the first-order corrections for the wavefunctions through degenerate unperturbed wavefunctions $|\psi_{n\mu}^{(0)}\rangle$ and non-degenerate wavefunctions $|\psi_{m}^{(0)}\rangle$:

$$|\psi_{n\mu}^{(1)}\rangle = \sum_{\nu} b_{\mu\nu} |\psi_{n\nu}^{(0)}\rangle + \sum_{m} a_{nm} |\psi_{m}^{(0)}\rangle . \quad (5.21)$$

Inserting this into the first order equation (5.20), we obtain,

$$\sum_{\nu} b_{\mu\nu} (E_{n}^{(0)} - E_{n}^{(0)}) |\psi_{n\nu}^{(0)}\rangle + \sum_{m} a_{nm} (E_{m}^{(0)} - E_{n}^{(0)}) |\psi_{m}^{(0)}\rangle = (E_{n\mu}^{(1)} - \hat{H}^{(1)}) |\psi_{n\mu}^{(0)}\rangle . \quad (5.22)$$

The first term disappears. Inserting the expansion (5.18),

$$\sum_{m} a_{nm} (E_{m}^{(0)} - E_{n}^{(0)}) |\psi_{m}^{(0)}\rangle = (E_{n\mu}^{(1)} - \hat{H}^{(1)}) \sum_{\nu} c_{\mu\nu} |n, \nu\rangle . \quad (5.23)$$

1 Another example would be the preference for the coupled base $|(l, s)_{j}, m_{j}\rangle$ in comparison to the decoupled base $|l, m, s, m_{s}\rangle$ knowing that the degeneracy in $j$ is lifted, when there is an energy associated with interacting angular momenta and the degeneracy in $m_{j}$ is lifted, when we apply a magnetic field.

2 Note that we label all states which are not degenerate with the state under investigation $|\psi_{n\mu}^{(1)}\rangle$ with the index $m$, even if there are degeneracies between them.
and multiplying the two sides with \( \langle n, \mu \rangle \), we get zero on the left-hand side, since we can choose the non-degenerate states to be orthogonal \( \langle n, \nu \rangle_m = \delta_{m,n} \). Hence,

\[
\sum_{\nu} c_{\mu\nu} \left[ E^{(1)}_{n\mu} \langle n, \mu | n, \nu \rangle - \langle n, \mu | H^{(1)} | n, \nu \rangle \right] = 0.
\]

This secular equation (one for each \( \mu \)) represents, in fact, a set of \( r \) linear equations for the coefficients \( c_{\mu\nu} \). The condition for having non-trivial solutions is,

\[
\det \left( \langle n, \nu | H^{(1)} | n, \mu \rangle - E^{(1)}_{n\mu} \delta_{\mu,\nu} \right)_{\mu,\nu} = 0.
\]

The solution of this secular determinant yields the solicited energies \( E^{(1)}_{\mu} \). Now, the solution of the secular equation (5.24) for each energy value produces those coefficients, which represent the best linear combinations adapted to the perturbation. Unlike in previous calculations with degenerate states, here we consider linear combinations of vectors of the degenerate subspace prior to switching on the perturbation.

In practice, we apply perturbation theory only to the lowest relevant order. That is, we only calculate the second order correction if first order corrections vanish. One famous example is the quadratic Stark effect discussed in Sec. 9.3. In the case of eigenvalues, which are degenerate in the absence of perturbation, the first order will always produce a remarkable correction, as in the example of the linear Stark effect, also discussed in Sec. 9.3. For this reason, we need not discuss higher perturbation orders in the case of degenerate eigenvalues.

Example 27 (Perturbation in a system with two degenerate states): As an example, we consider the following Hamiltonian,

\[
\hat{H} = \begin{pmatrix} \Delta & \Omega \\ \Omega & \Delta \end{pmatrix}.
\]

The exact solution gives the eigenvalues and eigenvectors,

\[
E_1 = \Delta + \Omega, \quad E_2 = \Delta - \Omega, \quad |\psi_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |\psi_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}.
\]

Now we divide the Hamiltonian into an unperturbed part and a perturbation,

\[
\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \begin{pmatrix} \Delta & 0 \\ 0 & \Delta \end{pmatrix} + \begin{pmatrix} 0 & \Omega \\ \Omega & 0 \end{pmatrix}.
\]

We get in zero order,

\[
E_1^{(0)} = \Delta = E_2^{(0)}, \quad |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
\]

The application of non-degenerate perturbation theory in first order would give,

\[
\langle 1 | \hat{H}^{(1)} | 1 \rangle = 0 = \langle 2 | \hat{H}^{(1)} | 2 \rangle, \quad |\psi_1^{(1)}\rangle = |1\rangle \frac{(1|\hat{H}^{(1)}|2)}{E_1^{(0)} - E_2^{(0)}} \rightarrow \infty \rightarrow -|\psi_2^{(1)}\rangle.
\]

That is, the correction of the energy vanishes in first order, while the correction of the wavefunction diverges. Obviously, the \( |\nu\rangle \) obtained by the diagonalization
of the matrix $\hat{H}^{(0)}$ is not adapted to the calculation of the matrix elements $\hat{H}^{(1)}$. Now, applying degenerate perturbation theory, we obtain by the secular determinant,

$$0 = \det \left[ \langle \nu | \hat{H}^{(1)} | \mu \rangle - E^{(1)}_\mu \delta_{\mu, \nu} \right] = \det \begin{pmatrix} -E^{(1)}_\mu & \Omega \\ \Omega & -E^{(1)}_\mu \end{pmatrix} = (E^{(1)}_\mu)^2 - \Omega^2 ,$$

eigenvalues are $E^{(1)}_1 = \Omega$ and $E^{(1)}_2 = -\Omega$ allowing the establishment of the secular equation,

$$c_{11} \left[ E^{(1)}_1 - \langle 1 | \hat{H}^{(1)} | 1 \rangle \right] - c_{12} \langle 1 | \hat{H}^{(1)} | 2 \rangle = c_{11} [\Omega - 0] - c_{12} \Omega = 0$$

$$-c_{21} \langle 2 | \hat{H}^{(1)} | 1 \rangle + c_{22} \left[ E^{(1)}_2 - \langle 2 | \hat{H}^{(1)} | 2 \rangle \right] = -c_{21} \Omega + c_{22} [-\Omega - 0] = 0 .$$

We obtain $c_{11} = c_{12} e c_{21} = -c_{22}$ and with this,

$$|\psi^{(0)}_1\rangle = \sum_\nu c_{1\nu} |\nu\rangle = c_{11} |1\rangle + c_{12} |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} , \quad |\psi^{(0)}_2\rangle = c_{21} |1\rangle + c_{22} |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix} .$$

Thus, we can verify that the corrections for the eigenenergies,

$$E_1 = E^{(0)}_1 + \langle \psi^{(0)}_1 | \hat{H}^{(1)} | \psi^{(0)}_1 \rangle = \Delta + \Omega , \quad E_2 = E^{(0)}_2 + \langle \psi^{(0)}_2 | \hat{H}^{(1)} | \psi^{(0)}_2 \rangle = \Delta - \Omega ,$$

coincides with the exact calculation made at the beginning. The eigenfunctions $|\psi^{(0)}_1\rangle$ should have been already corrected in first order, which we verify by calculating,

$$|\psi^{(1)}_1\rangle = |\psi^{(0)}_1\rangle \frac{\langle \psi^{(0)}_1 | \hat{H}^{(1)} | \psi^{(0)}_2 \rangle}{E_1 - E_2} = 0 = |\psi^{(1)}_2\rangle .$$

In Exc. 5.1.3.8 we study a partially degenerate three-level system and the breakdown of the degeneracy due to a perturbation. And in Exc. 5.1.3.9 we will treat a perturbation in a box potential with degenerate energy levels.

### 5.1.3 Exercises

#### 5.1.3.1 Ex: One-dimensional well with a deformation in the centre

Consider a one-dimensional potential well between $-L/2$ and $L/2$ with infinitely high walls. In the center of the well is a small deformation,

$$H^{(1)} = \begin{cases} \varepsilon & \text{for } -\frac{a}{2} \leq x \leq \frac{a}{2} \\ 0 & \text{outside that region} \end{cases}$$

Calculate the correction for the eigenenergies in first order and discuss the limits $a \ll L$ and $a \to L$.

#### 5.1.3.2 Ex: Perturbation

Show that the scalar product $\langle \psi^{(0)}_n | \psi^{(1)}_n \rangle$ (from the first-order correction to the state of the 'perturbed' system with the $n$-th state of the free Hamiltonian), cancels out when we impose that the 'perturbed' state $|\psi(\lambda)\rangle$ be normalized and the the product $\langle \psi^{(0)}_n | \psi(\lambda) \rangle$ be real.\(^3\)

\(^3\)See [113], Cap XI, A-2.
5.1. STATIONARY PERTURBATIONS

5.1.3.3 Ex: Extended nucleus

The expression $V(r) = -e^2/4\pi\epsilon_0 r$ for the potential energy of an electron in the hydrogen atom implies that the nucleus (the proton) is treated as a point particle. Now suppose that, on the contrary, the charge of the proton $+e$ is evenly distributed over a sphere of radius $R = 10^{-13}$ cm.

a. Derive the modified potential $V_m$, which corresponds to this distribution of the nuclear charge.

b. Assume that the wavefunction of the hydrogen atom does not change much due to the modified potential. Calculate in lowest order in $R/a_B$ the average energetic displacement $\langle \Delta V \rangle$ for the state $(n = 1, \ell = 0, m = 0)$. How will the energy displacement be in comparison to the states $(n = 2, \ell = 0, m = 0)$ and $(n = 2, \ell = 1, m = 0)$?

c. Calculate in the same way $\langle \Delta V \rangle$ for muonic hydrogen in the ground state.

5.1.3.4 Ex: Perturbation of a 2-level system

We consider a two-level system. Without perturbation the system would have the Hamiltonian $H^{(0)}$, the eigenenergies $E^{(0)}_1$, $E^{(0)}_2$ and the eigenfunctions $\psi^{(0)}_1$, $\psi^{(0)}_2$. Now we switch on a stationary perturbation of the form $H^{(1)} = e(\langle 1 | 2 \rangle + \langle 2 | 1 \rangle)$.

a. Calculate the eigenenergies directly solving the perturbed Schrödinger equation.

b. Calculate the perturbed energies using TIPT and compare to the exact calculation of the eigenenergies.

c. Calculate the eigenstates directly solving the perturbed Schrödinger equation.

d. Calculate the perturbed states using TPIT and compare to the exact calculation of the eigenfunctions.

5.1.3.5 Ex: Stark effect for an electron in a box

Consider an electron in a one-dimensional box, that is, in a well inside the interval $x \in [0, a]$ delimited by infinite walls. When a uniform electric field $E$ is applied, also in $x$-direction, the electron experiences a force equal to $-eE$, being $-e$ the electron charge, so that the potential energy inside the box becomes $eE x$.

a. What is the energy of the ground state of the electron (in first order approximation)? We can assume that $eEa$ is much smaller than the ground state energy the electron would have in the absence of electric fields.

b. Use first-order TIPT to get an approximation for the ground state wavefunction by calculating the first term of the correction.

5.1.3.6 Ex: Perturbed 3-level system until second order TIPT

Consider the following perturbed Hamiltonian:

$$H = H_0 + H_\lambda = \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix} + \begin{pmatrix} 0 & \lambda & 0 \\ \lambda & 0 & \lambda \\ 0 & \lambda & 0 \end{pmatrix}.$$

a. Determine the perturbed eigenvalues and eigenfunctions in first order TIPT.

b. Determine the eigenvalues in second order TIPT.
5.1.3.7 Ex: Stark effect for a charge in a harmonic oscillator

Consider a charged harmonic oscillator, immersed in a uniform electric field $E$, described by the Hamiltonian $\hat{H}^{(1)} = \hat{H} + eE\hat{x}$, being $\hat{H} = \hat{p}^2/2m + m\omega^2\hat{x}^2/2$ the Hamiltonian of the free one-dimensional oscillator, and $e$ the charge of the oscillator.

a. Obtain, through TIPT, the eigenenergies (first and second order corrections). Compare the results obtained by TIPT with the analytical ones.\footnote{See [113], Complement A XI.}
b. Same thing for a perturbation of the form $\rho m\omega^2\hat{x}^2/2$.
c. Same thing for a perturbation $\sigma\hbar\omega\hat{x}^3$.

5.1.3.8 Ex: Three-level system with degeneracy

Consider the following Hamiltonian $\hat{H}^{(0)}$ and its perturbation $\hat{H}^{(1)}$

$$\hat{H}^{(0)} + \hat{H}^{(1)} = \begin{pmatrix} \Delta & 0 & 0 \\ 0 & \Delta & 0 \\ 0 & 0 & \Delta' \end{pmatrix} + \begin{pmatrix} 0 & \Omega & 0 \\ \Omega & 0 & \Omega \\ 0 & \Omega & 0 \end{pmatrix}.$$

Calculate the corrections for the eigenvalues and eigenfunctions up to first order.

5.1.3.9 Ex: Perturbation in a 3D well with degeneracy

Consider a particle confined to a three-dimensional, infinite cubic well described by the potential energy $V(x,y,z) = 0$ for $0 < x < a$, $0 < y < a$ and $0 < z < a$ and $V(x,y,z) = \infty$ outside this region. We know that the particle’s stationary states are $\Psi^{(0)}_{n_x,n_y,n_z}(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x\pi}{a}x\right) \sin\left(\frac{n_y\pi}{a}y\right) \sin\left(\frac{n_z\pi}{a}z\right)$, being $n_x$, $n_y$, $n_z$ positive integers. The associated energies are $E^{(0)}_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)$. Note that the ground state is not degenerate while the first excited state is three times degenerate.

Consider that the particle in this box is subject to a perturbation of the shape $H^{(1)} = V_0$ for $0 < x < a/2$ and $0 < y < a/2$ and $H^{(1)} = 0$ outside this region.

a. Obtain the first-order correction for the ground state energy.
b. Obtain the first-order correction for the (degenerate) energy of the first excited state, in addition to the optimal base (which follows from the linear combinations of degenerate states) which most closely approximates the perturbed states.

c. Same thing for a perturbation $\sigma\hbar\omega\hat{x}^3$.

5.1.3.10 Ex: Vanishing perturbation orders

Show that it is impossible to design a perturbation Hamiltonian of the form,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{pmatrix} + \begin{pmatrix} 0 & \Omega_{12} & \Omega_{13} \\ \Omega_{12}^* & 0 & \Omega_{23} \\ \Omega_{13}^* & \Omega_{23}^* & 0 \end{pmatrix}$$

such that the first and second order corrections vanish.
5.2 Variational method

5.2.1 The Rayleigh fraction

Let us assume that we want to calculate the ground state energy \( E_g \) of a system described by a Hamiltonian \( \hat{H} \), but we do not know the wavefunction, and we do not know how to solve the Schrödinger equation. If at least we had a good idea of the generic form of the solution (Gaussian, sinusoidal, ...), we could choose a trial function with a free parameter and optimize this parameter minimizing the energy, which ought to be minimal for the ground state. This is precisely the idea of the variational method. Note that the variational method only works for the ground state.

For any function \( \psi \) we know that the Rayleigh fraction \( \mathcal{E} \) satisfies,

\[
E_g \leq \frac{\langle \psi|\hat{H}|\psi \rangle}{\langle \psi|\psi \rangle} = \mathcal{E},
\]

not only when \( \psi \) is the wavefunction of an excited state, but even when it represents a (imperfect) trial to the ground state. Assuming normalized wavefunctions we can discard the denominator \( \langle \psi|\psi \rangle = 1 \). To verify the theorem, we expand the function \( \psi \) into orthonormal (unknown) eigenfunctions, \( |\psi\rangle = \sum_n c_n |\psi_n\rangle \). Since \( \psi \) is normalized,

\[
1 = \langle \psi|\psi \rangle = \sum_{m,n} \langle \psi_m|c_m^* c_n |\psi_n \rangle = \sum_n |c_n|^2.
\]

In the same way,

\[
\langle \psi|\hat{H}|\psi \rangle = \sum_{m,n} \langle \psi_m|c_m^* \hat{H} c_n |\psi_n \rangle = \sum_n E_n |c_n|^2.
\]

As the ground state is that of the lowest energy, \( E_g \leq E_n \), we have demonstrated the relationship (5.26)

\[
E_g = E_g \sum_n |c_n|^2 \leq \sum_n E_n |c_n|^2 = \langle \hat{H} \rangle.
\]

In practice, the ansatz \( \psi_\alpha \) for the ground state allows us to calculate an energy that must be minimized via

\[
\frac{\partial \langle \psi_\alpha|\hat{H}_\alpha|\psi_\alpha \rangle}{\partial \alpha} = 0.
\]

In the Excs. 5.2.3.1 and 5.2.3.2 we will approach the fundamental state of a quartic potential and a harmonic oscillator, respectively, by trying several trial wavefunctions and optimizing their free parameters.

5.2.2 Rayleigh-Ritz method

A modification of the variational method is the Rayleigh-Ritz method. Here, instead of using a trial function, we use a linear combination of eigenfunctions with variable
coefficients: \(|\psi\rangle = \sum_k c_k |k\rangle\). These variables are then optimized to minimize the Rayleigh fraction,

\[
E_g \leq \frac{\sum_{k,m} c_k c_m \langle k | \hat{H} | m \rangle}{\sum_{k,m} c_k c_m \langle k | m \rangle} = \mathcal{E}
\]

where we assume real coefficients and eigenfunctions. For this, the derivatives with respect to all coefficients must vanish:

\[
\frac{\partial \mathcal{E}}{\partial c_q} = \sum_k c_k \langle k | \hat{H} | q \rangle + \sum_m c_m \langle q | \hat{H} | m \rangle - \sum_{k,m} c_k c_m \langle k | m \rangle \langle \sum_k c_k | k \rangle + \sum_m c_m \langle q | m \rangle \rangle = 0,
\]

using the definition of \(\mathcal{E}\). The equation is satisfied when the numerator disappears:

\[
0 = \sum_m c_m \langle q | \hat{H} | m \rangle - \mathcal{E} \langle q | m \rangle.
\]

The condition for the existence of solutions is that the secular determinant disappears,

\[
0 = \text{det} (\langle q | \hat{H} | m \rangle - \mathcal{E} \langle q | m \rangle).
\]

The solution of this equation leads to a set of values \(\mathcal{E}\), and the lowest value, \(\mathcal{E}_{\text{min}}\), is the best approximation for the ground state energy. The coefficients of the wavefunction are obtained by solving the eigenvalue equation (5.33) with \(\mathcal{E}_{\text{min}}\).

In Exc. 5.2.3.3 we will use the Rayleigh-Ritz method to estimate the effect of a finite nuclear mass of the hydrogen atom on the energy levels. In Exc. 5.2.3.4 we will use the Rayleigh-Ritz method to find the maximum number of atoms allowing for a stable Bose-Einstein condensate made of atoms subject to an attractive interatomic force.

### 5.2.3 Exercises

#### 5.2.3.1 Ex: Variational method applied to a quartic potential

Determine the ground state energy of the quartic potential \(V(x) = bx^4\) making the variational ansatz \(\psi_\alpha(x) = (\alpha/\pi)^{1/4} e^{-\alpha x^2/2}\). \textbf{Formulae}:

\[
\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}, \quad \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = \frac{1}{2} \sqrt{\pi}, \quad \int_{-\infty}^{\infty} x^4 e^{-x^2} dx = \frac{3}{4} \sqrt{\pi}
\]

#### 5.2.3.2 Ex: Variational method applied to the harmonic oscillator

Obtain, through the variational method, the ground state energy of the one-dimensional harmonic oscillator described by the Hamiltonian \(\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2\), and the corresponding wavefunction from the test functions

a. \(\psi(x) = Ae^{-\alpha x^2}\) being \(\alpha\) a constant;
b. \(\psi(x) = A/(x^2 + \beta^2)\) being \(\beta\) a constant;
c. \(\psi(x) = A \cos(\pi x/a)\) between the limits \(\pm a/2\) being \(a\) a constant.
5.2.3.3 Ex: Effect of finite nuclear mass on hydrogen via Rayleigh-Ritz

Use the Rayleigh-Ritz method to estimate the impact of the finite mass of the nucleus of the hydrogen atom. To do this, calculate the ground state energy using the exact Hamiltonian, but a basis of wavefunctions assuming an infinitely heavy nucleus. Only take into account the states $\psi_{100}$ and $\psi_{200}$. Help: Express the exact Hamiltonian in terms of the infinite-mass Hamiltonian approximating for small corrections of the reduced mass: $m \equiv m_e/(1 + \gamma) \simeq (1 - \gamma)m_e$, where $\gamma \equiv m_e/m_p$.

5.2.3.4 Ex: Collapse of a condensate with attractive interactions

A Bose-Einstein condensate of $^7$Li may become unstable due to attractive interatomic force, the scattering length being $a_s = -27.3a_B$. Consider the radial Gross-Pitaevskii Hamiltonian derived in Exc. 3.1.5.2 with an external harmonic potential with the oscillation frequency $\omega_{trp}/(2\pi) = 50$ Hz. Using the variational method to determine the maximum number of atoms allowing for a stable condensate. (Note that the derived minimization condition must be evaluated numerically.)

5.3 WKB approximation

The **WKB approximation** (from Wentzel-Kramers-Brillouin) [86, 360, 627] is a method to find approximate solutions for linear differential equations with spatially variable coefficients. It is typically used for calculations in quantum mechanics where the wavefunction is reformulated as an exponential semi-classically expanded function, and then the amplitude or phase is slowly changed. In the following, we present the WKB approximation applied to the Schrödinger equation and exemplify it in some canonical systems.

5.3.1 WKB approximation applied to the Schrödinger equation

Starting from the time-independent Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x),$$

and rewrite it as follows,

$$\frac{d^2 \psi}{dx^2} = k(x)\psi(x).$$

with $k(x) = \sqrt{2m[E - V(x)]/\hbar^2}$. For now, we will restrict ourselves to energies $E > V(x)$. In this scheme, the wavefunctions are usually complex functions, so that we can write them in polar coordinates, containing an amplitude $A(x)$ and a phase $\phi(x)$, which are both real numbers:

$$\psi(x) = A(x)e^{i\phi(x)}.$$  

Substituting this function into the Schrödinger equation we obtain a system of coupled equations in terms of $A(x)$ and $\phi(x)$,

$$A'' = A\left[(\phi')^2 - k^2\right] \quad \text{and} \quad (A^2\phi')' = 0.$$
The equations (5.39) and (5.37) are completely equivalent to the Schrödinger equation. The second Eq. (5.38) is easy to solve, \( A = \frac{C}{\sqrt{\phi'}} \), (5.39)
being \( C \) a real constant. We can not say the same thing about the solution of the first Eq. (5.38). In order to solve it we are going to use the WKB approach, assuming that \( A \) varies slowly, so the term \( A'' \rightarrow 0 \). By doing this approximation we can rewrite Eq. (5.39) in this way:
\[ (\phi')^2 = k^2. \] (5.40)
Solving this last expression we obtain two linearly independent solutions, \( \phi' = \pm k \).
So we get the expression for the phase:
\[ \phi(x) = \pm \int k(x) dx. \] (5.41)
We write this indefinite integral, because the constant term can be absorbed by the constant \( C \). Finally, we obtain the expression for the wavefunction in the WKB approximation:
\[ \psi(x) = \frac{C}{\sqrt{|k(x)|}} e^{\pm \int |k(x)| dx}. \] (5.42)
Here, taking the absolute value of the wavevector, we have already generalized for the case that the energy \( E \) of the particle is lower than the potential \( V(x) \) (classically forbidden region).

**Example 28 (WKB approximation):** The WKB approach is a semiclassical method for the solution of the Schrödinger equation that does not require the potential to be a perturbation of a soluble problem. Instead, it only assumes that certain classical quantities having the dimension of an action (energy per time) are much larger than Planck’s constant. Inserting the ansatz
\[ \psi(x) = Ae^{iS(x)/\hbar}, \]
into the one-dimensional time-independent Schrödinger equation, we find,
\[ -\frac{i\hbar}{2m} S''(x) + \frac{1}{2m} S'(x)^2 + V(x) - E = 0. \]
Now we expand the exponent in orders of \( \hbar \),
\[ S(x) = S_0(x) + \hbar S_1(x) + \frac{\hbar^2}{2} S_2(x) + ... , \]
and insert it in the above equation. Collecting the orders in \( \hbar \), we find in the first orders,
\[ \left[ \frac{1}{2m} S_0'(x)^2 + V(x) - E \right] \hbar^0 = 0 \]
\[ -\frac{i\hbar}{2m} S''_0(x) + \frac{1}{m} S_0'(x)S_1'(x) \hbar^1 = 0 \]
\[ \left[ \frac{1}{2m} S_1'(x)^2 - \frac{1}{2m} S_0''(x) \right] \hbar^2 = 0. \]
The solution of the zeroth order equation, \( S_0(x) = \pm \int_x^z \sqrt{2m|E - V(x')} dx' \),
gives
\[ \psi(x) = Ae^{\pm \frac{i}{\hbar} \int_x^z \sqrt{2m|E - V(x')} dx'}. \]
5.3. WKB APPROXIMATION

The WKB approximation can be used to describe continuous potentials (or barriers) by stepwise constant potentials. The transmission $|T|^2$ through these parts can be obtained by multiplying the individual tunneling probabilities,

$$\ln |T|^2 \simeq -2 \int_{\text{barrier}} \kappa(x) dx ,$$

with $\kappa(x) = \frac{1}{\hbar} \sqrt{2m[V(x) - E]}$.

5.3.2 Connection formulas

Now let us derive the connection formulas that interconnect solutions with $E$ above and below $V(x)$ at the turning points, precisely those regions where WKB fails. We will apply the derivation to a generic confining potential shown in Fig. 5.1.

Let us start with the right turning point Fig. 5.1(a)]. First, we shift the coordinate system so that the turning point coincides with zero, as shown in Fig. 5.1(b). As seen above, the WKB solutions will be given by the following equations:

$$\psi(x) \approx \begin{cases} \frac{1}{\sqrt{k(x)}} \left[ Be^{i \int_{0}^{x} k(x') dx'} + Ce^{-i \int_{0}^{x} k(x') dx'} \right] & \text{if } x \leq 0 \\ \frac{1}{\sqrt{k(x)}} De^{-i \int_{0}^{x} |k(x')| dx'} & \text{if } x \geq 0 \end{cases} . \quad (5.43)$$

In the vicinity of the turning point we approximate the potential by a straight line (Taylor series expansion up to first order) with the following functional dependence,

$$V(x) \approx E + V'(0)x . \quad (5.44)$$

The Schrödinger equation for this potential acquires the following format,

$$\frac{d^2 \psi_t}{dx^2} = \alpha^3 x \psi_t , \quad (5.45)$$

with $\alpha = \left[\frac{2m}{\hbar^2} V'(0)\right]^{1/3}$. Through a change of variables, $z = \alpha x$, we fall back on Airy’s equation,

$$\frac{d^2 \psi_t}{dz^2} = z \psi_t , \quad (5.46)$$
having as solution a linear combination of the two solutions of the Airy equation,

$$\psi_t(x) = a \text{Ai}(\alpha x) + b \text{Bi}(\alpha x). \quad (5.47)$$

Now let’s have a look at the WKB solutions in the two regions in the vicinity of the turning point. In the classically forbidden region we have \( k(x) = \alpha^{3/2} \sqrt{-x} \), thus being \( \int_0^x |k(x')|dx' = \frac{2}{3}(\alpha x)^{3/2} \). Thus, the WKB solution in the classically forbidden region near the turning point will be given by:

$$\psi(x) \approx \frac{D}{\sqrt{\hbar \alpha^{3/4} x^{1/4}}} e^{-\frac{2}{3}(\alpha x)^{3/2}}. \quad (5.48)$$

Using the asymptotic forms of Airy functions in the solution (5.47) we obtain the following expression for \( \psi_t(x) \),

$$\psi_p(x) \approx \frac{a}{2\sqrt{\pi} (\alpha x)^{1/4}} e^{-\frac{2}{3}(\alpha x)^{3/2}} + \frac{b}{\sqrt{\pi} (\alpha x)^{1/4}} e^{\frac{2}{3}(\alpha x)^{3/2}}, \quad (5.49)$$

which when compared to equation (5.48) shows us that \( a = \sqrt{\frac{4\pi}{\hbar}} D \) and \( b = 0 \). Repeating the previous steps in the negative region we see that the WKB solution in the asymptotic forms of the Airy solutions for approximately linear potentials takes the following format (with \( b = 0 \)):

$$\psi(x) \approx \frac{1}{\sqrt{\hbar \alpha^{3/4} (-x)^{1/4}}} \left[ B e^{i\frac{2}{3}(-\alpha x)^{3/2}} + C e^{-i\frac{2}{3}(-\alpha x)^{3/2}} \right], \quad (5.50)$$

and

$$\psi_p(x) \approx \frac{a}{\sqrt{-\pi (-\alpha x)^{1/4}}} \frac{1}{2i} \left[ e^{i\pi/4} e^{i\frac{2}{3}(-\alpha x)^{3/2}} - e^{-i\pi/4} e^{-i\frac{2}{3}(-\alpha x)^{3/2}} \right]. \quad (5.51)$$

When compared, \( \frac{a}{2i\sqrt{\pi}} e^{i\pi/4} = \frac{B}{\sqrt{\hbar \alpha}} \) and \(- \frac{a}{2i\sqrt{\pi}} e^{-i\pi/4} = \frac{C}{\sqrt{\hbar \alpha}} \). Having all this information we can rewrite the WKB solutions for all positions in the potential, including the turning points \(^5\):

$$\psi(x) \approx \begin{cases} \frac{2D}{\sqrt{k(x)}} \sin \left[ \int_x^{x_2} k(x')dx' + \frac{\pi}{4} \right], & \text{if } x \leq x_2 \\ \frac{D}{\sqrt{k(x)}} e^{-\int_{x_2}^{x} |k(x')|dx'}, & \text{if } x \geq x_2 \end{cases}. \quad (5.52)$$

Repeating the process for a decreasing turning point [left turning point of the potential of Fig. 5.1(a)], we obtain the following expression:

$$\psi(x) \approx \begin{cases} \frac{D'}{\sqrt{k(x)}} e^{-\int_{x_1}^{x_1} |k(x')|dx'}, & \text{if } x \leq x_1 \\ \frac{2D'}{\sqrt{k(x)}} \sin \left[ \int_{x_1}^{x} k(x')dx' + \frac{\pi}{4} \right], & \text{if } x \geq x_1 \end{cases}. \quad (5.53)$$

**Example 29 (Harmonic oscillator):** Now we apply the WKB method to a well-known system: the harmonic oscillator. We will calculate its energy levels

\(^5\)Note that we shifted the turning point to an arbitrary position \( x_2 \).
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and the respective eigenfunctions.

**Eigenenergies:** First, note that for a confining potential, and more specifically in the region where \( E \geq V(x) \), we have the solutions obtained for the left and right turning point, these two solutions must match each other, that is,

\[
\frac{2D}{\sqrt{k(x)}} \sin \left[ \int_x^{x_2} k(x')dx' + \frac{\pi}{4} \right] \simeq \frac{2D'}{\sqrt{k(x)}} \sin \left[ \int_{x_1}^{x} k(x')dx' + \frac{\pi}{4} \right],
\]

and hence the zeros of these functions, so the arguments of those sines must be equal (except for a multiple of \( \pi \)),

\[
\int_x^{x_2} k(x')dx' + \frac{\pi}{4} = -\int_{x_1}^{x_1} k(x')dx' - \frac{\pi}{4} + n\pi \quad (5.54)
\]

with \( n = 1, 2, ... \). With this information we take a harmonic potential of the type \( V(x) = \frac{1}{2}\kappa x^2 \). In this case, the turning points for a given energy \( E \) will be at \(-\sqrt{\frac{2E}{\kappa}}\) and \( \sqrt{\frac{2E}{\kappa}}\). For this potential we will have that \( k(x) = \sqrt{\frac{2m}{\kappa}(E - \frac{1}{2}\kappa x^2)} \). Calculating the integral of \( k(x) \) between these two turning points we get,

\[
\int_{x_1}^{x_2} k(x)dx = \frac{2m}{\kappa} \int_{-\sqrt{\frac{2E}{\kappa}}}^{\sqrt{\frac{2E}{\kappa}}} \sqrt{E - \frac{1}{2}\kappa x^2} dx = \pi E \frac{m}{\kappa} = \left( n - \frac{1}{2} \right) \pi \hbar,
\]

isolating \( E \) and taking \( \omega = \sqrt{\kappa/m} \) we have,

\[
E = \left( n - \frac{1}{2} \right) \hbar \omega,
\]

with \( n = 1, 2, ... \), the exact spectrum of the harmonic oscillator, but this is just a coincidence.

**Eigenstates:** Now we will calculate the eigenstates of the harmonic oscillator. The eigenfunctions were calculated on a computer. The first graph (Fig. 5.2) compares the first exact excited state with that obtained using the WKB method.

Note that the WKB approach is very good when \( x \to 0 \) and \( x \to \infty \), regions where the difference between the oscillator energy and the potential are large (\( E \gg V(x \to 0) \) and \( E \ll V(x \to \infty) \)), because in these regions the wavelength \( \lambda(x) \) acquires the lowest values, since it is proportional to \( \frac{1}{\sqrt{E - V(x)}} \). Hence, the spatial region in which the potential needs to be practically constant is smaller, which explains why the approximation is closer to the exact solution. In the intermediate regions the difference between \( E \) and \( V(x) \) begins to decrease, and the WKB approximation delivers its worst results.

As we increase the energy of the harmonic oscillator, the approximation becomes better (for the same reason as discussed in the previous paragraph). The following graph illustrates this effect for \( n = 10 \).

---

Note that \( n \neq 0 \), because the integral (5.54) has to be greater than zero.
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Figure 5.2: First excited state calculated accurately and through the WKB approximation.

Figure 5.3: Wavefunction of the vibrational state $n = 10$ calculated exactly and using the WKB approximation.

Example 30 (Hydrogen atom): Eigenenergies: For the hydrogen atom the effective potential is given by,

$$V(x) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}. $$

Note that the WKB method for this case obeys the relation (5.54), hence we get,

$$\int_{r_1}^{r_2} p(r) dr = \sqrt{2m} \int_{r_1}^{r_2} \sqrt{E + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}} dr$$

$$= \sqrt{-2mE} \int_{r_1}^{r_2} \frac{1}{r} \sqrt{-r^2 - \frac{e^2}{4\pi\epsilon_0 E} r + \frac{\hbar^2}{2mE} l(l+1)} dr.$$  

Notice that $E < 0$. Let us make the following substitution to facilitate algebraic manipulations,

$$B = -\frac{e^2}{4\pi\epsilon_0 E} \quad \text{and} \quad C = -\frac{\hbar^2}{2mE} l(l+1).$$

The turning points $r_1$ and $r_2$ are given by the following expressions,

$$r_1 = \frac{B - \sqrt{B^2 - 4C}}{2} \quad \text{and} \quad r_2 = \frac{B + \sqrt{B^2 - 4C}}{2}.$$
Thus, returning to the integral we will have the following:

\[
\int_{r_1}^{r_2} p(r)dr = \sqrt{-2mE} \int_{r_1}^{r_2} \frac{1}{r} \sqrt{(r-r_1)(r_2-r)}dr = \sqrt{-2mE} \frac{\pi}{2} (\sqrt{r_2} - \sqrt{r_1})^2
\]

\[
= \sqrt{-2mE} \frac{\pi}{2} (r_1 + r_2 - 2r_1r_2) = \sqrt{-2mE} \frac{\pi}{2} (B - 2\sqrt{C})
\]

\[
= \frac{\pi}{2} \left( - \frac{e^2 \sqrt{2m\epsilon_0}}{4\pi \epsilon_0 \sqrt{-E}} - 2\hbar \sqrt{l(l+1)} \right) = \left( n - \frac{1}{2} \right) \pi \hbar .
\]

Isolating \( E \) we obtain the energy spectrum of the hydrogen atom in the WKB approximation:

\[
E = -\frac{m}{2\hbar} \left( \frac{e^2}{4\pi \epsilon_0} \right)^2 \left( \frac{1}{n - 1/2 + l(l+1)} \right)^2 = -\frac{13.6}{\left[ n - 1/2 + l(l+1) \right]^2} eV .
\]

For high energies \( (n \gg l) \), we recover Bohr’s expression.

### 5.3.3 Exercises

#### 5.3.3.1 Ex: Energy levels of hydrogen via WKB

Use the WKB approach to calculate the energy levels of the hydrogen atom.

### 5.4 Time-dependent perturbations

Temporal perturbations typically occur when we suddenly switch on an external field that influences the motion or spin of the particles, or when the field varies over time, for example, an electromagnetic field. Let us first study a two-level system subject to a temporal perturbation.

#### 5.4.1 Two-level systems

We write the perturbation as

\[
\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}(t) .
\]

As in the case of a stationary perturbation, we write the eigenenergies and eigenfunctions of the unperturbed system as

\[
\hat{H}^{(0)}|n\rangle = E_n|n\rangle .
\]

Recalling that this stationary Schrödinger equation was obtained from the time-dependent Schrödinger equation via a separation ansatz (2.55), the temporal evolution of these eigenfunctions is given by,

\[
|\psi_n^{(0)}(t)\rangle = |n\rangle e^{-iE_n t/\hbar} .
\]

For small perturbations we can expect that the ansatz,

\[
|\psi^{(1)}(t)\rangle = a_1(t)|\psi_1^{(0)}(t)\rangle + a_2(t)|\psi_2^{(0)}(t)\rangle ,
\]

where \( a_1(t) \) and \( a_2(t) \) are slowly varying functions of time, the perturbation Hamiltonian can be approximated as

\[
\hat{H}^{(1)}(t) = \sum_{n,m} V_{nm} |n\rangle \langle m| e^{-iE_n t/\hbar} .
\]

As a result, the time-dependent Schrödinger equation can be written as

\[
\frac{d}{dt}|\psi(t)\rangle = \left( \hat{H}^{(0)} + \hat{H}^{(1)}(t) \right) |\psi(t)\rangle = \hat{H}^{(0)}|\psi(t)\rangle + \hat{H}^{(1)}(t)|\psi(t)\rangle .
\]

Solving this equation for \( |\psi(t)\rangle \) gives the time-dependent wave function in the perturbed Hamiltonian.
be good. Note that not only do eigenfunctions oscillate, but the coefficients also depend on time, because the composition of the states can change. The instantaneous probability of finding the system in state \( n \) is \( |a_n(t)|^2 \). Importing the above linear combination into the Schrödinger equation,

\[
\left[ \hat{H}^{(0)} + \hat{W}^{(1)}(t) \right] |\psi^{(1)}(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi^{(1)}(t)\rangle ,
\]

we find,

\[
a_1 \hat{H}^{(0)} |\psi_1^{(0)}\rangle + a_2 \hat{H}^{(0)} |\psi_2^{(0)}\rangle + a_1 \hat{H}^{(1)} |\psi_1^{(0)}\rangle + a_2 \hat{H}^{(1)} |\psi_2^{(0)}\rangle \\
= i\hbar \left[ \frac{\partial a_1}{\partial t} |\psi_1^{(0)}\rangle + \frac{\partial a_2}{\partial t} |\psi_2^{(0)}\rangle + a_1 \frac{\partial |\psi_1^{(0)}\rangle}{\partial t} + a_2 \frac{\partial |\psi_2^{(0)}\rangle}{\partial t} \right] \quad (5.60)
\]

\[
\implies a_1 \hat{H}^{(1)} |\psi_1^{(0)}\rangle + a_2 \hat{H}^{(1)} |\psi_2^{(0)}\rangle = i\hbar a_1 |\psi_1^{(0)}\rangle + i\hbar a_2 |\psi_2^{(0)}\rangle ,
\]

because the other terms satisfy the Schrödinger equation of zero order. Replacing the stationary eigenfunctions,

\[
a_1 e^{-iE_1 t/\hbar} \hat{H}^{(1)} |1\rangle + a_2 e^{-iE_2 t/\hbar} \hat{H}^{(1)} |2\rangle = i\hbar a_1 e^{-iE_1 t/\hbar} |1\rangle + i\hbar a_2 e^{-iE_2 t/\hbar} |2\rangle ,
\]

and multiplying this equation with \( |1\rangle \times \text{and} \langle 2| \times \), we find with the abbreviation \( \hbar \omega_0 \equiv E_2 - E_1 \),

\[
\hbar \dot{a}_1 = a_1 \langle 1| \hat{H}^{(1)} |1\rangle + a_2 e^{-i\omega_0 t} \langle 1| \hat{H}^{(1)} |2\rangle \quad (5.62)
\]

\[
\hbar \dot{a}_2 = a_1 e^{i\omega_0 t} \langle 2| \hat{H}^{(1)} |1\rangle + a_2 \langle 2| \hat{H}^{(1)} |2\rangle .
\]

Frequently, the perturbation induces only a coupling, but does not directly influence the energies, \( \langle n| \hat{H}^{(1)} |n\rangle = 0 \),

\[
\dot{a}_1 = a_2 \frac{e^{i\omega_0 t}}{i\hbar} \langle 1| \hat{H}^{(1)} |2\rangle \quad \text{and} \quad \dot{a}_2 = a_1 \frac{e^{i\omega_0 t}}{i\hbar} \langle 2| \hat{H}^{(1)} |1\rangle .
\]

Without perturbation, \( \langle m| \hat{H}^{(1)} |n\rangle = 0 \), no dynamics develops; the eigenfunctions evolve independently.

### 5.4.2 The time-dependent perturbation method

Now let us turn our attention to systems with many levels.

In **time-dependent perturbation theory** (TDPT) we separate the Hamiltonian into a stationary part and a time-dependent part \(^7\),

\[
\hat{H}(t) = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}(t) .
\]

\(^7\)See Becker-Sauter II, p.118ff e [591], p.104ff. An alternative treatment is found in [382], p.191ff or in Blochinzew, p.322ff.

\(^8\)Note that by substituting \( \hat{W} \) by \( \hat{H}^{(1)} \), the equation (5.65), \( i\hbar \dot{a}_1 |\psi_1(t)\rangle = \hat{H}^{(1)}(t)|\psi_1(t)\rangle \), corresponds to a first-order perturbative approximation, i.e., the perturbation eigenvalues \( \hat{H}^{(1)} \) are calculated with the eigenvectors of the unperturbed system. Thus, in first order TDPT we can substitute \( \hat{W} \) for \( \hat{H}^{(1)} \).
As usual, this Hamiltonian satisfies the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle.$$  \hfill (5.64)

Now we do a unitary transformation into the interaction picture with $S(t) = e^{-i\hat{H}(0)t/\hbar}$ substituting $|\psi(t)\rangle \equiv S(t)|\psi(t)\rangle$ and $\hat{H}^{(1)}(t) \equiv S(t)\hat{W}(t)S^{-1}(t)$ in the Schrödinger equation. This procedure removes the stationary part, as shown in Sec. 2.4.4,

$$i\hbar \frac{\partial}{\partial t} |\psi_I(t)\rangle = \lambda \hat{W}(t) |\psi_I(t)\rangle.$$  \hfill (5.65)

If $\hat{W}(t)$ were also independent of time, the solution would simply be $|\psi_I(t)\rangle = e^{-i\hat{W}t/\hbar}|\psi_I(0)\rangle$. Otherwise, we integrate the equation,

$$|\psi_I(t)\rangle = |\psi_I(0)\rangle + \lambda \int_0^t \hat{W}(\tau) |\psi_I(\tau)\rangle d\tau.$$  \hfill (5.66)

Substituting $|\psi_I(\tau)\rangle$ by $|\psi_I(t)\rangle$ we iterate this equation,

$$|\psi_I(t)\rangle = |\psi_I(0)\rangle + \lambda \int_0^t \hat{W}(\tau_1) |\psi_I(\tau_1)\rangle + \lambda \int_0^{\tau_1} \hat{W}(\tau_2) |\psi_I(\tau_2)\rangle d\tau_1$$

$$= |\psi_I(0)\rangle + \lambda \int_0^t \hat{W}(\tau_1) |\psi_I(\tau_1)\rangle + \lambda^2 \int_0^t \hat{W}(\tau_1) \hat{W}(\tau_2) |\psi_I(\tau_2)\rangle d\tau_2 d\tau_1$$

$$= \left[ \sum_{n=1}^N \left( \frac{\lambda}{i\hbar} \right)^n \int_0^t \hat{W}(\tau_1) \int_0^{\tau_1} \hat{W}(\tau_2) \cdots \int_0^{\tau_{n-1}} \hat{W}(\tau_n) d\tau_1 d\tau_2 \cdots d\tau_n \right] |\psi_I(0)\rangle + o(\lambda^{N+1}).$$

This is called the Dyson series. For $N = 1$, we get the first order of the perturbation series 9,

$$|\psi_I(t)\rangle = (1 + \lambda \int_0^t \hat{W}(\tau) d\tau) |\psi_I(0)\rangle.$$  \hfill (5.68)

The stationary states of the unperturbed Hamiltonian are given by $\hat{H}(0)|f\rangle = E_f |f\rangle$. Now, the perturbed states are expanded on this basis, $|\psi_I(t)\rangle = \sum_f |f\rangle a_f(t)$. The expansion coefficients are 10,

$$a_f(t) = \langle f|\psi_I(t)\rangle = \langle f|\psi_I(0)\rangle + \lambda \langle f| \int_0^t S^{-1}(\tau)\hat{H}^{(1)}(\tau)S(\tau)|\psi_I(0)\rangle d\tau.$$  \hfill (5.69)

Now, we assume that the system be initially in the eigenstate $|\psi_I(0)\rangle = |i\rangle$. The amplitudes then are,

$$a_{i\to f}(t) = \langle f|i\rangle + \lambda \int_0^t e^{iE_f t/\hbar} \langle f|\hat{H}^{(1)}(\tau)|i\rangle e^{-iE_i t/\hbar} d\tau$$

$$= \delta_{if} + \lambda \int_0^t \langle f|\hat{H}^{(1)}(\tau)|i\rangle e^{i\omega_f t/\hbar} d\tau.$$  \hfill (5.70)

9For higher orders, $|\psi_I(t)\rangle \approx \left[ \sum_{n=1}^N \left( \frac{\lambda}{i\hbar} \right)^n \int_0^t \hat{W}(\tau) d\tau \right] |\psi_I(0)\rangle = T \left[ \exp \left( \frac{\lambda}{i\hbar} \int_0^t \hat{W}(\tau) d\tau \right) \right] |\psi_I(0)\rangle$.

10We could define the coefficients in Schrödinger’s picture, $a_f \equiv \langle f|\psi\rangle$, but this would only introduce a phase factor, $a_{i\to f} \rightarrow a_{i\to f} e^{i(E_f - E_i)t/\hbar}$, which is unimportant for absolute values $|a_{i\to f}|^2$. This corresponds to a transformation to a rotating system, which will be discussed in Sec. 14.2.1.
The varying potential is considered a perturbation, and a variation of the system’s state is observed. As the energy is not conserved, $[\partial_t, \hat{H}(t)] \neq 0$, the time-dependence is not separable and the system exchanges energy with the potential. In first-order perturbation theory we only consider weak perturbations, i.e. the initial state is gradually emptied, $a_{i \to i}(dt) \simeq a_{i \to i}(0) = 1$. For an initially empty state the growth is obviously considerable. For $i \neq f$ we have,

$$
\frac{da_{i \to f}(t)}{dt} = a_{i \to f}(t + dt) - a_{i \to f}(t) = \frac{\lambda}{\hbar} \langle f | \hat{H}^{(1)}(t) | i \rangle e^{i \omega_{if} t} dt.
$$

This formula is nothing more than a generalization of the formula (5.63) obtained for a two-level system assuming that the initial state does not deplete considerably. In Exc. 5.4.6.1 we calculate the dynamics of a harmonic oscillator perturbed by a decaying force.

5.4.3 Specific perturbations

5.4.3.1 Sudden switch-on of a constant perturbation

To begin with, we consider a constant perturbation $\hat{H}^{(1)}$ suddenly switched on at $t = 0$. In Schrödinger’s picture we can write,

$$
a_{i \to f}(t) = \delta_{if} + \frac{\lambda}{\hbar} \langle f | \hat{H}^{(1)} | i \rangle \int_0^t e^{i \omega_{if} \tau} d\tau = \delta_{if} + \frac{\lambda}{\hbar} \langle f | \hat{H}^{(1)} | i \rangle \frac{1 + e^{i \omega_{if} t}}{i \omega_{if}}.
$$

We obtain for $i \neq f$,

$$
|a_{i \to f}(t)|^2 = \frac{\lambda^2}{\hbar^2} |\langle f | \hat{H}^{(1)} | i \rangle|^2 \frac{\sin^2(\omega_{if} t/2)}{(\omega_{fi}/2)^2}.
$$

For long times we calculate the rate \(^{11}\),

$$
\frac{d}{dt} |a_{i \to f}(t)|^2 = \frac{\lambda^2}{\hbar^2} |\langle f | \hat{H}^{(1)} | i \rangle|^2 \frac{\sin \omega_{fi} t}{\omega_{fi}/2} \quad \Rightarrow \quad \frac{2 \pi \lambda^2}{\hbar^2} |\langle f | \hat{H}^{(1)} | i \rangle|^2 \delta(\omega_f - \omega_i),
$$

where we use the representation of the Dirac function,

$$
\delta(x) = \lim_{t \to \infty} \frac{1}{2\pi} \int_{-t}^t e^{ikx} dk = \lim_{t \to \infty} \frac{i}{\pi} \text{sinc} xt.
$$

The $\delta$-function in (5.74) ensures that, for infinitely sharp steps, transitions are impossible, unless the energy of the final state is the same as the one of the initial state. This points to the fact that infinitely sharp steps are not a realistic physical concept.

In practice, the changes applied to a system are often slow and the observation times are long, because the frequencies of the transitions are high $\omega_{fi}/2\pi \simeq \text{THz}$. Let us assume that the perturbation be switched on within a time constant $\gamma^{-1}$. In Exc. 5.4.6.2 we will study how the rapidity of a perturbation influences the transition rate. We will see via a temporal analysis of $|a_{i \to f}(t)|^2$, that for slow variations, $\gamma \ll \omega_{fi}$, the system adiabatically approaches the final situation. For $\gamma \simeq \omega_{fi}$, the system receives a shock and exhibits oscillating transients. For $\gamma > \omega_{fi}$, we observe violent oscillations with largest amplitudes.

\(^{11}\)We use the trigonometric rule $\sin x = 2 \sin \frac{x}{2} \cos \frac{x}{2}$.
5.4.3.2 Periodic perturbations

We now consider the case of an oscillatory perturbation, for example an electromagnetic field. In principle, knowledge of the system’s response to periodic perturbations allows us to treat arbitrary perturbations, since we can expand them in Fourier series.

We first treat transitions between discrete levels, before considering states embedded in continua,

\[ \hat{H}^{(1)}(t) = \begin{cases} 0 & \text{for } t < 0 \\ 2\hbar \hat{\Omega}_0 \cos \omega t & \text{for } t \geq 0 \end{cases} \]  

(5.76)

With the abbreviation \( \Omega_{fi} \equiv \langle f | \hat{\Omega}_0 | i \rangle \) the transition rate is,

\[ a_{i \rightarrow f}(t) = -i \Omega_{fi} \int_0^t e^{i\Omega_{fi} \tau} \cos \omega \tau d\tau \]  

(5.77)

\[ = -i \Omega_{fi} \left[ \frac{e^{i(\omega_{fi}+\omega)t} - 1}{i(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi}-\omega)} \right] . \]

The first term being small, we neglect it in the rotating wave approximation (RWA). We obtain,

\[ |a_{i \rightarrow f}(t)|^2 = |\Omega_{fi}|^2 \sin^2 \frac{1}{2} \frac{(\omega_{fi} - \omega)t}{(\omega_{fi} - \omega)^2} \]  

(5.78)

This result coincides with the Rabi formula (5.73), except that the energy difference between the states \( \omega_{fi} \) is shifted by the frequency of the perturbation \( \omega \). The quantity \( \Delta_{fi} \equiv \omega - \omega_{fi} \) is called a detuning. The transition probability is maximal, when we are at resonance, that is \( \Delta_{fi} = 0 \). In this case,

\[ |a_{i \rightarrow f}(t)|^2 \longrightarrow |\Omega_{fi}|^2 t^2 . \]  

(5.79)

This can be seen by expanding the numerator in a Taylor series for small \( (\omega_{fi} - \omega)t \).

Note, that the probability exceeds 1 for long times, which can not be. In fact, the restriction to the first order in the Taylor expansion used in the derivation of the last equation is no longer valid for long times, when \( (\omega_{fi} - \omega)t > 1 \), and we need to take into account higher orders.

**Example 31 (The Rabi formula):** Let us now consider a periodic perturbation oscillating at frequency \( \omega = \omega_0 + \Delta \), where \( \Delta \) is called the detuning from the resonance \( \omega_0 \),

\[ H^{(1)} = -e \mathbf{E}(\mathbf{r},t) \cdot \mathbf{r} = -e E_0 \delta \cos(kz - \omega t) \cdot \mathbf{r} . \]  

(5.80)

Then,

\[ \langle 2 | H^{(1)} | 1 \rangle = -e E_0 \cos(kz - \omega t) \langle 2 | \mathbf{r} | 1 \rangle = \hbar \Omega \cos(kz - \omega t) , \]  

(5.81)

where we call

\[ \Omega \equiv -\frac{e E_0 \langle 2 | \mathbf{r} | 1 \rangle}{\hbar} \]  

(5.82)

the Rabi frequency. With this abbreviation the Eqs. (5.63) become,

\[ \dot{a}_1 = -i \Omega a_2 e^{-i\omega_0 t} \cos(kz - \omega t) \quad \text{and} \quad \dot{a}_2 = -i \Omega^* a_1 e^{i\omega_0 t} \cos(kz - \omega t) . \]  

(5.83)
Neglecting fast-rotating terms doing the so-called rotating wave approximation (RWA) and choosing the position of the atom to be \( z = 0 \),

\[
\dot{a}_1 \simeq -i \frac{\Omega}{2} a_2 e^{i \Delta t} \quad \text{and} \quad \dot{a}_2 \simeq -i \frac{\Omega^*}{2} a_1 e^{-i \Delta t} .
\] (5.84)

With the equations of motion we can, starting from initial values for \( a_1(0) \) and \( a_2(0) \), calculate the temporal evolution.

We solve this system of differential equations by differentiating one and substituting the other,

\[
\dot{a}_2 = -i a_1 \frac{\Omega^*}{2} e^{-i \Delta t} - a_1 \Delta \frac{\Omega^*}{2} e^{-i \Delta t} = -\frac{|\Omega|^2}{4} a_2 - i \Delta \dot{a}_2 .
\] (5.85)

We find solutions via the ansatz \( a_2 = e^{-i \Delta t/2} (A e^{i \Omega t/2} + B e^{-i \Omega t/2}) \). The equation for \( a_2 \) yields,

\[
\left( \frac{i}{2} G - \frac{i}{2} \Delta \right)^2 A e^{i(G - \Delta)t/2} + \left( \frac{-i}{2} G - \frac{i}{2} \Delta \right)^2 Be^{-i(G - \Delta)t/2} = -\frac{|\Omega|^2}{4} A e^{-i \Delta t/2} + \frac{|\Omega|^2}{4} B e^{i \Delta t/2}.
\] (5.86)

Separating the parts in \( A \) and in \( B \) we obtain two equations with the same result,

\[ G^2 = |\Omega|^2 + \Delta^2 . \] (5.87)

\( G \) is called the generalized Rabi frequency. Using the initial conditions, \( a_1(0) = 1 \) and \( a_2(0) = 0 \), we can fix one of the coefficients \( A \) and \( B \), since \( a_2(0) = A + B = 0 \),

\[ a_2 = 2i A e^{-i \Delta t/2} \sin \frac{G}{2} t . \] (5.88)

We now import this solution into the differential equation for \( a_1 \),

\[ \dot{a}_1 = -i \frac{\Omega}{2} a_2 e^{i \Delta t} = \Omega A e^{i \Delta t/2} \sin \frac{G}{2} t . \] (5.89)

The integral is,

\[ a_1(t) = \int_0^t \Omega A e^{i \Delta t'/2} \sin \frac{G}{2} t' dt' = -\frac{2A}{\Omega^*} e^{i \Delta t/2} \left( G \cos \frac{G}{2} t - i \Delta \sin \frac{G}{2} t \right) . \] (5.90)

Using the normalization condition,

\[
1 = |a_1|^2 + |a_2|^2 = \left| -\frac{2A}{\Omega^*} e^{i \Delta t/2} \left( G \cos \frac{G}{2} t - i \Delta \sin \frac{G}{2} t \right) \right|^2 + \left| 2i A e^{-i \Delta t/2} \sin G t \right|^2
= \frac{4A^2}{|\Omega|^2} \left( G^2 \cos^2 \frac{G}{2} t + \Delta^2 \sin^2 \frac{G}{2} t \right) + 4A^2 \sin^2 \frac{G}{2} t = 4A^2 \frac{G^2}{|\Omega|^2} .
\] (5.91)

Hence, \( A = |\Omega|/2G \). In general, we can choose \( \Omega \) real, and the final solution is,

\[
\frac{a_1(t)}{G} = -e^{i \Delta t/2} \left( \cos \frac{G}{2} t + \frac{-i \Delta}{G} \sin \frac{G}{2} t \right) \quad \text{and} \quad \frac{a_2(t)}{G} = \frac{i}{G} e^{-i \Delta t/2} \sin \frac{G}{2} t .
\] (5.92)

This result has already been obtained in 2.4.6.1 using a different approach. When the energies \( E_n \) are degenerate, under the influence of the perturbation, the populations of the system oscillate with the Rabi frequency \( \Omega \). When the energies are different, the oscillation frequency \( G \) is higher, but the amplitude
decreases as well. The initially empty state never reaches unitary population. In Exc. 5.4.6.3 we calculate the time required to allow the perturbation to invert the population of a two-level system, in Exc. 5.4.6.4 we study the maximum achievable inversion as a function of detuning, and in Exc. 5.4.6.5 we analyze the dynamics of a system subject to sequences of pulses.

Figure 5.4: (code) Probability $|a_2(t)|^2$ for the atom to be in the excited state for $\Omega = \Gamma$ and $\Delta = 0$ (blue), $\Delta = \Gamma$ (green), and $\Delta = 2.5\Gamma$ (red). Time is in units of $1/\Gamma$.

Note, that the Rabi formula (5.92) can be derived exactly without perturbative calculus. In Exc. 5.4.6.6 we show a derivation using the Laplace transformation method.

5.4.3.3 Transitions to continuous levels

When there are several final states, $f \in F$, the formula (5.78) must be generalized. The total transition probability,

$$P_{i \rightarrow F}(t) = \sum_{f \in F} |a_{i \rightarrow f}(t)|^2,$$

(5.93)

corresponds to the probability of the initial state $|i\rangle$ to be depleted. When the final state lies within a continuum, the sum in (5.93) must be replaced by an integral. With the density of states written in the form $\rho(E)$, where $\rho(E)dE$ is the number of states found in the energy range between $E$ and $E + dE$, the transition probability is

$$P_{i \rightarrow F}(t) = \int_{E_{\text{min}}}^{E_{\text{max}}} |a_{i \rightarrow f}(t)|^2 \rho(E_f)dE_f,$$

(5.94)

where $E \in [E_{\text{min}}, E_{\text{max}}]$ is the regime of energies within reach of the periodic perturbation. Now,

$$P_{i \rightarrow F}(t) = \int_{E_{\text{min}}}^{E_{\text{max}}} |\Omega_{fi}|^2 \frac{\sin^2 \frac{1}{2\hbar}(E_{fi} - E)t}{\frac{1}{4\pi^2}(E_{fi} - E)^2} \rho(E_f)dE_f .$$

(5.95)

Using the representation of the Dirac function,

$$\delta(x) = \lim_{t \rightarrow \infty} \frac{1}{\pi} \sin^2 \pi x t ,$$

(5.96)

12With $\rho(E) \equiv \sum_{f \in F} \delta(E_f - E)$ the integral is converted back into a sum.
with the substitution \( x \equiv (E_{fi} - E) / \hbar \), we obtain after sufficiently long times \(^{13}\),

\[
P_{i \rightarrow F}(t) = \int_{E_{\text{min}}}^{E_{\text{max}}} |\Omega_{fi}|^2 t^2 \frac{\pi}{\hbar} \delta\left(\frac{E_{fi} - E}{\hbar}\right) \rho(E_f) dE_f = 2\pi \hbar t |\Omega_{fi}|^2 \rho(E_i + E) .
\]

(5.97)

The transition rate is,

\[
\frac{dP_{i \rightarrow F}(t)}{dt} = \pi |\Omega_{fi}|^2 \rho(E_i + E) .
\]

(5.98)

For narrow distributions we may substitute the density of states \( \rho \) by a \( \delta \)-distribution,

\[
\frac{dP_{i \rightarrow F}}{dt} = \frac{2\pi}{\hbar} |\langle f | \hat{H}^{(1)} | i \rangle|^2 \delta(E_{fi} - E) ,
\]

(5.99)

where we went back to the definition of the perturbation Hamiltonian (5.76). This expression is called Fermi’s Golden rule. In Exc. 5.4.6.7 we will calculate the photoelectric effect.

### 5.4.3.4 Continuous frequency distribution

To derive Eq. (5.78), we considered perturbations with fixed oscillation frequencies. To handle frequency distributions \( \varrho(\omega) \), we must generalize this equation by calculating the integral,

\[
| a_{i \rightarrow f}(t) |^2 = |\Omega_{fi}|^2 \int \varrho(\omega) \frac{\sin^2 \frac{1}{2} (\omega_{fi} - \omega)t}{\frac{1}{4} (\omega_{fi} - \omega)^2} d\omega
\]

\[
\simeq |\Omega_{fi}|^2 t \varrho(\omega_{fi}) \int_{-\infty}^{\infty} \text{sinc}^2 x dx = \pi t |\Omega_{fi}|^2 \varrho(\omega_{fi} - \omega) ,
\]

(5.100)

again using the representation (5.96) of the Dirac function. The approximation \( \varrho(\omega) = \varrho(\omega_{fi}) \) can be used if the width of the sinc function is much narrower than the frequency distribution, which is the case for sufficiently long times, \( t \gg \pi / 2\Delta_{fi} \).

### 5.4.4 Numerical methods

The softwares ‘Maple’ or ‘Mathematics’ are useful for analytical calculations, that is, multiplying matrices or determining eigenvalues. For numerical calculations the software ‘Matlab’ is more adapted. For example, the time evolution of a Schrödinger equation,

\[
|\psi(t)\rangle = e^{-i \hat{H}t/\hbar} |\psi(0)\rangle ,
\]

(5.101)

can be calculated in a single command line using the Matlab ‘expm’ function.

When the system varies temporally, \( \hat{H}(t) \), we may divide time into small units \( dt \) and propagate the wavefunction as,

\[
|\psi(t + dt)\rangle = e^{-i \hat{H}(t)dt/\hbar} |\psi(t)\rangle \simeq |\psi(t)\rangle \left( 1 - i \frac{\hat{H} dt}{\hbar} \right) ,
\]

(5.102)

\(^{13}\)Remember \( \delta(ax) = \frac{1}{a} \delta(x) \).
continuously reinserting the solution into the equation. This Newton method does not converge quickly \((dt\) should be chosen small enough, when \(\hat{H}(t)\) varies rapidly), but there are other more sophisticated methods like the Runge-Kutta method.

A variation of this method is called steepest descent method. This method is similar to the Newton Eq. (5.102), but replaces the time \(dt\) with an imaginary time. Thus, the coherent temporal evolution of the Schrödinger equation is replaced by a dissipative evolution. The loss of energy automatically takes the system to the ground state. The method also applies to more complicated equations than the Schrödinger equation, for example, the Gross-Pitaevskii equation.

Figure 5.5: Condensate wavefunction (red) in a double-well potential (blue) numerically calculated using the steepest descent method. Also shown is the chemical potential (green).

Another numerical method often used in quantum mechanics is the method called the quantum Monte Carlo simulation of the wavefunction [429]. This method simulates trajectories of quantum systems treating intrinsic quantum noise as random processes disrupting the uniformity of the trajectory. The advantage of this method is that it also applies to dissipative systems.

### 5.4.5 Transition rates for higher-order perturbations

The evolution from an initial state \(\ket{i}\) that the system occupies at time \(t_0\) to some final state \(\ket{\psi}\), which may be a superposition, occupied at time \(t\) is ruled by the solution of the Schrödinger equation,

\[
\ket{\psi} = e^{-i\hat{H}(t-t_0)/\hbar}\ket{i}.
\]  

The probability to encounter \(\ket{\psi}\) in a given state \(\ket{f}\) is \(|\langle f | \psi \rangle|^2\), and has the transition rate is simply the derivative of this. The transition rate out of the initial state into any other final state is, consequently

\[
\frac{1}{\tau} = \sum_f \frac{d}{dt} |\langle f | e^{-i\hat{H}(t-t_0)/\hbar}|i \rangle|^2. 
\]  

Let us now consider a time-independent perturbation in the Schrödinger picture,

\[
\hat{H}(t) = \hat{H}^{(0)} + \hat{H}^{(1)},
\]  

(5.105)
where the time dependence is entirely left to the wavefunction. Now, we expand the propagator $e^{-i\hat{H}(t-t_0)}$ in a perturbative series. Unfortunately, $[\hat{H}^{(0)}, \hat{H}^{(1)}] \neq 0$, so that $e^{-i\hat{H}t} \neq e^{-i\hat{H}^{(0)}t}e^{-i\hat{H}^{(1)}t}$. But we can calculate,

$$i \frac{d}{dt} e^{i\hat{H}^{(0)}t} e^{-i\hat{H}t} = -\hat{H}^{(0)} e^{i\hat{H}^{(0)}t} + e^{i\hat{H}^{(0)}t} \hat{H}(t) e^{-i\hat{H}t} = e^{i\hat{H}^{(0)}t} \hat{H}(1) e^{-i\hat{H}t}. \quad (5.106)$$

Integrating both sides and resolving for $e^{-i\hat{H}t}$,

$$e^{-i\hat{H}t} = e^{-i\hat{H}^{(0)}t} \left\{ 1 - i \int_{-\infty}^{t} e^{i\hat{H}^{(0)}t_1} \hat{H}(1) e^{\varepsilon t_1} e^{-i\hat{H}t_1} dt_1 \right\}. \quad (5.107)$$

We want to analyze a steady-state situation, that is, we assume that the interaction as gradually built up in an infinitely remote past. Hence, we can set $\hat{H} = \hat{H}^{(0)}$ for $t_0 \to -\infty$,

$$e^{-i\hat{H}t} = e^{-i\hat{H}^{(0)}t} \left\{ 1 - i \int_{-\infty}^{t} e^{i\hat{H}^{(0)}t_1} \hat{H}(1) e^{\varepsilon t_1} e^{-i\hat{H}t_1} dt_1 \right\}, \quad (5.108)$$

where the term $e^{\varepsilon t_1}$, where $\varepsilon \to 0$, is inserted to guarantee a smooth switch-on. We iterate,

$$e^{-i\hat{H}t} = e^{-i\hat{H}^{(0)}t} \left\{ 1 - i \int_{-\infty}^{t} e^{i\hat{H}^{(0)}t_1} \hat{H}(1) e^{\varepsilon t_1} \times \right.$$  

$$\left. \times \left. e^{-i\hat{H}^{(0)}t} \left\{ 1 - i \int_{-\infty}^{t_1} e^{i\hat{H}^{(0)}t_2} \hat{H}(1) e^{\varepsilon t_2} e^{-i\hat{H}t_2} dt_2 \right] dt_1 \right\}. \quad (5.109)$$

We calculate the matrix elements up to second order substituting $\hat{H}$ with $\hat{H}^{(0)}$ in the last integral,

$$\langle f | e^{-i\hat{H}t} | i \rangle \quad (5.110)$$

$$\simeq \langle f | e^{-i\hat{H}^{(0)}t} \left\{ 1 - i \int_{-\infty}^{t} e^{i\hat{H}^{(0)}t_1} \hat{H}(1) e^{\varepsilon t_1} e^{-i\hat{H}^{(0)}t_1} \right\} \left\{ 1 - i \int_{-\infty}^{t_1} e^{i\hat{H}^{(0)}t_2} \hat{H}(1) e^{\varepsilon t_2} e^{-i\hat{H}^{(0)}t_2} dt_2 \right\} dt_1 \right\} | i \rangle$$

$$= e^{-i\omega_f t} \langle f | i \rangle - i e^{-i\omega_f t} \int_{-\infty}^{t} e^{i\omega_f t_1} \langle f | \hat{H}(1) | i \rangle e^{\varepsilon t_1} e^{-i\omega_f t_1} dt_1$$

$$- e^{-i\omega_f t} \int_{-\infty}^{t} e^{i\omega_f t_1} \langle f | \hat{H}(1) | i \rangle e^{-i\omega_f t_1} \sum_m |m\rangle \langle m| \int_{-\infty}^{t_1} e^{i\hat{H}(0)t_2} \hat{H}(1) | i \rangle e^{\varepsilon t_2} e^{-i\omega_f t_2} dt_2 dt_1 .$$

where we separated the perturbation orders and inserted $\sum_m |m\rangle \langle m| = 1$ using the

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14 We drop the $\hbar = 1$ for the following calculation to simplify the notation.
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They are also called closure relation. Using the time-independence of \( \hat{H}^{(1)} \),

\[
\langle f | e^{-i \hat{H}t} | i \rangle \simeq e^{-i \omega_f t} \delta_{f_i} - ie^{-i \omega_f t} \langle f | \hat{H}^{(1)} | i \rangle \int_{-\infty}^t e^{i (\omega_f - i \omega_i + \varepsilon) t_1} dt_1 \\
- e^{-i \omega_f t} \sum_m \langle f | \hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i \rangle \int_{-\infty}^t e^{i (\omega_f - i \omega_i + \varepsilon) t_1} \int_{-\infty}^{t_1} e^{i (\omega_m - i \omega_i + \varepsilon) t_2} dt_2 dt_1
\]

\[
= e^{-i \omega_f t} \delta_{f_i} - ie^{-i \omega_f t} \langle f | \hat{H}^{(1)} | i \rangle \frac{e^{i (\omega_f - i \omega_i + \varepsilon) t}}{i (\omega_f - \omega_i) + \varepsilon}
\]

\[
- e^{-i \omega_f t} \sum_m \frac{\langle f | \hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i \rangle}{i (\omega_m - \omega_i) + \varepsilon} \int_{-\infty}^t e^{i (\omega_f - i \omega_i + \varepsilon) t_1} dt_1
\]

\[
= e^{-i \omega_f t} \delta_{f_i} - i \langle f | \hat{H}^{(1)} | i \rangle \frac{e^{i (\omega_f - i \omega_i + \varepsilon) t}}{i (\omega_f - \omega_i) + \varepsilon}
- \sum_m \frac{\langle f | \hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i \rangle}{i (\omega_m - \omega_i) + \varepsilon} \frac{e^{i (\omega_f - i \omega_i + \varepsilon) t}}{i (\omega_f - \omega_i) + 2 \varepsilon}.
\]

These three terms represent the zeroth, first, and second perturbation orders of the propagation operator (5.103). They are also called Feynman propagators. Now, we can calculate the transition rate up to second order,

\[
\frac{1}{\tau} = \frac{d}{dt} \sum_f \left| \langle f | e^{-i \hat{H}t} | i \rangle \right|^2 \quad \text{(5.112)}
\]

\[
= \lim_{\varepsilon \to 0} \sum_f \left| \langle f | \hat{H}^{(1)} | i \rangle - \sum_m \frac{\langle f | \hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i \rangle}{-i i (\omega_m - \omega_i) - i \varepsilon} \right|^2 \frac{d}{dt} \frac{e^{i (\omega_f + \varepsilon) t}}{i (\omega_f - \omega_i) + \varepsilon} + \frac{2 \varepsilon e^{\varepsilon t}}{(\omega_f - \omega_i)^2 + \varepsilon^2}.
\]

The last fraction is a representation of the \( \delta \)-function. Reintroducing \( h \), we finally obtain,

\[
\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f | \hat{H}^{(1)} | i \rangle + \frac{1}{\hbar} \sum_m \frac{\langle f | \hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i \rangle}{\omega_i - \omega_m} \right|^2 \delta(\omega_f - \omega_i) \quad \text{(5.113)}
\]

The first term is Fermi’s Golden rule, the second order corresponds to the Kramers-Heisenberg formula, which serves to describe Thomson, Rayleigh and Raman scattering. The generalization of this transition rate to all perturbation orders can be written,

\[
\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f | \hat{H}^{(1)} | i \rangle + \frac{1}{\hbar} \sum_m \frac{\hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i \rangle}{\omega_i - \omega_m} + \ldots \right|^2 \delta(\omega_f - \omega_i) \quad \text{(5.114)}
\]

\[
+ \frac{1}{\hbar^{n-1}} \sum_{m_1, \ldots, m_{n-1}} \frac{\hat{H}^{(1)} | m_1 \rangle \langle m_1 | \ldots | m_{n-1} \rangle \langle m_{n-1} | \hat{H}^{(1)} | i \rangle}{(\omega_i - \omega_{m_1}) \ldots (\omega_i - \omega_{m_{n-1}})} \delta(\omega_f) .
\]
5.4.6 Exercises

5.4.6.1 Ex: Perturbed harmonic oscillator

Consider a one-dimensional harmonic oscillator (HO) initially prepared \((t = -\infty)\) in the ground state \(|0\rangle\) of the unperturbed Hamiltonian \(H(0) = \hbar \omega \hat{a}^{\dagger} \hat{a}\), such that \(H(0)|n\rangle = E_n|n\rangle\) with \(E_n = n\hbar \omega\).

a. Through the expression, \(a_f(t) \approx \frac{1}{\hbar} \int_{t_i}^{t_f} W_f e^{i\omega_f t} dt\), and the perturbative Hamiltonian \(W(t) = -e \mathcal{E} x e^{-t^2/\tau^2}\) (\(x\) is the position operator of the HO), applied between \(t = -\infty\) and \(t = +\infty\), calculate the probability of the system to be in the excited state \(|n\rangle\), specifying \(n\), at \(t = +\infty\). Analyze the result.

b. Do the same for a shape-changing perturbation, \(W(t) = \Lambda x^2 e^{-t^2/\tau^2}\).

5.4.6.2 Ex: Impact of the rapidity of a perturbation

Here we consider a slow variation, 

\[
\dot{W}(t) = \begin{cases} 
0 & \text{for } t < 0 \\
W_0(1 - e^{-\gamma t}) & \text{for } t \geq 0 
\end{cases}
\]

with \(\gamma \ll \omega_f\).

a. Calculate the transition rate for long times, \(t \gg \gamma^{-1}\).

b. Analyze the transition rate at a given time as a function of \(\gamma\).

5.4.6.3 Ex: Rabi oscillation

The population of a degenerate two-level system be initially in state \(|1\rangle\). What should be the duration of a perturbation to transfer the population to state \(|2\rangle\)?
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5.4.6.4 **Ex: Rabi method**

Free atoms be illuminated by light pulses characterized by the Rabi frequency $\Omega$, whose pulse area is (i) $\int_0^t \Omega \, dt = \pi$ and (ii) $= 2\pi$. For which frequency tuning $\Delta = \omega - \omega_0$ the excited state population is maximum? Draw the spectral profile of the population in the range $-5 < \Delta/\Omega < 5$.

5.4.6.5 **Ex: Ramsey fringes**

a. Consider a two-level atom illuminated by a $\pi/2$-pulse of nearly resonant light, $G \simeq \Omega$, and calculate the ground and excited state amplitudes.

b. How do the amplitudes evolve after the pulse, if the detuning $\Delta$ is small but non-zero?

c. Derive the solution for $|a_2(t)|^2$ of the equations (5.63) for the resonant case ($\Delta = 0$) assuming the following initial conditions, $a_2(0) = e^{i\phi}/\sqrt{2}$ and $a_2(t = \pi/\Omega) = 0$ if $\phi = 0$.

d. Discuss the case of two consecutive $\pi/2$-pulses separated by a time interval $T$.

5.4.6.6 **Ex: Two-level atom via Laplace transformation**

Solve the problem of a two-level atom interacting with a laser using the Laplace transformation method.

5.4.6.7 **Ex: Photoelectric effect**

A hydrogen atom ground state in the ground state 1s is placed in an electric field $E(t) = E_0 \cos \omega t$, such that $W(t) = -e \mathbf{r} \cdot \mathbf{E}(t) = W_0 e^{-i\omega t} + W_0^* e^{i\omega t}$ with $W_0 = e \mathbf{r} \cdot \mathbf{E}_0/2$. Find, via Fermi’s Golden rule, $R = 2\pi \hbar |\langle f | W(t)|i \rangle|^2 \rho(E_f - E_i \mp \hbar \omega)$, using the density of states $\rho(E_k)dE_k = V/(2\pi)^3 k^2 dk d\Omega$, the probability per unit of time for the atom to be ionized, by exciting from the ground state $\psi_{100}(\mathbf{r}) = e^{-r/a_B}/(\pi a_B^3)^{1/2}$ to the state described by the plane wave $\psi_k(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{r}} / V^{1/2}$. Simplify the calculation by assuming $\mathbf{E}_0 = E_0 \mathbf{e}_z$ and $\mathbf{k} = k \mathbf{e}_z$.

5.4.6.8 **Ex: Kicked harmonic oscillator in second order perturbation**

Consider a one-dimensional harmonic oscillator initially in its ground state kicked via the $\hat{H}^{(1)}(t) = e^{ikz} \Theta(t)$, as discussed in Sec. 4.5.2. Calculate the transition rate (5.104) to the final state $|f\rangle = |0\rangle$ in first and second order perturbation theory.
Chapter 6

Periodic systems

Many physical systems treat quantum particles in periodic potential. Examples are electrons in crystals or cold atoms in optical lattices. The periodicity adds a wealth of new phenomena.

6.1 The Bloch model

The motion of an electron inside a crystal is ruled by a spatially periodic potential $V(r)$ originating from the positively charged crystal atoms and the mean field produced by the quasi-free electrons,

$$V(r) = V(r + R) \quad ,$$

(6.1)

where $R$ is a vector connecting two arbitrarily chosen atoms of the lattice. With the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (6.2)$$

we can write the Schrödinger equation,

$$[\hat{H} + V(r)] \psi(r) = E \psi(r) \quad .$$

(6.3)

Since $V$ and $\nabla$ are invariant under translations $U_{tr}(R) \psi(r) \equiv \psi(r + R)$ by a fixed distance $R$, where the translation operator has been defined in Eq. (2.171), we have,

$$\hat{H} U_{tr}(R) \psi(r) = EU_{tr}(R) \psi(r) \quad .$$

(6.4)

That is, for a non-degenerate eigenvalue $^1$,

$$\psi(r + R) = f(R) \psi(r) \quad .$$

(6.5)

This relation holds for all vectors $R$ of the lattice, such that,

$$f(R_1 + R_2) \psi(r) = \psi(r + R_1 + R_2) = f(R_1) \psi(r + R_2) = f(R_1) f(R_2) \psi(r) \quad .$$

(6.6)

The relationship $f(R_1 + R_2) = f(R_1) f(R_2)$ is satisfied by the ansatz $f(R) \equiv e^{i k \cdot R}$, where $k$ is an arbitrary vector of reciprocal space. We get the famous Bloch theorem,

$$\psi_k(r + R) = e^{i k \cdot R} \psi_k(r) \quad ,$$

(6.7)

$^1$This also holds true for degenerate eigenvalues if we choose suitable basis of eigenvectors.
which represents a necessary condition for any eigenfunction \( \psi_k \) of the Schrödinger equation with periodic potential. Bloch’s theorem simply postulates that, apart from a phase factor, the wavefunction has the same periodicity as the potential.

The *Bloch function*,

\[
\psi_k(r) \equiv u_k(r)e^{ik \cdot r} \quad \text{with} \quad u_k(r + R) = u_k(r),
\]

(6.8)

automatically satisfies Bloch’s theorem. That is, the wave function of the electron \( \psi \) is a plane wave \( e^{ik \cdot r} \) modulated by a function \( u_k \) having the same periodicity as the lattice [351]. Although the vector of the electronic wave is arbitrary, it is possible (and useful) to restrict its value to the first Brillouin zone defined by \( k \in [-\pi/a, \pi/a] \), where \( a \) is an elementary vector of the lattice. The reason is that we can reduce a wavevector \( k \) in a wavefunction trespassing the first Brillouin zone by an appropriate vector \( G \) of reciprocal lattice,

\[
k' = k + G,
\]

(6.9)
yielding,

\[
\psi_k(r) = u_k(r)e^{ik \cdot r} = u_k(r)e^{-iG \cdot r}e^{ik' \cdot r}.
\]

(6.10)

We now define another function \( u_{k'}(r) \equiv u_k(r)e^{-iG \cdot r} \), which also satisfies the requirement (6.8), knowing that \( G \cdot R = n2\pi \), we see,

\[
u_{k'}(r + R) = u_k(r + R)e^{-iG \cdot (r + R)} = u_k(r)e^{-iG \cdot r} = u_k(r).
\]

(6.11)

Hence,

\[
\psi_k(r) = u_{k'}(r)e^{ik' \cdot r} = \psi_{k'}(r).
\]

(6.12)

### 6.1.1 Approximation for quasi-bound electrons

We now assume that the behavior of the electron near an atom is not influenced by atoms farther apart,

\[
\psi_k(r) = \sum_{i \in \text{lattice}} c_i(k)\phi(r - R_i).
\]

(6.13)

That is, we neglect superposition states of the electron at various sites of the lattice. The atom is subject to a potential \( U_{at}(r - R_i) \) located near the atom at the position \( R_i \), and it is described by the eigenfunction \( \phi(r - R_i) \) (only defined for the site \( i \)) with energy \( E_0 \),

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + U_{at}(r - R_i) \right] \phi(r - R_i) = E_0\phi(r - R_i).
\]

(6.14)

Even so, the function \( \psi_k(r) \) must satisfy Bloch’s theorem. This is the case when \( c_i(k) = e^{ik \cdot R_i} \), and therefore,

\[
\psi_k(r) = \sum_{i \in \text{lattice}} e^{ik \cdot R_i}\phi(r - R_i).
\]

(6.15)

**Example 32** (*Ansatz for a quasi-bound electron wavefunction*): The ansatz (6.15) satisfies Bloch’s theorem because,

\[
\psi_k(r + R_j) = \sum_i e^{ik \cdot R_i}\phi(r - (R_i - R_j)) = e^{ik \cdot R_j}\sum_i e^{ik \cdot (R_i - R_j)}\phi(r - (R_i - R_j)) = e^{ik \cdot R_j}\psi_k(r).
\]
We now calculate the energy \( E(\mathbf{k}) \) of an electron with the wavevector \( \mathbf{k} \) inserting the function \( \psi_\mathbf{k}(\mathbf{r}) \) of (6.15) in the Schrödinger equation and obtain,

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} \phi(\mathbf{r} - \mathbf{R}_i) = E(\mathbf{k}) \sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} \phi(\mathbf{r} - \mathbf{R}_i) .
\] (6.16)

\( U(\mathbf{r}) \) is the potential energy of the electron illustrated in Fig. 6.1 together with the energy \( U_{at}(\mathbf{r} - \mathbf{R}_i) \) of a free electron.

Substituting the kinetic energy term of (6.16) by the kinetic energy of (6.14), we calculate,

\[
\sum_i e^{i\mathbf{k}\cdot\mathbf{R}_i} [-U_{at}(\mathbf{r} - \mathbf{R}_i) + E_0 + U(\mathbf{r}) - E(\mathbf{k})] \phi(\mathbf{r} - \mathbf{R}_i) = 0 .
\] (6.17)

Now, multiplying this equation with \( \psi_\mathbf{k}^*(\mathbf{r}) = \sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j} \phi^*(\mathbf{r} - \mathbf{R}_j) \) and integrating over the volume of the crystal, we obtain,

\[
[E(\mathbf{k}) - E_0] \sum_{i,j} e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)} \int \phi^*(\mathbf{r} - \mathbf{R}_j) \phi(\mathbf{r} - \mathbf{R}_i) dV = \sum_{i,j} e^{i\mathbf{k}\cdot(\mathbf{R}_j - \mathbf{R}_i)} \int \phi^*(\mathbf{r} - \mathbf{R}_j) [U(\mathbf{r}) - U_{at}(\mathbf{r} - \mathbf{R}_i)] \phi(\mathbf{r} - \mathbf{R}_i) dV .
\] (6.18)

The functions \( \phi^*(\mathbf{r} - \mathbf{R}_j) \) and \( \phi(\mathbf{r} - \mathbf{R}_i) \) overlap only a little, even for adjacent atoms, such that we can neglect the terms \( i \neq j \) on the left side. The sum then corresponds to the number \( N \) of sites in the lattice. On the right side we can not neglect the terms involving other sites, because even if the wavefunctions of adjacent sites overlap little, the contribution of the potential difference \( |U(\mathbf{r}) - U_{at}(\mathbf{r} - \mathbf{R}_i)| \) is much lower for \( \mathbf{r} = \mathbf{R}_i \) than for \( \mathbf{r} = \mathbf{R}_j \). On the other hand, as the wavefunctions \( \phi(\mathbf{r} - \mathbf{R}_i) \) disappear quickly when \( |\mathbf{r} - \mathbf{R}_i| > |\mathbf{R}_m - \mathbf{R}_i| \), we can focus on adjacent sites (called \( \mathbf{R}_m \))

\[
N[E(\mathbf{k}) - E_0] = N \int \phi^*(\mathbf{r} - \mathbf{R}_i) [U(\mathbf{r}) - U_{at}(\mathbf{r} - \mathbf{R}_i)] \phi(\mathbf{r} - \mathbf{R}_i) dV
\] (6.19)

\[
+ N \sum_{m=\text{adjacent}} e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_m)} \int \phi^*(\mathbf{r} - \mathbf{R}_m) [U(\mathbf{r}) - U_{at}(\mathbf{r} - \mathbf{R}_i)] \phi(\mathbf{r} - \mathbf{R}_i) dV .
\]

Now we further suppose that the eigenfunction \( \phi \) exhibits radial symmetry corresponding to an \( s \) orbital. We obtain for the eigenvalues from the Schrödinger equation,

\[
E(\mathbf{k}) = E_0 - \alpha - \gamma \sum_{m=\text{adjacent}} e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_m)}
\] (6.20)

with \( \alpha = \int \phi^*(\mathbf{r} - \mathbf{R}_i) [U_{at}(\mathbf{r} - \mathbf{R}_i) - U(\mathbf{r})] \phi(\mathbf{r} - \mathbf{R}_i) dV \)

and \( \gamma = \int \phi^*(\mathbf{r} - \mathbf{R}_m) [U_{at}(\mathbf{r} - \mathbf{R}_i) - U(\mathbf{r})] \phi(\mathbf{r} - \mathbf{R}_i) dV \).

The interpretation is as follows: The combination of the atoms in a lattice produces an energy displacement \( \alpha \). In addition, it generates a splitting into a continuous band of energies as a function of reduced wavevector \( \mathbf{k} \)...
6.1.2 Approximation for quasi-free electrons

Here we assume an essentially homogeneous potential acting on the free electrons and consider the impact of the periodic lattice as a small perturbation. The periodic potential can be decomposed into a Fourier series by the vectors $\mathbf{G}$ of the reciprocal lattice,

$$U(r) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i \mathbf{G} \cdot \mathbf{r}}. \quad (6.21)$$

Consequently, we can make for Bloch functions (6.10) the following periodic ansatz,

$$\psi_k(r) = u_k(r) e^{i \mathbf{k} \cdot \mathbf{r}} \quad \text{with} \quad u_k(r) = \frac{1}{\sqrt{V_c}} \sum_{\mathbf{G}} u_{\mathbf{G}}(\mathbf{k}) e^{i \mathbf{G} \cdot \mathbf{r}}, \quad (6.22)$$

where $V_c$ is the volume of the crystal.

Without periodic potential, the eigenfunctions would be those of a free particle,

$$\psi_k(r) = \frac{1}{\sqrt{V_c}} e^{i \mathbf{k} \cdot \mathbf{r}} \quad (6.23)$$

with the eigenenergies

$$E_0(\mathbf{k}) = V_0 + \frac{\hbar^2 k^2}{2m}. \quad (6.24)$$

Inserting the functions (6.21) and (6.22) in the Schrödinger equation, we obtain,

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \sum_{\mathbf{G}''} U_{\mathbf{G}''} e^{i \mathbf{G}'' \cdot \mathbf{r}} \right] \frac{1}{\sqrt{V_c}} e^{i \mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{G}'}(\mathbf{k}) e^{i \mathbf{G}' \cdot \mathbf{r}} = E(\mathbf{k}) \frac{1}{\sqrt{V_c}} e^{i \mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{G}'}(\mathbf{k}) e^{i \mathbf{G}' \cdot \mathbf{r}},$$

that is,

$$\frac{1}{\sqrt{V_c}} \sum_{\mathbf{G}'} \left[ -\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G}')^2 - E(\mathbf{k}) \right] u_{\mathbf{G}'}(\mathbf{k}) e^{i \mathbf{k} + \mathbf{G}' \cdot \mathbf{r}} + \frac{1}{\sqrt{V_c}} \sum_{\mathbf{G}''} U_{\mathbf{G}''} e^{i \mathbf{G}'' \cdot \mathbf{r}} \sum_{\mathbf{G}'} u_{\mathbf{G}'}(\mathbf{k}) e^{i \mathbf{G}' \cdot \mathbf{r}} = 0. \quad (6.25)$$

Now multiplying with $\frac{1}{\sqrt{V_c}} e^{i (\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$ and integrating over the volume of the crystal (knowing $\frac{1}{V_c} \int_{V_c} e^{i \mathbf{G} \cdot \mathbf{r}} dV = \delta_{\mathbf{G} \cdot \mathbf{G}}$), we obtain,

$$\left[ \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 - E(\mathbf{k}) \right] u_{\mathbf{G}}(\mathbf{k}) + \sum_{\mathbf{G}'} U_{\mathbf{G} - \mathbf{G}'} u_{\mathbf{G}'}(\mathbf{k}) = 0, \quad (6.27)$$
6.1. THE BLOCH MODEL

for any value of $\mathbf{G}$.

To estimate the dependence of the Fourier components $u_{\mathbf{G}}(\mathbf{k})$ for $\mathbf{G} \neq 0$ we insert the unperturbed eigenenergies into the equation (6.27) only considering, in the sum over $\mathbf{G}'$, the terms of the first perturbative order, that is, those containing $U_0$ or $u_0(\mathbf{k})$,

$$\frac{\hbar^2}{2m}[(\mathbf{k} + \mathbf{G})^2 - \mathbf{k}^2]u_{\mathbf{G}}(\mathbf{k}) - U_0u_{\mathbf{G}}(\mathbf{k}) + U_0u_{\mathbf{G}}(\mathbf{k}) + U_{\mathbf{G}}u_{\mathbf{G}}(\mathbf{k}) = 0$$  \hfill (6.28)

$$u_{\mathbf{G}}(\mathbf{k}) = \frac{U_{\mathbf{G}}u_0(\mathbf{k})}{\frac{\hbar^2}{2m}[k^2 - (\mathbf{k} + \mathbf{G})^2]}.$$  \hfill (6.29)

Since the Fourier coefficients $U_{\mathbf{G}}$ have, for $\mathbf{G} \neq 0$, small values, the function $u_{\mathbf{G}}(\mathbf{k})$ is not negligible only for $k^2 \simeq (\mathbf{k} + \mathbf{G})^2$ that is,

$$-2\mathbf{k} \cdot \mathbf{G} \simeq |\mathbf{G}|^2.$$  \hfill (6.30)

We now want to find out the meaning of this condition ...

For the coefficients $u_0(\mathbf{k})$ and $u_{\mathbf{G}}(\mathbf{k})$ we obtain,

$$\left[\frac{\hbar^2}{2m}k^2 - E(\mathbf{k})\right]u_0(\mathbf{k}) + U_0u_0(\mathbf{k}) + U_{-\mathbf{G}}u_{\mathbf{G}}(\mathbf{k}) = 0$$  \hfill (6.31)

$$\left[\frac{\hbar^2}{2m}k^2 - E(\mathbf{k})\right]u_{\mathbf{G}}(\mathbf{k}) + U_{\mathbf{G}}u_{\mathbf{G}}(\mathbf{k}) + U_0u_{\mathbf{G}}(\mathbf{k}) = 0.$$  

From this follows,

$$\left[\frac{\hbar^2}{2m}k^2 + U_0 - E(\mathbf{k})\right]^2 = U_{\mathbf{G}}U_{-\mathbf{G}} = 0.$$  \hfill (6.32)

Since the potential $U(\mathbf{r})$ is real, $U_{-\mathbf{G}} = U_{\mathbf{G}}^*$. Therefore, introducing the eigenenergies $E_0(\mathbf{k})$ of free electrons (6.24),

$$E(\mathbf{k}) = E_0(\mathbf{k}) \pm |U_{\mathbf{G}}|.$$  \hfill (6.33)

Under the influence of the periodic perturbation potential we find at the surfaces of a Brillouin zone an energy splitting developing a forbidden gap in the spectrum. We can understand this observation as follows: In the crystal all electronic waves with wavevectors ending on a surface of a Brillouin zone are reflected by Bragg reflection. In the example of a one-dimensional lattice we understand that the superposition of an incident wave ($k = n\pi/a$) with the reflected one ($k = -n\pi/a$) produces a standing electronic probability density wave $\rho$ being proportional to $\rho_1 \propto \cos^2 n\pi/a$ or $\rho_2 \propto \sin^2 n\pi/a$. The charge density $\rho_1$ is maximal at the location of the atom in this site, which corresponds to an increased interaction energy; the density $\rho_2$ is minimal at the location of the atom. This explains the splitting.

The Bloch model can explain many properties of metals, semiconductors and insulators.

6.1.3 Application to one-dimensional optical lattices

In the following, we restrict ourselves to a one-dimensional potential, $V(z) = V(z + a)$, acting on (the center-of-mass of) atoms. Such a potential can be generated by two
counterpropagating plane wave laser beams with wavevectors $k_L$ and $-k_L$ and tuned to the red side of an atomic transition. In this situation the atoms are attracted to the maxima of the light intensity, the antinodes. Therefore, we can write the potential as

$$V(z) = -V_0 |e^{ik_Lz} + e^{-ik_Lz}|^2 = -V_0(1 + \cos 2k_Lz)$$

or, by letting $K = 2k_L$,

$$V(z) = -2V_0 \cos^2 Kz . \quad (6.34)$$

In the Fourier expansion, $V(z) = \sum_K U_K e^{iKz}$, this potential corresponds to the Fourier coefficients $U_0 = -V_0$ and $U_{\pm K} = -V_0/2$,

$$V(z) = -V_0(1 + \frac{1}{2} e^{2ik_Lz} + e^{-2ik_Lz}) . \quad (6.35)$$

We also expand the wavefunction into plane waves,

$$\psi(z) = \sum_q c_q e^{iqz} , \quad (6.36)$$

and we insert these expansions into Schrödinger’s stationary equation $\hat{H}\psi = \varepsilon\psi$, yielding,

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \sum_K U_K e^{iKz} \right] \sum_q c_q e^{iqz} = \varepsilon \sum_q c_q e^{iqz} . \quad (6.37)$$

Defining $q = k + nK$, where $k \in [-K/2, K/2]$ and $n \in \mathbb{Z}$,

$$\left[ \frac{\hbar^2}{2m} (nK + k)^2 - V_0 \right] c_{nK+k} - \frac{1}{2} V_0 c_{nK+k-K} - \frac{1}{2} V_0 c_{nK+k+K} = \varepsilon c_{nK+k} . \quad (6.38)$$

In matrix notation,

$$\hat{H} c = \varepsilon c . \quad (6.39)$$

where the matrix is around $n = ..., -1, 0, +1, ..:$

$$\hat{H} = \begin{pmatrix} \vdots & \vdots & \vdots \\ \frac{\hbar^2}{2m} (k - K)^2 - V_0 & -\frac{1}{2} V_0 & \frac{\hbar^2}{2m} k^2 - V_0 \\ -\frac{1}{2} V_0 & \frac{\hbar^2}{2m} k^2 - V_0 & -\frac{1}{2} V_0 \\ \vdots & \vdots & \vdots \end{pmatrix} , \quad c = \begin{pmatrix} \vdots \\ c_{k-K} \\ c_k \\ c_{k+K} \\ \vdots \end{pmatrix} . \quad (6.40)$$

For shallow potentials, $V_0 \ll \hbar^2 K^2/2m$, we can neglect the coefficients $V_0$ in the Eq. (6.38) and we find,

$$\varepsilon \simeq \hbar^2 q^2 / 2m , \quad (6.41)$$

which corresponds to the dispersion relation for free particles. On the other hand, looking at the bottom of deep potentials, $V_0 \gg \hbar^2 K^2/2m$, we can harmonically approximate the cosine potential by $V(z) \approx -2V_0 + \frac{\omega^2}{2} z^2$ with $\omega = K \sqrt{V_0/m} = h^{-1} \sqrt{2V_0 E_r}$. For this case we expect,

$$\varepsilon \simeq -2V_0 + \hbar \omega \left( n + \frac{1}{2} \right) . \quad (6.42)$$
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The exact spectrum of eigenvalues $\varepsilon$ can be calculated by numerically determining the eigenvalues of the matrix (6.40) for the first Brillouin zone, $k \in [-K/2, K/2]$, and the above limits are confirmed.

To estimate the width of the forbidden band, we cut out a $2 \times 2$ matrix within the matrix $\hat{H}$ and neglect its coupling with the others submatrices,

$$\hat{H}_s = \begin{pmatrix} \frac{\hbar^2}{2m}(k - K)^2 - V_0 & -\frac{1}{2}V_0 \\ -\frac{1}{2}V_0 & \frac{\hbar^2}{2m}k^2 - V_0 \end{pmatrix}. \quad (6.43)$$

At the edges of the Brillouin zone, $k = \frac{1}{2}K$, we get the eigenvalues $\varepsilon = \frac{\hbar^2K^2}{m} - V_0 \pm \frac{V_0}{2}$, that is, the band gap is $\Delta \varepsilon = V_0^2$. Bloch’s theorem says that Schrödinger’s equation can be solved for any Bloch states. These are superpositions of plane wave momentum states [20],

$$\psi_k(z) = e^{ikz}u_k(z), \quad (6.44)$$

with $u_k(z) = u_k(z + a)$.

The requirement that $\psi(z)$ satisfies the Schrödinger equation is equivalent to the condition that $c$ satisfies an eigenvalue equation. Let $U$ be the matrix of the eigenvectors of $\hat{H}$ and $\hat{E}$ the diagonal matrix of eigenvalues: $\hat{H} = U^{-1}\hat{E}U$ gives $\hat{E}Uc = \varepsilon Uc$, such that $Uc$ can be understood as eigenvectors.

Alternatively, we define $d_{nK+k} \equiv c_{nK+k+K}/c_{nK+k}$, consequently Eq. (6.38) becomes,

$$d_{nK+k-K} = \frac{V_0}{\frac{\hbar^2}{m}(nK+k)^2 - 2\varepsilon - V_0(2 + d_{nK+k})}. \quad (6.45)$$

For Bose-Einstein condensates, the procedure should be generalized taking into account the energy of the mean field.
6.1.4 Bloch oscillations

A Bloch oscillation is a phenomenon in solid state physics. It is the oscillation of a particle (e.g., an electron) confined to a periodic potential (e.g., a crystal), when a constant force (e.g., generated by a continuous electric field) acts on it. This phenomenon is very difficult to observe in solid crystals because, due to electron scattering by defects of the lattice [131, 465], the coherent evolution is limited to a small fraction of the Brillouin zone. However, Bloch oscillations were observed in semiconducting superlattices, in ultrathin Josephson junctions and with cold atoms in optical lattices [258, 396].

Let us first show a simple treatment for electrons subject to a constant electric field $E$. The one-dimensional equation of motion is,

$$\frac{\hbar \, dk}{dt} = -eE ,$$

with the solution,

$$k(t) = k(0) - \frac{eE}{\hbar} t .$$

The velocity $v$ of the electron is given by,

$$v(k) = \frac{1}{\hbar} \frac{d\mathcal{E}}{dk} ,$$

where $\mathcal{E}(k)$ denotes the dispersion relation for a given energy band. We now assume that it has the following form (tight-binding limit),

$$\mathcal{E} = A \cos ak ,$$

where $a$ is the lattice parameter and $A$ a constant. Then, $v(k)$ is given by,

$$v(k) = -\frac{Aa}{\hbar} \sin ak ,$$

and the position of the electron by,

$$x(t) = \int v(k(t))dt = -\frac{A}{eE} \cos \left( \frac{aeE}{\hbar} t \right) .$$

This shows, that the electron is oscillating in real space. The oscillation frequency is given by,

$$\omega_B = \frac{ae|E|}{\hbar} .$$

6.1.4.1 Bloch oscillations of atoms in optical lattices

Neutral atoms in a lattice can be accelerated by gravitation. To treat this case, we simply replace the electric force $-eE$ in the above calculation by the gravitational force $mg$, and we obtain the result,

$$\omega_B = \frac{mg\lambda_L}{2\hbar} .$$
with the wavelength of the retroreflected laser \( \lambda_L = 2a \) generating the standing wave. The Bloch oscillations can be understood in various pictures. The first one, illustrated in 6.3(a), is as Bragg reflection: Being constantly accelerated, the matter wave reduces its de Broglie wavelength from \( \infty \) to a value, where it is commensurable with the periodicity of the standing light wave potential. At this moment Bragg reflection comes into play scattering the atoms back.

How does the matter wave interact with the standing light wave? This is only possible if the atom has an internal transition capable of scattering photons from the light beams. As any absorption and emission process transfers a recoil momentum to the atom, we can understand the Bragg scattering process as a Raman scattering process: a photon of the laser beam generating the optical lattice coming from the left is absorbed and re-emitted to the left. This is best illustrated in the momentum domain sketched in Fig. 6.3(b). This Raman scattering transfers twice the photonic recoil to the atom. The requirement for commensurability of the Broglie wavelength and wavelength of the standing light wave is equivalent to saying that the matter wave momentum is equal to the recoil of a single photon. In other words, the matter wave always Bragg-reflected at the edge of a Brillouin zone.

In the Bloch picture, the dispersion relation of a free particle is distorted due to the periodicity of the potential generated by the standing light wave such as to open a forbidden band. As a consequence, instead of being accelerated without limits, the atom enters the second Brillouin zone, which is to say that it is reflected to the other side of the first Brillouin zone.

![Figure 6.3: Illustration of Bloch oscillations (a) in real space, (b) in momentum space, and (c) in the moving frame. You may also run a movie of Bloch oscillations clicking on (watch movie)!](image)

To reproduce the dynamics of the matter wave, we start from the time-dependent Schrödinger equation with the same periodic potential. We now expand the time-dependent wavefunction into plane waves. By inserting this ansatz into the Schrödinger equation, we obtain a set of equations for the expansion coefficients \( c_n \), which can be simulated numerically.

Now, we also allow an external force whose potential can be added to Schrödinger’s potential. The additional term can be removed by a transformation into the moving
frame. This modifies the equations of motion for the population amplitudes of the momenta \( c_n \),

\[
\hbar \frac{\partial \hat{\psi}}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \hat{\psi}}{\partial x^2} + \frac{\hbar W_0}{2} \sin(2k_l x) \hat{\psi} - mgx \hat{\psi}.
\]  

(6.54)

The additional term, which contains the frequency of the Bloch oscillation \( \nu_b \), increases linearly over time. As time goes by, a resonance is crossed when \( t = -n \tau_b \), and the crossing is periodically repeated at every \( n = -1, -2, 0, ... \). Tracing the matter wave evolution in the laboratory system, we see that whenever the resonance is crossed, the momentum undergoes a change of sign corresponding to a reflection of its motion. We expand the population of the momentum states into plane (Bloch) waves with \( |c_n(t)|^2 \) [523, 524],

\[
\hat{\psi}(x,t) = \sum_{n=-\infty}^{\infty} c_n(t)e^{2i k_l x} \cdot e^{imgx/t}/\hbar
\]  

(6.55)

transform into the moving frame, and obtain the time dependent solution with the usual definition of the recoil frequency \( \omega_r = \frac{\hbar k_l^2 m}{2} \) and

\[
\nu_b = \frac{g}{\omega_r}.
\]  

(6.56)

The equations of motion are now written,

\[
\frac{dc_n}{dt} = -4i\omega_r (n + \nu_b t)^2 c_n + \frac{W_0}{2} (c_{n+1} - c_{n-1})
\]  

(6.57)

and the center-of-the mass momentum is,

\[
\langle p \rangle_{lab} = \sum_n n|c_n(t)|^2 + \nu_b t
\]  

(6.58)

Figure 6.4: (code) Dynamics of Bloch’s oscillations.

Of course there are some conditions that need to be met to observe Bloch oscillations. The transfer of momentum is efficient only in the rapid adiabatic passage (ARP) regime characterized by the conditions \( 2(\nu_b/\omega_r) \ll (W_0/4\omega_r)^2 \ll 16 \). The first condition requires that the force that drives the atoms to perform the Bloch
oscillations must be weak enough to avoid transitions between Bloch bands, which guarantees the adiabaticity of the process. The other condition requires that the optical lattice be weak enough so that the dynamics involves only two adjacent momentum states at the same time and the transfer between the two is successful. A talk on this subject can be watched at (watch talk).

6.1.5 Perspectives: Three-dimensional optical lattices and the Mott insulator

6.1.6 Exercises

6.1.6.1 Ex: Gaussian approximation for Wannier function

Consider a stationary light wave producing a dipolar potential of the $V(x) = W_0 \sin^2(kx) = \frac{W_0}{2} - \frac{W_0}{2} \cos 2kx \cos W_0 \gg E_r = (\hbar k)^2 / 2m$.

a. Approximate the potential of a single site around $x = 0$ for a harmonic potential.

b. Calculate for which depth of the dipolar potential the approximate potential supports at least one connected state.

c. Calculate the spacing of the levels and the length of the harmonic oscillator $a_{ho}$.

d. Use the appropriately normalized ground state of this harmonic oscillator as an approximation for the Wannier function $\omega_{0,0}(x)$. It assumes the same depth of the network in all directions of a 3D cubic network. Derive the formula $U^{3d} = \frac{8}{\pi} k a_d \left( \frac{W_0}{E_r} \right)^{3/4}$ starting from,

$$U^{3D} = g^{3D} \int \omega^4_{(0,0)}(x, y, z) d^3r$$

$$\text{com } g^{3D} = \frac{4\pi \hbar a_d}{m}.$$ 

![Figure 6.5](image)

Figure 6.5: (a) Approximation of a periodic potential by a potential harmonic. (b-c) An infinite periodic potential should be considered as free or confining?

6.1.6.2 Ex: Perturbative treatment of a weak lattice

A weak lattice potential with $V_0 < E_r$ can be treated in perturbation theory to motivate the resulting opening of a gap in the refolded energy parabola. The unperturbed Hamiltonian $\hat{H}_0 = p^2 / 2m$ contains only the kinetic energy and the perturbation is $V(x) = V_0 \sin^2(kx) = \frac{1}{2} V_0 - \frac{1}{4} V_0 (e^{2ikx} + e^{-2ikx})$.

a. Calculate $\hat{V}(x) \phi_p(x)$ and show that $\langle \phi_{p\pm\hbar k} | \hat{V} | \phi_p \rangle$ are the only non-zero matrix
elements of the perturbation $V(x)$ between the eigenstates of $\hat{H}_0$ (which are the orthonormal plane waves $\phi_p = e^{ipx/\hbar}$). Neglect the constant term of the potential, which only yields a global energy shift.

b. This coupling is relevant around those momenta $p$, where $\phi_p$ has the same energy $\phi_{p+\hbar k}$ or $\phi_{p-\hbar k}$. Show that these momenta are $p = \mp \hbar k$.

c. Consider the perturbed system restricted to the basis $\{|p = -\hbar k\rangle, |p = +\hbar k\rangle\}$ and give the Hamiltonian as 2x2 matrix.

d. Diagonalize the matrix and consider the difference of the eigenenergies. Use them to estimate the size of the gap, that the lattice opens between the two lowest bands.

e. Calculate the eigenstates and interpret them by comparing the probability density to the lattice potential.

### 6.2 The Kronig-Penney model

The Kronig-Penney model describes the band structure of a lattice. Let us assume a periodic potential of rectangular wells with valleys of widths $a$ and peaks of widths $b$,

$$V(x) = U_0 \theta_{\text{mod}(x,a+b)\in[a,a+b]}.$$  \hspace{1cm} (6.59)

Inserting into the Schrödinger equation the plane wave ansatz $\psi = Ae^{iKx} + Be^{-iKx}$ for the wavefunction in the valley, $0 < x < a$, and $\psi = Ce^{Qx} + De^{-Qx}$ in the peak, $-b < x < 0$, we obtain $\varepsilon = \hbar^2 K^2/2m$ and $U_0 - \varepsilon = \hbar^2 Q^2/2m$. Choosing the constants $A, B, C, D$ such that $\psi$ and $\dot{\psi}$ are continuous in $x = 0, a$, we derive, using the periodicity of the Bloch wave $\psi(a < x < a + b) = \psi(-b < x < 0)e^{ik(a+b)}$,

$$\begin{pmatrix} iK & 1 & -1 & -1 \\ e^{iKa} & e^{-iKa} & -Q & Q \\ iKe^{iKa} & -iKe^{-iKa} & -e^{Qb+ik(a+b)} & -e^{Qb+ik(a+b)} \\ \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = 0.$$  \hspace{1cm} (6.60)

The determinant of the matrix must be zero, or,

$$\frac{Q^2 - K^2}{2QK} \sin Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a + b).$$  \hspace{1cm} (6.61)

For $\delta$-shaped peaks, we let $b = 0$ and $U_0 = \infty$ such that $Q^2 ba/2 = P$, this simplifies to,

$$\frac{P}{Ka} \sin Ka + \cos Ka = \cos ka.$$  \hspace{1cm} (6.62)

The dispersion relation for light is different. According to [405],

$$-\sqrt{\varepsilon} + \sqrt{\varepsilon}^{-1} \sin(\sqrt{\varepsilon} \omega a/c) \sin(\omega a/c) + \cos(\sqrt{\varepsilon} \omega a/c) \cos(\omega a/c) = \cos ka.$$  \hspace{1cm} (6.63)

For $\varepsilon = 1$ the equation simplifies to $ka = 2\omega a/c$. 

6.2. THE KRONIG-PENNEY MODEL

6.2.0.1 Photonic density of states

The photonic density of states in free space in three dimensions is evaluated from [602],

\[ dN = 2 \left( \frac{L}{2\pi} \right)^3 \int d^3k = 2 \left( \frac{L}{2\pi} \right)^3 k^2 dk \int d\phi d\cos \theta = \frac{L^3 \omega^2}{\pi^2 c^3} d\omega \equiv D(\omega) d\omega. \] (6.64)

In one dimension,

\[ dN = 2 \frac{L}{2\pi} dk = \frac{L}{\pi c} d\omega. \] (6.65)

The density is normalized \( \int_0^{\pi c/L} D(\omega) d\omega = 1 \) and the total energy, if all states are populated, is \( E \equiv \int_0^{\pi c/L} \omega D(\omega) d\omega = \pi c/L. \) However, this applies only if \( \omega = ck \). If the dispersion relation is more complicated, for example, inside a cavity or a forbidden photonic band, \( \omega = \omega(k) \), we must generalize,

\[ D(\omega) = \frac{L}{\pi} \frac{dk}{d\omega}. \] (6.66)

Assuming that the dispersion relation is given by the Kronig-Penney model, we obtain gaps in the density-of-states for those values of \( \omega \) which do not belong to any \( k \).

![Figure 6.6: Dispersion ratio and state density for a one-dimensional optical lattice.](image)
Chapter 7

Appendices to ’Quantum Mechanics’

7.1 Tables for quantum mechanics

7.1.1 Constants in atomic physics

<table>
<thead>
<tr>
<th>Physical constants:</th>
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<td>Velocity of light</td>
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<tr>
<td>Planck’s constant</td>
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<td>Atomic mass unit</td>
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<td>Boltzmann constant</td>
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<td>Faraday constant</td>
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<tr>
<td>Muon mass</td>
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<tr>
<td>Proton mass</td>
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<tr>
<td>Neutron mass</td>
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<tr>
<td>Deuteron mass</td>
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<td>g-factor of the electron</td>
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<tr>
<td>g-factor of the proton</td>
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<tr>
<td>g-factor of the neutron</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Derived constants:</th>
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<tbody>
<tr>
<td>Fine-structure constant</td>
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<tr>
<td>Avogadro constant</td>
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<td>Gas constant</td>
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<td>Classical electron radius</td>
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<td>Rydberg constant</td>
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<td>Compton wavelength</td>
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<tr>
<td>Thomson cross section</td>
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</table>

<table>
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<tr>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c = 299792458 \text{ m/s}$</td>
<td>$\hbar = 1.05457266 \times 10^{-34} \text{ Js}$</td>
<td>$u = 1.6605402 \times 10^{-27} \text{ kg}$</td>
</tr>
<tr>
<td>$k_B = 1.380658 \times 10^{-23} \text{ J/K}$</td>
<td>$F = 96485.309 \text{ C/mol}$</td>
<td>$\mu_0 = 10^{-7} \text{ Vs/Am}$</td>
</tr>
<tr>
<td>$\gamma = 6.67259 \times 10^{-11} \text{ m}^3\text{kg}^{-1}\text{s}^{-2}$</td>
<td>$m_e = 9.1096 \times 10^{-31} \text{ kg}$</td>
<td>$e = 1.60217733 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>$m_{\mu} = 105.658389 \text{ MeV}$</td>
<td>$m_p = 938.27231 \text{ MeV}$</td>
<td>$m_n = 939.56563 \text{ MeV}$</td>
</tr>
<tr>
<td>$m_d = 1875.61339 \text{ MeV}$</td>
<td>$g = 2.002319304386$</td>
<td>$g = 5.5858$</td>
</tr>
<tr>
<td>$g = -3.8261$</td>
<td>$\alpha = e^2/4\pi\varepsilon_0\hbar c \approx 1/137$</td>
<td>$N_A = 1/u_A \times 1\text{ g/mol} = 6.0221367 \times 10^{23} \text{ 1/mol}$</td>
</tr>
<tr>
<td>$R = N_A k_B = 8.314510 \text{ J/mol K}$</td>
<td>$\varepsilon_0 = 1/\mu_0 c^2 = 8.8542 \times 10^{-12} \text{ As/Vm}$</td>
<td>$a_B = 4\pi\varepsilon_0 h^2/m_e e^2 = 0.529 \times 10^{-10} \text{ m}$</td>
</tr>
<tr>
<td>$\mu_B = e\hbar/2m_e = 9.27 \times 10^{-24} \text{ J/T}$</td>
<td>$r_e = \alpha^2 a_B$</td>
<td>$R_\infty = m_e c^2/2\hbar = 13.7 \text{ eV}$</td>
</tr>
<tr>
<td>$\lambda_C = h/m_e c$</td>
<td>$\sigma_e = (8\pi/3)r_e^2$</td>
<td>$\lambda_C = h/m_e c$</td>
</tr>
</tbody>
</table>
7.1.2 Atomic units

A system of units commonly used in atomic physics is the one of atomic units. This system is based on the system of Gaussian units (CGS) defined by,

\[ e_{\text{cgs}} = e / \sqrt{4 \pi \varepsilon_0} \quad , \quad a_B = 1 / \alpha \times \hbar / m_e c = \hbar^2 / m_e e_{\text{cgs}}^2 \quad , \quad \hbar = 1. \] (7.1)

With this fixing we give the energy in terms of \( e_{\text{cgs}}^2 / a_B \), the wavevector in terms of \( 1 / a_B \), the distance in terms of \( m_e \) and the mass in terms of \( m_e \), such that,

\[ \tilde{E} = E / (e_{\text{cgs}}^2 / a_B) \quad , \]
\[ \tilde{k} = k a_B \quad , \]
\[ \tilde{R} = R / a_B \quad , \]
\[ \tilde{\mu} = \mu / m_e . \]

This notation simplifies the formulas. For example:

\[ k = \sqrt{\frac{2 \mu}{\hbar^2} (E - V)} \quad \text{becomes} \quad \tilde{k} = \sqrt{2 \tilde{\mu} (\tilde{E} - \tilde{V})} , \]
\[ V = C_0 \frac{e_{\text{cgs}}^2 a_B^2}{R^6} \quad \text{becomes} \quad \tilde{V} = \frac{\tilde{C}_0}{\tilde{R}^6} . \] (7.3)

7.1.3 Clebsch-Gordan and Wigner symbols

7.1.3.1 \{3j\}-symbols

The \textit{Clebsch-Gordan coefficient} describes spin coupling. The Clebsch-Gordans are related to Wigner’s \{3j\}-symbols,

\[
\begin{pmatrix} j_1 & j_2 & j \cr m_1 & m_2 & m \end{pmatrix} = \begin{pmatrix} j_1 & j_2 & j \cr m_1 & m_2 & -m \end{pmatrix} = (-1)^{j_1 - j_2 + m} \sqrt{\Delta(j_1j_2j_3)} \times \] (7.4)

\[
\times \sqrt{(j_1 + m_1)! (j_1 - m_1)! (j_2 + m_2)! (j_2 - m_2)! (j + m)! (j - m)!} \]

\[
\sum_t t! (m_1 - j_2 + j + t)! (-j_1 - m_2 + j + t)! (j_1 + j_2 - j - t)! (j_1 - m_1 - t)! (j_2 + m_2 - t)! ,
\]

with the abbreviation,

\[ \Delta(j_1j_2j_3) \equiv \frac{(j_1 + j_2 - j_3)! (j_1 - j_2 + j_3)! (-j_1 + j_2 + j_3)!}{(j_1 + j_2 + j_3 + 1)!} . \] (7.5)

7.1.3.2 \{6j\}-symbols

The \{6j\}-symbols describes the recoupling of two spins. They can be evaluated by,

\[
\begin{pmatrix} j_1 & j_2 & j_3 \cr J_1 & J_2 & J_3 \end{pmatrix} = \sqrt{\Delta(j_1j_2j_3) \Delta(j_1J_2J_3) \Delta(j_1j_2J_3) \Delta(J_1J_2j_3) \Delta(J_1j_2J_3) \Delta(J_1J_2j_3)} \sum_t \frac{(-1)^t (t + 1)!}{f(t)} ,
\] (7.6)

where \( f(t) = (t + j_1 + j_2 + j_3)! (t - j_1 - J_2 - J_3)! (t - j_1 - J_2 - J_3)! (t - J_1 + j_2 - j_3)! (j_1 + j_2 + J_1 + J_2 - t)! (j_2 + j_3 + J_2 + J_3 - t)! (j_3 + j_1 + J_3 + J_1 - t)! .\)

\(^1\text{See the script Electrodynamics by the same author Scripts/EletroMagnetcismoScript .}\)
\(^2\text{See [24], p.111 or [591], p.119.}\)
7.1.3.3 \(\{9j\}\)-symbols

The \(\{3j\}\)-symbols describes the recoupling of three spins. They can be evaluated by,

\[
\begin{pmatrix}
  j_1 & j_2 & J_{12} \\
  j_3 & j_4 & J_{34} \\
  J_{13} & J_{24} & J
\end{pmatrix} = \sum_g (-)^{2g}(2g+1) \begin{pmatrix}
  j_1 & J_{34} & j_2 \\
  j_3 & J_{12} & j_4 \\
  J_{13} & J_{24} & g
\end{pmatrix} \begin{pmatrix}
  J_{13} & J_{24} & J
\end{pmatrix}. \tag{7.7}
\]

\(\{9j\}\)-symbols satisfy the following orthogonality relation,

\[
\sum_{J_{12},J_{34}} \hat{J}_{12} J_{34} \hat{H}_{13} \hat{H}_{24} \begin{pmatrix}
  j_1 & J_{12} \\
  j_3 & j_4 \\
  J_{13} & J_{24} & J
\end{pmatrix} \begin{pmatrix}
  j_1 & J_{12} \\
  j_3 & J_{34} \\
  J_{13} & J_{24} & J
\end{pmatrix} = \delta_{J_1 J_3} \delta_{J_2 J_4} \delta_{J_{12} J_{34}}. \tag{7.8}
\]

7.1.4 Functions and polynomials

7.1.4.1 The Gauss function

Indefinite integrals:

\[
\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a} \quad \text{and} \quad \int_{0}^{\infty} x^n e^{-ax^2} dx = \frac{\Gamma\left(\frac{n+1}{2}\right)}{2a^{n+1}}. \tag{7.9}
\]

Higher momenta:

\[
\int_{x_0}^{x_1} e^{-ax^2} dx = xe^{-ax^2}\bigg|_{x_0}^{x_1} + 2a \int_{x_0}^{x_1} x^2 e^{-ax^2} dx. \tag{7.10}
\]

7.1.4.2 Bessel functions

The integral definition of the Bessel function, the von Neumann function, and the Hankel function of the first and second kind are:

\[
J_k(x) = \frac{1}{\pi} \int_{0}^{\pi} \cos(k\tau - x\sin\tau) d\tau = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i(x\sin\tau - k\tau)} d\tau \tag{7.11}
\]

\[
N_k(x) = \ldots
\]

\[
H_k^{(1,2)} = J_k \pm iN_k.
\]

The derivative,

\[
2 \frac{dJ_k(x)}{dx} = J_{k-1}(x) - J_{k+1}(x). \tag{7.12}
\]

Sum rules (empirically found),

\[
\sum_{k=-\infty}^{\infty} J_k(x) = \sum_{k=-\infty}^{\infty} J_k(x)^2 = 1 \neq \sum_{k=-\infty}^{\infty} |J_k(x)|^2. \tag{7.13}
\]
The spherical Bessel function, the spherical von Neumann function, and the spherical Hankel function of the first and second kind are defined by:

\[ j_k(x) = \sqrt{\frac{\pi}{2x}} J_{k+1/2}(x) \]  
\[ n_k(x) = \sqrt{\frac{\pi}{2x}} N_{k+1/2}(x) = (-1)^{k+1} \sqrt{\frac{\pi}{2x}} J_{-k-1/2}(x) \]  
\[ h_k^{(1,2)} = j_k \pm in_k. \]

The series,

\[ j_k(x) = (-x)^k \left( \frac{1}{x} \frac{d}{dx} \right)^k \frac{\sin x}{x}, \quad n_k(x) = -(-x)^k \left( \frac{1}{x} \frac{d}{dx} \right)^k \frac{\cos x}{x}. \]  
\[ (7.15) \]

The derivative,

\[ j_k'(x) = \frac{k}{x} j_k(x) - j_{k+1}(x). \]  
\[ (7.16) \]

7.1.4.3 Hermite polynomials

The definition of the Hermite polynomials:

\[ H_n(x) = \left( 2x - \frac{d}{dx} \right)^n \cdot 1 = (-1)^n x^n e^{-x^2} \frac{d^n}{dx^n} e^{-x^2} = \frac{2^n}{\sqrt{\pi}} \int_{-\infty}^{\infty} (x + it)^n e^{-t^2} dt \]  
\[ (7.17) \]

\[ H_n(x) \equiv 2^{-n/2} H_n(x). \]

Orthogonality and normalization:

\[ \int_{-\infty}^{\infty} e^{-x^2} H_m(x) H_n(x) dx = \sqrt{\pi} 2^n n! \delta_{mn}. \]  
\[ (7.18) \]

Recursion:

\[ \frac{d}{dx} H_n(x) = 2H_{n-1}(x) \]  
\[ (7.19) \]
\[ \frac{d}{dx} e^{-x^2} H_n(x) = e^{-x^2} H_{n+1}(x) \]
\[ H_{n+1}(x) = 2x H_n(x) - 2n H_{n-1}(x). \]

Particular values:

\[ H_{2n+1}(0) = 0 \]  
\[ H_{2n+1}(0) = (-1)^n 2^n (2n - 1)!! \]  
\[ (7.20) \]

Series:

\[ H_{2n}(x) = \sum_{k=0}^{\infty} \frac{(2n)!}{(2k)! (n-k)!} \frac{(-1)^{n-k}}{(2x)^{2k}} \]  
\[ (7.21) \]
\[ H_{2n-1}(x) = \sum_{k=0}^{\infty} \frac{(2n+1)!}{(2k+1)! (n-k)!} \frac{(-1)^{n-k}}{(2x)^{2k+1}} \]
\[ H_n(x) = n! \sum_{k=0}^{\text{int}(n/2)} \frac{1}{k! (n-2k)!} (-1)^k (2x)^{n-2k}. \]
7.1.4.4 Laguerre polynomials

The definition of the Laguerre polynomials is:

\[ L_n^{(m)}(x) = \frac{e^x x^{-m}}{m!} \frac{d^n}{dx^n} (e^{-x} x^{n+m}) \]  \hspace{1cm} (7.22)

\[ L_n(x) = L_n^{(0)}(x). \]

Series:

\[ L_n^{(m)}(x) = \sum_{k=0}^{n} \frac{(n+m)!}{n!} \frac{(-x)^k}{k!}. \]  \hspace{1cm} (7.23)

Recursion:

\[ \frac{d}{dx} L_n^{(m)}(x) = -L_{n-1}^{(m+1)}(x). \]  \hspace{1cm} (7.24)

Related functions:

\[ u_{mn}(\varepsilon) \equiv e^{-\varepsilon^2} \cdot (i\varepsilon)^{n-m} \cdot \sqrt{\frac{m!}{n!}} \cdot L_n^{(0)}(\varepsilon^2) \]  \hspace{1cm} (7.25)

\[ u_{mn}(0) \approx (i\varepsilon)^{n-m} \cdot \sqrt{\frac{n!}{m! (n-m)!}} \]

\[ u_{n+1,n}(0) \approx i\varepsilon \cdot \sqrt{n+1}. \]

Fourier transforms:

\[ \int_{-\infty}^{\infty} e^{-ax^2} x^{2k} \cos xp \cdot dx = \frac{(-1)^k \sqrt{\pi}}{2^{k+1} \sqrt{a}} \cdot e^{p^2/4a} \cdot He_{2k}(p/\sqrt{2a}) \]  \hspace{1cm} (7.26)

\[ \int_{-\infty}^{\infty} e^{-x^2/2} x^{2m} L_n^{(2m)}(x^2) \cos xp \cdot dx = \frac{(-1)^m \sqrt{\pi}}{2^{m+1} \sqrt{n!}} \cdot e^{-p^2/2} \cdot He_n(p) He_{n+2m}(p) \]

\[ \int_{-\infty}^{\infty} e^{-x^2/2} x^{2m+1} L_n^{(2m+1)}(x^2) \sin xp \cdot dx = \frac{(-1)^m \sqrt{\pi}}{2^{m+1} \sqrt{n!}} \cdot e^{-p^2/2} \cdot He_n(p) He_{n+2m+1}(p) \]

\[ \int_{-\infty}^{\infty} e^{-ax-bp} f(|x-p|) \cdot dx dp = \frac{1}{a+b} \left[ \int_{-\infty}^{\infty} e^{-ax} f(x) dx + \int_{-\infty}^{\infty} e^{-bp} f(p) dp \right]. \]

7.1.4.5 Legendre polynomials

The definition of Legendre polynomials is:

\[ P_n(x) \equiv \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n \]  \hspace{1cm} (7.27)

\[ P_n^{(-m)}(x) \equiv (1 - x^2)^{m/2} \frac{d^n}{dx^n} P_l(x). \]

Series:

\[ P_n^{(m)}(x) = \frac{(-1)^m (n+m)!}{2^m m!(n-m)!} (1-x^2)^{m/2} \left[ \frac{1}{2} - \frac{(n-m)!}{2!(m+1)!(m+n)!} \left( \frac{1-x}{2} \right)^2 + \frac{(n-m)!(n-m+1)!(m+n+1)!}{2(m+1)!(m+n+2)!} \left( \frac{1-x}{2} \right)^4 - \ldots \right]. \]  \hspace{1cm} (7.28)
7.1.4.6 Spherical harmonics

The definition of spherical harmonics is [626]:

\[
Y_{\ell m}(\vartheta, \phi) \equiv \sqrt{\frac{2\ell + 1}{4\pi}} \frac{(\ell - |m|)!}{(\ell + |m|)!} P_{\ell}^{|m|}(\cos \vartheta) e^{im\phi}.
\] (7.29)

The lowest spherical harmonics are:

\[
Y_{00} = \frac{1}{2} \sqrt{\frac{1}{\pi}}, \quad Y_{10} = \frac{1}{2} \sqrt{\frac{3}{4\pi}} \cos \theta
\]

\[
Y_{\pm 1} = \pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi} \
\]

\[
Y_{20} = \frac{1}{4} \sqrt{\frac{5}{16\pi}} (3\cos^2 \theta - 1)
\]

\[
Y_{\pm 1} = \mp \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm 2i\phi}.
\] (7.30)

7.1.4.7 Vector spherical harmonics

The definition of vector spherical harmonics is [626]:

\[
Y_{j\ell m}(r) \equiv (-1)^{1-\ell-m} \sqrt{2j+1} \sum_q \left( \begin{array}{ccc}
\ell & 1 & j \\
m - q & q & -m
\end{array} \right) Y_{\ell m - q}(\vartheta, \phi) \hat{e}_q.
\] (7.31)

7.1.4.8 The Gamma function

The definition of the Gamma function is:

\[
\Gamma(x+1) = x\Gamma(x), \quad \Gamma(1/2) = \sqrt{\pi}.
\] (7.32)

7.1.4.9 Riemann zeta-function

The definition of the Riemann zeta-function is,

\[
g_\eta(1) = \zeta(\eta),
\] (7.33)

where,

\[
g_\eta(z) = \sum_{t=1}^{\infty} \frac{\pm(z)^t}{t^\eta} = \frac{1}{\Gamma(\eta)} \int_0^\infty \frac{x^{\eta-1}dx}{z^{-1}e^x + 1},
\] (7.34)

is also called the Bose/Fermi function. The upper sign holds for bosons, the lower for fermions. The Sommerfeld expansion,

\[
\int_0^\infty \frac{g(x)dx}{e^{x-y} + 1} = \int_0^y g(x)dx + \int_0^\infty \frac{g(y + x)^{\eta-1}dx}{e^x + 1} - \int_0^x \frac{g(y - x)^{\eta-1}dx}{e^x + 1}
\]

\[
\approx \int_0^y g(x)dx + \frac{\pi^2}{6} g'(x) + ...
\] (7.35)

holds for \( z \gg 1 \) and yields,

\[
f_\eta(e^y) \approx \frac{x^\eta}{\Gamma(\eta + 1)} \left( 1 + \frac{\pi^2 \eta(\eta - 1)}{6x^2} + \frac{7\pi^4 \eta(\eta - 1)(\eta - 2)(\eta - 3)}{360x^4} + ... \right).
\] (7.36)
For small $z$ both functions converge towards,

$$c_\eta(z) = \frac{1}{\Gamma(\eta)} \int_0^\infty \frac{x^{\eta-1} dx}{z^{-1} e^x} = c_{\eta-1}(z) = z . \quad (7.37)$$

The derivative is,

$$\frac{\partial f_\eta(Z)}{\partial Z} = \frac{1}{\Gamma(\eta)} \frac{\partial}{\partial Z} \sum_{t=1}^\infty (-Z)^t \frac{(-Z)^{t-1}}{t^{\eta-1}} = \frac{1}{Z} \sum_{t=1}^\infty -\frac{(-Z)^t}{t^{\eta-1}} = f_{\eta-1}(Z) \frac{\Gamma(\eta)}{Z} , \quad (7.38)$$

or,

$$\frac{\partial f_\eta(Z)}{\partial Z} = \frac{1}{\Gamma(\eta)} \frac{\partial}{\partial Z} \int_0^\infty \frac{x^{\eta-1} dx}{Z^{-1} e^x + 1} = \frac{1}{\Gamma(\eta)} \int_0^\infty \frac{x^{\eta-1} Z^{-2} e^x dx}{(Z^{-1} e^x + 1)^2} \quad (7.39)$$

$$= \frac{1}{Z \Gamma(\eta)} \int_0^\infty x^{\eta-1} \frac{d}{dx} \frac{-1}{Z^{-1} e^x + 1} dx = \frac{\eta - 1}{Z \Gamma(\eta)} \int_0^\infty \frac{x^{\eta-2}}{Z^{-1} e^x + 1} dx = f_{\eta-1}(Z) \frac{1}{Z} .$$
Part II

Atomic and Molecular Physics
The electron spin and the atomic substructure

The energy structure of hydrogen calculated by Bohr’s model from the non-relativistic Hamiltonian agrees very well with the experimental measurements. However, in high-resolution experiments, small deviations were observed as energy shifts and splittings of spectral lines. These deviations, called fine structure, were not predicted by theory, which suggests that there are weak additional effects that do not strongly affect the position of the spectral lines but remove the energy degeneracy of the orbital quantum number $\ell$: $E = E_{n,\ell}$.

As a possible explanation we have the fact that the electrons present relativistic mass and momentum. In order to estimate the relevance of relativistic corrections let us estimate the electron velocity in the fundamental hydrogen states given by $E_1 = -\hbar^2/2m_e a_B^2$. Using the definitions of the Bohr radius, $a_B = 4\pi\varepsilon_0\hbar^2/(m_e e^2)$, and the fine structure constant

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0\hbar c} \simeq \frac{1}{137}, \quad (8.1)$$

we obtain,

$$v = \sqrt{\frac{2E_1}{m_e}} = \frac{\hbar}{m_e a_B} = \frac{e^2}{4\pi\varepsilon_0 \hbar} = \alpha c, \quad (8.2)$$

which shows that the electron velocity is very high and that relativistic effects may indeed be not negligible.

8.1 The Dirac equation

8.1.1 The Klein-Gordon equation for bosons

The Schrödinger equation for a free particle is based on the non-relativistic energy-momentum dispersion relation,

$$E = \frac{p^2}{2m_e}. \quad (8.3)$$

and the definitions of the quantum operators for energy and momentum,

$$E = i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad p = -i\hbar \nabla. \quad (8.4)$$
As already discussed in Sec. 2.1.2 we can, in order to find a relativistic wave equation, try the approach of inserting the quantum operators into the relativistic energy-momentum relation 1. 

\[ E^2 = c^2 p^2 + m_e^2 c^4. \] 

We obtain, 

\[ \left[ \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 + \left( \frac{m_e c}{\hbar} \right)^2 \right] \psi = 0. \] 

This is the *Klein-Gordon equation*. The stationary solution of this equation is a spherical wave, 

\[ \psi = \psi_0 \frac{1}{r} e^{-2\pi r/\lambda_C}, \] 

where \( \lambda_C = h/m_e c \) is the *Compton wavelength*. We show this in Exc. 8.1.5.1. For example, in the case of heavy bosonic particles, such as a field of \( \pi \)-mesons, \( \psi \) is the *Yukawa potential*.

In the framework of the *standard model*, it is believed that matter is composed of two fundamental types of particles, bosons and fermions. Bosons are exchanged between fermions conveying the interaction between them. A typical example is the one of two electrons whose Coulomb interaction is mediated by the exchange of photons. Bosons obey the Klein-Gordon equation, fermions the Dirac equation derived in the following section.

### 8.1.2 The Dirac equation for fermions

In 1928 Paul Dirac, at the age of 26, developed an approach to a relativistic wave equation which differed from the Klein-Gordon equation. Motivated by the observation that the photon, being the relativistic particle *par excellence*, obeys a linear energy-momentum relation of the form \( \omega = ck \), he attempted to derive a linear dispersion relation in \( E \) and \( p \) for heavy particles via the following ansatz: 

\[ E = \alpha_0 m_e c^2 + \alpha_1 cp_x + \alpha_2 cp_y + \alpha_3 cp_z. \] 

Replacing energy and momentum with their respective operators 2, 

\[ i\hbar \frac{\partial}{\partial t} \phi = \alpha_0 m_e c^2 \phi - i\hbar \left( \alpha_1 \frac{\partial}{\partial x} + \alpha_2 \frac{\partial}{\partial y} + \alpha_3 \frac{\partial}{\partial z} \right) \phi. \] 

We must now ensure that the relativistic energy-momentum condition (8.5) be satisfied.

**Example 33 (Derivation of the Dirac equation):** Taking the square on the right-hand side of the equation (8.9),

\[
[\alpha_0 m_e c^2 - i\hbar(\alpha_1 \partial_x + \alpha_2 \partial_y + \alpha_3 \partial_z)][\alpha_0 m_e c^2 - i\hbar(\alpha_1 \partial_x + \alpha_2 \partial_y + \alpha_3 \partial_z)]
= m_e^2 c^4 \alpha_0^2 - i\hbar m_e c^2 [(\alpha_0 \alpha_1 + \alpha_1 \alpha_0) \partial_x + (\alpha_0 \alpha_2 + \alpha_2 \alpha_0) \partial_y + (\alpha_0 \alpha_3 + \alpha_3 \alpha_0) \partial_z]
- c^2 \hbar^2 [\alpha_1^2 \partial_x^2 + \alpha_2^2 \partial_y^2 + \alpha_3^2 \partial_z^2]
- c^2 \hbar^2 [(\alpha_1 \alpha_2 \partial_x \partial_y + \alpha_2 \alpha_1 \partial_y \partial_x) + (\alpha_2 \alpha_3 \partial_y \partial_z + \alpha_3 \alpha_2 \partial_z \partial_y) + (\alpha_3 \alpha_1 \partial_z \partial_x + \alpha_1 \alpha_3 \partial_x \partial_z)].
\]

1 Using the covariant notation with \( p_\mu \equiv (E/c, \mathbf{p}) \): \( p_\mu p^\mu = E^2/c^2 - p^2 = m_e^2 c^2 \) is a Lorentz invariant.
2 We introduce the abbreviation \( \partial_k \equiv \frac{\partial}{\partial x_k} \).
For this expression to be identical to the relativistic energy-momentum condition (8.5),
\[ m^2 c^4 - c^2 \hbar^2 \left[ \partial_x^2 + \partial_y^2 + \partial_z^2 \right], \]
we need to postulate for all \( i = 0, \ldots, 4 \), that \( \alpha_i \alpha_j + \alpha_j \alpha_i = 2 \delta_{ij} \).

Obviously, the condition
\[ [\alpha_i, \alpha_j]_+ = 2 \delta_{ij} \quad (8.10) \]
can not be satisfied if the \( \alpha_i \) are numbers. The idea of Dirac was to interpret the variables \( \alpha_i \) as matrices. These matrices act as operators on appropriate states, which are no longer scalar wavefunctions but vectors. Each component of the vector is a wavefunction in the usual sense. The Hilbert space is extended to be the product space of the usual spatial wavefunctions and a finite-dimensional vector space.

**Example 34 (Calculation with matrices of operator):** To give an idea of how the algebra works we consider a general situation. As the operator we choose the product,
\[
\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{\partial}{\partial x}
\]
and as the wavefunction vector we choose,
\[
\begin{pmatrix} e^{ik_1 x} \\ e^{ik_2 x} \end{pmatrix}.
\]

Applying the operator on the state vector we get,
\[
\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{\partial}{\partial x} \begin{pmatrix} e^{ik_1 x} \\ e^{ik_2 x} \end{pmatrix} = \begin{pmatrix} 0 & \frac{\partial}{\partial x} e^{ik_1 x} \\ \frac{\partial}{\partial x} e^{ik_2 x} & 0 \end{pmatrix} = \begin{pmatrix} i k_2 e^{ik_2 x} \\ i k_1 e^{ik_1 x} \end{pmatrix}.
\]

The matrices \( \alpha_i \) must satisfy the condition (8.10). It is possible to show that this requires at least four-dimensional matrices of the following form:
\[ \alpha_0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad \text{and} \quad \alpha_j = \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix}, \quad (8.11) \]
where \( j = x, y, z = 1, 2, 3 \). In this notation the components of the matrices are also matrices:
\[ I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (8.12) \]
called **Pauli spin matrices**. The state vector must also have four dimensions,
\[
\vec{\Phi}(\mathbf{r}, t) = \begin{pmatrix} \phi(\mathbf{r}, t) \\ \chi(\mathbf{r}, t) \end{pmatrix} \quad \text{with} \quad \vec{\phi}(\mathbf{r}, t) = \begin{pmatrix} \phi_1(\mathbf{r}, t) \\ \phi_2(\mathbf{r}, t) \end{pmatrix} \quad \text{and} \quad \vec{\chi}(\mathbf{r}, t) = \begin{pmatrix} \chi_1(\mathbf{r}, t) \\ \chi_2(\mathbf{r}, t) \end{pmatrix}. \quad (8.13)
\]

\( \Phi_j \) are called **large components**, \( \chi_j \) are called **small components**. This designation is explained later. Combining the matrices \( \alpha_j \) to a three-dimensional vector \( \vec{\alpha} \), we can now write the Dirac equation (8.9) like,
\[
i \hbar \partial_t \vec{\Phi}(\mathbf{r}, t) = \left( m c^2 \alpha_0 + c \vec{\alpha} \cdot \mathbf{p} \right) \vec{\Phi}(\mathbf{r}, t). \quad (8.14)
\]
Or, using the notation (8.11) and combining the Pauli matrices $\sigma_j$ to a three-dimensional vector $\vec{\sigma}$, we can write the Dirac equation as:

$$\frac{i\hbar}{\partial t} \begin{pmatrix} \phi \\ \chi \end{pmatrix} = \begin{bmatrix} m_e c^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + c \begin{pmatrix} \vec{\sigma} \cdot \vec{p} & \vec{\sigma} \cdot \vec{p} \\ \vec{\sigma} \cdot \vec{p} & 0 \end{pmatrix} \end{bmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix}.$$  \hfill (8.15)

The non-diagonal matrix,

$$\begin{pmatrix} 0 & \vec{\sigma} \cdot \vec{p} \\ \vec{\sigma} \cdot \vec{p} & 0 \end{pmatrix}$$  \hfill (8.16)

couples large and small components.

**Example 35 (Covariant and relativistically invariant form of Dirac’s equation):** To demonstrate its relativistic invariance it is useful to rewrite the Dirac equation in a way in which time and space appear on equal footings. For this we introduce new matrices,

$$\gamma^0 \equiv \alpha_0 \quad \text{and} \quad \gamma^k = \gamma^0 \alpha_k.$$  \hfill (8.17)

We obtain,

$$\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad \gamma^k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix}.$$  \hfill (8.18)

We also define another important matrix by,

$$\gamma_5 \equiv i\gamma_0 \gamma_1 \gamma_2 \gamma_3 = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}.$$  \hfill (8.19)

With this, using Einstein’s notation $^3$, the Dirac equation (8.13) adopts the form,

$$i\hbar \gamma^\mu \partial_\mu \psi - mc \psi = 0.$$  \hfill (8.20)

The complete system is summarized in the Minkowski metrics of time-space in the form,

$$[\gamma^\mu, \gamma^\nu]_+ = 2\eta^\mu\nu,$$  \hfill (8.21)

for $\mu, \nu = 0, ..., 5$, that is, all matrices $\gamma_k$ anticommute.

The Dirac equation can now be interpreted as an eigenvalue equation, where the rest mass is proportional to the eigenvalue of a momentum quadrivector, the proportionality constant being the speed of light:

$$P_{\text{op}} \psi = m c \psi.$$  \hfill (8.22)

Using $\partial_0$ in the Feynman slash notation, which includes the $\gamma$-matrices, as well as a summation over the components of the spinor in the derivative, the Dirac equation becomes:

$$i\hbar \slashed{\partial} \psi - mc \psi = 0.$$  \hfill (8.23)

A fundamental theorem states that, if two distinct sets of matrices are given, which both satisfy Clifford’s relations, then they are connected to each other by a similarity transformation:

$$\gamma'^\mu = S^{-1} \gamma^\mu S.$$  \hfill (8.24)

If, in addition, the matrices are all unitary, as is the case of Dirac’s set, then $S$ is unitary,

$$\gamma'^\mu = U^\dagger \gamma^\mu U.$$  \hfill (8.25)

---

$^3 \partial_0 \equiv \frac{1}{\epsilon} \partial_t$
8.1.2.1 Anti-particles

Disregarding for a moment the non-diagonal matrix, the Dirac equation separates into two independent equations,

\[
\frac{i\hbar}{\partial t} \vec{\partial} \phi = m_e c^2 \vec{\phi} \quad \text{and} \quad \frac{i\hbar}{\partial t} \vec{\partial} \chi = -m_e c^2 \vec{\chi}.
\] (8.26)

These are eigenenergy equations with the eigenvalues \(m_e c^2\) and \(-m_e c^2\). The state with negative energy is interpreted as anti-particle. Therefore, the non-diagonal matrix mixes particles and anti-particles. We will study in Exc. 8.1.5.2 the so-called Zitterbewegung as a solution of the Dirac equation.

8.1.2.2 Particles and anti-particles in the non-relativistic limit

To reduce the Dirac equation to the non-relativistic Schrödinger equation, we first need to get rid of the rest energy. To do so, we separate a fast oscillation, whose frequency corresponds to the rest mass of the electron via the following ansatz, where \(u\) and \(v\) vary slowly in time:

\[
\vec{\Phi}(r,t) = e^{-i\omega_0 t} \begin{pmatrix} u(r,t) \\ v(r,t) \end{pmatrix}, \quad \hbar \omega_0 = m_e c^2,
\] (8.27)

with the temporal derivative,

\[
i\hbar \dot{\vec{\Phi}} = \begin{bmatrix} m_e c^2 (u) + i\hbar (\dot{u}) \\ \dot{v} \end{bmatrix} e^{-i\omega_0 t}.
\] (8.28)

We insert this into the Dirac equation,

\[
\begin{bmatrix} m_e c^2 (u) + i\hbar (\dot{u}) \\ \dot{v} \end{bmatrix} e^{-i\omega_0 t} = \begin{bmatrix} m_e c^2 (u) + c\vec{\sigma} \cdot \vec{p} (v) \\ \dot{u} \end{bmatrix} e^{-i\omega_0 t}
\] (8.29)

finally obtaining,

\[
i\hbar \dot{u} = c(\vec{\sigma} \cdot \vec{p})v, \quad i\hbar \dot{v} = c(\vec{\sigma} \cdot \vec{p})u - 2m_e c^2 v.
\] (8.30)

Since \(u\) and \(v\) only vary slowly in time, the derivatives on the left-hand side are small quantities. However, the condition that both derivatives must zero is too strong, because it leads to the trivial solution \(u = 0\) and \(v = 0\). We find the first non-trivial solution by the condition \(\dot{v} = 0\). The second equation then becomes,

\[
v = \frac{1}{2m_e c} (\vec{\sigma} \cdot \vec{p})u.
\] (8.31)

Inserted into the first equation,

\[
i\hbar \dot{u} = c(\vec{\sigma} \cdot \vec{p})^2 \frac{u}{2m_e c}.
\] (8.32)

We need, therefore, to evaluate the expression \((\vec{\sigma} \cdot \vec{p})^2\),

\[
\vec{\sigma} \cdot \vec{p} = \begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix} \quad \text{and} \quad (\vec{\sigma} \cdot \vec{p})^2 = \vec{p}^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.
\] (8.33)
Inserted into the differential equation (8.32) for $u$ we obtain precisely the Schrödinger equation for a free particle,

$$i\hbar \dot{\hat{u}} = \frac{p^2}{2m_e} u. \quad (8.34)$$

Let us return to the question, why we call $u$ the strong component. We have from the equation (8.31),

$$v^\dagger v = \frac{1}{(2m_e c)^2} (\vec{\sigma} \cdot \vec{p})^2 u^\dagger u = \frac{1}{2m_e c^2} \frac{p^2}{2m_e} u^\dagger u, \quad (8.35)$$

and since $\frac{p^2}{2m_e} \ll m_e c^2$ follows immediately $v^\dagger v \ll u^\dagger u$.

In this non-relativistic approximation the components $u$ are much larger than the components $v$. The mixture between particles and antiparticles only matters when $\frac{p^2}{2m_e} \simeq m_e c^2$, resp., $\frac{1}{2} m_e v^2 \simeq m_e c^2$ or $|v| \simeq c$. The electron only receives small positronic contributions as it approaches the speed of light. In the ground state of the hydrogen atom the electron has a velocity of of $v = \alpha c \simeq c/137$. That is, the contribution of the weak components is small, but present.

**Example 36 (Vanishing rest mass):** Let us note that for the case of vanishing rest mass, $m_e = 0$, the Dirac equation (8.15) dramatically simplifies. Taking the time derivative of the upper equation (8.15) and inserting the lower equation (8.15), we find,

$$\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \phi = \frac{1}{c^2} \frac{\partial}{\partial t} \chi = -\frac{(\vec{\sigma} \cdot \vec{p})^2}{\hbar^2} \phi = -\frac{p^2}{\hbar^2} \phi = \nabla^2 \phi. \quad (8.36)$$

I.e. we recover a Helmholtz type wave equation.

### 8.1.2.3 The spin

We consider the operator defined by [164, 165],

$$\hat{s} \equiv \frac{\hbar}{2} \vec{\sigma}, \quad (8.37)$$

and we calculate the commutation relations between its components. From the definitions (8.12) we obtain the rule,

$$[\hat{s}_x, \hat{s}_y] = \frac{\hbar^2}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} - \frac{\hbar^2}{4} \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar^2}{4} \begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix} = i\hbar \hat{S}_z. \quad (8.38)$$

In general terms the following holds true: $[s_i, s_j] = \epsilon_{ijk} i\hbar s_k$. It is interesting to compare this with the commutation relation for the orbital angular momentum $[\hat{l}_i, \hat{l}_j] = \epsilon_{ijk} i\hbar \hat{l}_k$. The coincidence suggests a generalization of the concept of angular momentum: We now call angular momentum operator every three-dimensional vector operator satisfying this commutation relation. We consider the eigenvalue equation for $\hat{S}_z$,

$$\hat{S}_z \phi = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = m_s \hbar \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}. \quad (8.39)$$

\footnote{This concept can be derived from the requirement of symmetry under rotation of space as discussed in Sec. 2.5.}
The eigenvalues are obviously $m_s = \pm \frac{1}{2}$. The angular momentum related to the matrices $S$ is obviously half-integer. We are dealing here with a new type of angular momentum, which is not included in the usual definition of orbital angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. The new angular momentum is called intrinsic angular momentum or spin of the particle. The spin represents a new structure or dimension additional to space comparable to the polarization of light. The photons of a circularly polarized light beam also contribute to an intrinsic angular momentum, which however in this case is integer.

In Exc. 8.1.5.3 we will see that neither $\hat{l}_z$ nor $\hat{s}_z$ are constants of motion of the Hamiltonian (8.15), but the sum $\hat{j}_z \equiv \hat{l}_z + \hat{s}_z$,

$$[\hat{j}_z, \hat{H}] = 0.$$  

(8.40)

#### 8.1.2.4 The stationary Dirac equation

By a similar treatment as in the Schrödinger equation one can deduce a stationary Dirac equation (8.14) via a separation of the time variable. Making for the time an exponential ansatz,

$$\vec{\phi}(\mathbf{r}, t) = \vec{\phi}(\mathbf{r}) e^{-\frac{iEt}{\hbar}} \quad \text{and} \quad \vec{\chi}(\mathbf{r}, t) = \vec{\chi}(\mathbf{r}) e^{-\frac{iEt}{\hbar}},$$  

(8.41)

we obtain coupled stationary equations for the large and small components,

$$(E - m_e c^2)\vec{\phi}(\mathbf{r}) = c\sigma \cdot \mathbf{p} \vec{\chi}(\mathbf{r}) \quad \text{and} \quad (E + m_e c^2)\vec{\chi}(\mathbf{r}) = c\sigma \cdot \mathbf{p} \vec{\phi}(\mathbf{r}).$$  

(8.42)

#### 8.1.3 The relativistic electron in a central Coulomb field

##### 8.1.3.1 Minimal coupling

In atomic physics we are mainly interested in electrons bound to a potential (e.g., generated by an atomic nucleus), that is, we must introduce electromagnetic forces into the Dirac equation. Therefore, we now consider the interaction of a charged particle with an electromagnetic field given by the vector potential $\mathbf{A}$ and by the electrostatic potential $U$, such that the electric and magnetic fields,

$$\vec{E} = -\nabla U - \frac{\partial \mathbf{A}}{\partial t} \quad \text{and} \quad \vec{B} = \nabla \times \mathbf{A},$$  

(8.43)

allow to calculate the Coulomb-Lorentz force. In the Hamiltonian formulation of electrodynamics the interaction can be described simply by the transition $^5$

$$\hat{p} \rightarrow \hat{p} - q\mathbf{A} \equiv \vec{\pi} \quad \text{and} \quad \hat{H} \rightarrow \hat{H} + qU,$$  

(8.44)

called the minimal coupling. These rules will be derived in Sec. 9.1. In addition to the substitution of the momentum, we must add the scalar potential $qU$, and we obtain the Dirac equation for a particle inside an applied electromagnetic field,

$$i\hbar \frac{\partial \vec{\Phi}}{\partial t} = \left( m_e c^2 \alpha_0 + c\vec{\alpha} \cdot \vec{\pi} + qU \right) \vec{\Phi}.$$  

(8.45)

---

$^5$In quadrivector notation: $\pi_\mu = p_\mu - qA_\mu$ with $p_\mu = \left(\frac{E/c}{\mathbf{p}}\right)$ and $A_\mu = \left(\frac{U/c}{\mathbf{A}}\right)$. 

---
8.1.3.2 Solving the stationary Dirac equation

Let us, for now, disregard external magnetic fields, \( A = 0 \). Then, the stationary Dirac equation becomes,

\[
[E - qU(r) - m_e c^2] \tilde{\phi}(r) = c \sigma \cdot p \chi(r) \\
[E - qU(r) + m_e c^2] \chi(r) = c \sigma \cdot p \tilde{\phi}(r).
\]

For the Coulomb potential,

\[
q U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}
\]

the Dirac equation can be solved algebraically [166, 233, 238, 208]. The calculation is more complicated than the resolution of the Schrödinger equation for hydrogen derived in Secs. 3.1.4 and 3.2.1 and will be sketched in the following.

**Example 37 (Dirac equation in spherical coordinates):** The goal of the following calculation is to express the Dirac equation for an electron in a central Coulomb field in spherical coordinates, i.e. \( r \) and \( p_r = -i \hbar \partial_r \) instead of \( p \). The starting point is the Dirac equation (8.15),

\[
\hbar \partial_t \Phi(r, t) = \hat{H} \Phi(r, t),
\]

with the Hamiltonian in the minimal coupling (8.44),

\[
\hat{H} \equiv m_e c^2 \alpha_0 + c \alpha \cdot [p - qA(r)] + qU(r)
\]

with \( A = 0 \) and \( U(r) = -\frac{e^2}{4\pi\epsilon_0 r} \).

We adopt the standard procedure from non-relativistic physics, which consists in rewriting the Hamiltonian in terms of observables, which commute with the Hamiltonian.

The goal is to calculate the quantity \( \alpha \cdot p \) appearing in the above Hamiltonian. As a first steps we define the following quantities,

\[
\begin{align*}
L & \equiv r \times p \quad \text{satisfying} \quad L \times L = \hbar L \\
S & \equiv \frac{\hbar}{2} \equiv \frac{\hbar}{2} \gamma_5 \alpha \\
J & \equiv L + S \\
\hbar j' & \equiv \alpha_0 (\gamma_5 \alpha \cdot L + \hbar) \\
r\varepsilon & \equiv \alpha \cdot r
\end{align*}
\]

remembering that \( \gamma_5 = -\alpha_1 \alpha_2 \alpha_3 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \) is the transformation exchanging particles and anti-particles. The first important relationship we have to derive is,

\[
(\alpha \cdot B)(\alpha \cdot C) = (B \cdot C) + r\gamma_5 \alpha \cdot (B \times C).
\]

---

6See also http://einstein.drexel.edu/~bob/Term_Reports/Whitehead_3.pdf
7Typical examples are the Hamiltonian of the harmonic oscillator (4.60) written in terms of \( \hat{n} \equiv \hat{a}^\dagger \hat{a} \) or the Hamiltonian of the hydrogen atom (3.33) written in terms of \( L^2 \).
It holds for \([\alpha, B] = 0 = [\alpha, C]\) and will be proven in 8.1.5.4. Exploiting this relationship, we see that the scalar quantity \(\varepsilon\) satisfies,

\[
\varepsilon^2 = \frac{1}{r^2}(\vec{\alpha} \cdot \vec{r})^2 = \frac{1}{r^2}[\vec{r} \cdot \vec{r} + i\vec{a} \cdot (\vec{r} \times \vec{r})] = 1 .
\]

Furthermore, with the definition of \(\vec{j}'\) we show,

\[
r\varepsilon \vec{a} \cdot \vec{p} = (\vec{\alpha} \cdot \vec{r})(\vec{\alpha} \cdot \vec{p}) = r \cdot \vec{p} + r\gamma_5 \vec{\alpha} \cdot (\vec{r} \times \vec{p}) = r \cdot \vec{p} + i\gamma \vec{r} \cdot \vec{L} = rp_r + i\alpha_0 hj' - ih ,
\]

where the relationship \(r \cdot \vec{p} = rp_r\) is verified in Exc. 8.1.5.5(c). Hence,

\[
\vec{\alpha} \cdot \vec{p} = \varepsilon \left(p_r + \frac{i\hbar(\alpha_0 j' - 1)}{r}\right) ,
\]

The final radial Hamiltonian is,

\[
\hat{H} = mc^2\alpha_0 + c\varepsilon \left(p_r - \frac{\hbar}{r}\right) + \frac{ue\alpha_0 hj'}{r} - \frac{e^2}{4\pi\varepsilon_0 r} .
\]

For now the choice of the quantities \(\varepsilon\) and \(j'\) must seem arbitrary, so we will have to discover their properties. We will see that \(j'\) is a non-zero integer related to the total angular momentum \(j\). The following properties will be proven in Exc. 8.1.5.5(a) and (b),

\[
(hj')^2 = J^2 + \frac{\hbar^2}{4} ,
\]

\[
[hj', \hat{H}]_\varepsilon = [\varepsilon, \hat{H}]_\varepsilon = [\alpha_0, \hat{H}]_\varepsilon = 0 .
\]

Hence, we got a collection of radial variables being constants of motion of the Dirac Hamiltonian.

**Example 38 (Resolving the spherical Dirac equation):** We will now search a solution to the spherical Dirac equation with the Hamiltonian (8.55). Noticing that the matrix \(\alpha_0\) is diagonal and the matrix \(\varepsilon\) counter-diagonal (just like the Dirac matrices \(\vec{\alpha}\)), we may break down the stationary radial Dirac equation into 2 by 2 matrices. Using the fact that \(\varepsilon\) commutes with all other terms and anti-commutes with \(\alpha_0\) and that \(\varepsilon^{-1} = \varepsilon^\dagger\) is a unitary transformation, we may go to a new basis via,

\[
\begin{pmatrix}
mc^2 & -\frac{e^2}{4\pi\varepsilon_0 r} \\
icpr + c\frac{h}{r} - c\frac{bj'}{r} & -mec^2 - \frac{e^2}{4\pi\varepsilon_0 r}
\end{pmatrix}
\begin{pmatrix}
\vec{\phi} \\
\varepsilon \vec{\chi}
\end{pmatrix}
= E
\begin{pmatrix}
\vec{\phi} \\
\varepsilon \vec{\chi}
\end{pmatrix} .
\]

Substituting \(\alpha = \frac{e^2}{4\pi\varepsilon_0 hc}\) and \(a_{\pm} = \frac{h}{mc^2}E/c\) (that is, \(\pm mc^2 - E \equiv \pm \hbar c a_{\pm}\)), we find,

\[
\begin{pmatrix}
\frac{1}{a_+} - \frac{a}{r} & -\frac{d}{a_+} - \frac{j'+1}{r} \\
\frac{d}{a_-} - \frac{j'-1}{r} & -\frac{1}{a_-} - \frac{a}{r}
\end{pmatrix}
\begin{pmatrix}
\vec{\phi} \\
\varepsilon \vec{\chi}
\end{pmatrix}
= 0 .
\]

Assuming the existence of solutions of the form,

\[
\begin{pmatrix}
\vec{\phi} \\
\varepsilon \vec{\chi}
\end{pmatrix}
= \frac{e^{-r/a}}{r}
\begin{pmatrix}
\vec{f} \\
\vec{g}
\end{pmatrix} ,
\]

\[
\begin{pmatrix}
\vec{f} \\
\vec{g}
\end{pmatrix}
= \begin{pmatrix}
\frac{e^{-r/a}}{r} \\
\frac{e^{-r/a}}{r}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\vec{f} \\
\vec{g}
\end{pmatrix}
= \begin{pmatrix}
\frac{e^{-r/a}}{r} \\
\frac{e^{-r/a}}{r}
\end{pmatrix} .
\]
where \( a \equiv \sqrt{a_+a_-} = \hbar \left( m_e^2 c^2 - \frac{E^2}{c^2} \right)^{-1} \) [that is, \( \frac{d}{dr} \frac{e^{-r/a}}{r} = \frac{e^{-r/a}}{r} \left( -\frac{1}{a} - \frac{1}{r} \right) \)],

we find,

\[
\left( \frac{d}{dr} - \frac{1}{a} - \frac{j'}{r} \right) \left( \frac{f}{g} \right) = 0 .
\] (8.60)

Next we expand the unknown function \( \vec{f} \) and \( \vec{g} \) as series,

\[
\vec{f}(r) = \sum_{s=-\infty}^{\infty} f_s r^s \quad \text{and} \quad \vec{g}(r) = \sum_{s=-\infty}^{\infty} g_s r^s .
\] (8.61)

These are then substituted into our system of equations. In order for the equation to go to zero as required, each term in the resulting series must separately go to zero. The coefficient of the \( r^s \) terms are,

\[
f_s a_+ - \alpha f_{s+1} - (s + 1 + j')g_{s+1} + \frac{g_s}{a} = 0 \quad \text{(8.62)}
\]

\[
g_s a_- - \alpha g_{s+1} - (s + 1 - j')f_{s+1} + \frac{f_s}{a} = 0 .
\]

These can be combined by multiplying the first equation (8.62) by \( a_+ \) and and the second by \( a_- \) and then subtracting the former from the latter. Exploiting \( \frac{a_+}{a_+} = \frac{a_-}{a_-} \), this gives us an expression directly relating the \( f_s \) coefficients with the \( g_s \) coefficients,

\[
[\alpha a - a_+(s - j')]f_s + [\alpha a_- + a(s + j')]g_s = 0 .
\] (8.63)

To obtain the values of the coefficients we consider the boundary conditions. The functions \( \vec{f}(r) \) and \( \vec{g}(r) \) must go to zero at \( r = 0 \), because the functions \( \vec{\phi} \) and \( \vec{\chi} \) would otherwise diverge there due to the \( r^{-1} \) term. This means that there is some smallest \( s \) below which the series does not continue. We call this \( s_0 \), and it has the property,

\[
f_{s_0 - 1} = g_{s_0 - 1} = 0 .
\] (8.64)

Plugging this into the equations (8.62), we find,

\[
\alpha f_{s_0} + (s_0 + j')g_{s_0} = 0 \quad \text{(8.65)}
\]

\[
\alpha g_{s_0} - (s_0 - j')f_{s_0} = 0 .
\]

Combining these equations we can write the value \( s_0 \) in a very simple form,

\[
s_0 = \sqrt{j'^2 - \alpha^2} .
\] (8.66)

This places a lower bound on the series. Note that this bound becomes imaginary if \( \alpha > j' \). This will be discussed in more detail shortly.

The upper bound of the series is also useful. It can be shown that the series must terminate if the energy eigenvalue is to be less than \( m_e c^2 \) [166]. The implication of this result is that if the series terminates at index \( s_1 \) such that,

\[
f_{s_1 + 1} = g_{s_1 + 1} = 0 .
\] (8.67)

Then, using equations (8.62) and (8.63), we have,

\[
\frac{s_1}{a} = \frac{1}{2} \left( \frac{1}{a_-} - \frac{1}{a_+} \right) \alpha = \frac{E}{\hbar c} \alpha ,
\] (8.68)
where we have used the definitions of the coefficients $a_{\pm}$ to expand them. Squaring this expression and expanding $a$ using its definition, we get,

$$s_1^2 \left( m_e c^2 - \frac{E^2}{c^2} \right) = \alpha^2 \frac{E^2}{c^2}. \tag{8.69}$$

This can be solved for the energy eigenvalues,

$$E = \pm m_e c^2 \left( 1 + \frac{\alpha^2}{s_1^2} \right)^{-1/2}. \tag{8.70}$$

Note that the ‘negative energy’ solution corresponds to positron energy levels. From here forward, we drop the negative root and look only at the electron solution.

The two end points of the series, the indices $s_0$ and $s_1$ are separated by an integer number of steps. Calling this integer $n'$ we can write,

$$s_1 = n' + s_0 = n' + \sqrt{j'^2 - \alpha^2}. \tag{8.71}$$

Plugging this into (8.70) gives a result for the energy eigenvalues in terms of only the two quantum numbers $n'$ and $j'$,

$$E_{n',j'} = m_e c^2 \left[ 1 + \frac{\alpha^2}{(n' + \sqrt{j'^2 - \alpha^2})^2} \right]^{-1/2}. \tag{8.72}$$

This is the final result quoted for the energy eigenvalues of the hydrogenic atom by Dirac [166]. It turns out that later developments in the field [233, 238] prefer to use an equivalent set of quantum numbers that maps more closely to the familiar ones. The number $j'$ is closely related to the total angular momentum quantum number $j$. $j'$ has the range 1, 2, 3, while $j$ has the range $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. It is natural, and in fact correct, to make the identifications,

$$j' = j + \frac{1}{2}, \tag{8.73}$$

and

$$n' = n - j' = n - j - \frac{1}{2}, \tag{8.74}$$

for the principal quantum number $n$ [233]. Combining these two adjustments with equation (8.72), we get the **Sommerfeld fine-structure formula**,

$$E_{n,j} = m_e c^2 \left[ 1 + \frac{\alpha^2}{\left( n - j - \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - \alpha^2} \right)^2} \right]^{-1/2}, \tag{8.74}$$

with $j = |\ell \pm \frac{1}{2}|$ and $\ell = 0, 1, \ldots$ The derivation of the form of the actual wave functions $\phi(r)$ and $\chi(r)$ is very tedious [233] and will not be reproduced here.

The energy predicted by the Sommerfeld fine-structure formula (8.74) depends on two quantum numbers. The degeneracy of the orbital angular momentum $j$ is lifted, and the new quantum number besides the main quantum number $n$ is that of the total angular momentum $j$. The intransparent expression can be expanded by $\alpha$,

$$E_{n,j} \approx m_e c^2 \left[ 1 - \frac{\alpha^2}{2n^2} - \frac{\alpha^4}{2n^3} \left( \frac{1}{j + 1/2} - \frac{3}{4n} \right) \right]. \tag{8.75}$$
The second term reproduces the energy of Bohr’s model, but there are correction terms proportional to $\alpha^4$. We will show in Secs. 8.1.4, that the energy levels, called \textit{fine structure}, result from several relativistic corrections of different origins.

In the expression (8.75) for the electron energy in the Coulomb potential, the last term is positive and proportional to $1/n^4$. It describes relaxation of the binding due to the contribution of weak components. The term containing the quantum number $j$ is called the spin-orbit coupling. To better understand this contribution we must first analyze more deeply the matrices $\hat{\sigma}$.

### 8.1.3.3 \textbf{Dirac’s Hamiltonian in the sub-relativistic limit}

Defining the energy $E' = E - m_e c^2$, the stationary Dirac equation (8.46) for an electron of charge $q = -e$ in an external electrostatic potential $U(r)$ can be written,

$$ [E' - qU(r)] \vec{\phi} = c \vec{\sigma} \cdot \vec{p} \vec{\chi} \quad \text{and} \quad [E' - qU(r) + 2m_e c^2] \vec{\chi} = c \vec{\sigma} \cdot \vec{p} \vec{\phi} . \quad (8.76) $$

resolving the second equation for the wavefunction $\vec{\chi}$ and substituting it into the first,

$$ E' \vec{\phi} = qU(r) \vec{\phi} + \vec{\sigma} \cdot \vec{p} \frac{1}{2m_e} \left( 1 + \frac{E' - qU(r)}{2m_e c^2} \right)^{-1} \vec{\sigma} \cdot \vec{p} \vec{\phi} . \quad (8.77) $$

In the non-relativistic limit,

$$ E' - qU \simeq \frac{p^2}{2m_e} \ll m_e c^2 , \quad (8.78) $$

we get,

$$ E' \simeq qU(r) \vec{\phi} + \vec{\sigma} \cdot \vec{p} \frac{1}{2m_e} \left( 1 - \frac{E' - qU(r)}{2m_e c^2} \right) \vec{\sigma} \cdot \vec{p} \vec{\phi} . \quad (8.79) $$

Now, $\vec{\sigma} \cdot \vec{p}$ is an operator entity, which acts on the subsequent operators and wavefunctions. We thus have to apply the product rule, $(\vec{\sigma} \cdot \vec{p})V\psi = V(\vec{\sigma} \cdot \vec{p})\psi + [(\vec{\sigma} \cdot \vec{p})V]\psi$, to the first occurrence of operator this operator in equation (8.77),

$$ E' \vec{\phi} \simeq qU(r) \vec{\phi} + \frac{1}{2m_e} \left( 1 - \frac{E' - qU(r)}{2m_e c^2} \right) (\vec{\sigma} \cdot \vec{p})^2 \vec{\phi} + \frac{q}{4m_e^2 c^4} [(\vec{\sigma} \cdot \vec{p})U(r)](\vec{\sigma} \cdot \vec{p}) \vec{\phi} . \quad (8.80) $$

In the following we will make use of a general relationship which is similar to (8.51),

$$ (\vec{\sigma} \cdot \vec{B})(\vec{\sigma} \cdot \vec{C}) = (\vec{B} \cdot \vec{C}) + i\vec{\sigma} \cdot (\vec{B} \times \vec{C}) . \quad (8.81) $$

It holds for $[\vec{\sigma} , \vec{B}] = 0 = [\vec{\sigma} , \vec{C}]$ and will be demonstrated in Exc. 8.1.5.4. The relationship yields,

$$ (\vec{\sigma} \cdot \vec{p})^2 = \vec{p}^2 \quad \text{and} \quad [\vec{\sigma} \cdot \vec{p}U(r)](\vec{\sigma} \cdot \vec{p}) = \vec{p}U(r) \cdot \vec{p} + i\vec{\sigma} \cdot [\vec{p}U(r) \times \vec{p}] , \quad (8.82) $$

so that expressing the momentum operator by $\vec{p} = -i\hbar \nabla$ wherever it acts on the potential,

$$ E' \vec{\phi} \simeq qU(r) \vec{\phi} + \frac{1}{2m_e} \left( 1 - \frac{E' - qU(r)}{2m_e c^2} \right) \vec{p}^2 \vec{\phi} - \frac{\hbar^2 q}{4m_e^2 c^2} \nabla U(r) \cdot \nabla \vec{\phi} + \frac{\hbar q}{4m_e^2 c^2} \vec{\sigma} \cdot [\nabla U(r) \times \vec{p}] \vec{\phi} . \quad (8.83) $$
Also, with \( U(r) = U(r) \),

\[
\nabla U(r) = \frac{\partial U}{\partial r} \nabla r = \frac{\partial U}{\partial r} r \quad \text{and} \quad \nabla U(r) \cdot \nabla = \frac{\partial U}{\partial r} \hat{e}_r \cdot \nabla = \frac{\partial U}{\partial r} \frac{\partial}{\partial r}.
\]

We get,

\[
E' \tilde{\phi} = qU(r) \tilde{\phi} + \frac{1}{2m_e} \left( 1 - \frac{E' - qU(r)}{2m_e c^2} \right) \frac{p^2}{2m_e} - \frac{\hbar^2}{4m_e^2 c^2} \frac{\partial qU}{\partial r} \frac{\partial}{\partial r} \tilde{\phi} + \frac{\hbar q}{4m_e^2 c^2} \cdot \left[ \frac{1}{r} \frac{\partial U}{\partial r} r \times p \right] \tilde{\phi}.
\]

The first two terms are those arising from Bohr's atom model, the third one is a correction due to the relativistic velocity of the electron, the forth comes from the electron's spin-orbit coupling, and the fifth is called the Darwin term. All contributions represent perturbations to the non-relativistic Schrödinger theory of Bohr's atom and will be discussed extensively in Secs. 8.2. We will show in 8.1.5.6 that \( \hat{l}^2, \hat{s}^2, \) and \( \hat{j}^2 \) are constants of motion of the above Hamiltonian.

8.1.4 The Pauli equation

When we calculated the electron's energy in the Coulomb potential (8.86), we only considered the electrostatic potential of the nucleus, letting the potential vector \( \mathbf{A} \) be zero. As long as we do not apply an external magnetic field this is correct, because the internal magnetism of the atom is already completely enclosed in the Dirac equation. On the other hand, we know that the atom contains moving charges, that is, currents which generate magnetic fields. Furthermore, the spins of the electron and of the proton produce magnetic moments, which ought to interact with the magnetic fields. Hence, the existence of magnetic effects in an atom is to be expected.

These magnetic effects can be discussed in a more transparent way applying a Schrödinger-like equation with minimal coupling to electromagnetic fields (8.44) to a two-component spinor \( \tilde{\phi} \). This Schrödinger-like equation can be obtained from Dirac's equation (8.76) via a stronger non-relativistic approximation, which consists in completely neglecting the weak component \( [E' - qU(r)] \tilde{\chi} \). On the other hand, we allow for the existence of magnetic fields via the substitution \( p \to \tilde{p} \). The equation for the strong component (8.77) then becomes,

\[
E' \tilde{\phi} = [qU(r)] \tilde{\phi} + \frac{(\tilde{\sigma} \cdot \tilde{p})^2}{2m_e} \tilde{\phi}.
\]

8The spin of the electron does not generate a magnetic field, in contrast to the angular momentum caused by its orbital motion. It only interacts with the environment through the requirement of symmetrization for being a fermion.
We can again apply the formula (8.81) to calculate,

\[
(\vec{\sigma} \cdot \vec{\pi})^2 \psi = \vec{\pi}^2 \psi + iq \vec{\sigma} \cdot \left\{ \nabla \times [A(\mathbf{r}) \psi] + A(\mathbf{r}) \times \nabla \psi \right\} = \vec{\pi}^2 \psi + iq \vec{\sigma} \cdot [\mathbf{p} - qA(\mathbf{r})] \psi = \vec{\pi}^2 \psi - \frac{\hbar}{2m_e} \vec{\sigma} \cdot \vec{B}(\mathbf{r}) \psi .
\]

In the case of an electron \((e = -q)\) we obtain the so-called Pauli equation,

\[
E' \phi = \left[ \frac{1}{2m_e} (-i\hbar \nabla + eA)^2 + \frac{e\hbar}{2m_e} \vec{\sigma} \cdot \vec{B} - eU(\mathbf{r}) \right] \phi ,
\]

which corresponds to a Schrödinger-like equation for a two-component spinor \(\phi\) with the Hamiltonian,

\[
\hat{H} \simeq \frac{\mathbf{p}^2}{2m_e} - \frac{1}{4\pi \varepsilon_0} \frac{e^2}{r} - \frac{i\hbar e}{2m_e} (\nabla \cdot \mathbf{A} + \mathbf{A} \cdot \nabla) + \frac{e}{m_e} \mathbf{s} \cdot \vec{B} ,
\]

neglecting terms in \(A^2\). Note however, that the kinetic energy is calculated with the momentum projected onto the spin, \(\vec{\sigma} \cdot \vec{\pi}\). The third term can be simplified within the Coulomb gauge \(\nabla \cdot \mathbf{A} = 0\) yielding,

\[
\hat{H}_{int} = \frac{e}{m_e} (\mathbf{A} \cdot \mathbf{p}) .
\]

The Pauli equation serves for a classical (non-relativistic) approach to the electron’s spin-orbit coupling, as we will see below and in the discussion of the fine structure in Sec. 8.2.2.

### 8.1.4.1 Dipole moment of the orbital angular momentum

The rotational motion of a charge, \(-e\), creates a current \(I\), corresponding to a current density,

\[
\mathbf{j}(\mathbf{r}') = I \delta(r - r') \delta(z') = -e \frac{\mathbf{v}}{2\pi r} \delta(r - r') \delta(z') .
\]

Hence, the dipole moment caused by the circular motion of an electron is,

\[
\mathbf{\vec{\mu}}_l = \frac{1}{2} \int_V \mathbf{r} \times \mathbf{j}(\mathbf{r}') d^3r' = \frac{1}{4\pi r} \int_0^{2\pi} d\phi' \int_{-\infty}^{\infty} dz' \int_0^{\infty} r' dr' \frac{e \mathbf{v}}{r} \delta(r - r') \delta(z') = -\frac{1}{2} \mathbf{r} \times \mathbf{v} = -\frac{e}{2m_e} \mathbf{l} ,
\]

with the angular momentum \(\mathbf{l} = \mathbf{r} \times m_e \mathbf{v}\). The quotient \(\gamma_e \equiv -e/2m_e\) is called gyromagnetic ratio of the electron. We often use the Bohr magneton, \(\mu_B \equiv \hbar/e/2m_e\), which represents the elementary unit of spin,

\[
\frac{\mu_B}{\mu_s} = -g_e \frac{1}{\hbar} .
\]

The \(g\)-factor of a system having any angular momentum \(\mathbf{l}\) is defined as a proportionality constant between the normalized dipole moment and the normalized angular momentum. \(g_e \equiv \mu_s/\mu_B = 1\) takes into account possible corrections between our classical derivation and quantum mechanics.
8.1.4.2 Pauli’s model of spin-orbit coupling

The aim of this section is to demonstrate the relationship between the spin-orbit coupling term in Dirac’s Hamiltonian (8.86) and the spin-magnetic field coupling term in Pauli’s Hamiltonian (8.90).

A comparison of Pauli’s expression with the energy of a magnetic moment in the field $\vec{B}$,

$$\hat{H}_{ls} = -\vec{\mu}_s \cdot \vec{B},$$

suggests the following connection between the spin and the magnetic moment:

$$-\vec{\mu}_s \cdot \vec{B} = \frac{e\hbar}{2m_e} \vec{\sigma} \cdot \vec{B} = \frac{e}{m_e} \vec{s} \cdot \vec{B}.$$  (8.96)

We conclude, that the electron carries, besides mass, charge and spin, also a magnetic dipole moment,

$$\vec{\mu}_s \mu_B = -\frac{e}{m_e} \vec{s} = -2\frac{\vec{s}}{\hbar},$$  (8.97)

For the $g$-factor of the electron, we obtain $g_e = 2$ \(^9\). Neutron and proton are also fermions with spin $\frac{1}{2}$, but they do not obey the Dirac equation! Their $g$-factors are $g_{proton} = 5.58585$ and $g_{neutron} = -3.8261$. The large deviation from $g = 2$ points to the existence of an internal structure.

The rapid motion of the electron within the electrostatic field $\vec{E}$ of the nucleus produces, following the theory of relativity, in the electron’s reference frame a magnetic field $\vec{B}'$ with which the electronic spin can interact. As we will show in 8.1.5.7, the field seen by the electron can be approximated in first order in $v/c$ by

$$\vec{B}' \approx \frac{v}{c^2} \times \vec{E}.$$  (8.98)

With this the interaction energy (8.95) becomes,

$$\hat{H}_{ls} = -\vec{\mu}_s \cdot \vec{B}' = \frac{e}{m_e c^2} \vec{s} \cdot (\vec{v} \times \vec{E}) = -\frac{e}{m_e c^2} \vec{s} \cdot (\vec{p} \times \nabla U)$$

$$= -\frac{e}{m_e c^2} \vec{s} \cdot \left( \vec{p} \times \frac{r dU}{r dr} \right) = -\frac{1}{m_e c^2} \vec{s} \cdot \frac{1}{r} \frac{dV(r)}{dr},$$

with $V(r) = -eU(r)$.

The resulting interaction energy coincides, apart from a factor $\frac{1}{2}$ [592], with the one obtained in the from Dirac’s equation (8.86). The deviation, called Thomas factor, is due to the necessity to transform back into the inertial system of the nucleus. This transformation, called Thomas precession, must be done by a Lorentz transformation, which is not trivial with electron continuously changing its propagation direction on its circular orbit. The transformation introduces the additional factor of $\frac{1}{2}$ \(^{10}\).

\(^9\)The exact value is $g_e \equiv \frac{\mu_s}{e\mu_B} = 2.002319314\ldots$ The deviation $g_e - 2 \approx \frac{\alpha}{\pi} - 0.164\frac{\alpha^2}{\pi^2}$ is due to the coupling of the spin to the fluctuations of the electromagnetic vacuum. We need to use quantum electrodynamical methods to calculate the corrections.

\(^{10}\)This is a kinematic effect in space-time: the Lorentz transformations for systems moving with non-collinear velocities can not simply be concatenated, but must be rotated, too [208, 313].
8.1.5 Exercises

8.1.5.1 Ex: Yukawa potential

Show, that Yukawa’s potential satisfies the Klein-Gordon equation.

8.1.5.2 Ex: Zitterbewegung

Zitterbewegung is a hypothetical rapid motion of elementary particles, in particular electrons, that obey the Dirac equation. The existence of such motion was first proposed by Erwin Schrödinger in 1930 as a result of his analysis of the wave packet solutions of the Dirac equation for relativistic electrons in free space, in which an interference between positive and negative energy states produces what appears to be a fluctuation (at the speed of light) of the position of an electron around the median, with a frequency of $2m_e c^2 /\hbar$, or approximately $1.6 \cdot 10^{21}$ rad/s. For the hydrogen atom, the Zitterbewegung produces the Darwin term which plays the role in the fine structure as a small correction of the energy level of the $s$-orbitals.

Use the Heisenberg equation to derive, from Dirac’s Hamiltonian, equations of motion for the position operator $\hat{r}$ and the ‘velocity operator’ $\vec{\hat{\alpha}}$. Solve the equation of motion and identify the Zitterbewegung.

8.1.5.3 Ex: Constants of motion of Dirac’s Hamiltonian 1

Show that $\hat{L}_z$ with $\hat{L} \equiv \vec{r} \times \hat{p}$ and $\hat{S}_z$ with $\hat{S} \equiv \frac{\hbar}{2} \gamma_5 \vec{\alpha}$ defining $\gamma_5 \equiv -i\alpha_1\alpha_2\alpha_3$ are not constants of motions, but $\hat{J} = \hat{L} + \hat{S}$, that is,

$$[\hat{H}, \hat{J}_z] = [\hat{H}, \hat{L}_z + \hat{S}_z] = 0 . \tag{8.100}$$

8.1.5.4 Ex: Calculating with Dirac matrices

a. Prove that, if $[\hat{B}, \vec{\sigma}] = 0 = [\hat{C}, \vec{\sigma}]$ where $\vec{\sigma}$ are the Pauli matrices, then,

$$(\vec{\sigma} \cdot \hat{B})(\vec{\sigma} \cdot \hat{C}) = \hat{B} \cdot \hat{C} + i \vec{\sigma} \cdot (\hat{B} \times \hat{C}) . \tag{8.101}$$

b. Prove that, if $[\hat{B}, \vec{\alpha}] = 0 = [\hat{C}, \vec{\alpha}]$ where $\vec{\alpha}$ are the Dirac matrices, then,

$$(\vec{\alpha} \cdot \hat{B})(\vec{\alpha} \cdot \hat{C}) = \hat{B} \cdot \hat{C} + i \gamma_5 \vec{\alpha} \cdot (\hat{B} \times \hat{C}) . \tag{8.102}$$

c. Show that the spin defined as,

$$\vec{S} = \frac{\hbar}{2} \vec{\varsigma} \quad \text{where} \quad \vec{\varsigma} \equiv \gamma_5 \vec{\alpha} = \mathbb{I} \otimes \vec{\sigma} \tag{8.103}$$

obeys different commutation rules than the Dirac matrices.

d. Conclude that,

$$(\vec{\varsigma} \cdot \hat{B})(\vec{\varsigma} \cdot \hat{C}) = \hat{B} \cdot \hat{C} + i \vec{\varsigma} \cdot (\hat{B} \times \hat{C}) . \tag{8.104}$$
8.2. **FINE STRUCTURE OF HYDROGEN-LIKE ATOMS VIA TIPT**

### 8.1.5.5 Ex: Constants of motion of Dirac’s Hamiltonian 2

In this exercise we will prove the relationships (8.56):

a. Prove,
\[(\hbar j')^2 = J^2 + \frac{\hbar^2}{4} . \tag{8.105}\]

b. Prove,
\[[\hbar j', \hat{H}]_\pm = 0 . \tag{8.106}\]

c. Prove,
\[r \cdot p = -\hbar r \frac{\partial}{\partial r} . \tag{8.107}\]

d. Prove,
\[[\varepsilon, \hat{H}]_\pm = 0 . \tag{8.108}\]

### 8.1.5.6 Ex: Constants of motion in the L · S-coupling

Consider a particle of mass \(\mu\) described by the Hamiltonian \(\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) + \xi(r)\mathbf{L} \cdot \mathbf{S}\), being \(V(r)\) a central potential, \(\mathbf{L}\) and \(\mathbf{S}\) its orbital angular momentum and spin.

a. Obtain the commutation relations \([\mathbf{L}, \hat{H}]\), \([\mathbf{S}, \hat{H}]\) and \([\mathbf{L} + \mathbf{S}, \hat{H}]\) for the cases without and with spin-orbit interaction \(\xi(r)\mathbf{L} \cdot \mathbf{S}\) introduced by relativistic corrections.

b. Calculate \([\mathbf{L}^2, \hat{H}]\), \([\mathbf{S}^2, \hat{H}]\) and \([\mathbf{J}^2, \hat{H}]\).

### 8.1.5.7 Ex: Magnetic field generated by the orbiting proton at the location of the electron

Calculate the magnetic field generated by the orbiting proton as it is perceived by the electron.

### 8.2 Fine structure of hydrogen-like atoms via TIPT

The wave equation that simultaneously satisfies the requirements of quantum mechanics and special relativity is the **Dirac equation**. In free space including electromagnetic interactions it describes all massive particles of semi-integer spin with parity as a symmetry, such as electrons and quarks. It was the first theory to fully explain special relativity in the context of quantum mechanics. The Dirac equation describes the fine structure of the hydrogen spectrum in a completely rigorous manner. The equation also implied the existence of a new form of matter, antimatter, previously unsuspected and unobserved. The equation also justifies a posteriori the introduction of spinors, that is, of the vector wavefunctions introduced by Pauli in a heuristic way. We have seen in the last section that, in the limit of high but non-relativistic velocities, the Dirac equation adopts the form of a Schrödinger equation with the modified Hamiltonian (8.86),

\[
\hat{H} = \hat{H}_0 + \hat{H}_{rl} + \hat{H}_{ls} + \hat{H}_{dw} + \hat{H}_{lamb} \tag{8.109}
\]

\[
= \left( \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi \varepsilon_0 r} \right) - \frac{p^4}{8m_e^3 c^2} + \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{1} \cdot \mathbf{s} + \frac{\pi \hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi \varepsilon_0} \delta^3(\mathbf{r}) + \hat{H}_{lamb} .
\]
We will discuss the various terms in the following sections. Note that the expression for the Darwin term differs from that of (8.86). We will see in Exc. 8.2.6.1, that they are, in fact, equivalent.

8.2.1 Correction for relativistic velocities

The first correction in the expression, $\hat{H}_{rl}$ in Eq. (8.109), comes from the expansion of the relativistic energy for small velocities up to second order,

$$E_{kin} = \sqrt{p^2c^2 + m_e^2c^4} \simeq m_ec^2 + \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3c^2} + ... .$$ \hspace{1cm} (8.110)

The correction is of the order of magnitude,

$$\frac{H_{rl}}{H_0} = \frac{\frac{p^4}{8m_e^3c^2}}{\frac{p^2}{2m_e}} = \frac{v^2}{4c^2} \simeq \frac{\alpha^2}{4} \approx 0.01\%.$$ \hspace{1cm} (8.111)

Due to the degeneracy of these states, it would be appropriate to use perturbation theory with degenerate states. However, as $\hat{H}_{rl}$ only depends on spatial coordinates commuting with $\mathbf{l}$ and $\mathbf{s}$, the degeneracy is not very important, since $\hat{H}_{rl}$ is already diagonal in the base $|n, \ell, m\rangle$, that is, $\langle n, \ell, m'|n', \ell', m'\rangle = \delta_{\ell \ell'}\delta_{mm'}$. Starting from,

$$\hat{H}_{rl} = -\frac{p^4}{8m_e^3c^2} = -\frac{1}{2m_e} \left(\frac{p^2}{2m_e}\right)^2 = -\frac{1}{2m_e} \left(\dot{\hat{\mathbf{r}}} - \frac{2E_n n^2}{\ddot{\mathbf{r}}}\right)^2$$ \hspace{1cm} (8.112)

with $\ddot{\mathbf{r}} \equiv \frac{Ze}{\alpha n}$ and using as an abbreviation the energies of hydrogen following Bohr’s model,

$$E_n = \langle n, \ell|\hat{H}_0|n, \ell\rangle = -\frac{Z^2c^2}{4\pi \varepsilon_0} \frac{1}{2a_B n^2} = -\frac{m_ec^2}{2} \frac{Z^2\alpha^2}{n^2}.$$ \hspace{1cm} (8.113)

We have

$$\Delta E_{rl} = \langle n, \ell|\hat{H}_{rl}|n, \ell\rangle$$ \hspace{1cm} (8.114)

$$= -\frac{1}{2m_e c^2} \left[\langle n, \ell|\hat{\mathbf{r}}^2|n, \ell\rangle - \langle n, \ell|\frac{4E_n n}{\ddot{\mathbf{r}}}\hat{\mathbf{r}}|n, \ell\rangle + \langle n, \ell|\left(\frac{2E_n n}{\ddot{\mathbf{r}}}\right)^2|n, \ell\rangle\right]$$

$$= \frac{Z^2\alpha^2}{4E_n n^2} \left[\frac{E_n^2}{n^2} - 4E_n^2 n^2 \frac{1}{n^2} + 4E_n^2 n^4 \frac{1}{n^3(\ell + \frac{1}{2})}\right],$$

using the eigenvalues calculated in (3.49). Finally, we obtain the following relativistic correction,

$$\Delta E_{rl} = E_n (Z\alpha)^2 \left[\frac{1}{n(\ell + \frac{1}{2})} - \frac{3}{4n^2}\right].$$ \hspace{1cm} (8.115)

Obviously, the degeneracy with respect to the angular momentum $\ell$ is lifted by this correction.
8.2.2 Correction due to spin-orbit coupling

The second correction, \( \hat{H}_{\ell s} \) in the expression (8.109), called spin-orbit interaction, is a relativistic correction due to the fact that the electron moves rapidly within the electrostatic field \( \vec{E} \) generated by the nucleus. Considering the fundamental orbit and the fact that the angular momenta are of the order of \( \hbar \) we can estimate the importance of this effect,

\[
\frac{H_{\ell s}}{H_0} = \frac{1}{2m_e c^2} \frac{e^2}{4\pi \varepsilon_0 r^2} \frac{1}{r} \frac{e^2}{4\pi \varepsilon_0 \alpha_B^2} \approx \frac{1}{2m_e c^2} \frac{\hbar^2}{\alpha_B^2} = \frac{\alpha^2}{2} \approx 0.01\% .
\]  

(8.116)

Example 39 (Classical derivation of the spin-orbit interaction): In the following, we will derive the expression from classical arguments borrowed from electrodynamic theory. Seen from the rest system of the electron being at position \( x = 0 \), it is the proton that orbits around the electron. This orbit creates a current, \(-j(r')\), which generates a magnetic field. Following the Biot-Savart law the potential vector and the amplitude of the field are,

\[
\vec{A}(x) = \frac{\mu_0}{4\pi} \int_V \frac{-j(r')d^3r'}{|x - r'|} , \\
\vec{B}(x) = \nabla \times \vec{A}(x) = \frac{\mu_0}{4\pi} \int_V \frac{(x - r') \times j(r')}{|x - r'|^3} d^3r' ,
\]

(8.117)

respectively,

\[
\vec{B}(0) = \frac{Ze}{4\pi} \frac{\mu_0}{r^3} \left( -\frac{r \times v}{e} \right) = \frac{Ze}{4\pi} \frac{\mu_0}{r} \frac{dV(r)}{dr} = \frac{Ze}{4\pi} \frac{\hbar^2}{r} ,
\]

(8.120)

with the Coulomb potential between the electron and the proton and its radial derivative,

\[
V(r) = -\frac{Ze^2}{4\pi \varepsilon_0 r} , \quad \frac{1}{r} \frac{dV(r)}{dr} = \frac{Ze^2}{4\pi \varepsilon_0 r^3} ,
\]

(8.119)

we have at the position of the electron,

\[
\vec{B}(0) = \frac{Ze\mu_0}{4\pi} \frac{-r \times v}{r^3} = \frac{-\varepsilon_0 \mu_0}{e} \frac{r \times v}{r} - \frac{1}{e} \frac{dV(r)}{dr} = -\frac{\hbar^2}{em_e c^2 r} \frac{dV(r)}{dr} .
\]

The advantage of introducing the potential \( V \) is, that this expression also holds for more complicated atoms with many electrons, where the potential may deviate considerably from the Coulombian potential. Note, that the magnetic field is very strong, \( B \approx \xi(a_B)h/\mu_B \approx 5 \text{ T} \). Inserting the magnetic field into Pauli’s expression (8.95) together with the magnetic moment of the spin (8.97),

\[
\hat{H}_{\ell s} = -\vec{\mu}_s \cdot \vec{B}(0) = \frac{1}{m_e^2 c^2} \frac{1}{r} \frac{dV(r)}{dr} ,
\]

(8.121)

where we still have to apply the corrective Thomas factor of \( \frac{1}{2} \).
The interaction operator can be written,

$$\hat{H}_{ls} = \xi(r) \hat{l} \cdot \hat{s} ,$$  \hspace{1cm} (8.122)

with the abbreviation,

$$\xi(r) \equiv \frac{-1}{2m_e^2c^2r} \frac{dV}{dr} = -\frac{Ze^2}{8\pi\varepsilon_0m_e^2c^2} \frac{1}{r^3} = \frac{E_nZ^2\alpha^2n^2}{\hbar^2} \frac{1}{\tilde{r}^3} ,$$  \hspace{1cm} (8.123)

with $\tilde{r} \equiv Zr/a_B$ and using the formulas (3.49).

After the introduction of the spin, the Hilbert space of the particles’ wavefunctions must be extended. The wavefunctions are now products of spatial wavefunctions and spin eigenvectors:

$$|n, \ell, m, m_s\rangle = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) \begin{pmatrix} s_1 \\ s_2 \end{pmatrix} .$$  \hspace{1cm} (8.124)

The new Hilbert space is the tensorial product of position space and spin space. The radial Hamiltonian for the hydrogen atom including the centrifugal term and the spin-orbit coupling now takes the form:

$$\hat{H} = \frac{p^2}{2m} + V(r) + \frac{l^2}{2m_e r^2} + \xi(r) \hat{l} \cdot \hat{s} .$$  \hspace{1cm} (8.125)

We may again consider the energy term $V_{ls}$ as a small perturbation, and calculate it using unperturbed wavefunctions,

$$\Delta E_{ls} = \langle n, \ell, s, m, m_s|V_{ls}|n, \ell, s, m, m_s\rangle = \langle n, \ell|\xi(r)|n, \ell\rangle \langle \ell, s, m, m_s|s_1\hat{l} s_2|\ell, s, m, m_s\rangle .$$  \hspace{1cm} (8.126)

Assuming a Coulombian potential, we first look at the radial part (8.123), which can easily be calculated using the formulae (3.49),

$$\langle n, \ell|\xi(r)|n, \ell\rangle = E_nZ^2\alpha^2n^2 \frac{1}{\hbar^2} \frac{n^3\ell(\ell+1/2)(\ell+1)}{n^3(\ell+1/2)(\ell+1)} .$$  \hspace{1cm} (8.127)

To diagonalize the angular part of the Hamiltonian, we need the common wavefunctions of $j^2$, $l^2$, and $s^2$. We can rewrite the coupling term as:

$$l \cdot s = \frac{1}{2}(j^2 - l^2 - s^2) .$$  \hspace{1cm} (8.128)

In the common eigensystem of $j^2$, $l^2$, and $s^2$ the Hamiltonian, therefore, is diagonal. We know the basis of this system from the theory of the addition of angular momenta. The states of the basis are linear combinations of the functions $|n, \ell, m, m_s\rangle$. Since the spins precess around each other, $\ell_z$ and $s_z$ are not good observables. But $s^2$, $l^2$, and $j^2$ are good observables. In the coupled basis $\{n, (\ell, s)j, m_j\}$,

$$\langle n, (\ell, s)j, m_j|s_1\hat{l} s_2|n, (\ell, s)j, m_j\rangle = \frac{\hbar^2}{2} [j(j+1) - \ell(\ell+1) - s(s+1)] .$$  \hspace{1cm} (8.129)

Since $j = \ell \pm 1/2$, we find that every level splits into two levels, one with the energy $E_{n\ell} + \ell \zeta_{n\ell}$ and the degeneracy $2\ell + 2$ and the other with the degeneracy $E_{n\ell} - (\ell+1)\zeta_{n\ell}$ with the degeneracy $2\ell$, where we introduced the abbreviation,

$$\zeta_{n\ell} \equiv \frac{\hbar^2}{2} \langle \xi(r) \rangle .$$  \hspace{1cm} (8.130)
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All in all, we get an energy correction due to the spin-orbit interaction of,

\[ \Delta E_{\ell s} = -E_n(Z\alpha)^2 \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{2n\ell(\ell+1/2)(\ell+1)} \] (8.131)

Note, that the coupling \( l \cdot s \) lifts the degeneracy with respect to \( l \), but not with respect to \( \ell_z \) (see Fig. 8.1). As we have already seen in Exc. 8.1.5.6, in the presence of an energy associated with the coupling \( l \cdot s \), only the total angular momentum \( l + s \) is a constant of motion.

8.2.3 Non-local electron-core interaction

Let us now discuss the third correction in the expression (8.109). The electron-nucleus interaction that we have considered so far is local, that is, the interaction at the point \( r \) sensed by the electron depends essentially on the field at that point in space. However, when relativistic theory is correctly applied, the electron-nucleus interaction becomes non-local, and the electron is then affected by all values of the nuclear field in a region around \( r \). The size of this region is of the order of the Compton wavelength of the electron, \( \lambda_C / 2\pi \equiv h/m_e c \). This correction was introduced by Sir Charles Galton Darwin through a substitution in the Dirac equation that solved the problem of normalization of the wavefunction.

Imagine that instead of the potential \( V(r) \), the potential of the electron is given by the integral,

\[ \int f(r')V(r + r')d^3r' \] (8.132)

where \( f(r') \) is a radially symmetric and normalized density-type function that takes significant values only in the vicinity of \( r \) within a volume \( (\lambda_C / 2\pi)^3 \) centered at \( r' = 0 \). Expanding the potential \( V(r + r') \) near the origin,

\[ V(r + r') = V(r) + [r' \cdot \nabla_r]V(r) + \frac{1}{2!} [r' \cdot \nabla_r]^2 V(r) + \ldots \] (8.133)

and inserting into the integral,

\[ \int f(r')V(r + r')d^3r' \] (8.134)

\[ = V(r) \int f(r')d^3r' + \int r'f(r')d^3r' \cdot \nabla_r V(r) + \frac{1}{2} \int r'^2 f(r')[\hat{e}_r \cdot \nabla_r]^2 d^3r' V(r) + \ldots \]

\[ = V(r) + 0 + \frac{1}{2!} \int r'^2 f(r')d^3r' \nabla^2 V(r) + \ldots \]

The second term is null due to the parity of \( f(r') \) and the third produces the Darwin correction using \( V(r) = \tilde{V}(r) \). Letting the function be constant within the volume, \( f(r) \simeq f_0 \), and with the normalization,

\[ 1 = \int_{-h/2m_e c}^{h/2m_e c} \frac{h}{2m_e c} \int_{-h/2m_e c}^{h/2m_e c} \int_{-h/2m_e c}^{h/2m_e c} f(r)dx dy dz = f_0 \left( \frac{h}{m_e c} \right)^3 \] (8.135)

The smearing out of the electron’s position is also known as Zitterbewegung. See Exc. 8.1.5.2.
we get the integral

$$\int r^2 f(r) d^3r = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(r) r^2 dx dy dz = \left( \frac{\hbar}{2m_e c} \right)^2 . \quad (8.136)$$

Also,

$$\nabla^2 V(r) = -e \nabla^2 \frac{Ze}{4\pi\varepsilon_0 r} = -e \frac{\rho(r)}{\varepsilon_0} = -\frac{Ze^2 \delta^3(r)}{\varepsilon_0} . \quad (8.137)$$

Hence,

$$\int f(r') V(r + r') d^3r' = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\pi\hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \delta^3(r) + ... , \quad (8.138)$$

which is precisely the electrostatic energy with the Darwin correction in the expressions (8.86) and (8.109).

To estimate the importance of this effect we consider the ground state, inserting its wavefunction (3.48),

$$\langle \hat{H}_{dw} \rangle = \int d^3r \psi_{100}^*(r) \frac{\pi\hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \delta^3(r) \psi_{100}(r) \quad (8.139)$$

$$= \frac{\pi\hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} |\psi(0)|^2 = \frac{\pi\hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{\alpha_B^3} .$$

We obtain,

$$\frac{H_{dw}}{H_0} = \frac{\pi\hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{1}{\alpha_B^3} = \frac{\hbar^2}{2m_e^2 c^2} \frac{Z}{\alpha_B^3} \approx 0.01% . \quad (8.140)$$

Darwin’s correction does not depend on the angular momentum \( l \) nor on the spin \( s \), such that,

$$\Delta E_{dw} = \langle \hat{H}_{dw} \rangle = -E_n(Z\alpha)^2 \quad (8.141)$$

### 8.2.4 Summary of the corrections

Combining the \( l \cdot s \) and relativistic corrections, we obtain,

$$\Delta E_{fs} = \Delta E_{rl} + \Delta E_{ls} + \Delta E_{dw}$$

$$= E_n(Z\alpha)^2 \left[ \frac{1}{n(l+\frac{1}{2})} - \frac{3}{4n^2} \right] - E_n(Z\alpha)^2 \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{2n\ell(\ell+\frac{1}{2})(\ell+1)} - E_n(Z\alpha)^2$$

$$= E_n(Z\alpha)^2 \left\{ \begin{array}{ll}
\frac{1}{nj} - \frac{3}{4n^2} - \frac{j(j+1)-(\ell+\frac{1}{2})(\ell-\frac{1}{2})}{2n(\ell+\frac{1}{2})(\ell+1)} - 1 & \text{para } \ell = j - \frac{1}{2} \\
\frac{1}{n(j+1)} - \frac{3}{4n^2} - \frac{j(j+1)-(\ell+\frac{1}{2})(\ell+\frac{1}{2})}{2n(\ell+\frac{1}{2})(\ell+1)} - 1 & \text{para } \ell = j + \frac{1}{2}
\end{array} \right\} .$$

That is, the levels are now degenerate in \( j \) (see Fig. 8.1) \(^{12}\). Obviously the levels which are most affected by relativistic corrections are those with low values of \( n \) and \( \ell \).

\(^{12}\)It is interesting that the quantum treatment presented here, including relativistic corrections, coincidentally agrees with the corrections of Arnold Johannes Wilhelm Sommerfeld.
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The levels are labeled by $n\ell_j$. For example, the state $3d_{5/2}$ has the main quantum number $n = 3$, the orbital angular momentum $\ell = 2$, and the total angular momentum $j = 5/2$. For large $n$ or $j$ the fine structure disappears. The new energy scheme is shown in Fig. 8.1. We note that, taking into account all relativistic corrections (but without the Lamb shift), we still have a partial degeneracy of the quantum number $j$. For example, the states $2s_{1/2}$ and $2p_{1/2}$ have the same energy. This is a particularity of the hydrogen atom.

8.2.5 Lamb shift

Only remains to discuss the fourth correction, $\hat{H}_{\text{lamb}}$ in the expression (8.6). The origin of the Lamb shift lies in quantum electrodynamics. Being due to the quantum nature of the electromagnetic field, this correction is not predicted within the Dirac equation.

We may imagine the Coulomb force between charged particles being mediated by a continuous exchange of virtual photons. But each isolated charge also continuously emits and reabsors virtual photons, with the result that the position of the electron is smeared over a region of 0.1 fm. This reduces the overlap between the electronic orbits and the nucleus. Hence, the Lamb shift causes corrections that are stronger for small $n$ and small $\ell$. For example in hydrogen, the $2p_{1/2}$ is $4.4 \cdot 10^{-6} \text{ eV} = 1 \text{ GHz}$ below the $2s_{1/2}$ (see Fig. 8.1).

8.2.6 Exercises

8.2.6.1 Ex: The Darwin term

Show that the expressions for the Darwin correction (8.86) and (8.109) are equivalent.

8.3 Hyperfine structure

Rutherford’s measurements suggested a point-like and infinitely heavy atomic nucleus. In fact, the mass is finite and the nuclear charge is distributed over a finite volume and often in a non-isotropic manner, which leads to multipolar interactions with the electrons. In addition, many nuclei have a spin that can interact with the magnetic moment of the electrons. The energy corrections due to these effects are
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called *hyperfine structure*\(^{13}\).

Because many of the following considerations will remain valid for many-electron systems to be discussed later, we will switch to a notation denoting by \( \mathbf{L} \) the total orbital angular momentum of the electronic shell, \( \mathbf{S} \) the total spin of the electronic shell, and \( \mathbf{J} \) the total angular momentum of the electronic shell, remembering that for hydrogen \( \mathbf{S} = \frac{\hbar}{2} \mathbf{\hat{s}} \).

### 8.3.1 Coupling to the nuclear spin

#### 8.3.1.1 Dipole moment of the nuclear spin

The nucleus may also have an angular momentum interacting with the angular momentum of the electrons. However, the momentum depends inversely on the masses. That is, the angular momentum of the nucleus is \( \mu_N / \mu_B = m_e / m_p \simeq 10^{-3} \) times smaller, where \( \mu_N = \frac{\hbar e}{2 m_p} \) is an abbreviation called nuclear magneton. Thus, we can assume that the interaction between the nucleus and the electron will not interfere with the \( \mathbf{L} \cdot \mathbf{S} \)-coupling between the orbital angular momentum and the spin of the electron. The spin of the nucleus will be oriented along the total momentum of the electrons \( \mathbf{J} \). However, this interaction will have the ability to lift the hydrogen degeneracy, even though the splitting will only be *hyperfine*. Indeed, the order of magnitude of *hyperfine splitting* is \( 10^{-6} \) eV.

Analogously to the expressions (8.94) and (8.97), we write the dipole moment of the nucleus,

\[
\frac{\mu_I}{\mu_N} = \frac{e}{2 m_p \mu_N} g_p I = g_p \frac{I}{\hbar},
\]

(8.143)

where \( g_p = \mu_I / I \) is once again a factor taking into account possible corrections between the classical derivation and quantum mechanics\(^{14}\).

#### 8.3.1.2 Hyperfine splitting

In the derivation of the Pauli equation (8.90) from the Dirac equation (8.77) we discarded non-relativistic terms and reintroduced electronic spin-orbit coupling by hand allowing for \( A(r, t) \neq 0 \). By an analogous calculation directly applied to the Dirac equation we may unravel the *hyperfine structure*. Instead of setting the vector potential to \( A(r, t) = 0 \), as we did in (8.46), we now generalize the Dirac equation (8.77),

\[
E' \tilde{\phi} = qU(r) \tilde{\phi} + \tilde{\sigma} \cdot \tilde{\pi} \frac{1}{2 m_e} \left( 1 + \frac{E' - U(r)}{2 m_e c^2} \right)^{-1} \tilde{\sigma} \cdot \tilde{\pi} \tilde{\phi}.
\]

(8.144)

Assuming \( \langle qA \rangle \ll \langle p \rangle \), we may only retain terms to the lowest order in \( A \) and neglect terms containing \( qA \frac{E' - U(r)}{2 m_e c^2} \). Using the result of the calculation (8.88),

\[
(\tilde{\sigma} \cdot \tilde{\pi})(\tilde{\sigma} \cdot \tilde{\pi}) = |p - qA|^2 - \hbar q \tilde{\sigma} \cdot \tilde{B},
\]

(8.145)

\(^{13}\)See [113] p. 1229 and [604] p. 23 for further reading.

\(^{14}\)In fact, the proton factor \( g \) is anomalous, \( g_p = 5.58 \), which reduces the fraction \( \mu_I / \mu_L \). For the neutron we have: \( g_n = -3.83 \).
we find the generalization of the total energy (8.66),
\[
\hat{H} \simeq \frac{[\mathbf{p} - q \mathbf{A}(r)]^2}{2m_e} - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r} - \frac{\mathbf{p}^4}{8m_e^2c^2} - \frac{e}{2m_e^2c^2} \frac{1}{r} \frac{\partial U}{\partial r} \mathbf{S} \cdot \mathbf{L} - \frac{\hbar^2e}{4m_e^2c^2} \frac{1}{r} \frac{\partial U}{\partial r} - \frac{\hbar q}{m_e} \hat{\mathbf{S}} \cdot \mathbf{B}(r),
\]
and expanding the bracket
\[
[p - qA]^2 \simeq p^2 - qp \cdot A - qA \cdot p = p^2 - 2qA \cdot p
\]
in the Coulomb gauge, we see that two new terms are added to the energy called the hyperfine structure,
\[
\hat{H} = \hat{H}_{B} + \hat{H}_{fs} + \hat{H}_{hfs}
\]
with \(\hat{H}_{hfs} = \hat{H}_{L} + \hat{H}_{S} = \frac{e}{m_e} \mathbf{A}(r) \cdot \mathbf{p} + \frac{2eB}{\hbar} \mathbf{S} \cdot \mathbf{B}(r),\)
with \(\hat{\mu}_S = -\frac{e}{m_e} \mathbf{S}.
\]

Up to now we did not say anything about the origin of the magnetic field. We only notice that any magnetic field will interact with the electron’s orbit and with its spin. We now make use of our knowledge that the proton has a spin of its own which produces, at the position of the electrons, a magnetic vector potential,
\[
\mathbf{A}(r) = \frac{\mu_0}{4\pi} \frac{\hat{\mu}_I \times r}{r^3},
\]
interacting with the angular momentum of the electron \(\mathbf{L}\) in the form,
\[
\hat{H}_{L} = \frac{e}{m_e} \mathbf{A} \cdot \hat{\mathbf{p}} = \frac{e}{m_e} \frac{\mu_0}{4\pi r^3} (\hat{\mu}_I \times r) \cdot \mathbf{p}
\]
\[
= \frac{e}{m_e} \frac{\mu_0}{4\pi r^3} \frac{\mu_N}{\hbar} g_p (I \times r) \cdot \mathbf{p} = \frac{\mu_0}{2\pi r^3} \frac{\mu_B}{\hbar} \frac{\mu_N}{\hbar} g_p \mathbf{L} \cdot \mathbf{I},
\]
using the definition of Bohr’s magneton.

In addition, the potential vector generated by the nuclear spin produces a magnetic field [313],
\[
\mathbf{B} = \nabla \times \mathbf{A} = \frac{\mu_0}{4\pi r^3} [3(\hat{\mu}_I \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \hat{\mu}_I] + \frac{2}{3} \mu_0 \mu_I \delta^3(\mathbf{r}),
\]
as will be shown in Exc. 8.3.3.1. This field interacts with the spin of the electron \(\mathbf{S}\) in the form,
\[
\hat{H}_{S} = -\hat{\mu}_S \cdot \mathbf{B} = -\frac{\mu_0}{4\pi r^3} [3(\hat{\mu}_I \cdot \hat{\mathbf{r}})(\hat{\mu}_S \cdot \hat{\mathbf{r}}) - (\hat{\mu}_S \cdot \hat{\mu}_I)] - \frac{2}{3} \mu_0 \hat{\mu}_S \cdot \hat{\mu}_I \delta^3(\mathbf{r})
\]
\[
= \frac{\mu_0}{4\pi r^3} \frac{\mu_B}{\hbar} \frac{\mu_N}{\hbar} g_p \frac{3}{\hbar} [3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r}) - (\mathbf{S} \cdot \mathbf{I})] + \frac{2}{3} \mu_0 g_p \mu_B \mu_N \mathbf{I} \cdot \mathbf{r} \delta^3(\mathbf{r}),
\]
inserting the expressions (8.97) and (8.143). The first term gives the energy of the nuclear dipole in the field due to the electronic orbital angular momentum. The second term gives the energy of the 'finite distance' interaction of the nuclear dipole with the field due to the electron spin magnetic moments. The final term, often known as the Fermi contact term relates to the direct interaction of the nuclear dipole with the spin dipoles and is only non-zero for states with a finite electron spin density at the position of the nucleus (those with unpaired electrons in s-subshells).

We now discuss the two cases in which \(L = 0\) or \(L \neq 0\) separately in the following subsections [113, 520, 313].
CHAPTER 8. THE ELECTRON SPIN AND THE ATOMIC SUBSTRUCTURE

8.3.1.3 Orbital angular momentum \( L = 0 \)

For vanishing orbital angular momenta, \( L = 0 \), we only need to consider the contribution \( \hat{H}_{SI} \). Furthermore, this contribution will be dominated by the Dirac term, because the \( s \)-orbitals have a high probability at the nuclear region, but fall off quickly at larger distances. Hence,

\[
\hat{H}_{SI} \simeq \frac{2}{3} \mu_0 g_e \mu_B s \cdot g_p \mu_N \frac{I}{\hbar} \delta^3(r) . \tag{8.153}
\]

Defining the complete total angular momentum of the atom,

\[
\mathbf{F} \equiv \mathbf{I} + \mathbf{S} , \tag{8.154}
\]

we calculate from (8.152),

\[
\Delta E_{hfs}^{L=0} = \langle (S, I) F, m_F | \hat{H}_{SI} | (S, I) F, m_F \rangle = \frac{2 \mu_0 g_e g_p \mu_B \mu_N}{3 \hbar^2} \langle \mathbf{S} \cdot \mathbf{I} \rangle \langle \delta^3(r) \rangle \tag{8.155}
\]

\[
= \frac{2}{3} \mu_0 g_e g_p \mu_B \mu_N [F(F + 1) - I(I + 1) - S(S + 1)] \int \psi_{n00}^* \psi_{n00} \delta^3(r) \rho d^3r \]

\[
= \frac{2}{3} \mu_0 g_e g_p \mu_B \mu_N [F(F + 1) - I(I + 1) - S(S + 1)] \left| \frac{1}{\sqrt{\pi}} \left( \frac{Z}{n a_B} \right)^{3/2} \right|^2 .
\]

As an example consider the hyperfine structure of the state \( 1s_{1/2} \) of the hydrogen atom. With \( J = I = \frac{1}{2} \) and \( Z = n = 1 \) we obtain,

\[
\Delta E_{hfs}^{L=0}(F = 1) - \Delta E_{hfs}^{L=0}(F = 0) = \frac{2}{3} \mu_0 g_e g_p \mu_B \mu_N 2 \frac{1}{\pi} \left( \frac{Z}{n a_B} \right)^3 \tag{8.156}
\]

\[
= \frac{2 g_e g_p m_e^2 c^2}{3 m_p} \alpha^4 \approx (2 \pi \hbar) \cdot 1.420 \text{ GHz} .
\]

The experimental value is 1.4204057518 GHz. This frequency corresponds to the spectral line used in radio astronomy, where the measurement of the angular distribution of this radiation allows the mapping of the spatial distribution of interstellar hydrogen.

8.3.1.4 Orbital angular momenta \( L \neq 0 \)

In the case \( L \neq 0 \) both contributions, \( \hat{H}_{SI} \) and \( \hat{H}_{LI} \) have to be considered, however, we may neglect the Dirac term, because the orbitals with orbital angular momentum have vanishing probabilities at the nuclear region. Combining the two terms (8.150) and (8.152), we obtain,

\[
\hat{H}_{JL} = \hat{H}_{LI} + \hat{H}_{SI} = \frac{\mu_0}{4 \pi r^3} \frac{\mu_B}{\hbar} g_e \frac{\mu_N}{\hbar} g_p [3(\mathbf{I} \cdot \hat{r})(\mathbf{S} \cdot \hat{r}) + \mathbf{L} \cdot \mathbf{I} - \mathbf{S} \cdot \mathbf{I}] \tag{8.157}
\]

\[
= \frac{\mu_0}{4 \pi r^3} \frac{\mu_B}{\hbar} g_e \frac{\mu_N}{\hbar} g_p \mathbf{N} \cdot \mathbf{I} ,
\]

introducing \( \mathbf{N} \) as a quantity that only depends on the electronic shell:

\[
\mathbf{N} = 3(\mathbf{S} \cdot \hat{r})\hat{r} + \mathbf{L} - \mathbf{S} . \tag{8.158}
\]
8.3. HYPERFINE STRUCTURE

Generalizing the complete total angular momentum of the atom (8.154),
\[ F ≡ I + J , \] (8.159)
is useful for calculating the coupling \( I \cdot J = \frac{1}{2}(F^2 - I^2 - J^2) \). Now, as the \( L \cdot S \)-coupling is strong, we project the two angular momenta onto the total electronic angular momentum \( J \),
\[ N \rightarrow \frac{N \cdot J}{|J|} \quad J , \quad I \rightarrow \frac{I \cdot J}{|J|} \] (8.160)
We get for the coupling between the projected spins (8.160) of the electronic layer and the nucleus,
\[ N \cdot I = \frac{(N \cdot J)(I \cdot J)}{|J|^2} = \frac{(N \cdot J)(F^2 - I^2 - J^2)}{2|J|^2} \] (8.161)
We calculate
\[ \Delta E_{L,\neq 0}^{hfs} = \langle((L, S)J, I)F, m_F|\hat{H}_{IJ}|((L, S)J, I)F, m_F\rangle \]
\[ = \frac{\mu_0}{4\pi} \frac{\mu_B}{\hbar} \hbar c \frac{\mu_N}{\hbar} g_p \left\langle \frac{N \cdot I}{r^3} \right\rangle \]
\[ = \frac{\mu_0}{4\pi} \frac{\mu_B}{\hbar} \hbar c \frac{\mu_N}{\hbar} g_p \frac{N \cdot J[F(F + 1) - I(I + 1) - J(J + 1)]}{2J(J + 1)} \left( \frac{Z}{a_B} \right)^3 \frac{n}{n^4L(L + \frac{1}{2})(L + 1)} \]
Introducing the interval factor,
\[ A_J = \frac{\mu_0}{4\pi} \frac{\mu_B}{\hbar} \hbar c \frac{\mu_N}{\hbar} g_p \left( \frac{Z}{a_B} \right)^3 \frac{N \cdot J}{2J(J + 1)} \frac{n}{n^4L(L + \frac{1}{2})(L + 1)} , \]
(8.163)
as a quantity that only depends on the electronic shell, we can write
\[ \Delta E_{L,\neq 0}^{hfs} = \frac{A_J}{2} [F(F + 1) - J(J + 1) - I(I + 1)] , \]
(8.164)
Note, that the \( J \cdot I \)-coupling breaks the degeneracy of \( J \) in the hydrogen atom, but not of \( J_z \). We can derive the following interval rule,
\[ \Delta E_{F+1} - \Delta E_F = A_J(F + 1) \]
(8.165)
Besides the magnetic interaction between the angular momenta of the nucleus and the electronic shell there is an interaction between the nucleus, when it is not spherically symmetric, and the shell. This interaction causes deviations from the interval rule and an additional splitting of the hyperfine states.

8.3.2 Electric quadrupole interaction

The fact that the nucleus is not perfectly spherical gives rise to new electron-nucleus corrections that are called quadrupolar interaction. The starting point is,
\[ \hat{H}_{quad} = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{|r_e - r_N|} - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|r_e|} , \]
(8.166)
where \( r_e \) is the electronic coordinate and \( r_N \) is the nuclear coordinate, both having their origin in the center mass of the nucleus. For \( r_e > r_N \) this interaction can be obtained after several mathematical steps as [403],

\[
\hat{H}_{\text{quad}} = B_J \frac{3(I \cdot J)(2I \cdot J + 1) - 2I^2J^2}{2I(I - 1)2J(J - 1)},
\]  
(8.167)

where \( B_J \) is called the constant of the quadrupolar electron-nucleus interaction. With this expression we can calculate,

\[
\Delta E_{\text{quad}} = \langle IJKm_K|\hat{H}_{\text{quad}}|IJKm_K \rangle = B_J \frac{\frac{3}{2}K(K + 1) - 2I(I + 1)J(J + 1)}{2I(2I - 1)2J(2J - 1)},
\]  
(8.168)

where \( K \equiv 2\langle J \cdot I \rangle = F(F + 1) - I(I + 1) - J(J + 1) \). It is important to remember that a nucleus with \( I = 0 \) or \( I = \frac{1}{2} \) has no quadrupole moment, \( B_J = 0 \). Also for \( J = \frac{1}{2} \) there will be no contribution.

Joining the contributions \( J \cdot I \) of Eq. (8.164) and the quadrupolar contribution (8.168), the hyperfine structure can be described by,

\[
\Delta E_{\text{hfs}} = \Delta E_{JI} + \Delta E_{\text{quad}} = \Delta E_{JI} + \Delta E_{\text{quad}} = \frac{A_J}{2} K + \frac{B_J}{8IJ(2I - 1)(2J - 1)}[3K(K + 1) - 4I(I + 1)J(J + 1)],
\]  
(8.169)

where the constants \( A_J \) and \( B_J \) depend on the atom and the total electronic angular momentum.
8.3. HYPERFINE STRUCTURE

Table 8.1: List of atomic data [573] showing the natural linewidth of the $D_2$ line, frequencies of the $D_1$ and $D_2$ lines, and the hyperfine splitting.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\gamma D_2/2\pi$ [MHz]</th>
<th>$D_1$ [cm$^{-1}$]</th>
<th>$D_2$ [cm$^{-1}$]</th>
<th>$\nu_{HFS}[S_{1/2}]$ [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>99.58</td>
<td>82264.000</td>
<td>82264.366</td>
<td>1420.4</td>
</tr>
<tr>
<td>$^2$H</td>
<td>99.58</td>
<td>82264.000</td>
<td>82264.366</td>
<td>228.2</td>
</tr>
<tr>
<td>$^6$Li</td>
<td>5.92</td>
<td>14901.000</td>
<td>14901.337</td>
<td>803.5</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>5.92</td>
<td>14901.000</td>
<td>14901.337</td>
<td>1771.6</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>10.01</td>
<td>16956.000</td>
<td>16973.190</td>
<td>461.7</td>
</tr>
<tr>
<td>$^{35}$K</td>
<td>6.09</td>
<td>12985.170</td>
<td>13042.876</td>
<td>-1285.8</td>
</tr>
<tr>
<td>$^{40}$K</td>
<td>6.09</td>
<td>12985.170</td>
<td>13042.876</td>
<td>254.0</td>
</tr>
<tr>
<td>$^{85}$Rb</td>
<td>5.98</td>
<td>12578.920</td>
<td>12816.469</td>
<td>3035.7</td>
</tr>
<tr>
<td>$^{87}$Rb</td>
<td>5.98</td>
<td>12578.920</td>
<td>12816.469</td>
<td>6834.7</td>
</tr>
<tr>
<td>$^{133}$Cs</td>
<td>5.18</td>
<td>11182.000</td>
<td>11737.000</td>
<td>9192.6</td>
</tr>
<tr>
<td>$^{135}$Cs</td>
<td>5.18</td>
<td>11182.000</td>
<td>11737.000</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2: Hyperfine constants of some alkaline atoms.

<table>
<thead>
<tr>
<th>atom</th>
<th>n</th>
<th>$A_J(n^2S_{1/2})$ [MHz·h]</th>
<th>$A_J(n^2P_{1/2})$ [MHz·h]</th>
<th>$A_J(n^2P_{3/2})$ [MHz·h]</th>
<th>$B_J(n^2P_{3/2})$ [MHz·h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H, $I = \frac{1}{2}$</td>
<td>1</td>
<td>46.17</td>
<td>-3.07</td>
<td>-0.18</td>
<td></td>
</tr>
<tr>
<td>$^7$Li, $I = \frac{3}{2}$</td>
<td>2</td>
<td>401.75</td>
<td>46.17</td>
<td>-3.07</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13.5</td>
<td></td>
<td>-0.96</td>
<td></td>
</tr>
<tr>
<td>$^{23}$Na, $I = \frac{3}{2}$</td>
<td>3</td>
<td>885.82</td>
<td>94.3</td>
<td>18.65</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>202</td>
<td>28.85</td>
<td>6.00</td>
<td>0.86</td>
</tr>
<tr>
<td>$^{85}$Rb, $I = \frac{9}{2}$</td>
<td>5</td>
<td>1011.9</td>
<td>120.7</td>
<td>25.029</td>
<td>26.03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>239.3</td>
<td>39.11</td>
<td>8.25</td>
<td>8.16</td>
</tr>
<tr>
<td>$^{87}$Rb, $I = \frac{9}{2}$</td>
<td>5</td>
<td>3417.3</td>
<td>409.1</td>
<td>84.852</td>
<td>12.510</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>809.1</td>
<td>132.5</td>
<td>27.70</td>
<td>3.947</td>
</tr>
</tbody>
</table>

In Excs. 8.3.3.2 and 8.3.3.3 we determine the hyperfine structures of sodium and rubidium atoms.

8.3.3 Exercises

8.3.3.1 Ex: Field of a magnetic moment

a. Calculate the vector potential $\mathbf{A}(\mathbf{r})$ and the magnetic dipole moment $\mathbf{\mu}$ produced by an orbiting electron by Biot-Savart’s law using the expansion of $|\mathbf{r} - \mathbf{r}'|^{-1}$ in Legendre polynomials.

b. Calculate the magnetic field $\mathbf{B}(\mathbf{r})$. 
8.3.3.2 Ex: Hyperfine structure of sodium

Determine the hyperfine structure of the $^2S$ and $^2P$ states of the sodium atom including energy shifts. See Tab. 13.1 for the hyperfine constants $A_J$ and $B_J$.

8.3.3.3 Ex: Hyperfine structure of rubidium

Given the following energy distances $\nu_{F,F'}$ of the hyperfine levels of the rubidium isotopes $^{87}\text{Rb}$ and $^{85}\text{Rb}$ [39],

- $^{87}\text{Rb}, S_{1/2}$ splits into $\nu_{1,2} = 6834.7$ MHz
- $^{87}\text{Rb}, P_{3/2}$ splits into $\nu_{0,1} = 72.3$ MHz, $\nu_{1,2} = 157.1$ MHz, $\nu_{2,3} = 267.2$ MHz
- $^{85}\text{Rb}, S_{1/2}$ splits into $\nu_{1,2} = 3035.7$ MHz
- $^{85}\text{Rb}, P_{3/2}$ splits into $\nu_{1,2} = 29.4$ MHz, $\nu_{2,3} = 63.4$ MHz, $\nu_{3,4} = 120.7$ MHz

calculate the positions of the barycenters.

8.3.3.4 Ex: Two particles

Consider a two-particle system of masses $\mu_1$ and $\mu_2$, exposed to a central potential $V(r)$ and an interaction potential $V(|r_1 - r_2|)$ which only depends on the distance between the particles. The Hamiltonian of the system in the interaction representation is $H = H_1 + H_2 + V(|r_1 - r_2|)$ with $H_\ell = -\frac{\hbar^2}{2\mu_\ell} \nabla_\ell^2 + V(r_\ell)$. Show that the individual angular momenta $L_\ell$ are not, in general, constants of the motion, unlike the total angular momentum $L = L_1 + L_2$.

8.4 Exotic atoms

'Normal’ atoms consist of a nucleus made of protons and neutrons and an electronic shell. But other two-particle systems are possible, e.g. where the nucleus or electron is replaced by another hadron or lepton (anti-proton, positron, muon, etc.). Such a system is called exotic atom. Atoms in Rydberg states also belong to this category.

8.4.1 Positronium and muonium

Positronium ($e^+e^-$) is a hydrogen-like system consisting of leptons, that is, an electron and a positron, which is the antiparticle of the electron. The muonium ($\mu^+e^-$) is similar to positronium, except that here the positron is replaced by a muon whose mass is $m_{\mu^+} = 207m_e$. Leptons are, according to the present understanding, particles without internal structure. Both systems are unstable: the two particles annihilate each other producing $\gamma$-photons. The energy levels and orbits of the two particles are similar to that of the hydrogen atom. However, because of the reduced mass, the frequencies of the spectral lines are less than half of the corresponding hydrogen lines.

The fundamental state of positronium, like that of hydrogen, has two possible configurations depending on the relative orientation of the electron and positron spins.
The singlet state with antiparallel spins ($S = 0, M_s = 0$) is known as para-positronium (p-Ps) and denoted by $^1S_0$. It has an average lifetime of

$$\tau = \frac{2\hbar}{m_e c^2 e^5} = 124.4 \text{ ps}$$

and decays preferably in two gamma rays with energy of 511 keV each (in the center-of-mass). The triplet state with parallel spins ($S = 1, M_s = -1, 0, 1$) is known as ortho-positronium (o-Ps) and denoted as $^3S_1$. It has an average life of 138.6 ns, and the most common form of decay produces three photons. Other forms of decay are negligible. For example, the decay channel producing five photons is $10^{-6}$ times less likely. Measurements of these lifetimes and the positronium energy levels have been used in precision tests of quantum electrodynamics.

While the precise calculation of the positronium energy levels is based on the Bethe-Salpeter equation, the similarity between positronium and hydrogen allows for an approximate estimate. In this approach, the energy levels are supposed to be different from those of hydrogen because of the difference in the value of the reduced mass $\mu$, used in the energy equation. Since $\mu = m_e/2$ for positronium, we have

$$E_n = -\frac{\mu q_e^4}{8\hbar^2 \varepsilon_0^2 n^2} = -\frac{1}{2} \frac{m_e q_e^4}{8\hbar^2 \varepsilon_0^2 n^2} = -6.8 \text{ eV}.$$  \hspace{1cm} (8.171)

A di-positronium molecule, that is, a system of two bound positronium atoms, has already been observed. Positronium in high energy states has been conjectured to become the dominant form of atomic matter in the universe in the very distant future if the proton decay becomes tangible.

### 8.4.2 Hadronic atoms

In contrast to leptons (such as the electron $e^-$, the positron $e^+$ and the muons $\mu^+$ and $\mu^-$) that participate only in electromagnetic interactions and weak interactions, hadrons also participate in strong (nuclear type) interactions. There are two types of hadrons, baryons (such as the proton $p$ and antiproton $\bar{p}$, the neutron $n$ and antineutron $\bar{n}$, hyperons $\Sigma$, $\Xi$, ...) that have semi-integer spin and behave like fermions and mesons (like the $\pi$-meson, $K$-meson, ...) that have an integer spin. Every negatively charged hadron can be used to form a hydrogen-type hadronic atom. These systems contain a nucleus and negative hyperon and are known as hyperonic atoms. All of these are unstable and due to the fact that they have a sufficiently long lifetime, some of their spectral lines have now been observed.

Since the hadrons interact strongly with the nucleus, the theory developed for hydrogen systems (in which only exist Coulomb interaction) can not be directly applied. In this way the values shown in Tab. 8.3 give only an estimate of the ‘radius’ and the ionization potential of the hadronic atoms $p\pi^-$, $pK^-$, $p\bar{p}$ and $p\Sigma^-$.  

### 8.4.3 Muonic hydrogen

The muon mass is $m_\mu = 207 m_e$. When a muon is attached to a proton we have muonic hydrogen. Its size is smaller because of the reduced mass $a_\mu = a_B \frac{1/m_e}{1/m_\mu + 1/m_p}$.
and the binding energy and the energies of excitation are greater for the same reason. F.ex. while for $H = p^+ e^-$ the transition $2S - 2P_{1/2}$ is at 10 eV $\Delta = 121$ nm, for $p^+ \mu^-$ it is at 1900 eV. Muonic atoms are interesting because they have amplified Lamb shifts, hyperfine interactions, and quantum electrodynamical corrections. Therefore, the displacement due to the finite distribution of charges in the proton $r_p = 0.8$ fm should influence the spectrum. While in $p^+ e^-$ the 2S level is shifted upward by the Lamb shift by a value of $4.4 \times 10^{-6}$ eV, in $p^+ \mu^-$ it is shifted down by a value of 0.14 eV. In Exc. 8.4.5.2 we calculate the spectrum of the muonic hydrogen and in Exc. 5.1.3.3 we compare the energy corrections due to the finite extension of the nuclei for muonic and for standard hydrogen in first order TIPT.

### 8.4.4 Rydberg atoms

An atom excited to a state whose main quantum number is very high is called Rydberg atom. These atoms have a number of peculiar properties, including high sensitivity to electric and magnetic fields, long decay times, and wavefunctions that approximate classical electron orbits. The inner electrons protect the outer electron from the electric field of the nucleus such that, from a distance, the electric potential looks identical to that seen by the electron of a hydrogen atom.

Despite its flaws, Bohr’s atom model is useful in explaining these properties. In Exc. 1.1.6.6 we derive Bohr’s expression for the orbital radius in terms of the principal quantum number $n$:

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{e^2 m}.$$

(8.172)

Thus, it is clear why Rydberg atoms have peculiar properties: the radius goes as $n^2$ (such that for example the state with $n = 137$ of hydrogen has a radius of $\sim 1$ mm) and the geometric cross section goes as $n^4$. Thus, Rydberg atoms are extremely large, with loosely bound valence electrons that are easily perturbed or ionized by collisions or external fields.

Since the binding energy of a Rydberg electron is proportional to $1/r$, and therefore falls as $1/n^2$, the spacing between energy levels falls as

$$\Delta E = E_1 \left( \frac{1}{(n + 1)^2} - \frac{1}{n^2} \right) \xrightarrow{n \to \infty} E_1 \left( -\frac{2}{n^3} + \frac{3}{n^4} + ... \right)$$

(8.173)
leading to less and less spaced levels. These Rydberg states form the Rydberg series.

### 8.4.4.1 Correspondence principle in Rydberg atoms

To calculate the oscillation frequency of an electron confined to a proton, we use the classical planetary model,

\[ m\omega_n^2 = \frac{e^2}{4\pi\varepsilon_0 r} \quad \text{and} \quad m\omega r^2 = n\hbar. \]  

(8.174)

Eliminating \( r \),

\[ \omega_n = \frac{me^4}{(4\pi\varepsilon_0)^2n^3\hbar^3}. \]  

(8.175)

Radiation of this frequency will be emitted by an atomic antenna. On the other hand, the Bohr model predicts frequencies between orbitals,

\[ \omega_n = \frac{E_{n+1} - E_n}{\hbar} = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} \left( \frac{1}{(n+1)^2} - \frac{1}{n^2} \right) \xrightarrow{n\to\infty} \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2} \frac{2}{n^3}. \]  

(8.176)

### 8.4.4.2 Production of Rydberg atoms

In the hydrogen atom only the ground state \((n = 1)\) is actually stable. Other states must be excited by various techniques such as electron impact or charge exchange. In contrast to these methods, which produce a distribution of excited atoms at various levels, the optical excitation method allows to produce specific states, but only for alkali metals whose transitions fall into frequency regimes which are accessible to lasers.

### 8.4.4.3 Potential in a Rydberg atom

The valence electron in a Rydberg atom with \( Z \) protons in the nucleus and \( Z - 1 \) electrons in closed layers sees a spherically symmetric Coulomb potential:

\[ U_{\text{cou}} = -\frac{e^2}{4\pi\varepsilon_0 r}. \]  

(8.177)

The similarity of the effective potential 'seen' by the outer electron and the authentic hydrogen potential suggests a classical treatment within the planetary model. There are three notable exceptions:

- An atom can have two (or more) electrons in highly excited states with comparable orbital radii. In this case, the electron-electron interaction gives rise to a significant deviation from the hydrogen potential. For an atom in a multiple Rydberg state the additional term \( U_{ee} \) includes a sum over each pair of highly excited electrons:

\[ U_{ee} = \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \]  

(8.178)
If the valence electron has very low angular momentum (interpreted classically as an extremely eccentric elliptical orbit), it can pass close enough to the nucleus to polarize it, giving rise to an additional term,

\[ U_{\text{pot}} = -\frac{e^2 \alpha_d}{(4\pi\varepsilon_0)^2 r^4}. \] (8.179)

If the outer electron penetrates the inner electronic shells, it sees more of the charge of the nucleus and therefore feels a larger force. In general, the modification of the potential energy is not simple to calculate and should be based on some knowledge of the nucleus’ geometry.

In hydrogen the binding energy is given by:

\[ E_B = -\frac{E_1}{n^2}. \] (8.180)

The binding energy is weak at high values of \( n \), which explains the fragility of the Rydberg states that can easily be ionized, e.g. by collisions.

Additional terms modifying the potential energy of a Rydberg state require the introduction of a quantum defect, \( \delta \ell \), in the expression for the binding energy:

\[ E_B = -\frac{E_1}{(n - \delta \ell)^2}. \] (8.181)

The long lifetimes of Rydberg states with high orbital angular momentum can be explained in terms of overlapping wavefunctions. The wavefunction of an electron in a state with high \( \ell \) (large angular momentum, 'circular orbit') has little overlap with the wavefunctions of the internal electrons and therefore stays relatively unperturbed. Also, the small energy difference between adjacent Rydberg states decreased the decay rate according to the result (13.37).

### 8.4.4.4 Rydberg atoms in external fields

The large distance between the electron and ionic nucleus in a Rydberg atom gives rise to an extremely large electric dipole moment \( d \). There is an energy associated with the presence of an electric dipole in an electric field \( \vec{E} \), known as Stark shift,

\[ E_S = -d \cdot \vec{E}. \] (8.182)

Depending on the sign of the projection of the dipole moment onto the vector of the local electric field, the energy of a state increases or decreases with the intensity of the field. The narrow spacing between adjacent levels \( n \) in the Rydberg series means that the states can approach degeneracy even for relatively weak fields. Theoretically, the force of the field in which a level crossing would occur (assuming no coupling between the states) is given by the Inglis-Teller limit,

\[ F_{\text{IT}} = \frac{e}{12\pi\varepsilon_0 a_0^2 n^5}. \] (8.183)

In hydrogen the pure Coulomb potential does not couple the Stark states of an \( n \) level, which results in a real crossover. In other elements, deviations from the ideal \( 1/r \)-potential allow for avoided crossings.
8.4.5 Exercises

8.4.5.1 Ex: Positronium

Calculate and compare the fine and hyperfine structure of positronium.

8.4.5.2 Ex: Hidrogênio muônico

Muonic hydrogen consists of a proton and a negatively charged muon. Calculate the binding energy of the ground state of muonic hydrogen in eV and write down the ground state’s wavefunction.
Chapter 9

Atoms with spin in external fields

9.1 Charged particles in electromagnetic fields

9.1.1 Lagrangian and Hamiltonian of charged particles

A charge subject to an electromagnetic field feels the Lorentz force,

\[ F = q\vec{E} + q\dot{\vec{r}} \times \vec{B}, \]  

(9.1)

where

\[ \vec{E} = -\nabla \Phi - \frac{\partial \vec{A}}{\partial t} \quad \text{and} \quad \vec{B} = \nabla \times \vec{A}, \]  

(9.2)

where \( \Phi \) and \( \vec{A} \) are called scalar and vector potential, respectively.

It is important to realize here, that the momentum \( p \) not only involves the momentum of the particle \( m\vec{v} \), but the field also carries a momentum \( q\vec{A}(\vec{r}) \). As we learned in electrodynamics it is possible to derive this force from a Lagrangian for the electronic motion,

\[ L(\vec{r}_i, \dot{\vec{r}}_i) = \frac{m}{2}\dot{\vec{r}}^2 - q\Phi(\vec{r}) + q\dot{\vec{r}} \cdot \vec{A}(\vec{r}). \]  

(9.3)

With this aim we first determine the momentum by,

\[ p_i = \frac{\partial L}{\partial \dot{r}_i} = m\dot{r}_i + qA_i, \]  

(9.4)

and the Hamiltonian by,

\[ H = \sum_i p_i\dot{r}_i - L(\vec{r}_i, \dot{\vec{r}}_i) = (m\vec{v} + q\vec{A}) \cdot \dot{\vec{r}} - \frac{m}{2}\dot{\vec{r}}^2 + q\Phi - q\dot{\vec{r}} \cdot \vec{A} = \frac{m}{2}v^2 + q\Phi. \]  

(9.5)

That is,

\[ H(\vec{r}_i, p_i) = \frac{1}{2m}(p - q\vec{A})^2 + q\Phi \]  

(9.6)

The following equations hold,

\[ \dot{\vec{r}}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H}{\partial r_i}. \]  

(9.7)
The first equation is easily verified by inserting the Hamiltonian (9.5). The second
leads to the Lorentz force,

\[ F_i = m \dot{v}_i = \dot{p}_i - q \dot{A}_i = -\frac{\partial H}{\partial r_i} - q \dot{A}_i = q \mathcal{E}_i + q (\mathbf{v} \times \mathbf{B})_i , \]  

(9.8)

where the last step of the derivation will be shown in the Exc. 9.1.3.1 using the
Coulomb gauge \( \nabla \cdot \mathbf{A} = 0 \).

### 9.1.2 Minimal coupling

Note that the same result (9.6) can be obtained by a canonical substitution,

\[ m \mathbf{v} \rightarrow \mathbf{p} - q \mathbf{A} \quad \text{and} \quad H \rightarrow H + q \Phi . \]  

(9.9)

This substitution rule, called minimal coupling, can be applied in quantum mechanics,

\[ m \dot{\mathbf{v}} \rightarrow -i\hbar \nabla - q \mathbf{A} \quad \text{and} \quad \hat{H} \rightarrow \hat{H} + q \Phi . \]  

(9.10)

In the case of the electron (\( q = -e \)) trapped in a central Coulomb potential
\( q \Phi = -\frac{Ze^2}{4\pi \varepsilon_0 r} \) and in the presence of any magnetic potential \( \mathbf{A} \), we thus obtain,

\[
\hat{H} = \frac{m_e}{2} \dot{\mathbf{v}}^2 + q \Phi = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{ihe}{2m_e} \mathbf{A} \cdot \nabla - \frac{ihe}{2m_e} \nabla \cdot \mathbf{A} + \frac{e^2 \mathbf{A}^2}{2m_e} + q \Phi .
\]  

(9.11)

The fourth term called diamagnetic term is quadratic in \( \mathbf{A} \) and usually so small
that it can be neglected. The second and third terms describe the interaction of the
electron through its momentum \( \mathbf{p} \) with the potential vector \( \mathbf{A} \) produced by magnetic
moments inside the atom or outer magnetic fields. Within the Coulomb gauge we
have \( (\nabla \cdot \mathbf{A}) \psi = (\mathbf{A} \cdot \nabla) \psi + \psi (\nabla \cdot \mathbf{A}) = (\mathbf{A} \cdot \nabla) \psi \), such that,

\[
\hat{H}_{\text{int}} = \frac{e}{m_e} \mathbf{A} \cdot \hat{\mathbf{p}} .
\]  

(9.12)

**Example 40 (Interaction Hamiltonian in dipolar approximation):** Note
that the Hamiltonian (9.11) has been obtained from a gauge transformation in
(2.201). With the particular choice for the gauge field,

\[ \chi(r, t) \equiv -\mathbf{A}(r, t) \cdot \mathbf{r} , \]

assuming that the potential only weakly varies in space, such that,

\[
\nabla \chi(r, t) \simeq -\mathbf{A}(r, t) \quad \text{and} \quad \frac{\partial \chi(r, t)}{\partial t} \simeq -\mathbf{r} \cdot \frac{\partial \mathbf{A}(r, t)}{\partial t} = -\mathbf{r} \cdot \mathcal{E}(r, t) ,
\]

we get with \( \mathbf{d} \equiv q \mathbf{r} , \)

\[
\hat{H} = \frac{1}{2m_e} (\mathbf{p} - q \mathbf{A} + \nabla \chi)^2 + q \Phi + q \frac{\partial \chi(r, t)}{\partial t} = \frac{\mathbf{p}^2}{2m_e} + q \Phi - \mathbf{d} \cdot \mathcal{E}(r, t) ,
\]  

(9.13)

Which is the interaction Hamiltonian in the dipolar approximation.
9.2. Interaction with magnetic fields

9.2.1 Normal Zeeman effect of the fine structure

The dipole moments of atoms can interact with external magnetic fields. The interaction leads to a shift of levels, which depends on the magnetic quantum number. Thus, the ultimate degeneracy in the energetic structure of the atom is lifted. This is called Zeeman splitting. We consider a uniform magnetic field \( \vec{B} = \hat{B} \hat{e}_z \) with the potential vector,

\[
\vec{A} = \frac{1}{2} \vec{B} \times \vec{r} = -\frac{\vec{B}}{2} (y \hat{e}_x + x \hat{e}_y).
\]

(9.14)

Thus the interaction energy between the electron and the field is given by the Hamiltonian (9.12),

\[
V_{zee}(B) = -\frac{i \hbar e}{m_e} \vec{A} \cdot \nabla = -\frac{i \hbar e}{2m_e} \vec{B} \times \vec{r} \cdot \nabla = -\frac{i \hbar e}{2m_e} \vec{B} \cdot (\vec{r} \times \nabla)
\]

(9.15)

\[
= -\frac{e}{2m_e} \vec{B} \cdot \vec{L} = -\frac{\mu_B}{\hbar} g_L \hat{L} \cdot \vec{B} = -\frac{\mu_B}{\hbar} \hat{L}_z B,
\]

with \( g_L = 1 \) using the relation (8.94), \( \vec{\mu}_L = \frac{e}{2m_e} \vec{L} \), between the angular momentum of the electron and the resulting magnetic moment. This relationship holds for an atom without spin (two electrons can couple their spins to a singlet state) and no hyperfine structure (or an unresolved hyperfine structure). The energies are therefore,

\[
\Delta E_{zee}(B) = -\frac{\mu_B}{\hbar} B \langle n, L, m_L | \hat{L}_z | n, L, m_L \rangle = -\mu_B m_L B.
\]

(9.16)

In the Excs. 9.2.8.1 and 9.2.8.2 we represent the interaction between an atomic angular momentum and a magnetic field in different bases characterized by different quantization axes.

9.2.2 Anomalous Zeeman effect

The anomalous Zeeman effect occurs when the ensemble of electrons has a spin. Using the already known expressions for the dipole moments of the orbital momentum and the spin of the electron, we obtain for the magnetic dipole moment,

\[
\vec{\mu}_J = \vec{\mu}_L + \vec{\mu}_S = \frac{\mu_B}{\hbar} g_L \vec{L} + \frac{\mu_B}{\hbar} g_s \vec{S} = \frac{\mu_B}{\hbar} (\vec{L} + 2 \vec{S}),
\]

(9.17)

with \( g_L = 1 \) and \( g_S = g_e = 2 \). We can see that the dipole moment of the atom is not parallel to the total momentum, \( \vec{J} = \vec{L} + \vec{S} \).
When the magnetic field is weak, $V_{ls} \gg V_{zee}(B)$, the total momentum $J$ will be a good observable. Therefore, we must first project the momenta $L$ and $S$ onto $J$,

$$L \rightarrow \left( L \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|}, \quad \text{and} \quad S \rightarrow \left( S \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|},$$  \hspace{1cm} (9.18)

before projecting the result onto the $\vec{B}$-field. The potential is,

$$V_{zee}(B) = -\mu B \cdot \vec{B} = -\frac{\mu B}{\hbar} (L + 2S) \cdot \vec{B} \rightarrow -\frac{\mu B}{\hbar} \left[ \left( L \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|} + 2 \left( S \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|} \right] = -\frac{\mu B}{\hbar} \frac{1}{2} \frac{3}{|J|^2} J^2 - \frac{S^2}{|J|^2} J \cdot \vec{B}. \hspace{1cm} (9.19)$$

And the energy is,

$$\Delta E_{zee}(B) = \left\langle \frac{\mu B}{\hbar} \left( 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right) \hat{J} \cdot \vec{B} \right\rangle. \hspace{1cm} (9.20)$$

Introducing the Landé factor,

$$g_J \equiv 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \hspace{1cm} (9.21)$$

we can write

$$\Delta E_{zee}(B) = -\frac{\mu B}{\hbar} g_J \langle \hat{J}_z B \rangle = -\mu_B g_J m_J B. \hspace{1cm} (9.22)$$

This expression describes the anomalous Zeeman effect, for which $S \neq 0$. For the normal Zeeman effect, for which the spin is zero, we find again $g_J = 1$.

Figure 9.1: Coupling angular moments for the effect (a) Normal Zeeman effect, (b) anomalous Zeeman effect, (c) Paschen-Back effect, (d) Zeeman effect of the hyperfine structure, and (e) Paschen-Goudsmith effect.

### 9.2.3 Paschen-Back effect and intermediate magnetic fields

A very strong external magnetic field ($> 1$ T), such that $V_{ls} \ll V_{zee}(B)$, can break the $L \cdot S$-coupling. Both spins $L$ and $S$ now couple separately to the field,

$$L \rightarrow \left( L \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|}, \quad \text{and} \quad S \rightarrow \left( S \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|}. \hspace{1cm} (9.23)$$
Therefore,

\[ V_{ph}(B) = -\frac{\mu_B}{\hbar} (\hat{L} + 2\hat{S}) \cdot \vec{B} \rightarrow -\frac{\mu_B}{\hbar} \left[ \frac{\vec{L} \cdot \vec{B}}{|\vec{B}|} \right] \vec{B} + 2\left( \vec{S} \cdot \frac{\vec{B}}{|\vec{B}|} \right) \vec{B}, \]

(9.24)
such that

\[ \Delta E_{ph}(B) = -\mu_B(m_L + 2m_S)B. \]

(9.25)
This is the Paschen-Back effect.

The derivations we have made so far have focused on simple situations well described by CSCOs in various coupling schemes. The projections on the different quantization axes [the total spin (9.18) in the Zeeman case or the applied magnetic field (9.23) in the Paschen-Back case] ensure that the Hamiltonians \( V_{ls} \) and \( V_{zee}(B) \) in these CSCOs are described by diagonal matrices. However, in regimes intermediate between Zeeman and Paschen-Back, \( V_{ls} \simeq V_{zee}(B) \), it is generally not possible to find a diagonal representation.

In order to calculate the energy spectrum in intermediate regimes we must, therefore, determine all the components of the matrix,

\[ V_{ls} + V_{zee}(B) = \xi(r) \hat{L} \cdot \hat{S} + \frac{\mu_B}{\hbar} (\hat{L} + 2\hat{S}). \]

(9.26)

Using \( \hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y \) and \( \hat{S}_\pm \equiv \hat{S}_x \pm i\hat{S}_y \), we can easily rewrite the energy in the following way,

\[ V_{ls} + V_{zee}(B) = \xi(r) \left( \hat{L}_z \hat{S}_z + \frac{1}{2} \hat{L}_+ \hat{S}_- + \frac{1}{2} \hat{L}_- \hat{S}_+ \right) + \frac{\mu_B}{\hbar} (\hat{L} + 2\hat{S}) \cdot \vec{B}. \]

(9.27)
This operator acts on the uncoupled states,

\[ \Delta E_{ls} + \Delta E_{zee}(B) \]

\[ = \langle L'm_L'; S'm_S' | \xi_{nl}(\hat{L}_z \hat{S}_z + \frac{1}{2} \hat{L}_+ \hat{S}_- + \frac{1}{2} \hat{L}_- \hat{S}_+) + \mu_B(\hat{L}_z + 2\hat{S}_z)B | Lm_L; Sm_S \rangle \]

\[ = \hbar^2 \xi_{nl} \left( \delta_{m_L,m'_L} \delta_{m_S,m'_S} + \frac{1}{2} \delta_{m_L,m'_L} \delta_{m_S,m'_S - 1} \right) \]

\[ + \hbar \mu_B (m_L + 2m_S) B \delta_{m_L,m'_L} \delta_{m_S,m'_S}, \]

(9.28)
with the abbreviations \( L_\pm \equiv \sqrt{L(L+1)} - m_L(m_L \pm 1) \). The energies are now the eigenvalues of this matrix. The factor \( \xi_{nl} \) is usually determined experimentally by letting \( B = 0 \). In Exc. 9.2.8.3 we calculate the re-coupling of the spins of two electrons in an external magnetic field.

### 9.2.4 Zeeman effect of the hyperfine structure

When the energy of the interaction with the magnetic field is comparable to the hyperfine interactions, but much weaker than that of the fine interactions, the fields do not disturb the coupling between the total electronic momentum \( J \) and the spin of the nucleus \( I \). Hence, \( J, I, F \), and \( m_F \) are good quantum numbers. Therefore, to calculate the interaction energy,

\[ V_{hfs} + V_{zee}(B) = V_{hfs} - \mu_F \cdot \vec{B}, \]

(9.29)
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Figure 9.2: Transition between the Zeeman regime and the Paschen-Back regime for the case $L = 1$ and $S = 1/2$.

where $\vec{\mu}_F$ is the total magnetic momentum,

$$\vec{\mu}_F = \vec{\mu}_J + \vec{\mu}_I = -\frac{\mu_B}{\hbar} g_J \hat{J} + \frac{\mu_N}{\hbar} g_p \hat{I}.$$  \hspace{1cm} (9.30)

we project the nuclear spin and the total electronic momentum separately in the direction of $\hat{F}$,

$$\hat{J} \rightarrow \left( \hat{J} \cdot \frac{\vec{F}}{|\vec{F}|} \right) \frac{\vec{F}}{|\vec{F}|} \quad \text{and} \quad \hat{I} \rightarrow \left( \hat{I} \cdot \frac{\vec{F}}{|\vec{F}|} \right) \frac{\vec{F}}{|\vec{F}|}.$$  \hspace{1cm} (9.31)

Note the negative sign in (9.30) due to the negative charge of the electron. The Landé factor $g_J$ [see (9.21)] is the one caused by the coupling of the orbital angular momentum $\vec{L}$ and the electron spin $\vec{S}$ and depends on the state under consideration. Thereby,

$$V_{zee}(B) = \left[ -\frac{\mu_B}{\hbar} g_J \left( \hat{J} \cdot \frac{\vec{F}}{|\vec{F}|} \right) \frac{\vec{F}}{|\vec{F}|} + \frac{\mu_N}{\hbar} g_p \left( \hat{I} \cdot \frac{\vec{F}}{|\vec{F}|} \right) \frac{\vec{F}}{|\vec{F}|} \right] \vec{B}$$  \hspace{1cm} (9.32)

Using $\hat{J} \cdot \hat{F} = \frac{1}{2}(\hat{F}^2 + \hat{J}^2 - \hat{I}^2)$ and $\hat{I} \cdot \hat{F} = \frac{1}{2}(\hat{F}^2 - \hat{J}^2 + \hat{I}^2)$ we write,

$$V_{zee}(B) = -\frac{\mu_B}{\hbar} g_J \frac{\hat{F}^2 + \hat{J}^2 - \hat{I}^2}{2|\vec{F}|^2} BF_z + \frac{\mu_N}{\hbar} g_p \frac{\hat{F}^2 - \hat{J}^2 + \hat{I}^2}{2|\vec{F}|^2} BF_z,$$  \hspace{1cm} (9.33)

such that

$$\Delta E_{hfs} + \Delta E_{zee}(B) \simeq \Delta E_{hfs} + \mu_B g_F m_F B,$$  \hspace{1cm} (9.34)

using the Landé factor $g_F$ for the state $F$,

$$g_F \simeq g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g_J \frac{\mu_N}{\mu_B} \frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)},$$  \hspace{1cm} (9.35)
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where the second term can be neglected.

The splitting of electronic states with the momentum $\hat{F}$ into $2F + 1$ sublevels $m_F = -F, \ldots, F$ is called Zeeman effect of the hyperfine structure. The result (9.32) only applies to weak fields. For strong fields the Zeeman splitting becomes a Paschen-Back splitting of the hyperfine structure.

9.2.5 Paschen-Back effect of the hyperfine structure

When the interaction with the magnetic field exceeds the hyperfine interaction, the nuclear spin $\hat{I}$ decouples from the total momentum $\hat{J}$, and both couple separately to the external magnetic field,

$$\hat{J} \rightarrow \left( \hat{J} \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|} \quad \text{and} \quad \hat{I} \rightarrow \left( \hat{I} \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|}. \quad (9.36)$$

The Zeeman effect of the hyperfine structure becomes a hyperfine structure of the Zeeman effect, also called Paschen-Back effect of the hyperfine structure or Paschen-Goudsmith effect. We can diagonalize the potential on a basis, where $I, m_I, J, m_J$ are good quantum numbers. Using the expression (8.169) but disregarding the quadrupolar contribution to the hyperfine interaction, $B_J \simeq 0$, we obtain,

$$V_{hfs} + V_{zee}(B) = V_{hfs} - (\vec{\mu}_J + \vec{\mu}_I) \cdot \vec{B} \simeq \frac{A_J}{\hbar^2} \hat{J} \cdot \hat{I} + \vec{\mu}_J \cdot \vec{B}. \quad (9.37)$$

$$\rightarrow \frac{A_J}{\hbar^2} \left( \hat{J} \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|} \cdot \left( \hat{I} \cdot \frac{\vec{B}}{|\vec{B}|} \right) \frac{\vec{B}}{|\vec{B}|} + \mu_{Jz}B = \frac{A_J}{\hbar^2} \hat{J}_z \hat{I}_z + \mu_{Jz}B,$$

where we neglect the interaction of the dipole moment of the nucleus with the external magnetic field, $\vec{\mu}_I \simeq 0$. We obtain,

$$\Delta E_{hfs} + \Delta E_{zee}(B) \simeq A_J m_J m_I \mu_B m_I. \quad (9.38)$$

The re-coupling of the state $|F m_F\rangle$ to $|m_I m_J\rangle$ in strong magnetic fields is described by Clebsch-Gordan coefficients,

$$|F m_F\rangle = \sum_{m_I + m_J = m_F} |m_I m_J\rangle \langle m_I m_J | F m_F\rangle. \quad (9.39)$$

9.2.6 Hyperfine structure in the intermediate field regime

Knowing the dipolar magnetic $A_J$ and quadrupolar $B_J$ interval factors, it is possible to calculate the Zeeman shift of the hyperfine structure in magnetic fields intermediate between the Zeeman and Paschen-Back regimes. For this, we must determine all the components of the matrix $V_{hfs} + V_{zee}(B)$ and calculate the eigenvalues. The relevant terms of the Eqs. (8.169) and the Eq. (9.36) are,

$$V_{hfs} + V_{zee}(B) = \frac{A_J}{\hbar^2} \hat{I} \cdot \hat{J} + \frac{B_J}{\hbar^2} \frac{6(\hat{I} \cdot \hat{J})^2 + 3\hat{I} \cdot \hat{J} - 2\hat{J}^2\hat{I}^2}{2I(2I-1)2J(2J-1)} + g_J \mu_B \vec{B} \cdot \hat{J} - g_I \mu_N \vec{B} \cdot \hat{I}. \quad (9.40)$$

We develop the complete matrix representation of this Hamiltonian within the uncoupled base, where $m_I, m_J$ are good quantum numbers, introducing the abbreviations $I_+ \equiv \sqrt{I(I+1) - m_I(m_I \pm 1)}$ and $I_{\pm \pm} \equiv \sqrt{I(I+1) - (m_I \pm 1)(m_I \pm 2)}.
The SU(2) algebra provides useful expressions, $\mathbf{\hat{I}} \cdot \mathbf{\hat{J}} = \mathbf{\hat{I}}_z \mathbf{\hat{J}}_z + \frac{1}{2} (\mathbf{\hat{I}}_+ \mathbf{\hat{J}}_- + \mathbf{\hat{I}}_- \mathbf{\hat{J}}_+ )$. The elements of the matrix are,

$$
\langle m'_I m'_J | H_{hfs} + H_B | m_I m_J \rangle = \left[ A_J + \frac{3B_J}{2(J+1)} \right] \times
$$

$$
\times \left\{ m_I m_J \delta_{m'_I m_I} \delta_{m'_J m_J} + \frac{1}{2} I_+ J_+ \delta_{m'_I m_I+1} \delta_{m'_J m_J-1} + \frac{1}{2} I_- J_- \delta_{m'_I m_I-1} \delta_{m'_J m_J+1} \right\}
$$

$$
+ \frac{6B_J}{2I(2I-1)2J(2J-1)} \langle m'_I m'_J | \left( \frac{\mathbf{\hat{I}}}{\hbar} \right)^2 | m_I m_J \rangle
$$

$$
+ \left[ - \frac{B_J 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)} + (g_I m_J - g_I \mu_B m_I) \mu_B B \right] \delta_{m'_I m_I} \delta_{m'_J m_J}
$$

where

$$
\langle m'_I m'_J | \left( \frac{\mathbf{\hat{I}}}{\hbar} \right)^2 | m_I m_J \rangle = \left[ (m_I m_J)^2 + \frac{1}{4} I_+^2 J_+^2 + \frac{1}{4} I_-^2 J_-^2 \right] \delta_{m'_I m_I} \delta_{m'_J m_J} + \frac{1}{2} \left( m'_I m'_J + m_I m_J \right) I_+ J_+ \delta_{m'_I m_I+1} \delta_{m'_J m_J-1} + \frac{1}{2} \left( m'_I m'_J + m_I m_J \right) I_- J_- \delta_{m'_I m_I-1} \delta_{m'_J m_J+1} + \frac{1}{4} I_+ J_+ I_- J_- \delta_{m'_I m_I+2} \delta_{m'_J m_J-2} + \frac{1}{4} I_- J_+ I_- J_- \delta_{m'_I m_I-2} \delta_{m'_J m_J+2} .
$$

The matrix $\langle m'_I m'_J | H_{hfs} + H_B | m_I m_J \rangle$ is divided into $2F + 1$ diagonal blocks, each labeled $m_F$. The total number of levels is,

$$
\sum_{F=|I-J|,..,I+J} 2F+1 = (2I+1)(2J+1) = \sum_{m_F=\pm F,..,F} \left( \sum_{m_I=\pm I,..,I} \sum_{m_J=\pm J,..,J} \sum_{m_I+m_J=m_F} 1 \right).
$$

In this form the matrix can be programmed, e.g. using computational software such as MATLAB, and all eigenvalues of the Hamiltonian for any state $^{2S+1}X_J$ and nuclear spin $I$ can be calculated numerically. Obviously, the eigenvalues follow from a diagonalization of the matrix and do not depend on the chosen base. Fig. 9.3 shows the result obtained for $^6$Li ($I = \frac{3}{2}$) in the state $^2S \left( ^2P_{3/2} \right)$ knowing that $A_J/\hbar = -1.17$ MHz and $B_J = 0$.

![Figure 9.3: (code) Hyperfine and Zeeman structure of the state $^2P_{3/2}$ of $^6$Li.](image.png)
Example 41 (Fully stretched states): It is interesting to analyze the so-called fully stretched states defined by $F = I + J$. For these states, the spin $K$ defined in (8.168) becomes,

$$K \equiv 2(J \cdot I) = F(F+1) - I(I+1) - J(J+1) = (I+J)(I+J+1) - I(I+1) - J(J+1) = 2JI,$$

the hyperfine structure (8.169),

$$\Delta E_{hfs} = \frac{A J}{2} K + \frac{B J}{8I(2I-1)J(2J-1)} [3K(K+1) - 4I(I+1)J(J+1)] = A J I J + \frac{B J}{4}.$$

That is, the hyperfine structure does not depend on the magnetic quantum number at any $B$-field amplitude, which means that the $m_J$, $m_I$, and $m_F$ are good quantum numbers at arbitrary $B$-field strengths. So see this, we calculate the Landé-factor (9.35),

$$g_F = g_J \frac{J}{F} - g_I \frac{\mu_N I}{\mu_B F},$$

and demonstrate, using $m_F = F$, $m_J = J$, and $m_I = I$,

$$V_{hfs} + V_{zee}(B) = A J I J + \frac{B J}{4} + g_J \mu_B \vec{B} \cdot \hat{J} - g_I \mu_N \vec{B} \cdot \hat{I}$$

$$= A J I J + \frac{B J}{4} + \mu_B g_F m_F B = A J I J + \frac{B J}{4} + (\mu_B g_J - \mu_N g_I) B.$$

The energy displacement of the fully stretched states is linear in the magnetic field. We can also look at the matrix elements $I_+ = 0$ and $I_- = \sqrt{2I}$ and note that all non-diagonal terms vanish.

When one of the spins, $J$ or $I$, is equal to 1/2 only two possible hyperfine states exist: $F = I \pm J$. For this case there is an approximate analytic formula called the Breit-Rabi formula [31], which will be derived in Exc. 9.2.8.4,

$$\Delta E_{hfs} + \Delta E_{zee}(B) = \left( \frac{A J}{7} \right) \hat{I} \cdot \hat{J} + g_J \mu_B \vec{B} \cdot \hat{J} - g_I \mu_N \vec{B} \cdot \hat{I}$$

$$= - \frac{A J}{4} + \mu_N g_N m_F B \pm \frac{A J (I + \frac{1}{2})}{2} \sqrt{1 + \frac{4m_F}{2I+1} x + x^2},$$

with the abbreviation $x \equiv \frac{2(\mu_B g_J - \mu_N g_I) B}{A J}$. Resolve also Exc. 9.2.8.5.

Atoms with paired electrons have no spin and therefore no magnetic dipole moment. For example, helium or strontium in their ground state $^1S_0$. These systems are diamagnetic due to the Hamiltonian term (9.11) being quadratic in $\vec{B}$, as we shall see in Exc. 9.2.8.6.

9.2.7 Landau levels in two-dimensional systems subject to magnetic fields

Consider a two-dimensional system of non-interacting particles with charge $q$ and spin $S$ confined to an area $A = L_x L_y$ in the $x$-$y$ plane. We apply a uniform magnetic field,

$$\vec{B} = B \hat{e}_z$$

(9.44)
along the $z$ axis. The Hamiltonian of this system is,

$$\hat{H} = \frac{1}{2m} (\hat{p} - q\hat{A})^2,$$  \hfill (9.45)

where $\hat{p}$ is the operator of the canonical momentum and $\hat{A}$ is the potential vector, related to the magnetic field by $\vec{B} = \nabla \times \hat{A}$. The vector potential,

$$A = \frac{1}{2} \begin{pmatrix} -B_y \\
B_x \\
0
\end{pmatrix},$$  \hfill (9.46)

reproduces the field (9.44). However, we have the freedom in choosing the potential vector, given by the gauge transformation, to add the gradient of a scalar field, for example,

$$\chi \equiv \frac{1}{2} B_{xy} \implies \nabla \chi = \frac{1}{2} \begin{pmatrix} B_y \\
B_x \\
0
\end{pmatrix} \implies \mathbf{A}' = \mathbf{A} + \nabla \chi = B_x \hat{e}_y. \hfill (9.47)$$

The potential vector $\mathbf{A}'$ gives the same magnetic field and only changes the general phase of the wavefunction, but the physical properties do not change. In this gauge, which is called *Landau gauge*, the Hamiltonian is,

$$\hat{H} = \frac{p_x^2}{2m} + \frac{1}{2m} \left( \hat{p}_y - \frac{qB}{c} \hat{x} \right)^2. \hfill (9.48)$$

The operator $\hat{p}_y$ commutes with this Hamiltonian, since the $y$ operator is absent due to the choice of the gauge. Thus, the operator $\hat{p}_y$ can be replaced by its eigenvalue $\hbar k_y$. Hence, by introducing the *cyclotron frequency*,

$$\omega_c \equiv \frac{qB}{mc},$$  \hfill (9.49)

we obtain,

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{m\omega_c^2}{2} \left( \hat{x} - \frac{\hbar k_y}{m\omega_c} \right)^2. \hfill (9.50)$$

This is exactly the Hamiltonian of the quantum harmonic oscillator, except that the minimum of the potential is displaced in position space by the value,

$$x_0 \equiv \frac{\hbar k_y}{m\omega_c}. \hfill (9.51)$$

To find the energies, we note that the translation of the potential of the harmonic oscillator does not affect the energies. The energies of this system are therefore identical to those of the standard quantum harmonic oscillator,

$$E_n = \hbar \omega_c \left( n + \frac{1}{2} \right), \hfill (9.52)$$

for $n \geq 0$. Since the energy does not depend on the quantum number $k_y$, we will have degeneracy. To derive the wavefunctions, we remember that $\hat{p}_y$ commutes with
the Hamiltonian. Then the wavefunction splits into a product of eigenstates of the
momentum in $y$-direction and eigenstates of the harmonic oscillator $|\phi_n\rangle$ shifted by a
value $x_0$ in $x$-direction:

$$
\Psi(x, y) = e^{ik_y y} \phi_n(x - x_0) .
$$

That is, the state of the electron is characterized by two quantum numbers, $n$ and $k_y$.

Each set of wavefunctions with the same $n$ is called Landau level. Effects due
to Landau levels are only observed, when the average thermal energy is lower than
the separation of the energy levels, which means that low temperatures and strong
magnetic fields are required. Each Landau level is degenerate, because of the second
quantum number $k_y$, which can adopt the values,

$$
k_y = \frac{2\pi N}{L_y} ,
$$

with $N \in \mathbb{N}$. The allowed values of $N$ are further restricted by the condition that the
center of force of the oscillator, $x_0$, must be physically inside the system, $0 \leq x_0 < L_x$.
This gives the following range for $N$,

$$
0 \leq N < \frac{m\omega_c L_x L_y}{2\pi \hbar} .
$$

For particles with charge $q = Ze$, the upper limit in $N$ can simply be written as a
ratio of fluxes,

$$
Z \frac{\Phi}{\Phi_0} = \frac{ZBL_x L_y}{(hc/e)} = N_{\text{max}} ,
$$

where $\Phi_0 = \hbar/2e$ is the fundamental flux quantum and $\Phi = BA$ the flux through the
system (with area $A = L_x L_y$). Thus, for particles with spin $S$, the maximum number
of particles per Landau level is,

$$
N_{\text{max}} = Z(2S + 1) \frac{\Phi}{\Phi_0} .
$$

### 9.2.7.1 Integer and fractional quantum Hall effect

In general, Landau levels are observed in electronic systems with $Z = 1$ and $S = 1/2$.
As the magnetic field increases, more and more electrons can fit a certain Landau
level. The occupation of the highest Landau level ranges from entirely full to entirely
empty, leading to oscillations in various electronic properties (see de Haas-van Alphen
effect, Shubnikov-de Haas effect and quantum Hall effect. The most direct observation
of the Landau levels is done via the quantum Hall effect. To discuss this effect let
us briefly recapitulate the Hall effect. In the scheme 9.4, charges are deviated by the
Lorentz force exerted by an applied magnetic field $\vec{B}$ from a driven current density $j_x$ into a current density $j_y$ until a sufficient amount of surface charge density has accumulated to generate an electric field exerting a Coulomb force on the charges which neutralizes the Lorentz force, $\vec{F} = q(\vec{E} + \vec{v} \times \vec{B}) = 0$. Resolving this condition by $\vec{v}$, we obtain for the current density,

$$
\vec{j} = \rho q \vec{v} = \frac{\rho q}{\vec{\sigma} \cdot \vec{E}} = \sigma \vec{E} ,
$$
where the last equation is Ohm’s law and
\[
\varsigma = \begin{pmatrix} \varsigma_{xx} & \varsigma_{xy} \\ -\varsigma_{xy} & \varsigma_{yy} \end{pmatrix} \quad \text{and} \quad \rho = \varsigma^{-1} = \frac{1}{\varsigma_{xx}^2 + \varsigma_{yy}^2} \begin{pmatrix} \varsigma_{xx} & -\varsigma_{xy} \\ \varsigma_{xy} & \varsigma_{yy} \end{pmatrix}
\] (9.59)
the conductivity and the resistivity, respectively. The Hall resistivity does therefore depend linearly on the magnetic field,
\[
\rho_{xy} = \frac{\mathcal{E}}{j} = \frac{B}{\varrho q} .
\] (9.60)

In two-dimensional systems this is, however, not observed. Instead, plateaus emerge whenever the magnetic field is ramped across a value where a new Landau level is possible binding one more electron,
\[
\rho_{xy} = \frac{2\pi \hbar}{e^2} \frac{1}{\nu} \quad \text{with} \quad \nu \in \mathbb{Z} .
\] (9.61)
9.2. INTERACTION WITH MAGNETIC FIELDS

Hamiltonian $V(B) = -\vec{\mu}_J \cdot \vec{B}$
a. choosing the quantization axis $\hat{e}_x$ in the direction of the magnetic field,
b. choosing the quantization axis $\hat{e}_z$ perpendicular to the direction of the magnetic field.

9.2.8.2 Ex: Zeeman shift and quantization axes

Choosing the fixed quantization axis $\hat{e}_z$ and a magnetic field $\vec{B}$ in an arbitrary direction, calculate the Hamiltonian of the Zeeman interaction with an angular momentum $J = 1$ and show that the energy shift depends only on absolute value $|\vec{B}|$.

9.2.8.3 Ex: Coupling of two electrons

Consider a two-electron system.
a. Show that the operator $(\hbar A/\hbar^2)\hat{s}_1 \cdot \hat{s}_2$ distinguishes the triplet from the singlet states.
b. Consider now, that the electrons are exposed to a magnetic field $B$ applied in the direction $\hat{e}_z$, so that they acquire the interaction energies with the field $(\mu_B B/\hbar)(g_1 \hat{s}_1 + g_2 \hat{s}_2)$. Obtain the matrix associated with the total Hamiltonian and demonstrate that in the regime $\hbar A \gg \mu_B B$, the representation that favors the total momentum is more adequate.
c. Show that in the regime $\hbar A \ll \mu_B B$, it is convenient to use the representation that privileges the individual spins of the total momentum.
d. Analyze the intermediate regime $\hbar A \approx \mu_B B$.

9.2.8.4 Ex: Breit-Rabi formula

Derive the analytical Breit-Rabi formula for the hyperfine structure (9.43) supposing $J = \frac{1}{2}$.

9.2.8.5 Ex: Reciprocal pollution of the Paschen-Back and Zeeman regimes

a. Determine the interaction matrix $\langle m_j m_I | \hat{V}_{hfs} + \hat{V}_{zee}(B) | m_j m_I \rangle$ of an atom with electron spin $J$ and nuclear spin $I$ in the decoupled base without considering the quadrupolar terms.
b. Determine the interaction matrix explicitly for the case of $^6$Li ($I = 1$) in its ground state $^2S_{1/2}$ ($A_J = \hbar \cdot 152.137$ MHz) for a magnetic field of $B = 100$ G.
c. For the system defined in (b) determine the eigenvalues $E(B)$ of the interaction matrix and the eigenvectors $|\alpha(B)\rangle$ on the decoupled base $|m_j m_I\rangle$.
d. For the system defined in (c) determine the eigenvalues $|\alpha(B)\rangle$ in the coupled base $|Fm_F\rangle$.
e. How good are the selection rules for transitions $S_{1/2} \rightarrow P_{3/2}$ in the intermediate regime between Zeeman and Paschen-Back? We start by calculating the Zeeman shifts for both levels ($s$ denotes the structure $S_{1/2}$, $p$ the structure $P_{3/2}$)

\[
B\langle m^s_j m^s_I | H_{hfs} + H_B | m^s_j m^s_I \rangle_B = E^s(B)
\]
\[
B\langle m^p_j m^p_I | H_{hfs} + H_B | m^p_j m^p_I \rangle_B = E^p(B) .
\]
For the level $P_{3/2}$ the interval factor is less. In particular for $^6$Li it is so small that we are immediately in the Paschen-Back scheme. This means that the matrix elements in the pure Zeeman regime can be expressed by [Deh07, unpublished],

$$
\langle m_J^p m_J^P | T_q^{(E\kappa)} | m_J^s m_J^s \rangle = 0
$$

$$
\langle m_J^p m_J^P | T_q^{(E\kappa)} | m_J^s m_J^s \rangle_0
$$

$$
= \left( \begin{array}{cc} J^s & J^p \\ m_J^s & -m_J^p \end{array} \right) \sum_{m_J^s} \left\{ \begin{array}{ccc} J^p & J^s & \kappa \\ F^p & F^s & I \end{array} \right\} (2F^s + 1)(2F^p + 1)(2\kappa + 1) \frac{2I + 1}{2I + 1}.
$$

Discuss the pure Paschen-Back regime via $\langle m_J^p m_J^P | T_q^{(E\kappa)} | m_J^s m_J^s \rangle$.

9.2.8.6 Ex: Diamagnetism of the ground states of H atoms

Calculate the quadratic Zeeman effect for the ground state of the hydrogen atom caused by the (usually neglected) diamagnetic term of the Hamiltonian in first order TPIT. Write down the energy shift as $\Delta E = -\frac{3}{2} B^2$ assuming a constant magnetic field in order to obtain the diamagnetic susceptibility $\chi$.

9.3 Interaction with electric fields

9.3.1 Stark Effect

Electric fields interact with the electrons of the atom. Describing the atom by its dipole moment, according to (9.13), the interaction energy is,

$$
V_{\text{stark}} = -\hat{d} \cdot \hat{E}.
$$

This is the Stark effect. This effect is usually weak, and its observation requires strong fields or high spectral resolution. Stationary perturbation theory TIPT gives,

$$
E^{(1)}_n = \langle \psi_n^{(0)} | -\hat{d} \cdot \hat{E} | \psi_n^{(0)} \rangle = e\vec{E} \cdot \int_{\mathbb{R}^3} z |\psi_n^{(0)}|^2 d^3 r = 0.
$$

This only applies when the states have well-defined parity and are NOT degenerate in $\ell$. When they ARE degenerate in $\ell$, which is the case of hydrogen, the states have no defined parity. For example, the states $s$ and $p$ contributing to the same state $|\psi_{n,j}\rangle$ have different parities. In this case, the condition (9.63) does not have to be satisfied, and the first perturbation order yields a value. This is the case of the linear Stark effect. In the Excs. 9.3.2.1 and 9.3.2.2 we explicitly calculate the Stark energy shift for a hydrogen atom subject to an electric field.
9.3. INTERACTION WITH ELECTRIC FIELDS

Other atoms do not have this degeneracy, and we must calculate the quadratic Stark effect in second order TIPT,

\[ |\psi_n^{(1)}\rangle = eE_z \sum_{n' \neq n} |\psi_{n'}^{(0)}\rangle \frac{\langle \psi_{n'}^{(0)} | \hat{z} | \psi_{n}^{(0)} \rangle}{E_n - E_{n'}}. \quad (9.64) \]

and

\[ E_n^{(2)} = e^2 E_z^2 \sum_{n' \neq n} \frac{|\langle \psi_{n'}^{(0)} | \hat{z} | \psi_{n}^{(0)} \rangle|^2}{E_n - E_{n'}}. \quad (9.65) \]

To simplify the matrix elements, we separate the radial part from the angular part,

\[ \langle \psi_{n'}^{(0)} | \hat{z} | \psi_{n}^{(0)} \rangle = \langle n' J' m' J | \hat{z} | n J m J \rangle = \int_0^\infty r^3 R_{n' J'} R_{n J} dr \int Y_{n' m' J}^* r Y_{n J m} d\Omega. \quad (9.66) \]

The radial part, written as

\[ \langle n' J' | \hat{z} | n J J \rangle \equiv \int_0^\infty r^3 R_{n' J'} R_{n J} dr, \quad (9.67) \]

and called the irreducible matrix element, no longer depends on the magnetic quantum number. On the other hand, the angular part may be expressed by Clebsch-Gordan coefficients, as will be discussed more extensively in Sec. 13.2.3. The result is called Wigner-Eckart theorem,

\[ \frac{\langle n' J' m' J | \hat{z} | n J m J \rangle}{\langle n' J' | \hat{z} | n J J \rangle} = \int Y_{n' m' J}^* r Y_{n J m} d\Omega = \frac{1}{2J' + 1} \begin{pmatrix} J & 1 & J' \\ m_J & 0 & -m'_{J} \end{pmatrix}. \quad (9.68) \]

With \([\hat{z}, \hat{L}_2] = 0\), which was shown in Exc. 3.3.4.2 we find,

\[ 0 = \langle J' m' J | [\hat{z}, \hat{J}_z] | J m J \rangle = (m_J - m'_{J}) \langle J' m' J | \hat{z} | J m J \rangle. \quad (9.69) \]

This means that for \( m_J \neq m'_{J} \), the matrix elements \( \langle J' m' J | \hat{z} | J m J \rangle \) should disappear. Therefore, the matrix is diagonal in \( m_J \). We consider dipole transitions with \(|J - J'| \leq 1\),

\[ \begin{pmatrix} J & 1 & J + 1 \\ m_J & 0 & -m_J \end{pmatrix} = \frac{(J + 1)^2 - m_J^2}{(2J + 1)(J + 1)}, \quad (9.70) \]

\[ \begin{pmatrix} J & 1 & J \\ m_J & 0 & -m_J \end{pmatrix} = \frac{m_J^2}{J(J + 1)}, \quad (9.70) \]

\[ \begin{pmatrix} J & 1 & J - 1 \\ m_J & 0 & -m_J \end{pmatrix} = \frac{J^2 - m_J^2}{J(2J + 1)}. \quad (9.70) \]

States with the same \(|m_J|\) lead to the same quadratic Stark effect,

\[ \Delta E \sim A + B|m_J|^2. \quad (9.71) \]

The factors \( A \) and \( B \) depend on the main quantum number \( n \) and also on \( L, S, J \). Moreover, they depend on the energy distance of all contributing levels, because of the denominator in the perturbation equation (9.64). Only levels with different parity \((-1)^L\) contribute. The formulae (9.70) will be derived explicitly in Exc. 9.3.2.3.

\(^1\)For it is possible to show that \( \langle n' J' | \hat{z} | n J J \rangle = 0 \) for \(|J - J'| > 1\).
9.3.2 Exercises

9.3.2.1 Ex: Stark effect in hydrogen

Consider the hydrogen atom immersed in a uniform electric field \( \vec{E} \) applied along the \( \hat{e}_z \)-direction. The term corresponding to this interaction in the total Hamiltonian is \( \hat{H}^{(1)} = -e\vec{E}\hat{z} \). For typical electric fields produced in laboratory, the condition \( \hat{H}^{(1)} \ll \hat{H}_0 \), which allows the use of TIPT, is satisfied. The effect of the perturbation \( \hat{H}^{(1)} \), called Stark effect, is the removal of the degeneracy of some of the hydrogen atom states. Calculate the Stark effect for the state \( n = 2 \).

9.3.2.2 Ex: Stark effect in 1\( s \) hydrogen level

Calculate the Stark shift of the hydrogen ground state by taking into account the contributions of the excited states \( n = 2, 3, ... \).

9.3.2.3 Ex: Stark effect

Derive the Eqs. (9.70) from the formula (7.4).
Chapter 10

Atoms with many electrons

10.1 Symmetrization of bosons and fermions

Quantum mechanics must be formulated in a way to avoid any possibility of distinguishing identical particles. However, the language of mathematics automatically assigns a particle to a wavefunction; for example, $\psi_a(x_1)$ is the wavefunction $a$ of particle 1 and $\psi_b(x_2)$ the wavefunction $b$ of particle 2. In the absence of interactions, the total wavefunction, $\Psi = \psi_a(x_1)\psi_b(x_2)$, solves the Schrödinger equation of two particles. Now, by changing the coordinates of the particles we get a different state $\Psi' = \psi_a(x_2)\psi_b(x_1)$ \(^1\). This erroneously suggests that the wavefunction of a particle plays the role of a label (or ‘soul’) characterizing the particle beyond its set of quantum numbers. Why this is a problem, we will see in the following example \(^2\).

**Example 42 (Indistinguishability of particles):** We consider a system of two non-interacting spinless particles in an infinite potential well. The total wavefunction is,

$$\Psi^{(1,2)} \equiv \psi_a(x_1)\psi_b(x_2) = C \cos \frac{n_a \pi x_1}{L} \cos \frac{n_b \pi x_2}{L} \quad (10.1)$$

with the energy,

$$E_{a,b} = \frac{\pi^2 n_a^2}{2mL^2} + \frac{\pi^2 n_b^2}{2mL^2}.$$

For observable quantities, such as $|\Psi^{(1,2)}|^2$, we must ensure, $|\Psi^{(1,2)}|^2 = |\Psi^{(2,1)}|^2$, that is,

$$C^2 \cos^2 \frac{n_a \pi x_1}{L} \cos^2 \frac{n_b \pi x_2}{L} = C^2 \cos^2 \frac{n_a \pi x_2}{L} \cos^2 \frac{n_b \pi x_1}{L},$$

\(^1\)We note that states are orthogonal, because

$$\int \psi^{*(1,2)}(x_1)\psi^{(2,1)}(x_1)dx_1dx_2 = \int \psi^{*(a)}(x_1)\psi^{(a)}(x_2)\psi^{(b)}(x_1)dx_1dx_2$$

$$= \int \psi^{*(a)}(x_1)\psi^{(b)}(x_1)dx_1 \int \psi^{*(b)}(x_2)\psi^{(a)}(x_2)dx_2 = \delta_{n_a,n_b}.$$

\(^2\)Ultimately, all this is simply a consequence of the uncertainty principle, which forbids us to specify a wavefunction as a function of two non-commuting coordinates: We have to choose one coordinate on which the wavefunction depends and treat the other as a quantum number, for example, $\psi_k(r) = e^{ik \cdot r}$ or $\psi_n(x) = \cos \frac{n \pi x}{L}$. When we now exchange the coordinates of two particles without changing their quantum numbers, we get obviously different states. In classical physics, the wavefunction of a particle would be written $\psi(x, p)$. If two classical particles are not distinct by any other mean, an exchange of all their coordinates would reproduce exactly the same state.
but this is not valid for $n_a \neq n_b$. If $n_a = n_b$, we have $\psi_a = \psi_b$. That is, the particles stay in the same state, and we do not need to worry about indistinguishability:

$$\Psi^{(2,1)}(x_2) = \psi_a(x_2)\psi_b(x_2) = \Psi^{(1,2)}(x_1)$$

and $E_{a,b} = E_{b,a}$.

However, the fact that this state is never observed with two electrons shows, that theory must be corrected to allow a true description of reality. Will deepen this argument in Exc. 10.1.3.1.

We need to construct the total wavefunction in another way. Let us consider linear combinations of $\Psi^{(1,2)}$,

$$\Psi^{S,A} \equiv \frac{1}{\sqrt{2}}(\Psi^{(1,2)} \pm \Psi^{(2,1)}) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1)] . \quad (10.2)$$

This *symmetrized wavefunction* (or anti-symmetrized) represents a trick to eradicate the label sticking to the particles. For, under position exchange described by the operator $P_x\psi_a(x_1)\psi_b(x_2) \equiv \psi_a(x_2)\psi_b(x_1)$, the (anti-)symmetrized functions behave like $^3$,

$$P_x\Psi^{S,A} = \pm \Psi^{S,A} \quad \text{while} \quad P_x\Psi^{(1,2)} = \Psi^{(2,1)} \neq \mp \Psi^{(1,2)} . \quad (10.3)$$

The (anti-)symmetrized function solves the Schrödinger equation, as well. As $[\hat{H}, P_x] = 0$, we can say that the system exhibits an *exchange symmetry* or *exchange degeneracy* upon particle exchange. Observables such as $\Psi^{S,A}\Psi^{S,A}$ stay conserved, for example, the probability

$$|\Psi^{S,A}|^2 = \frac{1}{2} [ |\psi_a(x_1)\psi_b(x_2)|^2 + |\psi_a(x_2)\psi_b(x_1)|^2 ] \quad (10.4)$$

$$\pm \frac{1}{2} [ \psi_a^*(x_1)\psi_b^*(x_2)\psi_a(x_2)\psi_b(x_1) + \psi_a^*(x_2)\psi_b^*(x_1)\psi_a(x_1)\psi_b(x_2) ] = P_x|\Psi^{S,A}|^2$$

does not change, when we exchange $x_1$ for $x_2$. For $x_1 = x_2$, we observe,

$$|\Psi^{S,A}|^2 = |\psi_a(x)\psi_b(x)|^2 \pm |\psi_a^*(x)\psi_b^*(x)|^2 . \quad (10.5)$$

That is, for a symmetric system, the probability of finding two particles at the same location is doubled, whereas for an anti-symmetric system, this probability is zero.

Wolfgang Pauli showed that the (anti-)symmetric character is related to the spin of the particles. Particles with *integer spin* called *bosons* must be symmetric. Particles with *semi-integer spin* called *fermions* must be anti-symmetric. Electrons are fermions. Therefore, in an atom, they can not be in the same state (location), but must be distributed over a complicated shell of orbitals. We note, that this applies not only to elementary particles, but also to composed particles such as, for example, atoms. We will determine in Exc. 25.1.5.1 the bosonic or fermionic character of several atomic species.

### 10.1.1 Pauli’s Principle

Two electrons with anti-parallel spins can be separated by inhomogeneous magnetic fields, even if they are initially in the same place. Therefore, they are distinguishable

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$^3$To guarantee $|P_x\Psi^{(1,2)}|^2 = |\Psi^{(1,2)}|^2$, we have $P_x\Psi^{(1,2)} = e^{i\phi}\Psi^{(1,2)}$. From this, $P_xP_x\Psi^{(1,2)} = e^{2i\phi}\Psi^{(1,2)} = \Psi^{(1,2)}$. Hence, $P_x\Psi^{(1,2)} = \pm \Psi^{(1,2)}$. 

and the wavefunction need not be anti-symmetric. But if we exchange the spin along
with the position, the particles must be indistinguishable. This must be taken into
account in the wavefunction by assigning a spin coordinate, $\psi(x_1, s_1)$. The exchange
operator should now be generalized,

$$P_{x,s} \Psi^{(1,2)} \equiv P_{x,s} \psi_a(x_1, s_1) \psi_b(x_2, s_2) = \psi_a(x_2, s_2) \psi_b(x_1, s_1) = \Psi^{(2,1)}.$$ (10.6)

We now assume that the electrons not only do not interact with each other, but
there is also no interaction between the position and the spin of each electron. That is,
we will discard $L \cdot S$-coupling \textsuperscript{4}. We can then write the total wavefunction of an electron
as the product of a spatial function, $\psi(x)$, and a spin function, $\chi(s) = \alpha \uparrow + \beta \downarrow$, where
$\alpha$ and $\beta$ are probability amplitudes of finding the electron in the respective spin state,
such that,

$$\psi(x, s) = \psi(x) \chi(s).$$ (10.7)

For two particles, the total spin function is,

$$X^{(1,2)} = \chi_a(s_1) \chi_b(s_2).$$ (10.8)

The (anti-)symmetrized version is

$$X^{S,A} = \frac{1}{\sqrt{2}} (X^{(1,2)} \pm X^{(2,1)}) = \frac{1}{\sqrt{2}} [\chi_a(s_1) \chi_b(s_2) \pm \chi_a(s_2) \chi_b(s_1)],$$ (10.9)
as we have already seen in Sec. 3.4.1. Since there are only two spin directions, there
are four possibilities to attribute the spins $\uparrow$ and $\downarrow$ to the functions $\chi_m(s_n)$,

$$X^S = \begin{cases}
\frac{1}{\sqrt{2}} (\uparrow \downarrow + \downarrow \uparrow) = \chi_{1,1} \\
\frac{1}{\sqrt{2}} (\uparrow \downarrow - \downarrow \uparrow) = \chi_{0,0}
\end{cases} \quad \text{and} \quad X^A = \frac{1}{\sqrt{2}} (\uparrow \downarrow - \downarrow \uparrow) = \chi_{0,0}$$ (10.10)

For the total wavefunction, which must be anti-symmetric for electrons, there are two
possibilities,

$$\Theta^A = \begin{cases}
\Psi^A X^A = \frac{1}{2} (\Psi^{(1,2)} + \Psi^{(2,1)}) (X^{(1,2)} - X^{(2,1)}) = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) + \psi_a(x_2) \psi_b(x_1)] \chi_{0,0} \\
\Psi^A X^S = \frac{1}{2} (\Psi^{(1,2)} - \Psi^{(2,1)}) (X^{(1,2)} + X^{(2,1)}) = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) - \psi_a(x_2) \psi_b(x_1)] \chi_{1,1}
\end{cases}$$ (10.11)

That is, the two electrons may be in a triplet state with the anti-symmetric spatial
wavefunction, or in a singlet state with the symmetric spatial wavefunction \textsuperscript{5}.

How to generalize these considerations to $N$ particles? The symmetric wavefunctions
contain all permutations of the label $a_k$, where we understand by $a_k$ the set of quantum numbers unambiguously specifying the state of the particle $k$,

$$\Theta^S = N \sum_{P_{x_1, a_k}} \psi_{a_1}(x_1) \ldots \psi_{a_N}(x_N),$$ (10.12)

\textsuperscript{4}In the case of $L \cdot S$-coupling, the total wavefunction can not be written as a product of spatial
and spin functions, but it must be anti-symmetric anyway.

\textsuperscript{5}In the coupled image, the total spin $S = s_1 + s_2$ can have the following values $S = |s_1 - s_2|, \ldots, s_1 + s_2 = 0, 1$. In the case $S = 0$ the magnetic quantum number can only have one value (singlet), $m_S = 0$. In the case $S = 1$ it can have three values $m_S = -1, 0, +1$ (triplet) (see Exc. 9.2.8.3).
with a normalization factor $\mathcal{N}$\footnote{It is possible to show $\mathcal{N} = \sqrt[\sum_{k=1}^{N} n_k]{\prod_{k=1}^{N} n_k!}$, where $n_k$ is the population of state $\psi_{a_k}$, that is, the number of particles with the same set of quantum numbers $a_k$.}. The (anti-)symmetrized wavefunction is obtained from the Slater determinant,

$$\Theta^{A} = \frac{1}{N!} \det \psi_{a_k}(x_n) = \frac{1}{N!} \begin{vmatrix} \psi_{a_1}(x_1) & \cdots & \psi_{a_1}(x_N) \\ \vdots & \ddots & \vdots \\ \psi_{a_N}(x_1) & \cdots & \psi_{a_N}(x_N) \end{vmatrix}. \tag{10.13}$$

This function satisfies

$$P_{x,s}^{A}(1,\ldots,i,j,\ldots,N) = \Theta^{A}(1,\ldots,j,i,\ldots,N) = -\Theta^{A}(1,\ldots,i,j,\ldots,N). \tag{10.14}$$

The Slater determinant is zero, when two sets of quantum numbers are identical, $a_i = a_j$. For example, for two electrons in an electronic shell, $|n_i,l_i,m_i,s_i\rangle = |n_j,l_j,m_j,s_j\rangle$. This is Pauli’s strong exclusion principle:

*The total wavefunction must be antisymmetric with respect to the exchange of any pair of identical fermions and symmetrical with respect to exchange any pair of identical bosons.*

**Pauli’s weak exclusion principle** (usually sufficient for qualitative considerations) says that two fermions in identical states can not occupy the same region in space. That is, their Broglie waves interfere destructively, as if Pauli’s principle exerted a repulsive interaction on the particles. This ‘force’ has a great impact on the phenomenology of the bonds between atoms, as we will discuss in the following sections.

### 10.1.2 Consequences for quantum statistics

The indistinguishability of quantum particles has interesting consequences on the statistical behavior of bosons and fermions. This becomes obvious when we consider two particles 1 and 2 being able to adopt two different states $a$ and $b$. Distinguishable particles can be in one of the following four states,

$$\Psi = \{\psi_a(x_1)\psi_a(x_2), \psi_a(x_1)\psi_b(x_2), \psi_b(x_1)\psi_a(x_2), \psi_b(x_1)\psi_b(x_2)\} \tag{10.15}$$

with the same probability of $p = 1/4$. Bosonic indistinguishable particles can stay in one of the following three states,

$$\Psi = \{\psi_a(x_1)\psi_a(x_2), \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)], \psi_b(x_1)\psi_b(x_2)\} \tag{10.16}$$

with the same probability of $p = 1/3$. Finally, fermionic indistinguishable particles can only be in a state,

$$\Psi = \{\frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]\} \tag{10.17}$$

with the same probability of $p = 1$. We see that a simple two-particle system already exhibits qualitative modifications of its statistical behavior. These differences generate different physics as we deal with systems of large numbers of particles, as we can see in the cases of the free electron gas and the Bose-Einstein condensate.

We finally note a result of the standard model of particle physics assigning a fermionic character to all fundamental constituent particles of matter while the mediators of fundamental forces are always bosons.
10.2. HELIUM

10.1.3 Exercises

10.1.3.1 Ex: Indistinguishability of particles

Consider the observable quantity \( \int_0^{L/2} \int_0^{L/4} |\Psi(x_1, x_2)|^2 dx_1 dx_2 \) for the case of the wavefunction defined in (10.1) and show, that it does depend on particle exchange.

10.1.3.2 Ex: Bosonic and fermionic isotopes

Consulting an isotope table determine the bosonic or fermionic character of the following atomic species: \(^{87}\text{Sr}\), \(^{86}\text{Sr}\), \(^{87}\text{Rb}\), \(^{39}\text{K}\), and \(^{40}\text{K}\).

10.2 Helium

The simplest atom to discuss Pauli’s principle is helium. The helium atom has a charged nucleus \( Z = +2e \) and mass \( m_{He} \approx 4m_H \).

10.2.1 The ground state

The ground state of the helium atom brings together the two electrons, that is, \((1s)^2\). To treat the helium atom, we can, as a first trial, describe the atom by the Bohr model, assuming independent electrons. Neglecting the electronic repulsion term (which depends on \( r_{12} \)), we can separate the total wavefunction:

\[
\Psi(r_1, r_2) = \Psi_1(r_1)\Psi_2(r_2),
\]

and we get two Schrödinger equations, the Hamiltonian being equal to the one of hydrogen-like atoms:

\[
\left[ -\frac{\hbar^2}{2\mu} \nabla_i^2 - \frac{e^2}{4\pi\varepsilon_0 r_i} \right] \Psi_i(r_i) = E^{(i)}_n \Psi_i(r_i),
\]

with \( i = 1, 2 \). For hydrogen-like atoms we have,

\[
E = E^{(1)}_n + E^{(2)}_n = E_B Z^2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right),
\]

with \( E_B = -13.6 \text{ eV} \). With this, we get the energy for the ground state:

\[
E_{He}(1s) = -2Z^2E_B = -108.8 \text{ eV}.
\]

The value predicted by Bohr’s model is far from experimental reality: The ionization energy measured for the first electron is 24.6 eV, for the second 54.4 eV, totaling a binding energy for two electrons of \(-78.983 \text{ eV}\). This corresponds to an error of about 38%. The lower energy of the first electron is due to the shielding of the nucleus by the second.
10.2.1.1 First-order perturbation of the energy

Treating the repulsion term between the electrons as a perturbation \cite{24} and using the eigenfunctions of hydrogen atoms $|n, \ell, m\rangle$, the total wavefunction is $|n_1, \ell_1, m_1; n_2, \ell_2, m_2\rangle$, we obtain as first order TIPT correction for the energy:

$$\Delta E = \langle n_1, \ell_1, m_1; n_2, \ell_2, m_2 | -\frac{e^2}{4\pi \varepsilon_0 r_{12}} | n_1, \ell_1, m_1; n_2, \ell_2, m_2 \rangle \rangle .$$ \hspace{1cm} (10.22)

This correction is called the Coulomb integral and has the value:

$$\Delta E = \frac{e^2}{4\pi \varepsilon_0} \int |\Psi_{n_1, \ell_1, m_1}(r_1)|^2 \left( \frac{1}{r_{12}} \right) |\Psi_{n_2, \ell_2, m_2}(r_2)|^2 dV_1 dV_2 .$$ \hspace{1cm} (10.23)

This integral is always positive. The term $|\Psi_{n_1, \ell_1, m_1}(r_1)|^2 dV_1$ is the probability of finding the electron inside the volume element $dV_1$ and, when multiplied by $-e$, gives the charge associated with that region. Thus, the integral represents the Coulomb interaction energy of the confined charges within the two volume elements $dV_1$ and $dV_2$. $\Delta E$ is the total contribution to the potential energy. Calculating the Coulomb integral for the ground state, which will be done in Exc. 10.2.3.1, we obtain,

$$\Delta E = \frac{5Z}{4} \left( \frac{e^2}{4\pi \varepsilon_0 2a_B} \right) = \frac{5Z}{4} E_B ,$$ \hspace{1cm} (10.24)

with $a_B$ the Bohr radius. $\Delta E$ corresponds to 34 eV. Thus, the ground state energy is $E_{He}(1s) = -108.8 \text{ eV} + 34 \text{ eV} = -74.8 \text{ eV}$. Comparing with the experimental value of $-78.983 \text{ eV}$ we have an error around 5.3%.

10.2.1.2 Shielding of the nuclear charge

We can make the approximation in which we consider that each electron moves in a Coulombian potential, with respect to the nucleus, shielded by the charge distribution of the other electron \cite{153}. The resulting potential will be generated by an effective charge $\zeta e \equiv (Z - B)e$. The quantity $B \in [0, 1]$ is called the shielding constant.

The first electron feels a total nuclear charge $Ze$, while the second feels an effective nuclear charge $\zeta e$. We exchange $Z$ for $\zeta$ in the energy term for hydrogen-like atoms,

$$E_n = -\zeta \frac{E_B}{n^2} ,$$ \hspace{1cm} (10.25)

and the energy for the ground state becomes, assuming total shielding, $B = 1$,

$$E = E_1 + E_2 = -Z^2 E_B - \zeta^2 E_B = -4E_B - E_B = -5E_B = -67.5 \text{ eV} .$$ \hspace{1cm} (10.26)

Comparing with the experimental value of $-78,983 \text{ eV}$ we have an error around 15%. For a shielding constant of around $B = 0.656$ the experimental value is reproduced. This means that the effective nuclear charge felt by the second electron is only partly shielded by the former. The TPIT method (10.22) and the shielding concept (10.25) can be combined in a variational calculation, where the effective charge $\zeta$ is the variational parameter. In Exc. 10.2.3.2 we study the reciprocal shielding of the electrons at the example of the helium-type ion $\text{H}^-$. 


10.2.2 Excited states

Let us now investigate the excited states of helium, in particular those, where only one electron is excited, the other one being in the ground state, \((1s)^1(2s)^1\) and \((1s)^1(2p)^1\). All energies are considerably higher (weaker binding) than predicted by Bohr’s model with \(Z = 2\), because of the interaction with the other electron. Also, the \((2s)\) and \((2p)\) levels are no longer degenerate, because the electrostatic potential is no longer Coulombian (see Fig. 10.1).

![Figure 10.1: Helium levels for the excitation of the first electron and allowed singlet and triplet transitions. Note that the state \((1s)^{1\uparrow\uparrow}\) does not exist.](image)

As we have seen in the discussion of the fine structure, the energy of the \(l \cdot s\)-coupling given by (8.131) is \(\propto E_n(Z\alpha)^2 \propto Z^4\). For helium which still has a small \(Z\), the energy of the coupling is weak \((\sim 10^{-4} \text{ eV})\), so that we can count on a direct coupling of the spins of the two electrons. Since the orbits of the electrons are now different, we can construct combinations of symmetric or antisymmetric spatial wavefunctions \(\Psi^{S,A}\), are therefore combinations \(X^{A,S}\) of anti-parallel or parallel spins. When the spins are parallel \((S = 1)\), the spatial wavefunction is antisymmetric, when they are antiparallel \((S = 0)\), it is symmetric. From the symmetry of the wavefunction depends the energy of the coulombian interelectronic interaction, because in the symmetric state the average distance of the electrons is much smaller than in the antisymmetric state, where the total spatial function disappears for zero distance. Consequently, the configuration \((1s)^1(2s)^1\) has two states with \(S = 0\) and \(S = 1\), with energy \(E_{S=0} > E_{S=1}\). Likewise, all configurations are split, as shown in Fig. 10.1. The energy difference \((\sim 1 \text{ eV})\) is considerable and well above the energy of fine structure interaction. This explains why the two spins first couple to a total spin, \(s_1 + s_2 = S\), before this spin couples to the total orbital angular momentum, \(S + L = J\). This is the \(L \cdot S\)-coupling.
10.2.2.1 Exchange energy

The energy difference between the two states $S = 0$ and $S = 1$ is called exchange energy. It comes out of a first-order perturbation calculation. For example, for the two possible states $(1s)^1(2s)^1$, we write the total anti-symmetric wavefunctions,

$$
\Theta^A_{\pm} = \frac{1}{\sqrt{2}} [\psi_{100}(r_1)\psi_{200}(r_2) \pm \psi_{100}(r_2)\psi_{200}(r_1)] \cdot \chi^{A,S},
$$

(10.27)

where the (+) sign holds for $\chi^A (S = 0)$ and the (−) sign for $\chi^S (S = 1)$. The energies are,

$$
\Delta E^{S,A} = \frac{1}{2} \int dr_1^3 \int dr_2^3 \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \Theta^A_{\pm}
$$

(10.28)

$$
= \frac{1}{2} \int dr_1^3 \int dr_2^3 \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \left[|\psi_{100}(r_1)|^2|\psi_{200}(r_2)|^2 + |\psi_{100}(r_2)|^2|\psi_{200}(r_1)|^2\right]
$$

$$
\pm \frac{1}{2} \int dr_1^3 \int dr_2^3 \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} 2\psi_{100}^*(r_1)\psi_{200}^*(r_2)\psi_{100}(r_2)\psi_{200}(r_1)
$$

$$
\equiv \Delta E_{\text{coulomb}} \pm \Delta E_{\text{exchange}}.
$$

The first integral,

$$
\Delta E_{\text{coulomb}} = \int dr_1^3 \int dr_2^3 \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} |\psi_{100}(r_1)|^2|\psi_{200}(r_2)|^2,
$$

(10.29)

is the Coulomb energy (10.23) between the electronic orbitals. We note that this part can be calculated from the Hamiltonian using non-symmetrized orbitals. The second integral,

$$
\Delta E_{\text{exchange}} = \int dr_1^3 \int dr_2^3 \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \psi_{100}^*(r_1)\psi_{200}^*(r_2)\psi_{100}(r_2)\psi_{200}(r_1),
$$

(10.30)

called exchange energy corresponds to the interference terms of the symmetrization and must be added or subtracted according to their symmetry character. It is interesting to note that up to this point the spin does not enter directly into the helium Hamiltonian,

$$
\hat{H}^{S,A} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(r_1) + V(r_2) + V(|r_1 - r_2|) \pm \Delta E_{\text{exchange}}.
$$

(10.31)

but only through the symmetry character of the spatial wavefunction. On the other hand, on a much smaller energy scale, the spin enters through the $\mathbf{L} \cdot \mathbf{S}$-interaction.

The potential is not spherically symmetric, the term $r_{12}$ depends on the angle between $r_1$ and $r_2$. Thus, the total wavefunction $\Psi(r_1, r_2)$ is not separable into a radial and an angular part. By consequence, unlike for hydrogen, the Schrödinger equation with the Hamiltonian (10.21) has no analytical solution.

**Example 43 (TIPT for excited helium states):** We consider the two electrons of a helium atom occupying different orbits described by wavefunctions denoted by $\psi_a(1) \equiv \psi_{n_1,\ell_1, m_{\ell_1}}(r_1)$ and $\psi_b(2) \equiv \psi_{n_2,\ell_2, m_{\ell_2}}(r_2)$. Applying the Hamiltonian without the interelectronic interaction term, the total states
\[\Theta = \psi_a(1)\psi_b(2)\text{ and } \psi_a(2)\psi_b(1)\] have the same energy \(E_a + E_b\). To calculate the energy correction, we use TIPT for degenerate states. We have to calculate the secular determinant \(\det(\langle n, \nu | H^{(1)} | n, \mu \rangle - E_{n, \mu} \delta_{\mu, \nu})\). The terms of the matrix \(H^{(1)}\) are:

\[
\begin{align*}
H_{11}^{(1)} &= \langle \psi_a(1)\psi_b(2) | \frac{e^2}{4\pi\varepsilon_0 r_{12}} | \psi_a(1)\psi_b(2) \rangle \\
H_{22}^{(1)} &= \langle \psi_a(2)\psi_b(1) | \frac{e^2}{4\pi\varepsilon_0 r_{12}} | \psi_a(2)\psi_b(1) \rangle \\
H_{12}^{(1)} &= \langle \psi_a(1)\psi_b(2) | \frac{e^2}{4\pi\varepsilon_0 r_{12}} | \psi_a(2)\psi_b(1) \rangle = H_{21}^{(1)}.
\end{align*}
\]

The terms \(J \equiv H_{11}^{(1)} = H_{22}^{(1)}\) are Coulomb integrals. The term \(K \equiv H_{12}^{(1)}\) is called exchange integral:

\[K = \frac{e^2}{4\pi\varepsilon_0} \langle \psi_a(1)\psi_b(2) | \frac{1}{r_{12}} | \psi_a(2)\psi_b(1) \rangle.
\]

Hence, as \(J\) and \(K\) are positive, the determinant is:

\[
\begin{vmatrix}
J - E & K \\
K & J - E
\end{vmatrix} = 0,
\]

yielding, \(E^{(1)} = J \pm K\).

That is, the states that were previously degenerate with energy \(E = E_a + E_b\) are now split into two states with energies \(E = E_a + E_b + J \pm K\). And the corresponding eigenfunctions are:

\[\Psi^{S,A}(1, 2) = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)].\]

This result shows that the repulsion between the two electrons breaks the degeneracy (of separable functions written in product form) into states with an energy difference \(2K\). Note that the eigenfunctions are symmetric, which is discussed in the next section.

### 10.2.2.2 The spectrum of helium

So far we have seen that, if the electrons are in the same orbital, we have an energy term \(E = 2E_a + J\) and, when they are in different orbitals, we have \(E = E_a + E_b + J \pm K\), with a separation between levels of \(2K\).

In practice, we consider only the excitation of one electron, because the energy to excite the two electrons exceeds the ionization energy of the helium atom. To find the selection rules for transition between symmetric and antisymmetric states, we calculate the dipole moment of the transition. For a two-electron system the dipole moment is \(\hat{d} = -e \mathbf{r}_1 - e \mathbf{r}_2\), which is symmetric with respect to a permutation of the two electrons. The matrix element for the dipolar transition is:

\[
\langle \Psi^{A} | \hat{d} | \Psi^{S} \rangle = -e \int \Psi^{+A}(\mathbf{r}_1, \mathbf{r}_2)(\mathbf{r}_1 + \mathbf{r}_2)\Psi^{S}(\mathbf{r}_1, \mathbf{r}_2)dV_1dV_2 .
\]

If we exchange the electrons, the above integral changes sign, because \(\Psi^{A}(\mathbf{r}_1, \mathbf{r}_2)\) changes sign. But the integral can not depend on the nomenclature of the integration...
variables, so it must be zero. The transition between a symmetric and an antisymmetric state can not occur. Looking at the spin wavefunction in $\Theta = \Psi^S \chi^A$ or $\Psi^A \chi^S$, we find that transitions are only allowed between singlet states or between triplet states. That is, there is a selection rule for the spin postulating $\Delta S = 0$ \(^7\),\(^8\).

Because of the differences observed in the singlet and the triplet spectrum of helium, illustrated in Fig. 10.1, it was first believed that they belong to different atomic species, called para-helium and ortho-helium. A chemical analysis showed later that it was the same element.

10.2.3 Exercises

10.2.3.1 Ex: Helium atom

Compare the measured binding energy with the prediction of Bohr’s model considering the inter-electronic interaction up to first order TIPT.

10.2.3.2 Ex: Shielding in helium

The helium atom (or helium-like atoms such as $H^-$) has two interacting electrons in its composition, which means that these systems have no exact solution. To circumvent this problem we have to come up with a series of approximate methods for calculating their eigenstates and their respective eigenenergies. Among these methods, a widely used one, due mainly to its ease and practicality, is the variational method, in which we calculate the fundamental state of a given problem through a test function that is not a solution of the original problem. This method, when applied to a helium atom, uses as test function the solution of the problem without coulombian interaction between the electrons, which only feel the interaction with the original charge of the nucleus. However, this method could be further improved if we considered an effective nuclear charge, due to its interaction with the electrons themselves, and then obtaining the test function. Apply this correction to the case of helium. Interpret the result. Help:

$$\int \frac{\sin \theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_2}} d\theta_2 = \frac{\sqrt{r_1^2 + r_2^2 - 2r_1^2r_2^2 \cos \theta_2}}{r_1r_2}$$

and

$$\langle \frac{1}{r} \rangle = \frac{Z}{a_B}.$$

10.3 Electronic shell structure

The interelectronic interaction and the need to antisimetrize the wavefunction of the electrons both contribute to excessively increase the complexity of multielectronic

\(^7\)Moreover, transitions between the states $^1S_0$ and $^3S_1$ are impossible, because they violate the selection rule for the angular momentum, $\Delta L = \pm 1$.

\(^8\)We can understand the selection rules as follows: As long as the wavefunction can be written as a product, $\Theta = \Psi(x)\chi(s)$, the symmetry character is preserved for the two functions separately. The eigenvalues of the operators $P_x$ and $P_s$ are then good quantum numbers. But this only holds for weak $L \cdot S$-coupling. The electric dipole operator for the transition does not act on the spin (which prevents the recoupling $S = 1 \leftrightarrow S = 0$ via $E1$-radiation) and also does not act on the symmetry character of the orbitals (which prevents transitions $\Psi^S \leftrightarrow \Psi^A$).

In principle, this holds for any species of atoms with two valence electrons. In reality however, the influence of the $L \cdot S$-coupling grows with $Z$, which weakens the interdiction of the intercombination transition. In this case, only the operator $P_{x,s}$ yields good eigenvalues.
atoms. The Hamiltonian describing a multielectronic atom of atomic number \( Z \),

\[
\hat{H} = E_{\text{kin}} + V_{ncl-ele} + V_{ele-ele} = \sum_{i=1}^{Z} \frac{p_i^2}{2m} - \sum_{i=1}^{Z} \frac{Ze^2}{4\pi\varepsilon_0 |r_i|} + \sum_{i<j=1}^{Z} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|},
\]

is extremely complicated to solve, even for the simplest case \( Z = 2 \) we must use approximation methods.

## 10.3.1 TIPT method

Note that, if we assume independent electrons \( (V_{ele-ele} = 0) \), that is, each electron moves independently of the others within the electrostatic potential generated by the nucleus and the other \( Z-1 \) electrons, the problem would be easily solvable: We could solve the Schrödinger equation for a product state of all the electronic wavefunctions, and we would know the eigenfunctions and individual eigenenergies of each electron (as for the hydrogen atom). In principle, we should use antisymmetric wavefunctions, but as a first approach we can choose to only respect Pauli’s weak principle, that is, assign an \textit{individual and unique} set of quantum numbers to each electron. The total energy would be the sum of the energy of every electron, and the associated physical eigenstates would be obtained by means of an antisymmetrization of the tensor product of the multielectronic state.

Thus, as a first approximation, we use the states of individual electrons (orbital approximation) and consider \( V_{ele-ele}(|r_i - r_j|) \) as a perturbation making use of \textit{time-independent perturbation theory}. However, this term is not small enough to justify this procedure, since approximating

\[
V_{ncl-ele} \simeq \frac{Z^2 e^2}{a_B} \quad \text{and} \quad V_{ele-ele} \simeq \frac{Z(Z-1)e^2}{2a_B},
\]

we realize that \( V_{ele-ele}/V_{ncl-ele} \) varies between \( \frac{1}{4} \) for \( Z = 2 \) and \( \frac{1}{2} \) for \( Z \gg 1/2 \). For this reason the use of alternative methods to describe multielectronic atoms is necessary. Nevertheless, the set of quantum numbers derived from Bohr’s atomic model are still the same as those used for many-electron atoms, and the orbitals are used as starting points for more sophisticated methods.

To calculate most of the atomic properties we need reasonably realistic potentials. The most important terms of the Hamiltonian are the Coulombian potential between the nucleus and the electrons, \( V_{ne} \), being naturally spherical, and the interaction potentials between the electrons, \( V_{ee} \), which we will try to approximate by a spherical potential and treat the deviations caused by the approximation afterward. Knowing the effect of the shielding of the nucleus by electronic charges, we already know the asymptotes (see Fig. 10.2),

\[
V_{\text{eff}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad \text{for} \quad r \to 0 \quad \text{and} \quad V_{\text{eff}} = -\frac{e^2}{4\pi\varepsilon_0 r} \quad \text{for} \quad r \to \infty. \]
Figure 10.2: (code) External potential (shielded Coulombian) $V_{cl} \propto \frac{e^2}{r}$ (blue, upper curve), interior potential (non-shielded Coulombian) $V_{bl} \propto \frac{Ze^2}{r}$ (green, lower curve), and effective potential (red, middle curve).

10.3.2 Thomas-Fermi model for an electron gas

A first approach to getting a reasonable effective potential $V_{eff}$ is provided by the Thomas-Fermi model. This is a semi-classical model that aims to roughly describe the total energy of the electrons as a density functional of atomic/molecular electrons. It serves as a basis for more sophisticated methods aiming at determining the electronic structure, such as density functional theory (DFT), and the wavefunctions determined by this method often serve as a starting point for the Hartree method discussed below. One of the important predictions of the Thomas-Fermi model is that the average radius of an atom depends on the nuclear charge as $\bar{R} \propto \frac{1}{Z^{1/3}}$.

The Thomas-Fermi model allows us to understand the electronic configuration of the fundamental states and provides the basis for the periodic system of elements. In this model, the electrons are treated as independent particles, on one side forming an effective radial electric potential, on the other side being subjected to this potential. Instead of requiring anti-symmetry of the wavefunction, it is only necessary to ensure that all electrons are distinguished by at least one quantum number. The orbitals of complex atoms are similar to the wavefunctions of hydrogen. So, we can use these quantum numbers $n$, $\ell$, $m_\ell$, and $m_s$ for every electron.

However, the effective radial potential depends very much on the species and is quite different from the Coulomb potential. So, the degeneracy in $\ell$ is lifted. In general, electrons with small $\ell$ are more strongly bound, because they have a higher probability of being near the nucleus, where the potential is deeper (see Fig. 10.2). The same argument explains why electrons with small $n$ are more strongly bound. We will discuss these effects in more depth in Sec. 10.4.1 by comparing the excitation levels of the valence electron in different alkalis.

10.3.2.1 Density of states in the Fermi gas model

Even though the real potential sensed by the electrons bound to a nucleus is very different from the three-dimensional well, we can roughly imagine that the atom is subdivided into small volumes, understood as box potentials, all filled with electrons. From this we can calculate the distribution of the electronic charge, such that the
average local energy is homogeneous and the electronic cloud in equilibrium. The distribution, in turn, serves to determine the shape of the electrostatic potential which, when subdivided into small volumes filled with electrons, produces the same charge distribution. This principle is called self-consistency.

According to the Fermi gas model, we consider an infinite potential well, that we gradually fill up with electrons. The Pauli principle allows us to place at most two electrons in each orbital,

\[ \Psi = \psi_{1,\uparrow}(x_1)\psi_{1,\downarrow}(x_2)\psi_{2,\uparrow}(x_3)\psi_{2,\downarrow}(x_4) \ldots \] (10.36)

This total wavefunction satisfies the weak Pauli principle, but is obviously not anti-symmetric. The approximation is good, when the interaction between the electrons is negligible. Otherwise, we need to consider the exchange energy terms. This model, called Fermi gas model, is often used to describe the behavior of electrons that can freely move within the conductance band of a metal.

We divide the atom into small volumes (cells) containing \( N \) uniformly distributed non-interacting electrons, whose total number is \( N_t \), and we analyze each cell individually. The whole volume can be modeled by a box potential: \( V(r) = 0 \) for \( 0 \leq x, y, z \leq L \) and \( V(r) = \infty \) in all other places. In this case we find the possible states \( \{ n_x, n_y, n_z \} \) with \( n_x, n_y, n_z = 1, 2, 3 \) and the single electron energies,

\[ E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m_e L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\hbar^2}{2m_e} k_{n_x, n_y, n_z}^2, \] (10.37)

where \( k_{n_x, n_y, n_z} = k_x^2 + k_y^2 + k_z^2 = \left( \frac{n_x \pi}{L} \right)^2 + \left( \frac{n_y \pi}{L} \right)^2 + \left( \frac{n_z \pi}{L} \right)^2 \). Each set of values \( k = (k_x, k_y, k_z) \) corresponds to a accessible state of the system, and each state is associated with a volume element \( (\pi/L)^3 \) in \( k \)-space. Defining the density of states \( \eta(E) \), we can express the total number of states below a particular energy \( E \) by,

\[ n(E) = \int_0^E \eta(E') dE' \equiv \frac{1}{(2\pi)^3} \int d^3 r d^3 k = \frac{L^3}{(2\pi)^3} \frac{4\pi}{\hbar^3} \int k^2 dk \] (10.38)

\[ = \frac{L^3}{(2\pi)^3} \frac{4\pi}{\hbar^3} \left( \frac{2m_e}{\hbar^3} \right)^{3/2} \int_0^E \sqrt{E'} dE' = \frac{L^3}{3\pi^2} \left( \frac{2m_e}{\hbar^3} \right)^{3/2} E^{3/2} \].

\( \eta(E)dE \) is the number of states with energies between \( E \) and \( E + dE \).

At temperature \( T = 0 \) K all \( N \) electrons are in their energetically lowest available state, obeying the Pauli exclusion principle and considering the spin. The energy of the \( N \)-th electron (the most energetic one) is then called the Fermi energy \( E_F \), that is, below \( E_F \) all states are occupied and all those above \( E_F \) are unoccupied. The total energy is given by the sum of the energies of the \( N \) less energetic states, and the final physical state is given by the antisymmetrization of the corresponding wavefunction. With the formula (10.38), we can express the Fermi energy via \( n(E_F) \equiv N \), such that,

\[ E_F = \frac{\hbar^2}{2m_e L^2} (3\pi^2 N)^{2/3}, \] (10.39)

so that the density of states can be expressed as,

\[ \eta(E) = \frac{dn(E)}{dE} = \frac{L^3}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} E^{1/2} = \frac{3N}{2} \frac{E^{1/2}}{E_F^{3/2}}. \] (10.40)
10.3.2.2 Thomas-Fermi energy

Fermi’s box potential trick allowed us to model the impact of Pauli’s principle on the spatial distribution of fermions in a restricted volume, but we did not take into account yet the fact that electrons are charged and will interact. Hence, the energy calculated so far is purely kinetic and will have to be complemented by potential energy.

The total kinetic energy of the electrons with the system in its ground state is,

\[
E_{\text{tot}} = \int_0^{E_F} E \eta(E) dE = \frac{L^3}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \int_0^{E_F} E^{3/2} dE \tag{10.41}
\]

\[
= \frac{L^3}{5\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} E_F^{5/2} = \frac{\hbar^2 3^{5/3} \pi^{4/3}}{10m_e} L^3 \left( \frac{N}{L^3} \right)^{5/3} = CL^3 \rho^{5/3},
\]

where \( \rho \equiv N/L^3 \) is the density of electrons per unit volume and \( C \) just a proportionality constant. Now understanding \( \rho \) as a quantity depending on position in space, we calculate the total number of electrons as,

\[
N_t = \int_{\mathbb{R}^3} \rho(r) d^3r,
\]

and the kinetic energy density by,

\[
\rho_{\text{kin}}(r) = C \rho^{5/3}(r),
\]

such that the total kinetic energy of the electrons in the electronic shell is,

\[
T[\rho] = C \int \rho^{5/3}(r) d^3r.
\]

The potential associated with the electron-nucleus interaction is,

\[
V_{\text{ep}}[\rho] = -\frac{Ze^2}{4\pi\varepsilon_0} \int \frac{\rho(r')}{r'} d^3r' = \int V_p(r') \rho(r') d^3r',
\]

with the electrical potential generated by the nucleus,

\[
\Phi_p(r) = \frac{V_p(r)}{-e} = \frac{Ze}{4\pi\varepsilon_0 r}
\]

The potential associated with the electron-electron interaction is,

\[
V_{\text{ee}}[\rho] = \frac{e^2}{2} \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(r)\rho(r')}{|r - r'|} d^3r d^3r' = \int V_e(r') \rho(r') d^3r',
\]

with the electrical potential generated by the electron cloud,

\[
\Phi_e(r) = \frac{V_e(r)}{-e} = \frac{e}{2} \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(r')}{|r - r'|} d^3r'.
\]

Thus, the total energy (Thomas-Fermi energy) can be written as a functional of the electronic density of the atom,

\[
H_{ TF}[\rho] = T[\rho] + V_{ ep}[\rho] + V_{ ee}[\rho].
\]
10.3. ELECTRONIC SHELL STRUCTURE

### 10.3.2.3 Electronic density and the Thomas-Fermi equation

Exploiting the variational principle, we are interested in the electronic density $\rho(r)$ which minimizes the Thomas-Fermi energy. We can perform this process via Lagrange multipliers under the constraint, that the number of electrons remains constant in the atom. Thus,

$$0 = \frac{\delta}{\delta \rho(r)} \left\{ H_{TF}[\rho] - \mu \left( \int \rho(r) d^3 r - N_t \right) \right\} .$$

(10.50)

Inserting the Thomas-Fermi energy (10.49) we calculate,

$$\mu = \frac{\delta}{\delta \rho(r)} \left\{ C \rho^{5/3}(r) + V_p(r) \rho(r) + V_e(r) \rho(r) \right\} = \frac{5}{3} C \rho^{2/3}(r) + V_p(r) + V_e(r) .$$

(10.51)

Resolving for the electronic density,

$$\rho(r) = \left( \frac{3}{5C} \right)^{3/2} \mu - V_p(r) - V_e(r) \right]^{3/2} .$$

(10.52)

The above expression is called the Thomas-Fermi equation and describes the electron density of the atom in its ground state. The expression (10.48) can be rewritten as a Poisson equation,

$$\nabla^2 V_e(r) = \frac{e^2}{2 \varepsilon_0} \rho(r) ,$$

(10.53)

so that,

$$\nabla^2 V_e(r) = \frac{e^2}{2 \varepsilon_0} \left( \frac{3}{5C} \right)^{3/2} \mu - V_p(r) - V_e(r) \right]^{3/2} .$$

(10.54)

For the effective potential introduced via $V_{eff} = V_p + V_e$, we find,

$$\nabla^2 V_{eff}(r) = \nabla^2 \left( \frac{Z e^2}{4 \pi \varepsilon_0} \frac{1}{r} \right) + \nabla^2 V_e(r)$$

$$= - \frac{Z e^2}{\varepsilon_0} \delta^3(r) + \frac{e^2}{2 \varepsilon_0} \left( \frac{3}{5C} \right)^{3/2} \mu - V_{eff}(r) \right]^{3/2} .$$

(10.55)

It is interesting to note that, as with (10.50), we can identify the Lagrange multiplier $\mu$ as a chemical potential. In particular, for non-interacting neutral atoms, we have $\mu = 0$. In addition, since for an atom both the potential and the electronic density must have spherical symmetry, we can write for $r \neq 0$,

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} [r V_{eff}(r)] = \frac{e^2}{2 \varepsilon_0} \left( \frac{3}{5C} \right)^{3/2} \left[-V_{eff}(r)\right]^{3/2} .$$

(10.56)

We now make the ansatz,

$$V_{eff}(r) \equiv - \frac{Z}{r} \chi(\alpha r) \quad \text{setting} \quad \alpha \equiv \frac{3 e^{4/3}}{5C \varepsilon_0^{2/3}} Z^{1/3} .$$

(10.57)

This transforms the expression (10.56) into,

$$\frac{\partial^2}{\partial r^2} \chi(\alpha r) = - \frac{e^2}{Ze_0} \left( \frac{3Z}{5C} \right)^{3/2} \frac{\chi^{3/2}(\alpha r)}{r^{1/2}} ,$$

(10.58)
or, substituting $x \equiv \alpha r$,

$$\frac{d^2 \chi}{d x^2} = -\frac{\chi^{3/2}}{x^{1/2}}.$$  \hfill (10.59) 

It is important to note the last equation does not depend on the parameter $Z$, thus being a general result for any neutral atom. The function $\chi(x)$ is determined numerically, but we can analyze its asymptotic values given the expected behavior of the effective potential $V_{eff}(r)$: for $r \to 0$ we expect that $V_{eff}(r) = V_p(r)$, hence $\chi(0) = 1$. On the other hand, for $r \to \infty$, we expect $V_{eff}(r) = 0$, hence $\chi(\infty) = 0$.

With $\chi(x)$ known, we obtain the charge density $\rho(x)$, and hence we are able to calculate the total energy of the atom under investigation. Thus, it is possible to show that [24],

$$H_{TF}[\rho] = -0.7687 \frac{e^2}{4\pi\varepsilon_0 a_B} Z^{7/3}. \hfill (10.60)$$

It is important to highlight some points:

1. The result holds for neutral atoms.

2. There is no electronic shell structure assumed; apart from the fact that the kinetic energy was derived in a way as to respect Pauli’s principle, the whole calculation was done within the laws of classical electromagnetism; no quantum mechanics was involved and, hence, no set of quantum numbers has been found.

3. Apart from the Pauli principle used to calculate the density of states (10.40), quantum statistical effects of identical particles (such as wavefunction antisymmetrization) are not taken into account.

A more refined model which deals with third criticism and, in addition, is closer to density functional theory (DFT) is the Thomas-Fermi-Dirac model.

### 10.3.3 Hartree method

The effective potential obtained from the Thomas-Fermi model can serve as a starting point for quantum treatment. Assuming that all electrons are subject to the same effective potential $V_{eff}$, we numerically solve the Schrödinger equation for each electron independently,

$$\hat{H}_i = \left( -\frac{\hbar^2}{2m} \nabla_i^2 + V_{eff} \right) \psi_i(r_i) = e_i \psi_i(r_i). \hfill (10.61)$$

With this we calculate all energies and eigenfunctions (only the radial parts are of interest) minimizing the total energy and respecting the weak Pauli principle, that is, we classify the states in the order of increasing energies $e_i$ and fill them successively with electrons. For the total wavefunction we obtain,

$$\left( \sum_{i=1}^{N} \hat{H}_i \right) \Psi_N = E_n \Psi_N \quad \text{with} \quad \Psi_N = \psi_1 \cdots \psi_N \quad \text{and} \quad E_n = \sum_{i=1}^{N} e_i. \hfill (10.62)$$

With the eigenfunctions we calculate the charge densities $e |\psi_j(r_j)|^2$. We integrate the field to obtain a potential that represents an improved estimation for the electronic
mean field,
\[ V_{\text{eff}} \rightleftharpoons -\frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{j \neq i} \int d^3r_j \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|} |\psi_j(r_j)|^2 \quad (10.63) \]

We replace that potential in the Schrödinger equation, and repeat the whole process from the beginning, until the total energy \( \sum_i \epsilon_i \) does not get any lower. This self-consistent method is called Hartree method. Fock improved these calculations using antisymmetric wavefunctions for the valence electrons. This method is called Hartree-Fock method.

### 10.3.4 Hartree-Fock method

The Hartree-Fock method used to treat atomic or molecular many-body systems aims at obtaining the electronic wavefunction of the system. Dealing with anti-symmetrized wavefunctions, it represents a refinement of the Hartree method. The method is based on the variational principle and on the assumption that we can write the global wavefunction as a Slater determinant, with each electron occupying a specific orbital state (spin-orbital) and interacting with an effective potential stemming from the electrons which occupy other orbitals. Instead of solving the Schrödinger equation, we must now solve a set of equations called Hartree-Fock equations of the type \( \hat{F}\psi_k(1) = \epsilon_k \psi_k(1) \). The method is performed iteratively until convergence of the atomic orbitals and their respective energies is reached. The procedure is then called self-consistent: Starting from an initial trial global wavefunction we calculate the effective potential in each orbital and a new set of wavefunctions which, in turn, generate a new effective potential. This new potential is then used in a new set of Hartree-Fock equations.

#### 10.3.4.1 Hartree-Fock equations

To start with, we write the Hamiltonian (10.33) of a multi-electronic atom as [24],

\[ \hat{H} = \sum_{i=1}^{Z} \hat{h}_i + \frac{1}{2} \sum_{i \neq j} \hat{V}_{ij} \quad (10.64) \]

where \( \hat{h}_i \) is the Hamiltonian only of the electron \( i \), and \( \hat{V}_{ij} \) is the interaction term between the electrons \( i \) and \( j \). To implement the method we must suppose that the multi-electronic state can be written as the product of the individual states of each electron:

\[ \Psi(1, ..., Z) = \psi_1(1)\psi_2(2)...\psi_{Z}(Z) \quad (10.65) \]

where \( \psi_i(1) = \phi_i(r_1)\chi(\alpha) = \psi_i^{\alpha}(r_1) \) represents the spin-orbital state of electron 1, that is, the spatial wavefunction of the electron in the state \( i \) and with spin \( \alpha \). However, due to the symmetrization postulate, the physical state of the system must be expressed by a Slater determinant,

\[ \Psi(1, ..., Z) = \frac{1}{\sqrt{Z!}} \det [\psi_1(1)\psi_2(2)...\psi_{Z}(Z)] \quad (10.66) \]
Now, we use the variational principle to minimize the expectation value of the ground state energy by varying the functions \( \psi_k(n) \). In this way, the correct orbitals are those that minimize the energy. The expectation value is written as,

\[
E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \sum_{i=1}^{Z} \hat{h}_i | \Psi \rangle + \langle \Psi | \frac{1}{2} \sum_{i \neq j} \hat{V}_{ij} | \Psi \rangle .
\]  

(10.67)

It is possible to show that,

\[
\langle \Psi | \sum_{i=1}^{Z} \hat{h}_i | \Psi \rangle = \sum_{i=1}^{Z} \langle \psi_i | \hat{h}_i | \psi_i \rangle \quad \text{and} \quad \langle \Psi | \frac{1}{2} \sum_{i \neq j} \hat{V}_{ij} | \Psi \rangle = \frac{1}{2} \sum_{i,j} \left[ \langle \psi_i \psi_j | \hat{V}_{ij} | \psi_i \psi_j \rangle - \langle \psi_j \psi_i | \hat{V}_{ij} | \psi_j \psi_i \rangle \right].
\]  

(10.68)

Hence,

\[
E = \sum_{i=1}^{Z} \hat{h}_i | \Psi \rangle + \frac{1}{2} \sum_{i,j} \epsilon_{ij} \left[ \langle \psi_i \psi_j | \hat{V}_{ij} | \psi_i \psi_j \rangle - \langle \psi_j \psi_i | \hat{V}_{ij} | \psi_j \psi_i \rangle \right].
\]  

(10.69)

The above expression can be minimized via Lagrange multipliers under the constraint that the states are orthogonal \( \langle \psi_i | \psi_j \rangle = \delta_{ij} \),

\[
\delta \left\{ \langle \Psi | \hat{H} | \Psi \rangle - \sum_{i,j} \epsilon_{ij} \left[ \langle \psi_i \psi_j | \hat{V}_{ij} | \psi_i \psi_j \rangle - \langle \psi_j \psi_i | \hat{V}_{ij} | \psi_j \psi_i \rangle \right] \right\}
\]  

(10.70)

Thus, we obtain the following set of Hartree-Fock equations:

\[
\hat{F} \psi_k(1) = \epsilon_k \psi_k(1) \quad \text{where} \quad \hat{F} = \hat{h}_1 + \sum_i (2\hat{J}_i - \hat{K}_i)
\]  

(10.71)

is the Fock operator and \( \epsilon_k \) is the energy associated with the spin-orbital \( \psi_k \). The operator \( \hat{J}_i \), called Coulomb operator, represents the mean potential sensed by electron 1 in the orbital \( k \) due to the presence of electron 2 in the orbital \( i \):

\[
\hat{J}_i \psi_k(1) = \left\{ \int \psi_i^*(2) V_{12} \psi_i(2) dr_2 \right\} \psi_k(1).
\]  

(10.72)

The operator \( \hat{K}_i \), denominated exchange operator, is a consequence of the symmetrization process and therefore a purely quantum effect, that is, without classical analogue:

\[
\hat{K}_i \psi_k(1) = \left\{ \int \psi_i^*(2) V_{12} \psi_k(2) dr_2 \right\} \psi_k(1).
\]  

(10.73)

Once we know all wavefunctions, the energies of the orbitals can be obtained in the following way:

\[
\int dr_1 \psi_k^*(1) \left\{ \hat{h}_1 + \sum_i (2\hat{J}_i - \hat{K}_i) \right\} \psi_k(1) = \epsilon_k \int dr_1 \psi_k^*(1) \psi_k(1) = \epsilon_k,
\]  

(10.74)
that is,
\[ \epsilon_k = \int dr_1 \psi^*_k(1) \hat{h}_1 \psi^*_k(1) + \sum_i (2\hat{J}_{ki} - \hat{K}_{ki}), \]  
(10.75)

where,
\[ \hat{J}_{ki} = \int dr_1 \psi^*_k(1) \hat{J}_i \psi_k(1) \]  
(10.76)
\[ \hat{K}_{ki} = \int dr_1 \psi^*_k(1) \hat{K}_i \psi_k(1) \]  

is the exchange integral.

The total atomic energy can be calculated by,
\[ E = 2 \sum_k \epsilon_k - \sum_{k,i} (2\hat{J}_{ki} - \hat{K}_{ki}). \]  
(10.77)

Furthermore, if assuming that, taking an electron away from the orbital \( \psi_k \) the electronic distribution remains unchanged, it is possible to associate the energy \( \epsilon_k \) with the ionization energy of the electron in this orbital, \( I_k \simeq \epsilon_k \). This equality is known as Koopman’s theorem.

### 10.4 The periodic system of elements

Completely filled principal layers \( n, \ell \) are isotropic, \( \Psi_N(r) = \Psi(r) \), as we will show in Exc. 10.4.4.1. It is important to distinguish three different energetic sequences:

1. Tab. 10.5 shows, for a given atom, the excited orbitals of the last electron. 2. The energy sequence shown in Tab. 10.6 tells us in which orbital the next electron will be placed, when we go to the next atom in the periodic table 10.8 which has one more proton in the nucleus. 3. The inner electrons are subject to different potentials and, hence, follow a different sequence energetic sequence: While for the inner electrons we find,
\[ E_{n,\ell} < E_{n,\ell+1} \ll E_{n+1,\ell}, \]  
(10.78)

the sequence is partially inverted for the outermost electron. Note that it is the outermost electrons that determine the chemical reactivity of the atom. The sequence is illustrated in Fig. 10.4.

Noble gases have small radii, high excitation energies and high ionization energies. The outermost electrons in a noble gas atom must overcome a large energy the gap to any higher quantum numbers. Halogens have strong electro-affinities, since the outer electron layer \( (n_{max}) \) is incomplete and therefore malleable, such that an electron approaching the halogen perceives the nucleus through a partially transparent shield. Alkalis are similar to hydrogen and have excitation energies in the optical regime. Their fundamental state \( ^2S_{1/2} \) is determined by a valence electron only in the \( \ell = 0 \) orbital. Unlike hydrogen, excitation energies are highly dependent on \( \ell \), since orbits with small \( \ell \) have higher probabilities to be in the unshielded region \( -Z^2e^2/r \) than orbits with large \( \ell \), who spend more time in the shielded region \( -e^2/r \). For the same reason, energies corresponding to larger \( n \) resemble more those of the hydrogen spectrum.
10.4.0.1 Inner shell electrons

The interior shell structure of the atoms can be analyzed by X-ray scattering. Electrons decelerated by atoms emit a continuous spectrum called \textit{Bremsstrahlung}, but they can also expel electrons from the inner layers leaving a hole behind. When a hole is filled by cascades of electrons falling down from higher layers, the atom emits a specific X-ray spectrum (\(\approx 10^4\) eV). The selection rules \(\Delta \ell = \pm 1\) and \(\Delta j = \pm 1\) split the lines in two components. X-ray spectra of neighboring elements in the periodic table are very similar, because the inner layers not being shielded, they see a potential close to \(\propto Z^2/r\). Therefore, the \(Z\)-dependency of inner energy levels along a horizontal rows in the periodic table is more or less \(\omega \propto Z^2\), as predicted by Bohr’s atomic model.

10.4.1 Electronic shell model

Each of the energy levels in this sum contains several states. Each of these states can be occupied by a single electron, according to the Pauli principle. In this way, we obtain the electronic configuration for the atoms of the periodic system. In this picture, the energies of the ground states of the elements, normalized by \(1/Z^2\), can be arranged in the scheme 10.3:

```
N  4s  3p\textsuperscript{\textasciicircum 1}  4p
M  3s  2p\textsuperscript{\textasciicircum 1}  3p\textsuperscript{\textasciicircum 2}  3d\textsuperscript{\textasciicircum 1}  \textsuperscript{\textasciicircum 2}Mg  \textsuperscript{\textasciicircum 2}Al  3p\textsuperscript{\textasciicircum 2}  3p\textsuperscript{\textasciicircum 3}  \textsuperscript{\textasciicircum 2}Si  3p\textsuperscript{\textasciicircum 2}  3p\textsuperscript{\textasciicircum 3}  3p\textsuperscript{\textasciicircum 4}  \textsuperscript{\textasciicircum 2}P  \textsuperscript{\textasciicircum 3}S  3p\textsuperscript{\textasciicircum 3}  \textsuperscript{\textasciicircum 2}Cl  3p\textsuperscript{\textasciicircum 2}  3p\textsuperscript{\textasciicircum 3}  3p\textsuperscript{\textasciicircum 4}  \textsuperscript{\textasciicircum 2}Ar
L  2s  \textsuperscript{\textasciicircum 2}Li  \textsuperscript{\textasciicircum 2}Be  2p\textsuperscript{\textasciicircum 1}  \textsuperscript{\textasciicircum 2}B  \textsuperscript{\textasciicircum 2}C  \textsuperscript{\textasciicircum 3}N  \textsuperscript{\textasciicircum 2}O  \textsuperscript{\textasciicircum 2}F  \textsuperscript{\textasciicircum 2}Ne
K  1s
```

This only works for atoms with up to 18 electrons. When the layer 3\(p\) is completely filled, the next to be occupied is not 3\(d\) but the 4\(s\). The new scheme is illustrated in 10.4. The anomalies beginning at \(Z = 18\) arise due to electron-electron interaction. The real potential evolves from one to the other Coulombian potential, as distance from the nucleus is increased, as illustrated in Fig. 10.2. Near the nucleus, the electrons shield the positive charge less than for large \(r\). Thus, those states that have a high probability near the nucleus are energetically lowered. That is,

\[ E_{2s} < E_{2p} \quad \text{and} \quad E_{6s} < E_{6p} < E_{6d}. \] (10.79)

The degeneracy of the orbital angular momentum in the Schrödinger model is thus lifted. The shielding is, as can be seen in the example of the excited states of lithium, a large effect in the range of some eV.

The shielding also accounts for the anomalies in the periodic system, such as in K or Ca. Since \(E_{4s} < E_{3d}\), the 4\(s\) state is filled before the 3\(d\). Similar anomalies
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Figure 10.4: Illustration of the sequence of filling the orbitals with electrons.

also occur in Rb (5s), Cs (6s), and Fr (7s). In rare earths the shielding effect is even more pronounced. Here, the energy of the state 6s is even below the energy of the 4f, which means that the shells 6s, 5s, 5p, and 5d protect the 4f shell very well. Resolve Exc. 10.4.4.2.

10.4.1.1 Alkalines

The electronic shell structure of alkalines consists of a completed noble gas shell and an additional valence electron. Their spectrum is therefore very similar to hydrogen. An empirical approach can be stressed to describe this feature,

\[ E_{n,l} = -\frac{1}{2} \mu_{EG} c^2 \frac{c^2}{n - \Delta(n,l)} \],

(10.80)

where \( \mu_{EG} \) is the reduced mass relative to the noble gas shell and \( \Delta(n,l) \) is called quantum defect. The quantum defect is tabulated for most alkaline states and is particularly important for low energy states. For sodium, for example, the values are:

For states with a large angular momentum, the quantum defect disappears. In these states, the electron is far from the nucleus and the potential is similar to that of hydrogen. Alkalines are currently widely studied in quantum optics laboratories, for being comparatively simple, but having a sufficiently rich structure to be interesting. The fundamental electronic transitions typically lie in the visible and near-infrared spectral range and can be excited with comparatively simple laser sources. The lifetime of excited states is typically longer than 20 ns, which corresponds natural linewidths of approximately \( (2\pi) \times 10 \text{ MHz} \).

\[ ^9 \text{An example of this is Nd:YAG (Neodymium in Yttrium Aluminum Garnet). In this crystal, optical transitions can be excited within the 4f shell of the Nd. However, these transitions are only allowed due to perturbations of the crystalline field. The very strong shielding ensures a long life of the excited state. For this reason this crystal is an excellent laser material.} \]
10.4.1.2 Excited states

The experimentally easiest and most precise approach to determining orbital energies consists in measuring excitation spectra of valence electrons. The table 10.5 compares such excitation spectra for various alkaline atoms. Although this is not to be confused with the binding energies of valence electrons of different atoms, it gives us a qualitative idea of the impact of shielding and indicates, which orbital will be occupied by the additional valence electron of the next species in the periodic table.

<table>
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<tr>
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<th>n = 4</th>
<th>n = 5</th>
<th>n = 6</th>
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<tr>
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<tr>
<td>f</td>
<td>-</td>
<td>0.00</td>
<td>-0.01</td>
<td>0.008</td>
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</tbody>
</table>

Figure 10.5: Comparison of the excitation energies of the *valence electron* for several alkaline atoms.
10.4.2 LS and jj-coupling

Following Hund’s rule, the $\mathbf{L} \cdot \mathbf{S}$-coupling is energetically favorable compared to the $\mathbf{j} \cdot \mathbf{j}$-coupling, which means that the spins of the outermost electrons, that is, the electrons outside of filled subshells $(n, \ell)$, prefer to orient their spins in parallel in order to anti-symmetrize the spatial wavefunctions and thus maximize the distance between the electrons. Every sub-layer of the series shown in Fig. 10.4 must be filled in the listed order before placing new electrons in the next layer.

In the case of helium, we have seen that the Pauli principle first determines the relative orientation of the electron spins. The spins $\mathbf{s}_i$ of the individual electrons therefore add up to a total angular momentum $\mathbf{S}$. The orbital angular momenta $\mathbf{l}_i$ also adopt a relative orientation. It is determined by a residual spherically non-symmetric Coulomb interaction: A certain combination $\mathbf{L}$ of orbital angular momenta leads to a certain spatial distribution of the electrons and thus to a certain electrostatic energy distribution.

The total spin $\mathbf{S}$ and the total orbital angular momentum $\mathbf{L}$ subsequently couple to a total angular momentum $\mathbf{J}$ very similar to the $\mathbf{l} \cdot \mathbf{s}$ spin-orbit coupling in single electron systems. States with different $\mathbf{J}$ then have the respective energies that the total spin $\mathbf{S}$ adopts in the field generated by the total orbital angular momentum $\mathbf{L}$.\(^\text{10}\)

---

\(^{10}\)In addition, there are the small contributions due to $\mathbf{l}_i \cdot \mathbf{l}_j$-coupling and to $\mathbf{s}_i \cdot \mathbf{s}_j$-coupling, where $i \neq j$.  

---

![Figure 10.6: Illustration of Hund’s rule.](image-url)
The above coupling scheme is called *Russel-Saunders coupling* or *LS-coupling*. It works when the spin-orbit coupling is small. In this case, intercombination is forbidden, which means that there can be no electromagnetic transition between states with different spins (see metastable helium).

Since \( E_{LS} \approx Z \alpha^4 \approx Z^4 \), for heavy atoms, the coupling of an electronic spin to its own orbital momentum grows strongly with \( Z \), as well as the symmetrization and the exchange energy, which mutually orient the spins, and the residual Coulomb interaction, which mutually couples the angular orbital momenta. In this case, the orientation of \( L_i \) relative to \( S_i \) delivers more energy than the exchange energy and the residual energy cost. Hence, the spin and the orbital angular momentum of an individual electron couple first,

\[
\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i .
\]

We obtain a new Hamiltonian of fine structure of the form,

\[
H_{FS} \propto \mathbf{j}_i \cdot \mathbf{j}_j .
\]

Pure \( jj \)-coupling only exists for very heavy nuclei. Normally, we have a so-called *intermediate coupling*, which is a mixture of *LS* and *jj*-coupling. This can considerable relax the intercombination prohibition. When the coupling is pure, we have the following dipolar selection rules:

- *LS-coupling*: \( \Delta S = 0, \Delta L = \pm 1, \Delta \ell = \pm 1 \)
- *jj-coupling*: \( \Delta j = 0, \pm 1 \) for one \( e^- \), \( \Delta j = 0 \) for all others

In addition we have the following two couplings: \( \Delta J = 0, \pm 1 \), but \( J, J' = 0 \) is forbidden, \( \Delta m_J = 0, \pm 1 \) when \( \Delta J = 0 \) but \( m_J, m_{J'} = 0 \) is forbidden.

### 10.4.3 Summary of contributions to the atomic energy levels

The total Hamiltonian of a single atom is composed of the kinetic energy of the nucleus and the electrons, of various interaction potentials between the nucleus and
10.4. THE PERIODIC SYSTEM OF ELEMENTS

the electrons, and of interactions with various types of external electromagnetic fields.

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla_R^2 + \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_{r_i}^2 \right) + V(r_1, s_1, \ldots, r_N, s_N) + V_{\text{ext}} . \tag{10.83} \]

Of course, with the presence of other atoms, other interactions may generate other relevant contributions to the Hamiltonian.

The following interactions contribute to the potential \( V \): The Coulomb interactions,

\[ V_{\text{ncl-ele}} = -\sum_{i=1}^{Z} \frac{Ze^2}{4\pi\varepsilon_0 |r - r_i|} \quad \text{and} \quad V_{\text{ele-ele}} = \sum_{i<j=1}^{Z} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|} , \tag{10.84} \]

the antisymmetry of the wavefunction, that is, exchange integrals,

\[ V_{\text{sym}} , \tag{10.85} \]

the energies of spin-orbit couplings,

\[ V_{ls} = -\sum_{i=1}^{Z} \frac{1}{e^2m^2c^2} \frac{1}{|r - r_i|} \frac{dV_{\text{el}}}{dr_i} (l_i \cdot s_i) , \tag{10.86} \]

the energies of spin-spin couplings,

\[ V_{ss} = \sum_{i \neq j=1}^{Z} \frac{e^2}{m^2} \left[ \frac{\sigma_i \cdot \sigma_j}{|r_i - r_j|^3} - 3 \frac{[\sigma_i \cdot (r_i - r_j)][\sigma_j \cdot (r_i - r_j)]}{(r_i - r_j)^5} \right] , \tag{10.87} \]

the energies of orbit-orbit couplings,

\[ V_{ll} = \sum_{i \neq j=1}^{Z} c_{ij} (l_i \cdot l_j) , \tag{10.88} \]

interactions between the spin of the electrons and the nuclear spin and between the orbital angular momentum of the electrons and the nuclear spin,

\[ V_{\text{hfs}} = \frac{A}{\hbar^2} J \cdot I , \tag{10.89} \]

and relativistic corrections.

\[ V_{\text{rel}} , \tag{10.90} \]

In addition, static external fields may displace energy levels and can influence the internal coupling of angular momenta and spins,

\[ V_{\text{ext}} = -d \cdot E , \quad -\tilde{\mu} \cdot B . \tag{10.91} \]

What quantum numbers are good depends on the relative amplitudes of intra-atomic interactions:

Case 1: fine structure with \( L \cdot S \)-coupling plus Zeeman splitting of hyperfine structure:
\(V_{\text{ncl-ele}}, V_{\text{ele-ele}} \gg V_{\text{ele-ele}}, \ V_{\text{sym}} \gg V_{ls} \gg V_{hfs} \gg V_{B}\) the quantum number are \(|n_i, l_i, L, S, J, F, m_F\).

Case 2: fine structure with \(j \cdot j\)-coupling plus Zeeman splitting of hyperfine structure: \(V_{\text{ncl-ele}}, V_{\text{ele-ele}} \gg V_{ls} \gg V_{hfs} \gg V_{B}\) the quantum number are \(|n_i, l_i, j_i, J, m_J, m_F\).

Case 3: fine structure with \(L \cdot S\)-coupling plus hyperfine structure of Zeeman splitting: \(V_{\text{ncl-ele}}, V_{\text{ele-ele}} \gg V_{ls} \gg V_{B} \gg V_{hfs}\) the quantum number are \(|n_i, l_i, L, S, J, m_J, m_F\).

Case 4: fine structure with \(L \cdot S\)-coupling plus Paschen-Back splitting of fine structure: \(V_{\text{ncl-ele}}, V_{\text{ele-ele}} \gg V_{ls} \gg V_{B} \gg V_{hfs}\) the quantum number are \(|n_i, l_i, L, S, m_L, m_S, m_F\).

10.4.4 Exercises

10.4.4.1 Ex: Filled electronic shells

Show at the example of hydrogen that completely filled electronic layer are isotropic.

10.4.4.2 Ex: Electronic excitation levels of alkaline

Explain why
a. state \([\text{Li}]\ (2s)^2S_J\) has lower energy than \([\text{H}]\ (2s)^2S_J;\)
b. state \([\text{Li}]\ (2s)^2S_J\) has lower energy than \([\text{Li}]\ (2p)^2P_J;\)
c. state \([\text{Na}]\ (3d)^2D_J\) has lower energy than \([\text{Na}]\ (4p)^2P_J;\)
### Periodic Table of the Elements

#### Atomic Properties of the Elements

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<td>Lr</td>
<td>Rf</td>
<td>Db</td>
</tr>
</tbody>
</table>

#### Frequently used fundamental physical constants

- **Speed of light in vacuum, \( c \):** 299,792,458 m/s
- **Planck constant, \( h \):** 6.6261 x 10^{-34} J s
- **Elementary charge, \( e \):** 1.6022 x 10^{-19} C
- **Electron mass, \( m_e \):** 9.1094 x 10^{-31} kg
- **Proton mass, \( m_p \):** 1.6726 x 10^{-27} kg
- **Fine-structure constant, \( \alpha \):** 1/137.036
- **Rydberg constant, \( R_\infty \):** 109,737.3 m
- **Bohr magneton, \( \mu_B \):** 1.3067 x 10^{-20} J/T

For a description of the atomic data, visit [physics.nist.gov/atomdata](http://physics.nist.gov/atomdata)
Chapter 11

Molecular dimers

In systems of many particles (gases, fluids, or solids) interatomic interactions must be considered. These interactions usually have electrostatic origins, but generally cannot be given in the form of closed expressions. For example, the collision of two atoms $i$ and $j$ can occur in a multitude of channels, that is, interaction potentials $V(r_i - r_j)$. Interatomic forces do not only govern collisions, but can sustain molecular bound states. This introduces new degrees of freedom in the systems of many particles through possible excitations of vibration or rotation movements.

Figure 11.1: (code) Example of an interatomic potential spaghetti: The lowest states of the molecule $^{85}\text{Rb}_2$.

In this course, we will not go beyond homo- or heteronuclear dimers, that is, molecules consisting of two identical or different atoms.

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11.1 Molecular binding

11.1.1 Ionic and covalent binding

There are two fundamental ways of binding two atoms together, the ionic bond and the covalent bond. The *ionic bond* is ruled by the quantities *electroaffinity* (EA), *electronegativity* (EN), and *ionization energy* (IE):

- **Ionization energy**: This energy is needed for the release of an electron by a neutral atom, e.g. \( \text{Na} + 5.1 \text{ eV} \rightarrow \text{Na}^+ + e^- \).

- **Electroaffinity**: This energy is released by the capture of an electron by a neutral atom, e.g. \( \text{Cl} + e^- \rightarrow \text{Cl}^- + 3.8 \text{ eV} \).

- **Electronegativity**: This quantity measures the stability of a valence orbital, e.g. that of fluorine (3.98) is more stable than that of cesium (0.79), such that fluorine holds its electrons tighter than cesium.

At short distances, the exchange of an electron between atoms can decrease energy. The so-called *ionic bond* is then sustained by the Coulombian attraction between two ions, and the binding energy can be estimated through electrostatic interaction.

**Example 44 (Ionic binding in NaCl)**: For example, a sodium and a chlorine atom gain energy by forming a molecule,

\[
\begin{align*}
\text{Na} + 5.1 \text{ eV} & \rightarrow \text{Na}^+ + e^- \\
\text{Cl} + e^- & \rightarrow \text{Cl}^- + 3.8 \text{ eV} \\
\text{Na}^+ + \text{Cl}^- & \rightarrow \text{NaCl} + 4.9 \text{eV} \\
\end{align*}
\]

\[
\text{Na} + \text{Cl} \rightarrow \text{NaCl} + (-5.1 + 3.8 + 4.9) \text{ eV}.
\]

---

1 We are not considering metallic bonds nor hydrogen bridge bonds, here.
The molecules are polar and, therefore, have a permanent electric dipole moment. The bond has no preferential direction, since each atom is perfectly isotropic. Therefore, this type is well suited for the construction of crystalline lattices.

To understand covalent bond, we consider the example \( \text{H}_2^+ \) and estimate the interaction energy for each distance \( R \) between the nuclei. In this case, in contrast to atoms, the spherical symmetry is broken, and therefore the energy degeneracy with respect to parity is abolished, that is, for wavefunctions \( \psi(-x) = \pm \psi(x) \) the energies vary differently with \( R \). The even wavefunction, which has an increased probability of the electron of being between the nuclei, is binding, which means that the interaction potential exhibits a minimum at a certain distance. The odd wavefunction, which disappears between the nuclei, is anti-binding, which means that the interaction potential is repulsive at all distances. In fact, an electron located at the center between two positive charges can overcome the Coulomb repulsion between the nuclei, whose mutual distance is twice. Obviously, the energy can not fall below that of the fundamental state of \( \text{He}^+ \), being approximately \( -4 \times 13.6 \) eV. With two electrons, as in the case of the neutral molecule \( \text{H}_2 \), the anti-parallel orientation of the spins, \( \uparrow \downarrow \), allows us to place the two electrons in the same orbital, while for parallel orientation, \( \uparrow \uparrow \), we expect anti-binding. Each electron without a partner in an orbital can form a covalent bond, for example, phosphorus \([\text{P}]=[\text{Ne}]3s^23p^{\uparrow \uparrow \uparrow}\) has three available orbitals corresponding to different magnetic quantum numbers. The covalent bond is directional \((sp^1, sp^2, \text{or } sp^3 \text{ hybridization})\), which is essential for the molecular structure such as in \( \text{CH}_4 \). Do the Exc. 11.1.6.1.

### 11.1.2 Born-Oppenheimer approximation and the \( \text{H}_2^+ \) molecule

The Born-Oppenheimer approximation in molecular physics consists in considering, at first, the positions of the nuclei as being fixed in space. This allows us to study the stationary states of the electrons subject to the potential created by the nuclei for a given internuclear distance \( R \). Varying \( R \), the electronic energies (computed for a fixed \( R \)) remain the same, because the electronic wavefunctions adjust instantaneously due to their mass being much lower than that of the nuclei. The non-varying electronic energies play the role of interaction potential energies between the nuclei [24].
11.1.2.1 Separation of the center-of-mass

Let us consider two heavy masses, \( M_{a,b} = M \) separated by a distance \( R \) and interacting through a potential \( V_{nn}(R) \). Furthermore, there is a light-weighted mass \( m_e \) interacting with the other masses through \( V_{ne}(r) \). The Hamiltonian is,

\[
\hat{H} = -\frac{\hbar^2}{2M} \nabla_a^2 + \frac{\hbar^2}{2M} \nabla_b^2 + \frac{\hbar^2}{2m_e} \nabla_c^2 + V_{nn}(|R_a - R_b|) + V_{ne}(|R_a - R_e|) + V_{ne}(|R_b - R_e|). \tag{11.2}
\]

We transform to the center-of-mass system of the two heavy masses anchored at \( \mathbf{X} \equiv \frac{M_a \mathbf{R}_a + M_b \mathbf{R}_b}{M} = \frac{1}{2}(\mathbf{R}_a + \mathbf{R}_b) \). The distance of the heavies is \( \mathbf{R} \equiv \mathbf{R}_a - \mathbf{R}_b \), and the coordinate of the light mass counting from the center-of-mass is \( \mathbf{r} = \mathbf{R}_a - \frac{1}{2} \mathbf{R} - \mathbf{R}_e \).

Introducing the reduced mass of the heavies \( M_r = \frac{M}{2} \),

\[
\begin{align*}
\left[ -\frac{\hbar^2}{2M} \nabla_X^2 + \frac{\hbar^2}{2M_r} \nabla_R^2 + V_{nn}(R) + \frac{\hbar^2}{2m_e} \nabla_e^2 + V_{ne}(|\mathbf{r} + \frac{1}{2} \mathbf{R}|) + V_{ne}(|\mathbf{r} - \frac{1}{2} \mathbf{R}|) \right] \Theta(\mathbf{X}) \Psi(\mathbf{R}, \mathbf{R}_e) &= E_{tot} \Theta(\mathbf{X}) \Psi(\mathbf{R}, \mathbf{R}_e),
\end{align*}
\]

Here, we made the ansatz for the total wavefunction \( \Psi = \Theta(\mathbf{X}) \Psi(\mathbf{R}, \mathbf{R}_e) \), assuming that the center-of-mass is only determined by the heavy masses,

\[
\begin{align*}
-\frac{\hbar^2}{2M} \nabla_X^2 \Theta(\mathbf{X}) &= E_{cm} \Theta(\mathbf{X}), \tag{11.4} \\
\left[ -\frac{\hbar^2}{2M_r} \nabla_R^2 + V_{nn}(R) + \frac{\hbar^2}{2m_e} \nabla_e^2 + V_{ne}(|\mathbf{r} + \frac{1}{2} \mathbf{R}|) + V_{ne}(|\mathbf{r} - \frac{1}{2} \mathbf{R}|) \right] \Psi(\mathbf{R}, \mathbf{R}_e) &= E \Psi(\mathbf{R}, \mathbf{R}_e),
\end{align*}
\]

where \( E_{tot} = E_{cm} + E \).

11.1.2.2 Adiabatic approximation

The Born-Oppenheimer approximation now consists in assuming that the movement of the heavies is independent of the position of \( m_e \), which allows us to separate the corresponding wavefunction \( \phi \) via the ansatz \( \Psi(\mathbf{R}, \mathbf{R}_e) = \psi(\mathbf{R}, \mathbf{r}) \phi(\mathbf{R}) \). On the other hand, the orbital \( \psi \) of the light mass \( m_e \) does not change much, when we vary the distance of the heavies, \( \nabla_R \psi(\mathbf{R}, \mathbf{r}) \approx 0 \). This is only valid, as long as the heavies are inert on the time scale of the movement of \( m_e \). Therefore, we can approximate the second derivative,

\[
\nabla_R^2 [\psi(\mathbf{R}, \mathbf{r}) \phi(\mathbf{R})] = \phi(\mathbf{R}) \nabla_R^2 \psi(\mathbf{R}, \mathbf{r}) + 2 \nabla_R \phi(\mathbf{R}) \cdot (\nabla_R \psi(\mathbf{R}, \mathbf{r}) - \psi(\mathbf{R}, \mathbf{r}) \nabla_R \phi(\mathbf{R})) \simeq \psi(\mathbf{R}, \mathbf{r}) \nabla_R^2 \phi(\mathbf{R}), \tag{11.5}
\]
postulating that the first two terms are negligible compared to the third. We can now separate the second equation (11.4) in two parts, the first being,

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + V_{ne}(|r + \frac{1}{2}R|) + V_{ne}(|r - \frac{1}{2}R|) \right] \psi(r, R) = \varepsilon(R)\phi(r, R).$$  \hspace{1cm} (11.6)

We solve this equation for the electronic degree of freedom \( r \) by choosing a fixed internuclear distance \( R \), and we substitute in the second expression (11.4), which gives,

$$\left[ -\frac{\hbar^2}{2M_r} \nabla^2_R + V_{nn}(R) + \varepsilon(R) \right] \phi(R) = E\phi(R). \hspace{1cm} (11.7)$$

Treating the interatomic distance \( R \) as a fixed parameter, the solution of Eq. (11.6) provides the electronic orbitals and their energies \( \varepsilon(R) \). The Born-Oppenheimer potential is composed of the electrostatic repulsive potential of the nuclei and the kinetic energy of the electron, \( V_{nn}(R) + \varepsilon(R) \). In other words, the presence of the electrons generates an additional interaction energy between the nuclei. By inserting this complete interatomic potential into Eq. (11.7), we can determine its vibrational structure \( \phi_{vib}(R) \).

Fig. 11.5 shows an example of binary effective nuclear potentials, as a function of the distance \( R \) between the two nuclei. Each curve corresponds to a different solution of the electronic equation, that is, to a different electronic state. In many cases, such nuclear potentials have a stable equilibrium region. The bound states located in these regions are molecular bound states of two atoms.

Figure 11.5: Effective nuclear potentials for the interaction between two rubidium atoms (Rb\(_2\)).

In practice, the calculation of adiabatic Born-Oppenheimer potentials is difficult and makes it the subject of sophisticated theories, such as the molecular orbital model or the valence bond model\(^2\). We study in Exc. 11.1.6.2 a generalization of the Born-Oppenheimer approximation.

\(^2\)Note that the Born-Oppenheimer approximation is no longer good in the presence of relativistic or spin-orbit coupling effects.
11.1.3 Linear combination of orbitals and the \( \text{H}_2 \) molecule

In the following we will discuss the electronic structure of the simplest neutral molecule: \( \text{H}_2 \). For the low electron states of this molecule, the Born-Oppenheimer approximation is totally satisfactory, that is, we want to solve a Schrödinger type equation (11.6), but with two electrons. We are, therefore, interested in the electronic Hamiltonian,

\[
\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + \frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{R_{ab}} - \frac{1}{|r_1 - R_a|} - \frac{1}{|r_2 - R_b|} - \frac{1}{|r_1 - R_a|} - \frac{1}{|r_2 - R_b|} + \frac{1}{r_{12}} \right),
\]

where '1' and '2' denote the two electrons and 'a' and 'b' the nuclei.

This problem cannot be solved analytically. The standard procedure begins with choosing a suitable basis, i.e. a very compact basis which does not depend on the configuration of the molecule. That is, we want the basis to be composed of functions that do not depend on the distance between the two nuclei, \( R_{ab} \), to avoid calculations for different bond lengths.

The most natural basis functions are the available atomic orbitals of the individual hydrogen atoms. When the bond length is too large, the system approaches the limit of two non-interacting hydrogen atoms. In this case, the electron wavefunction can be approximated by the product of atomic orbitals (AO) of atom 'a' and atom 'b'. Therefore, the smallest basis that gives us a realistic picture of the fundamental state of the \( \text{H}_2 \) molecule must contain two functions: \( |1s_a\rangle \) and \( |1s_b\rangle \). For finite bond lengths, it is advisable to allow the AOs to polarize and deform in response to the presence of the other electron (and the other nucleus). However, the \( |1s_a\rangle \) and \( |1s_b\rangle \) functions do not have to be exactly the hydrogenic eigenfunctions. It is sufficient to require them to be similar to the 1s orbitals and be centered on them. Since the actual shape of the orbitals is not yet fixed, we will give all the expressions in abstract matrix form, leaving the spatial integration for once the shape of the orbitals has been specified. This is the method of linear combination of atomic orbitals (LCAO).

11.1.4 Molecular orbital theory

We are now in a position to discuss the basic principles of the molecular orbital method (MO), which is the basis of the theory of the electronic structure of real molecules. The first step in any MO approach is to separate the Hamiltonian into two parts, one part describing the electrons '1' and '2' separately and one part counting for the interaction between them:

\[
\hat{H} = \hat{h}(1) + \hat{h}(2) + \hat{V}_{12} + \frac{e^2}{4\pi \varepsilon_0 \frac{1}{R_{ab}}}
\]

with

\[
\hat{h}(i) = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{|r_i - R_a|} + \frac{1}{|r_i - R_b|} \right)
\]

and

\[
\hat{V}_{12} = \frac{e^2}{4\pi \varepsilon_0 \frac{1}{r_{12}}}
\]

where \( i = 1, 2 \). We must remember that, within the BO approximation, \( R_{ab} \) is just a number. We choose the Hamiltonian \( \hat{h}(i) \) as the one-electron part of the complete Hamiltonian in matrix representation on the minimum basis:

\[
\begin{pmatrix}
\langle 1s_a | \hat{h} | 1s_a \rangle & \langle 1s_a | \hat{h} | 1s_b \rangle \\
\langle 1s_b | \hat{h} | 1s_a \rangle & \langle 1s_b | \hat{h} | 1s_b \rangle
\end{pmatrix} = \begin{pmatrix}
\epsilon & h_{ab} \\
h_{ab} & \epsilon
\end{pmatrix}
\]

(11.10)
defining the average one-electron energy \( \epsilon \equiv \langle 1s_a | \hat{H} | 1s_a \rangle \) and the non-diagonal coupling (often called *resonance integral*) \( h_{ab} \equiv \langle 1s_a | \hat{H} | 1s_b \rangle = \langle 1s_b | \hat{H} | 1s_a \rangle \). We can immediately diagonalize this matrix, the eigenvalues and the eigenvalues being:

\[
\epsilon_{\pm} = \epsilon \pm h_{ab} \quad \text{and} \quad |\phi_{\pm}\rangle \propto \frac{1}{\sqrt{2}} (|1s_a\rangle \pm |1s_b\rangle) .
\]

The one-electron effective Hamiltonian eigenstates are called *molecular orbital* (MO). They are one-electron wavefunctions delocalized over the spatial regions of the molecule.

![Figure 11.6: Illustration of the atomic orbitals.](image)

We need to first normalize the MOs, which is more complicated than it might seem, because the AOs are not orthogonal. For example, when the atoms approach each other, their AOs may have the shape shown in Fig. 11.6. However, by defining the overlap integral by

\[
S \equiv \langle 1s_a | 1s_b \rangle ,
\]

we can normalize as follows:

\[
|\phi_{\pm}\rangle = \frac{1}{\sqrt{2(1 \pm S)}} \left( |1s_a\rangle \pm |1s_b\rangle \right) ,
\]

since,

\[
\langle \phi_{\pm}|\phi_{\pm}\rangle = \frac{1}{2(1 \pm S)} \left( \langle 1s_a|1s_a\rangle \pm \langle 1s_a|1s_b\rangle \pm \langle 1s_b|1s_a\rangle + \langle 1s_b|1s_b\rangle \right) = 1 .
\]

These eigenfunctions merely show the symmetry of the molecule. The two hydrogen atoms are equivalent and, therefore, the eigenorbital must give equal weight to each \(1s\) orbital. Thus, our choice of the one-electron Hamiltonian does not really matter that much, because every one-electron Hamiltonian exhibiting the symmetry of the molecule would give the same molecular orbitals. For historical reasons, \(|\phi_{+}\rangle\) is denoted by \(|\sigma\rangle\) and \(|\phi_{-}\rangle\) by \(|\sigma^*\rangle\).

The second step in MO theory consists of constructing the determinant from the MOs corresponding to the wanted states. For illustration we will look at the lowest singlet state constructed from molecular orbitals. We note that \(h_{ab} < 0\), such that \(|\sigma\rangle\) has an energy inferior to \(|\sigma^*\rangle\). Neglecting the interaction, the lowest singlet state,

\[
|\Phi_{MO}\rangle = |\sigma\rangle|\sigma^*\rangle ,
\]

is the molecular ground state of \(H_2\). To estimate the validity of the approximation, we calculate the expectation value of the energy, \(\langle \sigma| \langle \sigma^*| \hat{H} | \sigma \rangle |\sigma^*\rangle\), decomposing the wavefunction into spin and spatial parts, noting that the spin part is normalized:

\[
\left| \langle \sigma| \langle \sigma^*| \hat{H} | \sigma \rangle |\sigma^*\rangle\right| = \langle \sigma(1)|\langle \sigma(2)| \hat{H} | \sigma(1) \rangle |\sigma(2)\rangle \langle \Phi_{\text{spin}}| \Phi_{\text{spin}} \rangle
\]

\[
= \langle \sigma(1)|\langle \sigma(2)| \hat{H} | \sigma(1) \rangle |\sigma(2)\rangle .
\]
Hence, with (11.10) we get,

\[ \langle \sigma(1) | (\sigma(2) | \hat{h}(2) | \sigma(1)) | \sigma(2) \rangle = \langle \sigma(1) | \sigma(1) \rangle \langle \sigma(2) | h(2) | \sigma(2) \rangle = \langle \sigma(2) | h(2) | \sigma(2) \rangle \equiv \epsilon_\sigma \]
\[ \langle \sigma(1) | (\sigma(2) | \hat{h}(1) | \sigma(1)) | \sigma(2) \rangle = \langle \sigma(1) | h(1) | \sigma(1) \rangle \langle \sigma(2) | \sigma(2) \rangle = \langle \sigma(1) | h(1) | \sigma(1) \rangle \equiv \epsilon_\sigma \]
\[ \langle \sigma(1) | (\sigma(2) | \hat{V}_{12} | \sigma(1)) | \sigma(2) \rangle \equiv J_{\sigma\sigma} . \]

Putting these facts together, we can write,

\[ \langle \Phi_{MO} | \hat{H} | \Phi_{MO} \rangle = \langle \Phi_{MO} | \hat{h}_1 | \Phi_{MO} \rangle + \langle \Phi_{MO} | \hat{h}_2 | \Phi_{MO} \rangle + \langle \Phi_{MO} | \hat{V}_{12} | \Phi_{MO} \rangle + \frac{e^2}{4\pi\varepsilon_0 R_{ab}} \]
\[ = 2\epsilon_\sigma + J_{\sigma\sigma} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}} . \]

Each of the first two terms represents the energy of a single electron (either 1 or 2) in the field produced by both the nuclei (\( \hat{h} \)), while the third is the average repulsion between the two electrons. Note that the first and second term are both positive, such that the bond must come from the one-electron part. This is the MO energy for the ground state of the \( H_2 \). We can try a more reasonable ansatz for the 1s-type basis functions \(^3\) by determining the unknown quantities from above (\( \epsilon_\sigma \) and \( J_{\sigma\sigma} \)) numerically and plot the total energy as a function of \( R_{ab} \) (blue dotted curve in Fig. 11.7). The exact adiabatic energy function determined from experimental data (solid black curve) agrees well at low energies. Summarizing the results with some key numbers, we note that MO theory predicts a bond distance of 0.072 nm in reasonable agreement with the exact value of 0.074 nm. We can also compare the

\(^3\)It turns out that it is more convenient to adjust the exponential decomposition of the hydrogenic orbitals to a sum of Gaussians.
11.1. MOLECULAR BINDING

binding energies,

\[ D_e = E_{H_2}(R_{\text{equil}}) - 2E_H . \]  

(11.18)

MOs theory predicts a binding energy of 5.0 eV compared to the experimental value of 4.75 eV. In view of the simplicity of the wavefunction and the absence of adjustable parameters the agreement is not so bad. Unfortunately, far away from the equilibrium distance, we have an unpleasant surprise: the molecule does not dissociate into two hydrogen atoms!

To get an idea of what is happening near dissociation, we expand the fundamental MO state in terms of AO configurations:

\[
|\Phi_{MO}\rangle \propto |\sigma(1)|\sigma(2)|\Phi_{spin}\rangle \\
= \frac{1}{2(1+S)}(|1s_a(1) + 1s_b(1)|1s_a(2) + 1s_b(2))|\Phi_{spin}\rangle \\
= \frac{1}{2(1+S)}(|1s_a(1)|1s_a(2) + 1s_a(1)|1s_b(2) + 1s_b(1)|1s_a(2) + 1s_b(1)|1s_b(2))|\Phi_{spin}\rangle .
\]

The two terms in the middle of the last line, called \textit{covalent configurations}, are exactly what we expect near dissociation: one electron in each hydrogen atom. However, the first and last term (which are called \textit{ionic configurations}) correspond to having two electrons in one atom and none in the other, which gives us $H^+$ and $H^-$ at dissociation! Since the weight of these terms is fixed, it is obvious that we got the wrong wavefunction (and therefore the wrong energy) when dissociating the molecule. Near the equilibrium point, the ionic terms contribute significantly to the true wavefunction, such that the MO theory is good at this point. But it is always terrible at dissociation.
11.1.5 Valence binding

An alternative to MO theory represents the valence bond theory (VB). Here, we use significantly more physical intuition and discard the ionic configurations from the MO wavefunction. Thus, the VB ground state wavefunction is:

\[
|\Psi\rangle \propto \frac{|1s_a(1)|1s_a(2) + |1s_b(1)|1s_a(2) \rangle |\uparrow(1)|\downarrow(2) + |\downarrow(1)|\uparrow(2)\rangle}{\sqrt{2}}
\]

\[
\equiv |\Psi_{space}\rangle|\Psi_{spin}\rangle.
\] (11.20)

VB theory assumes that this wavefunction is a good approximation to the true wavefunction at all binding distances and not only at large distances \(R_{ab}\). To verify this approximation, we can calculate the average energy for this VB state. First, we normalize the VB wavefunction,

\[
\langle \Psi | \Psi \rangle = \langle \Psi_{space}|\langle \Psi_{spin}| \Psi_{space}\rangle|\Psi_{spin}\rangle = \langle \Psi_{space}|\Psi_{space}\rangle
\]

\[
= \frac{1}{2} \left( (|1s_a(1)|1s_b(2)) + (|1s_b(1)|1s_a(2)) \right) \left( (|1s_a(1)|1s_a(2)) + (|1s_b(1)|1s_a(2)) \right)
\]

\[
= \frac{1}{2} \left( (|1s_a(1)|1s_b(2)) + (1s_b(1)|1s_a(2)) + (1s_a(1)|1s_b(2)) + (1s_b(1)|1s_a(2)) \right)
\]

\[
+ (1s_b(1)|1s_a(2)) (|1s_a(1)|1s_b(2)) + (1s_b(1)|1s_a(2)) (1s_b(1)|1s_a(2))
\]

\[
= \frac{1}{2} (1 + S^2 + S^2 + 1) = 1 + S^2 .
\] (11.21)

Therefore, the correctly normalized VB wavefunction is:

\[
|\Psi_{VB}\rangle = \frac{1}{2\sqrt{1 + S^2}} \left( |1s_a(1)|1s_a(2) \rangle + |1s_b(1)|1s_a(2)\rangle \right) \left( |\uparrow(1)|\downarrow(2)\rangle - |\downarrow(1)|\uparrow(2)\rangle \right).
\] (11.22)

Now we want to calculate \(\langle \hat{H}_{el}\rangle\) for this state. We note that the spin part does not matter, since the Hamiltonian is independent of spin:

\[
\langle \Psi_{VB}|\hat{H}|\Psi_{VB}\rangle = \langle \Psi_{spin}|\langle \Psi_{space}| \hat{H}| \Psi_{space}\rangle|\Psi_{spin}\rangle
\]

\[
= \langle \Psi_{space}|\hat{H}| \Psi_{space}\rangle \langle \Psi_{spin}|\Psi_{spin}\rangle = \langle \Psi_{space}|\hat{H}| \Psi_{space}\rangle
\] (11.23)

The only remnant of the spin state is the fact that the spatial wavefunction is symmetric, which is only possible when the spin part is antisymmetric. Treating each term in \(\langle \hat{H}\rangle\) separately,

\[
\langle \Psi|\hat{h}_1|\Psi\rangle = \frac{1}{2} \left( (|1s_a(1)|1s_b(2)) + (1s_b(1)|1s_a(2)) \right) \hat{h}_1 \left( (|1s_a(1)|1s_a(2)) + |1s_b(1)|1s_a(2)) \right)
\]

\[
= \frac{1}{2} \left( (|1s_a(1)|1s_b(2)) \hat{h}_1 |1s_a(1)|1s_b(2)\rangle + (1s_b(1)|1s_b(2)) \hat{h}_1 |1s_b(1)|1s_a(2)\rangle
\]

\[
+ (1s_b(1)|1s_a(2)) \hat{h}_1 |1s_a(1)|1s_b(2)\rangle + (1s_b(1)|1s_a(2)) \hat{h}_1 |1s_b(1)|1s_a(2)\rangle \right)
\]

\[
= \frac{1}{2} (e + Sh_{ab} + e + Sh_{ab}) ,
\] (11.24)

or,

\[
\langle \Psi_{VB}|\hat{h}_1|\Psi_{VB}\rangle = \frac{e + Sh_{ab}}{1 + S^2}.
\] (11.25)
Since the two electrons are identical, the elements of the $\hat{h}_2$ are the same as those of $\hat{h}_1$. The only remaining term is the average value of the interaction:

$$
\langle \Psi | \hat{V}_{12} | \Psi \rangle = \frac{1}{2} \left( \langle 1s_a(1)|s_b(2) \rangle + \langle 1s_b(1)|s_a(2) \rangle \right) \hat{V}_{12} \left( \langle 1s_a(1)|1s_a(2) \rangle + |1s_b(1)|1s_b(2) \rangle \right)
$$

$$
= \frac{1}{2} \left( \langle 1s_a(1)|1s_b(2) \rangle \hat{V}_{12} |1s_a(1)\rangle |s_b(2) \rangle + \langle 1s_a(1)|1s_b(2) \rangle \hat{V}_{12} |1s_b(1)\rangle |s_a(2) \rangle \\
+ \langle 1s_b(1)|1s_a(2) \rangle \hat{V}_{12} |1s_a(1)\rangle |s_b(2) \rangle + \langle 1s_b(1)|1s_a(2) \rangle \hat{V}_{12} |1s_b(1)\rangle |s_a(2) \rangle \right)
$$

The second and third terms are the same. They are called exchange integrals, because the 'bra' orbitals have switched order as compared to the 'kets':

$$
K = \langle 1s_a(1)|1s_b(2) \rangle \hat{V}_{12} |1s_a(1)\rangle |s_b(2) \rangle = \langle 1s_b(1)|1s_a(2) \rangle \hat{V}_{12} |1s_b(1)\rangle |s_a(2) \rangle .
$$

The first and forth terms are also the same. They are called Coulomb integrals, because they seem to be due to the Coulomb interaction between two charge densities:

$$
J = \langle 1s_b(1)|1s_a(2) \rangle \hat{V}_{12} |1s_a(1)\rangle |s_b(2) \rangle = \langle 1s_a(1)|1s_b(2) \rangle \hat{V}_{12} |1s_b(1)\rangle |s_a(2) \rangle .
$$

Therefore, we have the result,

$$
\langle \Psi_{VB} | \hat{V}_{12} | \Psi_{VB} \rangle = \frac{J + K}{1 + S^2} .
$$

Adding all terms, we get:

$$
\langle \Psi_{VB} | \hat{H} | \Psi_{VB} \rangle = \langle \Psi_{VB} | \hat{h}_1 | \Psi_{VB} \rangle + \langle \Psi_{VB} | \hat{h}_2 | \Psi_{VB} \rangle + \langle \Psi_{VB} | \hat{V}_{12} | \Psi_{VB} \rangle + \frac{1}{R_{ab}}
$$

$$
= 2 \epsilon + S h_{ab} + \frac{J + K}{1 + S^2} + \frac{1}{R_{ab}} .
$$

The Coulomb and exchange terms are positive. Nuclear repulsion is clearly positive. Thus, the only terms that lead to binding in this picture are the average energy of an electron $\epsilon$ and the resonance integral $h_{ab}$. If the first term is dominant, the bond is due to electronic delocalization, since an electron located near one of the atoms would only contribute the atomic value to $\epsilon$, which does not imply a bound state. If $h_{ab}$ is large, the bond involves some resonance character, which can be related to the familiar concept of resonance between different Lewis point structures.

A numerical evaluation of all integrals gives the potential curve presented in Fig. 11.7 for VB theory. As expected, this simple VB wavefunction gives the correct dissociation threshold, where MO theory fails. In addition, the accuracy of the simple VB result is surprisingly good even near the equilibrium distance: The VB predicts a bond distance of 0.071 nm (compared to the correct value of 0.074 nm) and $D_\epsilon = 5.2$ eV (compared to 4.75 eV). Thus, the VB wavefunction also gives a good agreement without adjustable parameters. But more importantly, it indicates a way of improving the wavefunction whenever we encounter an obvious error: in this case, we saw that the description of the dissociation was weak, and we constructed a VB ansatz curing the problem. This approach to VB is often generalized as follows.
when dealing with polyatomic molecules. We write the wavefunction as a product of a spatial part and a spin:
\[ |\Psi\rangle = |\Psi_{\text{space}}\rangle |\Psi_{\text{spin}}\rangle. \] (11.31)

The main assumption in VB theory is that the spatial part can be well represented by a product of atomic-like functions. For example, for water, we would immediately write a spatial part as:
\[ |\Psi_{\text{space}}\rangle \approx |1s_Ha\rangle |1s_Hb\rangle |1s_O\rangle |2s_O\rangle |2p_xO\rangle |2p_yO\rangle |2p_zO\rangle. \] (11.32)

However, there are two things wrong with this wavefunction. First, we know that atomic orbitals hybridize in a molecule. Therefore, we need to make appropriate linear combinations of AOs (in this case \(sp^3\) hybrids) to obtain the hybridized AOs. In this case, the four \(sp^3\) hybrids can be written symbolically as:
\[ |sp^3\rangle = c_{s,i} |2s\rangle + c_{x,i} |2p_x\rangle + c_{y,i} |2p_y\rangle + c_{z,i} |2p_z\rangle. \] (11.33)

and therefore, a more appropriate spatial configuration is:
\[ |\Psi_{\text{space}}\rangle \approx |1s_Ha\rangle |1s_Hb\rangle |1s_O\rangle |2s_O\rangle |sp^3_{1O}\rangle |sp^3_{1O}\rangle |sp^3_{2O}\rangle |sp^3_{2O}\rangle |sp^3_{3O}\rangle |sp^3_{4O}\rangle. \] (11.34)

The other problem with this state is that it lacks the adequate symmetry to describe fermions; the general state must be antisymmetric. In the case of two electrons this concept is easy to apply - singlets have symmetric space parts and triplets antisymmetric ones. However, in the case of many electrons, the rules are not so simple; in fact, the time of numerical computation grows exponentially with the number of electrons.

Formally, we will leave the derivation at this point to defining an operator \(A\) which ‘antisymmetrizes’ the wavefunction. In this case,
\[ |\Psi_{\text{space}}\rangle \approx A \left[ |1s_Ha\rangle |1s_Hb\rangle |1s_O\rangle |2s_O\rangle |sp^3_{1O}\rangle |sp^3_{1O}\rangle |sp^3_{2O}\rangle |sp^3_{2O}\rangle |sp^3_{3O}\rangle |sp^3_{4O}\rangle \right]. \] (11.35)

In general, the results of VB theory are very accurate for small systems, where it can be applied. The predicted bond lengths are rather short, and the binding energies tend to be too small, but the results are nevertheless qualitatively excellent. In addition, the correct hybridized atomic orbitals fall directly off the calculation, giving a good qualitative insight. Also, note that the atomic configurations should not change (or very little) when the geometry of the molecule changes (since the orbitals depend on the atom and not on the molecular structure). Therefore, these VB wavefunctions have a strong connection to the diabatic states discussed above. However, the exponential amount of time that one must invest to perform these calculations makes them impractical for most molecules of interest.

11.1.6 Exercises

11.1.6.1 Ex: Classical model of the covalent binding

Consider the molecule \(H_2^+\) with the two nuclei separated by 1 nm and an electron located in the middle between the nuclei. Calculate the electrostatic force acting on the nuclei.
11.1.6.2 Ex: Beyond the Born-Oppenheimer approximation for molecules

For molecules, the Born-Oppenheimer approximation may fail in some situations. Therefore, it is common to use another approach known as Born-Huang. To illustrate this approach, we consider a diatomic molecule in the laboratory frame.

a. Write down the many-body Hamiltonian of the molecule in atomic units.

\[ -\frac{\nabla_R^2}{2\mu_{AB}} - \sum_{i,j} \frac{1}{2M} \nabla_i \nabla_j - \sum_i \frac{\nabla_i^2}{2} + V \]

where that the coulombian interactions are included in the fifth term. Write down the time-independent Schrödinger equation for this molecule.

c. The Born-Huang approximation consists in assuming that the total wavefunction can be expanded on a basis of wavefunctions of the nuclei and the electrons, that is,

\[ \Psi(r, R) = \sum_k |\chi_k(R)\rangle |\phi_k(r, R)\rangle, \]

where \( \chi \) and \( \phi \) are the wavefunctions of the nuclei and the electrons, respectively. For the Schrödinger equation calculated in the previous item, use the Born-Huang approximation and obtain the set of coupled equations

\[
\left\{ \begin{aligned}
\sum_k \left[ -\frac{1}{2\mu_{AB}} \left( \nabla_R^2 \phi_k + \langle \phi_k | \nabla_R^2 | \phi_k \rangle + 2 \langle \phi_k | \nabla_R | \phi_k \rangle, \nabla_R \right) \right] - \\
\sum_k \left[ \frac{1}{2M} \left( \sum_{i,j} \langle \phi_i | \nabla_i \cdot \nabla_j | \phi_k \rangle \right) + \frac{1}{2} \sum_i \langle \phi_i | \nabla_i^2 | \phi_k \rangle - \langle \phi_i | V | \phi_k \rangle \right] \end{aligned} \right\} |\chi_k\rangle = E \sum_k |\chi_k\rangle
\]

which includes, although approximately, the kinetic energy of nuclei and electrons. **Help:** Use \( \nabla^2(\alpha\beta) = \alpha \nabla^2 \beta + \beta \nabla^2 \alpha + 2 \nabla \alpha \cdot \nabla \beta \).

d. Make a brief comparison between the Born-Huang approximation (and the coupled equations obtained in the previous equation) and the Born-Oppenheimer approximation.

11.1.6.3 Ex: Classical model of the covalent bond

Calculate the energies of the ground state and the last bound state of the potential \( V_n = -\frac{C}{r^n} \) for any \( n \).

11.1.6.4 Ex: Homonuclear collision

We consider the example of homonuclear collisions of \(^{85}\text{Rb}\) atoms. For ground state collisions in the channel \(^3\Sigma^+_2\), \(|f = 2, m_f = -2\rangle\), the long-range part of the potential is fixed by \( C_6 = 4550, C_8 = 550600, \) and \( C_{10} = 7.67 \times 10^7 [294, 509] \), where \( R_m = 9.8a_B, D_m = 0.13, \) and \( E_m = 1/2.5a_B \). The potentials can be merged at a given distance \( R_t = 27.6a_B \). Prepare a plot of potential.
11.2 Rovibrational structure of molecular potentials

The separation of the motion of the nuclei from the electronic dynamics made in the Born-Oppenheimer approximation led to equations (11.6) and (11.7). In a preceding section we analyzed in detail the equation (11.6) with the objective of understanding the phenomenon of molecular binding.

In the following section we will analyze the equation (11.7), which determines the motion of the nuclei. By separating the radii and angular parts of the motion, we will discover vibrational and rotational states.

11.2.1 The radial and angular equations

The interaction between two identical atoms is described by the following Hamiltonian, where $M_r = (M_a^{-1} + M_b^{-1})^{-1} = M/2$ is the reduced mass of the nuclei,

$$\hat{H} = \frac{\mathbf{P}^2}{2M_r} + V_{mol}(R) \quad \text{with} \quad V_{mol}(R) = \frac{e^2}{4\pi\epsilon_0 R} + V_{BO}(R).$$  \hspace{1cm} (11.36)

The interaction potential $V_{mol}$ is composed of a repulsive internuclear Coulomb force and a Born-Oppenheimer adiabatic potential due to the interaction of the electrons with each other and with the two nuclei. The kinetic energy is that of the relative motion (the center-of-mass motion has already been separated in Sec. 11.1.2, such that this inertial system is free of translational kinetic energy). In spherical coordinates,

$$\frac{\mathbf{P}^2}{2M_r} \phi(R) = -\frac{\hbar^2}{2M_r} \left[ \frac{1}{R} \frac{\partial}{\partial R} [R \phi(R)] + \frac{1}{R^2} \hat{L}^2 \phi(R) \right].$$  \hspace{1cm} (11.37)

The wavefunction can be separated into an angular part and a radial part, $\phi(R) = R_y(R)v_m(\theta, \phi)$. The angular part, which was discussed in Sec. 3.1.3, describes a rigid rotation of the homonuclear atoms around their center-of-mass with the rotation energy,

$$V_\ell(R) = \frac{\mathbf{L}^2}{2M_r R^2} = \frac{\hbar^2 \ell(\ell + 1)}{2M_r R^2},$$  \hspace{1cm} (11.38)

also called centrifugal barrier. The radial part is ruled by,

$$\left[ -\frac{\hbar^2}{2M_r} \frac{\partial^2}{\partial R^2} + V_\ell(R) + V_{BO}(R) \right] u_v(R) = E u_v(R),$$  \hspace{1cm} (11.39)

where $u_v(R) = rR_y(R)$ is the radial wavefunction of nuclear motion. The interatomic potential causes a motion of vibration. The vibrational states of the adiabatic potential are quantized and characterized by a well-defined vibrational energy. We will discuss the ro-vibrational structure in the following sections.

\footnote{We note here that at great distances other forces called \textit{van der Waals forces} dominate the interatomic interaction. These will be discussed in Sec. 11.3.}
11.2. ROVIBRATIONAL STRUCTURE OF MOLECULAR POTENTIALS

11.2.1.1 Rotational and vibrational bands

Molecules have much more degrees of freedom than atoms. For example, the atoms of a molecular dimer may vibrate inside the mutual interaction potential. In the center-of-mass system we can imagine these vibrations as oscillations of an atom with reduced mass and quantized energy. The molecule can rotate and have a momentum of inertia. These degrees of freedom contribute energies to the molecule’s Hamiltonian, either directly or through interactions with other degrees of freedom. Therefore, molecular spectra are characterized by a much greater complexity.

Figure 11.9: Molecular energy scales.

However, the energy regimes of the strongest excitations are quite different. A typical range for binding energies (depth of the interatomic potential) is $\Delta E_p \simeq 20..200$ THz (0.1..1 eV). Electronic excitations occur in the regime $\Delta E_e \simeq 100..1000$ THz (1..10 eV). The spacing between vibrational excitations typically is $E_{v+1} - E_v \simeq$ THz (0.01 eV). Finally, the rotational excitations are on the scale of $E_{\ell+1} - E_\ell \simeq 100$ MHz ($10^{-6}$ eV). Since at room temperature (a gas of molecules in thermal equilibrium at $T = 300$ K) the energy is on a scale of $2.5 \times 10^{-2}$ eV, the degree of freedom of the electronic excitation is frozen, while a wide distribution of vibrational and rotational states can be excited (e.g. by intermolecular collisions). The large difference of scales facilitates their separation and, therefore, the identification of the origin of the observed states in experimental measurements.

11.2.2 Vibrational molecular states

The potential energy of a molecule grows when the nuclei are displaced from their equilibrium positions. When the displacement, $x \equiv R - R_e$ is small, we can expand the potential energy,

$$V_{mol}(x) = V_{mol}(0) + \frac{dV_{mol}(0)}{dx} x + \frac{1}{2} \frac{d^2 V_{mol}(0)}{dx^2} x^2 + \ldots$$  \hfill (11.40)

5 Electronically excited states (that is, one of the valence electrons moves to an excited orbital) are more weakly bound, because the electrons are not in the most binding orbital.
The equilibrium energy is not of interest here, and the first derivative disappears in equilibrium. Therefore,

\[ V_{\text{mol}}(x) \simeq \frac{1}{2} k^2 x^2 \quad \text{with} \quad k \equiv \frac{d^2 V_{\text{mol}}(0)}{dx^2}. \]  

(11.41)

Using the effective mass we can write the Hamiltonian,

\[ \hat{H}_{\text{mol}} = -\frac{\hbar^2}{2m_1} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m_2} \frac{d^2}{dx_2^2} + \frac{1}{2} k x^2 = -\frac{\hbar^2}{2M_r} \frac{d^2}{dx^2} + \frac{1}{2} k x^2. \]  

(11.42)

The energy spectrum of this degree of freedom, therefore, is

\[ E_v = \hbar \omega (v + \frac{1}{2}). \]  

(11.43)

with \( \omega = \sqrt{k/M_r} \). That is, at the bottom of deep potentials, the energy levels are equidistant.

![Energy vs R/Re](image)

Figure 11.10: Many potentials are approximately harmonic at the center such as, for instance, the Morse potential (blue). The red curve shows the approximate harmonic potential.

### 11.2.2.1 Anharmonic vibrations in the Morse potential

For larger displacements we can no longer despise the anharmonic terms in the Taylor expansion. A better approximation is the Morse potential. This potential (blue in Fig. 11.10), unlike the harmonic potential (red in Fig. 11.10), is characterized by an asymptote for large interatomic distances. Therefore, it is often used as an analytical approximation to molecular potentials,

\[ V_{\text{morse}} = D_e \left(1 - e^{-a(R-R_e)}\right)^2, \]  

(11.44)

where \( r \) is the interatomic distance, \( r_e \) the equilibrium bond distance, \( D_e \) the depth of the potential measuring from the dissociation limit, and \( a \) a parameter controlling the range of the potential. At the bottom of the potential we can make the harmonic approximation, \( V_{\text{morse}}(R) \simeq \frac{k}{2} (R - R_e)^2 \) with \( k = 2a^2D_e \). Rewriting the potential in the form,

\[ \tilde{V}(R) \equiv V(R) - D_e = D_e \left(e^{-2a(R-R_e)} - 2e^{-a(R-R_e)}\right), \]  

(11.45)

we see, that it is a combination of a short-range repulsive potential and long-range attractive potential (similar to the Lennard-Jones’s potential).
The calculation of the energy spectrum of this potential is more difficult [132],

\[ E_v = \hbar \omega (v + 1/2) - \hbar \omega \chi_e (v + 1/2)^2 - D_e, \]  

(11.46)

with \( \omega \chi_e \equiv \frac{\hbar a^2}{2M_r} \) and \( \omega \equiv \sqrt{\frac{k}{M_r}} \), but the availability of an analytical expression is interesting for the calibration of numerical methods. The second term of the expression (11.46), which is proportional to the anharmonicity constant \( \chi_e \), becomes dominant at high excitations. The potential is finite with a dissociation energy of,

\[ D_0 = D_e - E_0. \]  

(11.47)

The number of vibrational states is limited \( v = 0, 1, \ldots, v_{\text{max}} \). With \( E < 0 \), we find,

\[ v_{\text{max}} < \frac{1}{2} - \frac{1}{2}. \]  

(11.48)

**Example 45 (Morse potential):** To solve the Schrödinger equation

\[ \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + V(R) \right) \Psi_R(v) = E_v \Psi(v), \]

it is convenient to introduce new variables,

\[ x = aR, \quad \lambda = \frac{\sqrt{2mD_e}}{\hbar}, \quad \varepsilon_v = \frac{2m}{a^2 \hbar^2} E_v, \]

such that,

\[ \left( -\frac{\partial^2}{\partial x^2} + V(x) \right) \Psi_n(x) = \varepsilon_n \Psi_n(x) \quad \text{with} \quad V(x) = \lambda^2 \left( e^{-2(x-x_e)} - 2e^{-(x-x_e)} \right). \]

The eigenvalues and eigenfunctions are [132]:

\[ \varepsilon_n = 1 - \frac{1}{x^2} \left( \lambda - n - \frac{1}{2} \right)^2 = \frac{2}{\lambda} (n+\frac{1}{2})^2 - \frac{1}{\lambda^2} (n+\frac{1}{2})^2 \quad \text{and} \quad \Psi_n(z) = N_n z^{\lambda-n-rac{1}{2}} e^{\lambda-z} L_n^{(2\lambda-2n-1)}(z), \]

where \( z = 2\lambda e^{-(x-x_e)} \) e \( N_n = \left[ \frac{n!(2\lambda-2n-1)!}{\Gamma(2\lambda-n)} \right]^{\frac{1}{2}} \) and,

\[ L_n^{(\alpha)}(z) = \frac{z^{-\alpha} e^{-\frac{z}{n}}}{n!} \frac{d}{dz} \left( z^n e^{-z} \right) = \frac{\Gamma(\alpha + n + 1) / \Gamma(\alpha + 1)}{\Gamma(n + 1)} 1_F(1, -n, \alpha + 1, z), \]

is the generalized Laguerre polynomial. The matrix elements of the spatial operator \( \hat{x} \) are (assuming \( m > n \) and \( N = \lambda - \frac{1}{2} \)),

\[ \langle \Psi_m | x | \Psi_n \rangle = \frac{2(-1)^{m-n+1}}{(m-n)(2N-n-m)} \left( \frac{N-n}{2} \right)^{N-n-m} \frac{[(N-n)(2N-n-m)!(2N-n-m+1)m!]}{\Gamma(2N-n+1)n!}. \]

In the original variables the eigenenergies are:

\[ E_v = \hbar \omega (v + 1/2) - \frac{[\hbar \omega (v + 1/2)]^2}{4D_e}, \]

where \( v \) is the vibrational quantum number and \( \omega = a \sqrt{\frac{2D_e}{m}} \). The energy difference between adjacent levels decreases with \( v \),

\[ E_{v+1} - E_v = \hbar \omega - (\hbar \omega) \frac{v+1}{2D_e}. \]
This fact describes well the vibrational structure of non-rotating molecules. However, the equation fails above some value of $v > v_{\text{max}}$, where $E_{v_{\text{max}}+1} - E_{v_{\text{max}}}$ is zero or negative,

$$v_{\text{max}} = \frac{2D_e - \hbar \omega}{\hbar \omega}.$$  

This failure is due to the finite number $v_{\text{max}}$ of bound states in the Morse potential. For energies above $v_{\text{max}}$ all energies are possible, and the equation for $E_v$ is no longer valid.

11.2.2.2 Vibrational selection rules

Electromagnetic fields of the type $E_1$, e.g., black body radiation, can induce transitions between vibrational states and redistribute their populations such as to establish a thermal equilibrium. However, as the stronger transitions are induced by dipole migrations of charges, we need to analyze in more detail the selection rules imposed on the dipole moment $\langle f|d|i \rangle$.

The states which are relevant for vibrational transitions are specified by $|\epsilon,v\rangle$, where $\epsilon$ denotes the electronic state of the molecule, since the vibrational spectrum depends on the electronic structure. The Born-Oppenheimer approximation allows us to consider the slow vibrations separately from the dynamics of the electrons. The time scale for electronic transitions is $1/\Delta E_e = 10^{-16}$ s$^{-1}$, and for a nuclear vibration it is $1/\Delta E_v = 10^{-13}$ s$^{-1}$. For each internuclear distance the electrons form an adapted stationary state, minimizing their energy for that distance. This is equivalent to the formation of an adiabatic interaction potential between the nuclei on which the nuclei can vibrate. To find out which vibrational transitions are possible, we need to calculate the matrix,

$$\langle \epsilon',v' | \hat{d} | \epsilon,v \rangle = \langle v'|\hat{d}_{\epsilon}|v \rangle .$$  \hspace{1cm} (11.49)$$

The dipole moment, $d_\epsilon = \langle \epsilon|\hat{d}|\epsilon \rangle$, of the molecule depends on the distance of the nuclei, since the electronic orbitals $|\epsilon\rangle$ depend on distance. Therefore, we can expand,

$$\hat{d} = \hat{d}_0 + \frac{d\hat{d}_0}{dx} \hat{x} + \frac{1}{2} \frac{d^2\hat{d}_0}{dx^2} \hat{x}^2 + .. .$$  \hspace{1cm} (11.50)$$

Therefore, the transition matrix is,

$$\langle \epsilon',v'|\hat{d}|\epsilon,v \rangle = \delta_{v,v'} \hat{d}_0 + \frac{d\hat{d}_0}{dx} \langle v'|\hat{x}|v \rangle + \frac{d^2\hat{d}_0}{dx^2} \langle v'|\hat{x}^2|v \rangle + .. .$$  \hspace{1cm} (11.51)$$

The first term disappears, that is, transitions can only occur, when the dipole moment varies with the distance. Therefore, homonuclear dimers do not undergo vibrational transitions.

For heteronuclear molecules with electronic charges that do not depend on the interatomic distance, the dipole moment varies linearly with small displacements. In this case, we only need the second term of the expansion. Within the harmonic approximation, the position operator can be expressed by, $\hat{x} \propto \hat{a} + \hat{a}^\dagger$. Therefore, only transitions $\Delta v = \pm 1$ are possible. However, due to anharmonicities, higher
order terms, \( \hat{x}^n \propto (\hat{a} + \hat{a}^\dagger)^n \) become influential, and transitions with \( \Delta v = \pm 2, \pm 3, \ldots \) become possible.

Thus, in anharmonic potentials, the vibrational selection rules are replaced by the concept the overlapping wavefunctions called \textit{Franck-Condon factor}.

Raman spectroscopy is a very useful tool to analyze ro-vibrational spectra. In this method, inelastic Raman scattering gives rise to Stokes and anti-Stokes lines in the spectrum at frequencies corresponding to \( \Delta v = \pm 1, \pm 2 \). The ground state spectrum is asymmetric, because of the absence of the lower state. In homonuclear dimers, the nuclear spins have a major impact on the Raman spectra. Parity considerations show that there can only be odd or even lines.

11.2.3 The Franck-Condon principle

The intensity of molecular transitions are, qualitatively, described by the \textit{Franck-Condon principle}, whose \textit{classical} formulation goes as follows:

\begin{quote}
\textit{The jump of an electron in a molecular transition occurs during a very small time compared to the time scale of the nuclear motion, so that immediately after the jump, the nuclei remain practically at the same positions and at the same velocities as before the jump [277].}
\end{quote}

For this reason, the transitions are drawn vertically in the scheme of potentials shown in Fig. 11.11(right). To yield considerable rates, transitions must occur when the nuclear velocities in the two coupled states are similar, which is the case at the classical turning points. At these points, the wavefunctions are maximal \(^6\).

![Figure 11.11](image)

Figure 11.11: (Left, code) Molecular wavefunctions in a potential for three different vibrational states. (Right) Pictorial representation of the classical statement of the Franck-Condon principle. Transition (a) has high intensity (or probability), because here both, the position and the relative velocity of the nuclei do not change. Transitions (b) and (c) are unlikely, because they necessitate either a change in the position of the nuclei (case b) or in velocity (case c).

\(^6\)Note that the presence of a hyperfine structure can modify the selection rules.
With this Franck-Condon principle, we can determine which are the strongest transitions between vibrational levels of a molecule, as represented in Fig. 11.11(left). In particular, we are interested in transitions between vibrational levels of different electronic states.

The exact transition probabilities are calculated via the square module of the transition dipole moment (TDM). The TDM is an out-of-diagonal matrix element of the electric dipole operator $\hat{M}$, given by:

$$M_{AB} = \langle \Psi(A) | \hat{M} | \Psi(B) \rangle ,$$

being $|\Psi(A)\rangle$ and $|\Psi(B)\rangle$ two molecular states.

Still within the Born-Oppenheimer approximation, we can split the dipole moment operator into two terms, a nuclear and an electronic term, according to:

$$\hat{M}(r,R) = \hat{M}_e(r,R) + \hat{M}_n(R) .$$

Thus, the TDM is:

$$M_{AB} = \int \psi_e^*(A) \psi_e^*(B) dR dr
\int \psi_e(A) \psi_e(B) dR dr
\int \psi_n^*(A) \psi_n^*(B) dR
\int \psi_n(A) \psi_n(B) dR .$$

Since the electronic wavefunctions of different states are orthogonal, it follows that $
\int \psi_e^*(A) \psi_e^*(B) dr = 0,$ canceling the second term.

Looking at the first term, we note that the electronic dipole moment $\hat{M}_e(r,R)$ also depends on the nuclear coordinates as a parameter. The quantum formulation of the Franck-Condon principle consists in stating that, in a molecular state, the electronic dipole moment varies little with the nuclear coordinates. Thus, along with the condition of the Born-Oppenheimer approximation, we can split the first TDM term into electronic and nuclear integrals:

$$M_{AB} = \int \hat{M}_e \psi_e^*(A) \psi_e(B) dR dr
\int \psi_e(A) \psi_e(B) dR
\int \psi_n^*(A) \psi_n(B) dR
\int \psi_n(A) \psi_n(B) dR .$$

Thus, we have a comparative expression for the transition probability given by:

$$P_{AB} \propto |M_{AB}|^2 = \left| \int \hat{M}_e \psi_e^*(A) \psi_e(B) dR \right|^2 \left| \int \psi_e(A) \psi_e(B) dR \right|^2 .$$

The second factor in equation (11.56) is called Franck-Condon factor. When we study the transitions between two electronic states, this factor compares the intensities of the transitions between distinct pairs of vibrational levels.

**Example 46 (Ultracold molecules):** Ultracold molecules have been proposed for a variety of applications, such as ultra high resolution spectroscopy [407], test of fundamental laws of physics [151, 536], quantum computation [150] and others[98]. Most of these applications, however, require that the molecular sample be in a single quantum state. This is an experimental challenge, since molecules have more degrees of freedom than atoms, such as rotation and
vibration.
To create a sample of molecules trapped in the ground state of vibration, a possible method is to first produce the molecules from ultracold atoms using a process called \textit{photo association}, and then pump these molecules to the vibrational ground state.

Photoassociation consists in the excitation of a pair of free atoms to the bound state of an excited electronic potential by the absorption of a photon. The pair then decays by spontaneous emission either back to the state of two free atoms (which is not desirable), or to a bound state of the fundamental electronic potential. For Rb\(_2\) molecules, photoassociation is efficient at certain frequencies [411], with the \(A^1\Sigma^+_u\) potential as the excited state (see Fig. 11.12).

Soon after being formed, the molecules are usually in levels of high vibrational energy (around \(\nu \approx 80\)), because these levels connect best (high Franck-Condon overlap) to the excited state. The transfer of population to the fundamental state of vibration is done by 'optical pumping'.

Vibrational cooling via optical pumping can be done by irradiating a broad frequency band of light that excites transitions to vibrational levels of the excited nuclear potential. These excited states are chosen such that their Franck-Condon overlap with the ground states of lower vibrational energy is larger. As a consequence, a molecule sent to an excited state returns with higher probability to a level of lower vibrational energy. The absorption and emission cycles are repeated, until the molecules reach the fundamental vibrational state.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11_12.png}
\caption{Photoassociation scheme to form Rb\(_2\) molecules. In process (a), a pair of free atoms absorbs a photon of the incident radiation, forming a bound state in the excited potential. Then, in (b), the newly formed molecule decays by spontaneous emission to a bound state of the fundamental potential, or it can return to a state of two free atoms.}
\end{figure}
11.2.4 Rotational progression

Until now we neglected the centrifugal energy (11.38),

\[ V_{\ell}(R) = \frac{L^2}{2M_rR^2} = \frac{\hbar^2\ell(\ell + 1)}{2M_rR^2} . \tag{11.57} \]

As we shall now see, this energy creates a substructure of the vibrational levels.

The moments of inertia in the three axes of space are,

\[ I_{qq} = \sum_i m_i r_i^2(q) . \tag{11.58} \]

The kinetic energy of the rotation is,

\[ E_{\text{rot}} = \frac{1}{2} \sum_{q=1,2,3} m_q v_q^2 = \frac{1}{2} \sum_{q=1,2,3} I_{qq} \omega_q^2 = \frac{L_x^2}{2I_{xx}} + \frac{L_y^2}{2I_{yy}} + \frac{L_z^2}{2I_{zz}} , \tag{11.59} \]

with the angular momentum \( L_q = I_{qq} \omega_q \).

Many molecules have a symmetry axis, such that there are two different moments of inertia, \( I_\perp \equiv I_{xx} = I_{yy} \) and \( I_\parallel \equiv I_{zz} \). Interpreting angular momenta as quantum operators,

\[ \hat{H} = \frac{\hat{L}_z^2}{2I_\perp} + \left( \frac{1}{2I_\parallel} - \frac{1}{2I_\perp} \right) \hat{L}_z^2 . \tag{11.60} \]

We must first consider the rotation of the molecule relative to the symmetry axis of the molecule. Forgetting external fields we calculate the energy of the molecule associated with the observables \( \hat{L}_z^2 \) with the quantum number \( \ell \) and \( \hat{L}_z \) with the quantum number \( K \). We find the eigenvalues,

\[ E(\ell, K, M_\ell) = \frac{\hbar^2\ell(\ell + 1)}{2I_\perp} + \left( \frac{1}{2I_\parallel} - \frac{1}{2I_\perp} \right) \hbar^2 K^2 = B\ell(\ell + 1) + (A - B)K^2 , \tag{11.61} \]

with \( \ell = 0, 1, \ldots, K = -\ell, \ldots, \ell \), and \( M_\ell = -\ell, \ldots, \ell \) and introducing the rotational constants, \( A \equiv \hbar^2/2I_\parallel \) and \( B \equiv \hbar^2/2I_\perp \). We then analyze this equation in the context of applying an external field that defines both, the direction \( \hat{e}'_z \) in the laboratory as well as the projection of the angular motion \( \hat{L}_z^2 \) on this direction, \( m_\ell \). That is, we have two axes, the internuclear axis \( \hat{e}_z \) and the rotation axis of the molecule \( \hat{e}'_z \).

Each level \( |\ell, m_\ell\rangle \) is \( 2(2\ell + 1) \) times degenerate, because \( K = -\ell, \ldots, \ell \) and \( K \) can be positive or negative. Each level \( \ell \) contains \( 2\ell + 1 \) states. Note that for spherical molecules, \( A = B \), and the degree of freedom \( K \) disappears. In Exc. 11.2.6.2 we calculate the rotational spectrum of a homonuclear diatomic molecule.

The rotational constant can be approximated by,

\[ E_{\text{rot}} = \frac{\hbar^2\ell(\ell + 1)}{2M_r\langle R^2 \rangle} , \tag{11.62} \]

where \( \sqrt{\langle R^2 \rangle} \) is the expectation value for the outer turning point of the vibrational level. As an example, the rotational constant for the vibrational state of \(^{87}\text{Rb}_2\) which is 5.9 cm\(^{-1}\) below the dissociation limit is \( B_v = \nu_{\text{rot}}^{\ell=1} - \nu_{\text{rot}}^{\ell=0} = 81 \) MHz. To be more precise, we would need to calculate \( \langle R^2 \rangle_v = \langle \psi_v | R^2 | \psi_v \rangle \).
Transitions between vibrational levels occur together with rotational transitions \( \Delta \ell = \pm 1 \). Therefore, the frequencies of transitions depend on the rotational constant \( B_v \), which depends on the vibrational state. The energies of the molecule are,

\[
E_{\nu, \ell} = \hbar \omega (v + 1/2) - \hbar \omega v (v + 1/2)^2 + \ldots + \hbar c B_v (\ell + 1) - \hbar c D_v (\ell + 1)^2 + \ldots .
\] (11.63)

Under the influence of a rapid rotation, the atoms of the molecule are subjected to centrifugal force and, hence, are further away from each other. Since at ambient temperatures many rotational levels are populated, we experimentally observe many lines known as \( P \)-branch, when \( \Delta \ell = -1 \), as \( Q \)-branch, when \( \Delta \ell = 0 \), and as \( R \)-branch, when \( \Delta \ell = 1 \). See Exc. 11.2.6.3.

### 11.2.4.1 Rotational selection rules

For transitions between electronic states, the selection rules are \( \Delta r = 0, \pm 1 \). Rotational transitions can occur between levels \( \Delta r = \pm 1 \). \( \Delta r = 0 \) is not allowed, because it violates the conservation of parity. Note also that the nuclear isotope influences the ro-vibrational levels via the reduced mass.

We consider a linear molecule in the state \( |\epsilon, \ell, M_{\ell}\rangle \), where \( \epsilon \) denotes the electronic and vibrational state of the molecule. To find out which transitions are possible, we need to calculate the matrix,

\[
\langle \ell', \ell', M_{\ell}' | d | \epsilon, \ell, M_{\ell}\rangle = \langle \ell', M_{\ell}' | d | \epsilon, \ell, M_{\ell}\rangle ,
\] (11.64)

with \( d = \langle \epsilon | d | \epsilon \rangle \). Here, we apply the Born-Oppenheimer approximation, which allows us to separate the dynamics of the electrons and also the vibrations of the molecule, because these movements are so fast, that they are always in a steady state, adiabatically following the slow movement of the rotation.

The selection rules can now be derived from the Wigner-Eckart theorem,

\[
\frac{\langle \ell', \ell, M_{\ell}' | d | \ell, M_{\ell}\rangle|^2}{\langle \ell' | d | \ell, M_{\ell}\rangle^2} = \frac{1}{2\ell' + 1} \left( \frac{\ell}{m_{\ell}} \begin{pmatrix} 1 & \ell' \\ \kappa & -m'_{\ell} \end{pmatrix} \right) .
\] (11.65)

We find \( \Delta \ell = 1 \) e \( \Delta M_{\ell} = 0, \pm 1 \). See Exc. 11.2.6.4.

### 11.2.5 Computation of vibrational states

#### 11.2.5.1 Localization energy

One consequence of Heisenberg’s uncertainty relation is that a certain localization energy is always required to localize a particle. As an example, we consider the attractive potential,

\[
V = -\frac{C}{R^{2\alpha}} .
\] (11.66)

The space available for the particle is limited between the classical turning point, which for a given energy is \( r_t = \left( \frac{C}{|E|} \right)^{1/\alpha} \). The momentum corresponding to this energy is \( k_t = \left( \frac{2m|E|}{\hbar^2} \right)^{1/2} \). Heisenberg’s uncertainty relation requires \( k_t r_t > 2 \), that

\[ \text{See [24], p.326} \]
is, at least half of the wavelength must fit within the potential (between 0 and \( r_t \)) at the height of the bound state. Therefore,

\[
|E|^{1-2/\alpha} > \frac{2\hbar^2}{mC^2/\alpha}.
\] (11.67)

For a Coulomb potential, with \( \alpha = 1 \) and \( C = e^2/4\pi\varepsilon_0 \), we obtain the energy of the ground state of the hydrogen atom,

\[
E > E_1 = -\frac{e^2}{4\pi\varepsilon_0 2a_B},
\] (11.68)

but there is no state higher than all others. That is, all energies \( E_n = E_1/n^2 \) exist.

For \( \alpha = 2 \), we do not get a condition for the energy. For the Casimir-Polder potential, \( \alpha = 3 \), we obtain,

\[
E < -\frac{8\hbar^6}{m^3C^2}.
\] (11.69)

This means that, in contrast to the Coulomb potential, the binding energy must be lower than a certain limit.

11.2.5.2 The LeRoy-Bernstein method

The LeRoy-Bernstein method allows us to estimate the highest bound levels. It only applies near the dissociation limit, where the semi-classical formula of quantization is valid,

\[
v + \frac{1}{2} = \sqrt{\frac{8M_v}{\hbar^2}} \int_0^{R_1} dR \sqrt{E(v) - V(R)}.
\] (11.70)

Inserting the potential

\[
V(R) = D_e - \frac{C}{R^n},
\] (11.71)

we get

\[
E(v^*) = D_e - \left( \frac{(n - 2)\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)}{2\Gamma\left(\frac{1}{2} + \frac{1}{n}\right)} (v^* + v_D) \right)^{\frac{2n}{n-2}} \left( \frac{\hbar^{2n}}{(2\pi M_v)^n C^2} \right)^{\frac{n-2}{n}},
\] (11.72)

where \( v^* \) is a number counting the vibrational levels from the top to the bottom starting at the dissociation limit.

11.2.5.3 Open channels

For a given interatomic potential \( V(R) \), neglecting the spin structure [327], the relative wavefunction of a two-atom system satisfies the Schrödinger equation,

\[
\left[ -\frac{1}{2\mu} \Delta + V(R) \right] \psi(R) = E\psi(R).
\] (11.73)

Separating the radial and angular contributions, \( \psi(R) \equiv Y(\vartheta, \phi)f(R)/R \), we obtain,

\[
\left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + V(R) + \frac{l(l + 1)}{2\mu R^2} \right] f(R) = Ef(R).
\] (11.74)
Figure 11.13: (code) Highest vibrational states obtained by the LeRoy-Bernstein method.

Now, we introduce the local wavevector, $k(R) = \sqrt{2\mu[E - V(R)] - l(l + 1)/R^2}$ and write,

$$f'' = -k^2 f .$$

This differential equation can be solved numerically [see Fig. 11.14(a)].

Figure 11.14: (code) (a) Numerical computation of the relative wavefunction for a low energy collision, $E \gtrsim 0$ and $\ell = 0$. The blue curve shows the interatomic Li-Rb potential (a)$^3\Sigma$, the red curve illustrates the relative Broglie wavefunction of the molecule. The asymptote of this extrapolated wavefunction (green curve) cuts the abscissa at $a_\text{s} = -120a_B$, which is just the scattering length for collisions in this channel. (b) Numerical computation of the wavefunction for a vibrational state. The potential is an interpolation (black) between a short-range Morse potential (green), and a long range potential (blue). The red curve illustrates the relative wavefunction for the ninth vibrational state (counting from ground state).

11.2.5.4 Bound states

For bound states, we must simultaneously satisfy the eigenvalue problem. We can, for example, guess an eigenvalue $E$, calculate the associated wavefunction $f(R)$, check whether it diverges for $R \rightarrow \infty$, and vary $E$ until $f(R)$ no longer diverges. Fig. 11.14(b) shows the wavefunction of a vibrational state obtained by solving the Schrödinger equation and adjusting the energy until the function stops diverging in the classically forbidden range.
11.2.5.5 The Fourier grid method

Another, extremely rapid, numerical method for determining the spectrum of vibrational states of a potential, is the Fourier grid method. It is based on the discretization of the Hamiltonian along the interatomic potential. We write the Hamiltonian as,

\[ H \psi(R) = [T(R) + V(R)]\psi(R) = E\psi(R) \]  

and put it in a matrix form using the set of functions of the basis \( \phi_i(R_j) = \delta(R_i - R_j) \) with \( i = 1, \ldots, N \), where \( R_i = R_0 + i(R_N - R_0)/N \). This problem has \( N \) eigenvalues \( E_i \).

The Fourier grid method now evaluates the kinetic energy at each point in the grid. We insert the local terms \( H_{ii} = H(R_i) \) and the non-local terms \( H_{ij} = H(R_i, R_j) \) into the Hamiltonian, as well as the potential energies \( V_{ij} = V(R_i) \delta_{ij} \). The kinetic energy is the inverse Fourier transform from momentum space of \( T_{rs} = T(k_r)\delta_{rs} = (k_r^2/2\mu)\delta_{rs} \) and becomes [177],

\[ H_{ij} = \frac{\pi^2}{4\mu(R_N - R_1)^2} (-1)^{i-j} \left( \frac{1}{\sin^2 \frac{\pi(i-j)}{2N}} - \frac{1}{\sin^2 \frac{\pi(i+j)}{2N}} \right) \text{ for } i \neq j \]  

\[ H_{ij} = \frac{\pi^2}{4\mu(R_N - R_1)^2} \left( \frac{2N^2 + 1}{3} - \frac{1}{\sin^2 \frac{\pi(i)}{2N}} \right) + V(R_i) \text{ for } i = j . \]

To improve the wavefunction, we can interpolate,

\[ \psi(q) = \sum_{j=1}^{n} \psi(q_j) \text{sinc} \frac{\pi(q - q_j)}{\Delta q} . \]  

The method can be extended to coupled channels \( \sigma = A, B \) via,

\[ H_{(i\sigma)(j\tau)} = T_{ij}\delta_{\sigma\tau} + V_{\sigma\tau}(R_i)\delta_{ij} . \]

The Hamiltonian has the general form,

\[ H = \begin{pmatrix} T & 0 \\ 0 & T \end{pmatrix} + \begin{pmatrix} V_A & 0 \\ 0 & V_B \end{pmatrix} + \begin{pmatrix} W_{AA} & W_{AB} \\ W_{BA} & W_{BB} \end{pmatrix} , \]

where all matrices \( V_k \) and \( W_k \) are diagonal \(^8\).

11.2.6 Exercises

11.2.6.1 Ex: Transitions between vibrational states

Calculate the dipole moment between two arbitrary vibrational states of (a) a harmonic potential and (b) a Morse potential.

11.2.6.2 Ex: Rotational spectrum of diatomic molecules

Calculate the rotational spectrum for a diatomic molecule from the result (11.59).

\(^8\)Note that the Fourier grid method can be improved by using a grid with spacings adjusted to the potential gradient [350, 597, 380].
11.2. ROVIBRATIONAL STRUCTURE OF MOLECULAR POTENTIALS

Figure 11.15: (code) Numerical computation of the wavefunction using the Fourier grid method at example of the interatomic potential Li-Rb (1)\(^1\)Π. (a) Short range Morse potential (green), long range (blue), interpolation (black) and \([352]\). (b) Vibrational wavefunctions, (c) external turning point (red) and center of mass (green), (d) rotational progression, and (e) Franck-Condon overlap with the tenth vibrational state.

11.2.6.3 Ex: Ro-vibrational spectrum

Determine the frequency spectra of ro-vibrational transitions for the branches \(P\), \(Q\), and \(R\).

11.2.6.4 Ex: Rotational spectrum

Determine the rules and the spectrum of rotational transitions for a spherical molecule.

11.2.6.5 Ex: The Fourier grid method

The Fast Fourier Transform (FFT) is defined by,

\[
H_n = \sum_{k=0}^{N-1} e^{-2\pi i nk/N} h_k
\]

\[=
\sum_{k=0}^{N-1} e^{-2\pi i k/(N/2)} h_{2k} + e^{-2\pi i k/N} \sum_{k=0}^{N/2-1} e^{-2\pi i k/(N/2)} h_{2k+1}
\]

\[=
\text{even} + \text{odd} .
\]

the inverse transform is,

\[
h_k = \frac{1}{N} \sum_{k=0}^{N-1} e^{2\pi i nk/N} H_n .
\]
The sinus transform of a real vector $s_k$ is,

$$S_n = \frac{2}{N} \sum_{k=1}^{N-1} s_k \sin \frac{\pi nk}{N} .$$

Calculate the inverse transform of the matrix $T_{rs} = k_r^2 \delta_{rs}$.

### 11.3 Van der Waals forces and spin coupling

The individual atoms have a complex substructure due to the angular momenta of the electronic motion, its spins and the nuclear spin. All of these angular momenta can interact, couple and generate new energy terms, which need to be taken into account when calculating the various potentials of interatomic interaction,

$$\hat{H} = \frac{P^2}{2M_r} + V_{\text{coulomb}}(R) + \sum_{k=1,2} \left( V_{hfs}^{(k)} + V_{\text{zeeman}}^{(k)} \right) + V_{\text{dipole,spin-spin}}(R) + V_{\text{dipole,spin-orbit}}(R) .$$

The Coulomb interaction for interacting alkaline gases can be expressed as:

$$V_{\text{coulomb}}(R) = V_{\text{coulomb}}^{S=0} P_{S=0} + V_{\text{coulomb}}^{S=1} P_{S=1} .$$

The projectors $P_{S=0,1}$ will be required to expand the Hilbert space for the degrees of freedom of the spins.

The **van der Waals forces** include all intermolecular forces. These are long-range forces that occur between permanent and induced atomic dipoles $\sim 1/r^6$.

#### 11.3.1 Analytical models for short and long-range potentials

In general, the potentials are estimated by ab initio Hartree-Fock calculations. A short-range potential, or *Morse potential*, can be approximated by,

$$V_{\text{morse}} = D_m \left( \left[ 1 - e^{-B_m (R - R_m)} \right]^2 - 1 \right) .$$

Here, $B_m$ is the width of the minimum, $R_m$ the position of the minimum, $D_m$ the length. A long-range potential can be written,

$$V_{\text{vdw}}(R) = D_e - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} .$$

$D_e$ is the energy of dissociation. The *van der Waals coefficients* $C_k$, which determine the potential shape at large distances, can be calculated using other methods with higher precision. To obtain a closed formula, the short and long range parts can be joined by,

$$V = V_{\text{morse}} F + V_{\text{vdw}} (1 - F) ,$$

where $F \equiv e^{-(R/R_i)^6}$.

---

9They also occur, in a pure form, in optical resonators such as in the **Casimir effect**. Since the lowest frequency in a cavity is $\omega = \sqrt{2\pi c/L}$, the zero point energies inside and outside the cavity are different. This causes an attractive force between the cavity mirrors $\sim 1/r^3, 1/r^4$. 
11.3. VAN DER WAALS FORCES AND SPIN COUPLING

The situation is different for collisions of identical atoms in excited states, which has a much larger range because of the resonant interaction between dipoles. In this case, an additional *Movre-Pichler potential* dominated by a coefficient $C_3$ arises,

$$V_{vdw}^e = V_{movre}^e + V_{dispersion}^e.$$  \hfill (11.86)

In contrast, excited state collisions of different species are purely short ranged.

11.3.2 Spin coupling in dimers, molecular quantum numbers

We consider two interacting alkaline atoms, each being described by a set of quantum numbers of internal angular momenta, they couple their spins:

$$l_i \quad \text{angular momentum of the individual atom} \quad (11.87)$$

$$s_i \quad \text{electronic spin}$$

$$i_i \quad \text{nuclear spin}$$

$$l_i + s_i = j_i \quad \text{total electronic angular momentum}$$

$$j_i + i_i = f_i \quad \text{total angular momentum}.$$  

When the atoms approach each other, at intermediate distances, they couple their spins:

$$\ell \perp \hat{e}_z \quad \text{molecular rotation} \quad (11.88)$$

$$\Lambda \equiv |M_L|\hat{e}_z \quad \text{projection of } L \text{ onto the interatomic } \hat{e}_z$$

$$\Sigma \equiv M_S\hat{e}_z \quad \text{projection of } S \text{ onto the interatomic } \hat{e}_z$$

$$\Omega \equiv \Lambda + \Sigma \quad \text{projection of } L + S \text{ onto the interatomic } \hat{e}_z.$$  

At short distances, they form a molecular dimer described by the quantum numbers:

$$L = l_1 + l_2 \quad \text{total electronic angular momentum} \quad (11.89)$$

$$S = s_1 + s_2 \quad \text{electronic spin}$$

$$I = i_1 + i_2 \quad \text{nuclear spin}$$

$$f = f_1 + f_2 \quad \text{total angular momentum or } (L, S)k + I$$

$$J = \Omega + \ell$$

$$F = f + \ell.$$  

The quantum numbers couple like,

$$l_1 + l_2 = L \xrightarrow{\hat{e}_z} \Lambda$$

$$s_1 + s_2 = S \xrightarrow{\hat{e}_z} \Sigma$$

$$j_1 + j_2 = j \xrightarrow{\hat{e}_z} \Omega + \ell = J$$

$$i_1 + i_2 = I \xrightarrow{=} = I$$

$$f_1 + f_2 = f + \ell = F.$$  \hfill (11.90)
Obviously, the atomic angular momentum is no longer a conserved quantity, but its projection onto the interatomic molecular axis is. The various possibilities how $L$, $S$, and $J$ are projected onto the internuclear axis or directly couple to the rotational angular momentum $\ell$ are handled by Hund’s cases (a) to (e). The spin coupling is described by $\{9j\}$-symbols, as discussed below.

### 11.3.3 Hund’s coupling cases

The coupling force between atomic spins depends on the distance between the atoms. Due to the variety of spins appearing in atoms, there are many possibilities how they can couple. These were classified by Hund into five cases.

#### 11.3.3.1 Hund’s case (a)

The molecular interaction is so strong that $L$ and $S$ couple to the $z$-axis instead of coupling to each other. This case is analogous to the Paschen-Back effect,

$$L \rightarrow \Lambda \quad \text{and} \quad S \rightarrow \Sigma$$

(11.91)

A common notation is to label the states $\Lambda = \Sigma, \Pi, \Delta, ...$. That is, in the symbol $X(2S+1\Lambda\Omega)_{\sigma}^{\pm}$, where $\sigma = g, u$ is the inversion symmetry, $X, A, B, ..$ and $a, b, ..$ are the singlet and triplet series starting from the lowest energy levels. An alternative notation is to assign labels ordered by energy $X = (1), (2), ...$ Finally, $\pm$ is the symmetry upon reflection. For example, $X^{1}\Sigma_{g}^{+}$.
11.3.3.2 Hund’s case (b)

$L$ is projected onto the $z$-axis before coupling to $\ell$. The resulting angular momentum afterward directly couples to $S$.

\[ L \rightarrow \Lambda \quad (\ell, k, S) J. \]  

(11.92)

11.3.3.3 Hund’s case (c)

$L$ and $S$ couple together instead of projecting themselves onto the $z$-axis. This case is analogous to the Zeeman effect,

\[ (L, S) j \rightarrow \Omega \quad (\Omega, \ell) J. \]  

A common notation is to label the states by $\Omega = 0, 1, 2, \ldots$. That is, in the symbol $X(\Omega)$, the letter $X = 1, 2, \ldots$ is a label ordered by energy. For example $2(0^-_s)$.

11.3.3.4 Hund’s case (d)

$L$ is not projected on the $z$-axis, but directly couples to the rotational angular momentum. The resulting angular momentum afterward only couples to the $S$

\[ ((L, \ell) k, \ell) J. \]  

(11.94)

11.3.3.5 Hund’s case (e)

$L$ and $S$ mutually couple as in the case (c), but are not projected on the $z$-axis, but couple directly with $\ell$, which is quantized,

\[ ((L, S) j, \ell) J. \]  

(11.95)

11.4 Molecular hyperfine structure

The scattering length in specific channels can be expressed via singlet and triplet scattering lengths,

\[ a_{|f_1, m_{f_1}+|f_2, m_{f_2}|} = P_{S=0}a_s + P_{S=1}a_t. \]  

(11.96)

The projectors are $P_S = |\langle S|((f_1 f_2)f)\rangle|$. According to [90]DOI or [416]DOI the recoupling from the uncoupled hyperfine representation into the short range representation is given by,

\[ \langle S m_S I m_l l' m' f_1 m_{f_1} f_2 m_{f_2} \ell m_{\ell} \rangle = \delta_{ll'}\delta_{m_m'} \sum_{f, m_f} \langle S m_S I m_I f f_1 m_{f_1} f_2 m_{f_2} f m_f \rangle \times \left\{ \begin{array}{ccc} s_1 & s_2 & S \\ i_1 & i_2 & I \\ f_1 & f_2 & f \end{array} \right\} \sqrt{\hat{S}\hat{I}\hat{f_1}\hat{f_2}} \left( \frac{1 - (1 - \delta_{f_1 f_2})(-1)^{S+I+\ell}}{2 - \delta_{f_1 f_2}} \right). \]  

(11.97)

The last bracket is dropped for unsymmetrized recoupling. We will study examples of spin recoupling in the ground state channels in Exc. 11.4.1.1, 11.4.1.2, and 11.4.1.3.
11.4.1 Exercises

11.4.1.1 Ex: Spin recoupling of identical $^{87}$Rb ground state channels

a. Unravel the molecular hyperfine structure of identical $^{87}$Rb ground state channels.
b. Project the collisional channels $|f_1m_{f_1} f_2m_{f_2}\rangle = |1 - 1 1 - 1\rangle$ and $|22 22\rangle$ on the singlet and triplet potentials, $S = 0, 1$.

11.4.1.2 Ex: Spin recoupling of $^6$Li$^{87}$Rb ground state channels

a. Unravel the molecular hyperfine structure of $^6$Li$^{87}$Rb ground state channels.
b. Project the collisional channels on short range potentials.

11.4.1.3 Ex: Hyperfine structure of $^6$Li$^{23}$Na and $^6$Li$^{87}$Rb

a. Unravel the molecular hyperfine structure of $^6$Li$^{23}$Na and $^6$Li$^{87}$Rb bound state.
b. How about the open channels?
Chapter 12

Collisions

12.1 Motion of interacting neutral atoms

The following sections, devoted to the relative motion of two neutral atoms, are adapted from J. Walraven’s excellent lectures on Quantum Gases available at [616]. The atoms are presumed to move slowly, typically at large separation, and to interact pair wise through a potential of the Van der Waals type. The term slowly refers to,

\[ k_{\text{therm}} r_0 \ll 1 \quad \text{where} \quad \lambda_{\text{therm}} = \frac{2\pi}{k_{\text{therm}}} = \sqrt{\frac{2\pi \hbar^2}{mk_B T}} \]  \hspace{1cm} (12.1)

is the thermal de Broglie wavelength and \( r_0 \) the range of the interaction potential. As the Van der Waals interaction gives rise to elastic collisions, the total energy of the relative motion is conserved in time. As the potential energy vanishes at large interatomic separation the total energy is usually expressed in the form \( E = \frac{\hbar^2 k^2}{2m} \). This implies that also the wavenumbers for the relative motion before and after the collision must be the same and shows that, far from the potential center, the collision can only affect the phase of the wavefunction - not its wavelength. Apparently, the appearance of a shift in phase relative to the free atomic motion provides the key to the quantum mechanical description of elastic collisions. This being said, we postpone the discussion of the actual collisional behavior to Sec. 12.2. First we prepare ourselves for this discussion by analyzing the stationary states for the motion in the presence of an interaction potential.

An important simplifying factor in the description of ultracold collisions is the emergence of universal behavior in the relative motion of the atoms. The latter applies to low-energy collisional states as well as to weakly bound states. Universal means in this context that, asymptotically (for \( r \gg r_0 \)), the wavefunctions become independent of the details of the interaction potential but can be characterized in terms of a few parameters, each representing some characteristic length scale of the collisional system. In other words, very different short-range physics can give rise to the same scattering behavior. From a theory point of view this universality has the enormous advantage that the essential features of ultracold collisions can be described with the aid of simple model potentials for which analytical solutions can be obtained.

In our analysis of the collisional motion three characteristic length scales will appear, the interaction range \( r_0 \) the scattering length \( a \) and the effective range \( r_e \), each expressing a different aspect of the interaction. The range \( r_0 \) is the distance beyond which the interaction may be neglected even for \( k \to 0 \). The second characteristic
length, the s-wave scattering length $a$, acts as an effective hard-sphere diameter. It is a measure for the interaction strength and determines the collision cross section in the limit $k \to 0$ as will be elaborated on in Sec. 12.2. The third characteristic length, the effective range $r_e$ expresses how the potential affects the energy dependence of the cross section and determines when the $k \to 0$ limit is reached.

The s-wave scattering length is the central parameter for the theoretical description of bosonic quantum gases. It determines both the thermodynamic and the collisional properties of these gases. In single-component fermionic gases the s-wave scattering length plays no role because the wavefunction for the relative motion of the atoms has to be antisymmetric. In two-component fermionic gases this restriction is absent for collisions between atoms of different components. As a consequence, in these systems the inter-component s-wave scattering length determines the collision related properties - for instance the thermalization rate.

In Sec. 12.1.1 we show how the phase shift appears as a result of interatomic interaction in the wavefunction for the relative motion of two atoms. For free particles the phase shift is zero. An integral expression for the phase shift is derived. In Sec. 12.1.2 and beyond we specialize to the case of low-energy collisions ($kr_0 \ll 1$). The basic phenomenology is introduced and analyzed for simple model potentials like the hard-sphere (Sec. 12.1.2) and the spherical well (Sec. 12.1.3), where the existence of a short range is manifest. For the discussion of arbitrarily shaped potentials, we refer to the script [616].

12.1.1 The collisional phase shift

12.1.1.1 Schrödinger equation

The starting point for the description of the relative motion of two atoms at energy $E$ is the Schrödinger equation (3.32),

$$\left[ \frac{1}{2m_r} \left( \frac{p_r^2}{r^2} + \frac{L^2}{r^2} \right) + V(r) \right] \psi(r, \vartheta, \varphi) = E \psi(r, \vartheta, \varphi) . \quad (12.2)$$

Here $m_r$ is the reduced mass of the atom pair and $V(r)$ the interaction potential. As discussed in Sec. 3.1.3 the eigenfunctions $\psi(r, \vartheta, \varphi)$ can be separated in a radial and an angular part, $\psi = R_\ell(r) Y_{\ell m}(\vartheta, \varphi)$, where the functions $Y_{\ell m}$ are spherical harmonics and the functions $R_\ell(r)$ satisfy the radial wave equation,

$$\left[ \frac{\hbar^2}{2m_r} \left( - \frac{d^2}{dr^2} - \frac{2}{r} \frac{d}{dr} + \frac{\ell(\ell + 1)}{r^2} \right) + V(r) \right] R_\ell(r) = E R_\ell(r) . \quad (12.3)$$

By the separation procedure the angular momentum term is replaced by a repulsive effective potential,

$$V_{\text{rot}}(r) = \frac{\hbar^2 \ell(\ell + 1)}{2m_r r^2} , \quad (12.4)$$

representing the rotational energy of the atom pair at a given distance and for a given rotational quantum number $\ell$. In combination with an attractive interaction it gives rise to a centrifugal barrier for the radial motion of the atoms. This is illustrated in Fig. 12.1 for the example of hydrogen.
12.1. MOTION OF INTERACTING NEUTRAL ATOMS

Figure 12.1: Example showing the high-lying bound states near the continuum of the singlet potential $^1\Sigma^+_g$ (the bonding potential) of the hydrogen molecule; $v$ and $J$ are the vibrational and rotational quantum numbers, respectively. The dashed line shows the effect of the $J = 3$ centrifugal barrier. The presence of a rotational barrier gives rise to an exponential suppression of the radial wavefunction for $r < r_{tp}$ and is negligible at distances where the interaction becomes noticeable $r \ll r_0$.

To analyze the radial wave equation we introduce reduced energies,

$$\varepsilon = \frac{2m_r E}{\hbar^2} = \begin{cases} k^2 & \text{for } k > 0 \\ -\kappa^2 & \text{for } k < 0 \end{cases} \quad \text{and} \quad \tilde{V}(r) = \frac{2m_r V(r)}{\hbar^2}, \quad (12.5)$$

choosing $k$ and $\kappa$ as real positive number. This puts Eq. (12.3) in the form,

$$R''_{\ell} + \frac{2}{r} R'_{\ell} + \left[ \varepsilon - \tilde{V}(r) - \frac{\ell(\ell + 1)}{r^2} \right] R_{\ell} = 0 \quad (12.6)$$

With the substitution $u_{\ell}(r) = r R_{\ell}(r)$ it reduces to a 1D Schrödinger equation,

$$u''_{\ell} + \left[ \varepsilon - \tilde{V}(r) - \frac{\ell(\ell + 1)}{r^2} \right] u_{\ell} = 0, \quad (12.7)$$

12.1.1.2 Low-energy limit: the $s$-wave regime

For two atoms with relative angular momentum $\ell > 0$ there exists a distance $r_{tp}$, called the classical turning point, below which the rotational energy exceeds the total energy $E$,

$$k^2 = \frac{\ell(\ell + 1)}{r_{tp}^2}. \quad (12.8)$$

This is illustrated in Fig. 12.1. In the classically inaccessible region of space ($r < r_{tp}$) the radial wavefunction is exponentially suppressed \(^1\). Combining Eq. (12.8) with the

\(^1\)At this point we exclude tunneling through the barrier and the occurrence of shape resonances.
condition (12.1) we obtain the inequality,
\[ kr_0 = \sqrt{\ell (\ell + 1)} \frac{r_0}{r_{tp}} \ll 1 , \quad (12.9) \]
which implies that, for \( \ell \neq 0 \), the classical turning point is found at a distance much larger than the range \( r_0 \) of the interaction. As the range \( r_0 \) defines the distance beyond which the potential can be neglected, this inequality shows that the radial motion is not affected by the presence of the potential \( V(r) \) in the radial wave equation. The notable exception is the case \( \ell = 0 \), where the barrier is absent and the potential gives rise to a substantial distortion of the radial waves. In other words, for \( kr_0 \ll 1 \) phase shifts (i.e. scattering) can only arise from collisions with zero angular momentum. The range of collision energies where the inequalities (12.9) are valid is called the \( s \)-wave regime.

12.1.1.3 Free particle motion

We first have a look at the case of free particles or particles in a homogeneous potential, \( V(r) = V_0 \). By introducing the dimensionless variable \( \varrho = kr \), where \( k \equiv \sqrt{2m(E - V_0)/\hbar^2} \), the radial wave equation (12.6) can be rewritten in the form of the spherical Bessel differential equation,
\[ R''_\ell + \varrho R'_\ell + \left[ 1 - \frac{\ell (\ell + 1)}{\varrho^2} \right] R_\ell = 0 . \quad (12.10) \]
Here, the derivatives are with respect to the new variable.

The general solution of Eq. (12.10) for angular momentum \( \ell \) is a linear combination of two particular solutions, one regular with amplitude \( A_\ell \), the spherical Bessel function \( j_\ell(\varrho) \), and one irregular with amplitude \( B_\ell \), the spherical Neumann function \( n_\ell(\varrho) \):
\[ R_\ell(\varrho) = A_\ell j_\ell(\varrho) + B_\ell n_\ell(\varrho) = c_\ell \left[ \cos \eta_\ell \ j_\ell(\varrho) + \sin \eta_\ell \ n_\ell(\varrho) \right] , \quad (12.11) \]
where the new parameters \( c_\ell \) and \( \eta_\ell \), defined by
\[ A_\ell \equiv c_\ell \cos \eta_\ell \quad \text{and} \quad B_\ell \equiv c_\ell \sin \eta_\ell , \quad (12.12) \]
represent the amplitude \( c_\ell \) and the asymptotic phase \( \eta_\ell \) of the wavefunction. Note that this equation is singular in the origin except for the case of vanishing phase shifts. Therefore, in the case of free particles we require \( \eta_\ell = 0 \) for all angular momentum values \( \ell \). This implies that the general solution reduces to the regular one,
\[ R_\ell(\varrho) = c_\ell \cos \eta_\ell \ j_\ell(\varrho) . \quad (12.13) \]

12.1.1.4 Significance of the phase shifts

To investigate the effect of a short-range interaction potential \( V(r) \) we return to the radial wave equation (12.6). As the potential is of short range it may be neglected for \( r \gg r_0 \) and the general solutions coincide with those of the spherical Bessel equation,
\[ R_\ell(k, r) \xrightarrow{r \gg r_0} c_\ell \left[ \cos \eta_\ell \ j_\ell(kr) + \sin \eta_\ell \ n_\ell(kr) \right] . \quad (12.14) \]
For \( r \gg 1/k \) the spherical Bessel and Neumann functions assume their asymptotic form and we find,

\[
R_{\ell}(k, r) \xrightarrow{kr \to \infty} \frac{c_{\ell}}{kr} \left[ \cos \eta_{\ell} \sin(kr - \frac{1}{2} \ell \pi) + \sin \eta_{\ell} \cos(kr - \frac{1}{2} \ell \pi) \right]
\]

\[= \frac{c_{\ell}}{kr} \sin(kr + \eta_{\ell} - \frac{1}{2} \ell \pi). \]

where we introduced the constant \( \eta_{\ell} \) representing the asymptotic phase shift. For a given value of \( k \) this phase shift fixes the general solution of the radial wavefunction \( R_{\ell}(k, r) \) up to an \( \ell \) dependent normalization constant \( c_{\ell} \). Note that in view of the \( k \) dependence of the phase shift, \( R_{\ell} \) is a function of \( k \) and \( r \) rather than a function of the product \( kr \). Whereas in the case of free particles the phase shifts must all vanish, in the presence of the interaction they provide the proper asymptotic form of the distorted waves. The non-zero asymptotic phase shift is the signature of the interaction at short distance; the motion becomes free-particle like (undistorted) only at large distance from the scattering center. In elastic scattering the relative energy \( \hbar^2 k^2 / 2m \) is conserved; hence, asymptotically also \( k \) and the de Broglie wavelength. This leaves only the asymptotic phase of the wave to be affected.

**Example 47 (Scattering matrix):** Rewriting Eq. (12.15) in complex notation,

\[
R_{\ell}(k, r) \simeq \frac{c_{\ell}}{2k} i \left[ e^{-i\eta_{\ell}} e^{-i(kr - \frac{1}{2} \ell \pi)} - e^{i\eta_{\ell}} e^{i(kr - \frac{1}{2} \ell \pi)} \right],
\]

we see that for \( r \to \infty \) the stationary solution \( R_{\ell}(k, r) \) can be regarded as an 'incoming' spherical wave interfering with an 'outgoing' spherical wave. It is convention to choose the phase of the normalization constant such that the phase of the incoming wave is zero,

\[
R_{\ell}(k, r) \xrightarrow{r \to \infty} \frac{c_{\ell}}{2k} \left[ e^{-ikr} - e^{-ikr} e^{2i\eta_{\ell}} \right],
\]

Apart from the sign, the ratio of the phase factors of the outgoing over the incoming wave is

\[
S_{\ell} = e^{2i\eta_{\ell}}. \]

This quantity is called the scattering matrix (\( S \) matrix) or, better, the \( l \)-wave contribution to the \( S \) matrix. Being unitary it does not suffer from the divergences of the ratio \( B_{\ell}/A_{\ell} = \tan \eta_{\ell} \). In the present context the name scattering matrix is a bit heavy because we only have a single matrix element (\( 1 \times 1 \) matrix). The term matrix finds its origin in the description of scattering of particles with an internal degree of freedom (like spin), for which the phase factor is replaced by a unitary matrix.

### 12.1.2 Hard-sphere potentials

We now turn to analytical solutions for model potentials in the limit of low energy. We first consider the case of two hard spheres of equal size. These can approach each other to a minimum distance equal to their diameter \( a \). For \( r \leq a \) the radial wave function vanishes, \( R_{\ell}(r) = 0 \): Outside the hard sphere we have free atoms, \( V(r) = 0 \),
with relative wave number \( k = [2m_r E/\hbar^2]^{1/2} \). Thus, for \( r \leq a \) the general solution for the radial wave functions of angular momentum \( \ell \) is given by the free atom expression (12.11), which asymptotically this takes the form (12.15) of a phase-shifted spherical Bessel function,

\[
R_\ell(k, r) = c_\ell [\cos \eta_\ell \, j_\ell(kr) + \sin \eta_\ell \, n_\ell(kr)] \approx \frac{c_\ell}{kr} \sin(kr + \eta_\ell - \frac{1}{2} \ell \pi) . \tag{12.19}
\]

To determine the phase shift we require as a boundary condition that \( R_\ell(k, r) \) vanishes at the surface of the hard sphere (see Fig. 12.2),

\[
\cos \eta_\ell \, j_\ell(ka) + \sin \eta_\ell \, n_\ell(ka) = 0 . \tag{12.20}
\]

Hence, the phase shift follows from the expression,

\[
\tan \eta_\ell = \frac{j_\ell(ka)}{n_\ell(ka)} . \tag{12.21}
\]

This expression allows to derive asymptotic expressions (for \( ka \ll 1 \) and for \( ka \gg 1 \)) for the radial wave function (12.19), as will be shown in Exc. 12.1.5.1.

![Figure 12.2: Radial wavefunctions (\( \ell = 0 \)) for various values of \( k \) (down to the \( k \to 0 \) limit) in the case of a hard sphere potential. The boundary condition is fixed by the requirement that the wavefunction vanishes at the edge of the hard sphere, \( R_0(ka) = 0 \).](image)

### 12.1.2.1 s-wave phase shifts for hard spheres

For the case \( \ell = 0 \), inserting the analytical expressions for the Bessel and von Neumann function, (12.19) becomes without approximation,

\[
R_0(k, r) = \frac{c_0}{kr} (\cos \eta_0 \sin kr + \sin \eta_0 \cos kr) = \frac{c_0}{kr} \sin(kr + \eta_0) . \tag{12.22}
\]

The phase shift follows from the boundary condition \( R_0(k, a) = 0 \), which can be written in the form,

\[
\cos \eta_0 \sin ka + \sin \eta_0 \cos ka = 0 . \tag{12.23}
\]

Hence, the phase shift is

\[
\eta_0 = -ka . \tag{12.24}
\]
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With this expression Eq. (12.22) reduces to

\[ R_0(k, r) = \frac{c_0}{kr} \sin[k(r - a)] . \]  

(12.25)

This expression is exact for any value of \( k \), as announced above. The linear \( k \) dependence of \( \eta_0 \) simply expresses its definition in which the shift of the wave (by \( a \)) is compared to the de Broglie wavelength \( \lambda_{dB} \), \( \eta_0 = -2\pi a/\lambda_{dB} \). As a consequence the phase shift vanishes for \( k \to 0 \),

\[ \lim_{k \to 0} \eta_0(k) = 0 . \]  

(12.26)

This result is obvious when comparing the finite shift \( a \) to the diverging wavelength \( \lambda_{therm} \). Interestingly, in the limit \( k \to 0 \) the expression (12.25) becomes \( k \) independent,

\[ R_0(r) \sim 1 - \frac{a}{r} \quad \text{for} \quad a \leq r \ll 1/k . \]  

(12.27)

This important result is illustrated in Fig. 12.2. In the limit \( k \to 0 \) the wavefunction is essentially constant throughout space (up to a distance \( 1/k \to \infty \) at which it starts to oscillate), except for a small region of radius \( a \) around the potential center.

12.1.3 Spherical wells with a flat bottom

The second model potential to consider is the spherical well of range \( r_0 \) sketched in Fig. 12.3,

\[ \tilde{V}(r) = \begin{cases} 2m_r V_0/\hbar^2 = \tilde{V}_0 = -\kappa_0^2 & \text{for} \ r \leq r_0 \\ 0 & \text{for} \ r > r_0 \end{cases} . \]  

(12.28)

Here \( |U_0| = \kappa_0^2 \) is called the well depth (\( \kappa_0 \) is chosen to be real and positive, \( \kappa_0 > 0 \)). The energy of the continuum states is given by \( \varepsilon = k^2 \). In analogy, the energy of the bound states is written as,

\[ \varepsilon_b = -\kappa^2 . \]  

(12.29)

We now have to solve the radial wave equation (12.6) with the spherical well potential (12.28). Since the potential is constant inside the well \( (r \leq r_0) \) the wavefunction has to be free-particle like with the wave number given by,

\[ K_+ = \sqrt{2m_r(E - V_0)/\hbar^2} = \sqrt{\kappa_0^2 + k^2} . \]  

(12.30)

As the wavefunction has to be regular in the origin, inside the well it is given by,

\[ R_\ell(r) = C_\ell j_\ell(K_+ r) \quad \text{for} \ r \leq r_0 , \]  

(12.31)

where \( C_\ell \) is a normalization constant. This expression holds for \( E > V_0 \) (both \( E > 0 \) and \( E \leq 0 \)).

Outside the well \( (r > r_0) \) we have for \( E > 0 \) free atoms, \( \tilde{V}(r) = 0 \), with relative wavevector \( k = [2m_r E/\hbar^2]^{1/2} \). Thus, for \( r > r_0 \) the general solution for the radial wave functions of angular momentum \( \ell \) is given by the free atom expression (12.11),

\[ R_\ell(k, r) = c_\ell [\cos \eta_\ell \ j_\ell(kr) + \sin \eta_\ell \ n_\ell(kr)] \quad \text{for} \ r > r_0 . \]  

(12.32)
The full solution [see Fig. 12.3(a)] is obtained by the continuity conditions for $R_\ell(r)$ and $R'_\ell(r)$ at the boundary $r = r_0$. These imply continuity of the logarithmic derivative with respect to $r$,

$$K_+ \frac{j'_\ell(q_i)}{j_\ell(q_i)} = \left. \frac{R'_\ell(r)}{R_\ell(r)} \right|_{r=r_0} = k \frac{\cos \eta_\ell j'_\ell(q_e) + \sin \eta_\ell n'_\ell(q_e)}{\cos \eta_\ell j_\ell(q_e) + \sin \eta_\ell n_\ell(q_e)},$$

(12.33)

where we defined the abbreviations $q_i \equiv K_+ r_0$ and $q_e \equiv k r_0$. This ratio suffices to determine $\eta_\ell$ independently of the normalization constants $C_\ell$ and $c_\ell$. Once the phase shift is known, the relation between $C_\ell$ and $c_\ell$ follows from the continuity condition for $R_\ell(r)$. Furthermore, it shows that the asymptotic phase shift $\eta_\ell$ can take any (real) value depending on the depth of the well. In view of the importance of the $S$ matrix in scattering theory Sec. 12.2, it is advantageous to determine $e^{2i\eta_\ell}$ rather than $\eta_\ell$ itself. Expressing $\sin \eta_\ell$ and $\cos \eta_\ell$ in terms of $e^{i\eta_\ell}$ and $e^{-i\eta_\ell}$ Eq. (12.33) becomes,

$$K_+ \partial_q \ln j_\ell(q_i) = k \frac{e^{2i\eta_\ell} h^{(2)}_\ell(q_e) + h^{(1)}_\ell(q_e)}{e^{2i\eta_\ell} h^{(2)}_\ell(q_e) + h^{(1)}_\ell(q_e)},$$

(12.34)

with the definition of the Hankel functions of the first and second kind: $h^{(1,2)}_\ell \equiv j_\ell \pm i n_\ell$. Solving for $e^{2i\eta_\ell}$ this leads to the following expression for the $\ell$-wave contribution to the $S$ matrix,

$$e^{2i\eta_\ell} = - \frac{h^{(1)}_\ell(q_e) K_+ \partial_q \ln j_\ell(q_i) - k \partial_q \ln h^{(1)}_\ell(q_e)}{h^{(2)}_\ell(q_e) K_+ \partial_q \ln j_\ell(q_i) - k \partial_q \ln h^{(2)}_\ell(q_e)},$$

(12.35)

where the expression $\partial_q \ln$ stands for the logarithmic derivative. This expression may look a bit heavy, but is valuable as it represents the exact result for arbitrary $\ell$. 

**Figure 12.3**: (code) (Left) Scheme of the flat bottom potential. (Right) (a) Radial wavefunctions for square wells: (a) continuum state ($\varepsilon = k^2 > 0$); (b) Zero energy state ($\varepsilon = k^2 = 0$) in the presence of an asymptotically bound level ($\varepsilon = -\kappa^2 = 0$); (c) bound state ($\varepsilon = -\kappa^2 < 0$). Note the continuity of $R_0(r)$ and $R'_0(r)$ at $r = r_0$. The wavefunctions are not normalized and are shifted relative to each other only for reasons of visibility.
In Exc. 12.1.5.2 we simplify this formula for \( \ell = 0 \). As the formula (12.35) lacks transparency from the physical point of view, we analyze in the coming sections the case \( \ell = 0 \) directly discussing the radial wavefunctions \( u_\ell \).

Figure 12.4: (code) The \( s \)-wave scattering length \( a \) normalized on \( r_0 \) as a function of the depth of a spherical square potential well (blue curve). Note that, typically, \( a \simeq r_0 \) (green line), except near the resonances at \( \kappa_0 r_0 = (n + \frac{1}{2})\pi \) being an integer.

12.1.3.1 \( s \)-wave scattering \((E > 0)\)

The analysis of spherical well potentials becomes particularly simple for the case \( \ell = 0 \). Let us first consider the case \( E > 0 \), for which the radial wave equation can be written as a 1D-Schrödinger equation (12.7) of the form,

\[
 u''_0 + [k^2 - \bar{V}(r)]u_0 = 0 .
\]

The solution is,

\[
 u_0(kr) = \begin{cases} 
 C_0 \sin(Kr) & \text{for } r \leq r_0 \\
 c_0 \sin(kr + \eta_0) & \text{for } r > r_0 
\end{cases} .
\]

(12.37)

To determine \( \eta_0(k) \) it is sufficient to apply the boundary condition for continuity of the logarithmic derivative at the edge of the well,

\[
 \left. \frac{u'_0}{u_0} \right|_{r=r_0} = K_+ \cot K_+ r_0 = k \cot(kr_0 + \eta_0) .
\]

(12.38)

Note that this expression coincides with the general result given by Eq. (12.33) for the case \( \ell = 0 \); i.e. the boundary condition of continuity for \( u'_0/u_0 \) coincides with that for \( R'_0/R_0 \), as we know from a calculation left to Exc. 12.1.5.3. Furthermore, for a vanishing potential \((\kappa_0 \to 0)\) we have \( K_+ \to k \) and the boundary condition properly yields a zero phase shift \((\eta_0 = 0)\).

At this point we introduce the effective hard-sphere diameter \( a(k) \) to describe, in analogy with Eq. (12.24), the behavior of the phase shift,

\[
 \eta_0(k) \equiv -ka(k) .
\]

(12.39)

By this procedure we extract the linear \( k \) dependence as well as the negative sign from the phase shift. This is a good idea because the linear \( k \)-dependence does not arise
from the potential but simply from the definition of the phase in which, as discussed earlier, the shift of the wave is compared to the de Broglie wavelength. In the limit \( k \to 0 \), we have \( K_+ r_0 \to \kappa_0 r_0 \) and with the definition,

\[
a \equiv \lim_{k \to 0} a(k) = -\lim_{k \to 0} \eta(k)/k
\]

(12.40)

the boundary condition (12.38) becomes,

\[
\left. \frac{u'_0}{u_0} \right|_{r=r_0} = \kappa_0 \cot \kappa r_0 = \frac{1}{r_0 - a}.
\]

(12.41)

Solving for \( a \) we find,

\[
a = r_0 \left( 1 - \frac{\tan \gamma}{\gamma} \right),
\]

(12.42)

where the dimensionless positive quantity,

\[
\gamma \equiv \kappa_0 r_0
\]

(12.43)

is called the well parameter. As shown in Fig. 12.4, the value of \( a \) can be positive, negative or zero depending on the value of \( \gamma \). Therefore, rather than using the pictorial term effective hard-sphere diameter the name scattering length is used for \( a \). Next to the range, the scattering length represents the second characteristic length that can be associated with the interaction potential. As the name suggest, it is a measure for the scattering behavior of atoms, and we elaborate on this in Sec. 12.2. Also, in Sec. ?? we will show that \( a \) is also a measure for the effective strength of the interaction.

Fig. 12.4 and Eq. (12.42) show that \( a \) is typically a quantity of the size of \( r_0 \), although for \( \gamma = \tan \gamma \) it is zero and for \( \gamma = \left( \nu + \frac{1}{2} \right) \pi \), with \( \nu \) being an integer, it diverges. The latter condition points to a resonance phenomenon occurring when (with increasing \( \gamma \)) a new bound level enters the potential well. For the square well potential the scattering length is mostly positive; it is negative in the regions with \( \gamma < \tan \gamma \), which become narrower for increasing \( \gamma \). This unlikely occurrence of negative \( a \) is atypical for the general case; e.g. for Van der Waals potentials the probability to find a negative scattering length is 25%.

For \( r \geq r_0 \) the radial wavefunction corresponding to Eq. (12.37) is of the form,

\[
R_0(k,r) = \frac{c_0}{kr} \sin[kr - ka(k)].
\]

(12.44)

Recalling the definitions (12.39) and (12.40) we find that for \( k \to 0 \) this radial wavefunction becomes \( k \)-independent,

\[
R_0(r) \sim 1 - \frac{a}{r} \quad \text{for} \quad r_0 < r \ll \frac{1}{k}.
\]

(12.45)

The latter two expressions for the radial wavefunction have the same formal appearance as the hard sphere results (12.25) and (12.27). However, whereas the diameter of the hard-sphere has a fixed value, the scattering length for the well depends on \( \gamma \). As shown in Fig. 12.5, for positive scattering length the \( s \)-wave has a characteristic node at \( r = a \); for negative scattering length this becomes a virtual node.
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Importantly, because Eq. (12.45) reaches the asymptotic value 1 only for distances \( r \gg a \), the use of this equation in the modeling of dilute gases is only justified if \( a \) is much smaller than the interparticle spacing,

\[
na^3 \ll 1.
\]  

(12.46)

Otherwise, the interaction with neighboring atoms will distort the relative motion of the colliding pair. This violates the binary scattering approximation on which Eq. (12.45) is based. The dimensionless quantity \( na^3 \) is called the gas parameter. When its value is small, the gas is called nearly ideal or weakly interacting.

12.1.3.2 Bound \( s \)-levels \((E \leq 0)\)

Let us turn to the case \( E \leq 0 \). We shall show that the divergences of the scattering length obtained by analyzing the continuum states \((E > 0)\) result from the appearance of the next bound \( s \)-level when increasing the well parameter. The 1D Schrödinger equation takes the form,

\[
\left(u_0'' + [-\kappa^2 - \tilde{V}(r)]u_0(r) = 0 \right).
\]  

(12.47)

where \( \epsilon = -\kappa^2 \) is the discrete energy eigenvalue of a bound state with \( \ell = 0 \). The

\[\text{Figure 12.5: Reduced radial wavefunctions } u_0(r) \text{ for continuum states } (\epsilon > 0) \text{ in the } k \to 0 \text{ limit for increasing well depth near the threshold value } \kappa_0 r_0 = \left(n + \frac{1}{2}\right)\pi: \text{ (a) presence of an almost bound state } (a < 0); \text{ (b) presence of zero-energy resonance } (\kappa_{0b} = 0, a \to \pm \infty); \text{ (c) presence of a weakly bound state } (a > 0); \text{ (d) deeper binding of the least bound state. For } r > r_0 \text{ the wavefunction is given by } u_0(r) = c_0(r - a); \text{ hence, the value of } a \text{ is given by the intercept with the horizontal axis. This gives rise to a characteristic node at } r = a, \text{ which is real for } a > 0 \text{ (just as for hard spheres of diameter } a), \text{ but virtual for } a < 0. \text{ The wavefunctions are not normalized.} \]

solutions are of the type (see Fig. 12.29),

\[
u_0(k, r) = \begin{cases} 
C_0 \sin K_+ r & \text{for } r \leq r_0 \\
C_0 e^{-\kappa r} & \text{for } r \leq r_0
\end{cases}
\]  

(12.48)

where \( \kappa > 0 \) because the bound state wavefunction has to be normalized. The bound state energy is obtained by requiring the continuity of the logarithmic derivative when

\(^2\text{Note that weakly interacting does not mean that that the potential is 'shallow'. Any gas can be made weakly interacting by making the density sufficiently small.}\)
connecting the inner part of the wavefunction to the outer part,

\[ \left. \frac{u'_0(r)}{u_0(r)} \right|_{r=r_0} = K_- \cot K_- r_0 = -\kappa , \quad (12.49) \]

where \( \kappa > 0 \) and

\[ K_- = \left[ 2m_r(E - V_0)/\hbar^2 \right]^{1/2} = (\kappa_0^2 - \kappa^2)^{1/2} . \quad (12.50) \]

With decreasing \( \gamma \), the least bound level disappears in the limit \( \kappa \to 0, K_- \to \kappa_0 \). In this limit Eq. (12.49) reduces to,

\[ \left. \frac{u'_0(r)}{u_0(r)} \right|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 \bigg|_{\kappa \to 0} = 0 , \quad (12.51) \]

Increasing from zero the vibrational levels appear sequentially for

\[ \gamma = (v + \frac{1}{2})\pi , \quad (12.52) \]

where \( v = 0, 1, \ldots, v_{\text{max}} \) is the vibrational quantum number. This shows that a minimum well parameter \( (\gamma = \pi/2) \) is required to bind the first state. For the least-bound level, \( v_{\text{max}} \), we have,

\[ (v_{\text{max}} + \frac{1}{2})\pi = \text{Int} \left( \frac{\gamma}{\pi} - \frac{1}{2} \right) \quad (12.53) \]

and the total number of bound s levels follows with,

\[ N_b = v_{\text{max}} + 1 = \text{Int} \left( \frac{\gamma}{\pi} + \frac{1}{2} \right) . \quad (12.54) \]

The relation between \( \kappa \) and \( v \) for a given vibrational level depends on the ratio \( \kappa/K_- \) and is given by

\[ \cot K_- r_0 = -\frac{\kappa}{K_-} . \quad (12.55) \]

Note that this relation corresponds to \( K_- r_0 \simeq (v_{\text{max}} + \frac{1}{2})\pi \) for the least-bound state \( (\kappa/K_- \ll 1) \) and to \( K_- r_0 \simeq (v_{\text{max}} + 1)\pi \) for deeply bound levels \( (K_-/\kappa \ll 1) \), as is illustrated in Fig. 12.7(a).

**12.1.3.3 Weakly bound s-level: halo states**

For weakly bound s levels \( (0 < \kappa r_0 \ll 1) \) we have \( K_- \to \kappa_0 \) and Eq. (12.49) may be approximated by

\[ \left. \frac{u'_0(r)}{u_0(r)} \right|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 = -\kappa , \quad (12.56) \]

Furthermore, we recall that in the presence of a weakly bound s-level the scattering length is large and positive, \( a \gg r_0 \). From Eq. (12.41) we recall that for \( k \to 0 \) the logarithmic derivative also satisfies the relation

\[ \left. \frac{u'_0(r)}{u_0(r)} \right|_{r=r_0} = \kappa_0 \cot \kappa_0 r_0 = \frac{1}{r_0 - a} \simeq -\frac{1}{a} , \quad (12.57) \]

\(^3\)This conclusion cannot be extended to lower dimensions; in two dimensions bound states appear for arbitrarily shallow potentials.
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Interestingly, for $a \gg r_0$ the logarithmic derivative of the continuum states becomes independent of $r_0$ and $\kappa_0$; i.e. it becomes independent of the shape of the potential well. As we shall see it only depends on the well parameter $\gamma$ and not on the well shape. This points to a universal limiting shape of the wavefunction for large scattering length. As is sketched in Fig. 12.7(b), for decreasing $\kappa$ the least-bound state turns into a halo state; i.e. for $KR_0 \ll 1$ most of the probability of the bound state is found in the classically inaccessible region outside the potential well, thus surrounding the potential center like a halo. This behavior holds for arbitrary short-range potentials.

With Eqs. (12.56) and (12.57) we have obtained two expressions for $\kappa_0 \cot \kappa_0r_0$ and arrive at the conclusion that in the presence of a weakly bound state the scattering length is given by,

$$a \simeq \frac{1}{\kappa}$$

(12.58)
This expression reveals the tight relation between the binding energy of the least-bound state, given by Eq. (12.29), and the scattering length,

$$E_b = -\frac{\hbar^2 \kappa^2}{2m_{\pi}} \xrightarrow{\kappa \rightarrow 0} -\frac{\hbar^2}{2m_{\pi} a^2}.$$  

(12.59)

### 12.1.3.4 s-wave resonances in the continuum: The Breit-Wigner formula

To obtain the $k$-dependence of the phase shift for large but otherwise arbitrary well parameter ($\gamma \gg 1$) we rewrite the boundary condition (12.38) in the form,

$$\eta_0(k) = -kr_0 + \arctan \frac{kr_0}{K+r_0 \cot K+r_0} \equiv \eta_{bg} + \eta_{res}.$$  

(12.60)

The first term of (12.60) is called the **background contribution** to the phase shift and the second term the **s-wave resonance contribution**. Note that the background contribution shows the same phase development as we found in Sec. 12.1.2 for hard spheres. The phase development of the resonance contribution is shown in Fig. 12.8(a) for the case of a large well parameter slightly detuned from the threshold value (at $\gamma = 31.5\pi \approx 98.960169$) such that the scattering length is negative ($\Delta \gamma = -0.5$).

For potentials with $\gamma \gg 1$ the argument of the arctangent is predominantly small, $kr_0/|K+r_0 \cot K+r_0| \ll 1$, because $K+r_0 = \kappa_0 r_0 (1 + k^2/\kappa_0^2)^{1/2} > \gamma \gg 1$.

However, the argument of the arctangent diverges when $\cot K+r_0$ passes through zero; i.e. for

$$K+r_0 = \kappa_0 r_0 (1 + k^2/\kappa_0^2)^{1/2} > \gamma \gg 1.$$  

(12.61)

where $\tilde{v}$ is an integer called the resonance index. This divergence is observed as a small resonant enhancement of $a(k)$, as shown in Fig. 12.8(b). The physical phase is a continuous function of $k$, which changes by $\pi$ when sweeping across the resonance. Because the arctangent remains finite for $\cot K+r_0 = 0$ also the resonant phase shift remains finite, having the value $\eta_{res}(k) = \frac{\pi}{2} \pi$ (modulo $\pi$) at the center of each resonance.

In the remainder of this section we shall analyze the width and separation of the s-wave resonances for the case $\gamma \gg 1$. Since $K_+ \geq \kappa_0 \geq K_-$, we have,

$$\tilde{v} \geq \frac{2}{\pi} - \frac{1}{2} \geq v_{max},$$  

(12.63)

which shows that for $\gamma \gg 1$ the value of $\tilde{v}$ is large ($\tilde{v}_{min} \geq \tilde{v}_{max} \gg 1$). Hence, the resonance numbering starts where the numbering of bound states ends. To discuss the resonances we denote the wavevectors $k$ and $K_+$ at resonance by $k_{res}$ and $K_{res} \equiv \sqrt{\kappa_0^2 + k_{res}^2}$, respectively. The resonance energies $\epsilon_{res} = k_{res}^2$ satisfy the condition,

$$\epsilon_{res} = K_{res}^2 - \kappa_0^2 = (\tilde{v} + \frac{1}{2})^2 \pi^2 - \kappa_0^2 \geq 0.$$  

(12.64)

The exceptional case for which the equal sign applies ($\tilde{v} = v_{max}$) corresponds to a resonant bound state ($\kappa = 0$) and the resonance is called a resonance at threshold or zero-energy resonance ($k_{res} = 0$).
Figure 12.8: (code) (a) Resonance contribution to the s-wave phase shift $\eta_0(k)$ for a large well parameter slightly detuned from the threshold value (at $\gamma = 31.5\pi$), such that the scattering length is negative ($\Delta \gamma = -0.5$): The linear shift of the background contribution is not included in the plot. Note that the $\pi$ phase jumps arise from the modulo-$\pi$ representation of the arctangent and do not represent an observable phenomenon; the physical phase increases monotonically and equals $\eta_{\text{res}} = \frac{1}{2}$ (modulo $\pi$) at the center of the resonances; (b) contribution of the resonances to the effective hard sphere diameter $a(k) = -\eta_0(k)/k$. As (in this example) the lowest resonance is not close to threshold the resonant enhancement is small, $|a_{\text{res}}(k)| = r_0 \ll 1$.

Let us first analyze s-wave resonances for large well parameters ($\tilde{v} = v_{\text{max}}$) and far from threshold, ($\kappa = 0$). The energy spacing between two subsequent resonances is,

$$\Delta \varepsilon_{\text{res}} = \varepsilon^{(\tilde{v}+1)}_{\text{res}} - \varepsilon^{(\tilde{v})}_{\text{res}} = 2(\tilde{v} + 1) \frac{\pi^2}{r_0^2} \approx \frac{2\pi\gamma}{r_0^2} .$$

To analyze a given resonance we expand $K_+ \cot K_+ r_0$ about the point of zero crossing. For this purpose we introduce the notation,

$$K_+ = \sqrt{\kappa_0^2 + (k_{\text{res}} + \delta k)^2} = K_{\text{res}} + \frac{\delta k \ k_{\text{res}}}{K_{\text{res}}} ,$$

where $\delta k = k - k_{\text{res}}$ is called the detuning from resonance. Thus, restricting ourselves to the low-energy (but not zero energy) s-wave resonances ($1 < k_{\text{res}} r_0 \ll K_{\text{res}} r_0 \approx \gamma$), we may approximate $K_+ \cot K_+ r_0 \approx K_{\text{res}} \cot K_{\text{res}} r_0$. Expanding cot $K_+ r_0$ about the zero crossing at $K_+ r_0 = (\tilde{v} + 1/2)\pi$ and retaining only the linear term we obtain (see Problem 3.4),

$$K_{\text{res}} \cot K_{\text{res}} r_0 = -\delta k \ k_{\text{res}} r_0 .$$

Hence, the diverging argument of the arctangent becomes,

$$\tan \eta_{\text{res}} = \frac{k}{K_+ \cot K_+ r_0} \approx -\frac{1}{\delta k \ r_0} = -\frac{k + k_{\text{res}}}{(k^2 - k_{\text{res}}^2) r_0} \approx -\frac{2k_{\text{res}}/r_0}{\varepsilon - \varepsilon_0} .$$
Figure 12.9: (code) (a) Transition from bound states to Breit-Wigner s-wave resonances plotted for $\Delta \gamma = -0.5$ with respect to the threshold at $\gamma = 31.5\pi$ (same conditions as Fig. 12.8). The bound states are indicated as zero-width spikes at energies $\varepsilon = -\kappa^2$, with $\kappa$ following from Eq. (12.49). For $\varepsilon > 0$ the plot is based on Eqs. (12.60). The width of the resonances increases with the square root of the energy. Note that the band of energies typical for the quantum gases ($kr_0 \ll 1$) corresponds to a narrow zone, unresolved on the energy scale of the plot.

The expansion (12.66) is valid over the full range of the resonant change in phase provided the following condition holds,

$$\delta k \, r_0 \ll \frac{K_{res}}{k_{res}} \simeq \frac{\gamma}{k_{res}r_0},$$

which is satisfied for the lowest resonances as long as the well parameter is sufficiently large ($\gamma \gg k_{res}r_0$). As long as $\delta k \ll k_{res}$ we may further approximate $k \simeq k_{res}$. With these approximations and after restoring the dimensions, Eq. (12.68) can be written as a function of the energy $E = \hbar^2 k^2 / 2m$, 

$$\tan \eta_{res} = \frac{k}{\frac{K_+}{\cot K_+} r_0} \simeq \frac{-\Gamma^2}{\varepsilon - \varepsilon_{res}},$$

where

$$\Gamma/2 = 2k_{res}/r_0$$

is called the spectral width of the resonance. Comparing the expressions for $\Gamma$ and $\Delta E_{res}$ we find that for given $r_0$ the width $\Gamma$ is independent of $\gamma$, whereas the resonance spacing is proportional to $\gamma$. Thus, only for sufficiently large well parameters ($\gamma \gg 1$) the spectral width becomes smaller than the resonance spacing,

$$\Gamma \ll \Delta \varepsilon_{res} \iff k_{res}r_0 \ll \pi \gamma.$$}

Knowing the tangent of $\eta_{res}$, we readily obtain the sine and Eq. (12.70) is replaced by the Breit-Wigner formula,

$$\sin^2 \eta_{res} = \frac{(\Gamma/2)^2}{(\varepsilon - \varepsilon_0)^2 + (\Gamma/2)^2}.$$

For optical resonances this energy dependence is known as the Lorentz lineshape. Note that $\Gamma$ corresponds to the full-width-at-half-maximum (FWHM) of this line shape.
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The lowest energy resonances are plotted in Fig. 12.9 along with the highest-energy bound states.

The resonance near threshold (almost bound level) deserves special attention, as this type of resonance is the only one that can play an important role within the band of energies relevant for the quantum gases ($kr_0 \ll 1$). Fig. 12.9 shows that near the threshold (at $\gamma = 31.5\pi$) the resonance narrows down and becomes asymmetric, which means that the Breit-Wigner lineshape is lost. Using Eq. (12.54) we calculate $\tilde{v} = 31$. The narrow line is reminiscent of a bound level but the scattering length is negative (see Fig. 12.9). Under these conditions the wavefunction has a virtual node at $r = -|a|$ (see Fig. 12.29). Accordingly, the level is called a virtual level and the wavefunction is said to represent a virtual bound state. In analogy with the bound states its energy is written as $\varepsilon = \kappa^2_{res}$, where $\kappa$ is to be defined later.

12.1.4 Other types of potentials

12.1.4.1 Zero-range potentials

An important model potential is obtained by considering a spherical well in the zero-range limit $r_0 \rightarrow 0$. As illustrated in Fig. 12.10, it is possible to construct a zero-range well in such a way that the long-range properties of the wavefunction are unaffected;

![Wavefunctions](image)

Figure 12.10: Wavefunctions corresponding to the same binding energy ($\varepsilon = -\kappa^2$) plotted for three different values of $r_0$. Outside $r_0$ the wavefunctions fall off exponentially, always with the same decay exponent $\kappa$; this is the essence of the Bethe-Peierls boundary condition. The dashed lines show the extrapolation for $r \rightarrow 0$. (a) reference case; (b) for $kr_0 \ll 1$ most of the probability density of a bound state is found outside the well (halo state); (c) for zero-range potentials ($kr_0 = 0$) the oscillating part of the wavefunction is compressed into a delta function and only the decaying exponent remains (universal limit). Note that these wavefunctions do not share the same normalization.

i.e. the scattering length $a$ and the binding energy $\varepsilon = -\kappa^2$ of the least-bound state remain unchanged.

For $E < 0$ this can be demonstrated with the aid of the boundary condition (12.49),

$$-\kappa = K_- \cot K_- r_0 .$$  \hspace{1cm} (12.74)
Reducing the radius $r_0$ the value of the binding energy $\varepsilon = -\kappa^2$, can be conserved by increasing $\kappa_0$. In the limit $r_0 \to 0$ the well depth should diverge in accordance with,

$$-\frac{\kappa}{K_-} = \cot K_- r_0 \to 0 .$$

This condition is satisfied for $K_- r_0 \simeq \pi/2$. To elucidate this point we consider the least-bound level with vibrational quantum number $v = v_{\max}$, for which $K_- r_0 = (v_{\max} + 1/2)\pi$. Reducing $r_0$ by a factor of 2 the wavenumber $K_-$ has to be doubled to conserve the number of nodes in the wavefunction (i.e. to conserve $v_{\max}$). This means that the kinetic energy inside the well has to increases by a factor 4. Since for the least-bound level we have $K_- r_0 \simeq \gamma$, it means that in this case the binding energy can be conserved at effectively constant well parameter. Obviously, the freedom to conserve (for decreasing $r_0$) the binding energy of one of the levels can only be used once. It does not hold for the other levels because the level separation diverges with $\kappa_0$. In the zero range limit the potential only supports a single bound state and the wavefunction of that state is given by,

$$R_0(r) = c_0 e^{-\kappa r} \frac{r}{r} \quad \text{for} \quad r > 0 ,$$

and with $\kappa > 0$. Unit normalization, $\int r^2 R_0^2(r) dr = 1$, is obtained for $c_0 = \sqrt{2\kappa}$. For $E > 0$ we can arrive at the same conclusion. The boundary condition for $k \to 0$ and given value of $r_0$ is given by Eq. (12.41), which we write in the form,

$$\frac{1}{r_0 - a} = \kappa_0 \cot \kappa_0 r_0 .$$

Reducing the radius $r_0$, the scattering length $a$ can be conserved by increasing $\kappa_0$. In the limit $r_0 \to 0$ the well depth should diverge in accordance with,

$$-\frac{1}{\kappa_0 a} = \cot \kappa_0 r_0 \to 0 .$$

This is again satisfied for $\kappa_0 r_0 \simeq \pi/2$. In the zero-range limit the radial wavefunction for $k \to 0$ is given by,

$$R_0(k,r) = \frac{1}{kr} \sin[k(r - a)] \quad \text{for} \quad r > 0 ,$$

which implies $R_0(k,r) \simeq 1 - a/r$ for $0 < r \ll 1/k$.

### 12.1.4.2 Bethe-Peierls boundary condition

Note that Eq. (12.76) is the solution for $E < 0$ of the 1D-Schrödinger equation in the zero-range approximation,

$$u_0'' - \kappa^2 u_0 \quad \text{for} \quad r > 0 ,$$

under the boundary condition,

$$\frac{u_0'}{u_0} \bigg|_{r \to 0} = -\kappa .$$
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The latter relation is called the Bethe-Peierls boundary condition and was first used to describe the deuteron, the weakly bound state of a proton with a neutron \[?\]. It shows that for weakly bound states the wavefunction has the universal form of a halo state, which only depends on the binding energy, \(\varepsilon_0 = -\kappa^2\) (see Fig. 12.10).

For \(E > 0\) the 1D-Schrödinger equation in the zero-range approximation is given by,

\[
 u'_0 + k^2 u_0 = 0 \quad \text{for} \quad r > 0 .
\]

(12.82)

The general solution is \(u_0(k, r) = c_0 \sin[kr + \eta_0]\). Using the Bethe-Peierls boundary condition we obtain,

\[
 k \cot \eta_0(k) = -\kappa ,
\]

(12.83)

which yields after substituting \(\eta_0(k \to 0) \simeq -ka\) the universal relation between the scattering length and the binding energy in the presence of a weakly bound \(s\)-level, \(\varepsilon_0 = -\kappa^2 = -1/a^2\).

![Figure 12.11](a) Dependence of the scattering length on the potential depth.

12.1.4.3 Power-law potentials

The general results obtained in the previous sections presumed the existence of a finite range of interaction, \(r_0\). Thus far this presumption was based only on the heuristic argument presented in Sec. ???. To derive a proper criterion for the existence of a finite range and to determine its value \(r_0\) we have to analyze the asymptotic behavior of the interatomic interaction \[?\]. For this purpose we consider potentials of the power-law type,

\[
 V(r) = -\frac{C_s}{r^s} ,
\]

(12.84)
where \( C_s = V_0 r_s^6 \) is the power-law coefficient, with \( V_0 \equiv |V(r_c)| \equiv \hbar^2 \kappa_c^2/2m_r \) the well depth. These power-law potentials are important from the general physics point of view, because they capture major features of interparticle interactions.

For power-law potentials, the radial wave equation (12.85) takes the form,

\[
R'' + \frac{2}{r} R' + \left[ k^2 + \frac{\kappa_c^2 r_s^6}{r^6} - \frac{\ell(\ell + 1)}{r^2} \right] = 0 .
\]

(12.85)

Because this equation can be solved analytically in the limit \( k \to 0 \) it is ideally suited to analyze the conditions under which the potential \( V(r) \) may be neglected and thus to determine \( r_0 \). To solve Eq. (12.85) we look for a clever substitution of the variable \( r \) and the function \( R_\ell(r) \) to optimally exploit the known \( r \) dependence of the potential in order to bring the differential equation in a well-known form. To leave exibility in the transformation we search for functions of the type,

\[
G_\ell(x) = r^{-\nu} R_\ell(r) ,
\]

(12.86)

where the power \( \nu \) is to be selected in a later stage.

12.1.4.4 Computation of the scattering length

The scattering length depends on the binding energy \( E_v \) of weakly bound states. If \( a \) is positive and much greater than the range of the potential, then \[234, 204\] (12.59),

\[
E_v = -\frac{\hbar^2}{2m_r a^2} .
\]

(12.87)

More precisely, for a potential behaving at long range as,

\[
V = -\frac{C_6}{R^6} ,
\]

(12.88)

we get,

\[
E_v = -[(v_D - v)H(m_r, C_6)]^{-1/3} ,
\]

(12.89)

where \( v_D \) is the vibrational quantum number at the dissociation limit and \( H \) a constant. Also,

\[
a = \frac{\Gamma(3/4)}{2\sqrt{2}\Gamma(5/4)} \left( \frac{2\mu C_6}{\hbar^2} \right)^{1/4} \left[ 1 - \tan \pi(v_D + \frac{1}{2}) \right] .
\]

(12.90)

12.1.4.5 Second method

It yields for \( \gamma = \alpha, \beta \),

\[
\frac{d^2}{dR^2} \varepsilon_\gamma(R) = 2m_r V(R) \varepsilon_\gamma(R) .
\]

(12.91)

Successive approaches start with \( \varepsilon_\alpha^{(0)} = R \) and \( \varepsilon_\beta^{(0)} = 1 \) and get superior orders via,

\[
\frac{d^2}{dR^2} \varepsilon_\gamma^{(k+1)}(R) = 2m_r V(R) \varepsilon_\gamma^{(k)}(R) .
\]

(12.92)

We define \( \delta_\gamma^{(k)} \equiv \varepsilon_\gamma^{(k)} - \varepsilon_\gamma^{(k-1)} \) starting with \( \delta_\gamma^{(0)} = \varepsilon_\gamma^{(0)} \), such that,

\[
\frac{d^2}{dR^2} \delta_\gamma^{(k+1)}(R) = 2m_r V(R) \delta_\gamma^{(k)}(R) .
\]

(12.93)
\( \delta_\alpha(R \to \infty) = \delta_\beta(R \to \infty) = 0. \) Since \( \varepsilon_\alpha = \lim_{k \to \infty} \varepsilon^{(k)}_\alpha \), the wavefunction is thus obtained from,

\[
U(R) = \alpha(1 + \delta^{(1)}_\alpha + \delta^{(2)}_\alpha + \ldots) + \beta(R + \delta^{(1)}_\beta + \delta^{(2)}_\beta + \ldots).
\] (12.94)

This long-range expression must match the short-range value at a certain point \( R_0 \):

\[
U(R_0) = \alpha \varepsilon_\alpha(R_0) + \beta \varepsilon_\beta(R_0).
\] (12.95)

\[
U'(R_0) = \alpha \frac{d}{dR} \varepsilon_\alpha(R_0) + \beta \frac{d}{dR} \varepsilon_\beta(R_0)
\]

and

\[
a = -\frac{\beta}{\alpha} = \frac{U(R_0) \frac{d}{dR} \varepsilon_\alpha(R_0) - U'(R_0) \varepsilon_\alpha(R_0)}{U(R_0) \frac{d}{dR} \varepsilon_\beta(R_0) - U'(R_0) \varepsilon_\beta(R_0)} = \frac{\frac{d}{dR} \varepsilon_\alpha(R_0)}{\frac{d}{dR} \varepsilon_\beta(R_0)}.
\] (12.96)

Let us consider a specific potential,

\[
V(R) = \frac{1}{2} BR^m r e^{-\eta R} - \left( \frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} \right) f_c(R)
\] (12.97)

\[
f_c(R) = \theta(R_c - R) e^{-(R_c/R - 1)^2} + \theta(R - R_c).
\]

At very long range we have \( V(R) \simeq -\frac{C_6}{R^6} \), such that,

\[
\delta^{(k+1)}_\gamma = \int_0^R 2m_r V \delta^{(k)}_\gamma dR = \delta^{(k)}_\gamma(\infty) - \int_R^\infty -\frac{2m_r C_6}{R^6} \delta^{(k)}_\gamma dR
\] (12.98)

\[
= 2m_r C_6 \int_R^\infty \frac{\delta^{(k)}_\gamma}{R^6} dR.
\]

In particular,

\[
\delta^{(1)}_\alpha = 2m_r C_6 \frac{-1}{4R^4}, \quad \delta^{(2)}_\alpha = (2m_r C_6)^2 \frac{-1}{4 \cdot 9R^9}
\]

\[
\delta^{(1)}_\beta = 2m_r C_6 \frac{1}{5R^5}, \quad \delta^{(2)}_\beta = (2m_r C_6)^2 \frac{1}{5 \cdot 10R^{10}}.
\] (12.99)

12.1.4.6 Third method

To estimate the scattering length for a particular interaction consult [393, ?, 459]. Following [393] we write the Schrödinger equation in atomic units as,

\[
\frac{d^2 U}{dR^2} = 2m_r V(R)U(R).
\] (12.100)

The ansatz \( U(R) = \alpha \varepsilon_\alpha(R) + \beta \varepsilon_\beta(R) \) with \( \varepsilon_\alpha(R \to \infty) = R \) and \( \varepsilon_\beta(R \to \infty) = 1 \) shows that \( a = -\beta/\alpha \) is the desired scattering length.
12.1.4.7 Fourth method

The equation for the accumulated phase follows from the Schrödinger equation,

$$\phi(r_0) \equiv \int_0^{r_0} k(r) \, dr \quad \text{(12.101)}$$

$$k^2(r) = \frac{2m_r}{\hbar^2} \sqrt{E - V(r) - \frac{\hbar^2(l+1)}{2m_r r^2}}.$$  

According to [459] we start resolving,

$$\frac{d}{dR} \delta_{k,0}(R) = -k^{-1} V(R) \sin^2[kR + \delta_{k,0}(R)]. \quad (12.102)$$

12.1.4.8 Pseudo potentials

As in the low-energy limit \((k \to 0)\) the scattering properties only depend on the asymptotic phase shift it is a good idea to search for the simplest mathematical form that generates this asymptotic behavior. The situation is similar to the case of electrostatics, where a spherically symmetric charge distribution generates the same far field as a properly chosen point charge in its center. Not surprisingly, the suitable mathematical form is a point interaction. It is known as the pseudo potential and serves as an important theoretical Ansatz at the two-body level for the description of interacting many-body systems [195, 298]. The existence of such pseudo potentials is not surprising in view of the zero-range square well solutions discussed in Sec. 12.5.

As the pseudo potential cannot be obtained at the level of the radial wave equation, we return to the full 3D Schrödinger equation for a pair of free atoms,

$$\left( \nabla^2 + k^2 \right) \psi_k(r) = 0,$$  

where \(k = \sqrt{2m_r E/\hbar^2}\) is the wavenumber for the relative motion. Restricting ourselves to \(s\)-wave collisions we derived earlier the solution of this equation as being given by \(\psi_k(r) = \frac{c_0}{kr} \sin kr\). However, we are now looking a solution of the type \((12.37)\), which includes a phase shift \(\eta_0\),

$$\psi_k(r) = \frac{c_0}{kr} \sin(kr + \eta_0). \quad (12.104)$$

Inserting this expression into the wave equation \((12.103)\) we encounter the problem that the solution is irregular in the origin when \(\eta_0 \neq 0\). Apparently, we need to complement the wave equation by a (pseudo-)potential to remove this problem.

Our claim is now that the operator,

$$-\frac{4\pi}{k \cot \eta_0} \delta^3(r) \frac{\partial}{\partial r} r,$$  

is the wanted \(s\)-wave pseudo potential \(\tilde{V}(r)\). That is, the wave equation,

$$\left( \nabla^2 + k^2 + \frac{4\pi}{k \cot \eta_0} \delta^3(r) \frac{\partial}{\partial r} r \right) \psi_k(r) = 0 \quad (12.106)$$
lets the phase-shifted wavefunction (12.104) be regular at the origin.

The presence of the delta function makes the pseudo-potential act as a boundary condition at $r = 0$,

$$\frac{4\pi \delta^3(r)}{k \cot \eta_0} \left[ \frac{\partial}{\partial r} r \psi_k(r) \right]_{r=r_0} = 4\pi \delta^3(r) \frac{c_0}{k} \sin \eta_0$$

$$= -4\pi \delta^3(r) \frac{c_0}{k} \sin(kr) \simeq -4\pi ac_0 \delta^3(r),$$

where we used the expression for the $s$-wave phase shift, $\eta_0 = -ka$. This is the alternative boundary condition we were looking for. Substituting this into Eq. (12.106) we obtain the inhomogeneous equation

$$(\nabla^2 + k^2) \psi_k(r) \simeq -4\pi ac_0 \delta^3(r).$$

(12.108)

This inhomogeneous equation has the solution (12.104), as demonstrated in Exc. 12.1.5.4.

For functions $f(r)$ with regular behavior in the origin we have

$$\left[ \frac{\partial}{\partial r} r f(r) \right]_{r=0} = f(0) + r \left[ \frac{\partial}{\partial r} f(r) \right]_{r=0} = f(0),$$

(12.109)

and the pseudo potential takes the form of a delta function potential

$$\tilde{V}(r) = -\frac{4\pi}{k \cot \eta_0} \delta^3(r) \simeq \frac{4\pi a\delta^3(r)}{k}.$$

(12.110)

or, equivalently, restoring the dimensions,

$$V(r) = \frac{g}{2} \delta^3(r) \quad \text{with} \quad g = \frac{4\pi \hbar^2}{m_r}.$$

(12.111)

This expression, for $na^3 \ll 1$ valid in the zero energy limit, is convenient for calculating the interaction energy, as will be shown in Sec. 26.2.3.

### 12.1.4.9 Coupling of potentials

When molecular potentials cross and couple via collisions, via radiative coupling, or via a Feshbach resonance (cf. Sec. 12.4.2), new adiabatic potentials are formed. These

---

**Note** that the wavefunction $\psi_k$ is irregular,

$$\delta^3(r) \frac{\partial}{\partial r} [r \psi_k(r)] = \delta^3(r) \frac{\partial}{\partial r} \left( r \frac{c_0 \sin(kr + \eta_0)}{kr} \right) = \delta^3(r) c_0 \cos[k(r-a)] \quad k \to 0 \quad c_0 \delta^3(r).$$

On the other hand,

$$\delta^3(r) \frac{\partial}{\partial r} [r \psi_k(r)] = \delta^3(r) \frac{c_0 \sin(kr + \eta_0)}{kr} = \delta^3(r) \frac{c_0 \sin[k(r-a)]}{kr} \quad k \to 0 \quad c_0 \delta^3(r)[1 - \frac{a}{r}]$$

**Note** that the dependence on the relative position vector $r$ rather than its modulus $r$ is purely formal as the delta function restricts the integration to only zero-length vectors. This notation is used to indicate that normalization involves a 3-dimensional integration, $\int \delta^3(r) d^3r$. Pseudo potentials do not carry physical significance but are mathematical constructions that can chosen such that they provide wavefunctions with the proper phase shift.
are obtained as the $r$-dependent eigenvalues of the coupling Hamiltonian,

$$
\hat{H}_{cpl} = \begin{pmatrix} V_1(R) & \Omega \\ \Omega & V_2(R) \end{pmatrix}.
$$

(12.112)

Such calculations are known as *coupled channels* calculations.

![Figure 12.12](code) The coupling of molecular potentials (solid lines) generates new adiabatic potentials (dash-dotted lines).

### 12.1.5 Exercises

12.1.5.1 **Ex: Asymptotic radial function for hard-sphere potentials**

Using asymptotic expressions for the Bessel and von Neumann functions derive the radial function $R_\ell(k,r)$ for the two limiting cases $ka \ll 1$ and $ka \gg 1$.

12.1.5.2 **Ex: $s$-wave collision on flat bottom potentials**

Simplify the scattering matrix (12.35) for the collisional flat bottom potential for the case of $s$-wave collisions.

12.1.5.3 **Ex: Equivalence of boundary conditions**

Show that the radial wavefunction $R_\ell$ and $u_\ell$ satisfy equivalent boundary conditions at the surface of the spherical box potential.

12.1.5.4 **Ex: Derivation of a linear expansion**

Derive the linear expansion (12.67).

12.1.5.5 **Ex: Pseudo-potential for $s$-wave scattering**

Verify the equation $(\nabla^2 + k^2)\psi_k(r) = 4\pi\delta^3(r)\frac{1}{k}\sin\eta_0$ by direct substitution of the solution (12.104) setting $c_0 = 1$.

### 12.2 Scattering theory

In this chapter we discuss scattering by time independent potentials satisfying $rV(r \to \infty) \to 0$, that is short-range potentials. Such a potential may have attractive regions
supporting bound states with energy $E < 0$. Here, however, we only consider states $E > 0$. Since the potential is supposed independent of time, $\partial_t \hat{H} = 0$, we will focus on time-independent problems,

$$\hat{H}\psi_k(r) = E_k\psi_k(r), \quad (12.113)$$

with $\hat{H} = \frac{p^2}{2m} + V(r)$ and $E_k = \hbar^2 k^2 / 2m$. The boundary conditions are given by the scattering geometry in such a way that at long distances the wavefunction behaves as (see Fig. 12.13),

$$\psi_k(r) \sim e^{ik \cdot r} + f_k(\Omega) \frac{e^{ik_s \cdot r}}{r}. \quad (12.114)$$

For elastic scattering processes we have $k_s = k$. The scattering amplitude $f_k(\Omega)$ depends on the energy $E_k$ and on the scattering solid angle. Experimentally, we scatter individual particles described by wave packets. Since the scattering theory is linear, we can describe the packets by superpositions of stationary solutions $\psi_k$.

![Figure 12.13: Scattering of incident light (wavevector $k_0$) by a potential $V$.](image)

### 12.2.1 Lippmann-Schwinger equation

In order to consider the example of two particles involved in a collision we may go into the center-of-mass system (using reduced masses), fix the origin of the coordinate system on one of the particles, and analyze the trajectory of the second particle inside the interaction potential.

The scattering theory is based on Green’s method, which we already know from electrostatics. So, let us start of a brief reminder of the use of the Green’s function as a method to solve electrostatic problems.

**Example 48 (Green’s method in electrostatics):** From Maxwell’s third equation we obtain,

$$\nabla^2 \phi(r) = -\varepsilon_0^{-1} \rho(r).$$

Being defined by,

$$\nabla^2 G(r) = \delta^3(r),$$

the Green function is,

$$G(r) = \frac{-1}{4\pi |r|}.$$

With this, we find the solution of the Maxwell equation,

$$\phi(r) = \left(-G * \varepsilon_0^{-1} \rho(r)\right)(r) = -\frac{1}{\varepsilon_0} \int_V \rho(r_0) G(r-r_0) d^3 r_0 = \frac{1}{4\pi \varepsilon_0} \int_V \frac{\rho(x)}{|r-x|} d^3 x,$$

known as Poisson’s law.

\[\text{Note that } k \text{ is not a quantum number, since } \psi_k \text{ contains momentum components } \neq k.\]
12.2.1.1 Green’s method in quantum mechanics

Green’s method can be used to solve Schrödinger’s equation with the boundary condition (12.114). We start from the reduced stationary Schrödinger equation (12.113) [591],

\[(\Delta + k^2)\psi_k(r) = \frac{2m}{\hbar^2} V(r) \psi_k(r) .\] (12.115)

This equation is not a common eigenvalue problem, since any energy \(E_k\) generates a solution. The equation (12.115) is a partial inhomogeneous differential equation with the left side describing free propagation and the right side describing a source that depends on the solution. Such differential equations are usually solved using Green’s functions. We choose a point source and we solve,

\[(\Delta + k^2)G(r, k) = \delta^3(r) ,\] (12.116)

along with the boundary conditions. The solution takes the form [61],

\[G(r, k) = \frac{1}{4\pi} \frac{e^{ik|r|}}{|r|} ,\] (12.117)

such that,

\[\psi_k(r) = e^{ikr} + (G * \frac{2m}{\hbar^2} V \psi_k) (r) = e^{ikr} + \frac{2m}{\hbar^2} \int_V d^3r' G(r - r', k)V(r')\psi_k(r') .\] (12.118)

The equation (12.118) is called Lippmann-Schwinger equation. Of course, this equation does not solve, but only reformulate the problem taking into account the boundary conditions. It is more appropriate for an implementation of approximations. See Exc. 12.2.7.1 and 12.2.7.2.

Now let us consider the far field, \(r \to \infty\), to verify the asymptotic behavior and find an expression for \(f_k(\Omega)\) as a function of \(V(r)\). For \(r \to \infty\) we can approximate

\[k|\mathbf{r} - \mathbf{r}'| = kr\sqrt{\langle \hat{\mathbf{e}}_r - \mathbf{r}'/r \rangle^2} = kr\sqrt{1 - 2\hat{\mathbf{e}}_r \cdot \mathbf{r}'/r + (\mathbf{r}'/r)^2} \approx kr - \mathbf{k}' \cdot \mathbf{r}' \approx kr ,\]

with \(\mathbf{k}' = k\hat{\mathbf{e}}_r\). With this the Lippmann-Schwinger equation (12.118) becomes,

\[\psi(r) \to e^{ikr} - \frac{2m}{\hbar^2} \int_V \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} V(r')\psi(r')d^3r'\]

\[= e^{ikr} - \frac{2m}{4\pi\hbar^2 kr} \int_V e^{-ik' \cdot \mathbf{r}'} V(r')\psi(r')d^3r' \equiv \psi_{in} + f_k(\Omega)e^{ikr} ,\]

giving, in comparison with the expression (12.114), the scattering amplitude,

\[f_k(\Omega) = \frac{2m}{4\pi\hbar^2} \int_V e^{-ik' \cdot \mathbf{r}'} V(r')\psi(r')d^3r' .\] (12.121)

Starting from the wavefunctions \(\psi_{in} \equiv e^{ikr}\) and \(\psi_s \equiv f_k(\Omega)e^{ikr}/r\) we can calculate the current densities,

\[J_{in} = \frac{\hbar}{2mi}(\psi_{in}^\dagger \nabla \psi_{in} - c.c.) = \frac{\hbar k}{m} ,\] (12.122)

\[J_s = \frac{\hbar}{2mi}(\psi_s^\dagger \partial_r \psi_s - c.c.)\hat{\mathbf{e}}_r = \frac{\hbar k'}{m r^2} |f_k(\Omega)|^2 + O(r^{-3}) .\]
The number $dI(\Omega)$ of particles scattered per second into the solid angle $d\Omega$ is simply $dI(\Omega) = |J_s|r^2d\Omega$. With this we can calculate the differential effective cross section defined by the ratio between $dI(\Omega)$ and the number $|J_{in}|$ of incident particles per second,

$$\frac{d\sigma}{d\Omega} = \frac{dI(\Omega)}{|J_{in}|d\Omega} = |f_k(\Omega)|^2. \quad (12.123)$$

Finally we define the total effective cross section,

$$\sigma = \int d\Omega |f_k(\Omega)|^2. \quad (12.124)$$

12.2.2 Wave packets

We now let a wave packet defined at a time $t = t_0$,

$$\psi(r,t_0) = \int \frac{d^3k}{(2\pi)^3} a_k e^{ik\cdot r}, \quad (12.125)$$

impinge on a scattering potential. The amplitude $a_k$ be concentrated around $k_0$, such that the wave packet approaches the scatterer with the velocity $v_0 = \hbar k_0/m$. The time evolution of the wavefunction $\psi(r,t)$ determines the signal measured by a detector at a later time $t = t_0$. Our task is to determine $\psi(r, t > t_0)$. The scattered states $\psi_k$ solving the Schrödinger equation (12.113) are complete in the space of the extended wavefunctions, and we can write the temporal evolution as,

$$\psi(r,t) = \int \frac{d^3k}{(2\pi)^3} A_k \psi_k(r)e^{-iE_k(t-t_0)/\hbar}. \quad (12.126)$$

At time $t_0$ the results (12.125) and (12.126) must match. To verify this, we write (12.125) replacing the plane wave $e^{ik\cdot r}$ using the Lippmann-Schwinger equation (12.118) with Green’s function (12.117), and then we compare the coefficients,

$$\psi(r,t_0) = \int \frac{d^3k}{(2\pi)^3} a_k \left[ \psi_k(r) + \frac{m}{2\pi\hbar^2} \int d^3r' e^{ik|r-r'|} V(r') \psi_k(r') \right]. \quad (12.127)$$

The scattering process is illustrated in Fig. 12.14. To simplify the calculation of

![Figure 12.14: Scattering of wave packet at a potential.](image_url)

the second term in this equation, we assume that $\psi_k$ is smooth, that is, there are no
resonances, such that we can approximate, $\psi_k \simeq \psi_{k_0}$. With $k \simeq k \cdot \hat{e}_{k_0}$ we obtain,

$$\int \frac{d^3k}{(2\pi)^3} a_k e^{ik|r-r'|} \psi_k(r') = \int \frac{d^3k}{(2\pi)^3} a_k e^{ik(\hat{e}_{k_0}|r-r'|)} \psi_{k_0}(r')$$

$$\simeq \psi(\hat{e}_{k_0}|r-r'|, t_0) \psi_{k_0}(r').$$

Here, $\psi(\hat{e}_{k_0}|r-r'|, t_0)$ is the incident wave package evaluated to the right, where by definition it is $\simeq 0$. The expression (12.127) therefore has the form,

$$\psi(r, t_0) = \int \frac{d^3k}{(2\pi)^3} a_k \psi_k(r),$$

and a comparison of the coefficients with (12.126) gives, $A_k = a_k$. Finally, we evaluate $\psi(r, t)$ at the time of detection $t > t_0$ to understand, that the above stationary analysis is actually physically correct. According to (12.126) we have,

$$\psi(r, t) = \int \frac{d^3k}{(2\pi)^3} A_k \psi_k(r) e^{-iE_k(t-t_0)/\hbar}$$

$$\simeq \psi_0(r, t) + \int \frac{d^3k}{(2\pi)^3} a_k e^{ikr} f_k(\Omega) e^{-iE_k(t-t_0)/\hbar}.$$

Hence, $\psi_0(r, t)$ describes the evolution of the wave packet without scatterer,

$$\psi_0(r, t) = \int \frac{d^3k}{(2\pi)^3} a_k e^{ikr} e^{-iE_k(t-t_0)/\hbar}.$$

If $f_k$ it’s smooth around $k = k_0$, which allows us to place this amplitude ($f_k \simeq f_{k_0}$) in front of the integral, and with $k \simeq k \cdot \hat{k}_0$ we obtain,

$$\psi(r, t) \overset{t \text{ large}}{\Rightarrow} \psi_0(r, t) + \frac{f_{k_0}(\Omega)}{r} \psi_0(\hat{k}_0 r, t).$$

The scattering process is illustrated in Fig. 12.14: According to the last equation the scattering process involves the superposition of the non-scattered packet and a packet scattered in the direction $\Omega$. The latter involves the amplitude $\Psi_0(\hat{k}_0 r, t)$ of a packet propagating in forward direction, which only needs to be evaluated at the right time and distance. This packet will then be multiplied with the amplitude describing the angular dependency $f_{k_0}$; the angle, therefore, only appears through this amplitude and not in the wavefunction $\psi_0$. In two situations the above analysis can not be applied:

- when $V$ is long-ranged, f.ex., $V = 1/r$,
- when the incident energy $E_k$ is resonant.
12.2.3 Born approximation

The Lippmann-Schwinger equation suggests the following perturbative iteration called \textit{Born series} [61],

\[
\psi(r) = \psi_i(r) + \left( G \ast \frac{2m}{\hbar^2} V \psi \right)(r) = \psi_i(r) + \frac{2m}{\hbar^2} G * V \psi_i(r) + \left( \frac{2m}{\hbar^2} \right)^2 \left[ G * V \left( G * V \psi_i \right) \right](r)
\]

\[
= \psi_i(r) + \frac{2m}{\hbar^2} \int_V G(r-r')V(r')\psi_i(r')d^3r' + \left( \frac{2m}{\hbar^2} \right)^2 \int_V G(r-r')V(r')G(r-r'')V(r'')\psi_i(r'')d^3r'd^3r''.
\]

In the so-called \textit{Born approximation} we consider only the first perturbation order, and inserting a plane wave, \(\psi_i(r) = e^{ikz}/(2\pi)^{3/2}\), we obtain,

\[
\psi(r) = \frac{e^{ikz}}{(2\pi)^{3/2}} - \frac{m}{(2\pi)^{3/2}2\pi\hbar^2} \int_V \frac{e^{ik|r-r'|}V(r')}{|r-r'|} e^{ikz}d^3r'.
\]

The asymptotic behavior \(r \gg r'\), it follows with (12.119) using \(z'=r' \cdot \hat{e}_z\) and defining \(k_s = k \hat{e}_r\), \(k_i = k \hat{e}_z\),

\[
\psi(r) \simeq \frac{e^{ikz}}{(2\pi)^{3/2}} - \frac{m}{(2\pi)^{3/2}2\pi\hbar^2} \int_V \frac{e^{ik(r-r')/r}V(r')}{r} e^{ikr}d^3r' \quad (12.135)
\]

\[
= \frac{e^{ikz}}{(2\pi)^{3/2}} + \frac{m}{(2\pi)^{3/2}2\pi\hbar^2} \int_V V(r')e^{i(k_i-k_s) \cdot r'}d^3r' \equiv \frac{1}{(2\pi)^{3/2}} \left( e^{ikz} + \frac{e^{ikr}}{r} f(k_i, k_s) \right),
\]

with

\[
f(k_i, k_s) \equiv \frac{m}{2\pi\hbar^2} \int_V V(r')e^{i(k_i-k_s) \cdot r'}d^3r' = -\frac{m}{2\pi\hbar^2} \langle k_s | \bar{V} | k_i \rangle.
\]

12.2.4 Spherical potentials

For spherically symmetric scattering potentials, \(V(r) = V(r)\), the Hamiltonian \(\hat{H} = p^2/2m + V(r)\) commutes with the rotation operators \(U_\omega = e^{-i\omega L/\hbar}\) around any axis \(\hat{e}_\omega\). Therefore, we can separate the angular problem and decompose the scattering problem following the irreducible representations of the rotation group. This \textit{partial wave} decomposition can be written,

\[
\psi_k(r) = \sum_{\ell=0}^{\infty} (2\ell + 1)i^\ell P_\ell(\cos \theta)R_\ell(r),
\]

where the factor \((2\ell + 1)i^\ell\) is a convention facilitating the calculation later on. By inserting this separation ansatz for the radial and angular variables into the stationary Schrödinger equation (12.113), we obtain the radial Schrödinger equation,

\[
\left[ \frac{\partial^2}{\partial r^2} - \frac{\ell(\ell+1)}{r^2} + k^2 \right] rR_\ell(r) = \frac{2m}{\hbar^2} V(r) rR_\ell(r), \quad (12.137)
\]
where $\psi_k$ must satisfy the boundary conditions (12.144). Fortunately, we can also expand the incident wave by partial waves $^7$,

$$e^{ikz} = e^{i r \cos \theta} = \sum_{\ell = 0}^{\infty} (2\ell + 1) i^\ell j_\ell(kr) P_\ell(\cos \theta) . \quad (12.138)$$

We now use the result (12.138) to find the boundary conditions for the radial waves $R_\ell$. In the infinity we have $r V(r) \to \sim 0$. For this reason,

$$R_\ell(r) \to h_\ell^{(2)}(kr) + s_\ell h_\ell^{(1)}(kr) , \quad (12.139)$$

where the Hankel functions $h_\ell^{(1,2)}(kr) \sim e^{\pm i (\rho - (\ell + 1) \pi / 2)}$ describe, respectively, incident ($h_\ell^{(2)}$) and outgoing ($h_\ell^{(1)}$) spherical waves.

To determine the coefficients $\alpha_\ell$ and $s_\ell$ we note first that, without potential, $V(r) = 0$, the solution of the radial equation (12.137) is known,

$$R_\ell(r) = j_\ell(kr) = \frac{1}{2} [h_\ell^{(2)}(kr) + h_\ell^{(1)}(kr)] , \quad (12.140)$$

such that $\alpha_\ell = \frac{1}{2}$ and $s_\ell = 1$. For $V(r) \neq 0$ the incident wave $h_\ell^{(2)}$ is the same, but not the incident $h_\ell^{(1)}$, which results in $s_\ell \neq 1$. However, particle number conservation requires that the number of particles entering the potential is equal to the number of particles coming out. That is, the total radial flow must be,

$$0 = j_r^\ell(r) = \frac{\hbar}{2i m} [R_\ell^* \partial_r R_\ell - R_\ell \partial_r R_\ell^*] = \frac{\hbar}{4mkr^2} |s_\ell|^2 - 1 , \quad (12.141)$$

approximating $2 R_\ell \sim \frac{e^{-i(\rho + \omega)} + s_\ell e^{i(\rho + \omega)}}{kr}$. Hence, $|s_\ell| = 1$, that is,

$$s_\ell = e^{2i \delta_\ell(k)} , \quad (12.142)$$

where $\delta_\ell(k)$ is the scattering phase. The scattering phase determines the solution of the scattering problem, because it fixes the scattering amplitude: Evaluating the solution (12.136) in the asymptotic limit by the formula (12.138),

$$\psi_k(r) \sim \frac{1}{2} \sum_{\ell = 0}^{\infty} (2\ell + 1) i^\ell P_\ell(\cos \theta) [h_\ell^{(2)}(kr) + e^{2i \delta_\ell} h_\ell^{(1)}(kr)]$$

$$= e^{ikr} + \frac{1}{2} \sum_{\ell = 0}^{\infty} (2\ell + 1) i^\ell P_\ell(\cos \theta) [e^{2i \delta_\ell} - 1] h_\ell^{(1)}(kr) = e^{ikr} + f_k(\theta) e^{i \delta_\ell} \sin \delta_\ell , \quad (12.143)$$

we obtain the scattering amplitude in the form $^8$

$$f_k(\theta) = \frac{1}{k} \sum_{\ell} (2\ell + 1) P_\ell(\cos \theta) e^{i \delta_\ell} \sin \delta_\ell , \quad (12.144)$$

$^7$For the more general case of arbitrary vectors $k \cdot r$, we use the addition theorem for $Y_{\ell m}$ and express $P_\ell(\cos \theta)$ by spherical functions,

$$e^{i k \cdot r} = 4\pi \sum_{\ell = 0}^{\infty} \sum_{m = -\ell}^{\ell} i^\ell j_\ell(kr) Y_{\ell m}^*(\Omega_k) Y_{\ell m}(\Omega_r) .$$

$^8$Com $h_\ell^{(1)}(kr) \sim (-i)^{\ell + 1} e^{ikr} / kr$.
We call
\[ \frac{e^{2i\delta_\ell} - 1}{2ik} = \frac{e^{i\delta_\ell}}{k} \sin \delta_\ell \equiv f_\ell \] (12.145)
the \textit{amplitude of the partial wave} \cite{622, 80}.

### 12.2.5 Scattering phase and length

In summary, we can, within the Born approximation, express the collisional state of any type of particles by isotropic potentials,

\[ \psi(r) \sim e^{ikr} + e^{ikr}/r f_k(\Omega). \] (12.146)

The scattering cross section can be written,

\[ \sigma = \int d\Omega |f_k(\Omega)|^2 = \frac{1}{k^2} \int d\Omega \sum_\ell (2\ell + 1) P_\ell(\cos \theta) \sin \delta_\ell |^2 \] (12.147)

\[ = \frac{4\pi}{k^2} \sum_\ell (2\ell + 1) \sin^2 \delta_\ell = 4\pi \sum_\ell (2\ell + 1)|f_\ell|^2 . \]

The quantity
\[ \sigma_\ell = \frac{4\pi}{k^2} (2\ell + 1) \sin^2 \delta_\ell = \frac{4\pi}{k^2} (2\ell + 1)|f_\ell|^2 \] (12.148)
is called \textit{effective partial cross section}. Obviously, \( \sigma_\ell \leq \frac{4\pi}{k^2} (2\ell + 1) \) holds. The phase shift \( e^{2i\delta_\ell} \) has a simple physical interpretation: We consider the function,

\[ e^{i\delta_\ell} j_\ell(kr + \delta_\ell) = \frac{e^{i\delta_\ell}}{2} \left[ h_\ell^{(2)}(kr + \delta_\ell) + h_\ell^{(1)}(kr + \delta_\ell) \right] \] (12.149)
\[ \sim \frac{e^{i\delta_\ell}}{2} \left[ \left( -i \right)^\ell e^{i(kr + \delta_\ell)} + \left( +i \right)^\ell e^{-i(kr + \delta_\ell)} \right] \frac{kr \gg \delta_\ell}{\frac{1}{2} [h_\ell^{(2)} + e^{2i\delta_\ell} h_\ell^{(1)}]} \sim R_\ell . \]

Now comparing the case \( V = 0 \) giving \( R_\ell(r) = j_\ell(kr) \) with the case \( V \neq 0 \) giving \( R_\ell(r) \sim e^{i\delta_\ell} j_\ell(kr + \delta_\ell) \), we notice that a positive displacement, \( \delta_\ell > 0 \), pulls the wavefunction into the potential, while a negative displacement, \( \delta_\ell < 0 \), pushes the wavefunction out, as illustrated in Fig. 12.15.

### 12.2.6 Optical theorem

Consider the amplitude for forward scattering \( f(0) \) by writing its imaginary part as,

\[ \text{Im } f(0) = \frac{1}{k} \sum_k (2\ell + 1) P_\ell(\cos \theta) \sin^2 \delta_\ell \bigg|_{\theta=0} = \frac{1}{k} \sum_k (2\ell + 1) \sin^2 \delta_\ell \equiv \frac{k}{4\pi} \sigma . \] (12.150)

With this we obtain the \textit{optical theorem},

\[ \sigma = \frac{4\pi}{k} \text{Im } f(0) . \] (12.151)

The deeper meaning of the optical theorem is the conservation of particle number: The flux of scattered particles, \((\hbar k/m)\sigma = I_{sc} \), must be extracted from the incident
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Figure 12.15: Phase shift $\delta_{\ell}(k)$ of the scattered wavefunction. (a) An attractive potential increases the kinetic energy and the wavefunction oscillates faster, which causes a positive phase shift and a negative scattering length. (b) A repulsive potential slows down the wavefunction oscillation and produces a positive scattering length. (c,d) In an attractive potential deep enough to support vibrational states, the wavefunction performs several oscillations. The sign of the scattering length then depends on the distance of the last bound state to the continuum.

flux $I_0$ by scattering, and therefore, is missing in the forward direction. It is the interference of the scattered wave with the incident wave, which diminishes the non-scattered wave and therefore creates a shadow of the scatterer in the forward direction. The particles missing in the shadow of the scatterer are precisely those that have been scattered. This is the message of the optical theorem, which is always valid in the absence of possible (inelastic) processes leading to trapping or a transformation of the particles.

12.2.6.1 Born approximation for the scattering phase

The scattering problem can be considered as solved when we know the scattering amplitude $f_k(\theta)$, since this quantity gives us the flux measured by the detector. Now, $f_k(\theta)$ is known, when we know the scattering phases $\delta_{\ell,k}$. These are, in general, determined by integrating the radial equation (12.137). Here, we expect that only angular momenta $\ell < kR_0$ ($R_0$ is the range of potential) produce significant phase shifts. Particles with larger angular momenta have collision parameters $b \sim \ell/k$ out of the potential reach. We notice that partial s-waves are always scattered, whereas partial p-waves (or higher) are only weakly scattered when the energy is weak, $E < \hbar^2/2mR_0^2$. In these cases an approximate calculation of $\delta_{\ell}$ is sufficient:

We insert (12.136) and $e^{ikz} = \sum_{\ell} \frac{1}{2} \sqrt{4\pi(2\ell + 1)} \int_{-1}^{1} dz P_{\ell}(z)e^{ikz}$ into (12.121) and
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Table 12.1: List of scattering length for various alkaline species.

<table>
<thead>
<tr>
<th>Element</th>
<th>$a_{s}^{\text{mixed}}$</th>
<th>$a_{s}^{\text{triplet}}$</th>
<th>$a_{p}^{\text{triplet}}$</th>
<th>$B_{FB,s-\text{wave}}$</th>
<th>$B_{FB,p-\text{wave}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{H}$</td>
<td>1.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2\text{H}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6\text{Li}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^7\text{Li}$</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{23}\text{Na}$</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{39}\text{K}$</td>
<td>118</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{40}\text{K}$</td>
<td>158</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{41}\text{K}$</td>
<td>225</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{85}\text{Rb}$</td>
<td></td>
<td></td>
<td></td>
<td>156</td>
<td></td>
</tr>
<tr>
<td>$^{87}\text{Rb}$</td>
<td>105</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{133}\text{Cs}$</td>
<td></td>
<td></td>
<td></td>
<td>685.43, 911.74, 1007.34</td>
<td></td>
</tr>
<tr>
<td>$^{135}\text{Cs}$</td>
<td>163</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

integration over $\Omega'$ yields,

$$f_\ell(\theta) = \frac{2m}{4\pi\hbar^2} \int_V e^{-ik'|r'|}V(r')\psi(r')d^3r'$$

$$= -\frac{2m}{\hbar^2} \sum_{\ell=0}^{\infty} (2\ell + 1)P_\ell(\cos \theta) \int_0^{\infty} dr' r'^2 V(r') j_\ell(kr') R_\ell(r') \ .$$

Comparing this formula with (12.144) we find,

$$e^{i\delta_\ell} \sin \delta_\ell = -\frac{2mk}{\hbar^2} \int_0^{\infty} dr \ r^2 V(r) j_\ell(kr) R_\ell(r) \ .$$

The result (12.153) is the Born approximation for the scattering phase $\delta_\ell(k)$. Note that $R_\ell \approx j_\ell$ is not a good approximation, in ranges where $V$ is large and $R_\ell$ strongly suppressed (f.ex., inside hard cores). For $\ell$ large we have $j_\ell \sim r^\ell$, and $\delta_\ell$ is small for a limited potential $V(r)$.

12.2.6.2 Analyticity of $s_\ell(E)$

We consider a short-range potential that disappears at $r > R_0$. The radial solution out of the reach of the potential will then be given by,

$$R_\ell(r) = \frac{1}{2} [h_\ell^{(2)}(kr) + s_\ell h_\ell^{(1)}(kr)] \ ,$$

while for $r < R_0$ the solution $R_\ell$ must be found by integrating the radial equation (12.137). The scattering phase $s_\ell$ must be chosen in a way that $R_\ell$ and $\partial_r R_\ell$ be continuous at $R_0$. The normalization factor vanishes in the logarithmic derivative,
such that,
\[ \gamma_\ell \equiv \partial_r \ln R_\ell \bigg|_{R_0} = \frac{1}{R_\ell} \frac{\partial R_\ell}{\partial r} \bigg|_{R_0} = \left. \frac{\partial_r h_\ell^{(2)} + s_\ell \partial_r h_\ell^{(1)}}{h_\ell^{(2)} + s_\ell h_\ell^{(1)}} \right|_{R_0}. \]  

(12.155)

Now
\[ s_\ell - 1 = \frac{2(\partial_r - \gamma_\ell) j_\ell}{(\gamma_\ell - \partial_r) n_\ell} \bigg|_{R_0} \]  

(12.156)
or with
\[ s_\ell - 1 = \frac{2i}{\cot \delta_\ell - i} \]  

expressing \( \delta_\ell \) by \( \gamma_\ell \),
\[ \cot \delta_\ell = \frac{(\partial_r - \gamma_\ell) n_\ell}{(\partial_r - \gamma_\ell) j_\ell} \bigg|_{R_0}. \]  

(12.157)
The partial effective cross section is,
\[ \sigma_\ell = \frac{4\pi}{k^2} (2\ell + 1) \sin^2 \delta_\ell = \frac{4\pi}{k^2} \frac{2\ell + 1}{1 + \cot^2 \delta_\ell}. \]  

(12.158)

Analyzing the expressions for \( s_\ell(\cot \delta_\ell) \) and \( \sigma_\ell(\cot \delta_\ell) \) we find that

- for \( \cos \delta_\ell = i \) the scattering phase \( s_\ell \) has a pole and \( \sigma_\ell \to \infty \);
- for \( \cos \delta_\ell = 0 \) the scattering phase is \( s_\ell - 1 \) and \( \sigma_\ell = 4\pi(2\ell + 1)/k^2 \) is maximal.

The poles of \( s_\ell \) are just the bound states: A bound state asymptotically satisfies
\[ R_\ell(r) \sim h_\ell^{(1)}(i\kappa r) \propto e^{-\kappa r} \]  

with the binding energy \( E_B = -\hbar^2 \kappa^2/2m \). The condition of continuity is given by,
\[ \gamma_\ell = \left. \frac{\partial_r h_\ell^{(1)}}{h_\ell^{(1)}} \right|_{R_0}, \]  

(12.159)
and the insertion into the general continuity condition (12.157) gives,
\[ \cot \delta_\ell = \frac{h_\ell^{(1)} \partial_r n_\ell - n_\ell \partial_r h_\ell^{(1)}}{h_\ell^{(1)} \partial_r j_\ell - j_\ell \partial_r h_\ell^{(1)}} = i . \]  

(12.160)
In the same way the zero crossings of \( \cot \delta_\ell \) correspond precisely to the scattering resonances. To see this, we expand around a resonance,
\[ \cot \delta_\ell(E) \simeq \cot \delta_\ell(E_r) - \frac{1}{\sin^2 \delta_\ell} \frac{d \delta_\ell}{dE} \bigg|_{E_r} (E - E_r) = - \frac{d \delta_\ell}{dE} \bigg|_{E_r} (E - E_r) \equiv \frac{2}{\Gamma_r} (E - E_r) , \]  

(12.161)
defining the width \( \Gamma_r = \frac{2}{\sigma(E \delta_\ell) \bigg|_{E_r}} \) of the resonance peak in the effective section \( \sigma_\ell \) in the form,
\[ \sigma_\ell = \frac{4\pi}{k^2} (2\ell + 1) \frac{(\Gamma_r/2)^2}{(E - E_r)^2 + (\Gamma_r/2)^2} . \]  

(12.162)
See Fig. 12.16,
\[ s_\ell - 1 = \frac{-i\Gamma_r}{E - (E_r - i\gamma_r/2)} . \]  

(12.163)
The scattering phase \( \delta_\ell \) increases by \( \pi \). The value \( \delta_\ell(E = 0) \) gives the number of bound states, \( \delta_\ell(0) = n_\ell \text{_{ligado}} \pi \).

\(^9\)We have for the spherical Hankel functions: \( h_\ell^{(1,2)}(x) = j_\ell(x) \pm iy_\ell(x) \).
12.3. COLD ATOMIC COLLISIONS

12.2.7 Exercises

12.2.7.1 Ex: Green’s method

Show that, knowing the solution of (12.116), that is, knowing the Green function, we can write the solution of the scattering problem (12.115) as,

\[
\psi_k(r) = e^{ikr} + \frac{2m}{\hbar^2} \int d^3r' G(r - r', k)V(r')\psi_k(r).
\]

12.2.7.2 Ex: Green’s function

Calculate the Green function of the equation (12.116).

12.2.7.3 Ex: Rutherford scattering

Consider the scattering of a particle of charge \( Q \) by a static charge distribution \( \rho(r) = \rho_0 e^{-ar} \) totaling the charge \( Q' \). Derive from (12.136) the formula (1.10) describing the Rutherford scattering.

12.2.7.4 Ex: Scattering length for hard-core potentials

Calculate the scattering length for a spherical box barrier and a spherical box potential as a function of potential depth (see also Exs. 3.1.5.4 and 3.1.5.5 and [615]).

12.3 Cold atomic collisions

Modern techniques developed in the area of atomic optics allow to cool atomic gases to temperatures well below 1 \( \mu K \). We use the expansions \( j_\ell \sim x^\ell/(2\ell + 1)!! \) and \( n_\ell \sim (2\ell - 1)!!/x^{\ell+1} \) in the equation (12.157), and obtain for \( kR_0 \ll 1 \),

\[
\cos \delta_\ell \simeq \frac{2\ell + 1)!!(2\ell - 1)!!}{(kR_0)^{2\ell+1}} \frac{\ell + 1 + R_0 \alpha_\ell(E)}{\ell - R_0 \alpha_\ell(E)}.
\]  

(12.164)
A coarse approximation leads to

\[
\cos \delta_\ell = \frac{\cos \delta_\ell \delta_\ell \ll 1}{\sin \delta_\ell} \simeq \frac{1}{\sin \delta_\ell} \simeq \frac{1}{(R_0 k)^{2\ell+1}} ,
\]

that is,

\[
\sin \delta_\ell \simeq (R_0 k)^{2\ell+1} .
\]

In other words, the scattering phases decrease rapidly, in the regime of cold collisions, with increasing \( \ell \), and \( \ell = 0 \) type collisions dominate,

\[
k \cot \delta_0 \alpha_\ell(E) \simeq \frac{1 + R_0 \alpha_0(0)}{R_0^2 \alpha_\ell(E)} .
\]

The \( s \)-wave scattering length defined by,

\[
a_s = \frac{R_0^2 \alpha_\ell(E)}{1 + R_0 \alpha_0(0)} = \frac{\sin \delta_0}{k}
\]

then it is the only relevant parameter of the collision. For \( R_0 \alpha_0 \gg 1 \) we find \( a_s \simeq R_0 \). For example, for a hard sphere we have \( R_\ell(R_0) = 0 \), \( \alpha_\ell = \infty \), \( a = R_0 > 0 \) and \( \cot \delta_0 = -1/kR_0 \). For small \( kR_0 \) we obtain \( \delta_0 \simeq -kR_0 < 0 \), which corresponds to a negative phase shift for the repulsive potential, as expected. The effective cross section is,

\[
\sigma_0 = \frac{4\pi}{k^2} \left[ \frac{1}{1 + \cot^2 \delta_0} \right] \simeq \frac{4\pi}{k^2 + 1/\alpha_s^2} .
\]

In comparison to the effective cross section for higher angular momenta, \( \sigma_\ell \propto \frac{\sin^2 \delta_\ell}{k^2} \) behaves like,

\[
\sigma_\ell \propto R_0^2 (R_0 k)^{4\ell} \to 0 .
\]

In contrast, we find that the scattering at low energies has an \( s \)-wave character, \( \sigma \) being dominated by \( \sigma_0 \),

\[
\sigma(E = 0) = 4\pi a_s^2 .
\]

For a hard sphere \( (a = R_0) \) we find an effective cross section \textit{four times larger} than classically expected \( (\sigma_{cl} = \pi R_0^2) \).

Figure 12.17: The cold collision can be described by a hard core potential.
In summary, for kinetic energies below the centrifugal barrier, only s-wave collisions are significant. The higher-order partial waves are frozen behind the centrifugal barrier. That is, the energy of cold collisions is not enough to excite a rotational motion, not even the one with the lowest rotational energy allowed by quantum mechanics. Such a collision is called cold collision or s-wave collision.

The relative wavefunction tends asymptotically to $\psi(R) \xrightarrow{R \to \infty} k_{dB}^{-1} \sin[k_{dB}(R-a)]$ as $T \to 0$. This means that for temperatures so low that the length of the Broglie wave of the relative motion is much longer than the potential range $k_{dB}^{-1} \gg R_{\text{turning}}$, the scattering becomes independent of temperature, and the scattering length $a$ becomes well defined.

Generally, a repulsive interaction potential corresponds to a positive scattering length and an attractive potential to a negative one. However, if the attractive potential supports bound states, the value of the scattering length depends on the energy of the last bound state with respect to the dissociation threshold [615, 616].

### 12.3.1 Collision cross section, unitarity regime

Note that the scattering length $a$ may have a value quite different from $r_e$, especially in the presence of a Feshbach resonance. The meaning of universality, $|a| \gg r_e$, is that short-range properties play no role in the dynamics.

At low temperatures, $kr_e \to 0$, we have the equation (12.169). In contrast, in the unitary limit, $k \to \infty$, but $r_e \to 0$, we have,

$$\sigma = \frac{8\pi}{k^2},$$

(12.172)

and the cross section becomes independent of atomic particularities. What the equation (12.169) says is, that the maximum attainable cross-section is limited to the smallest of the values $8\pi a$ and $8\pi/k$. Even though $a(B)$ can be increased to divergent values near a Feshbach resonance, for finite collision energies it will never exceed an effective value $a_{eff} = 1/\sqrt{a^2 + 1/k^2}$. For a thermal gas, $k = h^{-1}\sqrt{2\pi mk_B T}$, while for a pure condensate $k = 2\pi/L$, where $L$ is the size of the condensate. Therefore, the effective scattering length can not exceed the size of the condensate. Unitarity also means that the kinetic energy exceeds the binding energy, $k_B T \equiv \frac{h^2 k^2}{2m} \leq \frac{h^2}{2ma^2}$.

The collision rate depends on the density, temperature and collisional cross section [338],

$$\gamma_{\text{coll.peak}} = \sqrt{2}\sigma_{\text{elast}}\bar{v}n_0,$$

$$\gamma_{\text{coll.aver}} = \gamma_{\text{coll.peak}}/2\sqrt{2}. \tag{12.173}$$

Note that at the unitary limit, as $\bar{v} \propto \sqrt{T}$, we have that $\sigma_{\text{elast}} \propto T$ and $n_0 \propto \bar{v}^{-3} \propto T^{-3/2}$, such that the collision rate is independent of temperature.

At low temperatures, $k \to 0$, the delocalization of the colliding particles is greater than its short-range structure. This is the Wigner threshold law [629, 622]. For elastic collisions of neutral ground state atoms, the cross section (12.169) becomes

---

10At temperatures at which the trajectory of atoms is described by de Broglie waves the only difference between an atom before and after an elastic collision is the phase shift $\delta_0$ of this wave.
temperature-independent. Thus, the rate coefficient decreases as \( \langle \sigma \bar{v} \rangle \propto \sqrt{T} \), while the collision rate increases as \( \langle \sigma \bar{v} n_0 \rangle \propto T^{-1} \).

For inelastic collisions, \( \sigma \propto T^{-1} \). For three-body collisions see [192].

### 12.3.2 Collisions between identical particles

We consider collisions of two identical particles. Separating the center-of-mass coordinates, \( \mathbf{R} = \mathbf{r}_1 + \mathbf{r}_2 \), from the relative ones, \( \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \), we see that \( \mathbf{R} \) is symmetric and \( \mathbf{r} \) antisymmetric in \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \). We separate the wavefunction into orbital and spin parts,

\[
\Psi(x_1, x_2) = e^{i \mathbf{P} \cdot \mathbf{R}} \psi(\mathbf{r}) \chi(s_1, s_2).
\]

For indistinguishable particles the result of the scattering has the asymptotic form,

\[
\psi(\mathbf{r}) \sim e^{i \mathbf{k} \cdot \mathbf{r}} + f(\theta) e^{i k r}. \tag{12.175}
\]

#### 12.3.2.1 Spin 0 bosons

For bosons with spin 0 we have \( \chi = 1 \) and, because of the symmetry of \( \Psi \), holds \( \psi(\mathbf{r}) = \psi(-\mathbf{r}) \). Consequently, we must symmetrize the result of the scattering. We make use of the fact that the exchange of particles via \( \mathbf{r} \to -\mathbf{r} \) in polar coordinates corresponds to the transformation \( \theta \to \pi - \theta, \ r \to r \),

\[
\psi \sim (e^{i \mathbf{k} \cdot \mathbf{r}} + e^{-i \mathbf{k} \cdot \mathbf{r}}) + [f(\theta) + f(\pi - \theta)] e^{i k r}. \tag{12.176}
\]

For the effective differential cross section we obtain,

\[
\frac{d\sigma}{d\Omega} = |f(\theta) + f(\pi - \theta)|^2 = |f(\theta)|^2 + |f(\pi - \theta)|^2 + 2 \Re[f^*(\theta) f(\pi - \theta)]. \tag{12.177}
\]

The first two terms are classical. The third (interference) term appears because of quantum statistics. The angles showing up in \( (12.177) \) are illustrated in Fig. 12.19.
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For bosons, the interference terms double the cross section as compared to the classical case, when $\theta = \pi/2$,

$$
\frac{d\sigma}{d\Omega} = 4|f(\frac{\pi}{2})|^2.
$$

(12.178)

Figure 12.19: The symmetrization of the collision wavefunction produces two paths with angles $\theta$ and $\pi - \theta$, which must be added coherently.

For the isotropic potential $V(r)$ we use the partial wave representation,

$$
f(\theta) = \sum_{\ell} i^\ell f_\ell(\cos \theta).
$$

(12.179)

With $P_\ell(\cos \theta) = (-1)^\ell P_\ell(\pi - \cos \theta)$ we get,

$$
f(\theta) - f(\pi - \cos \theta) = 2 \sum_{\ell=\text{par}} i^\ell f_\ell(\cos \theta),
$$

(12.180)

and we find that only even angular momenta appear.\(^{11}\)

12.3.2.2 Spin 1/2 fermions

In the case of fermions with spin $\frac{1}{2}$ two situations are possible.\(^{12}\):

1. The singlet spin state $\chi_s = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ is antisymmetric and, consequently, the orbital part,

$$
\psi(\mathbf{r}) = \psi(-\mathbf{r})
$$

must be symmetric. The cross section is the same as for spin 0 bosons,

$$
\left. \frac{d\sigma}{d\Omega} \right|_s = |f(\theta) + f(\pi - \theta)|^2.
$$

(12.182)

2. The triplet spin states,

$$
\chi_s = \left\{ \frac{1}{\sqrt{2}} (|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) \right\} \right\} \right\}
$$

(12.183)

---

\(^{11}\)For $\ell$ odd the Legendre polynomial changes sign, and the contributions vanish.

\(^{12}\)This is analogous to the case of helium, where the spatial function of the state $2s^2 \uparrow\uparrow$ is always antisymmetric, but for the $2s \uparrow 2p \uparrow$ exist symmetric spatial orbitals.
require an antisymmetric orbital wavefunction, \( \psi(r) = -\psi(-r) \), and we obtain a scattering amplitude, \( f(\theta) \to f(\theta) - f(\pi - \theta) \), which only contains odd angular momenta \( \ell \). With this, the cross section becomes,

\[
\left| \frac{d\sigma}{d\Omega} \right|_t = |f(\theta) - f(\pi - \theta)|^2 \quad (12.184)
\]

Note that polarized fermions only scatter in channels of odd angular momenta: cold bosonic atoms show a contact potential due to s-wave collisions \((12.180)\), polarized fermionic atoms only interact weakly in the p-channel. In the case of a statistically mixed ensemble of non-polarized fermions we have a the weighted average,

\[
\frac{d\sigma}{d\Omega} = \frac{3}{4} \left| \frac{d\sigma}{d\Omega} \right|_t + \frac{1}{4} \left| \frac{d\sigma}{d\Omega} \right|_s = |f(\theta)|^2 + |f(\pi - \theta)|^2 - \Re[f^*(\theta)f(\pi - \theta)] \quad (12.185)
\]

### 12.3.2.3 Molecular spectra

Here we consider rotational spectra of low energies \( E_{\text{rot}} = \hbar^2 \ell(\ell+1)/2\Theta \ll E_{\text{eletronico}} \sim eV \). In slow time scales we can consider the electronic shell to be rigid. We look at two examples of molecules with bosonic and fermionic nuclei:

- Molecules \((\text{C}^{12})_2\): the nuclei are 0-spin bosons, so only collisions with even \( \ell \) are allowed.
- Molecules \(\text{H}_2\): the nuclei are spin-\( \frac{1}{2} \) fermions, so we have for a spin wavefunction, \( \chi = \chi_s : \ell = \text{even}, \text{para-hydrogen}, \chi = \chi_t : \ell = \text{odd}, \text{ortho-hydrogen} \). (12.186)

The transformation of ortho-hydrogen into para-hydrogen is difficult (the nuclei being well shielded), such that we observe two types of gases with,

\[
E_{\text{rot,para}} = 0, \frac{3}{\Theta}, \frac{10}{\Theta}, \frac{21}{\Theta}, ... E_{\text{rot,ortho}} = \frac{1}{\Theta}, \frac{6}{\Theta}, \frac{15}{\Theta}, ... \quad (12.187)
\]

### 12.3.3 Collisions between hot atoms

Angular moments with \( \ell \leq kR_0 \) should contribute a lot to \( \sigma \), since the collision parameter is inside \( R_0 \). For a hard sphere we have \( \alpha_{\ell} = \infty \) and \( \cot \delta_{\ell} = n_{\ell}(kR_0)/j_{\ell}(kR_0) \). With the asymptotic expressions of \( j_{\ell} \) and \( n_{\ell} \) we obtain \( \cot \delta_{\ell} \sim -\cot(kR_0 - \ell\pi/2) \), that is, \( \delta_{\ell} = kR_0 + \ell\pi/2 \) \((+\pi)\). With these scattering phases we can calculate the scattering cross section,

\[
\sigma \simeq \frac{4\pi}{k^2} \sum_{\ell=0}^{kR_0} (2\ell + 1) \sin^2 \delta_{\ell} \quad (12.188)
\]

\[
\simeq \frac{4\pi}{k^2} \sum_{\ell=0}^{kR_0} (\ell + 1) \cos^2 [kR_0 - (\ell + 1)\pi/2] + \ell \sin^2 (kR_0 - \ell\pi/2)
\]

\[
= \frac{4\pi}{k^2} \sum_{\ell=0}^{kR_0} \ell (\cos^2 + \sin^2) = \frac{4\pi}{k^2} \frac{kR_0(kR_0 + 1)}{2} = 2\pi R_0^2, \quad (12.189)
\]

which is the double of the classical value.
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Figure 12.20: (a) Bound state for $\ell = 0$. (b) Bound state for $\ell > 0$ in a potential including the centrifugal barrier $\hbar^2 \ell(\ell+1)/2mr^2$. (c) Resonances for $\ell = 0$ are broad and possibly not defined with $\Gamma_r > E_r$. A defined resonance with $\Gamma_r < E_r$ requires that $|\partial E/\partial \alpha_0|$ be large. (d) For $\ell > 0$ we obtain narrow resonances called shape resonances, because the decay of the state is suppressed by the centrifugal barrier.

12.3.4 Photoassociation during ultracold collisions

Ultra-cold collisions are an interesting example of how light can control the result of inelastic or reactive collisions. Here we discuss as a specific example the photoassociation, which illustrates the utility of the dressed states pictures. The upper panel of Fig. 12.21 shows schematic curves of (bare) potentials relevant to our discussion. Two atoms in the ground state form a relatively shallow molecular ground state characterized by electrostatic dispersion

$$ V_1(r) = -\frac{C_6}{R^6}. \quad (12.190) $$

or long-range van der Waals potential. Two other molecular states arise from the interaction of an excited atom with the ground state atom. The predominant term of the interaction is the potential of resonant dipole-dipole interactions,

$$ V_{2,3}(r) = -\mp \frac{C_3}{R^3}. \quad (12.191) $$

which gives rise to an attractive and a repulsive potential. The $R^{-3}$ dependence of the resonant dipole interaction means that the associated potentials greatly modify the asymptotic level even at internuclear distances where the ground state van der Waals potential is still relatively shallow. The photoassociation process involves a slow approach of two identical ground state atoms. A mono-modal optical field, tuned to the red of the atomic resonance, is applied. When the two atoms reach an internuclear distance $R_C$ such that the energy of the applied field $\hbar \omega_C$ exactly coincides with the potential difference $V_2(R_c) - V_1(R_c)$, the probability of transferring population from the fundamental molecular state to the excited molecular state is maximal. This molecular resonance is sometimes called Condon point. The conventional way of calculating this probability follows the procedure elaborated in Sec. 13.1 for a two-level
atom. First, we would solve the time-independent molecular Schrödinger equation to obtain the molecular wavefunctions. Then, write down the coupled differential equations by describing the time dependence of the expansion coefficients of the relevant molecular wavefunctions, solve for the coefficients and calculate the square of their absolute values. Finally, we would need to integrate the transition probability inside a region $\Delta R$ around the Condon point, where the transition probability is not be negligible. The dressed states picture allows to reduce this rather laborious program, essentially, to a problem of a curve crossing of two levels. The bottom panel of Fig. 12.21 illustrates the photoassociation in the dressed states picture. The basis states are now product states made up of the field and the molecular levels. Furthermore, we approximate the molecular states themselves as products of atomic states. This approximation is justified by the long range, weakly perturbative influence of the van der Waals and resonant dipoles interactions. Calling the ground and excited states $|1\rangle$ and $|2\rangle$, respectively, we have

$$|1, n\rangle = |1\rangle |1\rangle |n\rangle,$$  \hspace{1cm} (12.192)

and for the field-molecule excited state

$$|2, n - 1\rangle = |2\rangle |1\rangle |n - 1\rangle.$$  \hspace{1cm} (12.193)

The two molecular curves intersect at the Condon point and optically couple to the applied field. This optical coupling produces an avoided crossing near $R_C$ and mixes the states of the molecule-field basis. The well-known Landau-Zener formula (LZ) expresses the probability of traversing from one adiabatic molecular state to another as a function of the interaction strength, the relative velocity of the collision partners, and the relative slopes of the two curves. The probability of LZ is given by,

$$\exp \frac{2\pi}{v} \langle 1, n | \Omega | 2, n - 1 \rangle | \frac{d}{dR} \Delta V_{12}(R_C) |,$$  \hspace{1cm} (12.194)

where $v$ is the relative radial velocity of the approaching particles and $\frac{d}{dR} \Delta V_{12}(R_C)$ is the difference of slopes of the two non-interacting potentials at the Condon point. The dipole-field interaction operator $\Omega$ must be taken with the dipole of the molecular transition. A reasonable approximation is to take the moment of molecular transition as twice the atomic moment and average over the whole space. The result is,

$$\exp \frac{2\pi}{\sqrt{3}} \langle 1, n | \Omega_{at} | 2, n - 1 \rangle | \frac{d}{dR} \Delta V_{12}(R_C) |,$$  \hspace{1cm} (12.195)

where $\Omega_{at}$ denotes the atomic operator of the dipole-field interaction. In the case of a crossing of an essentially flat potential $V_1$ and $V_2(R) = -\frac{C_3}{R^3}$, the absolute value of the derivative of the slope difference is,

$$\left| \frac{d}{dR} \Delta V_{12}(R_C) \right| = \frac{3C_3}{R_C^3}.$$  \hspace{1cm} (12.196)

Resolve Exc. 12.3.13.1.
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12.3.5 Ground state collisions

12.3.6 Hyperfine structure

We consider the scheme (11.90), we set \( l_j = 0 \), and concentrate on \( s \)-waves, \( \ell = 0 \),

\[
\begin{align*}
\mathbf{s}_1 + \mathbf{s}_2 &= \mathbf{S} \quad \rightarrow \quad \Omega \\
\mathbf{i}_1 + \mathbf{i}_2 &= \mathbf{I} \\
f_1 + f_2 &= f
\end{align*}
\]

(12.197)

At short distances the coupling \((S,I)f_1, f_2)f\) breaks up and a \((s_1, s_2)S, I)f\) coupling emerges. This does not hold for fully stretched spin states \( f_1 + f_2 = f \), because \( f \) is a good quantum number at all distances (and small enough magnetic fields). In contrast \( m_f \) is a good quantum number at all distances and at all fields.

In order to obtain the potentials coupled by hyperfine interaction, we first calculate for a single vibrational level the relative wavefunctions \( |\psi_{(s_1,f_2)}(R)\rangle \) from the known perturbed but uncoupled potentials \( V(R) + V_{h,f} \), where,

\[
V_{h,f} = h a_{h,f,1} \mathbf{s}_1 \cdot \mathbf{i}_1 + h a_{h,f,2} \mathbf{s}_2 \cdot \mathbf{i}_2 .
\]

(12.198)

The antisymmetric part is negligible [606], so that \( V_{h,f} \simeq \frac{1}{2} h a_{h,f,1} \mathbf{S} \cdot \mathbf{i}_1 + \frac{1}{2} h a_{h,f,2} \mathbf{S} \cdot \mathbf{i}_2 \). Then couple the channels via,

\[
|\psi_{(S,I)f}(R)\rangle = A \sum_{f_1,f_2} \sqrt{S^I} \hat{f}_1 \hat{f}_2 \left\{ \begin{array}{ccc} s_1 & s_2 & S \\ i_1 & i_2 & I \\ f_1 & f_2 & f \end{array} \right\} |\psi_{(f_1,f_2)}(R)\rangle
\]

(12.199)

\[
|\psi_{(f_1,f_2)}(R)\rangle = A^{-1} \sum_{S,I} \sqrt{S^I} \hat{f}_1 \hat{f}_2 \left\{ \begin{array}{ccc} s_1 & s_2 & S \\ i_1 & i_2 & I \\ f_1 & f_2 & f \end{array} \right\} |\psi_{(S,I)f}(R)\rangle.
\]

which satisfies the orthogonality relation (see Tables in 7.1.3).
12.3.7 Scattering length in specific channels

The scattering length in specific channels can be expressed via singlet and triplet scattering length,

\[ a_{|f_1,m_{f1}|,|f_2,m_{f2}|} = P_{S=0}a_s + P_{S=1}a_t. \] (12.200)

The projectors are \( P_s = |\langle S|(f_1,f_2)f\rangle|. \) According to [90] or [416] the recoupling from the uncoupled hyperfine representation into the short range representation is given by,

\[ \langle S|m_S I_{m_I} l' m_{l'}|f_1 m_{f1} f_2 m_{f2} l m_l\rangle = \delta_{ll'}\delta_{m'm_s'} \sum_{f,m_f} \langle S|m_S I_{m_I}|f_{1m_{f1}} f_{2m_{f2}}|m_f\rangle \times \]

\[ \times \left( \begin{array}{ccc} s_1 & s_2 & S' \\ i_1 & i_2 & f \end{array} \right) \sqrt{S'} I_{f_1 f_2} \left( \frac{1 - (1 - \delta_{f_1 f_2})(-1)^{S + l + l'}}{\sqrt{2} - \delta_{f_1 f_2}} \right). \] (12.201)

The last bracket is dropped for unsymmetrized recoupling. Calculations have been done for \(^{87}\text{Rb}\) collisions and for \(^{6}\text{Li}^{87}\text{Rb}\) collisions. It turns out that the fully stretched states have pure triplet character.

Note that in strong magnetic fields the coupling \((i_1, i_2)I\) easily breaks up, and the recoupling to be considered is rather \(\langle S|m_S m_{i1} m_{i2} l' m_{l'}|f_1 m_{f1} f_2 m_{f2} l m_l\rangle\).

12.3.8 Hyperfine coupling in magnetic fields

12.3.8.1 Zeeman splitting of bound states

The splitting of the bound state is described by [606],

\[ H_{int}^+ = V_{hf}^+ + V_{Zeeman} \]

\[ = E_B + \frac{1}{2} \hbar a_{hf,1} S \cdot i_1 + \frac{1}{2} \hbar a_{hf,2} S \cdot i_2 + \mu_B B (g_S S + g_{i1} i_1 + g_{i2} i_2), \] (12.202)

such that,

\[ \langle m_{i1}' m_{2'} m_{f2}' | H_{hf} + H_B | m_S m_{i2} m_{i1} \rangle \]

\[ = E_B + (g_S m_S + g_{i1} m_{i1} + g_{i2} m_{i2}) \mu_B B \delta_{m_{i1}' m_{i1}} \delta_{m_{i2}' m_{i2}} \delta_{m_{f2}' m_{f2}} \]

\[ + \frac{1}{2} \hbar (a_{hf,1} m_{i1} m_S + a_{hf,2} m_{i2} m_S) \delta_{m_{i1}' m_{i1}} \delta_{m_{i2}' m_{i2}} \delta_{m_{f2}' m_{f2}} \]

\[ + \frac{1}{4} \hbar a_{hf,1} (i_1, S_- \delta_{m_{f2}' m_{f2}} m_{s} + 1 \delta_{m_{i1}' m_{i1}} m_{i1} - 1 + i_1, S_+ \delta_{m_{i1}' m_{i1}} m_{i1} - 1 \delta_{m_{f2}' m_{f2}} m_{s} + 1) \delta_{m_{i2}' m_{i2}} \]

\[ + \frac{1}{4} \hbar a_{hf,2} (i_2, S_- \delta_{m_{f2}' m_{f2}} m_{s} + 1 \delta_{m_{i2}' m_{i2}} m_{i2} - 1 + i_2, S_+ \delta_{m_{i2}' m_{i2}} m_{i2} - 1 \delta_{m_{f2}' m_{f2}} m_{s} + 1) \delta_{m_{i1}' m_{i1}}. \] (12.203)

For an example on how to evaluate the matrix at various magnetic fields and obtain the hyperfine structure of a bound state in the Zeeman and the Paschen-Back regime, we propose the systems \(^{6}\text{Li}^{23}\text{Na}\) and \(^{6}\text{Li}^{87}\text{Rb}\).

12.3.8.2 Magnetic dipole interaction

Reads,

\[ V_{dd} = \frac{\mu_0}{4\pi R^3} [\mu_1 \cdot \mu_1 - 3(\mu_2 \cdot \mathbf{R})(\mu_2 \cdot \mathbf{R})] \] (12.204)

neglecting nuclear spin.
12.3. COLD ATOMIC COLLISIONS

12.3.8.3 Second-order spin-orbit interaction

First-order spin-orbit interaction disappears for ground state collisions. But second-order spin-orbit interaction may occur. These lead to inelastic losses (see next section).

12.3.8.4 Selection rules

The selection rules for bosonic homonuclear collisions are,

\[ S = 0, \ldots, s_1 + s_2 \]
\[ I = 0, \ldots, i_1 + i_2 \]
\[ f_j = |i_j - s_j|, \ldots, i_j + s_j \]
\[ |I - S| \leq F \leq I + S \]
\[ |f_1 - f_2| \leq F \leq f_1 + f_2 \]
\[ (-1)^I = (-1)^S \text{ for all } F \]
\[ (-1)^{f_1} = -(-1)^{f_2} \text{ for all odd } F \].

What does they look like for fermions? What does they look like for heteronuclear collisions?

12.3.9 Inelastic collisions

12.3.9.1 Spin changing collisions

These have their origin in spin exchange and spin dipole-dipole processes. Spin exchange occurs when the colliding electronic clouds overlap. At short distances the \((S, I)_{f_1, f_2}f\) breaks up and a \(((s_1, s_2)S, I)f\) coupling remixes according to Fig. ??.

Hence, collisions between atoms \(|f_1, m_{f_1}\rangle|f_2, m_{f_2}\rangle\) are subject to spin exchange induced by coupling of the spin states via the exchange interaction, e.g. \(|2, 1\rangle|2, 1\rangle \rightarrow |2, 2\rangle|2, 0\rangle\). Typical exchange rates are on the order of \(10^{-10}\) cm\(^3\)/s.

Since \(f\) is a good quantum number at all distances (for \(B = 0\)), spin exchange processes conserve \(\ell\) and \(f\). Hence, the fully stretched spin states \(f_1 + f_2 = f\) cannot decay into other states, except by higher-order processes, such as dipolar relaxation. Consequently, the relaxation rates for \(|2, 2\rangle + |2, 2\rangle\) or \(|1, -1\rangle + |1, -1\rangle\) states are only on the order of \(10^{-15}\) cm\(^3\)/s.

The cross section for inelastic spin exchange collisions is \([625, 123]\),

\[ \sigma = M_{if} \pi (a_t - a_s)^2 , \] (12.206)

where,

\[ M_{if} = \left[ \sum_{m_S, I, m_I} \left(C_{S=0} C'_{S=0} - C_{S=1} C'_{S=1}\right) \right]^2 \] (12.207)

\[ C = \langle S, m_S; I, m_I | F_1 m_1; F_2 m_2 \rangle . \]

See also [554]. The reason for the above dependence can be understood as follows. \(a_s\) and \(a_t\) determine the energy of the last bounds states of the singlet and triplet
potentials. The more those energies are different, the stronger the coupling \( \propto |E_t - E_s|^{-1} \). An alternative, physical picture is given in [91].

12.3.9.2 Dipolar relaxation

The fully stretched spin states, such as \(^{87}\text{Rb} |f = 2, m_f = 2\rangle\) are expected to be quite stable. However, relativistic effects (retardation?) (and 2\(^{nd}\) order spin-orbit coupling) break the degeneracy of the molecule-fixed projection \( |\Omega| = 0, 1 \) of the \(^3\Sigma\) potential [416]. When the atoms approach their spins recouple, i.e. from \([s_1, i_1)f_1, (s_2, i_2)f_2]\) towards \([(s_1, s_2)s, (i_1, i_2)i]\) as described by the \(9j\) coefficients Eq. (12.197). Due to the symmetry of the problem, \( f \) and its projection \( m_f \) are good quantum numbers at all distances. However, if there is a higher-order admixture of the orbit \( l_j \), the symmetry is broken, and the quantum number depends on the coupling schemes. Consequently, transitions between different \( m_f \) become possible, i.e. dipolar relaxation may change \( f, m_f \) or \( \ell = 0 \), e.g. a collision can be \( s\)-wave in the entrance and \( d\)-wave in the exit channel.

12.3.9.3 Three-body collisions

The trapped low-field seeking alkali gases are metastable versus 3-body recombination. 3-body recombination is the combination of two colliding atoms to a dimer in presence of a third atom receiving the excess energy as kinetic energy and results in trap loss of the molecule and of the atom. They are suppressed as the gas gets more and more dilute since the rate goes like \( n^3 \). There might be interesting 3-body resonance phenomena like the Efimov state predicted for Helium droplets [182], [378] and recently seen in experiment [359, 580, 80, 387].

3-body recombination is in contrast to the more controlled way of creating molecules via photoassociation or coherent free-bound coupling.

Ultracold collisions are crucial for BEC. They provide the thermalizing elastic collisions necessary for evaporative cooling, they are the cause for the condensate self-energy and give rise to nonlinearities in the condensate dynamics. But they are also interesting by themselves. The spectrum of two-body collisions exhibits interesting features like shape- and Feshbach resonances [294, 303]. Their analysis facilitates detailed conclusions on the nature of the interaction potentials. Three body collisions are important to investigate, because they constitute a decay mechanism of the intrinsically metastable system that represents a trapped Bose-gas.

Three body collisions are not a quantum statistical effect and don’t require the presence of a BEC, but they occur only at very high densities comparable to those necessary for BEC. It should be possible to detect them in photoassociation (PA) spectra. Photoassociation provides a tool to explore the level structure of excited states by shining in a laser with frequency \( \nu \) tuned between the colliding channel and a vibrational bound level of the excited state potential. Since the excited state preferentially decays into the continuum, where the atoms have high kinetic energy, the transition rate may be monitored via trap losses. Or we can shine in an additional laser that further excites the excited atoms into the ionized continuum where they can be registered by an ion detector.

Three-body photoassociation processes should reveal themselves by additional lines in the two-body photoassociation spectra. Those lines should only appear at
very high densities and their strength should scale as the density cubed,

\[ Rb + Rb + Rb + h\nu \rightarrow Rb_3^* . \]  \hspace{1cm} (12.208)

### 12.3.9.4 Other processes

Majorana spin flips and collisions involving higher partial waves \( \ell \) can eventually lead to spin relaxation. In Eq. (11.90) we see that \( f \) is not necessarily a good quantum number in contrast to \( F \), \( |2, 2\rangle|2, 2\rangle \rightarrow |2, 1\rangle|2, 0\rangle + E_{rot} \). However, the particles must tunnel across the centrifugal barrier, which sets temperature constraints.

### 12.3.9.5 Collisions between fermions

Very cold three-body collisions are suppressed for fermions, because two of them necessarily must have the same quantum state, which violates the Pauli exclusion principle. This is useful for employing Feshbach resonances to form molecular BECs made of fermions.

### 12.3.10 Excited states collisions

#### 12.3.10.1 Adiabatic potentials

We consider the scheme (11.90), we set \( I = 0 \), and we concentrate on \( s \)-waves, \( \ell = 0 \),

\[
\begin{align*}
I_1 + I_2 &= L \xrightarrow{\hat{z}} \Lambda \\
S_1 + S_2 &= S \xrightarrow{\hat{z}} \Sigma \\
J_1 + J_2 &= J \xrightarrow{\hat{z}} \Omega
\end{align*}
\]  \hspace{1cm} (12.209)

The *spin-orbit interaction* splits the potential curves. The recoupling is described by,

\[
|\psi_{(L,S)J}(R)\rangle \sim \sum_{j_1, j_2} \sqrt{L_S J_1 J_2} \begin{pmatrix} l_1 & l_2 & L \\ s_1 & s_2 & S \\ j_1 & j_2 & j \end{pmatrix} |\psi_{(j_1, j_2)J}(R)\rangle . \]  \hspace{1cm} (12.210)

#### 12.3.10.2 Homonuclear collisions

Let us consider the example of the fine structure in homonuclear \(^{87}\text{Rb}\) collisions. Without hyperfine, rotational and Zeeman splitting the recoupling goes like illustrated in Fig. 12.22.

From Fig. 12.22 we see that the molecular states are remixed at long range: Every state \( 0_g^-, 0_u^-, 0_g^+, 0_u^+ \) has several molecular states to which it connects, e.g. \( 0_g^- \) connects within the fine structure to \( (2)^3\Sigma_g^+ \) and \( (2)^3\Pi_g \). Those multiplets form a closed interacting subspace. According to Movre and Pichler [439, 598] we get
with $\Delta = E(2P_{3/2}) - E(2P_{1/2}) = \frac{3}{3} A_{so}$,

$$0^-_\sigma = \begin{pmatrix} E(3\Pi_\sigma) - \frac{1}{3} \Delta & \frac{\sqrt{2} \Delta}{3} \\ -\frac{\sqrt{2} \Delta}{3} & E(3\Sigma^+_\sigma) \end{pmatrix} , \quad 0^+_\sigma = \begin{pmatrix} E(3\Pi_\sigma) - \frac{1}{3} \Delta & -\frac{\sqrt{2} \Delta}{3} \\ -\frac{\sqrt{2} \Delta}{3} & E(1\Sigma^+_\sigma) \end{pmatrix}$$

$$1^-_\sigma = \begin{pmatrix} E(3\Pi_\sigma) & \frac{1}{3} \Delta & -\frac{1}{3} \Delta \\ \frac{1}{3} \Delta & E(1\Pi_\sigma) & -\frac{1}{3} \Delta \\ -\frac{1}{3} \Delta & -\frac{1}{3} \Delta & E(3\Sigma^+_\sigma) \end{pmatrix} , \quad 2^-_\sigma = (3\Pi_\sigma) .$$

At short range the potentials approximately go like,

$$E(1\Sigma^+_g), E(3\Sigma^+_u) \propto 2C_3/R^3$$

$$E(1\Pi_u), E(3\Pi_g) \propto C_3/R^3$$

$$E(1\Pi_g), E(3\Pi_u) \propto -C_3/R^3$$

$$E(1\Sigma^+_u), E(3\Sigma^+_g) \propto -2C_3/R^3 .$$

Inserting the short range potentials and defining $X = \sigma C_3/3\Delta R^3$, $Y = E/\Delta$ and
\( \sigma = + \) for \( g \) and \(-\) for \( u \),

\[
0^{-}_\sigma = \begin{pmatrix}
3X + \frac{1}{3} & \frac{\sqrt{2}}{3} \\
-\frac{\sqrt{2}}{3} & -6X + \frac{2}{3}
\end{pmatrix}, \quad 0^{+}_\sigma = \begin{pmatrix}
3X + \frac{1}{3} & \frac{\sqrt{2}}{3} \\
\frac{\sqrt{2}}{3} & 6X + \frac{2}{3}
\end{pmatrix}
\] (12.213)

\[
1_\sigma = \begin{pmatrix}
3X + \frac{1}{3} & \frac{1}{3} & -\frac{1}{3} \\
-\frac{1}{3} & -3X + \frac{1}{3} & -\frac{1}{3} \\
-\frac{1}{3} & -\frac{1}{3} & -6X + \frac{2}{3}
\end{pmatrix}, \quad 2_\sigma = (3X + 1).
\]

Note that the structure looks very much like the transition from the Zeeman to the Paschen-Back regime, where \( X \) plays the role of the magnetic field and \( Y \) the level shift. The characteristic equations are,

\[
Y^2 - (1 - 3X)Y - 18X^2 = 0 \quad \text{for} \quad 0^{-}_\sigma
\]

\[
Y^2 - (1 + 9X)Y + (4X + 18X^2) = 0 \quad \text{for} \quad 0^{+}_\sigma
\]

\[
Y^3 + (-2 + 6X)Y^2 + (1 - 8X - 9X^2)Y + (2X + 6X^2 - 54X^3) = 0 \quad \text{for} \quad 1_\sigma
\]

\[
Y - (1 + 3X) = 0 \quad \text{for} \quad 2_\sigma
\] (12.214)

### 12.3.11 Heteronuclear collisions

For a collision in the channel \( ^6\text{Li} P ^{87}\text{Rb} S \) we get the \( \{9j\}\)-symbol,

\[
\begin{pmatrix}
\ell_6 & \ell_{87} & L \\
\sigma_6 & \sigma_{87} & S \\
\jmath_6 & \jmath_{87} & j
\end{pmatrix} = \begin{pmatrix}
0 & 1 & 1 \\
\frac{1}{2} & \frac{1}{2} & S \\
\frac{1}{2} & \frac{1}{2} & \jmath \to \Omega
\end{pmatrix}.
\] (12.215)

We thus expect a fine structure \( j_{87} = \frac{1}{2}, \frac{3}{2} \) at long range and exchange interactions \( S = 0, 1 \) at short range. For the projection onto the internuclear axis \( |L - S| \leq \Omega \leq L + S \).

Let \( V_k(R) \) be the uncoupled potentials and,

\[
\Delta_{kl}(R) = D_{kl} + A_{kl}(1 - e^{-B_{kl}(R-R_{kl})})^2 - 1
\] (12.216)

the spin-orbit functions modeled as Morse potentials, where \( D_{kl} \) is related to the fine-structure splitting, \( D_{kl} = \frac{1}{3}(E_k - E_l) \), for diagonal and, \( D_{kl} = \frac{\alpha}{3}(E_k - E_l) \), for off-diagonal elements. For heteronuclear molecules like \( ^6\text{Li}^{87}\text{Rb} \) we have matrices like [52, 51],

\[
\begin{array}{cccccccc}
| & |^{3\Sigma^+} & |^{3\Pi} & |^{1\Sigma^+} & |^{3\Pi} & |^{3\Sigma^+} & |^{3\Pi} & |^{3\Pi} \\
\hline
\ell_\Pi = 0 & v^{(3\Sigma)} & \Delta_{ab} \sqrt{2} \\
\ell_\Pi = 0 & \Delta_{ab} \sqrt{2} & v^{(3\Pi)} - \Delta_{bb} \\
\ell_\Pi = 0 & v^{(1\Sigma)}(-2\Delta_{bb}) & -\Delta_{ab} \\
\ell_\Pi = 1 & -\Delta_{bb} & v^{(3\Pi)}(+\Delta_{bb}) \\
\ell_\Pi = 1 & v^{(3\Sigma)} & \Delta_{ab} & \Delta_{cb} \\
\ell_\Pi = 1 & \Delta_{ab} & v^{(1\Pi)} & -\Delta_{cb} \\
\ell_\Pi = 2 & \Delta_{cb} & -\Delta_{bb} & v^{(3\Pi)} \\
\ell_\Pi = 2 & v^{(3\Sigma)} & \Delta_{ab} & \Delta_{cb}
\end{array}
\] (12.217)

for every fine structure. For example, there is a matrix for the two \( ^6\text{Li} S_{1/2} ^{87}\text{Rb} P_{1/2,3/2} \) asymptotes and another one for the \( ^6\text{Li} P_{1/2,3/2} ^{87}\text{Rb} S_1 \) asymptotes. Additional terms enter via rotational effects [52].
Concretely,

\[ \Delta_{bb}(R \to \infty) = \frac{1}{3}(E_{3/2} - E_{1/2}) \]  
\[ \Delta_{cB}(R \to \infty) = \frac{1}{3}(E_{3/2} - E_{1/2}) \]  
\[ \Delta_{bB}(R \to \infty) = \frac{1}{3}(E_{3/2} - E_{1/2}) \]  
\[ \Delta_{cb}(R \to \infty) = \frac{1}{3}(E_{3/2} - E_{1/2}) \] .

12.3.11.1 Inelastic trap losses

Between ground and excited states fine changing collisions and radiative escape are possible. Between two ground states only hyperfine changing collisions may occur.

The nature of the collision process, whether it is a one-\(^{13}\), two-, or three-body collision, reveals itself via the temporal behavior of trap losses. Using the abbreviation,

\[ \langle \eta \rangle \equiv \frac{1}{N} \int \eta(r)n(r)d^3r \] ,

\(^{13}\)By one-body collision we mean collisions with atoms of the background gas.
we can write the loss rates due to inelastic one-, two-, and three-body collisions,
\[ B \langle 1 \rangle N , \quad K \langle n \rangle N , \quad L \langle n^2 \rangle N . \] (12.220)

the prefactors depend on the collision velocity (that is, the temperature of the sample) and atomic parameters (for example, the collision cross section for two-body collisions, which may itself depend on temperature). Hence, the total number of trapped atoms evolves according to,
\[ \dot{N} = -B \langle 1 \rangle N - K \langle n \rangle N - L \langle n^2 \rangle N . \] (12.221)

Assuming a gaussian density distribution,
\[ n(r) = \frac{N}{(2\pi)^{3/2}r^3} e^{-r^2/2r^2} , \] (12.222)

we calculate,
\[ \dot{N} = -BN - \frac{K}{(4\pi)^{3/2}r^3} N^2 - \frac{L}{3^{3/2}(2\pi)^{3}r^6} N^3 . \] (12.223)

Fig. 12.25 shows a simulation of Eq. (12.223).

For condensates in the Thomas-Fermi limit [564] found the following differential equations for two- and three-body collisions,
\[ \frac{\dot{N}}{N} = -Gc_2 N^{2/5} - \frac{1}{r} \quad \text{and} \quad \frac{\dot{N}}{N} = -Lc_3 N^{4/5} - \frac{1}{r} . \] (12.224)
12.3.12 Heteronuclear electric dipole moment

The *electric dipole moment* of a dimer is highest for big mass difference, as in the case of LiRb and for low vibrational quantum number [353, 25]. The electric dipole moment determines the rate for spontaneous and *black-body radiation*, \( \bar{n} = (e^{-\beta \hbar \omega} - 1)^{-1} \), induced transitions between rovibrational states [354], \( \Gamma_{vlm}^{\text{tot}} = \Gamma_{vlm}^{\text{spnt}} + \Gamma_{vlm}^{\text{bb}} \). With the transition rate between individual levels,

\[
\Gamma_{vlm \rightarrow \nu'\nu'm'}^\alpha = \frac{8\pi}{3} \frac{\omega^3}{\hbar c^3} |\langle \psi |d| \rangle|^2 ,
\]

we can estimate the rates for spontaneous emission,

\[
\Gamma_{vlm}^{\text{spnt}} = \sum_{\nu'\nu'm'} \Gamma_{vlm \rightarrow \nu'\nu'm'}^{\text{em}} ,
\]

and for black-body radiation,

\[
\Gamma_{vlm}^{\text{bb}} = \sum_{\nu'\nu'm'} \bar{n}\Gamma_{vlm \rightarrow \nu'\nu'm'}^{\text{em}} + \sum_{\nu''\nu''m''} \bar{n}\Gamma_{vlm \rightarrow \nu''\nu''m''}^{\text{abs}} .
\]

Note that selection rules require \( |l - l'| \leq 1 \) and \( |m - m'| \leq 1 \), rotational transitions are inhibited by small \( \omega^3 \), spontaneous emission is high for intermediate levels for which on one hand \( \omega^3 \) is large enough and enough final states are available.

From calculations of the \( R \)-dependence of the electric dipole moments [25] the dipole moment of a specific vibrational state is easily estimated from,

\[
d = \frac{\int \psi(R)R\psi(R) dR}{\int \psi(R)\psi(R) dR} .
\]

In electric fields the dipole moments will lead to Stark shifts. For \( |d| = 1 \) Debye in a field of 1 V/m we expect a Stark shift of \( H_{\text{Stark}} \approx 500 \text{ kHz} \). It may be possible to measure this by photoassociation spectroscopy. Note also that since homonuclear dimers do not have a permanent electric dipole moment, transitions between vibrational ground states are forbidden.
12.4. RESONANCES IN COLD COLLISIONS

Figure 12.26: (code) (a) Dipole moment at the example of LiRb as a function of interatomic distance. (b) Dipole moment at the example of LiRb as a function of vibrational quantum number.

12.3.13 Exercises

12.3.13.1 Ex: Photoassociation

Consider a laser focused into a cold, confined cloud of Na atoms at a temperature of 450 µK. For a detuning of 600 MHz, calculate the laser intensity (in W/cm$^2$) required to produce a 25% probability of photoassociation. The transition moment (a.u.) of Na is 2.55.

12.3.13.2 Ex: Vibrational structure of LiRb

Calculations of the vibrational structures of several ground states of the heteronuclear molecule LiRb.

12.4 Resonances in cold collisions

12.4.1 Shape resonances

The 'centrifugal' term can give rise to repulsive walls for attractive potentials. Behind these walls, quasi-bound states can develop and give rise to collision resonances. That is, resonances emerge in the collision cross section as a function of the collision temperature called shape resonances.

12.4.2 Feshbach resonances

The so-called Feshbach resonance is due to an energetic match between a collision channel and a bound molecular state [196, 594, 595, 426, 194, 427, 607]. They allow to vary the scattering length $a_s$ almost arbitrarily from zero, where the atomic cloud turns into an ideal gas, up to values exceeding the total size of the cloud.

The impact of a Feshbach resonance can be understood as a perturbation of the collisional channel leading to a modification of the depth of the scattering potential. When this leads to the promotion of one more vibrational state into (or from) the
continuum, this obviously leads to a dramatic modification of the scattering length \( a_s \).

Let us consider two very cold atoms colliding on an attractive interatomic potential \( V(R) \) (see Fig. 12.28,right). At long distances the relative wavefunction is a sine characterized by the Broglie wave vector \( k_{dB} \). As the atoms approach each other, they mutually accelerate, and the Broglie wave performs some small and rapid oscillations within the potential. The number of nodes of the wavefunction within the potential corresponds to the number of bound vibrational levels that the potential with a given depth can support. The scattering length \( a_s \) is defined as the phase slip, which the Broglie wave would acquire during the collision at the boundary \( k_{dB} \rightarrow \infty \).

With the possibility of gradually decreasing the depth of the molecular potential, at some point the last state below the ionization threshold goes to the continuum of unbound states, the wavefunction decreases the number of nodes by one unit, while the scattering cross section crosses a singularity. In fact, the potential \( V(R) \) can be manipulated with the help of radiation fields [194, 67, 427] or, near a collisional \textbf{Feshbach resonance}, by magnetic fields [595, 596]. Feshbach resonances were predicted in nuclear systems [196]. Its recent revival in the context of cold atomic collisions is due

\[ 14 \text{ Note that the divergence of the scattering length is an artifact of the hard core approximation, that is, the regularization of the interaction potential, since the matrix } \mathcal{T} \text{ by itself does not diverge.} \]
to the prospect of its use for manipulating the scattering length and thus controlling
the mean-field energy of a Bose-Einstein condensate.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.29}
\caption{(code) (a) Scattering length and (b) collision cross section upon crossing a
Feshbach resonance. The scattering length can be positive (solid red line) or negative (dashed
blue line). A movie on a simulation of a Feshbach resonance can be watched here.}
\end{figure}

The collisional \textit{Feshbach resonance} arises when the energy of the state of two
colliding atoms coincides with the energy of a vibrational molecular level belonging
to a higher energy asymptote (see Fig. 12.28, right). This coincidence can strongly
perturb the collisional channel, because the resonance shifts the phase of the relative
de Broglie wavefunction and allows the atoms to tunnel into the molecular state
for a short period of time, the duration of which is determined by the Heisenberg
uncertainty relation. If the sum of the magnetic dipole moments of the atoms is
different from the dipole moment of the molecule, the resonance can be tuned via
external magnetic fields exploring the Zeeman effect. When a Feshbach resonance is
crossed, the scattering length crosses a singularity, as shown in Fig. 12.29 (left).\textsuperscript{16}

\section{12.5 Light-assisted collisions}

\textsuperscript{15}It is even possible to invert the sign of the scattering length. This was a prerequisite for conden-
sation of the atomic species of \textsuperscript{85}Rb \textsuperscript{510}. In addition, Feshbach resonances are interesting because
they can install a coherent free-bound coupling between an \textit{open-channel} of colliding atoms and a
bound molecular state of the same atoms, as shown in Fig. 12.28. This coupling can lead to the
creation of molecular condensates.
Part III

Quantum Optics
Chapter 13

Interaction of light with mono-electronic atoms

13.1 Semiclassical theory of the excitation of atomic transitions

In Secs. 1.2 we introduced the Einstein coefficients $A$ and $B$, which we associated with Planck’s spectral distribution of black-body radiation. This procedure allowed us to connect the coefficients for spontaneous and stimulated transitions, but did not provide any method to calculate them from the intrinsic properties of the atoms. The purpose of this chapter is to find expressions for the rates of absorption and emission of atomic radiation using quantum mechanics and to relate them to the Einstein coefficients. As for all rates, we will find that these rates should be expressed in terms of probabilities for absorption and emission. Several disciplines such as spectrometry, spectroscopy and astrophysics have developed their own terminologies to describe absorption and emission of light by matter. We will explain how the most frequently used parameters are interrelated by placing particular emphasis on the simplest system, which is the two-level atom with no degeneracy and no spin.

In a model of an isolated atom, the atomic energy levels are eigenstates of the Hamiltonian and describe the system completely, i.e. they do not undergo any evolution. To accurately describe an atom, one has to consider its coupling to the field of the electromagnetic vacuum. The total system has different eigenstates and their projection on the unperturbed eigenstates changes over time. We will show in the following, that an excited atomic state has a constant probability, depending on the coupling to the electromagnetic field, to decay to another state. Thus, the probability of measuring a specific lifetime follows a Poisson distribution.

13.1.1 Time-dependent perturbation by a plane wave

Looking at the Hamiltonian (9.11) describing the interaction of a charged particle with an electromagnetic field, we find that the term $A \cdot \nabla \propto e^{i\omega t}$ oscillates with frequency $\omega$, while the term $A^2 \propto e^{2i\omega t}$ oscillates with twice that frequency. We will only consider the interaction term (9.12), which is linear in $A$, and we will treat this term as first-order perturbation by time-dependent perturbation theory (TPDT).

With this scope we separate the Hamiltonian in a stationary part and a time-
dependent part \(^1\),

\[ \hat{H}(t) = \hat{H}^{(0)} + \hat{H}_{\text{int}}(t) \quad \text{with} \quad \hat{H}_{\text{int}} = \frac{e}{m} \mathbf{A}(r, t) \cdot \hat{\mathbf{p}} , \] (13.1)

where \( \hat{H}^{(0)} \) contains the kinetic energy and the Colombian potential of Eq. (9.11). In Sec. 5.4.5, inserting the expansion,

\[ |\psi\rangle = \sum_k a_k(t)|k\rangle e^{-iE_k t/\hbar} , \] (13.2)

along with the Hamiltonian (13.1) in the Schrödinger equation, we obtained the first order perturbative approximation (5.71). Setting the initial condition to \( c_k(t \leq 0) = \delta_{ki} \) and supposing that the probability of finding the atom initially in the ground state \( |i\rangle \) for short times is 1, we got,

\[ a_f^{(1)}(t) \simeq \frac{1}{i\hbar} \int_0^t \langle f|\hat{H}_{\text{int}}|i\rangle e^{i\omega f t'} dt' . \] (13.3)

We now consider a perturbation by an electromagnetic plane wave within the Coulomb gauge,

\[ \Phi = 0 \quad \text{and} \quad \nabla \cdot \mathbf{A} = 0 . \] (13.4)

The solution of the wave equation can be written,

\[ \mathbf{A}(r, t) = \mathbf{A}_0^*(r)e^{i\omega t} + \mathbf{A}_0(r)e^{-i\omega t} . \] (13.5)

For plane waves,

\[ \mathbf{A}_0(r) = \mathbf{A}_0 e^{ik \cdot r} \] (13.6)

and \( k = \omega/c \) and \( k \cdot \mathbf{A}_0 = 0 \). With this, it is possible to show (see Exc. 13.1.4.1), that the energy density is,

\[ u(\omega) = \frac{\varepsilon_0}{2} \mathbf{E}^2 + \frac{1}{2\mu_0} \mathbf{B}^2 = 2\varepsilon_0 \omega^2 A_0^2 . \] (13.7)

On the other hand, the energy density is proportional to the number of photons \( N(\omega) \) inside the volume \( V \),

\[ u(\omega) = \frac{N(\omega)\hbar \omega}{V} . \] (13.8)

The intensity corresponds to a flow of energy,

\[ I(\omega) = u(\omega) c . \] (13.9)

Separating the polarization \( \hat{\epsilon} \) from the amplitude \( A_0 \),

\[ A = \hat{\epsilon} A_0 e^{i k \cdot r} e^{-i \omega t} + \text{c.c.} , \] (13.10)

\(^1\)The energy of the light field is not considered in the Hamiltonian, because it is treated as classical, that is, its energy commutes with the other observables of the system.
and inserting the perturbation (13.1) into the approximation (13.3),

\[
a^{(1)}_f(t) = -\frac{e}{m} \int_0^t dt' \langle f | A \cdot \nabla | i \rangle e^{i\omega_f t'} dt' \\
= -\frac{eA_0}{m} \langle f | e^{i\mathbf{k}\cdot\mathbf{r}^\dagger} \cdot \nabla | i \rangle \int_0^t dt' e^{i(\omega_f - \omega)t'} dt' - \frac{eA_0}{m} \langle f | e^{-i\mathbf{k}\cdot\mathbf{r}^\dagger} \cdot \nabla | i \rangle \int_0^t dt' e^{i(\omega_f + \omega)t'} dt'.
\]

Which of the two processes occurs, depends on the initial and final energies. For \( E_f = E_i + \hbar \omega \) the first term describing the process of absorption will dominate, for \( E_f = E_i - \hbar \omega \) the second term describing emission prevails.

### 13.1.2 Absorption and stimulated emission

#### 13.1.2.1 Absorption

We define the matrix element

\[
M_{fi} \equiv \langle f | e^{i\mathbf{k}\cdot\mathbf{r}^\dagger} \cdot \nabla | i \rangle,
\]

and concentrate on the absorption process. Defining the detuning by \( \Delta \equiv \omega - \omega_{fi} \) and evaluating the integral,

\[
\left| \int_0^t e^{-i\Delta t'} dt' \right|^2 = \left| e^{-i\Delta t} - 1 \right|^2 = 4 \frac{\sin^2 \frac{\Delta t}{2}}{\Delta^2} \simeq 2\pi \delta(\Delta),
\]

at short times \(^2\), the absorption probability becomes,

\[
|a^{(1)}_f(t)|^2 = \frac{e^2}{m^2} A_0(\omega)^2 |M_{fi}|^2 \left| \int_0^t dt' e^{i(\omega_{fi} - \omega)t'} dt' \right|^2 = \frac{e^2}{m^2} A_0(\omega)^2 |M_{fi}|^2 2\pi t \delta(\Delta).
\]

The \( \delta(\Delta = 0) \) function simply represents conservation of energy. Of course this is only an approximation not taking into account the finite width of the transition line.

Expressing the field by the intensity (13.10), we obtain the transition rate for absorption,

\[
W_{f_i}^{(ab)} = \frac{d}{dt} |a^{(1)}_f(t)|^2 = 2\pi \left( \frac{eA_0}{m} \right)^2 |M_{fi}|^2 \delta(\omega - \omega_{fi}) = \frac{\pi e^2}{\varepsilon_0 m^2 c} \frac{I(\omega)}{\omega^2} |M_{fi}|^2 \delta(\omega - \omega_{fi}).
\]

We note that the absorption rate is proportional to the intensity of the radiation, which characterizes a typically linear effect.

If we want to express the rate of absorption by atoms in terms of energy, we simply multiply \( W_{f_i} \) by \( \hbar \omega \) and, hence, we can define the cross section for the absorption of radiative energy as,

\[
\sigma_{i\rightarrow f} \equiv \frac{\text{absorption rate}}{\text{incident intensity}} = \frac{\hbar \omega W_{f_i}}{I(\omega)} = \frac{\pi e^2}{\varepsilon_0 m^2 c \omega} |M_{fi}(\omega_{fi})|^2 \delta(\omega - \omega_{fi}).
\]

\(^2\)\(\lim_{n \rightarrow \infty} \frac{n \sin^2 \frac{\pi x}{2}}{(nx)^2} = \delta(x)\).
13.1.2.2 Stimulated emission

For $E_f = E_i - \hbar \omega$ the equation describes the process of stimulated emission. Analogously to the calculation of the absorption, we obtain,

$$W_{if}^{(st)} = \frac{\pi e^2}{\varepsilon_0 m^2 c} \frac{I(\omega)}{\omega^2} |M_{ij}^*|^2 \delta(\omega + \omega_{fi}) ,$$  \hspace{1cm} (13.17)

with $M_{fi}^* = \langle f | e^{-ik \cdot r} \cdot \nabla | i \rangle$. Of course,

$$W_{if}^{(st)} = W_{fi}^{(ab)} .$$  \hspace{1cm} (13.18)

The fact that, in a coupled atom-radiation system in equilibrium, the radiation field excites the same number of transitions in absorption $i \rightarrow f$ as in stimulated emission $f \rightarrow i$ is called the principle of detailed balance.

Obviously, the situation is different, if instead of two states we have several states that can be excited by radiation or decay.

13.1.3 Spontaneous emission

Absorption and stimulated emission are due to the interaction of the atom with a radiation field. There is another emission process due to interaction with fluctuations of the electromagnetic vacuum called spontaneous emission. This interaction is understood in the framework of quantum electrodynamics. Here, we will adopt a heuristic treatment.

Replacing in Eq. (13.17) the intensity by the number of photons (13.8), we obtain,

$$W_{if}^{(st)} = \frac{\pi \hbar e^2}{\varepsilon_0 m^2 \omega V} |M_{fi}|^2 \delta(\omega - \omega_{fi}) .$$  \hspace{1cm} (13.19)

In fact, the introduction of the concept of photons already implies the quantization of the electromagnetic field. Adding to the number of photons a photon representing the vacuum fluctuations, $N(\omega) \rightarrow N(\omega) + 1$, we are able to include spontaneous emission,

$$W_{if}^{(st)} + W_{if}^{(sp)} = \frac{\pi \hbar e^2 [N(\omega) + 1]}{\varepsilon_0 m^2 \omega V} |M_{fi}|^2 \delta(\omega + \omega_{fi}) .$$  \hspace{1cm} (13.20)

This means that even in the absence of a classical radiation field, $N(\omega) = 0$, there is an emission probability. We note that $W_{if}^{(sp)}$ depends on the volume confining the atom, that is, the cavity, since it describes the transfer of energy to this volume. Here, it is clear that an argument is still missing, because the transfer rate must depend in some way on the number of states available to accommodate the emitted photon, that is, on the density of states within the cavity. The calculation of this density of states should allow us to evaluate the quantization volume $V$.

13.1.3.1 Density of states

To estimate the number of modes, that is, of photonic states within a solid angle $d\Omega$ of free space, we consider a cubic box of size $L$. The modes within this volume
are imposed by the periodic boundary conditions on the spatial part of the plane wavefunctions $e^{-ik \cdot r}$, 

$$k_{x,y,z} = \frac{2\pi}{L} n_{x,y,z} ,$$  \hspace{1cm} (13.21)

where $(n_x, n_y, n_z)$ is a set of integers representing the various states of the photon. In the limit of large $L$ the variation between successive $k$ is very small, such that we can treat the numbers as continuous variables. That is, the number of states with $k$ between $(k_x, k_y, k_z)$ and $(k_x + dk_x, k_y + dk_y, k_z + dk_z)$ is, 

$$dn_xdn_ydn_z = \frac{L^3}{(2\pi)^3} dkd\Omega = \frac{V}{(2\pi)^3} \omega^2 d\omega d\Omega \equiv \rho_c(\omega) d\omega d\Omega ,$$  \hspace{1cm} (13.22)

where the third expression is in spherical coordinates, the fourth one uses the relation $\omega = ck$, and the last one defines the density of states, 

$$\rho_c(\omega) = \frac{V}{(2\pi)^3} \omega^2 .$$  \hspace{1cm} (13.23)

Thus, the spontaneous emission rate of photons into the solid angle $d\Omega$ is, 

$$W_{if}^{(sp)} d\Omega = \left( \int \omega W_{if}^{(sp)} \rho_c(\omega) d\omega \right) d\Omega = \int_\omega \frac{\pi \hbar e^2}{\varepsilon_0 m^2 c^2 V} |M_{fi}|^2 \delta(\omega + \omega_{fi}) \frac{V}{(2\pi)^3} \omega^2 d\omega d\Omega$$

$$= \frac{\hbar e^2}{8\pi^2 \varepsilon_0 m^2 c^3} |M_{fi}|^2 \omega_{fi} d\Omega ,$$  \hspace{1cm} (13.24)

This simplified treatment with only two atomic states considers light as a scalar field. In fact, light is a vector field and can have two independent orthogonal polarizations. The transition matrix may depend on polarization, such that, 

$$W_{if}^{(sp)} = \frac{\hbar e^2}{8\pi^2 \varepsilon_0 m^2 c^3} \int \sum_{\lambda=1,2} |M_{fi}^\lambda|^2 \omega_{fi} d\Omega .$$  \hspace{1cm} (13.25)

### 13.1.4 Exercises

#### 13.1.4.1 Ex: Energy density of plane waves

Derive the result (13.7) for the temporal averages of the squares of the fields $\overline{E(r, t)^2} = \overline{[-\partial_t A(r, t)]^2}$ and $\overline{B(r, t)^2} = \overline{[\nabla \times A(r, t)]^2}$.

### 13.2 Dipolar transitions

#### 13.2.1 Dipolar approximation

So far, we have used the matrix element $M_{fi}^\lambda(\omega_{fi})$ without saying how it can be calculated, nor when it is significant. In many cases of interest the calculation of this matrix element is considerably simplified by an expansion of the term $e^{-ik \cdot r}$, which is part of the matrix element (13.12), 

$$e^{-ik \cdot r} = 1 - ik \cdot r - \frac{1}{2!}(k \cdot r)^2 + ... .$$  \hspace{1cm} (13.26)
This expansion is justified by the fact that the wavelength (∼ 600 nm in the visible spectrum) is much larger than the size of the scattering atom, \( k a_B \ll 1 \). The dipolar approximation supposes,
\[
e^{-i k \mathbf{r}} \simeq 1 ,
\]

such that we can remove the spatial dependence. In this approximation there is only an interaction of the electric field of the radiation with the atom via an electric dipole term \( \mathbf{d} \cdot \mathbf{E} \). Thus,
\[
M_{f_i}^\lambda(\omega_{fi}) = \langle f | e^{-i k \mathbf{r}} \hat{\mathbf{E}} \cdot \nabla | i \rangle \simeq \hat{\mathbf{E}} \frac{i m}{\hbar} \langle f | \mathbf{p} | i \rangle \cdot \hat{\mathbf{E}} \cdot \mathbf{d}_{fi} \ .
\]

(13.28)

We can calculate the expectation value of the velocity of the moving charge by the Heisenberg equation using the unperturbed Hamiltonian,
\[
M_{f_i}^\lambda(\omega_{fi}) \simeq \hat{\mathbf{E}} \frac{i m}{\hbar} \langle f | \frac{1}{i \hbar} \mathbf{r} | H_0 | i \rangle = \hat{\mathbf{E}} \frac{i m}{\hbar} (E_i - E_f) \langle f | \mathbf{r} | i \rangle \ .
\]

(13.29)

The interpretation of the last equation is, that the states \( | i \rangle \) and \( | f \rangle \) are connected through a displacement of the electronic cloud which, therefore, represents the induction of an electric dipole during the electronic transition. It is convenient to introduce the electric dipole moment \( ^3 \mathbf{d}_{fi} \equiv -e \langle f | \mathbf{r} | i \rangle \).

(13.30)

As a result, the matrix element becomes,
\[
M_{f_i}^\lambda(\omega_{fi}) \simeq \frac{m \omega_{fi}}{\hbar c} \hat{\mathbf{E}} \cdot \mathbf{d}_{fi} \ .
\]

(13.31)

and the absorption rate (13.15) is then, in the dipolar approximation,
\[
W_{f_i}^{(dp)} = \frac{\pi e^2}{\varepsilon_0 m^2 c} \frac{I(\omega_{fi})}{\omega_{fi}^2} |M_{f_i}|^2 \delta(\omega - \omega_{fi})
= \frac{\pi}{\varepsilon_0 \hbar^2 c} I(\omega_{fi}) |\hat{\mathbf{E}} \cdot \mathbf{d}_{fi}|^2 \delta(\omega - \omega_{fi}) = \frac{4\pi^2 \alpha}{\hbar} I(\omega_{fi}) |\hat{\mathbf{E}} \cdot \mathbf{r}_{fi}|^2 \delta(\omega - \omega_{fi}) .
\]

(13.32)

using the definition of the fine structure constant \( \alpha = e^2 / 4\pi \varepsilon_0 \hbar c \).

13.2.1.1 Polarization dependence

Following Eq. (13.31) the absorption rate depends on the orientation of the dipole moment with respect to the polarization of light, which therefore plays an important role in this transition. When \( \mathbf{d}_{fi} \) between two states is zero, the transition via electric dipole radiation is prohibited. This is not to say that there is no transition, since other terms of the expansion (13.26) are not necessarily zero, and there may be transitions of higher multipolar orders. Even the matrix element \( M_{f_i}^\lambda(\omega_{fi}) \) being zero for transitions involving one photon, there is still the possibility of two-photon transitions.

Setting \( \theta \) as the angle between \( \hat{\mathbf{E}} \) and \( \mathbf{d}_{fi} \) we obtain,
\[
W_{f_i}^{(dp)} = \frac{\pi}{\varepsilon_0 \hbar^2 c} I(\omega_{fi}) |\mathbf{d}_{fi}|^2 \cos^2 \theta \delta(\omega - \omega_{fi}) .
\]

(13.33)

\( ^3 \)In the presence of several atoms \( \mathbf{d} = -e \sum_j \mathbf{r}_j \), where the \( \mathbf{r}_j \) are the radii of the orbits of the various electrons of the atom.
In case of unpolarized (or randomly polarized) radiation we can replace the angular distribution \( \cos^2 \theta \) by its average value,

\[
\cos^2 \theta = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \cos^2 \theta \sin \theta d\theta d\phi = \frac{1}{3},
\]

such that,

\[
W_{f_i}^{(dp, no-pol)} = -\frac{\pi}{3\varepsilon_0 \hbar^2 c} I(\omega_{fi}) |d_{fi}|^2 \delta(\omega - \omega_{fi}).
\]

This expression also represents the stimulated emission rate in the electric dipole approximation.

The total spontaneous emission rate can be obtained from Eq. (13.25) integrating over all possible orientations,

\[
W_{f_i}^{(sp)} = \frac{\hbar e^2}{8\pi^2 \varepsilon_0 m^2 c^3} \sum_{\lambda=1,2} |M_{\lambda f_i}|^2 \omega_{fi} d\Omega
\]

\[
= \frac{\hbar e^2}{8\pi^2 \varepsilon_0 m^2 c^3} \int_0^{2\pi} \int_0^\pi \frac{m\omega_{fi}}{\epsilon \hbar c} \hat{e} \cdot d_{fi} |d_{fi}|^2 \omega_{fi} \sin \theta d\theta d\phi
\]

\[
= \frac{e^2}{4\pi^2 \varepsilon_0 \hbar c^3} \omega_{fi}^3 |r_{fi}|^2 \int_0^{2\pi} \int_0^\pi \cos^2 \theta \sin \theta d\theta d\phi = \frac{e^2}{3\pi \varepsilon_0 \hbar c^3} \omega_{fi}^3 |r_{fi}|^2,
\]

such that, for non-polarized light,

\[
W_{f_i}^{(sp)} = \frac{4\alpha}{3c^2} \omega_{fi}^3 |r_{fi}|^2 = \frac{4\alpha}{3c^2} \omega_{fi}^3 |r_{fi}|^2 = \Gamma.
\]

This is the rate of spontaneous decay of an excited atomic state. It can be measured experimentally which, in turn, allows the calculation of the dipole moment,

\[
d_{fi} = \sqrt{\frac{3\pi \varepsilon_0 \hbar \Gamma}{k^3}}.
\]

In Exc. 13.2.6.1 we calculate the Rabi frequency from the dipole moment of an atomic transition and the electric field of a radiation field.

### 13.2.1.2 Einstein transition probabilities

Considering the problem of the transfer of energy between the electromagnetic field and a sample of atoms in thermal equilibrium, Einstein realized that the processes of absorption and stimulated emission are not sufficient to understand the radiative coupling between two energy levels, that is, the coupling is not correctly described by Fermi’s Golden rule, and we need to introduce the notion of spontaneous emission.

Differently from the derivation of the preceding section, Einstein considered atoms whose populations of energy states are in thermal equilibrium with the electromagnetic field of a black-body. With this picture he came to the same result for the spontaneous emission rate (13.35). The famous Einstein coefficients \( A_{f_i} \) and \( B_{f_i} \) are given by,

\[
A_{f_i} N_f = W_{f_i}^{(sp)} \quad \text{and} \quad \frac{A_{f_i}}{B_{f_i}} = \frac{\hbar \omega_{fi}^3}{\pi^2 c^3},
\]
where \( N_f \) is the population of the excited state. This shows that, in fact, spontaneous emission is a necessary consequence of the interaction of an atom with a thermal bath (also called reservoir).

### 13.2.2 Einstein transition probabilities

We now consider the problem of energy transfer between an electromagnetic field and a sample of atoms. The rate of absorption of a light field is,

\[
R_{i \rightarrow f} \equiv \frac{1}{3} \dot{P}_{i \rightarrow f} = \frac{\pi}{6\hbar^2} \mathcal{E}_0^2 |d_{fi}|^2 \theta(\omega_{fi}) ,
\]

with \( W_0 = \mathcal{E}_0 d_{fi} \) and \( d_{fi} \) being the transition matrix element between atomic states. The factor \( \frac{1}{3} \) comes from the fact that the vector \( \vec{E} \) of the electric field can have any polarization, but only polarizations along the direction of the oscillation of the dipole moment contribute.

For a single atom, the result (13.40) is symmetric with respect to an exchange of the initial and final states, that is, the rates for absorption and induced emission of light are the same. For a sample of atoms being in thermal equilibrium, the populations \( N_i \) of the ground state and \( N_f \) of the excited state are unequal according to Boltzmann’s law. Therefore, as we have shown in Sec. 1.2.5,

\[
N_f R_{f \rightarrow i} \neq N_i R_{i \rightarrow f} .
\]

Thus, Einstein came to the conclusion that Fermi’s golden rule correctly describes absorption, but does not contain all contributions of emission. The rates being related to the Einstein coefficients by the equation (1.65), we find,

\[
R_{f \rightarrow i} = B_{fi} N_f u(\omega_{fi})
\]

and

\[
S_{f \rightarrow i} = A_{fi} N_f = \frac{\hbar \omega_{fi}^3}{\pi^2 \epsilon_0^2 c^3} B_{fi} N_f = \frac{\hbar \omega_{fi}^3}{\pi^2 \epsilon_0^2 c^3} \frac{R_{i \rightarrow f} \omega_{fi}}{u(\omega_{fi})} = \frac{\omega_{fi}^3}{3\pi \epsilon_0 \hbar c^3} |d_{fi}|^2 ,
\]

exploiting the relation (1.70). We shall return to the subject of transitions in chapter 13.1.

### 13.2.3 Selection rules and electronic transitions

The selection rules that determine which transitions between two sets of quantum numbers \( i \rightarrow f \) are allowed, reflect the symmetry properties of the system, e.g., the conservation of angular momentum (including the spin of the photon) or the change of parity, which can be understood by the fact that the emission of a photon in a particular direction must in some way alter the spatial isotropy of the atom. Note that symmetric oscillations of the shape of the charge distribution do not radiate.

Since the electronic transitions via electric dipole radiation are described by \( |\hat{e} \cdot r_{fi}| \), we expect a strong dependence between the polarization state of the light and the
existence of a displacement \( \mathbf{r}_{fi} \) in the transition between states. Let us express \( \hat{e} \) and \( \mathbf{r}_{fi} \) in spherical coordinates, which more adapted to the problem,  

\[
x = r \hat{e}_x = r \sin \theta \cos \phi \quad , \quad y = r \hat{e}_y = r \sin \theta \sin \phi \quad , \quad z = r \hat{e}_z = r \cos \theta .
\]  

(13.44)

Defining,  

\[
\hat{e}_{\pm 1} = -\frac{1}{\sqrt{2}} (\hat{e}_x \pm i \hat{e}_y) \quad , \quad \hat{e}_0 \equiv \hat{e}_z .
\]  

(13.45)

we obtain  

\[
r_{\pm 1} \equiv r \cdot \hat{e}_{\pm} = r \cdot \frac{1}{\sqrt{2}} (\mp \hat{e}_x - i \hat{e}_y) = \frac{1}{\sqrt{2}} \left( \mp x - iy \right) = \frac{1}{\sqrt{2}} r \sin \theta e^{\pm i \phi} = r Y_{1,\pm 1}(\theta, \phi) \]  

(13.46)

Similarly,  

\[
\epsilon_{\pm 1} \equiv \hat{\epsilon} \cdot \hat{e}_{\pm} \quad , \quad \epsilon_0 \equiv \hat{\epsilon} \cdot \hat{e}_0 .
\]  

(13.47)

Applying the expansion into spherical coordinates to the matrix element \( \mathbf{r}_{fi} = \langle f | \hat{r} | i \rangle \) with \( \hat{e}_q \cdot \hat{e}_{q'} = \delta_{qq'} \), it is easy to check,  

\[
\hat{\epsilon} \cdot \mathbf{r}_{fi} = \sum_{q=0, \pm 1} (\hat{\epsilon} \cdot \hat{e}_q) \hat{e}_q \cdot \sum_{q=0, \pm 1} (\mathbf{r}_{fi} \cdot \hat{e}_q) \hat{e}_q = \sum_{q=0, \pm 1} \epsilon_q \langle f | r_q | i \rangle = \sqrt{\frac{4\pi}{3}} \sum_{q=0, \pm 1} \epsilon_q \langle f | r Y_{1,q} | i \rangle .
\]  

(13.48)

The matrix elements are,  

\[
\langle f | r_q | i \rangle = \sqrt{\frac{4\pi}{3}} \langle n_f \ell_f m_f | Y_{1,q} | n_i \ell_i m_i \rangle = \sqrt{\frac{4\pi}{3}} \int_0^\infty r^3 R_{n_f,\ell_f} R_{n_i,\ell_i} dr \int Y^*_{\ell_f, m_f} Y_{1,q} Y_{\ell_i, m_i} d\Omega .
\]  

(13.49)

The radial integral, called \textit{reduced matrix element} or \textit{irreducible matrix element} with the notation,  

\[
\langle n_f \ell_f | r | n_i \ell_i \rangle \equiv \int_0^\infty r^3 R_{n_f,\ell_f} R_{n_i,\ell_i} dr ,
\]  

(13.50)

is always non-zero, while the angular integral is only non-zero, if the values of \( \ell_i, m_i, \ell_f, m_f \)

\[\text{4} \text{Generally, it is useful to choose the quantization axis along the axis of a magnetic field,}
\]

\[\hat{e}_0 = \frac{\mathbf{g}}{\mathbf{g}} .\]

The second axis may be chosen freely, for example,  

\[
\hat{e}_x = \frac{\hat{e}_0 \times \mathbf{g}}{|\hat{e}_0 \times \mathbf{g}|} ,
\]

where \( \mathbf{g} \) marks an arbitrary direction, for example, of gravity. The third axis must be perpendicular to the first two,  

\[
\hat{e}_y = \frac{\hat{e}_x \times \hat{e}_0}{|\hat{e}_x \times \hat{e}_0|} .
\]
and \( q \) satisfy certain conditions called \textit{selection rules}. We have \(^5\),

\[
\int Y^*_{\ell_f, m_f} Y_{\kappa, q Y_{\ell_i, m_i}} d\Omega = \sqrt{\frac{(2\ell_i+1)(2\ell_f+1)}{4\pi(2\kappa+1)}} \left( \begin{array}{c|c|c|c} \ell_i & \kappa & \ell_f \\ \hline 0 & 0 & 0 \end{array} \right) \left( \begin{array}{c|c|c|c|c|c} \ell_i & \kappa & \ell_f \\ \hline m_i & q & m_f \end{array} \right),
\]

(13.51)

here with \( \kappa = 1 \). Defining the electric dipole tensor operator,

\[
Q^q_{\ell_f}(r) = er^q(r) = \sqrt{\frac{4\pi}{3}} Y^q_1(\theta, \phi)er,
\]

(13.52)

we can write,

\[
\langle n_f \ell_f m_f | rY_{1,q} | n_i \ell_i m_i \rangle = \sqrt{\frac{(2\ell_i+1)(2\ell_f+1)}{3}} \langle n_f \ell_f || r || n_i \ell_i \rangle \left( \begin{array}{c|c|c|c} \ell_i & 1 & \ell_f \\ \hline 0 & 0 & 0 \end{array} \right) \left( \begin{array}{c|c|c|c} \ell_i & \kappa & \ell_f \\ \hline m_i & q & m_f \end{array} \right).
\]

(13.53)

This is the \textit{Wigner-Eckart theorem}. The electric dipole operator is a simpler example of a tensor operator \( Q^q_{\ell_f}(r) \) characterizing the transition between atomic states. In Excs. 13.2.6.2 and 13.2.6.3 we explicitly calculate, for a hydrogen atom subjected to a magnetic field, components of the electric dipole operator.

Selection rules may be violated in higher orders, e.g., by multipolar radiation, as in the cases of \textit{magnetic dipole transitions} or \textit{electric quadrupole transitions}. This also is the case of the phenomenon of \textit{phosphorescence}, which is a type of fluorescence emitted by metastable states.

\subsection*{13.2.3.1 Parity}

The \textit{parity} of a state has been defined as,

\[
\mathcal{P}\psi_{n\ell m}(r) = \psi_{n\ell m}(-r) = (-1)^\ell \psi_{n\ell m}(r),
\]

(13.54)

as shown above. That is, states with \( \ell \) pair (impair) have even (odd) parity. Now the integral (13.53) only does not vanish, when \( \ell_i + \ell_f + 1 = \text{even} \). Therefore, \textit{dipole transitions must change the parity of the states}. F.ex., transitions \( S \to P \) would be possible, while \( S \to S \) would be prohibited.

\subsection*{13.2.3.2 Angular momentum}

In the decomposition (13.53) with \( \kappa = 1 \) the first Clebsch-Gordan coefficient is only non-zero, when \( |\ell_f - \ell_i| \leq 1 \leq \ell_f + \ell_i \). That is, \textit{dipole transitions can not change the angular momentum by more than one unit}.

\subsection*{13.2.3.3 Magnetic quantum number}

In the decomposition (13.53) with \( \kappa = 1 \) the second Clebsch-Gordan coefficient is only non-zero, when \( |q| \leq 1 \). That is, \textit{dipole transitions can not change the magnetic quantum number by more than one unit}. This can also be seen from,

\[
\int Y^*_{\ell_f, m_f} Y_{\kappa, q Y_{\ell_i, m_i}} d\Omega \propto \int e^{i(m_i+q-m_f)} d\Omega \propto \delta_{m_i+q,m_f}.
\]

(13.55)

\(^5\)Frequently used are the \((3j)\)-symbols connected to the Clebsch-Gordans coefficients by,

\[
\langle j_i m_i, j_f m_f | J, M \rangle = (-1)^{j_i-j_f+M} \sqrt{2J+1} \left( \begin{array}{c|c|c} j_i & j_f & J \\ \hline m_i & m_f & -M \end{array} \right),
\]
13.2. DIPOLAR TRANSITIONS

13.2.4 Summary of selection rules including fine structure

The fine structure is due to a coupling of the type \( L + S = J \). In this case,

\[
\langle (L, S)Jm_J|er|(L', S')J'm_J \rangle = (-1)^{L'+L+2J'+S+m_j} \frac{1}{\sqrt{2L+1}} \frac{1}{\sqrt{2L'+1}} \frac{1}{\sqrt{2J+1}} \frac{1}{\sqrt{2J'+1}} \delta_{S,S'} \delta_{L,L'} \delta_{J,J'} \langle mJ|er|nL' \rangle ,
\]

where the first matrix represents a so-called \( \{6j\} \)-symbol.

Electric dipolar transitions are excited by Stark-like perturbations,

\[
\hat{V}_{\text{stark}} = -ed \cdot \mathcal{E} ,
\]

where \( \mathcal{E} = \mathcal{E}_0 \cos(k \cdot r - \omega t) \) is the electric field of an electromagnetic oscillating wave with polarization \( \mathcal{E}_0 \). With \( d = ez\hat{e}_z \), in order to determine which dipole transitions are possible, we must look at the matrix \( \langle J'm_J'|\hat{z}|Jm_J \rangle \). Applying the Wigner-Eckart theorem (9.68), it is already possible to determine, between which magnetic quantum numbers \( m_J \) and \( m'_J \) transitions may occur.

We can compare the amplitudes of the various transitions between states \( |m_J \rangle \) and \( |m'_J \rangle \) via the Clebsch-Gordan coefficients (see Exc. 9.3.2.1). Transitions are only possible between states for which the corresponding Clebsch-Gordan coefficient does not zero. This is called the selection rule. Looking at the equations (9.70), we find for dipolar transitions the following selection rules,

\[
\Delta J = 0, \pm 1 \quad \text{mas} \quad (J = 0) \rightarrow (J = 0) \quad \text{is prohibited}
\]

\[
\Delta m_J = 0, \pm 1 \quad \text{mas} \quad (m_J = 0) \rightarrow (m_J = 0) \quad \text{is prohibited when} \quad \Delta J = 0 .
\]

In addition, we have for the \( L \cdot S \) coupling,

\[
\Delta S = 0, \Delta L = \pm 1 \quad \text{and for the electron undergoing the transition} \quad \Delta l = \pm 1 .
\]

In the presence of a strong magnetic field (Paschen-Back regime) breaking up the \( L \cdot S \)-coupling the selection rules are,

\[
\Delta m_S = 0, \Delta m_L = 0, \pm 1 .
\]

For \( j \cdot j \)-coupling,

\[
\Delta j = 0, \pm 1 \quad \text{for one electron and} \quad \Delta j = 0 \quad \text{for all others} .
\]

For all dipole transitions the parity must change between even and odd.

**Example 49 (Transitions allowed and prohibited in the dipolar approximation):** Examples of allowed transitions are \(^2S_{1/2} \leftrightarrow ^2P_{1/2}, ^1S_0 \leftrightarrow ^1P_0\). Prohibited transitions are \(^1S_0 \leftrightarrow ^3P_1, ^2S_{1/2} \leftrightarrow ^2D_{3/2}, (5s)^2 ^3P_0 \leftrightarrow (5s6s)^3P_0\).

<table>
<thead>
<tr>
<th></th>
<th>(E1)</th>
<th>(M1)</th>
<th>(E2)</th>
<th>(M2)</th>
<th>(E3)</th>
<th>(M3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1, \pm 2, \pm 3$</td>
<td>$\Delta J = 0, \pm 1, \pm 2, \pm 3$</td>
</tr>
<tr>
<td>(2)</td>
<td>$\pi f = -\pi t$</td>
<td>$\pi f = \pi t$</td>
<td>$\pi f = -\pi t$</td>
<td>$\pi f = \pi t$</td>
<td>$\pi f = -\pi t$</td>
<td>$\pi f = \pi t$</td>
</tr>
<tr>
<td>(3)</td>
<td>one $e^-$ jump</td>
<td>no $e^-$ jump</td>
<td>none or one $e^-$ jump</td>
<td>one $e^-$ jump</td>
<td>one $e^-$ jump</td>
<td>one $e^-$ jump</td>
</tr>
<tr>
<td>(4)</td>
<td>if $\Delta S = 0$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td>$\Delta L = 0, \pm 1, \pm 2, \pm 3$</td>
<td>$\Delta L = 0, \pm 1, \pm 2, \pm 3$</td>
</tr>
<tr>
<td>(5)</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0, \pm 1$</td>
</tr>
<tr>
<td>(6)</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td>$\Delta L = 0, \pm 1, \pm 2, \pm 3$</td>
<td>$\Delta L = 0, \pm 1, \pm 2, \pm 3$</td>
</tr>
</tbody>
</table>

### 13.2.4.1 Selection rules for emission in certain directions

As shown in Eq. (13.48), the excitation rate induced by a light field depends on the relative orientation of the laser polarization $\hat{e}$ and the magnetic field $\vec{B}$. To take this dependence into account, we decompose the polarization vector (which can be linear or elliptical) on a coordinate basis, as shown in Eq. (13.47). Thus, the relative amplitude of the transitions $\Delta m_f = 0$ is proportional to the projection of the polarization vector onto the magnetic field axis, $\epsilon_0 \equiv \hat{e} \cdot \vec{e}_0$. To estimate the amplitude of the transitions $\Delta m_f = \pm 1$, we must project onto the coordinates $\hat{e}_\pm = \hat{e} \pm \hat{e}_y$. Note that the direction of incidence of the beam, given by the wavevector $\vec{k}$, does not influence the transition probability directly (after all, the spatial dependence $e^{i\vec{k} \cdot \vec{r}}$ was removed by the dipolar approximation (13.26)); only through the fact, that the polarization is perpendicular to the propagation vector, $\hat{e} \perp \vec{k}$.

Figure 13.1: Selection rules due to polarization $\hat{e}$ of the incident light. The projection of this vector onto the axes $\pi = \hat{e} \cdot \vec{e}_y$ and $\sigma_\pm = \hat{e} \cdot \vec{e}_\pm$ is proportional to the excitation probability (and, obviously, also to the emission probability).

### 13.2.5 Atomic transition rates

#### 13.2.5.1 Irreducible tensor operators

Irreducible tensor operators are defined by their commutation relation with the angular momentum $\vec{J}$,

$$[\vec{J}, T_q^{(k)}] = \sum_{q'} (kq|J|kq') T_{q'}^{(k)}.$$  (13.62)
13.2. DIPOLAR TRANSITIONS

Using the spherical unit vectors $\hat{e}_{\pm 1} = \frac{1}{\sqrt{2}}(\mp \hat{e}_x - i\hat{e}_y)$ and $\hat{e}_0 = \hat{e}_z$, we can reduce Cartesian vector operators to first-order tensor operators:

$$\vec{T} = \sum_q T_q^{(1)} \hat{e}_q \quad \text{resp.} \quad T_q^{(1)} = \vec{T} \cdot \hat{e}_q. \quad (13.63)$$

Examples for tensor operators are $\Pi_q^{(0)}$, $\hat{e}_q^{(1)}$, $J_q^{(1)}$, and $Y_q^{(k)}$. The most general tensor product is defined by:

$$\left( T^{(k)} \times U^{(k')} \right)_m^{(j)} = \sum_{q,q'} \left( \begin{array}{ccc} k & k' & j \\ q & q' & -m \end{array} \right) T_q^{(k)} U_{q'}^{(k')} . \quad (13.64)$$

With this product it is possible to represent scalar, vector or tensor products of higher ranks,

$$\left( T^{(1)} \times U^{(1)} \right)_0^{(0)} = \frac{1}{\sqrt{3}} \vec{T} \cdot \vec{U} \quad (13.65)$$

$$\left( T^{(1)} \times U^{(1)} \right)_m^{(1)} = \frac{1}{\sqrt{2}} (\vec{T} \times \vec{U}) \cdot \hat{e}_m$$

$$\left( T^{(1)} \times U^{(1)} \right)_m^{(2)} = -\frac{1}{\sqrt{6}} (3T_z U_z - \vec{T} \cdot \vec{U})$$

$$\left( T^{(1)} \times U^{(1)} \right)_{\pm 1}^{(2)} = \pm \frac{1}{2} \left((T_x U_x + T_y U_y) \pm i(T_y U_z + T_z U_y)\right)$$

$$\left( T^{(1)} \times U^{(1)} \right)_{\pm 2}^{(2)} = -\frac{1}{2} \left((T_x U_x - T_y U_y) \pm i(T_x U_y + T_y U_x)\right).$$

13.2.5.2 The Wigner-Eckart theorem

Be $T_q^{(k)}$ an irreducible tensor of rank $k$. Then, there exists then an irreducible matrix element $\langle j || T^{(k)} || j' \rangle$, which does not depend on the Zeeman sublevels:

$$\langle jm | T_q^{(k)} | j'm' \rangle = \left( \begin{array}{ccc} j' & k & j \\ m' & q & -m \end{array} \right) \frac{1}{\sqrt{2j+1}} \langle j || T^{(k)} || j' \rangle . \quad (13.66)$$

From the possible values for the Clebsch-Gordan coefficients follow directly the selection rules for multipolar radiation:

$$\langle jm | T_q^{(k)} | j'm' \rangle = 0 \quad \text{else} \quad E' - E = \hbar \omega \quad (13.67)$$

$$|j' - j| \leq k \leq j' + j$$

$$m' - m = q$$

$$\tau' = T.$$

For tensor products the reduced matrix element can be reduced:

$$\langle j || \left( T^{(k)} \times U^{(k')} \right) || j' \rangle = (-)^{j + \ell + j'} \sqrt{2\ell + 1} \sum_q \left\{ \begin{array}{ccc} k & k' & \ell \\ j' & j & q \end{array} \right\} \langle j || T^{(k)} || q \rangle \langle q || U^{(k')} || j' \rangle . \quad (13.68)$$
In particular, it is possible to show,
\[
\langle j||I(0)||j'\rangle = \sqrt{2j + 1}\delta_{jj'}
\]
\[
\langle j||I(1)||j'\rangle = \sqrt{2j + 1}\sqrt{j(j + 1)}\delta_{jj'}
\]
\[
\langle j||Y^{(k)}||j'\rangle = i^{j+k+j'}\frac{\sqrt{2j + 1}\sqrt{2k + 1}\sqrt{2j' + 1}}{4\pi} \left( \begin{array}{ccc} j & k & j' \\ 0 & 0 & 0 \end{array} \right).
\]

13.2.5.3 Matrix element for angular momentum coupling

We consider states \((l,s)j\rangle\). If the factors \(T\) and \(U\) of the tensor product act on different angular momenta, it can be reduced as follows:
\[
\langle (l,s)j||T^{(k)}\times U^{(k')}||(l',s')j'\rangle = \sqrt{2l + 1}\sqrt{2j + 1}\sqrt{2j' + 1} \left\{ \begin{array}{c} l' \\ k' \\ l \\ s \\ j' \\ j \end{array} \right\} \langle l||T^{(k)}||l'\rangle\langle s||U^{(k')}||s'\rangle.
\]
Assuming, in particular, \(U^{(k')} \equiv I^{(0)}\), we get, with \(T^{(k)} = (T^{(k)}\times I^{(0)})^{(k)}\),
\[
\langle (l,s)j||T^{(k)}||(l',s')j'\rangle = (-)^{l+s+j+k}\delta_{ss'}\sqrt{2j + 1}\sqrt{2j' + 1} \left\{ \begin{array}{c} l' \\ k' \\ l \\ s \\ j' \\ j \end{array} \right\} \langle l||T^{(k)}||l'\rangle.
\]

The last equation therefore applies when \(T^{(k)}\) only acts on the angular momentum component \(l\). If on the other hand, \(T^{(k)}\) only acts on \(j\), then we obviously have,
\[
\langle (l,s)j||T^{(k)}||(l',s')j'\rangle = \langle j||T^{(k)}||j'\rangle.
\]

13.2.6 Exercises

13.2.6.1 Ex: Rabi frequency

From the expression for the dipole moment \(d\) and the relationship between the intensity \(I\) and the electric field derive the Rabi frequency \(\Omega\) produced by a laser beam of intensity \(I\) by exciting an atomic dipole transition with the wavelength \(\lambda\) and decay width \(\Gamma\).

13.2.6.2 Ex: Non-stationary state

Construct a non-stationary hydrogen wavefunction with equal contributions of \((n = 1, \ell = 0, m = 0)\) and \((n = 2, \ell = 1, m = 1)\). Calculate the expectation values \(\langle |r| \rangle\) and \(\langle r \rangle\) as a function of time.

13.2.6.3 Ex: Transitions between Zeeman substates

Consider a hydrogen atom immersed in a uniform magnetic field, described by the Hamiltonian \(H = H^{(0)} + H^{(1)}\), being \(H^{(0)} = \hat{p}^2/2m + V(r)\) and \(H^{(1)} = -(\mu_B/\hbar)\hat{L} \cdot \vec{B}\) despising the spin.\(^6\)

a. Given the initial function, \(|\psi_m(0)\rangle = \cos \alpha |\phi_{000}\rangle + \sin \alpha |\phi_{21m}\rangle\), determine its shape at time \(t\).

\(^6\)See Cohen-Tannoudji, Complemento D.VII
b. Calculate the mean value \( \langle d \rangle_m(t) = \langle \psi_m(t) | d | \psi_m(t) \rangle \) of the electric dipole operator of the atom \( d = qR \).

c. Analyze the frequencies and polarizations of the emitted radiation by the transition of the excited states \( |\phi_{21m}\rangle \) to the ground state.

13.2.6.4 Ex: Derivation of selection rules

a. Prove \( \{L_k, r_m\} = i\hbar r_n \epsilon_{kmn} \) for an orbital angular momentum.

b. Using the commutator derived in (a) derive the selection rules for transitions \( \langle \alpha' L' m' | \hat{\epsilon} \cdot \hat{r} | \alpha L m \rangle \), where \( \hat{\epsilon} \) is the polarization vector of the radiation field chosen to be \( \hat{e}_0 \) or \( \hat{e}_\pm \).

c. Prove \( \{ \hat{L}^2, [\hat{L}^2, \hat{r}] \} = 2\hbar^2 (\hat{r} \hat{L}^2 + \hat{L}^2 \hat{r}) \) for an orbital angular momentum \( \hat{L} \).

d. Using the commutator derived in (b) derive the selection rule for \( \hat{L}^2 \).

13.3 Spectral lines and lifetimes

13.3.1 Natural linewidth of a transition

Be \( \Gamma \equiv \sum_f \mathcal{W}_{i_f}^{(sp)} \) the spontaneous decay rate of a state \( |i\rangle \). This means that its population is decreasing,

\[
\dot{N}_i = -\Gamma N_i . \tag{13.73}
\]

Since \( N_i = \langle \psi_i | \psi_i \rangle \), we have \( \dot{N}_i(t) = |\psi_i(0)\rangle e^{i\omega_i t - \Gamma t/2} \). The Fourier transform is,

\[
|\xi(\omega)| = \frac{1}{\sqrt{2\pi}} \int_0^\infty |\psi_i(t)\rangle e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{i\omega_i t - i\omega t - \Gamma t/2} dt |\psi_i(0)\rangle \tag{13.74}
\]

\[
= \frac{1}{\sqrt{2\pi}} \lim_{t \to \infty} \left. \frac{e^{i(\omega_i - \omega)t - \Gamma t/2} - 1}{i(\omega_i - \omega) - \Gamma/2} \right|_{t=0} |\psi_i(0)\rangle = \frac{1}{\sqrt{2\pi}} \left. \frac{1}{i(\omega - \omega_i) + \Gamma/2} \right|_{t=0} |\psi_i(0)\rangle .
\]

The spectrum,

\[
|\xi(\omega)|^2 = \frac{1}{2\pi} \left( \frac{1}{(\omega - \omega_i)^2 - \Gamma^2/4} \right) . \tag{13.75}
\]

is a Lorentz distribution. Note, that the natural linewidth can be blurred by line broadening effects, such as the Doppler broadening or collisions between atoms. These effects will be discussed in the Cap. 14.5.5.

Excited states can sometimes decay into various states of lower energy. In this case the linewidth is simply given by the sum of the partial decay rates, since the convolution of Lorentz distributions \( \mathcal{L}_k \) with widths \( \Gamma_k \) is again a Lorentzian with the total width \( \Gamma = \sum_k \Gamma_k \).

13.3.2 Beyond perturbative treatment

We look for an equation to describe the temporal evolution of atoms interacting with a radiation field. However, to portray systems that contain excitation and relaxation processes occurring simultaneously, a theory based on Schrödinger’s equation is no longer sufficient, because it is only capable of explaining stimulated processes, such as the absorption of a monochromatic wave. Dissipative process, such as spontaneous emission, require a more general approach to describe the evolution of a system.
A single wavefunction is, in general, not enough to represent such a system nor to quantify the probabilities associated with each of its states, but we rather need an ensemble of wavefunctions.

A comprehensive formalism, capable of dealing with ensembles of wavefunctions and dissipative processes is the so-called density operator formalism. The dynamics of the density operator is ruled by the Bloch equations [62], which provide equations of motion for the temporal evolution of populations, described by the diagonal terms of the operator, and coherences of the system, represented by the non-diagonal terms, as we shall see in the next chapter. The Bloch equations were initially developed to understand nuclear magnetic resonance (NMR) phenomena.

### 13.3.3 Line and oscillator strength

In addition to the Einstein coefficients $A_{21}$, $B_{21}$, and $B_{12}$, the amplitude of the transition dipole moments $d_{12}$ and the absorption cross-section $\sigma_0(\omega)$, three other quantities are sometimes used to characterize atomic transitions: the oscillator strength $f$, the line strength $S$, and the spectral absorption cross section $\sigma_\omega$. In the following sections, we will connect these different concepts.

The line strength $S$ is defined as the square of the transition dipole moment summed over all degeneracies of the ground and excited states,

$$S_{12} = S_{21} = \sum_{m_1,m_2} |\langle \psi_{1,m_1} | d | \psi_{2,m_2} \rangle|^2 . \quad (13.76)$$

The notion of the line strength becomes significant when working with real atoms characterized by degenerate ground and excited states. In such cases we need to extend the meaning of $d_{12}$ and consider transitions between each of the degenerate sublevels. For a non-degenerate two-level atom, the quantities $d_{12}$ and $A_{21}$ are simply related by,

$$A_{21} = \frac{\omega_0^3}{3\pi\epsilon_0 \hbar c^3} d_{12}^2 . \quad (13.77)$$

If the lower level would be degenerate, the spontaneous emission rate coefficient would be given by the sum of all possible deexcitation rates. In this case, $d_{12}^2$ is defined as the sum of the elements of the transition matrix coupling the excited and the lower states,

$$d_{12}^2 = \sum_{m_1} |\langle \psi_{1,m_1} | d | \psi_{2} \rangle|^2 . \quad (13.78)$$

Now, it can be shown that the spontaneous emission rate from any sublevel of a degenerate excited state toward a lower level (that is, the sum over all lower sublevels) is the same for all excited sublevels. This statement reflects the intuitively plausible idea that spontaneous emission must be isotropic and unpolarized, if the sublevels of an excited state are uniformly populated. Therefore, the insertion of Eq. (13.78) into (13.77) should produce correct results, even when the excited state is degenerate.

Comparing the sum over all upper and lower degeneracies with the line strength $S$,

$$S_{12} = \sum_{m_1,m_2} |\langle \psi_{1,m_1} | d | \psi_{2,m_2} \rangle|^2 = g_2 d_{12}^2 . \quad (13.79)$$

---

7This applies to Zeeman sublevels (summing up $(3j)$-coefficients). Check for other degeneracy (also summing up $(6j)$-coefficients)!
Therefore, the insertion of Eq. (13.79) into (13.77) must be accompanied by a factor of $1/g_2$ to correct for the fact that all excited sub-levels radiate at the same rate. Therefore, using the $S_{12}$ of Eq. (13.79) the correct expression relating the transition dipole between degenerate levels to the spontaneous emission rate is,

$$S_{12} = g_2 \frac{3\pi\epsilon_0 \hbar c^3}{\omega_0^3} A_{21} ,$$  

(13.80)

meaning that the line strength is proportional to the sum of the spontaneous emission rates $A_{21}$ from each one of the $g_2$ excited levels toward all fundamental levels.

For an atom with two levels separated by an energy $\hbar \omega_0$ the oscillator strength for emission is defined as a measure for the radiative decay rate $A_{21}$ as compared to the radiative decay rate $\gamma_e$ of a classical electronic oscillator with frequency $\omega_0$:

$$f_{21} = -\frac{1}{3} \frac{A_{21}}{\gamma_e} .$$  

(13.81)

In case of degeneracy the oscillator strength for absorption is consequently defined by,

$$f_{12} = -\frac{g_2}{g_1} f_{21} = \frac{g_2}{3g_1} \frac{A_{21}}{\gamma_e} .$$  

(13.82)

The transitions $S \leftrightarrow P$ in real atoms behave roughly as classical oscillators, that is, $A_{21} \approx \gamma_e$. The factor $1/3$ in the definition compensates for the triple degeneracy of the $P$ levels. So, a transition $S \leftrightarrow P$ which behaves exactly as a classical oscillator would be characterized by an oscillator strength for emission of $f_{21} = -\frac{1}{3}$ and an oscillator strength for absorption of $f_{12} = 1$. The classical expression for $\gamma_e$ derived from the Lorentz model is [237],

$$\gamma_e = \frac{e^2 \omega_0^2}{6\pi\epsilon_0 m_e c^3} .$$  

(13.83)

Therefore, in terms of the $A_{21}$ coefficient and of fundamental constants, the oscillator strength for absorption is given by,

$$f_{12} = A_{21} \frac{2\pi\epsilon_0 m_e c^3}{e^2 \omega_0^2} .$$  

(13.84)

Oscillator strengths obey certain sum rules that are useful for analyzing the relative intensities of atomic spectral lines. For example, atoms with single valence electrons (which are closer to the classical situation) obey the following sum rule,

$$\sum_k f_{ik} = 1 ,$$  

(13.85)

where the sum goes over all the excited states reached from the ground state. Alkaline atoms are approximately one-electron systems, and the oscillator strength of the first transition $S \rightarrow P$ is typically of the order of $f_{12} = 0.7 - 0.95$. The sum rule tells us that most of the total transition probability for the excitation of the valence electron is concentrated in the first transition $S \rightarrow P$, and that transitions to higher states will
be comparatively weaker. Another sum rule exists for the excitation and spontaneous emission from excited intermediate states \( j \):

\[
\sum_{i<j} f_{ji} + \sum_{k>j} f_{jk} = Z ,
\]

which is called the Thomas-Reiche-Kuhn sum rule. In the form of many electrons [Eq. (13.86)] this rule is very useful, when \( Z \) is the number of equivalent electrons, that is, electrons with the same quantum numbers \( n, l \). Note also, that the numbers are intrinsically negative. Oscillator strengths are often used in astrophysics and plasma spectroscopy \(^8\). They are sometimes tabulated as \( \log gf \), where,

\[
g_1 f_{12} = -g_2 f_{21} \equiv gf .
\]

### 13.3.4 Propagation of light in dielectric media

Let us now use Einstein’s theory to calculate the interaction of light with a gas being so diluted that we can treat the interaction as occurring with individual atoms. We first consider the propagation of light through a continuous (non-conducting) dielectric medium. The interaction of light with such a medium allows us to introduce important quantities, such as the polarization, the susceptibility, the index of refraction, the extinction coefficient, and the absorption coefficient. We shall see later that the polarization can be considered as densities of dipole moments induced into the dielectric medium by the oscillating light field. But for the moment, we simply begin by defining the polarization \( \tilde{\mathbf{P}} \) with respect to an applied electric field \( \tilde{\mathbf{E}} \) as,

\[
\tilde{\mathbf{P}} = \varepsilon_0 \tilde{\chi}_e \tilde{\mathbf{E}} .
\]

The tilde \( \sim \) ornamenting the quantities means that they are complex, and that measurable quantities must be taken from the real parts. \( \chi_e \) is the linear complex electric susceptibility, which is an intrinsic property of the medium responding to the light field. It is related to the medium’s dielectric constant,

\[
\tilde{\varepsilon} = \varepsilon_0 (1 + \tilde{\chi}_e) .
\]

Near resonances, the susceptibility is a strong function of frequency and can be spatially anisotropic. It is a complex quantity with a real dispersive part, \( \chi_e' \), and an imaginary absorptive part, \( \chi_e'' \),

\[
\tilde{\chi}_e = \chi_e' + i\chi_e'' .
\]

Several expressions that we already know become modified in a dielectric medium,

\[
\left( \frac{k_e c}{\omega} \right)^2 = 1 + \tilde{\chi}_e ,
\]
with $\chi_\varepsilon = 0$ in free space. In a dielectric medium, $kc/\omega$ becomes a complex quantity, conventionally expressed by,
\[
\frac{kc}{\omega} = \eta + i\kappa ,
\]
where $\eta$ is the \textit{refraction index} and $\kappa$ the \textit{extinction coefficient} of the dielectric medium. The relationships between the refractive index, the extinction coefficient and the two components of the susceptibility are,
\[
\eta^2 - \kappa^2 = 1 + \chi'_\varepsilon \quad \text{and} \quad 2\eta\kappa = \chi''_\varepsilon .
\]
Note, that in a transparent dielectric medium there is no absorption, such that, $\eta^2 = 1 + \chi'_\varepsilon = \varepsilon/\varepsilon_0$. Within a dielectric medium, we obtain the propagating wave solutions of Maxwell’s equations by substituting $k$ with the equation (13.92)
\[
\vec{E} = \vec{E}_0 e^{i(\omega t - \kappa z)} .
\]

The relationship between the amplitudes of the electric and magnetic fields is,\footnote{\textit{In a dielectric medium, $\mu \simeq \mu_0$.}}
\[
B_0^{(x)} = \sqrt{\varepsilon \mu} E_0 = \sqrt{\varepsilon_0 \mu_0 \varepsilon_0} \frac{1}{c} (\eta + i\kappa) E_0 = (\eta + i\kappa) B_0 .
\]

We use the subscript ($\chi$) to mark quantities within the dielectric medium. The average energy density is,
\[
\bar{u}^{(\chi)} = \frac{1}{2} \varepsilon_0 \eta^2 |\vec{E}|^2 = \eta^2 \bar{u} .
\]

Now, the intensity of the light beam in a dielectric medium is attenuated,
\[
I^{(\chi)} = \frac{1}{\mu_0} |\vec{E} \times \vec{B}| = \frac{1}{2} \varepsilon_0 \varepsilon_0 |\vec{E}|^2 = \frac{1}{2} \varepsilon_0 \varepsilon_0 \varepsilon^2_0 e^{-2\omega z/c} = I^{(0)} e^{-Kz} ,
\]
where
\[
I^{(0)} = \frac{1}{2} \varepsilon_0 \varepsilon_0 \varepsilon^2_0
\]
is the intensity at the point, where the light enters the medium, and
\[
K = 2\frac{\omega \kappa}{c} = \frac{\omega}{\eta \varepsilon}_e \chi''
\]
is called absorption coefficient. Note, that the energy flow $I^{(\chi)}$ in the dielectric medium is always the product of energy density and propagation velocity $c/\eta$. Note also, since the frequency $\omega$ of the light propagating through the dielectric remains the same, the wavelength shrinks like $\lambda = \frac{c/\eta}{\nu}$ [382].

**Example 50 (Energy density and Poynting vector in a dielectric medium):** The energy density in vacuum, $\bar{u} = \frac{\varepsilon}{4} |\vec{E}|^2 + \frac{1}{4\mu_0} |\vec{B}|^2$, becomes in a dielectric medium,
\[
\bar{u}^{(\chi)} = \frac{1}{4} \text{Re} (\varepsilon \vec{E} \cdot \vec{E}^* + \frac{1}{\mu_0} \vec{B} \cdot \vec{B}^*) = \text{Re} \frac{\varepsilon}{4} |\vec{E}|^2 + \frac{1}{4\mu_0} |\frac{\eta + i\kappa}{c} \vec{E}|^2
\]
\[
= \frac{\varepsilon_0}{4} (1 + \chi'_\varepsilon) \varepsilon^2_0 + \frac{\varepsilon_0}{4} |\eta + i\kappa|^2 \varepsilon^2_0 = (\eta^2 - \kappa^2 + \eta^2 + \kappa^2) \frac{\varepsilon_0}{4} \varepsilon^2_0 = \frac{\varepsilon_0}{2} \eta \varepsilon^2_0 e^{-2\omega z/c} ,
\]
where we only consider the real part of the susceptibility $\chi_\varepsilon$. On the other hand, the Poynting vector is,
\[
\vec{I} = \frac{1}{2\mu_0} \text{Re} [\vec{E} \times \vec{B}^*] = \frac{\varepsilon_0 e^2}{2} \varepsilon^2_0 \left[ e^{-2\omega z/c} \frac{\eta + i\kappa}{c} \right] = \frac{\varepsilon_0 c}{2} \eta \varepsilon^2_0 e^{-2\omega z/c} .
\]
13.3.5 Propagation of light in dilute gases

We are often interested in the attenuation of the intensity of a beam of light traversing a dilute gas of resonant scattering atoms. The equation (13.97) describes this attenuation via the properties of the dielectric material. What we are looking for in fact is a microscopic equivalent description in terms of absorption and light emission rates. The Einstein rate equation yields the temporal transition rates, but does not say how they relate to the spatial attenuation length of the light beam. We now consider a beam propagating through a cell containing an absorptive gas and assume that, along the optical axis, absorption and emission reach a steady state. We begin with the Einstein equation (1.65), and write

\[ 0 = -N_1 B_{12} u(\omega) + N_2 B_{21} u(\omega) + N_2 A_{21} . \]  

We now use the result (1.69) to write

\[ N_2 A_{21} = u(\omega) B_{12} (N_1 - N_2 \frac{g_1}{g_2}) . \]  

In steady state, the number of the excited atoms is,

\[ N_2 = \frac{u(\omega) B_{12} N_1}{A_{21} + \frac{g_1}{g_2} u(\omega) B_{12}} . \]  

Now, we must treat the refractive index of the dielectric medium carefully. The expression for the energy density must be modified following Eq. (13.96)

\[ u(\omega) = \frac{u(\chi)(\omega)}{\eta^2} . \]  

To use the Einstein coefficients, which suppose propagation at the speed of light in the vacuum \(^1\), we must correct the energy density in the dielectric medium before using it in the equation (13.102) [382]. Therefore, we should express \( u(\omega) \) in this equation by \( u(\chi)(\omega)/\eta^2 \),

\[ N_2 A_{21} = \frac{u(\chi)(\omega)}{\eta^2} B_{12} (N_1 - N_2 \frac{g_1}{g_2}) . \]  

Multiplying the two sides with \( \hbar \omega_0 \), we see that the left side describes the rate of energy scattered out of the beam by spontaneous emission, while the right side describes the energy loss of the beam, i.e., the difference between energy removed by absorption and energy returned to the beam by stimulated emission,

\[ \frac{d\bar{U}(\chi)}{dt} = -N_2 A_{21} \hbar \omega_0 = -\frac{u(\chi)(\omega)}{\eta^2} B_{12} (N_1 - N_2 \frac{g_1}{g_2}) \hbar \omega_0 . \]  

\(^1\)In Einstein’s model, what really matters for inducing transitions is the flux of photons, that is, the number of photons that traverse an atom per unit of time. This flux can not depend on the index of refraction. Therefore, we must use the spectral energy density calculated in the vacuum \( \bar{u}_\omega \).
13.3. Spectral Lines and Lifetimes

13.3.6 Susceptibility and polarization

Everything we have developed so far involves the coupling of a single-mode optical field with a two-level atom. For this system the Schrödinger equation would be perfectly adequate. If we want to include spontaneous emission, however, we need the density matrix formalism. The equations (5.63) do not respect the fact that the excited state is not only coupled to the incident light field (with the frequency $\omega$), but also with all modes of the electromagnetic vacuum. To take spontaneous emission into account, we need to go back to Sec. 1.2.7 and recalculate the absorption coefficient $K$ [Eqs. (13.99), (1.73)] from the relationship between susceptibility and polarization, Eq. (13.88). In order to obtain a new expression for the susceptibility, we will write the polarization in terms of an ensemble of individual transition dipoles. We will use the solutions for the coefficients of two coupled atomic levels, Eqs. (5.63). However, we will modify the expression for $C_2$ by adding a term that reflects the spontaneous emission from the upper state. The resulting expression for the susceptibility (and hence the absorption coefficient) will reflect the finite ‘natural’ life time of the upper state. For the present discussion we are only concerned with the temporal dependence of the actual light wave, which we write as,

$$\tilde{E}(t) = \tilde{E}_0 \cos \omega t = \frac{1}{2} [e^{i\omega t} + e^{-i\omega t}] . \tag{13.106}$$

Then we consider how to write the polarization in terms of a susceptibility when the field contains two conjugate frequencies, $\pm \omega$. Substituting into Eq. (13.88), we have,

$$\tilde{\mathcal{P}}(t) = \frac{1}{2} \epsilon_0 \tilde{E}_0 [\chi(\omega)e^{i\omega t} + \chi(-\omega)e^{-i\omega t}] . \tag{13.107}$$

The polarization can also be expressed in terms of the density of the transition dipoles in a gas of two-level atoms,

$$\tilde{\mathcal{P}}(t) = \frac{N}{V} \mathbf{d}_{12}(t) \longrightarrow \frac{N}{V} \langle \mathbf{d}_{12}(t) \rangle . \tag{13.108}$$

where $\mathbf{d}$ is the transition dipole of only one atom, $N = V$ is the atomic density, and the quantum expectation value for the transition dipole moment is,

$$\langle \mathbf{d}_{12} \rangle = -e \int \Psi \sum_j r_j \Psi d^3r . \tag{13.109}$$

Now, from Eq. (5.58),

$$\langle \mathbf{d}_{12} \rangle = -e \left[ a_1^* a_2 \langle \psi_1 | \sum_j r_j | \psi_2 \rangle e^{-i\omega_0 t} + a_1 a_2^* \langle \psi_2 | \sum_j r_j | \psi_1 \rangle e^{i\omega_0 t} \right] . \tag{13.110}$$

To simplify the notation we define $\langle \mathbf{r}_{mn} \rangle \equiv \langle \psi_m | \sum_j r_j | \psi_n \rangle$ and obtain,

$$\langle \mathbf{d}_{12} \rangle = -e [a_1^* a_2 \langle \mathbf{r}_{12} \rangle e^{-i\omega_0 t} + a_1 a_2^* \langle \mathbf{r}_{21} \rangle e^{i\omega_0 t}] . \tag{13.111}$$

Now, we only need to replace the solutions of the coupled equations by relating $a_1$ and $a_2$ of the Eqs. (5.63) in (13.111) which, in turn, can be inserted into the equation.
(13.107). Thus we obtain an expression for the polarization in terms of properties of the atoms and the incident field. However, the solution for \( a_2 \), Eq. (5.78), does not consider spontaneous emission. Now, we will introduce an ad hoc modification of Eq. (5.63) by including a radiative loss constant \( \gamma \),

\[
\Omega^* \cos \omega t e^{i\omega_0 t} a_1 - i\gamma a_2 = i\frac{da_2}{dt}.
\]  

This term does NOT EXPLAIN spontaneous emission. It simply takes into account the existence of the effect and characterizes its amplitude through \( \gamma \): If the incident field is turned off \( (\Omega^* = 0) \)

\[
-i\gamma a_2 = i\frac{da_2}{dt}.
\]  

and

\[
a_2(t) = a_2(0)e^{-\gamma t}.
\]  

Now the probability of finding an atom in the excited state (or the fraction of excited atoms in an ensemble) is,

\[
N_2/N = |a_2(t)|^2 = |a_2(0)|^2 e^{-2\gamma t}.
\]  

Comparing this behavior with the result obtained from the Einstein rate equation, we see immediately,

\[
A_{21} = 2\gamma \equiv \Gamma.
\]  

Now the solution for our improved \( a_2(t) \) coefficient is,

\[
a_2(t) = -\frac{1}{2} \Omega^* \left[ \frac{e^{i(\omega_0+\omega)t}}{\omega_0 + \omega - i\gamma} + \frac{e^{i(\omega_0-\omega)t}}{\omega_0 - \omega - i\gamma} \right].
\]  

Making the weak field approach, \( C_1(t) \approx 1 \), replacing the values obtained for \( a_{1,2} \) in the transition dipole (13.111) and replacing the average of the orientations, \( \langle r_{12} \rangle^2 \rightarrow \frac{1}{3} \langle r_{12} \rangle^2 \), in the polarization (13.108), we obtain,

\[
\vec{P}(t) = \frac{Ne^2}{6\hbar} \frac{\langle r_{12} \rangle^2 E_0^2}{V} \left[ e^{i\omega t} + e^{i\omega t} \frac{e^{i\omega t}}{\omega_0 - \omega - i\gamma} + \frac{e^{-i\omega t}}{\omega_0 - \omega + i\gamma} + \frac{e^{-i\omega t}}{\omega_0 + \omega + i\gamma} \right].
\]  

We compare this result with Eq. (13.107) and identify the susceptibility \( \chi(\omega) \) in terms of the atomic properties and the frequency of the incident field,

\[
\chi(\omega) = \frac{Ne^2}{3\epsilon_0 \hbar V} \frac{\langle r_{12} \rangle^2}{\omega_0 - \omega - i\gamma} \left[ \frac{1}{\omega_0 - \omega - i\gamma} + \frac{1}{\omega_0 + \omega - i\gamma} \right].
\]  

\[
= \frac{Ne^2}{3\epsilon_0 \hbar V} \frac{\langle r_{12} \rangle^2}{(\omega_0 - \omega)^2 + \gamma^2} \left[ \frac{1}{(\omega_0 - \omega)^2 + \gamma^2} + \frac{1}{(\omega_0 + \omega)^2 + \gamma^2} + i\gamma \left( \frac{1}{(\omega_0 - \omega)^2 + \gamma^2} + \frac{1}{(\omega_0 + \omega)^2 + \gamma^2} \right) \right].
\]  

In most practical situations in the laboratory \( \omega \) will not be tuned more than some 100 GHz away from \( \omega_0 \), hence \( |\omega_0 - \omega| \lesssim 10^{11} \) Hz. With optical frequencies \( \omega \approx 10^{15} \) Hz, it is clear that the second term on the right hand side of Eq. (13.119) will be negligible compared to the first one. Therefore, we can discard the second term and write the susceptibility as,

\[
\chi(\omega) \approx \frac{Ne^2}{3\epsilon_0 \hbar V} \frac{1}{\omega_0 - \omega - i\gamma} = \frac{Nd_{12}^2}{3\epsilon_0 \hbar V} \frac{\Delta + i\Gamma/2}{\Delta^2 + (\Gamma/2)^2} = \frac{n\hbar \Omega^2}{3\epsilon_0 E_0^2} \frac{-\Delta + i\Gamma/2}{\Delta^2 + (\Gamma/2)^2}.
\]  

(13.120)
We identify the real and imaginary parts, $\chi = \chi' + i\chi''$, and express, starting from Eq. (13.99), the absorption coefficient as,

$$K = \frac{\omega}{c n} \chi''(\omega) = \frac{\pi N d_1^2 \omega_0}{3\epsilon_0 h c V} \frac{\Gamma/2\pi}{\Delta^2 + (\Gamma/2)^2} = \frac{\pi N d_1^2 \omega_0}{3\epsilon_0 h c V} L(\omega - \omega_0) .$$ (13.121)

The Lorentzian profile term governs the frequency dependence of the absorption coefficient. We see that $K$ exhibits a peak at the resonance frequency $\omega_0$ and a width of $\Gamma$. The factor of $\pi$ inserted in the numerator and denominator of the right term of Eq. (13.121) allows to normalize the profile. We have also assumed in Eq. (13.121) that the gas is sufficiently dilute for $\eta \approx 1$ to hold, and that the line is sufficiently narrow to be able to replace $\omega$ with $\omega_0$, such that,

$$\frac{\omega}{c n} \rightarrow \frac{\omega_0}{c} .$$ (13.122)

The absorption cross section has the same lineshape, since from Eqs. (1.73) and (13.121) we have,

$$\sigma_{0a} = \frac{\pi d_1^2 \omega_0}{3\epsilon_0 h c V} L(\omega - \omega_0) ,$$ (13.123)

consistent with our previous expression for the frequency dependence of the absorption cross-section. We can also write the imaginary component of the susceptibility in terms of the cross section using the Eqs. (1.73) and (13.121)

$$\chi'' = \frac{c N}{\omega_0 V} \sigma_{0a} .$$ (13.124)

Do the Excs. 13.3.7.1 until 13.3.7.3.

### 13.3.6.1 Permittivity and permeability

The permittivity and relative permeability of a dense gas can be connected to the microscopic quantities through the Clausius-Mossotti formula,

$$\varepsilon_r = 1 + \frac{2}{3} \frac{N}{\varepsilon_0} \alpha_{pol,e} \left( 1 - \frac{1}{3} \frac{N}{\varepsilon_0} \alpha_{pol,e} \right) , \quad \mu_r = 1 + \frac{2}{3} \frac{N}{\mu_0} \alpha_{pol,m} \left( 1 - \frac{1}{3} \frac{N}{\mu_0} \alpha_{pol,m} \right) ,$$ (13.125)

that is, to the susceptibilities,

$$\chi_\varepsilon = \varepsilon_r - 1 = \frac{N}{\varepsilon_0} \alpha_{pol,e} \left( 1 - \frac{1}{3} \frac{N}{\varepsilon_0} \alpha_{pol,e} \right) , \quad \chi_\mu = \mu_r - 1 = \frac{N}{\mu_0} \alpha_{pol,m} \left( 1 - \frac{1}{3} \frac{N}{\mu_0} \alpha_{pol,m} \right) ,$$ (13.126)

where the induced electric and magnetic polarizabilities are,

$$\alpha_{pol,e} = \frac{2 d_{fi}}{|\mathcal{E}_p|} \rho_{i,f} , \quad \alpha_{pol,m} = \frac{2 m_{fi}}{|\mathcal{B}_p|} \rho_{i,f} .$$ (13.127)

$d_{fi}$ and $m_{fi}$ are the dipole moments for electric and magnetic transitions and $\rho_{i,f}$ the coherences excited in these transitions, which can be calculated from the Bloch equations. The relative strength between magnetic and electrical transitions is,

$$\frac{2\mu_B}{c e a_B} = \alpha .$$ (13.128)
13.3.7 Exercises

13.3.7.1 Ex: Solution for the susceptibility

Show that the solution of Eq. (13.112) is given by the result (13.117).

13.3.7.2 Ex: Width of the absorption band

The resonator of a dye laser with a large emission bandwidth additionally contains an absorbing (dense) gas. The absorption spectrum of the gas is Lorentzian with a width of 3 GHz, and the absorption coefficient has, in the middle of the absorption line (at 600 nm), the value of 0.2. What are the maximum and minimum relative spectral distances $\Delta f/\Delta f_0$ of the axial modes within the spectral range of the absorption, compared to the distances $\Delta f_0$ of the empty resonator?

13.3.7.3 Ex: Einstein’s rate equations

Show that the solution of the equations (5.63) is given by the result (13.117) using the approximation of short times, $C_1 \simeq 1$. 


Chapter 14

The Bloch equations

So far we mainly considered low amplitude light fields with broadband emission and incoherent phases that interact weakly with an atom or a dilute gas. The expression (5.79) allowed us to calculate the probability of finding a two-level atom exposed to a light field in the excited state. But these expressions were obtained by averaging over the spectral width of the line, ignoring any phase relationship between the incident field and the excited dipole, and basically assuming a negligible depopulation of the ground state. For the first half of the 20-th century these assumptions matched the available light sources, usually incandescent, arc or plasma discharge lamps. After the invention of the laser in 1958, single mode and pulsed lasers quickly replaced the lamps as a source for optical excitation. These new light sources initiated a revolution in optical science, the consequence of which continue to reverberate through modern sciences and applied technologies.

The characteristics of laser sources are far superior to the old lamps in all respects. They are intense, collimated, spectrally narrow and phase coherent. The laser gave rise to a multitude of new spectroscopic techniques and new disciplines, such as quantum electronics, the study of statistical properties of light in quantum optics, optical cooling and trapping of microscopic particles, the control of chemical reactivity, and new technologies for imaging and high resolution microscopy.

To tackle the problem from the base we need first to examine what happens when our two-level atom interacts with light sources, which are spectrally narrow in comparison to the natural width of optical transitions, and what happens when the states have a well-defined polarization and phase and the intensities are sufficient to significantly depopulate the ground state. We will look out for an equation that describes the temporal evolution of atoms interacting strongly with a single mode of the radiation field.

A first attempt to solve this problem could be to use the Schrödinger equation, which describes the temporal evolution of the state of any system. In fact, as long as we are only interested in stimulated processes, such as the absorption of a monochromatic wave, the Schrödinger equation would suffice. A problem arises when we want to describe relaxation processes at the same time as excitation processes, after all in most realistic situations the atom reaches a steady state, where the rate of excitation and relaxation are equal. Spontaneous emission (and any other dissipative process) must therefore be included in the physical description of the temporal evolution of our light-atom system. In this case, however, our system is no longer restricted to a single mode of the light field and the two atomic states of excitation. Spontaneous emission populates a statistical distribution of states of the light field and leaves the atom in
a superposition of many momentum states. This situation can not be described by a single wavefunction, but only by a distribution of wavefunctions, and we can only expect to calculate the probability of finding the system within this distribution. The Schrödinger equation, therefore, no longer applies, and we need to trace the time evolution of a system characterized by a density operator describing a statistical mixture of quantum states. The equations which describe the time evolution of the matrix elements of this density operator are the optical Bloch equations, and we must use them instead of the Schrödinger equation. In order to appreciate the origin and the physical content of the optical Bloch equations we begin by reviewing the rudiments of the density matrix theory.

14.1 Density matrix

14.1.1 The density operator

We define the statistical operator or density operator 1,

\[
\hat{\rho} \equiv \sum_k p_k \hat{P}_k \quad \text{where} \quad \hat{P}_k \equiv |\psi_k\rangle\langle \psi_k| ,
\]

where \(|\psi_k\rangle\) is a complete set of orthonormal states of the system under study. We have a statistical distribution of these states with \(p_k\) being the probability of finding \(|\psi_k\rangle\) in the set. Obviously, \(\sum_k p_k = 1\). That is, the density operator acts on a member of the set \(|\psi_k\rangle\) such as to extract the probability of finding the system in \(|\psi_k\rangle\),

\[
\hat{\rho}|\psi_m\rangle = \sum_k p_k |\psi_k\rangle\langle \psi_k| |\psi_m\rangle = p_m |\psi_m\rangle .
\]

If all members of the set are in the same state, for example \(|\psi_k\rangle\), the density operator reduces to,

\[
\hat{\rho} = |\psi_k\rangle\langle \psi_k| ,
\]

and the system is in a pure state with \(\hat{P}_k = 1\). Each time a quantum state can be expressed by a single wave function, it is a pure state, but it does not have to be an eigenstate. Starting from the equation (14.2) we find the diagonal elements of the density matrix, which are the probabilities of finding the system in \(|\psi_m\rangle\),

\[
\langle \psi_m|\hat{\rho}|\psi_m\rangle = p_m .
\]

1In the presence of degeneracy or a continuous spectrum we can generalize the definition:

\[
\hat{\rho} \equiv \sum_k p_k \hat{P}_k + \int p_\lambda \hat{P}_\lambda d\lambda \quad \text{where} \quad \hat{P}_k \equiv \sum_m |km\rangle\langle km| \quad \text{and} \quad \hat{P}_\lambda \equiv \int |\lambda\mu\rangle\langle \lambda\mu|d\mu .
\]

Here, \(m\) and \(\mu\) are degenerate quantum numbers, \(m, n\) are discrete, and \(\lambda, \mu\) are continuous quantum numbers. The set of quantum numbers is complete, when

\[
\sum_{k,m} |km\rangle\langle km| = \hat{1} = \int |\lambda\mu\rangle\langle \lambda\mu|d\lambda d\mu .
\]

The degree of degeneracy of a state \(|k\rangle\) is \(\text{Tr} \hat{P}_k = \sum_m 1\). The probability of finding the system in the state \(|k\rangle\) is \(\langle \hat{P}_k \rangle = p_n \sum_m 1\).
Assuming that all $|\psi_k\rangle$ are orthonormal, the non-diagonal elements are necessarily zero. Besides that,

$$\sum_k \langle \psi_k | \hat{\rho} | \psi_k \rangle = 1 .$$

(14.5)

So, $\hat{\rho}$ contains all information about the system. When a state is unknown, $\hat{\rho}$ describes the probability of finding the system in each state. When the state is fully known, $\hat{\rho}$ describes a pure state, that is, a vector in the Hilbert space, which is unequivocally determined by a complete set of observables with their respective quantum numbers.

The properties of the density operator are,

$$\hat{\rho} = \hat{\rho}^\dagger$$

$$\langle \hat{\rho} \rangle \geq 0$$

$$\text{Tr} \: \hat{\rho} = 1$$

$$\text{Tr} \: \hat{\rho}^2 \leq 1$$

$$\det \: \hat{\rho} = 0$$

$$\hat{\rho} = \hat{\rho}^2 \text{ for a pure state}$$

(14.6)

14.1.1.1 Entropy

In a very general sense, the entropy determines in what direction a reversible process will take place. It is related to the size of the available phase space on both sides of the reaction. For example, the coupling of discrete and continuous modes is governed by entropy considerations.

Entropy measures of the lack of information about a system from which we only know $\langle \hat{H} \rangle$,

$$S \equiv -k_B \langle \ln \hat{\rho} \rangle = -k_B \text{ Tr } (\hat{\rho} \ln \hat{\rho}) .$$

(14.7)

The information entropy (or von Neumann entropy) of statistically independent systems $\hat{\rho} \equiv \hat{\rho}_1 \otimes \hat{\rho}_2$ is additive $S = S_1 + S_2$. We can also define absolute temperatures by $T^{-1} \equiv \partial S / \partial \langle \hat{H} \rangle$. The entropy of a pure state is 0. Hamiltonian processes conserve entropy, for they correspond to non-dissipative unitary transformations. On the other side, relaxation increases the entropy and the phase space volume. Another common definition is the so-called purity or Renyi entropy,

$$S_R \equiv \langle 1 - \hat{\rho} \rangle = 1 - \text{Tr } (\hat{\rho}^2) .$$

(14.8)

Quantum states can exhibit coherences. For example, if we express a state $|\psi\rangle$ on a basis of eigenstates $|1\rangle$ and $|2\rangle$:

$$\hat{\rho} = |\psi\rangle \langle \psi| = \begin{pmatrix} \langle \psi |1 \rangle^2 & \langle 1 |\psi \rangle \langle \psi |2 \rangle \\ \langle 2 |\psi \rangle \langle \psi |1 \rangle & \langle \psi |2 \rangle^2 \end{pmatrix} .$$

(14.9)

The evolution of such a state is described by the von Neumann equation,

$$i\hbar \partial_t \hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)] .$$

(14.10)

The measurement process is not described by this equation. A pure state will always remain pure. If the eigenstates do not interact, the density operator will remain
diagonal. The von Neumann equation conserves the properties of hermiticity, \( \hat{\rho} = \hat{\rho}^\dagger \), completeness, Tr \( \hat{\rho} = 1 \), and purity \( \text{det} \hat{\rho} = 0 \).

The density operator for a statistical mixture in a canonical ensemble (where \( S \) is maximum, \( U \) is variable, and \( N \) is fixed) follows from a variational problem with the Lagrange parameters \( \delta(S - k_B \alpha(\hat{1}) - k_B \beta(\hat{H})) = 0 \), since Tr \( \hat{\rho} \) and \( \langle \hat{H} \rangle \) are fixed by boundary conditions. We find,

\[
\hat{\rho} = \frac{1}{Z} e^{-\hat{H}/k_B T} \quad \text{with} \quad Z \equiv \text{Tr} e^{-\hat{H}/k_B T}.
\] (14.11)

We also have the expectation values, \( \langle \hat{H} \rangle = -\partial \ln Z/\partial(1/k_B T) \) and \( (\Delta H)^2 = -\partial(\hat{H})/\partial(1/k_B T) \). All quantities are fixed, except the kinetic energy, which balances the interaction with a heat bath. \( T \) is the only equilibrium parameter. The density operator satisfies a Boltzmann distribution \(^2\),

\[
U = \langle \hat{H} \rangle = \frac{p^2}{2m} = -\frac{\partial}{\partial(1/k_B T)} \ln \int e^{-p^2/2mk_BT} dp = \frac{k_B}{2} T.
\] (14.12)

### 14.1.2 Matrix formalism

The next step is to develop matrix representations of the density operator by expanding the state vectors \( |\psi_k\rangle \) in a complete orthonormal basis,

\[
|\psi_k\rangle = \sum_n c_{nk} |n\rangle = \sum_n |n\rangle \langle n| \psi_k \rangle,
\] (14.13)

using the completeness relation (2.70), that is, \( \sum_n |n\rangle \langle n| = \mathbb{I} \), and defining,

\[
c_{nk} \equiv \langle n| \psi_k \rangle
\] (14.14)

as the projection of the state vector \( |\psi_k\rangle \) on the basis vector \( |n\rangle \). Now, we can write the density operator matrix representation within the basis \( \{|n\rangle\} \) using the definition of \( \hat{\rho} \) in Eq. (14.1) and replacing the expansions of \( |\psi_k\rangle \) and \( \langle \psi_k| \) of Eq. (14.13):

\[
\hat{\rho} = \sum_k p_k |\psi_k\rangle \langle \psi_k| = \sum_k p_k \sum_{m,n} |n\rangle \langle n| \psi_k \langle \psi_k| m \rangle \langle m| = \sum_k p_k \sum_{m,n} c_{nk}^* c_{mk} |n\rangle \langle m|.
\] (14.15)

The matrix elements of \( \rho \) in this representation are

\[
\rho_{nm} = \langle n| \hat{\rho} |m\rangle = \sum_k p_k c_{nk} c_{mk}^*
\] (14.16)

with the diagonal elements \( \langle n| \hat{\rho} |n\rangle = \sum_k p_k |c_{nk}|^2 e \),

\[
\rho_{nm}^* = \langle n| \hat{\rho}^\dagger |m\rangle = \sum_k p_k c_{nk}^* c_{mk} = \sum_k p_k \langle m| \psi_k \rangle \langle \psi_k| n \rangle = \langle m| \rho |n\rangle = \rho_{nm},
\] (14.17)

which means that the operator \( \hat{\rho} \) is hermitian.

\(^2\)The von Neumann entropy \( S \) of a mixture can be expressed in terms of the eigenvalues or in terms of the trace and the logarithm of the density operator \( \hat{\rho} \). Since \( \hat{\rho} \) is a semi-definite positive operator, its spectrum \( \lambda_i \), given by \( \rho = \sum_i \lambda_i |\varphi_i\rangle \langle \varphi_i| \) where \( \{|\varphi_i\rangle\} \) is an orthonormal basis, satisfies \( \lambda_i > 0 \) and \( \sum \lambda_i = 1 \). Then the entropy becomes \( S = -\sum_i \lambda_i \ln \lambda_i = -\text{Tr} (\rho \ln \rho) \).
**Example 51 (Density operator for a single atom):** For a very simple system such as a single atom with several levels, that without spontaneous emission can be described by a single wavefunction $|\psi_1\rangle$, we can let $p_k = \delta_{1k}$. That is, the equations (14.15) and (14.17) reduce to,

\[ \hat{\rho} = \sum_{m,n} c_{n1}^* c_{m1} |n\rangle\langle m| \quad \text{and} \quad \langle n|\rho|m\rangle = c_{n1} c_{m1}^* . \quad (14.18) \]

### 14.1.2.1 Measurement and trace

The sum of the diagonal elements of a matrix representing an operator is called the **trace**. This quantity represents a fundamental property of the density operator, since it is invariant with respect to any unitary transformation:

\[ \text{Tr} \hat{\rho} \equiv \sum_n \langle n|\rho|n\rangle . \quad (14.19) \]

With the definition of the density operator (14.1) we can write the Eq. (14.19) as,

\[ \text{Tr} \hat{\rho} \equiv \sum_{n,k} p_k \langle n|\psi_k\rangle\langle \psi_k|n\rangle . \quad (14.20) \]

Now, using the completeness relation,

\[ \text{Tr} \hat{\rho} \equiv \sum_{n,k} p_k \langle n|\psi_k\rangle\langle \psi_k|n\rangle = \sum_k p_k \langle \psi_k|\psi_k\rangle = 1 , \quad (14.21) \]

which shows that the trace of the density operator representation is always 1 regardless of the basis of the matrix representation.

Expectation values of observables are expressed by,

\[ \langle \hat{A} \rangle = \sum_k p_k \langle \psi_k|\hat{A}|\psi_k\rangle . \quad (14.22) \]

On the other side,

\[ \hat{\rho} \hat{A} = \sum_k p_k |\psi_k\rangle\langle \psi_k|\hat{A} \]

and in the basis $\{|n\rangle\}$,

\[ \langle n|\hat{\rho} \hat{A}|m\rangle = \langle n| \sum_k p_k |\psi_k\rangle \langle \psi_k|\hat{A}|m\rangle = \sum_k p_k \langle n|\psi_k\rangle \langle \psi_k|\hat{A}|m\rangle = \sum_k p_k \langle \psi_k|\hat{A}|m\rangle \langle n|\psi_k\rangle . \quad (14.24) \]

Now, along the diagonal, we have,

\[ \langle n|\hat{\rho} \hat{A}|n\rangle = \sum_k p_k \langle \psi_k|n\rangle \langle n|\hat{A}|\psi_k\rangle . \quad (14.25) \]
With the closing relation in the basis \( \{ \ket{n} \} \), we now have \(^3\),

\[
\text{Tr} \: \hat{\rho} \hat{A} = \sum_k p_k \langle \psi_k | \hat{A} | \psi_k \rangle = \langle \hat{A} \rangle .
\] (14.26)

The Eq. (14.26) says that the ensemble average of any dynamic observable \( \hat{A} \) can be calculated from the diagonal elements of the operator matrix \( \hat{\rho} \hat{A} \): Since the trace is independent of the basis (this will be shown in Exc. 14.1.5.1), each unitary transformation taking the matrix representation from a basis \( \{ \ket{n} \} \) to another one \( \{ \ket{t} \} \) leaves the trace invariant. Using the definition of a unitary transformation we can easily show that the trace of a cyclic permutation of a product is invariant. For example,

\[
\text{Tr} \left[ \hat{A} \hat{B} \hat{C} \right] = \text{Tr} \left[ \hat{C} \hat{A} \hat{B} \right] = \text{Tr} \left[ \hat{B} \hat{A} \hat{C} \right],
\] (14.27)

and in particular

\[
\text{Tr} \left[ \hat{\rho} \hat{A} \right] = \text{Tr} \left[ \hat{A} \hat{\rho} \right] = \langle \hat{A} \rangle .
\] (14.28)

In the Excs. 14.1.5.2 and 14.1.5.3 we apply the density operator to pure and mixed states of a two-level system. In Exc. 14.1.5.4 we study thermal mixtures.

### 14.1.2.2 Measurement process

If an observable \( \hat{A} \) has a spectral representation \( \hat{A} = \sum_n a_n \ket{a_n} \bra{a_n} = \sum_n a_n \hat{P}_n \), the measurement process will transform the density operator to,

\[
\hat{\rho} \to \hat{\rho} = \sum_n \hat{P}_n \hat{\rho} \hat{P}_n .
\] (14.29)

That is, after the measurement, the operator becomes diagonal on the basis of the eigenvalues of \( \hat{A} \) \(^4\).

We note that the density operator (14.29) describes the whole ensemble after the measurement. The sub-ensemble corresponding to a particular result \( a_n \) of the measurement is described by a different density operator,

\[
\hat{\rho}' = \frac{\hat{P}_n \hat{\rho} \hat{P}_n}{\text{Tr} \left[ \hat{\rho} \hat{P}_n \right]} .
\] (14.30)

This is true, when \( \ket{a_n} \) is the only eigenvector with the eigenvalue \( a_n \). If not, \( \hat{P}_n \) in the expression (14.30) should be replaced by the projection operator onto the sub-space of \( a_n \) \(^5\).

---

\(^3\)In the presence of degeneracy or a continuous part of the spectrum we can generalize the definition of the expectation,

\[
\langle \hat{X} \rangle \equiv \text{Tr} \: \hat{\rho} \hat{X} = \sum_{k,m} \langle km | \hat{\rho} \hat{X} | km \rangle .
\]

\(^4\)A projective measure always increases entropy. The entropy of a pure state is zero, while that of a mixture is always greater than zero. Therefore, a pure state can be converted into a mixture by a measurement, but the reverse can not happen. Thus, the action of measuring induces an irreversible change in the density matrix reminiscent of the collapse of the wavefunction. Strangely, the measurement reduces the amount of information by quenching the quantum interference of the compound system in a process called quantum decoherence. A subsystem can be taken from a mixed state to a pure state only at the price of increasing the von Neumann entropy elsewhere in the global system.

\(^5\)In general, assuming that \( f \) is a function associating each observable \( \hat{A} \) with a number \( f(\hat{A}) \)
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14.1.2.3 Systems and subsystems

Density operators are very useful for playing with systems and subsystems. Let us, for instance, assume that we have two quantum systems defined on the Hilbert spaces $H_1$ and $H_2$. The composite system is then the tensor product $H_1 \otimes H_2$. We now suppose that the compound system is in a pure state, $|\psi\rangle \in H_1 \otimes H_2$. If the state can be written in the form $|\psi\rangle = |\psi_1\rangle \otimes |\psi_2\rangle$, this means that the state of the first subsystem is $|\psi_1\rangle$. However, in general, $|\psi\rangle$ does not decompose like this. Of course, every vector in $H_1 \otimes H_2$ is a linear combination of tensorial products of $H_1$ and $H_2$. If $|\psi\rangle$ cannot be decomposed as a tensor product, we say that the two systems are entangled. In this case, there is no reasonable way of associating a pure state $|\psi_1\rangle \in H_1$ to the state $\psi \in H_2 \otimes H_2$. If, for example, in the case of a two particle wavefunction $\Psi(x_1, x_2)$ there is no way to construct a wavefunction (i.e. a pure state) $\psi_1(x_1)$ describing the state of the first particle, then $|\Psi(x_1, x_2)\rangle \neq \psi_1(x_1)\psi_2(x_2)$.

The point of the discussion is that, even if the total system is in a pure state, the various subsystems that compose it will normally be in mixed states. On the other hand, regardless of whether the composite system is in a pure or mixed state, we can perfectly construct a density matrix that describes the state. Therefore, the use of density matrices is inevitable. Let $\hat{\rho}$ be the density matrix of the system composed of two subsystems. Then the state in $H_2$ is described by a reduced density operator given by the partial trace of $\hat{\rho}$ over $H_2$. In the particular case, where the state the density matrix has the form $\hat{\rho} = \hat{\rho}_1 \otimes \hat{\rho}_2$, where $\hat{\rho}_1$ and $\hat{\rho}_2$ are the density matrices in $H_1$ and $H_2$, then the partial trace is simply, $\text{Tr}_{H_2} \hat{\rho}_{\rho_1}$.

14.1.3 Temporal evolution of the density operator

As shown in Secs. 2.4.2 to 2.4.4, the equations governing the temporal evolution of a quantum system depend on the choice of the picture, i.e. Schrödinger’s (2.127), Heisenberg’s (2.133), or the interaction picture (2.140). This, of course, also applies to a system represented by a density matrix.

Returning to the density operator definition (14.1), we can express its temporal dependence in terms of time-dependent quantum states and of the time evolution operator (2.130),

$$\hat{\rho}(t) = \sum_k p_k |\psi_k(t)\rangle \langle \psi_k(t)| = \sum_k p_k U(t, t_0) |\psi_k(t_0)\rangle \langle \psi_k(t_0)| U^\dagger(t, t_0).$$ (14.31)

Writing,

$$\hat{\rho}(t_0) = \sum_k p_k |\psi_k(t_0)\rangle \langle \psi_k(t_0)|,$$ (14.32)

we see immediately,

$$\hat{\rho}(t) = U(t, t_0) \hat{\rho}(t_0) U^\dagger(t, t_0),$$ (14.33)

(which we may imagine as the expectation value), we can state the following: If $f$ satisfies some natural properties (such as the one to produce positive values for positive operators), then there exists a unique density matrix $\hat{\rho}$, such that $f(\hat{A}) = \text{Tr} (\hat{\rho}\hat{A})$ for all $\hat{A}$. That is, every reasonable ‘family’ of expectation values’ can be represented by a density matrix, which suggests that the density matrix provides the most general description of a quantum state.
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where, for the common case of a time-independent Hamiltonian,

\[ U(t, t_0) = e^{-i\hat{H}(t-t_0)/\hbar}. \]  

(14.34)

Now we find the time derivative of the density operator differentiating the two sides of (14.33) and substituting the Eqs.

\[ \frac{dU}{dt} = \frac{1}{i\hbar} \hat{H}U \quad \text{and} \quad \frac{dU^\dagger}{dt} = -\frac{1}{i\hbar} U^\dagger \hat{H} \]  

(14.35)

for the time derivatives \( U \) and \( U^\dagger \). The result is

\[ \frac{d\hat{\rho}(t)}{dt} = \frac{i}{\hbar} [\hat{\rho}(t), \hat{H}] . \]  

(14.36)

The commutator itself can be considered as a superoperator acting, not any more on states but on operators, that is, we can write,

\[ \mathcal{L}\hat{\rho}(t) \equiv \frac{i}{\hbar} [\hat{\rho}(t), \hat{H}] , \]  

(14.37)

where \( \mathcal{L} \) is called Liouville operator. The equation (14.36) is called Liouville equation or von Neumann equation. The Liouville equation describes the time evolution of the density operator which, in turn, describes the distribution of an ensemble of quantum states. Even though the form of the Liouville equation resembles the Heisenberg equation, Eq. (14.31) shows that \( \rho(t) \) is in the Schrödinger picture.

For a two-level system perturbatively interacting with a light field, the Hamiltonian can be decomposed as in (2.137) into a stationary part and a time-dependent part,

\[ \hat{H} = \hat{H}_a + \hat{V}(t) , \]  

(14.38)

where \( \hat{H}_a \) is the part of the Hamiltonian describing the atomic structure and \( \hat{V}(t) \) the interaction of the dipole transition with the classical oscillating electric field. The interaction picture is the natural choice for this type of problem. In this case, we can transform the density operator into the interaction picture defined by (2.138),

\[ \hat{\rho}(t) = e^{i\hat{H}_0(t-t_0)/\hbar} \hat{\rho}(t_0) e^{-i\hat{H}_0(t-t_0)/\hbar} , \]  

(14.39)

where the 'tilde' decoration (replacing the 'hat') emphasizes, that we are now in the interaction picture. We look for the time evolution rate of \( \hat{\rho}(t) \) analogously to the Liouville equation. Calculating the time derivatives on both sides of (14.39) and substituting Eq. (14.36) for \( \frac{d\rho}{dt} \) results in,

\[ \frac{d\hat{\rho}(t)}{dt} = \frac{i}{\hbar} [\hat{\rho}(t), \hat{V}(t)] . \]  

(14.40)

This equation shows that the time evolution of the density operator in the interaction picture depends only on the time-dependent part of the total Hamiltonian.
14.1.4 Semi-classical two-level atom in the dipolar approximation

In the following sections we will derive a ready-to-use form of the Hamiltonian governing the interaction of a weak single-mode light field with a two-level atom in the dipolar approximation.

14.1.4.1 Transformation to the interaction picture

The semi-classical light-atom interaction Hamiltonian comprises two terms,

$$\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{atom-field}},$$  \hspace{1cm} (14.41)

which, in the dipolar approximation, can be written,

$$\hat{H} = \begin{pmatrix} 0 & 0 \\ 0 & \hbar \omega \end{pmatrix} - \hat{d} \cdot \vec{E}(r, t) \quad \text{where} \quad \hat{d} = -e \hat{r} = \begin{pmatrix} 0 \\ \langle 1|d|2 \rangle \\ \langle 2|d|1 \rangle \end{pmatrix}$$  \hspace{1cm} (14.42)

is the dipole operator and

$$\vec{E}(r, t) = \vec{\epsilon} \left[ E_0(r) e^{i(k \cdot r - \omega t)} + E_0^*(r) e^{-i(k \cdot r - \omega t)} \right]$$  \hspace{1cm} (14.43)

the electric field. Note that via $E_0(r) \to i \sqrt{\frac{\hbar \omega}{2 \varepsilon_0 V}} \hat{a}$, we can quantize the radiation mode, as will be shown in Sec. 15.1.2. Introducing the Rabi frequencies

$$\hbar \Omega(r) \equiv -E_0(r) \vec{\epsilon} \cdot \langle 2|d|1 \rangle \quad \text{and} \quad \hbar \Theta(r) \equiv -E_0^*(r) \vec{\epsilon} \cdot \langle 1|d|2 \rangle$$  \hspace{1cm} (14.44)

as an abbreviation, we can write the Hamiltonian,

$$\hat{H} = \hbar \begin{pmatrix} \Omega(r) e^{i(k \cdot r - \omega t)} & 0 \\ \frac{\Theta(r)}{2} e^{-i(k \cdot r - \omega t)} & \frac{\Theta^*(r)}{2} e^{-i(k \cdot r - \omega t)} + \frac{\Omega(r)}{2} e^{-i(k \cdot r - \omega t)} \end{pmatrix} \hbar \omega_0$$  \hspace{1cm} (14.45)

The transformation from the Schrödinger to Dirac’s interaction picture, is done via,

$$\hat{H} \equiv \hat{U}^\dagger \hat{H} \hat{U} + \hbar \hat{U}^\dagger \dot{\hat{U}} \quad \text{with} \quad \hat{U} = e^{-i\hat{H}_{\text{atom}} t/\hbar}.$$  \hspace{1cm} (14.46)

We obtain,

$$\hat{H} = \begin{pmatrix} 0 & \hbar \frac{\Omega(r)}{2} e^{-i(k \cdot r - \Delta t)} \\ \hbar \frac{\Theta(r)}{2} e^{-i(k \cdot r - \omega t)} & 0 \end{pmatrix} + \begin{pmatrix} 0 & \hbar \frac{\Theta^*(r)}{2} e^{-i(k \cdot r - \omega t)} \\ \hbar \frac{\Omega(r)}{2} e^{i(k \cdot r - \Delta t)} & 0 \end{pmatrix} \equiv \hat{H}_{\text{slow}} + \hat{H}_{\text{fast}}.$$  \hspace{1cm} (14.47)
14.1.4.2 The rotating-wave approximation

The transition amplitude in first-order perturbation theory is,

\[ a_{i \rightarrow f}(t) = \frac{1}{i \hbar} \int_0^t \langle 2 | \tilde{H}(\tau) | 1 \rangle d\tau = \frac{\hbar}{2} \int_0^t \left[ \Theta(r)e^{i(k \cdot r - \Delta t)} + \Theta^*(r)e^{-i(k \cdot r - \Delta t)} \right] d\tau \]

\[ = \frac{\Omega(r)e^{ik \cdot r}}{2\Delta} (e^{-i\Delta t} - 1) + \frac{\Theta^*(r)e^{-ik \cdot r}}{2(\omega + \omega_0)} \left( e^{-i(\omega + \omega_0)\Delta t} - 1 \right) \]

(14.48)

\[ \simeq \frac{\Omega(r)e^{ik \cdot r}}{2\Delta} (e^{-i\Delta t} - 1) , \]

where the last step corresponds to the rotating-wave approximation. This allows us to neglect \( \tilde{H}_{fast} \).

14.1.4.3 Transformation into the rotating frame

Now, we further transform into rotating frame using,

\[ \tilde{H}' = \hat{U}^\dagger \tilde{H} \hat{U} + i\hbar \dot{\hat{U}}^\dagger \hat{U} \quad \text{with} \quad \hat{U} = \begin{pmatrix} 1 & 0 \\ 0 & e^{-i\Delta t} \end{pmatrix} . \] (14.49)

This yields,

\[ \tilde{H}' = \begin{pmatrix} 0 & \frac{\hbar}{2} \Omega^*(r)e^{-ik \cdot r} \\ \frac{\hbar}{2} \Omega(r)e^{ik \cdot r} & -\hbar \Delta \end{pmatrix} . \] (14.50)

We always can write the Rabi frequency as \( \Omega = |\Omega|e^{i\phi} \) and attribute the phase to the atomic position if necessary. Locating the atom in the center of the coordinate system, we finally get,

\[ \tilde{H}' = \begin{pmatrix} 0 & \frac{\hbar}{2} \Omega \\ \frac{\hbar}{2} \Omega & -\hbar \Delta \end{pmatrix} . \] (14.51)

14.1.5 Exercises

14.1.5.1 Ex: Trace of an operator

The trace of an operator \( \hat{A} \) is defined by \( \text{Tr} \hat{A} = \sum_n \langle n | \hat{A} | n \rangle \).

a. Show that the trace is independent of the chosen basis!

b. Show that \( \text{Tr} \hat{A} \hat{B} = \text{Tr} \hat{B} \hat{A}! \)

14.1.5.2 Ex: Pure states and mixtures

Consider a system of two levels coupled by a light mode. The Hamiltonian can be written \((\hbar \equiv 1)\),

\[ \hat{H} = \begin{pmatrix} 0 & \frac{\hbar}{2} \Omega \\ \frac{\hbar}{2} \Omega & \omega_0 \end{pmatrix} . \]

Calculate \( \hat{\rho} \), \( \hat{\rho}^2 \) and \( \langle \hat{H} \rangle \) for the following two cases:

a. The atom is in a superposition state, \( |\psi\rangle = \alpha |1 \rangle + \beta |2 \rangle \)

b. The atom is a statistical mixture of eigenstates, \( \hat{\rho} = \mu |1 \rangle \langle 1 | + \nu |2 \rangle \langle 2 |. \)
14.1.5.3 Ex: Mixture of states

A two-level atom is initially in a superposition of two states \( |\psi\rangle = \frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{2}} |2\rangle \).

An apparatus measures the populations of the states, but the experimenter forgot to read the indicated result.

a. Describes the state the atom by the density operator.

b. Now the experimenter returns to the device. Calculate with which probability he reads the state \( |1\rangle \).

14.1.5.4 Ex: Thermal population of a harmonic oscillator

In thermal equilibrium the energy states of a system are populated following Boltzmann’s law,

\[
P_n = \frac{e^{-n\beta \omega}}{\sum_m e^{-m\beta \omega}} \quad \text{with} \quad \beta \equiv \frac{1}{k_B T} .
\]

Consider a one-dimensional harmonic oscillator characterized by the secular frequency \( \omega \) and, using the density operator, calculate the mean quantum number of the population and the mean energy.

14.2 Bloch equations for two-level atoms

In this chapter we will begin to apply the ideas and tools developed in the previous sections. Let us first make use of the density matrix to describe a two-level atom coupled to a single-mode light field without spontaneous emission. We will then introduce the atomic Bloch vector as a convenient and suggestive method to describe the time evolution of a coupled two-level atom. We will introduce spontaneous emission and the important concepts of polarization and susceptibility emanating from an excited sample of oscillating dipoles. Optical Bloch equations including spontaneous emission will be given and their stationary solutions will be discussed. Dissipative processes always broaden transition lines, and thus we will discuss various broadening mechanisms.

14.2.1 The matrix elements of the density operator

Since the optical Bloch equations are coupled differential equations relating the elements of the density operator matrix, we must examine the temporal dependence of these matrix elements, based on our knowledge of the operator’s properties. We begin with the Liouville equation (14.36) and evaluate the elements of the matrix,

\[
\langle m | \frac{d\hat{\rho}(t)}{dt} | n \rangle = \frac{i}{\hbar} \langle m | [\hat{\rho}(t), \hat{H}] | n \rangle = \frac{i}{\hbar} \langle m | [\hat{\rho}(t), \hat{H}_A + \hat{V}(t)] | n \rangle \quad (14.52)
\]

where \( |m\rangle \) and \( |n\rangle \) are members of a complete set of vectors of a basis \( \{ |k\rangle \} \) which are also eigen-kets of \( \hat{H}_A \) and span the space of \( \hat{H} \). Now, we insert the closing expression \( \sum_k |k\rangle \langle k| \) in the commutator on the right-hand side of Eq. (14.52):

\[
\langle m| [\hat{\rho}(t), \hat{V}(t)] | n \rangle = \sum_k \left[ \langle m | [\hat{\rho}(t) | k \rangle \langle k | \hat{V} | n \rangle - \langle m | \hat{V} | k \rangle \langle k | [\hat{\rho}(t) | n \rangle \right] . \quad (14.53)
\]
For our two-level atom the complete set only includes two states: \( |1(t)\rangle = |1\rangle \) and \( |2(t)\rangle = e^{-i\omega_0 t} |2\rangle \). In addition, the matrix elements of the dipole coupling operator \( \hat{V} \) are only non-diagonal,

\[
V \equiv \langle 1|\hat{V}|2\rangle = \langle 2|\hat{V}|1\rangle.
\]

Hence, Eq. (14.52) adopts the form,

\[
\begin{align*}
\frac{d\hat{\rho}_{11}}{dt} &= \frac{i}{\hbar} [\hat{\rho}_{12} V - \hat{\rho}_{21} V] \\
\frac{d\hat{\rho}_{22}}{dt} &= \frac{i}{\hbar} [\hat{\rho}_{21} V - \hat{\rho}_{12} V] = -\frac{d\hat{\rho}_{11}}{dt} \\
\frac{d\hat{\rho}_{12}}{dt} &= i\omega_0 \hat{\rho}_{12} + \frac{i}{\hbar} [V(\hat{\rho}_{11} - \hat{\rho}_{22})] \\
\frac{d\hat{\rho}_{21}}{dt} &= -i\omega_0 \hat{\rho}_{21} + \frac{i}{\hbar} [V(\hat{\rho}_{22} - \hat{\rho}_{11})] = \frac{d\hat{\rho}_{12}^*}{dt}
\end{align*}
\]

remembering that the dash of the diagonal terms, called populations, must be unitary, and that the non-diagonal terms, called coherences, must be complex,

\[
\hat{\rho}_{11} + \hat{\rho}_{22} = 1 \quad , \quad \hat{\rho}_{12} = \hat{\rho}_{12}^*.
\]

The above set of equations constitutes the optical Bloch equations in the Schrödinger picture. It does not include loss terms due to spontaneous emission. We transform the Bloch equations to the interaction picture by replacing the Liouville equation (14.36) by (14.40), and calculating the matrix elements. We obtain,

\[
\begin{align*}
\frac{d\hat{\rho}_{22}}{dt} &= \frac{i}{\hbar} V(\hat{\rho}_{21} - \hat{\rho}_{12}) \\
\frac{d\hat{\rho}_{12}}{dt} &= \frac{i}{\hbar} V(\hat{\rho}_{11} - \hat{\rho}_{22})
\end{align*}
\]

We would also have obtained this expression via the substitution, \( \hat{\rho}_{12} = \hat{\rho}_{12} e^{i\omega_0 t} \).

The interaction picture simplifies the expressions for the temporal dependence of the coherences by eliminating the first term on the right-hand side. Transforming to the interaction picture removes the temporal dependence of the basis vectors spanning the Hilbert space of the two-level atom.

We have derived the optical Bloch equations from the Liouville equation, which is the fundamental equation of motion of the density operator, and we have seen how a unitary transformation can be used to represent these equations in the Schrödinger, Heisenberg or interaction picture. So far, the Bloch equations do not include the possibility of spontaneous emission. We will learn later, how to include this phenomenon.

### 14.2.2 Rotating wave approximation

In the following, we will only consider exponentials rotating with the frequency \( \Delta \equiv \omega - \omega_0 \), and we will neglect terms rotating like \( \Delta \equiv \omega + \omega_0 \). This approximation, called rotating wave approximation (RWA) is good, when the Rabi frequency is sufficiently small, \( \Omega \ll \omega \). Otherwise, we observe an energy correction of the levels called Bloch-Siegert shift. The RWA can be implemented in the time dependence of the coupling operator,

\[
V(t) = \hbar \Omega \cos \omega t \rightarrow \frac{\hbar}{2} \Omega e^{-i\omega t},
\]
neglecting the part $\frac{1}{2} \hbar \Omega e^{i\omega t}$.

Once the RWA made, we can transform to the rotating system by the prescription,

$$\rho_{12} \equiv \hat{\rho}_{12} e^{-i\omega t}, \quad \rho_{22} \equiv \hat{\rho}_{22},$$

which, applied to the Bloch equations in the Schrödinger picture Eq. (14.55), yields,

$$\frac{d\rho_{22}}{dt} = i \frac{\Omega}{2} (\rho_{21} - \rho_{12}), \quad \frac{d\rho_{12}}{dt} = -i \Delta \rho_{12} + i \frac{\Omega}{2} (\rho_{11} - \rho_{22}).$$

In Exc. 14.2.5.1 we derive the Bloch equations from the equations of motion for the population amplitudes $a_1$ and $a_2$.

For arbitrary starting conditions, the solution of these equations is not simple. To solve the problem we write the equations in a matrix form,

$$\vec{\rho} \equiv \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{12} \\ \rho_{21} \end{pmatrix}, \quad M \equiv \begin{pmatrix} 0 & 0 & \frac{i}{2} \Omega & -\frac{i}{2} \Omega \\ 0 & 0 & -\frac{i}{2} \Omega & \frac{i}{2} \Omega \\ \frac{i}{2} \Omega & -\frac{i}{2} \Omega & 0 & i\Delta \\ -\frac{i}{2} \Omega & \frac{i}{2} \Omega & 0 & i\Delta \end{pmatrix}, \quad \dot{\vec{\rho}} = M \vec{\rho}.$$  

(14.61)

To solve this system of differential equations, we calculate the eigenvalues of the matrix,

$$\det(M - \lambda) = \lambda^2 (\Delta^2 + \Omega^2) + \lambda^4 = 0$$

$$\lambda = 0, \pm iG,$$

with the generalized Rabi frequency $G \equiv \sqrt{\Delta^2 + \Omega^2}$. Therefore, the general solution is,

$$\rho_{22}(t) = \rho_{22}^{(1)} + \rho_{22}^{(2)} e^{iGt} + \rho_{22}^{(3)} e^{-iGt}$$

$$\rho_{12}(t) = \rho_{12}^{(1)} + \rho_{12}^{(2)} e^{iGt} + \rho_{12}^{(3)} e^{-iGt}.$$  

(14.63)

The coefficients follow from the Bloch equations with particular starting conditions. With a little algebra we get

$$\rho_{22}^{(1)} = \rho_{22}(0) + \frac{1}{4G^2} [\Omega^2 (1 - 2\rho_{22}(0)) - \Delta (\Omega \rho_{12}^*(0) + \Omega^* \rho_{12}(0))],$$

$$\rho_{22}^{(2)} = \frac{1}{4G^2} [-\Omega^2 (1 - 2\rho_{22}(0)) + (\Delta + G) \Omega \rho_{12}^*(0) + (\Delta - G) \Omega^* \rho_{12}(0)],$$

$$\rho_{22}^{(3)} = \frac{1}{4G^2} [-\Omega^2 (1 - 2\rho_{22}(0)) + (\Delta - G) \Omega \rho_{12}^*(0) + (\Delta + G) \Omega^* \rho_{12}(0)],$$

$$\rho_{12}^{(1)} = \frac{\Delta - G}{4G^2} [\Omega^2 (1 - 2\rho_{22}(0)) + \Omega (\Omega^* \rho_{12}(0) + \Omega^* \rho_{12}^*(0))],$$

$$\rho_{12}^{(2)} = \frac{\Delta - G}{4G^2} [-\Omega^2 (1 - 2\rho_{22}(0)) + (\Delta + G) \Omega \rho_{12}^*(0) + (\Delta - G) \rho_{12}(0)],$$

$$\rho_{12}^{(3)} = \frac{\Delta + G}{4G^2} [\Omega^2 (1 - 2\rho_{22}(0)) + (\Delta - G) \Omega \rho_{12}^*(0) + (\Delta + G) \rho_{12}(0)].$$

(14.64)

We derive this solution in Exc. 14.2.5.2.

To begin the discussion of this solution, let us consider a sample of atoms initially in the ground state when the light field is switched on at time $t = 0$,

$$\rho_{11}(0) = 1 = 1 - \rho_{22}(0), \quad \rho_{12}(0) = 0 = \rho_{21}(0).$$  

(14.65)
In this case, the conditions (14.64) simplify to,

\[ \rho^{(1)}_{22} = \frac{\Omega^2}{2G^2}, \quad \rho^{(1)}_{12} = \frac{1}{2G^2} \Delta \Omega \]

\[ \rho^{(2)}_{22} = -\frac{\Omega^2}{4G^2}, \quad \rho^{(2)}_{12} = \frac{-\Delta}{4G^2} \Omega \]

\[ \rho^{(3)}_{22} = -\frac{\Omega^2}{4G^2}, \quad \rho^{(3)}_{12} = \frac{-\Delta}{4G^2} \Omega, \]

such that,

\[ \rho_{22} = \rho^{(1)}_{22} + \rho^{(2)}_{22} e^{iGt} + \rho^{(3)}_{22} e^{-iGt} = \frac{\Omega^2}{4G^2} (2 - e^{iGt} - e^{-iGt}) \]

\[ \rho_{12} = \rho^{(1)}_{12} + \rho^{(2)}_{12} e^{iGt} + \rho^{(3)}_{12} e^{-iGt} = \frac{\Delta \Omega}{2G^2} - \frac{\Delta - G}{4G^2} \Omega e^{iGt} - \frac{\Delta + G}{4G^2} \Omega e^{-iGt} \]

\[ = \frac{2\Omega}{4G^2} (\Delta - \Delta \cos Gt + iG \sin Gt). \]

Using \( \cos x = 1 - 2 \sin^2 \frac{x}{2} \) and \( \sin x = 2 \sin \frac{x}{2} \cos \frac{x}{2} \), we finally obtain,

\[ \rho_{22} = \frac{\Omega^2}{G^2} \sin^2 \frac{Gt}{2}, \quad \rho_{12} = \frac{\Omega}{G^2} \sin \frac{Gt}{2} \left( \Delta \sin \frac{Gt}{2} + iG \cos \frac{Gt}{2} \right). \] (14.68)

And comparing with the solutions of the Schrödinger equation for a coupled two-level atom 2.4.6.1 and (5.92), we verify,

\[ \rho_{22} = \left| \frac{i \Omega}{G} e^{-it\Delta/2} \sin \frac{Gt}{2} \right|^2 = |a_2|^2 \] (14.69)

\[ \rho_{12} = -e^{-it\Delta/2} \left[ \cos \frac{Gt}{2} - i \frac{\Delta}{G} \sin \frac{Gt}{2} \right] \frac{-i \Omega}{G} e^{it\Delta/2} \sin \frac{Gt}{2} = a_1 a_2^*. \] (14.70)

14.2.3 Pauli matrices and the atomic Bloch vector

The internal structure of atoms is analyzed in atomic physics, where we find that the energy levels are discrete (Bohr’s axiom). The center of mass motion of the atoms and collisions with other atoms are ignored, and concerning the interaction of the atoms with light, we are only interested in the aspect, that the interaction can induce transitions between internal states via absorption or emission of photons. It is the duty of atomic physics to calculate the frequencies and strengths of transitions (by Hartree-Fock or similar methods), as well as their behavior in external electric and magnetic fields. The results of these calculations are visualized in energy level schemes called Grotrian diagrams. In quantum optics we do not care, how the energies of the levels were calculated, but accept them as given. That is, we assume the Hamiltonian of the unperturbed atom to be diagonalized, so that its internal structure can be written as,

\[ \hat{H}_{\text{electron}} = \sum_j \hbar \omega_j |j\rangle \langle j| \] (14.71)

The electronic states are orthonormal \( \langle i | j \rangle = \delta_{ij}, \) and we define the transition operators by

\[ \hat{\sigma}_{ij} |k\rangle = \delta_{jk} |i\rangle, \] (14.72)
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and $\hat{\sigma}_{ij}^+ = \hat{\sigma}_{ji}$ satisfying the commutation relation,

$$[\hat{\sigma}_{ij}, \hat{\sigma}_{lk}] = \delta_{jl} \hat{\sigma}_{ik} - \delta_{ik} \hat{\sigma}_{lj}.$$  \hspace{1cm} (14.73)

Many times we will restrict ourselves to atoms of two or three levels. For a two-level system we obtain the Pauli spin matrix defined in (2.45). Every $2 \times 2$ matrix can be expanded on a Pauli matrix basis,

$$\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = |1\rangle \rho_{11} \langle 1| + |1\rangle \rho_{12} \langle 2| + |2\rangle \rho_{21} \langle 1| + |2\rangle \rho_{22} \langle 2|,$$

$$= \rho_{11}(\frac{1}{2} + \frac{1}{2} \hat{\sigma}_z) + \rho_{12} \hat{\sigma}^- + \rho_{21} \hat{\sigma}^+ + \rho_{22}(\frac{1}{2} - \frac{1}{2} \hat{\sigma}_z)$$

$$= \rho_{11} \hat{\sigma}^+ \hat{\sigma}^- + \rho_{12} \hat{\sigma}^- + \rho_{21} \hat{\sigma}^+ + \rho_{22} \hat{\sigma}^- \hat{\sigma}^+ = \begin{pmatrix} \langle \hat{\sigma}^- \hat{\sigma}^+ \rangle & \langle \hat{\sigma}^- \rangle \\ \langle \hat{\sigma}^+ \rangle & \langle \hat{\sigma}^+ \hat{\sigma}^- \rangle \end{pmatrix}.$$  \hspace{1cm} (14.74)

This formalism can easily be extended to an atom with many levels. Solve the Exc. 14.2.5.3.

For the two-level case it is useful to introduce an alternative notation based on the Bloch vector defined in (2.47),

$$\vec{\rho} \equiv \begin{pmatrix} 2 \text{Re} \rho_{12} \\ 2 \text{Im} \rho_{12} \\ \rho_{22} - \rho_{11} \end{pmatrix} = \begin{pmatrix} \langle \sigma^- \rangle + \langle \sigma^+ \rangle \\ i \langle \sigma^- \rangle - \langle \sigma^+ \rangle \\ \langle \sigma^+ \sigma^- \rangle - \langle \sigma^- \sigma^+ \rangle \end{pmatrix} = \begin{pmatrix} \langle \sigma_x \rangle \\ \langle \sigma_y \rangle \\ \langle \sigma_z \rangle \end{pmatrix}.$$  \hspace{1cm} (14.75)

We also define the torque vector,

$$\vec{G} \equiv \begin{pmatrix} \Omega \\ 0 \\ \Delta \end{pmatrix} \quad \text{with} \quad \|G^2\| = G = \sqrt{\Omega^2 + \Delta^2},$$

the length of which is simply the Rabi frequency. With this, we can write the Bloch equations,

$$\frac{d\vec{\rho}}{dt} = \vec{G} \times \vec{\rho},$$

as will be shown in Exc. 14.2.5.4. $\rho_{12}$ describes the polarization and $\rho_{22} - \rho_{11}$ the population inversion of the atom. The equation is analogous to the equation of motion for a rigid rotor or spinning top (for example, a dipole in a homogeneous field). It displays phenomena such as precession and nutation. The physical content and usefulness of the Bloch vector will become clearer when we use the formalism to analyze electric and magnetic couplings. In Exc. 14.2.5.5 we verify that the Bloch vector is normalized (as long as spontaneous emission is not considered).

14.2.4 State manipulations by sequences of radiation pulses

The temporal dependence of the three components of the atomic Bloch vector provides a useful illustration of the atom-field interaction. Resonant coupling, $\Delta = 0$ and $G = \Omega$, puts the solutions (14.68) into the form,

$$\rho_{22}(t) = \frac{1}{2}(1 - \cos \Omega t), \quad \rho_{12}(t) = \frac{i}{2} \sin \Omega t,$$

$$\rho_{21}(t) = \frac{i}{2} \sin \Omega t,$$

$$\rho_{11}(t) = \frac{1}{2}(1 + \cos \Omega t).$$

(14.78)
that is,

$$\vec{g}(t) = \begin{pmatrix} 0 \\ \sin \Omega t \\ -\cos \Omega t \end{pmatrix}. \tag{14.79}$$

That is, a resonant pulse rotates a Bloch vector initially pointing in the direction $-z$ within the plane $z$-$y$, until it arrives, at time $t = \frac{\pi}{2\Omega}$, at the $+y$ direction and at time $t = \frac{\pi}{\Omega}$ at the $+z$ direction. This means that the entire population has been transferred to the excited state. The Bloch vector continues to rotate (the movement is called \textit{nutation}) around the torque vector $G$ which, as can be seen from Eq. (14.77), points at the $+x$ direction when $\Delta = 0$. The nutation frequency is proportional to the force $\Omega$ of the atom-field interaction. With the Eq. (14.68) we see that the population oscillates between the ground and excited state with the frequency $\Omega$. This means that the energy $\hbar \omega$ is periodically exchanged between the atom and the field. A pulse of resonant light of duration such that $\tau = \pi/2\Omega$ is called a $\pi/2$-pulse. The nutation is illustrated in Fig. 14.1(a).

Once the coherence has been excited by a detuned radiation, $\Delta \neq 0$, the Bloch vector does not stand still, even after the radiation has been switched off. To see this, we consider again the general solution (14.64) now entering $\Omega = 0$. If the Bloch vector is initially at a point in the unitary circle of the plane $z$-$y$, it will rotate according to the formula,

$$\rho_{22}(t) = \rho_{22}(0), \quad \rho_{12}(t) = \rho_{12}(0)e^{-i\Delta t}, \quad \tag{14.80}$$

that is,

$$\vec{g}(t) = \begin{pmatrix} \rho_{12}(0) \sin \Delta t \\ \rho_{12}(0) \cos \Delta t \\ 2\rho_{22}(0) - 1 \end{pmatrix}. \tag{14.81}$$

That is, the Bloch vector performs a motion of \textit{precession} around the symmetry axis. The precession is illustrated in Fig. 14.1(b).

![Figure 14.1](image)

Figure 14.1: (code) (a) Nutation of the Bloch vector. The red circles show the evolution of the Bloch vector on the Bloch sphere for a resonant $\pi$-pulse. (b) Precession of the Bloch vector.

The evolution of the Bloch vector on the surface of the Bloch sphere under the influence of radiation fields can be considered a coherent trajectory of the wavefunction
of the atomic state, which is therefore subject to interference phenomena [299]. Interferometers can be realized by sequences of consecutive pulses splitting populations, exciting coherences, and remixing populations.

Sensors based on interferometry of atomic excitation are nowadays among the most accurate and most sensitive. We will discuss the method of radiation pulse sequences in several exercises: In the Excs. 14.2.5.6, 14.2.5.7, and 14.2.5.8 the Ramsey method.

14.2.4.1 Atomic ensembles

While it is technically challenging to observe the dynamics of single atoms, it is relatively easy monitor the dynamics of ensembles of atoms, provided that they react synchronously to incident radiation. The concentration of a sufficient number of atoms in a small volume can, however, introduce additional (desirable or undesirable) effects. Collisions, for instance, induce (irreversible) decoherence. On the other hand, if the ensemble is sufficiently dense that the mean distance between atoms is less than a resonant wavelength, then the transition dipoles of the individual atoms will couple to produce a collective dipole moment and generate effects known as superradiance.

Thermal motion of the atoms is another undesired effect, because every atom will interact with the radiation on a different Doppler-shifted frequency. This leads to diffusion of the individual atomic Bloch vectors in the \(x-y\)-plane, which in turn limits the resolution of interferometric applications. We will discuss in Exc. 14.2.5.9 the photon echo method, which allows to circumvent this problem.

14.2.5 Exercises

14.2.5.1 Ex: Derivation of Bloch equations

Derive the Bloch equations explicitly based on the temporal evolutions of the coefficients \(a_{1,2}\) (5.63) knowing that \(\rho_{ij} = a_i^* a_j\).

14.2.5.2 Ex: General solution of Bloch equations

Derive the solution (14.64) of the Bloch equations (14.61).

14.2.5.3 Ex: Expansion in Pauli matrices

Show explicitly \(\text{Tr} \hat{\rho} \hat{\sigma}^- \hat{\sigma}^+ = \rho_{11}\).

14.2.5.4 Ex: Bloch vector and Bloch equations

Show that Eq. (14.77) is equivalent to the Bloch equations (14.61).

14.2.5.5 Ex: Normalization of the Bloch vector

Verify \(\|\hat{\rho}\| = 1\).
14.2.5.6 **Ex: Sequence of Ramsey pulses**

Many atomic clocks work according to the Ramsey spectroscopy method: The two-level atom is resonantly excited by a microwave $\pi/2$-pulse. Then, the phase of atomic coherence precesses freely over a period of time $T$ accumulating an angle $\phi$. Finally, a second $\pi/2$-pulse is applied and the population of the upper-level is measured. Calculate this population as a function of the angle $\phi$. Neglect spontaneous emission.

14.2.5.7 **Ex: Analytical treatment of the Ramsey experiment**

Derive the analytic formula for the final population $\rho_{22}$ for the Rabi and Ramsey experiments. Derive and compare the line widths of the "interference fringes" in these two experiments.

14.2.5.8 **Ex: Atomic clocks by the Ramsey method with spontaneous emission**

In this exercise we study the Ramsey method used in atomic clocks. For this, we will consider a two-level system $|1\rangle$ and $|2\rangle$ excited by a microwave radiation field characterized by the Rabi frequency $\Omega_{12}$, and we will compare two cases: without and with spontaneous emission:

a. Write down the Hamiltonian of the system, propose a sequence of pulses allowing the observation of the Ramsey fringes, do a numerical simulation of the Schrödinger equation (based on the prescription (14.151)), and prepare a graph of the type 14.1 illustrating the temporal evolution of the Bloch vector during the sequence.

b. Calculate numerically from the Schrödinger equation the population $\rho_{22}$ immediately after the pulse sequence as a function of the detuning $\Delta_{12}$ of the radiation field, and prepare a graph of the spectrum. Also, assuming a decay rate of $\Gamma_{12} = 0.1\Omega_{12}$, calculate the population $\rho_{22}$ as a function of detuning $\Delta_{12}$ from the Bloch equations (making sequences of type (14.151)), prepare a new graph, and compare it with the previous graph obtained by the Schrödinger equation.

c. What happens to the width of the fringes, when the free precession time $\tau$ between the Ramsey pulses is increased? Prepare a graph of the inversion $2\rho_{22} - 1$ as a function of $\Delta_{12}$ and $\tau$ and interpret the results.

14.2.5.9 **Ex: Photon echo**

'Photon echo' is a powerful spectroscopic technique that allows circumvention of certain dephasing processes, for example, the Doppler shift due to the atomic motion in a thermal sample of atoms. The technique resembles the Ramsey method with the difference, that between the two Ramsey $\pi/2$-pulses, that is, during the free precession time, we apply an additional $\pi$-pulse, which inverts the imaginary part of the coherence. We will study this method by numerical simulation of the Schrödinger equation and the Bloch equations for a two-level system with and without spontaneous emission:

a. Write down the Hamiltonian of the system and do a numerical simulation of the Schrödinger equation (concatenating the pulses as explained in Eq. (14.151)) for the following temporal pulse sequence:

(i) resonant $\pi/2$-pulse ($\Delta_{12} = 0$) choosing $\Omega_{12} = 2$, ...
(ii) evolution for a time $T$ without radiation ($\Omega_{12} = 0$),
(ii) resonant $\pi/2$-pulse using the same parameters as in (i),
(iv) evolution for a time $T$ without radiation, and
(v) resonant $\pi/2$-pulse identical to the first pulse.
Prepare a graph of type 14.1 illustrating the temporal evolution of the Bloch vector
during the sequence. Now, repeat the sequence taking into account a possible Doppler
shift leading to $\Delta_{12} \neq 0$.

b. Repeat the calculation of (a), now numerically solving the Bloch equations, which
allow the occurrence of spontaneous emission ($\Gamma_{12} = 0.03\Omega_{12}$). Interpret the results.

### 14.3 Bloch equations with spontaneous emission

#### 14.3.1 Phenomenological inclusion of spontaneous emission

To find the Bloch equations including spontaneous emission, we insert the phenomeno-
logical term $-i\gamma a_2$ into the Eqs. (5.63), as we have already done for Eq. (13.112),
\[
\Omega^* \cos \omega t e^{i\omega t} a_1 - i\gamma a_2 = i \frac{d a_2}{d t} ,
\]
that is, the equations of motion can be corrected by simply replacing,
\[
\frac{d a_2}{d t} \sim \left( \frac{d}{d t} + \gamma \right) a_2 .
\]
Knowing $\rho_{mn} = a_m^* a_n$, it is easy to check,
\[
\frac{d \rho_{22}}{d t} \sim \left( \frac{d}{d t} + \Gamma \right) \rho_{22} \quad \text{and} \quad \frac{d \rho_{12}}{d t} \sim \left( \frac{d}{d t} + \gamma \right) \rho_{12} ,
\]
with $\gamma = \Gamma/2$, such that the Bloch equations become,
\[
\begin{pmatrix}
\frac{d}{dt} & \rho_{11} \\
\rho_{22} & \rho_{12} \\
\tilde{\rho}_{12} & \tilde{\rho}_{21}
\end{pmatrix}
= \begin{pmatrix}
0 & \Gamma & \frac{i}{2} \Omega & -\frac{i}{2} \Omega \\
0 & -\Gamma & -\frac{i}{2} \Omega & \frac{i}{2} \Omega \\
\frac{i}{2} \Omega & -\frac{i}{2} \Omega & -i\Delta - \gamma & 0 \\
-\frac{i}{2} \Omega & \frac{i}{2} \Omega & 0 & i\Delta - \gamma
\end{pmatrix}
\begin{pmatrix}
\rho_{11} \\
\rho_{22} \\
\tilde{\rho}_{12} \\
\tilde{\rho}_{21}
\end{pmatrix} .
\]

**Example 52 (Langevin equation):** The Heisenberg equation for the evolution
of the internal degrees of freedom, including the phenomenologically introduced
decay, is also called Langevin equation. It can be written as,
\[
i \frac{d \hat{\sigma}}{dt} = \frac{1}{\hbar}[\hat{\sigma}, \hat{H}] - \frac{i}{2} \Gamma \hat{\sigma} ,
\]
and analogously for $\hat{\sigma}_z$. With the Hamiltonian $\hat{H} = \hbar \Delta \hat{\sigma}^\dagger \hat{\sigma}^\dagger + \frac{1}{2} \hbar \Omega (e^{i\omega t} \hat{\sigma} + h.c.)$
we obtain, using the Pauli spin matrices, exactly the Bloch equations,
\[
i \dot{\hat{\sigma}} = \Delta [\hat{\sigma}, \hat{\sigma}^\dagger] + \frac{1}{2} \Omega e^{i\omega t} [\hat{\sigma}, \hat{\sigma}^\dagger] - \frac{1}{2} \Gamma \hat{\sigma} = -\Delta \hat{\sigma} - \frac{1}{2} \Omega e^{i\omega t} \hat{\sigma}_z - \frac{1}{2} \Gamma \hat{\sigma}
\]
\[
i \dot{\hat{\sigma}}_z = \Delta [\hat{\sigma}_z, \hat{\sigma}^\dagger] + \frac{1}{2} \Omega e^{i\omega t} [\hat{\sigma}_z, \hat{\sigma}^\dagger] + \frac{1}{2} \Omega e^{i\omega t} [\hat{\sigma}_z, \hat{\sigma}] - \frac{1}{2} \Gamma \hat{\sigma}_z = -\Omega (\hat{\sigma}^\dagger - \hat{\sigma}) - \frac{1}{2} \Gamma \hat{\sigma}_z .
\]
14.3.1.1 Stationary solution of the Bloch equations

The dissipation introduced by the spontaneous emission allows the system to reach a steady state. Letting the time derivatives be 0, we obtain the stationary solutions,

\[
\rho_{22}(\infty) = \frac{\frac{1}{4} |\Omega|^2}{\Delta^2 + \frac{1}{2} |\Omega|^2 + \frac{1}{4} \Gamma^2} \quad \text{and} \quad \rho_{12}(\infty) = e^{i \Delta t} \frac{\frac{1}{2} |\Omega| (\Delta - \frac{i}{2} \Gamma)}{\Delta^2 + \frac{1}{2} |\Omega|^2 + \frac{1}{4} \Gamma^2}.
\]

This will be shown in Exc. 14.3.5.1. We see that the populations and coherences both have a frequency dependence, which is similar but not identical to the one already found for the susceptibility \(\chi\), the absorption coefficient \(K\), and the absorption cross section \(\sigma_{0a}\) in the Eqs. (13.120), (13.121), and (1.73). But here the denominators have an extra term \(\frac{1}{2} |\Omega|^2\) contributing to an effective widths of \(\rho_{22}\) and \(\rho_{12}\),

\[
\Gamma_{\text{eff}} = \sqrt{2 |\Omega|^2 + \Gamma^2}.
\]

This effect, called power broadening or saturation broadening, has already been discussed in (1.102). The phase factor \(e^{i \Delta t}\) describes the optical precession of the Bloch vector.

By introducing the saturation parameter,

\[
s \equiv \frac{2 |\Omega|^2}{4 \Delta^2 + \Gamma^2},
\]

we can rewrite the stationary dipole moment and the excited state population (14.86) as,

\[
\rho_{22}(\infty) = \frac{s/2}{1 + s} , \quad \rho_{12}(\infty) = e^{i \Delta t} \frac{\Delta - i \frac{\Gamma}{2}}{\Omega} \frac{s}{1 + s}.
\]

and

\[
\rho_{12}(\infty)^2 = \frac{s/2}{(1 + s)^2}.
\]

Fig. 14.2(a) shows the Rabi oscillations damped by spontaneous emission. For long times the population of the excited state \(\rho_{22}\) converges to the asymptote (14.89). Fig. 14.2(b) shows the temporal evolution of the Bloch vector subject to spontaneous emission. In Exc. 14.3.5.2 we the behavior of the phase of the dipole moment \(\rho_{12}\) with respect to the driving field.

Example 53 (Resonant excitation and weak excitation): A case where the Bloch equations can be analytically treated is under resonant excitation, \(\Delta = 0\). In this case, for the initial conditions, \(\rho_{12}(0) = \rho_{22}(0) = 0\), the solution including decay is,

\[
\rho_{22}(t) = \frac{|\Omega|^2}{2 |\Omega|^2 + \Gamma^2} \left[ 1 - e^{-\frac{3 \Gamma t}{4}} \left( \cos \lambda t + \frac{3 \Gamma}{4 \lambda} \sin \lambda t \right) \right] \quad \text{and} \quad \rho_{12}(t) = 0,
\]

where \(\lambda \equiv \sqrt{|\Omega|^2 - \Gamma^2}\). This solution (which will be derived in Exc. 14.3.5.3), describes the optical mutation of the Bloch vector along the \(\rho_z\) axis. We note here that, due to spontaneous emission, the norm of the Bloch vector is NOT...
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Figure 14.2: (code) (a) Rabi oscillations damped by spontaneous emission for Rabi frequencies between $\Omega/\Gamma = 0.2, \ldots, 5$. (b) Evolution of the Bloch vector subject to spontaneous emission ($\Gamma_{12} = 0.05\Omega_{12}$) after of a resonant $\pi$-pulse (blue) and after a $\pi$-pulse with detuning $\Delta_{12} = \Omega_{12}/2$.

conserved, i.e., the Bloch vector evolves to the interior of the Bloch sphere. Another case that can be solved analytically is the weakly excited atom, $|\Omega| \ll \gamma$,

$$\rho_{22} \simeq \frac{\Omega^2}{4\Gamma^2} \left( 1 + e^{-2\Gamma t} - 2 \cos \Delta t \right) \quad (14.92)$$

and

$$\rho_{12}(t) \simeq \frac{-i\Omega}{2i\Delta + 2\Gamma} \left( e^{-i(\Delta+\Gamma)t} - 1 \right) + \rho_{12}(0) e^{-i(\Delta+\Gamma)t} .$$

14.3.2 Susceptibility and density operator

The frequency-dependent linear susceptibility completely describes the linear propagation of an electromagnetic wave within a medium. It is related to the index of refraction and the absorption coefficient. Nonlinear processes should be described by higher order susceptibilities. Electric fields $\vec{E} = \vec{E}_0 e^{i\omega t} + c.c.$ induce in media characterized by a given susceptibility $\chi$ the polarization $\vec{P} = \chi \vec{E}$. The polarization is the sum of the dipole moments of the individual atoms, $\vec{P} = n \langle \vec{d} \rangle$, where $n = N/V$ is the atomic density. The susceptibility can therefore be expressed by the Hamiltonian interaction $\hat{H} = -\vec{d} \cdot \vec{E}$,

$$\chi = -\frac{n}{|\vec{E}|^2} \langle \hat{H} \rangle . \quad (14.93)$$

Using the two-level Hamiltonian (13.119) we obtain,

$$\chi = -n \frac{\hbar \Omega}{2|\vec{E}|^2} \rho_{12} e^{i\Delta t} + c.c. \quad (14.94)$$

for the polarization,

$$\vec{P} = n \vec{d} \rho_{12} + c.c. \quad (14.95)$$
and for the susceptibility,
\[
\chi(\omega) = \frac{2nd^2}{3\varepsilon_0 \hbar} \left( \Delta + i\Gamma \right) \sqrt{4\Delta^2 + 2|\Omega|^2 + \Gamma^2} \quad \text{with} \quad d = \sqrt{\frac{3\pi\varepsilon_0\hbar\Gamma}{k^3}} .
\] (14.96)

We can insert the new expression (14.86) for \( \rho_{12} \) into our previous expression for \( \langle d_{12} \rangle \) (13.111) and get new expressions for the polarization \( \vec{P}(t) \), (13.108) and (13.118), and the susceptibility \( \chi \) (13.120). The modified expression for the susceptibility is,
\[
\chi = \frac{Nd_{12}^2}{3\varepsilon_0 \hbar V} \frac{-\Delta + \frac{1}{2}\Gamma}{\Delta^2 + \frac{1}{2}|\Omega|^2 + \frac{1}{4}\Gamma^2} .
\] (14.97)

In the imaginary component we obtain the new absorption coefficient,
\[
K = \frac{\omega}{c\eta} \chi''(\omega) = \frac{\pi Ne^2 |\langle r_{12} \rangle|^2 \omega_0}{3\varepsilon_0 \hbar c V} \frac{\Gamma/2\pi}{\Delta^2 + \frac{1}{2}|\Omega|^2 + \frac{1}{4}\Gamma^2} ,
\] (14.98)
and the absorption cross-section,
\[
\sigma_{0a} = \frac{\pi e^2 |\langle r_{12} \rangle|^2 \omega_0}{3\varepsilon_0 \hbar} \frac{\Gamma/2\pi}{\Delta^2 + \frac{1}{2}|\Omega|^2 + \frac{1}{4}\Gamma^2} .
\] (14.99)

The important new property is the effective width \( \Gamma_{\text{eff}} \), which appears in \( \chi \), \( K \), and \( \sigma_{0a} \). In Excs. 14.3.5.4 and 14.3.5.5 we calculate the impact of the spontaneous emission on the determinant of the density operator. Solve the Excs. 14.3.5.6, 14.3.5.7, 14.3.5.8, and 14.3.5.9.

### 14.3.3 Liouville equation for two levels

In this chapter we chose to include spontaneous emission in the Bloch equations by phenomenological arguments. We will show more ahead, that dissipation can be treated from general principles. This treatment, named after Weisskopf-Wigner, derives from a Liouville type equation (14.36), but which holds for a total density operator \( \rho_{\text{atom}\&\text{field}} \) describing the atom and the electromagnetic modes, an equation for the density operator of only the atom. The price to pay for this simplification is an additional term appearing in the equation now called master equation,
\[
\dot{\rho}(t) = (\mathcal{L}_0 + \mathcal{L}_{\text{sp}})\rho(t) \quad \text{with} \quad \mathcal{L}_0\rho(t) \equiv \frac{i}{\hbar} [\hat{\rho}(t), \hat{H}] \quad \text{and} \quad \mathcal{L}_{\text{sp}} = \frac{i}{2}(2\hat{\sigma}\hat{\rho}\hat{\sigma}^+ - \hat{\sigma}^+\hat{\rho}\hat{\sigma} - \hat{\rho}\hat{\sigma}^+\hat{\sigma})
\] (14.100)

where \( \hat{\sigma}^\pm \) are the Pauli matrices. We show in Exc. 14.3.5.10, that the known Bloch equations can be derived from the master equation.

### 14.3.4 Saturation effects by the effective Hamiltonian

The eigenvalues of the effective Hamiltonian of a two-level system excited by radiation,
\[
\hat{H} = \begin{pmatrix} 0 & \frac{1}{2}\Omega \\ \frac{1}{2}\Omega & \Delta - \frac{i}{2}\Gamma \end{pmatrix}
\] (14.101)

describe possible effects of line broadening and/or displacement due to coupling,

\[
\frac{1}{2} \left( \Delta - \frac{i}{2} \Gamma \right) \pm \frac{1}{2} \sqrt{\left( \Delta - \frac{i}{2} \Gamma \right)^2 + \Omega^2}.
\] (14.102)

The real parts of the eigenvalues \( \text{Re} \ E \) describe shifts and/or splittings of the transition line. The imaginary parts \( \text{Im} \ E \) describe broadening effects of the lines.

In the simplest case, \( \Delta = 0 \) and \( \Gamma > 4\Omega \), we find the saturation broadening already discussed in (14.87), and we will deepen it in Exc. 14.3.5.11. For the case \( \Gamma < 4\Omega \), we observe a splitting of the line called Autler-Townes splitting, which will be studied in Exc. 14.3.5.12. If \( \Omega \neq 0 \), the spectrum becomes asymmetrical. In the case of weak excitation, \( \Gamma \gg 4\Omega \), we observe a shift of the transition line with dispersive dependence (near the resonance) on the frequency of the incident radiation. This is the dynamic Stark shift (or light-shift). In the case of strong excitation, \( \Gamma \ll 4\Omega \), we observe again at the split spectrum, but now the two lines exhibit an avoided crossing-type dependence on the radiation frequency. We study these effects in Exc. 14.3.5.14.

Obviously, these effects can be studied by the Bloch equation formalism containing the terms of spontaneous relaxation.

**14.3.5 Exercises**

**14.3.5.1 Ex: Stationary solution of the Bloch equations**

Derive the stationary solution of the Bloch equations including spontaneous emission.

**14.3.5.2 Ex: Detuning-dependent phase-shift of the dipole moment**

Calculate the phase-shift of the dipole moment with respect to the driving field across resonance.

**14.3.5.3 Ex: Solution of the Bloch equations for resonant excitation**

Derive the solution (14.91) of the Bloch equations with spontaneous emission for resonant excitation.

**14.3.5.4 Ex: Determinant of the Bloch matrix**

In Sec. 14.1.1 we already saw that \( \det \hat{\rho} = 0 \) for conservative systems. Now, show explicitly for the Bloch matrix of a two-level system, that \( \det \rho = 0 \) only holds in the absence of spontaneous emission.

**14.3.5.5 Ex: Density operator with dissipation**

Discusses the phenomenon of dissipation in the example of

a. a thermal sample of two-level systems \( |i\rangle = |1\rangle, |2\rangle \) characterized by the density operator \( \rho = |i\rangle \langle i| \otimes |v\rangle \langle v| \), where \( |v\rangle \) is the velocity state of the atom and

b. a two-level atom coupled to a radiation field, \( \rho = |i\rangle \langle i| \otimes |n\rangle \langle n| \), where \( |n\rangle \) is the number of photons inside the mode.
14.3.5.6 Ex: Bloch vector
A two-level atom with decay rate $\Gamma = 2\pi \times 6$ MHz be excited by a light field detuned by $\Delta = 2\Gamma$ and whose intensity is a quarter of the saturation intensity. Write down the Bloch vector for $t \to \infty$.

14.3.5.7 Ex: Purity of two-level atoms with spontaneous emission
Calculate for a driven two-level atom in the stationary limit $\text{Tr } \rho$ and $\text{Tr } \rho^2$.

14.3.5.8 Ex: Bloch sphere
Check the temporal evolution of the norm of the Bloch vector defined by $\vec{\rho} \equiv (2\text{Re } \sigma_+ , 2\text{Im } \sigma_-, \sigma_z)$, where the $\sigma_k$ are the Pauli matrices, for a resonantly excited two-level system with and without spontaneous emission.

14.3.5.9 Ex: Atomic beam
An atomic beam is illuminated perpendicular to its propagation direction by (quasi-)monochromatic, collimated laser pulses having the intensity $I = 1$ W/cm$^2$, the wavelength $\lambda = 780$ nm, and the duration 200 ns. The laser is tuned to the center of an atomic resonance line ($\Gamma/2\pi = 6$ MHz).

a. How does the population of the upper atomic state develop?

b. How does the dynamics change, when the light is detuned by 100 MHz?

14.3.5.10 Ex: General form of the master equation
Show that the general form of the master equation: $\dot{\rho} = -\frac{i}{\hbar} [\hat{H}, \rho] - \frac{\Gamma}{2}(2\rho\sigma^+ \sigma^- \rho - \rho\sigma^+ \sigma^-)$, reproduces the Bloch equations including spontaneous emission.

14.3.5.11 Ex: Quantum Zeno effect and saturation broadening
In this exercise we study saturation broadening effect in a three-level system $|1\rangle$, $|2\rangle$, and $|3\rangle$ in $V$-configuration, as shown in Fig. 14.6(b), excited by two resonant lasers with the Rabi frequencies $\Omega_{12}$ and $\Omega_{23}$.

a. From the eigenvalues $E_{1,2}$ of the effective Hamiltonian (14.101) of the system, describe the behavior of the real part (energy shift) and the imaginary part (linewidth) as a function of the Rabi frequency. Prepare diagrams $\Omega_{12}$ versus $\text{Re } E_{1,2}$ and versus $\text{Im } E_{1,2}$ and discuss the limits $\Omega_{12} > \frac{1}{2}\Gamma_{12}$ and $\Omega_{12} < \frac{1}{2}\Gamma_{12}$.

Saturation broadening can be measured experimentally in a three-level system in $V$-configuration. To reproduce the experiment by numerical simulations of the Bloch equations (14.143),

b. write down the Liouville matrix $\mathcal{L}$ of the system and calculate the time evolution of the Bloch vector via equation (14.147) varying the Rabi frequency $\Omega_{23}$. Choosing the parameters $\Gamma_{23} = \Gamma_{12}$, $\Gamma_{13} = 0.001\Gamma_{12}$, $\Omega_{12} = 0.2\Gamma_{12}$, and $\Delta_{12} = 0 = \Delta_{23}$, prepare a 3D curve (similar to Fig. 14.2(a)) of the population $\rho_{33}(t)$.

c. Interpret the results in terms of broadening by saturation. The broadening can also be understood in terms of the quantum Zeno effect, where the transition $|1\rangle$-$|2\rangle$ plays the role of the 'observed system' and the transition $|2\rangle$-$|3\rangle$ the role of the
measuring device or 'meter' (for example, we can observe the light scattered on the 'meter transition' to infer the evolution of the 'system transition').

14.3.5.12 Ex: Saturation broadening and Autler-Townes splitting

In this exercise we study the Autler-Townes effect in a two-level system $|1\rangle$ and $|2\rangle$ resonantly excited ($\Delta_{12} = 0$) by a laser with the Rabi frequency $\Omega_{12}$:

a. From the eigenvalues $E_{1,2}$ of the effective Hamiltonian (14.101) of the system, describe the behavior of the real part (energy shift) and the imaginary part (linewidth) as a function of the Rabi frequency. Prepare diagrams $\Omega_{12}$ versus $\text{Re} \ E_{1,2}$ and versus $\text{Im} \ E_{1,2}$ and discuss the limits $\Omega_{12} > \frac{1}{2} \Gamma_{12}$ and $\Omega_{12} < \frac{1}{2} \Gamma_{12}$.

b. Write down the Liouville matrix $M_{\text{red}}$ reduced by the trace condition (14.148) and calculate the stationary Bloch vector from equation (14.150) varying the detuning of the probe laser $\Delta_{23}$ and the Rabi frequency $\Omega_{12}$ of the system under study ($|1\rangle$ and $|2\rangle$). Choosing the parameters $\Gamma_{23} = 0.5 \Gamma_{12}$, $\Gamma_{13} = 0.01 \Gamma_{12}$, $\Omega_{23} = 0.1 \Gamma_{12}$, prepare a 3D curve (similar to Fig. 14.2(a)) of the stationary population $\rho_{22}(\infty)$. Interpret the results.

c. Compute the stationary Bloch vector from equation (14.150) varying the detunings of the two lasers $\Delta_{12}$ and $\Delta_{23}$. Choosing the parameters $\Gamma_{23} = \Gamma_{12}$, $\Gamma_{13} = 0.01 \Gamma_{12}$, $\Omega_{23} = 0.1 \Gamma_{12}$, $\Omega_{12} = 0$, $\Omega_{12} = 0.5 \Gamma_{12}$, and $\Omega_{12} = 2 \Gamma_{12}$.

The Autler-Townes effect can be measured experimentally by probing the population of level $|2\rangle$ via excitation of a third (higher) level by a second laser with the Rabi frequency $\Omega_{23}$. Thus, we obtain a three-level system in cascade configuration, as shown in Fig. 14.6(c). In order to reproduce the experiment by numerical simulations of the Bloch equations (14.143),

14.3.5.13 Ex: Light-shift

Calculate the light-shift in a driven two-level system from the effective Hamiltonian,

$$\hat{H}_{\text{eff}} = \begin{pmatrix} 0 & \frac{1}{2} \Omega \\ \frac{1}{2} \Omega & \Delta - \frac{1}{2} \Gamma \end{pmatrix}.$$ 

Prepare spectra of the eigenvalues for $\Gamma/\Omega = 0$, 0.5, and 2.

14.3.5.14 Ex: Light-shift

In this exercise we study the effect of the dynamic Stark shift (or light shift) of the energy levels of a two-level system $|1\rangle$ and $|2\rangle$ excited by a laser with the Rabi frequency $\Omega_{12}$ and the detuning $\Delta_{12}$:

a. From the eigenvalues $E_{1,2}$ of the effective Hamiltonian (14.101) system, find approximations for weak coupling ($\Omega_{12} \ll \Gamma_{12}$) and strong coupling ($\Omega_{12} \gg \Gamma_{12}$). Prepare a graph showing the eigenvalue spectrum (separating the parts $\text{Re} \ E_{1,2}$ and $\text{Im} \ E_{1,2}$) as a function of detuning $\Delta_{12}$ for various values of $\Omega_{12}$. Also search for approximations valid for large detunings $\Delta_{12} \gg \Gamma_{12}, \Omega_{12}$ and add them to the graph.

The light shift can be experimentally measured in a three-level system in $\Lambda$-configuration, as illustrated in Fig. 14.6(a). To reproduce the experiment by numerical simulations of the Bloch equations (14.143),

b. Write the Liouville matrix $M_{\text{red}}$ reduced by the condition to the trace (14.148) and calculate the stationary Bloch vector from equation (14.150) varying the detunings of the two lasers $\Delta_{12}$ and $\Delta_{23}$. Choosing the parameters $\Gamma_{23} = \Gamma_{12}$, $\Gamma_{13} = 0.01 \Gamma_{12}$, $\Omega_{23} = 0.1 \Gamma_{12}$, $\Omega_{12} = 0$, $\Omega_{12} = 0.5 \Gamma_{12}$, and $\Omega_{12} = 2 \Gamma_{12}$. 

Prepare spectra of the eigenvalues for $\Gamma/\Omega = 0$, 0.5, and 2.
\( \Omega_{12} = 2\Gamma_{12} \), and \( \Omega_{23} = 0.2\Gamma_{12} \), prepare a 3D curve (similar to Fig. 14.2(a)) of the stationary population \( \rho_{22}(\infty) \). Interpret the results.

### 14.4 Line broadening mechanisms

The resolution of atomic spectroscopy is generally limited by several perturbative effects, many of them originating in the atomic motion. They manifest themselves as broadening and/or shifts of atomic resonances. Free atoms, as well as atoms confined in potentials, have kinetic energy and evolve on extended phase space trajectories. If the spatial localization is less than the effective cross section of the exciting laser beam, then the interaction time is limited and the resonance lines are broadened by the Fourier effect in a process called transit time broadening, and the efficiency of fluorescence collection is reduced. The same happens with the Doppler effect: Only those atoms that have a specific velocity along the optical axis defined by the laser beam can interact. Free as well as confined atoms can only scatter when they are in specific cells of the phase space.

There are two different fundamental types of broadening. The so-called homogeneous broadening affects all atoms in the same way regardless of their positions or velocities. It usually give rise to Lorentzian line profiles and can be included in the Bloch equations. It correspond to an acceleration of the relaxation. Examples are the natural linewidth, saturation broadening, and collision broadening.

The so-called inhomogeneous broadening is due to a displacement of atomic levels, which may be different for each atom. Averaging over a large sample of atoms, the displacements generate an effective broadening usually with a Gaussian line profile. It can not be included in the Bloch equations, but only as an average over all trajectories of all atoms. It does not correspond to an accelerated relaxation. Inhomogeneous broadening is often due to external perturbations, e.g., Doppler broadening and broadening due to temporal fluctuations or spatial inhomogeneities of external electric or magnetic fields. In Exc. 14.4.6.1 we calculate the optical density of atomic clouds. In Exc. 14.4.6.2 we present a spectroscopic technique bypassing the Doppler broadening called Doppler-free spectroscopy and calculate the Lamb-dip profile. Finally, in Exc. 14.4.6.3, we discuss a cooling technique allowing for the reduction of Doppler broadening, called Zeeman slower.

### 14.4.1 Saturation broadening

Eq. (14.87) shows that when the power of the incident light increases, the population of the excited state saturates at a limit value of \( \rho_{22} = \frac{1}{2} \). The saturation parameter defined in (14.88) measures the degree of saturation. When the narrowband light source is tuned to resonance, the saturation parameter is basically a measure for the ratio between the stimulated population transfer rate \( \Omega \) and the spontaneous decay rate \( A_{21} \). We can rewrite the stationary population of the excited level as in (14.89). In resonance and with the saturation parameter \( s = 1 \), we obtain

\[
\Omega = \frac{1}{\sqrt{2}}\Gamma.
\]
We can use equation (14.103) to define the saturation intensity \( I_{\text{sat}} \) for an atom with the transition dipole \( d_{12} \). From Eq. (1.41) we have,

\[
E_0 = \sqrt{\frac{2I}{\epsilon_0 c}}. \tag{14.104}
\]

Therefore, using the definition of the Rabi frequency, \( \hbar \Omega = d_{12} E_0 \), and the relationship between \( d_{12} \) and \( \Gamma \) given by Eq. (13.38), we have,

\[
I_{\text{sat}} = \frac{g_1}{g_2} \frac{2\pi^2 c \hbar}{3\lambda_0^3} \Gamma, \tag{14.105}
\]

taking into account the degeneracies \( g_j \) of the levels. In Exc. 14.4.6.4 we calculate the saturation intensity of popular atomic transitions.

### 14.4.2 Collision broadening

The theory of atomic collisions covers a large area of research, including elastic and inelastic, reactive and ionizing processes. In low-pressure gases at room temperature or hotter we need only consider the simpler processes: long-range van der Waals interactions that result in elastic collisions. The 'low pressure' criterion requires that the average free path between collisions be greater than any linear dimension of the gas volume. Under these conditions, collisions can be modeled with straight trajectories, along which the interaction time is short and the time between collisions is long in comparison with the radiative lifetime of the excited atomic state. Then, the impact of a collision on the emission of a radiating atom causes a loss of coherence due to a phase interruption of the excited state atomic wavefunction. The term 'elastic' means that the collision does not disturb the populations of the internal states, so we only need to consider the off-diagonal elements of the density matrix,

\[
\frac{d\rho_{12}}{dt} = i\frac{\Omega_0}{2} e^{i(\omega - \omega_0)t} (\rho_{11} - \rho_{22}) - \gamma' \rho_{12}, \tag{14.106}
\]

where \( \gamma' \) is the sum of the spontaneous emission \( \gamma \) and the collision rate \( \gamma_{\text{col}} \),

\[
\gamma' = \gamma + \gamma_{\text{col}}. \tag{14.107}
\]

The inverse of the collision rate is simply the time between phase interruptions or the time between collisions. Now, for collisions between hard cores of atoms of mass \( m \) (with reduced mass \( m_{\text{red}} = m/2 \)) and with radius \( \rho \) in a gas with density \( n \) consisting of a single species, a standard analysis based on the kinetic theory of dilute gases shows that the time between collisions is given by the collision rate,

\[
\gamma_{\text{col}} = \frac{1}{\tau_{\text{col}}} = \sigma n \bar{v}, \tag{14.108}
\]

where \( \bar{v} = \sqrt{\frac{8k_B T}{\pi m_{\text{red}}}} \) is the average collision velocity in a homogeneous gas at the temperature \( T \) and \( \sigma = \sqrt{8\pi \rho^2} \) the collision cross section. Thereby,

\[
\gamma_{\text{col}} = \frac{8\rho^2 n}{\sqrt{m_{\text{red}} / \pi k_B T}}. \tag{14.109}
\]

\(^6\)Some authors define the saturation for \( s = 2 \), as happens when \( \Omega = \Gamma \).
We can now relate this simple result of gas kinetics to the phase interruption rate by reinterpreting the meaning of the collision radius. When an excited atom propagating through space suffers a collision, the long-range interaction will produce a time-dependent perturbation of the energy levels of the radiating atom and a phase shift in the radiation,

$$\eta = \int_{-\infty}^{\infty} [\omega(t) - \omega_0] dt = \int_{-\infty}^{\infty} \Delta \omega(t) dt \, .$$  \hspace{1cm} (14.110)

The long-range van der Waals interaction is expressed by,

$$\Delta E = \hbar \omega = \frac{C_n}{[b^2 + (vt)^2]^{n/2}} \, ,$$  \hspace{1cm} (14.111)

where $b$ is the impact parameter of the collision trajectory and $v$ the collision velocity. The phase shift is then

$$\eta = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{C_n}{[b^2 + (vt)^2]^{n/2}} dt \, .$$  \hspace{1cm} (14.112)

The integral is easily assessed for the two most frequent cases: non-resonant van der Waals interactions $n = 6$ and resonant van der Waals interactions $n = 3$. The phase shifts are,

$$\eta_6(b) = \frac{2\pi}{3\hbar} \frac{C_6}{b_6^6 v} \quad \text{and} \quad \eta_3(b) = \frac{4\pi}{3\sqrt{3}\hbar} \frac{C_3}{b_3^3 v} \, .$$  \hspace{1cm} (14.113)

Now, if instead of using the hard core approximation, we define a collision as an encounter causing a phase shift of at least 1 radians, we have a new condition for the collision radius,

$$b_6 = \left(\frac{2\pi}{3\hbar} \frac{C_6}{v}\right)^{1/5} \quad \text{and} \quad b_3 = \left(\frac{4\pi}{3\sqrt{3}\hbar} \frac{C_3}{v}\right)^{1/2} \, .$$  \hspace{1cm} (14.114)

Replacing these collision radiiuses for the radius $\rho$ in Eq. (14.109) and inserting the average collision velocity, we find the collision rate,

$$\gamma_{c6} = 4n \left(\frac{\sqrt{2}\pi^2 C_6}{3\hbar}\right)^{2/5} \left(\frac{4\pi k_B T}{\mu}\right) \quad \text{and} \quad \gamma_{c3} = 4n \left(\frac{2}{3}\right)^{3/2} \left(\frac{\pi^2 C_3^2}{\hbar}\right)^{3/10} \, .$$  \hspace{1cm} (14.115)

Substituting the generalized $\gamma'$ of (14.107) for $\gamma$ in the Bloch equations (14.86), we find the stationary solutions,

$$\rho_{22} = \frac{\frac{1}{2} \frac{\gamma'}{\gamma} |\Omega|^2}{\Delta^2 + \frac{1}{2} \frac{\gamma'}{\gamma} |\Omega|^2 + \gamma'^2} \quad \text{and} \quad \rho_{12} = e^{i(\omega - \omega_0)t} \frac{\frac{1}{2} \Omega(\Delta - i\gamma')}{\Delta^2 + \frac{1}{2} \frac{\gamma'}{\gamma} |\Omega|^2 + \gamma'^2} \, .$$  \hspace{1cm} (14.116)

The effective linewidth (radiative and collisions) is,

$$\Gamma_{eff}' = 2\sqrt{\gamma'^2 + \frac{1}{2} \frac{\gamma'}{\gamma} |\Omega|^2} \, .$$  \hspace{1cm} (14.117)

When the excitation is sufficiently weak, so that power broadening can be neglected in comparison to collision broadening, the second term can be discarded,

$$\Gamma_{eff}' = 2(\gamma + \gamma_{col}) \, .$$  \hspace{1cm} (14.118)
14.4. LINE BROADENING MECHANISMS

The equations (14.87) and (14.118) express the linewidths in the limits of dominating power and collision broadening, respectively. Note that the susceptibility, absorption coefficient, and absorption cross-section retain their Lorentzian profile, but with a larger width due to collisions. Since each atom is subject to the same broadening mechanism, the broadening is homogeneous. Solve Excs. 14.4.6.5.

14.4.3 Doppler broadening

The **Doppler broadening** is simply the apparent frequency distribution of a sample of radiating atoms at temperature $T$. The contribution of each atom to the radiation appears detuned by the **Doppler shift** because of its velocity. The frequency shift for a non-relativistically moving particle is $\omega = \omega_0/(1 - v/c)$, such that,

$$\Delta \equiv \omega - \omega_0 \simeq \omega_0 \frac{v}{c} = k \cdot v = kv_z ,$$

(14.119)

where $k$ is the wavevector of the light and $v$ is the velocity of the atom. This distribution of Doppler shifts of a gaseous sample in thermal equilibrium follows the probability distribution of velocities,

$$P(v_z)dv_z \propto e^{-mv_z^2/2k_BT}dv_z = e^{-m\Delta^2/2\omega_0^2k_BT} \frac{c}{\omega_0} d\omega .$$

(14.120)

This frequency distribution is a Gaussian centered at $\omega = \omega_0$ and with the width,

$$\text{FWHM} = 2\omega_0 \left( \frac{2k_BT \ln 2}{mc^2} \right)^2 .$$

(14.121)

A measure of the width is also the **standard deviation**,

$$2\sigma = \frac{2\omega_0}{c} \sqrt{\frac{k_BT}{m}} = \frac{\text{FWHM}}{1.177} .$$

(14.122)

From Eq. (14.120) we can see that the line profile is,

$$D(\omega - \omega_0) \equiv \frac{1}{\sqrt{2\pi} k_BT m} e^{-(\omega - \omega_0)^2/2\sigma^2} d\omega .$$

(14.123)

The profile compares with the Lorentzian profile Eq. (1.74) associated with natural, power, or collision broadening. Doppler broadening is a property of the atomic ensemble, each atom suffering a unique but different displacement than the other atoms. Hence, it is called **inhomogeneous broadening**.

The Heisenberg equation used to derive the Bloch equations assumes immobile atoms. However, we can easily apply the Galilei transformation to a system, where the atoms move with the given velocity $v$,

$$(\partial_t + v \cdot \nabla)\rho(r, t) = -\frac{i}{\hbar} [\hat{H}, \rho(r, t)] .$$

(14.124)

Since the light fields propagate as $e^{i(\omega t - k \cdot r)}$, the solution of the above equation simply follows from the immobile solution with the substitution $\Delta \to \Delta - k \cdot v$. 
For a cloud obeying Maxwell’s velocity distribution, \( P(v) \sim e^{-m v^2 / k_B T} \),

\[
\bar{\rho}(\Delta) = \frac{1}{\sqrt{2\pi}\delta} \int_{\mathbb{R}} e^{-\frac{(k \cdot v)^2}{2\delta^2}} \rho(\Delta - k \cdot v) d(k \cdot v) .
\] (14.125)

The average of the density operator over all velocities, \( \bar{\rho} \), therefore follows as the convolution of the density operator \( \rho \) (obtained as the solution of the Bloch equation) and the Gaussian function \( G(\Delta) = (2\pi\delta^2)^{-1/2} e^{-\Delta^2 / 2\delta^2} \),

\[
\bar{\rho}(\Delta) = (G * \rho)(\Delta) .
\] (14.126)

### 14.4.4 Voigt profile

It is clear that in many practical circumstances homogeneous and inhomogeneous processes simultaneously contribute to the broadening of lines. In these cases, we can consider that the radiation of each atom, homogeneously broadened by phase-interruption processes (such as spontaneous emission or collisions), is displaced by the Doppler effect within the Maxwell-Boltzmann distribution corresponding to the temperature \( T \). The profile of the gaseous sample, therefore, is a convolution of homogeneous and inhomogeneous profiles. The resulting profile is called **Voigt profile**:

\[
V(\omega - \omega_0) = \int_{-\infty}^{\infty} L(\omega - \omega_0 - \omega') D(\omega - \omega_0) d\omega' 
= \frac{\gamma}{2\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{(\omega - \omega_0)^2}{2\sigma^2}} \frac{1}{(\omega - \omega_0 - \omega')^2 + (\gamma / 2)^2} d\omega' .
\] (14.127)

This integral has no analytical solution, but it is easy to solve numerically. Resolve Excs. 14.4.6.6 and 14.4.6.7.

### 14.4.5 Bloch equations with phase modulation

In some situations, the atom vibrates thus producing an oscillating Doppler shift. Also, external magnetic fields or oscillating laser frequencies can produce this effect. We incorporate this temporal modulation (frequency \( \Omega_a \)) of the light frequency shifts, induced by the Doppler effect, into the optical Bloch equations via the substitution \[540],

\[
\Delta_{ij} \rightarrow \Delta_{ij} + k_{ij} \cdot v \cos \Omega_a t .
\] (14.128)

The Bloch equations can then be brought into the form,

\[
\dot{\rho} = (L + 2X \cos \Omega_a t) \rho + b ,
\] (14.129)

where the matrix \( X \) contains the modulation index of the atomic motion \( k_{ij} v \). The stationary solution of the differential equation, averaged over the time of an oscillation period, can be expressed as an infinite continuous fraction:

\[
\rho(\infty) = -(L + S^+ + S^-)^{-1} b
\] (14.130)

where \( S^\pm = -X_L \pm i\Omega_a 1 - X_{L\pm i\Omega_a} X^{-1} \) .
This solution replicates the correct excitation spectra even for a multilevel system.

Let us be more specific for a two-level system. Its Hamiltonian is, $\hat{H}_{\text{int}} = \frac{1}{2} \hbar \Omega e^{-i[\omega t - k \cdot \mathbf{v}/\Omega a \sin \Omega a t]}$, such that the Bloch equation is,

$$\frac{d}{dt} \begin{pmatrix} \rho_{22} \\ \rho_{12} \\ \rho_{21} \end{pmatrix} = \begin{pmatrix} -\Gamma & -\frac{i}{2} \Omega & \frac{i}{2} \Omega \\ -\frac{i}{2} \Omega & -\Lambda & 0 \\ \frac{i}{2} \Omega & 0 & -\Lambda^* \end{pmatrix} + 2 \cos \Omega a t \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\frac{1}{2} k v & 0 \\ 0 & 0 & \frac{1}{2} k v \end{pmatrix} \begin{pmatrix} \rho_{22} \\ \rho_{12} \\ \rho_{21} \end{pmatrix} + \begin{pmatrix} 0 \\ \frac{1}{2} \Omega \\ -\frac{1}{2} \Omega \end{pmatrix}. \quad (14.131)$$

We look for the stationary solution by letting $\dot{\rho}_n = 0$ and $\rho = \sum_{n=-\infty}^{\infty} \rho_n e^{-in\Omega_a t}$ and projecting on $e^{-in\Omega_a t}$ by,

$$(L + in\Omega_a 1)\rho_n + X(\rho_{n+1} + \rho_{n-1}) + b\delta_{n0} = 0. \quad (14.132)$$

Now we define $\rho_{n \pm 1} = S^\pm \rho_n$ for $n \gtrless 0$. Then, equation (14.132) becomes,

$$\rho_0 = -[L + X(S_0^+ + S_0^-)]^{-1} b \quad \text{para} \quad n = 0, \quad (14.133)$$

$$S_{n+1}^\pm = -[L + in\Omega_a 1 + XS_n^\pm]^{-1} b \quad \text{for} \quad n \gtrless 0.$$ 

Substituting the equation below into the equation above,

$$\rho_0 = -\left[ L + \left( \frac{-X}{L + i\Omega_a} + \frac{-X}{L + 2i\Omega_a} + \ldots \right) + \left( \frac{-X}{L + i\Omega_a} + \frac{-X}{L + 2i\Omega_a} + \ldots \right) \right]^{-1} b. \quad (14.134)$$

Figure 14.3: (code) Spectral broadening due to the periodic movement of the atom.

### 14.4.6 Exercises

#### 14.4.6.1 Ex: Optical density of a cold cloud

The cross section of an atom with the resonant frequency $\omega_0$ moving with velocity $v$ and irradiated by a laser beam of frequency $\omega$ is,

$$\sigma(v) = \frac{6\pi}{k^2} \frac{\Gamma^2}{4(\omega - \omega_0 - kv)^2 + \Gamma^2}.$$
The normalized one-dimensional Maxwell distribution,

\[
\rho(v) dv = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv^2/2k_BT} dv.
\]

a. Calculate the absorption profile of the resonance line at 461 nm \((\Gamma_{461} = (2\pi) 30.5 \text{ MHz})\) of a strontium gas cooled to the Doppler limit \((k_B T_D = h\Gamma)\) of this transition.

b. Calculate the absorption profile of the resonance line at 689 nm \((\Gamma_{689} = (2\pi) 7.6 \text{ kHz})\) of a strontium gas cooled to the Doppler limit of the transition at 461 nm.

c. Compare the optical densities in case of resonance.

**Help:** To evaluate the convolution integral approximate the narrower distribution by a \(\delta\)-function maintaining the integral over the distribution normalized.

### 14.4.6.2 Ex: Saturated absorption spectroscopy

Saturated absorption spectroscopy is a technique to avoid Doppler enlargement. The diagram, shown in Fig. 14.4, consists of a cell filled with a rubidium gas (resonance frequency \(\omega_0 = ck = 2\pi c/780 \text{ nm}\), decay rate \(\Gamma = (2\pi) 6 \text{ MHz}\)) and two laser beams with the same frequency \(\omega\) but counterpropagating, one called saturation and another called proof. The one-dimensional and normalized Maxwell velocity distribution is,

\[
\rho(v) dv = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv^2/2k_BT} dv.
\]

The gas is at \(T = 300 \text{ K}\), where the partial pressure of rubidium is around \(P = 10^{-1} \text{ mbar}\). The length of the cell is \(L = 10 \text{ cm}\). The laser has an intensity below the saturation limit, such that the cross section of an atom moving at velocity \(v\) is,

\[
\sigma(v) = \frac{6\pi}{k^2} \frac{\Gamma^2}{4(\omega - \omega_0 - k\nu)^2 + \Gamma^2}.
\]

The saturation laser has high intensity. We suppose here, \(\Omega \equiv 10\Gamma\), where \(\Omega\) is the frequency of Rabi caused by the saturation beam. In this way it creates a population \(N_a nd\) of atoms in the excited state. As this population lacks in the ground state, \(N_g = N - N_e\), the absorption of the proof beam is decreased by the factor,

\[
\frac{N_e}{N} = \frac{\Omega^2}{4(\omega - \omega_0 + k\nu)^2 + 2\Omega^2 + \Gamma^2}.
\]

Calculate for laser proof spectrum of optical density, \(OD(\omega) = \ln \int_{-\infty}^{\infty} \frac{N_a - N_e}{N} \sigma(v) \rho(v) dv\), and the intensity of light transmitted through the cell, \(I/I_0 = e^{-OD}\).

![Figure 14.4: Scheme of saturation spectroscopy.](image)
14.4. LINE BROADENING MECHANISMS

14.4.6.3 Ex: The Zeeman slower

Consider a tube through which passes a collimated beam of atoms, all having the same initial velocity $v = v_0$. In the opposite direction to the atomic motion travels a collimated and monochromatic light beam with frequency $\omega = kc$. The absorption rate for photons by an atom has a Lorentzian profile, which can be written as:

$$W(v) = \frac{W_0}{2\pi} \left( \frac{\Gamma^2}{(\omega - \omega_0 + kv)^2 + (\Gamma/2)^2} \right),$$

where $\Gamma$ is the natural width of the spectral line at $\omega_0$, and $W_0$ is a constant. The frequency of the light is tuned in order to compensate for the Doppler effect at the beginning of the tube, $\delta = \omega - \omega_0 = -kv_0$ (the light is tuned to the red of the resonance). As the atoms are decelerated, they cease to be resonant with the light beam and fail to absorb photons. This can be avoided by employing the so-called Zeeman-slowing technique, which compensates for the effect using the Zeeman-shift induced by magnetic fields. In this exercise, we will study what happens if this technique is not used.

a. For an atom with velocity $v$, write an expression for the mean travel distance $\Delta s(v)$ before it absorbs a photon as a function of the parameters $\Gamma$, $v_0$, $k$, and $W_0$. (The mean time it takes to absorb a photon is $W(v)^{-1}$).

b. The velocity of the atom as a function of the number of absorbed photons is $v_n = v_0 - n\frac{\hbar k}{m}$, the second term being the recoil due to the absorption of a single photon. The average total distance traveled by an atom after absorbing $N$ photons is estimated by:

$$S = \sum_{n=0}^{N} \Delta s(v_n) \simeq \int_{0}^{N} \Delta s(v_n) dn .$$

Calculate the average distance required for the atoms to be slowed down to $v = 0$ (ignoring the Doppler limit). Write the expression as a function of $\Gamma$, $v_0$, $k$, and $W_0$. Help: Do the following change of variables to simplify the evaluation of the integral: $n \rightarrow v$.

c. Typically, the detuning of the light, $|\delta| = kv_0$, is much larger than the natural width $\Gamma$ of the transition. What happens to $S$ in the limit when $kv_0 \gg \Gamma$? Interpret this result, justifying the need for the Zeeman-slowing technique.

14.4.6.4 Ex: Saturation intensity

Calculate the saturation intensity for the sodium transition $3s^2S_{1/2}, F = 2 \leftrightarrow 3p^2P_{3/2}, F' = 3$. The natural width of the transition is $\Gamma/2\pi = 9.89$ MHz and the wavelength $\lambda = 590$ nm.
### 14.4.6.5 Ex: Pressure broadening

At what pressure the collision broadening [given by the expression (14.109)] between sodium atoms in the ground state dominates the width of the D2-transition at ambient temperature. The natural width of the D2-line is $\Gamma/2\pi = 6$ MHz.

### 14.4.6.6 Ex: Optical density of a hot cloud

Calculate and draw the effective Lorentz profile, Gauss profile and Voigt profile for the resonance line at 461 nm ($\Gamma = (2\pi) 32$ MHz) of a strontium gas heated to the temperature 400°C and the pressure $P = 10^{-4}$ mbar inside a 15 cm long cell.

### 14.4.6.7 Ex: Rate equations as a limiting case of Bloch equations

We show in this exercise that, in the limit $\Gamma \gg \Omega$, we can derive, from the Bloch equations, the Einstein rate equations. Proceed as follows:

a. Apply the condition $\dot{\rho}_{12} = 0$ to the Bloch equations for a two-level system (14.86), determine $\rho_{12}(\infty)$, and replace this stationary value in the equations for the populations $\rho_{kk}(t)$ using, as an abbreviation, the transition rate $R \equiv \gamma s$, where $s$ is the saturation parameter (14.88).

b. Integrate the rate equations over the entire spectrum, i.e. $\Delta \in [-\infty, \infty]$, and derive Einstein’s equations using the relations (13.7), (13.38), and (13.39).

### 14.4.6.8 Ex: Lorentzian versus Gaussian line profile

Beyond what detuning is a Doppler-broadened transition dominated by the Lorentzian profile of the transition?

### 14.5 Multi-level systems

The two-level system represents an idealization of the real atom, since at least one of the levels is usually degenerate. Many important phenomena in quantum optics are not found in this system, but conditioned to the existence of a third level. Examples are optical pumping (essential for laser operation), quantum jumps or dark resonances [which are at the basis of the phenomenon of electromagnetically induced transparency (EIT)].

To derive the Bloch equations for atoms with several levels excited by several lasers and coupled to free space (i.e. without external cavity), we can use the same master equation (14.100), but with a generalized Hamiltonian and Lindbladt operator,

\[
\hat{H}_{\text{atom}} = \sum_i \hbar \omega_i \hat{\sigma}_{ji} \hat{\sigma}_{ij} \\
\hat{H}_{\text{clas}} = \frac{\hbar}{2} \Omega_{ij} \left( e^{-i\omega_{ij}t} \hat{\sigma}_{ij} + e^{i\omega_{ij}t} \hat{\sigma}_{ji} \right) \\
L_{\text{atom}} \rho = \sum_{i,j} \Gamma_{ij} \left( [\hat{\sigma}_{ij}, \hat{\rho} \hat{\sigma}_{ij}] + [\hat{\sigma}_{ij} \hat{\rho}, \hat{\sigma}_{ij}^+] + 2\beta_{ij} [\hat{\sigma}_{ij} \hat{\sigma}_{ij}^+, \hat{\rho}] + [\hat{\sigma}_{ij}^+ \hat{\rho}, \hat{\sigma}_{ij} \hat{\sigma}_{ij}^+] \right) .
\]

The levels have the energy $\hbar \omega_i$ above the ground level.

Let us first have a look at the coherent part of the master equation. The Hamiltonian in the semiclassical approximation (that is, the atom is quantized and consists...
of several levels $|i\rangle$ with energies $\hbar \omega_i$, while the light fields are described by factors $e^{i\omega_{ij}t}$, with frequencies $\omega_{ij}$ tuned near the transitions $|i\rangle - |j\rangle$) includes the following contributions,

$$\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{atom-field}}$$

$$= \sum_i |i\rangle \hbar \omega_i \langle i| + \sum_{i < j \text{ with } E_i < E_j} |i\rangle \frac{\hbar}{2} \Omega_{ij} \langle j| e^{i\omega_{ij}t} + \text{c.c.} .$$

The Rabi frequency $\Omega_{ij}$ is a measure for the force at which the levels $|i\rangle$ and $|j\rangle$ are coupled by the resonantly irradiated light field. The master equation can be simplified by applying the rotating wave approximation and transforming to the coordinate system which rotates with the light frequencies $\omega_{ij}$:

$$\rho_{ij} \rightarrow \hat{\rho}_{ij} e^{i\omega_{ij}t} , \quad \hat{H}_{\text{atom-field}} \rightarrow e^{-i\hat{H}t/\hbar} \hat{H}_{\text{atom-field}} e^{i\hat{H}t/\hbar} .$$

Finally, the master equation can be reformulated by introducing a generalized Bloch vector $\tilde{\rho}$, and the matrix representation of the Liouville superoperator $\mathcal{L}$ as a linear system of $n^2$ coupled differential equations,

$$\frac{d}{dt} \tilde{\rho} = \mathcal{M} \tilde{\rho} , \quad \tilde{\rho} = (\rho_{11} \; \ldots \; \rho_{nn} \; \rho_{12} \; \rho_{21} \; \ldots \; \rho_{n-1 \; n} \; \rho_{nn} \; \rho_{n-1}) ,$$

where the Bloch matrix $\mathcal{M}$ is obtained from the Liouvillean $\mathcal{L}$ simply by rearranging the matrix elements.

Alternatively to the complex formulation, the differential equations can be written for the real and imaginary part of the Bloch vector. The components $\rho_{ii}$ correspond to the population probabilities of the levels $|i\rangle$, the non-diagonal elements $\rho_{ij}$ describe the coherences between $|i\rangle$ and $|j\rangle$. Now, we must insert the Hamiltonian (14.136) and the density operator $\rho_{ij}$ into the Liouville equation (14.36) in order to derive the generalized Bloch equations. In practice, these calculations are simple but heavy. Therefore, we describe in Sec. 14.5.4 a simplified recipe for compiling Bloch equations for arbitrary level systems for real atoms.

### 14.5.1 Liouville equation for many levels

The indices for the atomic levels are joined to a single index, such that the master equation takes a simpler form after having introduced a **Liouville operator**:

$$\hat{\rho} = (\ldots \rho_{ik} \ldots) \equiv \sum_{i,j} |i\rangle \rho_{ij} \langle j| ,$$

$$\dot{\rho} = \mathcal{L} \hat{\rho} , \quad \rho = e^{\mathcal{L} t} \hat{\rho}_0 .$$

The relation with the **von Neumann equation** with $\hat{H} = \sum_{i,j} |i\rangle H_{ij} \langle j|$ and $\hat{\rho} = \sum_{k,l} |k\rangle \rho_{kl} \langle l|$ and $\hat{\sigma}_{ij} = |i\rangle \langle j|$ is:

$$\mathcal{L}_0 \hat{\rho} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] = -i \sum_{k,l,j} H_{kl} \rho_{ij} |k\rangle \langle l| + i \sum_{k,l,i,j} H_{ij} \rho_{kl} |k\rangle |l\rangle \langle j| .$$

(14.140)
For example, for the two-level system with the definition of the external product (2.112):

\[ \mathcal{L}_0 = -i\hat{H} \otimes \mathbb{1} + i\mathbb{1} \otimes \hat{\rho}_t . \]  

(14.141)

The relaxation terms are,

\[ \mathcal{L}_d \hat{\rho} = \sum_{i,j} \gamma_{ij} \left( 2\sigma_{ji} \hat{\rho}\sigma_{ij} - \sigma_{ij} \sigma_{ji} \hat{\rho} - \hat{\rho}\sigma_{ij}\sigma_{ji} \right) \]  

(14.142)

\[ = \sum_{i,j,k} \left( 2\gamma_{ji}\delta_{kj}\rho_{ii} - \gamma_{ij}\rho_{kj} - \gamma_{ik}\rho_{kj} \right) |k\rangle\langle j| . \]

Example 54 (Liouville equation for two levels): For example, for the two-level system,

\[ \mathcal{L}_0 = \begin{pmatrix} 2\gamma_{11} & 0 & 0 & 2\gamma_{21} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2\gamma_{12} & 0 & 0 & 2\gamma_{22} \end{pmatrix} - \begin{pmatrix} 2(\gamma_{11} + \gamma_{12}) & 0 & 0 & 0 \\ 0 & \sum_{(kj)} \gamma_{(kj)} & 0 & 0 \\ 0 & 0 & \sum_{(kj)} \gamma_{(kj)} & 0 \\ 0 & 0 & 0 & 2(\gamma_{22} + \gamma_{21}) \end{pmatrix} . \]

Here, we consider \((kj) = (11 12 21 22)\) as a single index.

14.5.2 Bloch equations for three levels

In principle, three-level system can exist in there possible configurations, shown in Fig. 14.6. Note that it is not possible to describe a three-level system with all levels pairwise coupled by three lasers within the formalism of Bloch’s equations.\(^7\)

---

\(^7\)For the same reason that the three-body problem has no general analytic solution.
is,

\[ \dot{\rho} = \mathcal{M} \rho = \begin{pmatrix}
\Gamma_{13} & \frac{i}{2} \Omega_{12} & -\frac{i}{2} \Omega_{12} & 0 & 0 & 0 & 0 \\
0 & -\frac{i}{2} \Omega_{12} & \frac{i}{2} \Omega_{12} & 0 & 0 & \frac{i}{2} \Omega_{23} & -\frac{i}{2} \Omega_{23} \\
0 & 0 & 0 & 0 & 0 & -\frac{i}{2} \Omega_{23} & -\frac{i}{2} \Omega_{23} \\
\frac{i}{2} \Omega_{12} & \frac{i}{2} \Omega_{12} & 0 & -\Delta_{12} & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{i}{2} \Omega_{23} & 0 & -\Delta_{13} & 0 & -\frac{i}{2} \Omega_{12} & 0 \\
0 & 0 & 0 & 0 & -\frac{i}{2} \Omega_{23} & 0 & -\Delta_{13} & 0 & 0 \\
0 & \frac{i}{2} \Omega_{23} & -\frac{i}{2} \Omega_{23} & 0 & 0 & -\frac{i}{2} \Omega_{12} & 0 & -\Delta_{23} & 0 \\
0 & -\frac{i}{2} \Omega_{23} & \frac{i}{2} \Omega_{23} & 0 & 0 & 0 & \frac{i}{2} \Omega_{12} & 0 & -\Delta_{23}
\end{pmatrix}
\begin{pmatrix}
\rho_{11} \\
\rho_{22} \\
\rho_{23} \\
\rho_{24} \\
\rho_{25} \\
\rho_{26} \\
\rho_{27} \\
\rho_{28} \\
\rho_{29}
\end{pmatrix}
\]

with \( \Lambda_{mn} = i \Delta_{mn} + \gamma_{mn} \) and,

\[ \Delta_{13} = \Delta_{12} - \Delta_{23} \quad (14.144) \]

\[ \gamma_{12} = \frac{i}{2} (\Gamma_{12} + \Gamma_{23}) \quad , \quad \gamma_{23} = \frac{i}{2} (\Gamma_{12} + \Gamma_{23} + \Gamma_{13}) \quad , \quad \gamma_{13} = \frac{i}{2} \Gamma_{13} . \]

In Exc. 14.5.5.1 we will derive the matrix (14.143).

The coherent terms of the same matrix can be used for the V- and the cascade configurations shown in Figs. 14.6(b,c). Obviously, the incoherent terms, that is, the submatrix \( 3 \times 3 \) separated in the matrix (14.143) containing the population decay rates must be adjusted, as well as the decay rates of the coherences on the diagonal. Finally, the definition of the Raman detuning \( \Delta_{13} \) must be adjusted. For the system in V-configuration we have,

\[ \mathcal{M}_{\text{incoh}} = \begin{pmatrix}
-\Gamma_{12} - \Gamma_{13} & 0 & 0 \\
\Gamma_{12} & 0 & \Gamma_{23} \\
\Gamma_{13} & 0 & -\Gamma_{23}
\end{pmatrix} \quad , \quad \Delta_{13} = \Delta_{12} - \Delta_{23} \quad (14.145) \]

\[ \gamma_{12} = \frac{i}{2} (\Gamma_{12} + \Gamma_{13}) \quad , \quad \gamma_{23} = \frac{i}{2} \Gamma_{13} \quad , \quad \gamma_{13} = \frac{i}{2} (\Gamma_{12} + \Gamma_{13} + \Gamma_{23}) . \]

For the cascade system we have,

\[ \mathcal{M}_{\text{incoh}} = \begin{pmatrix}
0 & \Gamma_{12} & \Gamma_{13} \\
0 & -\Gamma_{12} & \Gamma_{23} \\
0 & 0 & -\Gamma_{13} - \Gamma_{23}
\end{pmatrix} \quad , \quad \Delta_{13} = \Delta_{12} - \Delta_{23} \quad (14.146) \]

\[ \gamma_{12} = \frac{i}{2} \Gamma_{12} \quad , \quad \gamma_{23} = \frac{i}{2} (\Gamma_{12} + \Gamma_{23} + \Gamma_{13}) \quad , \quad \gamma_{13} = \frac{i}{2} (\Gamma_{13} + \Gamma_{23}) . \]

These matrices serve to calculate, among others, the phenomena of Autler-Townes splitting treated in Exc. 14.3.5.12, of the light-shift treated in Excs. 14.3.5.13 and 14.3.5.14, the dark resonances treated in Exc. 14.5.5.3, the STIRAP method treated in Exc. 14.5.5.4, adiabatic sweeps treated in Exc. 14.5.5.5, the dispersive interaction between atoms and light treated in Exc. 14.5.5.6, Fano resonance-type line profiles of dark resonances treated in Exc. 14.5.5.7, and the quantum jumps, which will be studied in later chapters. In Excs. 14.5.5.8 and 14.5.5.9 we will show, that an atomic gas may have negative permittivity and negative permeability and, consequently, properties usually only found in artificial metamaterials, as for example, a negative refractive index.
14.5.3 Numerical treatment of Bloch equations

Since the differential Bloch equations are linear, they can be easily solved. For example, the prescription

\[ \vec{\rho}(t) = e^{\mathcal{M}t} \vec{\rho}(0) \]  

(14.147)

propagates the Bloch vector to later times.

The matrix \( \mathcal{M} \) is not invertible, but by applying the condition \( \text{Tr} \ \rho = 1 \), a component of the density matrix can be eliminated, for example by letting,

\[ \rho_{11} = 1 - \sum_k \rho_{kk} \ . \]  

(14.148)

The resulting state vector, \( \vec{\rho}_{\text{red}} \), has the length \( n^2 - 1 \), and from \( \mathcal{M} \) we obtain the (trace-)reduced, now invertible matrix \( \mathcal{M}_{\text{red}} \) and the inhomogeneity vector \( \mathbf{b} \). The differential equation is now,

\[ \frac{d}{dt} \vec{\rho}_{\text{red}} = \mathcal{M}_{\text{red}} \vec{\rho}_{\text{red}} + \mathbf{b} , \]

(14.149)

with the stationary and time-dependent solutions,

\[ \vec{\rho}_{\text{red}}(\infty) = -\mathcal{M}_{\text{red}}^{-1} \mathbf{b} , \quad \vec{\rho}_{\text{red}}(t) = e^{\mathcal{M}_{\text{red}}t} \vec{\rho}_{\text{red}}(0) + (1 - e^{\mathcal{M}_{\text{red}}t}) \vec{\rho}_{\text{red}}(\infty) . \]  

(14.150)

Once the matrix \( \mathcal{M} \) or the matrix \( \mathcal{M}_{\text{red}} \) and the inhomogeneity vector \( \mathbf{b} \) are determined for a system, the state of the atom can be calculated at any time, as well as the populations and coherences. The system’s free parameters are the natural transition linewidths and the detunings, as well as the intensities and emission bandwidths of the incident light fields.

14.5.3.1 Simulation of the Schrödinger and Bloch equation

Once we have written the solution of the Schrödinger equation in the form (5.101) with a time-independent Hamiltonian \( \hat{H} \), or of the Bloch equations in the form (14.147) or (14.150) with a time-independent Liouvillian \( \mathcal{M} \), we can easily simulate temporal evolutions of quantum systems. If the Hamiltonian or Liouvillian depend on time, for example, when the Rabi frequencies are pulsed or the detunings are ramped, we must solve the equations iteratively. That is, we chose time intervals \( \Delta t \) sufficiently short, so that the Hamiltonian (or the Liouvillian) can be considered constant during this interval, and we propagate the wavefunction (or the Bloch vector) to later times via:

\[ |\psi(t + \Delta t)\rangle = e^{i\hat{H}(t)\Delta t} |\psi(t)\rangle \quad \text{or} \quad \vec{\rho}(t + \Delta t) = e^{\mathcal{M}(t)\Delta t} \vec{\rho}(t) , \]

(14.151)

and insert the solution obtained again into equations (14.151) with the Hamiltonian \( \hat{H}(t + \Delta t) \) (or the Liouvillian \( \mathcal{M}(t + \Delta t) \)) adjusted to the new time.

Example 55 (Electromagnetically induced transparency): In some special cases, the three-level Bloch equations can be solved analytically. The system in Λ-configuration schematized in Fig. 14.6(a), where the two lasers satisfy the condition \( \Delta_{12} = \Delta_{23} \) can exhibit a dark resonance leading to the phenomena of
electromagnetically induced transparency (EIT) and electromagnetically induced absorption. In these resonances a dramatic change of the refractive index is observed despite the fact that the atom becomes transparent, \( \text{Re } \chi > 0 \) and \( |\text{Im } \chi| \ll \text{Re } \chi \):

\[
\text{Re } n = \sqrt{1 + \text{Re } \chi} > 0,
\]

resulting in a high group velocity,

\[
v_g = \frac{c}{n + \omega \frac{dn}{d\omega}},
\]

EIT is usually studied in \( \Lambda \)-type systems, but similar phenomena can be found in cascade-type systems [652, 644], which will be studied here. Disregarding the decay rate \( \Gamma_{13} \), the Bloch equations (14.143) and (14.146) give the coherences,

\[
\begin{align*}
\dot{\rho}_{12} &= -\Lambda_{12}\rho_{12} + \frac{i\Omega_{12}}{2} (\rho_{11} - \rho_{22}) - \frac{i\Omega_{23}}{2} \rho_{13} \\
\dot{\rho}_{13} &= -\Lambda_{13}^{*}\rho_{13} - \frac{i\Omega_{12}}{2} \rho_{23} - \frac{i\Omega_{23}}{2} \rho_{12} \\
\dot{\rho}_{23} &= -\Lambda_{23}\rho_{23} + \frac{i\Omega_{23}}{2} (\rho_{22} - \rho_{33}) - \frac{i\Omega_{12}}{2} \rho_{13} .
\end{align*}
\]

Assuming stationarity and negligible depletion of the ground state, \( \rho_{11} = 1 \),

\[
\begin{align*}
0 &= -\Lambda_{12}\rho_{12} + \frac{i\Omega_{12}}{2} - \frac{i\Omega_{23}}{2} \rho_{13} \\
0 &= -\Lambda_{13}^{*}\rho_{13} - \frac{i\Omega_{12}}{2} \rho_{23} - \frac{i\Omega_{23}}{2} \rho_{12} \\
0 &= -\Lambda_{23}\rho_{23} - \frac{i\Omega_{12}}{2} \rho_{13} .
\end{align*}
\]

Substituting the third into the first equation,

\[
\begin{align*}
0 &= -\Lambda_{12}\rho_{12} + \frac{i\Omega_{12}}{2} - \frac{i\Omega_{23}}{2} \rho_{13} \\
0 &= -\Lambda_{13}^{*}\rho_{13} - \frac{i\Omega_{12}}{2} \rho_{23} - \frac{i\Omega_{23}}{2} \rho_{12} \\
\rho_{12} &= \frac{i\Omega_{12}}{2} \frac{4\Lambda_{13}\Lambda_{23} + \Omega_{12}^{2}}{\Lambda_{12} (4\Lambda_{13}\Lambda_{23} + \Omega_{12}^{2}) + \Omega_{23}^{2}} .
\end{align*}
\]

The macroscopic polarization is now \( P = \frac{N}{\sqrt{\pi}} d_{12} \rho_{21} \), with the number of atoms \( N \). In the limit of weak probes, the dressed susceptibility follows from \( P = \varepsilon_0 \chi \tilde{\varepsilon}_{12} = \frac{N}{\sqrt{\pi}} d_{12} \rho_{21} \),

\[
\chi = \frac{N d_{12}}{\sqrt{\pi} \varepsilon_{12}} \rho_{21} = \frac{N |d_{12}|^2}{\sqrt{\pi} \varepsilon_0 \hbar \Omega_{12}} \rho_{21} .
\]

For a resonant probe laser, \( \Delta_{23} = 0 \) and with \( \Gamma_{13} \approx 0 \), we have \( \Lambda_{13} = \frac{1}{2} \Gamma_{23} + i \Delta_{12} \) and \( \Lambda_{23} = \frac{1}{2} (\Gamma_{23} + \Gamma_{12}) \). The susceptibility in the probe transition is now, using \( \Theta \equiv \Gamma_{23} + \frac{\Omega_{12}^{2}}{2\Delta_{23}} \),

\[
\chi = \frac{N |d_{12}|^2}{\sqrt{\pi} \varepsilon_0 \hbar \Omega_{12}} \frac{i\Omega_{12}}{\Gamma_{23} + \frac{\Omega_{12}^{2}}{2\Delta_{23}} - 2i \Delta_{12}} \frac{\gamma_{23} + \Theta^{2} - 2i \Delta_{12}}{(\Gamma_{23} + \frac{\Omega_{12}^{2}}{2\Delta_{23}} - 2i \Delta_{12}) (\Gamma_{23} + 2i \Delta_{12}) + \Omega_{23}^{2}} = \chi' + i\chi'' .
\]

We consider, for example, the intercombination line of atomic strontium \(^1S_0\)\(^3P_1 \) (\( \lambda_{12} = 689 \) nm and \( \Gamma_{12} = (2\pi) \) 7.6 kHz) be the 'dressing' transition \(^3P_1\)\(^5S_4d\)\(^3D_1 \) (\( \lambda_{23} = 2700 \) nm and \( \Gamma_{23} = (2\pi) \) 90.3 kHz), be the 'dressing' transition
$^{3}P_{1}-(5s5d)^{3}D_{1}$ ($\lambda_{23} = 497$ nm and $\Gamma_{23} = (2\pi) 2.3$ MHz), both characterized by $\Gamma_{23} \gg \Omega_{12}, \Gamma_{12}, |\Delta_{12}|$, such that $\Theta \simeq \Gamma_{23}$. Hence,

$$\chi' + i\chi'' = \frac{N|d_{12}|^{2} 2\Delta_{12} + i\Gamma_{23}}{V\varepsilon_{0}\hbar \Omega_{23}}.$$ 

The refraction index follows with,

$$n = \sqrt{1 + \chi} \simeq 1 + \frac{1}{2\chi}.$$ 

Its imaginary part originates from the decay term of the atom: it is here responsible for the absorbing nature of the cloud. EIT is characterized by a pronounced dispersion and a small concomitant absorption.

Figure 14.7: (code) EIT signal for the cascade system of strontium with the transitions at 689 nm and 497 nm with $\Omega_{12} = \Gamma_{12}, \Omega_{23} = \Gamma_{23}$ and $\Delta_{23} = 0$. The red lines are calculated by numerical integration of the Bloch equations. The dotted lines are obtained from analytical formulas based on the assumptions of weak ground state depletion (which is not really correct in the chosen parameter regime.

### 14.5.4 General rules for setting up multilevel Bloch equations

The canonical way of deriving multi-level Bloch equations starts from a von Neumann equation for the total density operator for the atom embedded in the electromagnetic mode structure of the environment including incident laser beams. After tracing over the degrees of freedom of the electromagnetic vacuum and using the Markov and the Born approximations, one arrives at a master equation of the form [214],

$$\dot{\hat{\rho}} = -\frac{i}{\hbar} [H, \hat{\rho}] + \mathcal{L}_{\Gamma} \hat{\rho} + \mathcal{L}_{\beta} \hat{\rho}.$$  

(14.152)
Here $H$ is the Hamiltonian of coupled atom-laser system. The Liouville superoperators,

$$\mathcal{L}_\Gamma \hat{\rho} = \sum_{k,l} \Gamma_{kl} \left( [\sigma_{kl}, \rho \sigma_{kl}^\dagger] + [\sigma_{kl} \rho, \sigma_{kl}^\dagger] \right)$$  \hspace{1cm} (14.153)$$

$$\mathcal{L}_\beta \hat{\rho} = \sum_{k,l} \Gamma_{kl} \left( [\sigma_{kl} \sigma_{kl}^\dagger, \hat{\rho} \sigma_{kl} \sigma_{kl}^\dagger] + [\sigma_{kl} \sigma_{kl}^\dagger \hat{\rho}, \sigma_{kl} \sigma_{kl}^\dagger] \right),$$

describe dissipation through spontaneous emission from the various excited states and decoherence due to phase fluctuations of the laser fields, respectively. The operators $\sigma_{kl} = |k\rangle \langle l|$ describe the transition between two states, $\Gamma_{kl}$ is the spontaneous decay of level $|k\rangle$ into $|l\rangle$, and $\beta_{kl}$ is the emission bandwidth of the laser coupling the two levels. Simple but tedious algebraic transformations of the master equation lead, in the rotating wave approximation, to a set of linear first-order differential equations in the populations of the atomic excitation levels and the coherences between them. The equations are called the optical Bloch equations.

Alternatively, the Bloch equations may be found by breaking down the multi-level scheme into a set of three-level systems. Respecting a few symmetry considerations, the multi-level Bloch equations can then be reassembled from the three-level Bloch equations corresponding to every possible combination of three levels. Based on such considerations, we provide in the following a simple recipe for setting up Bloch matrices for arbitrary level schemes. A movie showing a simulation of multi-level Bloch equations for Li atoms can be watched under the following link: (watch movie).

Let us regard a $n$-level atom. Its internal state is fully described by the populations $\rho_{kk}$ and the (complex) coherences $\rho_{kl}$, with $k, l = 1, \ldots, n$. In this work we describe the coherences by their real and imaginary parts. The labeling is such that the levels are sorted according to their excitation energy, $E_k < E_l$ for $k < l$. We define the Bloch vector,

$$\vec{\rho} \equiv (\rho_{11} \ldots \rho_{nn} \text{Im} \rho_{12} \text{Re} \rho_{12} \text{Im} \rho_{13} \text{Re} \rho_{13} \ldots \text{Im} \rho_{1n} \text{Re} \rho_{1n} \text{Im} \rho_{23} \text{Re} \rho_{23} \ldots \text{Im} \rho_{n-1,n} \text{Re} \rho_{n-1,n}) .$$  \hspace{1cm} (14.154)$$

The Bloch equations then formally read,

$$\dot{\vec{\rho}} = \mathcal{M} \vec{\rho} ,$$  \hspace{1cm} (14.155)$$

where in the given Bloch vector basis the matrix $\mathcal{M}$ has the following structure,

$$\mathcal{M} = \begin{pmatrix} (A) & (B_1) \\ (B_2) & (C) & (D) \\ (D) & (C) \end{pmatrix} .$$  \hspace{1cm} (14.156)$$

The different blocks of the matrix have the following significations. Block $A$ handles the transfer of populations by spontaneous decay. Its rank corresponds to the number of levels $n$. The diagonal elements of this block are the decay rates $\Gamma$ of the excited states. The off-diagonal elements $\Gamma_{kl}$ denote the gain of level $k$ from a decaying level $l$. Conservation of energy thus requires that the sum of the transition rates
cancels for every column of matrix $A$, $\Gamma = \sum_k \Gamma_{kl}$, as it is the case for the two-level Bloch matrix. If the levels are sublevels of a Zeeman and/or hyperfine split multiplet, the rates have to be weighted with Wigner’s $(3j)$ and $(6j)$ symbols, $\Gamma_{kl} = \Gamma S_{kl}$. The relative oscillator strengths $S_{kl}$ are given in Sec. 14.5.4.2.

The blocks $B_k$ treat the interdependence of the populations and the coherences. $B_1$ describes how the coherence between any pair of states driven by a light field generating a Rabi frequency $\Omega_{kl}$ influences the populations. The block consists of convoluted $2 \times 2$ matrices of the form,

$$
\begin{pmatrix}
\hat{\rho}_{kk} \\
\hat{\rho}_{ll}
\end{pmatrix} \sim 
\begin{pmatrix}
-\Omega_{kl} & 0 \\
\Omega_{kl} & 0
\end{pmatrix}
\begin{pmatrix}
\text{Im } \rho_{kl} \\
\text{Re } \rho_{kl}
\end{pmatrix}.
$$

(14.157)

$B_2$ describes how the populations in turn influence the coherences,

$$
\begin{pmatrix}
\text{Im } \hat{\rho}_{kl} \\
\text{Re } \hat{\rho}_{kl}
\end{pmatrix} \sim 
\begin{pmatrix}
\frac{1}{2} \Omega_{kl} & -\frac{1}{2} \Omega_{kl} \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
\rho_{kk} \\
\rho_{ll}
\end{pmatrix}.
$$

(14.158)

The Rabi frequencies have to be weighted not only with the relative oscillator strength $S_{kl}$, but also with the projection $H_{kl}$ of the laser polarization onto the orientation of the magnetic field and the laser polarization, $\Omega_{kl} = \Omega_x S_{kl} H_{kl}$. Here $\Omega_x$ is the Rabi frequency generated by a laser on a transition, whose oscillator strength is 1.

The projection is calculated in Sec. 14.5.4.3 for the three possible laser polarizations, i.e. for $\sigma^\pm$ and for $\pi$ light.

The matrix $C$ rules the influence of the decays of the coherences, of the detunings $\Delta_{kl} = \omega_x - \omega_{\text{atom}}$, and the laser linewidths $\beta_{kl}$. Note that the detuning of the laser frequency $\omega_x$ is negative for red-detuned light. In the chosen basis it breaks down into an array $2 \times 2$ matrices aligned along the diagonal of $\mathcal{M}$. Their shape is,

$$
\begin{pmatrix}
\text{Im } \hat{\rho}_{kl} \\
\text{Re } \hat{\rho}_{kl}
\end{pmatrix} \sim 
\begin{pmatrix}
-\frac{\gamma_{kl}}{2} & -\Delta_{kl} \\
\Delta_{kl} & -\frac{\gamma_{kl}}{2}
\end{pmatrix}
\begin{pmatrix}
\text{Im } \hat{\rho}_{kl} \\
\text{Re } \hat{\rho}_{kl}
\end{pmatrix}.
$$

(14.159)

where $\gamma_{kl} = \sum_{m,E_m} \Gamma_m (\Gamma_{km} + \Gamma_{lm}) + 2\beta_{kl}$. Often the levels are sublevels of a Zeeman and/or hyperfine split multiplets. In this case the frequency shift $Z_{kl}$ of the level is added to the detuning $\Delta_{kl}$. The shift is calculated in Sec. 14.5.4.4 for the example of the $^6\text{Li} D_2$ line.

The block $D$ governs the interdependences of all laser-driven coherences of the atom. The block contains $2 \times 2$ submatrices at any place of the matrix $\mathcal{M}$, where the row index pair $(mn)$ and the column index pair $(kl)$ have one index in common provided the two different indices correspond to the Rabi frequency of an incident laser:

$$
\begin{pmatrix}
\text{Im } \hat{\rho}_{mn} \\
\text{Re } \hat{\rho}_{mn}
\end{pmatrix} \sim 
\begin{pmatrix}
0 & \pm \frac{1}{2} \Omega_{kl} \\
\pm \frac{1}{2} \Omega_{kl} & 0
\end{pmatrix}
\begin{pmatrix}
\text{Im } \rho_{pq} \\
\text{Re } \rho_{pq}
\end{pmatrix}.
$$

(14.160)

The submatrix elements indexed by column $(pq)$ and row $(mn)$ are non-zero if one of the indices $p$ or $q$ is equal to one of the indices $m$ or $n$ and the unequal indices correspond to a laser-driven transition. In order to find the correct signs of the submatrix elements, we distinguish four cases: 1. For $m = p$, $n = k$, and $q = l$ the signs are: $(+ -)$; 2. for $n = q$, $m = k$, and $p = l$ the signs are: $(+ -)$; 3. for $m = q$, $n = k$, and $p = l$ the signs are: $(+ +)$; and 4. for $n = p$, $m = k$, and $q = l$ the signs are: $(+ -)$. A proper parametrization is proposed in the next section.
14.5.4.1 Recipe for $D$ transitions in alkalines

In order to give a simple algorithm we parametrize the particular choice of sorting the components of the vector, we define a new index $\mu$ running from 1 to $n^2$ by setting $(\varrho_\mu) \equiv (\rho_{kl})$, where,

$$\begin{align*}
\mu(k,k) &= k \\
\mu(k,l) &= 2nk - n - k^2 - k + 2l - 1 ,
\end{align*}$$

so that,

$$\begin{align*}
\varrho_{\mu(k,k)} &= \rho_{kk} \\
\varrho_{\mu(k,l)} &= \mathfrak{Im} \, \rho_{kl} \\
\varrho_{\mu(k,l)+1} &= \mathfrak{Re} \, \rho_{kl} .
\end{align*}$$

The Bloch equations then formally read,

$$\dot{\varrho}_\mu = \mathcal{M}_{\mu\nu} \varrho_\nu .$$

We illustrate the procedure by considering the case of the $^6\text{Li} \, D_2$ line with 6 ground states $k \in G \equiv \{1, \ldots, 6\}$ belonging to the $^2S_{1/2}$ hyperfine levels $F = \frac{1}{2}, \frac{3}{2}$ and 12 excited states $k \in E \equiv \{7, \ldots, 18\}$ belonging to the $^2P_{3/2}$ hyperfine levels $F = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$.

According to the parametrization (14.155) the block $A$ of the matrix $\mathcal{M}$ is filled with the following components,

$$\begin{align*}
\mathcal{M}_{\mu(kk),\mu(kk)} &= -\Gamma \text{ for } k \in E \\
\mathcal{M}_{\mu(kk),\nu(ll)} &= \Gamma S_{kl} \text{ for } k \in G \text{ and } l \in E ,
\end{align*}$$

where the relative oscillator strength $S_{kl}$ is given by Eq. (14.171).

The blocks $B_k$ of the matrix $\mathcal{M}$ are filled with the components,

$$\begin{align*}
\mathcal{M}_{\mu(k,k),\nu(k,l)} &= -\mathcal{M}_{\mu(l,l),\nu(k,k)} \\
&= -2\mathcal{M}_{\mu(k,l),\nu(k,k)} = 2\mathcal{M}_{\mu(k,l),\nu(l,l)} \\
&= -\Omega_{kl} S_{kl} H_{kl} ,
\end{align*}$$

for $k \in G$ and $l \in E$. The projection onto the quantization axis $H_{kl} = H_{kl} \left( \frac{\hat{z}_{kl}}{|\hat{z}_{kl}|}, \vec{B}, m_l - m_k \right)$ is given by Eq. (14.174).

The block $C$ contains the components,

$$\begin{align*}
\mathcal{M}_{\mu(k,l),\mu(k,l)} &= \mathcal{M}_{\mu(k,l)+1,\mu(k,l)+1} \\
&= -\frac{\Gamma}{2} - \frac{\Gamma}{2} \delta_{k\geq 7} - \beta_{pb} \delta_{2<k<7} - \beta_{rp} \delta_{k\leq 2} \\
\mathcal{M}_{\mu(k,l),\mu(k,l)+1} &= -\mathcal{M}_{\mu(k,l)+1,\mu(k,l)} \\
&= -\Delta_{pb} \delta_{k>2} - \Delta_{rp} \delta_{k<3} + Z_{kl}(B)
\end{align*}$$

for $k \in G \cup E$ and $l \in E$ and ,
for \( k \in G \) and \( l \in E \),
\[
M_{\mu(k,f),\mu(k,f)+1} = -M_{\mu(k,f)+1,\mu(k,f)}
\]
\[
= -\Delta_{pb} + \Delta_{rp} + Z_{k,10}(B) - Z_{f,10}(B)
\]
for \( k \in \{1,2\} \) and \( f \in \{3,..,6\} \). The Zeeman shift \( Z_{kl} \) is given by Eq. (14.175).

Finally, the block \( D \) is filled with the components,
\[
M_{\mu(k,f),\mu(f,l)+1} = \left( \delta_{l<f} - \frac{1}{2} \right) \Omega_{kl} S_{kl} H_{kl}
\]
\[
= \left( \delta_{l<f} - \frac{1}{2} \right) \Omega_{kl} S_{kl} H_{kl},
\]
where,
\[
\Omega_{kl} \equiv (\Omega_{rp}\delta_{k \leq 2} + \Omega_{pb}\delta_{k \geq 3})\delta_{l \geq 7}
\]
\[
\epsilon_{kl} \equiv (\epsilon_{rp}\delta_{k \leq 2} + \epsilon_{pb}\delta_{k \geq 3})\delta_{l \geq 7}.
\]

for \( k \in G \cup E \) and \( l \in E \) and \( f \in G \cup E \) but \( f \neq k,l \). The projection onto the quantization axis \( H_{kl} = H_{kl} \left( \frac{\hat{r}_{kl}}{|\hat{r}_{kl}|}, \vec{B}, m_l - m_k \right) \) is given by Eq. (14.174).

The Eqs. (14.164)-(14.169) form together an algorithm to generate the matrix allowing one to numerically solve the Bloch equations (14.163), as has been done in the main text.

### 14.5.4.2 Relative forces of oscillators

Spontaneous transitions between hyperfine- and Zeeman split levels have to be weighted according to the Wigner-Eckardt theorem using Clebsch-Gordan \((3j)\) and Wigner \(\{6j\}\) symbols. Consider the transition \(|(J_k,I)F_k,m_k\rangle \leftrightarrow |(J_l,I)F_l,m_l\rangle\). The relative oscillator strength is,
\[
S_{kl} = \left( \frac{F_k}{m_k} \begin{pmatrix} \kappa & F_l \\ \text{sign}(m_l - m_k) & -m_l \end{pmatrix} \right)^2
\]
\[
= \left( \frac{F_k}{m_k} \begin{pmatrix} J_l & J_k & \kappa \\ F_k & F_l & I \end{pmatrix} \right)^2 \frac{(2F_k + 1)(2J_l + 1)(2\kappa + 1)}{2I + 1}.
\]

### 14.5.4.3 Elliptical laser polarization

The transition rates additionally depend on the relative orientation of the laser polarizations and the magnetic field direction. This dependence is accounted for by decomposing the polarization vector into the,
\[
\hat{e}_3 = \frac{\vec{B}}{B}, \quad \hat{e}_2 = \frac{\hat{e}_3 \times \hat{g}}{|\hat{e}_3 \times \hat{g}|}, \quad \hat{e}_1 = \frac{\hat{e}_2 \times \hat{e}_3}{|\hat{e}_2 \times \hat{e}_3|},
\]
where \( \hat{g} \) is an arbitrarily chosen direction, e.g. gravity. The relative amplitude of the transitions \( \Delta m_J = 0 \) is proportional to the projection of the polarization vector on
the magnetic field axis \( \zeta_0 = (\hat{e} \cdot \hat{e}_3)^2 \) for \( \pi \)-polarized light. To estimate the amplitude of the transitions \( \Delta m_J = \pm 1 \), we must project onto the coordinates,

\[
\hat{e}_\pm = \frac{1}{\sqrt{2}} (\hat{e}_1 \mp i \hat{e}_2),
\]

and we obtain \( \zeta_{\pm 1} = (\hat{e} \cdot \hat{e}_\pm)^2 \) for \( \sigma^\pm \)-polarized light. Hence,

\[
H_{kl} = \zeta_{\Delta m_J} = \zeta_{m_l - m_k}.
\]

With this generalization the Bloch equations can e.g. be employed to calculate Hanle resonances quantum mechanically. The Hanle effect occurs when a magnetic and an optical field compete for the quantization axis.

### 14.5.4.4 Hyperfine and Zeeman splitting

The nuclear spin of the \( ^6\text{Li} \) atom is \( I = 1 \), its electron spin is \( S = \frac{1}{2} \). The excitation states are characterized by quantum numbers \( J_k, F_k, m_k \). The electron angular orbital momentum is \( L_k = \delta_{k \geq 7} \), and the electron angular orbital momentum is \( J_k = \frac{1}{2} \delta_{k \leq 6} + \frac{3}{2} \delta_{k \geq 7} \). The hyperfine structure of the excited state \( ^2P_{3/2} \) can be written as \( \nu_{hf1} = -2.8 \text{ MHz, } \nu_{hf2} = 0 \text{ MHz, } \) and \( \nu_{hf3} = 1.7 \text{ MHz.} \) Hence, the hyperfine splitting is inferior to the natural decay rate \( \Gamma = (2\pi) 6 \text{ MHz}, \)

\[
Z_{kl} = \frac{\mu_B |\vec{B}|}{2\pi \hbar} (g_F m_k - g_F m_l) + \nu_{hf1} \delta_{7 \leq l \leq 8} + \nu_{hf2} \delta_{8 \leq l \leq 13} + \nu_{hf3} \delta_{13 \leq l \leq 16},
\]

where \( g_{F_k} \) is the Landé factor of hyperfine level \( F_k \).

### 14.5.5 Exercises

#### 14.5.5.1 Ex: Bloch equations for three levels

An excited \( \Lambda \)-shaped atom consists of two ground states \( |1\rangle \) and \( |3\rangle \), which are coupled by two lasers with Rabi frequencies and detunings \( \Omega_{12} \) and \( \Delta_{12} \) respectively \( \Omega_{23} \) and \( \Delta_{23} \) through an excited level \( |2\rangle \). Derive the Bloch equations from this system from the general master equation.

#### 14.5.5.2 Ex: Adiabatic elimination

Derive the effective two-level Bloch equations for a \( \Lambda \)-type three-level system adiabatically eliminating the excited state under the Raman condition. *Help:* Start from the Liouvillean (14.143), set \( \rho_{22} = 0 \), assume \( \Gamma_{13} \ll \Gamma_{12}, \Gamma_{23} \ll |\Delta_{12}|, |\Delta_{23}| \), and \( \Delta_{12} = -\Delta_{23} \).

#### 14.5.5.3 Ex: EIT & dark resonances

In this exercise we study so-called *dark resonances*, which are responsible for the phenomenon of *electromagnetically induced transparency* (EIT). Such resonances are observed in three-level systems \( |1\rangle - |2\rangle - |3\rangle \) in \( \Lambda \)-configuration, as shown in Fig. 14.6(a), when the laser detunings are chosen so as to satisfy \( \Delta_{12} = \Delta_{23} \).
a. From the Bloch equations (14.143) show analytically that, in a stationary situation, the population of the excited state is $\rho_{22}(\infty) = 0$ in the center of the dark resonance. Dark resonances can be observed experimentally. To reproduce the experiment by numerical simulations of the Bloch equations (14.143), write down the Liouville matrix $\mathcal{M}_{\text{red}}$ reduced by the trace condition (14.147) and calculate the stationary Bloch vector from equation (14.148) varying the detunings of the two lasers $\Delta_{12}$ and $\Delta_{23}$. Choosing the parameters such that $\Gamma_{23} = \Gamma_{12}$, $\Gamma_{13} = 0$, $\Omega_{12} = 2\Gamma_{12}$, and $\Omega_{23} = 0.2\Gamma_{12}$, prepare a 3D curve [similar to Fig. 14.2(a)] of the population $\rho_{22}(\infty)$. Interpret the results.

14.5.5.4 Ex: STIRAP

In experiments with cold atoms it is often necessary to transfer populations between ground states, for example, between specific levels of a hyperfine structure. One possible procedure is the method of optical pumping, from the initial ground state to an excited state, which subsequently decays to the final state by spontaneous emission. The problem with this incoherent procedure is, that one can control into which ground state level the atom will decay, and that it heats atoms due to the photonic recoil associated with the scattering of light. In this exercise we studied an alternative method, called Stimulated Raman Adiabatic Passage (STIRAP), which allows the coherent transfer of population between two states by counter-intuitive pulse sequences:

a. Consider a three-level system in $\Lambda$-configuration, as shown in Fig. 14.6(a), initially being in the state $|1\rangle$. Write the system’s Hamiltonian in the interaction picture. Now, choose $\Delta_{12} = 0 = \Delta_{23}$, and a temporal variation of the Rabi frequencies described by $\Omega_{12}(t) = \Gamma_{12}\left(\frac{1}{2} + \frac{1}{\pi} \arctan \Gamma_{12} t\right)$ and $\Omega_{23}(t) = \Gamma_{12}\left(\frac{1}{2} - \frac{1}{\pi} \arctan \Gamma_{12} t\right)$. With this, solve the Schrödinger equation (14.151) iteratively within the time interval $t \in [-40/\Gamma_{12}, 40/\Gamma_{12}]$, while continuously adjusting the Rabi frequencies.

b. The dynamics can also be calculated via a numerical simulations of the Bloch equations (14.143). Write down the Liouville matrix and prepare a simulation using the same parameters as in (b) and additionally $\Gamma_{23} = \Gamma_{12}/2$, $\Gamma_{13} = \Gamma_{12}/500$.

c. Interpret the results.

14.5.5.5 Ex: Adiabatic sweeps

In experiments with cold atoms it is often necessary to transfer populations between ground states, for example, between specific levels of a Zeeman structure. One possible procedure is the method of optical pumping, from the initial ground state to an excited state, which subsequently decays to the final state by spontaneous emission. The problem with this incoherent procedure is, that one can control into which ground state level the atom will decay, and that it heats atoms due to the photonic recoil associated with the scattering of light. In this exercise we study an alternative method, called adiabatic sweep, which allows the coherent transfer of population between the two outer states of a degenerate multiplet, as shown in Fig. 14.8, via an adiabatic ramp of the frequency of the incident radiation:

a. Write down the Hamiltonian of the system in the interaction picture. Now, choose $\Omega/2\pi = 8$ kHz and apply a linear ramp of the radiation detuning between $-50$ kHz $< \Delta(t)/2\pi < 50$ kHz during a time interval of 2 ms. With this, solve the Schrödinger
equation (14.143) iteratively varying the detuning.

b. Write down the Liouville matrix of the system and do a numerical simulation of the Bloch equations (14.143) using the same parameters as in (a). Interpret the results. What you observe when you introduce a decay rate between adjacent levels of $\Gamma/2\pi = 200$ Hz?

---

14.5.6 Ex: Dispersive interaction between an atom and light

Radiation which is tuned far from a resonance can change the phase of an atomic dipole moment without changing the populations. We study this effect in a three-level system in cascade configuration excited by two radiation fields, as illustrated in Fig. 14.6(c), simulating the Schrödinger equation and the Bloch equations.

a. Write down the Hamiltonian $\hat{H}$ for this system letting $\Delta_{12} = 0$.

b. Now, consider the subsystem $\ket{2} - \ket{3}$, write down its Hamiltonian $\hat{H}_{23}$, determine the eigenvalues, and assume that this transition be excited very far-off resonance. That is, for $\Delta_{23} \gg \Omega_{23}, \Gamma_{23}$ expand the eigenvalues of $\hat{H}_{23}$ up to second order in $\Omega_{23}$. Finally, replace the submatrix $\hat{H}_{23}$ in the complete Hamiltonian $\hat{H}$ by the matrix of the expanded eigenvalues. This procedure corresponds to treating the transition $\ket{2} - \ket{3}$ as a perturbation of the transition $\ket{1} - \ket{2}$ until second order.

c. Assume that the atom is initially in the ground state and compute the time evolution of the state via the Schrödinger equation (14.151) using (a) the perturbed Hamiltonian and (b) the exact Hamiltonian for the following sequence of pulses:

(i) a $\pi/2$-pulse on the transition $\ket{1} - \ket{2}$,
(ii) a pulse with a variable duration between 0 and $\Delta t = \Omega_{23}^2/4\pi\Delta_{23}$ applied to the transition $\ket{2} - \ket{3}$,
(iii) a $\pi/2$-pulse on the transition $\ket{1} - \ket{2}$. What you observe?

d. Establish the Liouville matrix $\mathcal{L}$ for the same system and calculate the time evolution of the Bloch vector during the sequence by the Bloch equations (14.151) choosing the same parameters as in (c) and additionally $\Gamma_{23} = 1$, $\Gamma_{13} = \Gamma_{23}$, $\Gamma_{12} = 0.01\Gamma_{23}$, and $\Omega_{12} \gg \Delta_{23}, \Gamma_{23}$. Prepare a 3D curve [similar to Fig. 14.2(b)] of the population $\rho_{22}(t)$. Interpret the results.

---

8This type of interaction is used in the implementation of quantum gates in quantum computing.
14.5.5.7 Ex: Fano profile of in dark resonance

The dark resonance studied in Exc. 14.5.5.3 may in some circumstances adopt an asymmetric profile. Calculate, for a three-level system in Λ-configuration, as shown in Fig. 14.6(a), starting from the Bloch equations (14.143) with the Liouville matrix $\mathcal{M}_{\text{red}}$ reduced by the trace condition (14.147), the spectrum $\rho_{22}(\Delta_{23})$ for the following set of parameters: $\Gamma_{12} = 2$, $\Gamma_{23} = \Gamma_{12}/2$, $\Gamma_{23} = 0.1\Gamma_{12}$, $\Omega_{12} = 10\Gamma_{12}$, $\Omega_{23} = 5\Gamma_{23}$, $\Delta_{12} = -5\Gamma_{12}$ and $\Delta_{23} = [-1 : 0.01 : 1]\Gamma_{23}$. Interpret the spectrum in terms of a Fano resonance.

14.5.5.8 Ex: Gas with negative permittivity

Study EIT on the strontium cascade system consisting of the transitions 689 nm and 497 nm and draw a spectrum of the permittivity. Compare with the permittivity of the 689 nm two-level system. What densities are necessary to get a negative permittivity?

14.5.5.9 Ex: Gas with negative permeability

Theoretically, under certain conditions, gases may exhibit negative permittivity and permeability, and therefore refraction [550] DOI, [548] DOI, [549] DOI, [454] DOI, [366]. To study this phenomenon we consider a three-level system in Λ-configuration with an electric dipole transition and another magnetic dipole transition. The objective is to balance the electrical dipole moment excited by a probe laser and the magnetic dipole moment excited via a Raman transition by both, the probe laser and a control laser. The Raman transition simulates an effective magnetic field. Since the magnetic moment is smaller by a factor of $\alpha^2$, the electric moment must be reduced by detuning the probe laser, as shown in Fig. 14.9.

Figure 14.9:

a. Consider a three-level system in Λ-configuration. The transitions $|1\rangle \rightarrow |2\rangle$ and $|2\rangle \rightarrow |3\rangle$ are assumed to be electric dipoles and $|1\rangle \rightarrow |3\rangle$ a magnetic dipole, such that, $\Gamma_{12}, \Gamma_{23} \gg \Gamma_{13}$. Extract from the Bloch equation (14.143) the equations for the coherences $\rho_{12}$, $\rho_{13}$, and $\rho_{23}$.

b. Suppose, that the excitation on the probe transition be so weak, $\Omega_{12} \ll \Gamma_{12}$, that it does not succeed to empty the ground state. In this approximation eliminate the dynamics of $\rho_{23}$ and deduce the stationary solution for $\rho_{12}$ and $\rho_{13}$.

c. Calculate the magnetic susceptibility $\chi_m = [549]$ with the following parameters $\Gamma_{12} = 7 \cdot 10^7$ s$^{-1}$, $\Gamma_{23} = 3 \cdot 10^7$ s$^{-1}$, $\Gamma_{13} = 2 \cdot 10^7$ s$^{-1}$, $\Omega_{12} = 0.1\Gamma_{12}$, $\Omega_{23} = 2 \cdot 10^8$ s$^{-1}$.
\[ \Delta_{23} = 0 \text{ in the regime } \Delta_{12} = [-15\Gamma_{23}, 15\Gamma_{23}] \].

d. Simulate the Bloch equations (14.143) and compare with the numerical solution.

14.5.5.10 Ex: Magnetic dipole transitions in strontium

Magnetic dipole transitions are characterized by the selection rules \( \Delta J = 0, \pm 1 \), \( \Delta S = 0 \), \( \Delta L = 0 \), and \( \Delta n = 0 \). There are several transitions starting from the \( 5s5p \, 3P_J \) metastable states going to the \( 5p^2 \, 3P_J \) states with strong linewidths:

- \( 5s5p \, 3P_{1o} \leftrightarrow 5p^2 \, 3P_2 \) at 472.2278nm with \( \Gamma = (2\pi) \, 5.7\text{MHz} \)
- \( 5s5p \, 3P_{1o} \leftrightarrow 5p^2 \, 3P_1 \) at 478.4320nm with \( \Gamma = (2\pi) \, 4.8\text{MHz} \)

Check whether it is possible to reach negative permeability in a cold strontium gas.

14.5.5.11 Ex: Cascade EIT scheme in strontium

Consider the Bloch equations for the \(^{88}\text{Sr} \) 7-level system consisting of the following levels: \( |1\rangle \equiv (5s^2) \, ^1S_0 \), \( |2-4\rangle \equiv (5s5p) \, ^3P_1 \), and \( |5-7\rangle \equiv (5s5d) \, ^3D_1 \), and check under which circumstances it is possible to observed dark resonances. The Sr level scheme can be consulted under (Sr level scheme). The Liouvillean can be consulted at (Sr Liouvillean).
Chapter 15

Atoms in quantized radiation fields

So far we have treated the optical field only as a stationary or propagating classical wave, while our two-level atom has been regarded as an entity obedient to the laws of quantum mechanics and subject to an induced perturbation by an oscillatory electromagnetic field. This procedure naturally leads to oscillations of the atomic states’ populations and the coherences between them. However, in strong fields, when atomic energy spectrum is significantly modified, a non-perturbative, time-independent approach can be fruitful. Time-independent solutions for the Schrödinger equation for atoms coupled to fields is called dressed states. They were used for the first time to interpret the splitting of rotational molecular spectra in the presence of intense classical radiofrequency fields. While the semiclassical treatment is suitable for a wide variety of phenomena and has the virtue of mathematical simplicity and familiarity, it is sometimes worth considering the field as a quantum entity as well. In the dressed states picture, the atom-field interaction corresponds to an exchange of energy quanta between the field (photons) and the atom. This approach allows us to express photonic number states, also called Fock states, on equal footings with the discrete states of atom excitation and to write the state functions of the coupled atom-field system in a basis of photonic and atomic product states. Diagonalization of the dipole coupling terms in the system’s Hamiltonian generates time-independent solutions of dressed states in a completely quantum Schrödinger equation.

We begin this chapter with the quantization of the light field and then express the atom-field interaction in a fully quantized form. We will examine some examples illustrating how the dressed states picture can provide useful information on the light-matter interactions.

15.1 Quantization of the electromagnetic field

We have already seen that the energy of a monochromatic light field with frequency $\omega$ is quantized in small equal portions, such that the total energy is $n\hbar\omega$, where $n$ is an integer number. The energy spectrum is the same as the one of the harmonic oscillator. Therefore, we can identify a light mode with an oscillator and adopt the entire formalism developed for the harmonic oscillator. The formalism will be assumed as known in the following. We will, for simplicity use the term photon (respectively phonon) for excitations of a harmonic oscillator mode. It is however important to be
aware that a photon is not a particle, as it simply disappears when performing the transition from quantum to classical mechanics [367].

15.1.1 Field operators

The basic idea behind field quantization is the replacement of the classical harmonic oscillators discussed in Sec. 4.4 by quantum oscillators. The simplest approach to perform this quantization is to introduce the scalar potential $\Phi$ and the potential vector $A$ as done in electrodynamic theory. In free space, without charges nor currents, and within the Coulomb gauge we have the solution of the wave equation (13.5) generalized to a distribution of wavevectors $k$,

$$A(r, t) = \sum_k \bar{\epsilon}_k [A_{0k}^+ e^{i(k \cdot r - \omega_k t)} + A_{0k}^- e^{-i(k \cdot r - \omega_k t)}], \quad (15.1)$$

where we already isolated the vectorial character due to the polarization $\bar{\epsilon}_k$ of the light mode $k$. Obviously, $A_{0k}^- = (A_{0k}^+)^*$. As each amplitude and polarization of the wave given by the vector potential $A_{0k}$ and $A_{0k}^+$ must satisfy the wave equation separately, we arrive at the dispersion relation,

$$\omega_k = ck. \quad (15.2)$$

With the results (13.7) and (13.8) we know that the energy in each radiative mode is,

$$E_k = \hbar \omega_k N_k = u_k V = 2\varepsilon_0 V \omega_k^2 |A_{0k}|^2 = 2\varepsilon_0 V \omega_k^2 (A_{0k}^- A_{0k}^+ + A_{0k}^+ A_{0k}^-). \quad (15.3)$$

The second quantization now consists in interpreting the mode as a quantum harmonic oscillator, that is, we understand the observables as operators satisfying commutation rules, such as $[\hat{A}_{0k}, \hat{A}_{0k}^+] \propto \delta_{k,k'}$, and hence being affected by quantum fluctuations:

$$\hat{H}_k = \hbar \omega_k (\hat{N}_k + \frac{1}{2}) = 2\varepsilon_0 V \omega_k^2 (\hat{A}_{0k}^- \hat{A}_{0k}^+ + \hat{A}_{0k}^+ \hat{A}_{0k}^-). \quad (15.4)$$

Introducing normalized field operators following the commutation rule (4.58) via,

$$\hat{a}_k \sqrt{\frac{\hbar}{4\varepsilon_0 V \omega_k}} \equiv \hat{A}_{0k}^+ \quad \text{and} \quad \hat{a}_k^\dagger \sqrt{\frac{\hbar}{4\varepsilon_0 V \omega_k}} \equiv \hat{A}_{0k}^-, \quad (15.5)$$

such that,

$$\hat{H}_k = \hbar \omega_k (\hat{a}_k^\dagger \hat{a}_k + \frac{1}{2}). \quad (15.6)$$

The analogy allows us to interpret them as creation operator and annihilation operator of photons. Finally, we can rewrite (15.1) as,

$$\hat{A}_k(r, t) = \sqrt{\frac{\hbar}{4\varepsilon_0 V \omega_k}} \bar{\epsilon}_k \left[ \hat{a}_k e^{i(k \cdot r - \omega_k t)} + \hat{a}_k^\dagger e^{-i(k \cdot r - \omega_k t)} \right]. \quad (15.7)$$

---

1See the script Electrodynamics by the same author Scripts/EletroMagnetismoScript.

2The atom-light interaction may depend on the polarization of the light with respect to the quantization axis of the atom, as defined e.g. by a magnetic field. In these cases we need to extend the index $k$ to include the polarization state $(k, \lambda)$. 
We already know such combinations of operators and their complex conjugates from the HO (4.67).

The electric and magnetic field operators for the cavity modes can be constructed from,

\[
\hat{\vec{E}}_k = -\frac{\partial \hat{\vec{A}}_k}{\partial t} = i\sqrt{\frac{\hbar \omega_k}{2\varepsilon_0 V}} \left( \hat{a}_k e^{i(k \cdot r - \omega_k t)} - \hat{a}^\dagger_k e^{-i(k \cdot r - \omega_k t)} \right) \vec{\epsilon}_k.
\]

(15.8)

We can calculate the period-averaged energy of the \( k \)-th cavity mode from a quantum version of Eq. (15.9),

\[
\bar{E}_k = \frac{\varepsilon_0}{2} \int \langle n_k | \hat{\vec{E}}_k \cdot \hat{\vec{E}}_k | n_k \rangle dV.
\]

(15.9)

The result (15.6) is exactly Planck’s quantum hypothesis (although strictly speaking, he rather suggested a quantization of oscillators in the conducting walls of the cavity, not of the field) on the distribution of the spectral intensity radiated by a black body. We now can see that it follows naturally from the quantization of the cavity field modes. Solve Excs. 15.1.4.1, Exc. 15.1.4.2, and 15.1.4.3.

### 15.1.2 Interaction of quantized fields with atoms

Now, that we have a clear picture of the quantized field with the energies in the modes given by Eq. (15.9) and the photon number states given by the eigenstates \(| n \rangle\) of the quantized harmonic oscillator, we are in a position to consider our two-level atom interacting with this quantized radiation field. If for the moment, we exclude spontaneous emission and stimulated processes, the Hamiltonian of the combined atom-field system is,

\[
\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{field}} + \hat{H}_{\text{atom-field}}.
\]

(15.10)

We describe the atom by a two-level system,

\[
\hat{H}_{\text{atom}} = \Delta \hat{g} + \Delta \hat{e} = \hbar \omega_g |g\rangle \langle g| + \hbar \omega_e |e\rangle \langle e| + \hbar (\omega_g + \omega_0) |e\rangle \langle e|,
\]

(15.11)

where \( \hat{H}_{\text{field}} \) is the Hamiltonian of the quantized field, expressed by Eq. (15.6), and \( \hat{H}_{\text{atom-field}} \) the atom-field interaction. For the Hamiltonian without interaction, \( \hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{field}} \), the eigenstates are simply product states of the atomic states and the photon number states,

\[
|g, n\rangle = |g\rangle |n\rangle \quad \text{and} \quad |e, n\rangle = |e\rangle |n\rangle.
\]

(15.12)

The left side of Fig. 15.1 shows, how the eigenenergies of the product states consist of two ladders, being displaced by the energy difference \( \hbar \Delta \), which corresponds to the detuning. We write the Hamiltonian of the atom Eq. (15.11) as the sum of projectors on unperturbed eigenstates using the completeness relation and the orthogonality
of eigenstates. With the same idea we can rewrite the dipole operator defined in Eq. (13.30),

$$\hat{d} = \sum_i |\psi_i\rangle\langle\psi_i| = \sum_{i,j} |i\rangle e^{i(\omega_i - \omega_j)t} d_{ij} |j\rangle \langle j|.$$

(15.13)

using $|\psi_n(t)\rangle = e^{-i\omega_nt} |n\rangle$. Note that $d$ only has non-diagonal elements.

Figure 15.1: (Left) Photons number states and the two stationary states of the two-levels atom. (Center) Double ladder showing the basis of products states of photon number and atomic states. (Right) Dressed states constructed by diagonalization of the full Hamiltonian in the basis of the product states.

Now, let us use the electric field of Eqs. (15.8) to describe the atom-field interaction through the Hamiltonian $\hat{H}_{\text{atom-field}} = -\hat{d} \cdot \vec{E}$,

$$\hat{H}_{\text{atom-field}} = i \sum_k \sum_{i,j} \sqrt{\frac{\hbar \omega_k}{2\epsilon_0 V}} d_{ij} e^{i(\omega_i - \omega_j)t} |i\rangle \langle j| \cdot \vec{E}_k \left[ \hat{a}_k e^{i(k \cdot r - \omega_k t)} - \hat{a}_k^\dagger e^{-i(k \cdot r - \omega_k t)} \right].$$

(15.14)

For our two-level atom interacting with a single mode radiation field, we only have,

$$\hat{H}_{\text{atom-field}} = i \sqrt{\frac{\hbar \omega_k}{2\epsilon_0 V}} d_{ge} \left[ e^{i(\omega_e - \omega_g)t} |g\rangle \langle e| + e^{i(\omega_g - \omega_e)t} |e\rangle \langle g| \right] \cdot \vec{E}_k \left[ \hat{a}_k e^{i(k \cdot r - \omega_k t)} - \hat{a}_k^\dagger e^{-i(k \cdot r - \omega_k t)} \right].$$

(15.15)

15.1.2.1 Rotating wave approximation for dressed states

We can simplify the notation by identifying $\hat{\sigma}^+ = |e\rangle\langle g|$ and $\hat{\sigma}^- = |g\rangle\langle e|$ of the Eqs. (14.72) and introducing as an abbreviation the Rabi frequency,

$$\frac{1}{2} \hbar \Omega(r) \equiv \sqrt{\frac{\hbar \omega_k}{2\epsilon_0 V}} d_{ge} \cdot \vec{E}_k e^{ik \cdot r}.$$

(15.16)

The interaction Hamiltonian then becomes,

$$\hat{H}_{\text{atom-field}} = \frac{1}{2} \hbar \Omega(r) e^{-i(\omega_k - \omega_0)t} \hat{\sigma}^+ \hat{a}_k + \frac{1}{2} \hbar \Omega(r) e^{-i(\omega_k + \omega_0)t} \hat{\sigma}^+ \hat{a}_k^\dagger + \frac{1}{2} \hbar \Omega^*(r) e^{i(\omega_k + \omega_0)t} \hat{\sigma}^- \hat{a}_k^\dagger - \frac{1}{2} \hbar \Omega^*(r) e^{i(\omega_k - \omega_0)t} \hat{\sigma}^- \hat{a}_k.$$

(15.17)

This Hamiltonian contains four terms describing the following processes,
15.1. QUANTIZATION OF THE ELECTROMAGNETIC FIELD

15.1. QUANTIZATION OF THE ELECTROMAGNETIC FIELD

\[ |g, n\rangle \rightarrow |e, n - 1\rangle \text{ the atom is excited by the absorption of a photon;} \]
\[ |e, n\rangle \rightarrow |g, n - 1\rangle \text{ the atom is deexcited by the absorption of a photon;} \]
\[ |g, n\rangle \rightarrow |e, n + 1\rangle \text{ the atom is excited by the emission of a photon;} \]
\[ |e, n\rangle \rightarrow |g, n + 1\rangle \text{ the atom is deexcited by the emission of a photon;} \]

Obviously, only the first and forth terms respect energy conservation (in first-order processes) and can serve as initial and final states in real physical processes. Fig. 15.3 shows schemes of these four terms. We see, that neglecting the second and third process (i.e., terms \( \propto \hat{\sigma}^\pm \hat{a}^\pm \) of the Hamiltonian) is equivalent to making the rotating wave approximation (RWA), where we despise the terms rotating with the frequency \( \pm (\omega_k + \omega_0) \), and that we really only need to consider the coupling between the two dressed states \( |g, n\rangle \) and \( |e, n - 1\rangle \).

Finally, within the RWA the Hamiltonian reads,

\[
\hat{H}_{\text{atom-field}} = \frac{i}{2} \hbar \Omega(r) e^{-i \Delta_k t} \hat{\sigma}^+ \hat{a}_k - \frac{i}{2} \hbar \Omega^*(r) e^{i \Delta_k t} \hat{\sigma}^- \hat{a}^+_k , \tag{15.18}
\]

where we introduced the detuning \( \Delta_k \equiv \omega_k - \omega_0 \) as short hand notation.

It is important to note that the first and fourth term can be important in higher order processes, such as multiphotonic absorption or Raman scattering processes, where the excited state would be a virtual level. In fact, when the Rabi frequency is very large, \( \Omega \simeq \omega \), the excitation and deexcitation processes follow each other so rapidly, that energy conservation can be violated for short times. The energy shift caused by terms neglected in the RWA are called Bloch-Siegert shift \(^3\).

15.1.3 Dressed states

Within the new dressed states basis, the atom-light coupling problem is reduced to diagonalizing the Hamiltonian of a quasi-degenerate two-level atom (\( \Delta \ll \omega_0 \)), in which the non-diagonal elements are given by \( \frac{1}{2} \hbar \Omega \). The eigenenergies of the complete Hamiltonian \( \hat{H} \) are,

\[
E_{\pm} = \frac{\hbar}{2} (\omega_{g,n} + \omega_{e,n-1}) \pm \frac{\hbar}{2} G . \tag{15.19}
\]

where \( \hbar \omega_{g,n} \) and \( \hbar \omega_{e,n-1} \) are the energies of the product states \( \hbar \omega_g + n \hbar \omega_k \) and \( \hbar \omega_e + (n - 1) \hbar \omega_k \).

The atom-field product states offer a natural basis for the Hamiltonian of Eq. (15.10). The states resulting from the diagonalization of the Hamiltonian on this basis are

\[^3\]The shift is not observed, when the non-rotating terms \( \sigma^\pm a^\pm \) are forbidden by other conservation or selection rules. For example, when a resonance is excited by \( \sigma^\pm \) light, the RWA is accurate.
called dressed states. As indicated in Fig. 15.1, the neighboring doublets the double ladder ’repel’ each other under the influence of the interaction $\hat{H}_{\text{atom-field}}$ in Eq. (15.10). The mixed coefficients form the familiar problem of two levels, now called $|a\rangle$ and $|b\rangle$. From Fig. 15.1 we see,

$$
|a, N\rangle = \cos \theta |g, n\rangle + \sin \theta |e, n - 1\rangle,
$$

$$
|b, N\rangle = \cos \theta |e, n - 1\rangle - \sin \theta |g, n\rangle.
$$

(15.20)

with

$$
\tan 2\theta = \frac{\Omega}{\Delta},
$$

(15.21)

where the separation between constituents of the same dressed state is $G = \sqrt{\Omega^2 + \Delta^2}$. The numbers $n$ denote the amount of photons in the laser beam, the numbers $N$ denote the amount of energy packets within the system, that is, the photons plus the possible excitation of the atom.

### 15.1.4 Exercises

**15.1.4.1 Ex: Photon statistics**

An optical resonator contains 10 photons in the mode $TEM_{00q}$. What is the probability of finding, at any time, 1 photon resp. 10 photons, when the light is (a) thermal, (b) coherent? For case (a), what is the temperature of the light?

**15.1.4.2 Ex: Thermal mixture**

We consider a thermal non-interacting atomic gas in one dimension. Instead of describing the state of the atomic ensemble, we can consider a single atom with a distributed probability of having a given velocity $v$. The density operator of the continuous degree of freedom can be written,

$$
\hat{\rho} = \int dv \sqrt{\frac{m}{2\pi k_B T}} e^{-mv^2/2k_B T} |v\rangle \langle v|,
$$

and the trace of an arbitrary observable $\hat{A}$,

$$
\langle \hat{A} \rangle = \text{Tr} \hat{\rho} \hat{A} = \int du \langle u|\hat{\rho} \hat{A}|u\rangle.
$$
Now imagine a device capable of measuring the speed of a single atom randomly chosen within the cloud.

a. Express the probability of measuring a specific velocity \( v' \) for this atom using the density operator.

b. Express the expectation value of the average velocity by the density operator.

15.1.4.3 Ex: Converting a pure state into a mixture by incomplete measurement

Consider a dressed two-level atom with the atomic states \( |g\rangle \) and \( |e\rangle \) and the photon number state \( |n\rangle \).

a. Write down the general normalized dressed state and the density operator.

b. Now, perform a measurement of the atomic state tracing over the atomic degree of freedom and verify whether the resulting density operator represents a pure state.

c. Now, perform a measurement of the photon number and verify whether the resulting density operator represents a pure state.

15.2 Quantum correlations in the Jaynes-Cummings model

The Jaynes-Cummings model describes the dynamics of a single dressed two-level atom in a single monochromatic laser mode in the absence of spontaneous emission processes. The model has become a paradigm of quantum mechanics with applications in quantum information, where it applies to the formulation of entanglement protocols of atomic states and the implementation of quantum ports. In the following, we will first study the interaction of an atom with an optical mode neglecting dissipation effects, leaving the discussion on the impact of dissipation processes to later sections.

The dynamic evolution of pure states then follows the Schrödinger equation. The Hamiltonian of this system is given by (15.17). Letting \( \hbar = 1 \) and assuming that the atom is located at the origin \( [\text{such that } \Omega(0)e^{ikr} = \Omega(0)] \), we can write the Hamiltonian as,

\[
\hat{H} = \omega \hat{a}^\dagger \hat{a} + \omega_0 (\hat{\sigma}^+ \hat{\sigma}^- - \frac{1}{2}) + \frac{1}{2} \Omega (\hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a} \hat{\sigma}^-)
\]

(15.22)

where \( \omega \) is the frequency of the radiation, \( \omega_0 \) the frequency of the atomic transition, and \( \Omega \) the Rabi frequency generated by a single photon. We choose the Fock representation for the radiation mode, we represent the atomic transitions by Pauli matrices, and we span the product space \( \hat{\rho}_{\text{field}} \otimes \hat{\rho}_{\text{atom}} \) generalizing the operators \( \hat{\sigma}^\pm \sim \hat{\sigma}^\pm \otimes I \) and \( \hat{\sigma}^\pm \sim \sigma^\pm \otimes \hat{\sigma}^\pm \). Explicitly we get,

\[
\hat{a}^\dagger = \sum_n \sqrt{n+1} |n+1\rangle \langle 1 0 | \langle n| \quad \text{and} \quad \hat{\sigma}^+ = \sum_n |n\rangle \langle 0 \ 0 | \langle n|
\]

\[
\hat{a} = \sum_n \sqrt{n} |n-1\rangle \langle 0 1 | \langle n| \quad \text{and} \quad \hat{\sigma}^- = \sum_n |n\rangle \langle 0 \ 1 | \langle n|.
\]

(15.23)
The Hamiltonian $\hat{H}$ can be decomposed into sub-hyperspaces of $n$ photons $\hat{H}_n$:

$$\hat{H} = \sum_n \left[ |n\rangle \left( (n-1)\omega - \frac{\omega_0}{2} \frac{\omega - \frac{\omega_0}{2}}{n\omega + \frac{\omega_0}{2}} \right) + |n-1\rangle \left( 0 \frac{\omega_0}{2} \sqrt{n} 0 \right) + |n+1\rangle \left( 0 \frac{\omega_0}{2} \sqrt{n+1} 0 \right) \right] |n\rangle$$

$$= \left( \begin{array}{cccc}
-\frac{\omega_0}{2} & 0 & 0 & \omega - \frac{\omega_0}{2} \\
0 & \frac{\omega_0}{2} \sqrt{2} & \omega + \frac{\omega_0}{2} & 0 \\
0 & \omega - \frac{\omega_0}{2} & \frac{\omega_0}{2} \sqrt{2} & 2\omega - \frac{\omega_0}{2} \\
\omega - \frac{\omega_0}{2} & 0 & 2\omega - \frac{\omega_0}{2} & \cdots \\
\end{array} \right)$$

$$= \bigoplus_n \left( \frac{(n-1)\omega + \frac{\omega_0}{2}}{n\omega - \frac{\omega_0}{2}} \frac{\omega_0}{2} \sqrt{n} \right) = \bigoplus_n \hat{H}_n .$$

The density operator for the subspace is,

$$\hat{\rho}_n = \left( \begin{array}{cccc}
|n-1\rangle|2\rangle & |n-1\rangle|1\rangle & |n-1\rangle|1\rangle |n\rangle \\
|n\rangle|1\rangle & |n\rangle|1\rangle & |n\rangle|1\rangle |n\rangle \\
|n\rangle|1\rangle & |n\rangle|1\rangle & |n\rangle|1\rangle |n\rangle \\
\end{array} \right).$$

The eigenvalues can be easily calculated by $^4$,

$$\det \sum_n \hat{H}_n = \sum_n \det \hat{H}_n ,$$

(15.26)

defining the detuning between radiation and the atomic transition, $\Delta \equiv \omega - \omega_0$, and the generalized $n$-photon Rabi frequency, $\varpi_n \equiv \sqrt{\Delta^2 + n\Omega^2} = |\varpi_n|e^{ikR}$, which contains the spatial mode function of the radiation field. This gives the diagonal matrix of eigenvalues,

$$\hat{E}_n = \left( \begin{array}{cccc}
(n-1)\omega + \frac{\varpi_n}{2} & 0 & 0 & (n-1)\omega - \frac{\varpi_n}{2} \\
0 & (n-1)\omega + \frac{\varpi_n}{2} & 0 & (n-1)\omega - \frac{\varpi_n}{2} \\
0 & 0 & (n-1)\omega + \frac{\varpi_n}{2} & 0 \\
(n-1)\omega - \frac{\varpi_n}{2} & 0 & 0 & (n-1)\omega + \frac{\varpi_n}{2} \\
\end{array} \right).$$

(15.27)

From the transformation $\hat{H}_n U_n = U_n \hat{E}_n$, under the condition that $U_n$ is unitary and hermitian, $U_n^\dagger U_n$, and using the abbreviation tan $2\phi_n \equiv \sqrt{n}\Omega/\Delta$, we obtain:

$$U_n = \left( \begin{array}{cccc}
\cos \phi_n & \sin \phi_n \\
-\sin \phi_n & \cos \phi_n \\
\end{array} \right).$$

(15.28)

The eigenvectors corresponding to the eigenvalues $\hat{E}_n$ are obtained by $\hat{H}_n |x\rangle = e_{nx} |x\rangle$, that is, $\hat{E}_n U_n^{-1} |x\rangle = e_{nx} U_n^{-1} |x\rangle$. Knowing $\hat{E}_n |y\rangle = e_{ny} |y\rangle$, we obtain $|x\rangle = U_n |y\rangle$.

The temporal evolution of the Jaynes-Cummings state, $|\psi(t)\rangle = e^{-i\hat{H}t}|\psi(0)\rangle$, is described by the transformation,

$$e^{-i\hat{H}^\dagger t} = U_n e^{-i\hat{E}_n^\dagger t} U_n^{-1} = e^{-i(n-1/2)\omega t} \times 
$$

$$\times \left( \begin{array}{cccc}
\cos^2 \phi_n e^{i\varpi_n t/2} + \sin^2 \phi_n e^{-i\varpi_n t/2} & \cos \phi_n \sin \phi_n (e^{i\varpi_n t/2} - e^{-i\varpi_n t/2}) \\
\cos \phi_n \sin \phi_n (e^{i\varpi_n t/2} - e^{-i\varpi_n t/2}) & \sin^2 \phi_n e^{-i\varpi_n t/2} + \cos^2 \phi_n e^{i\varpi_n t/2} \end{array} \right).$$

(15.29)

$^4$The following rules apply to determinants,

$$\det(AB) = \det A \det B \quad \text{and} \quad (\det A)^{-1} = \det A^{-1}.$$
which is essentially the same, as the time evolution derived in Exc. 2.4.6.1. The
transition probability between dressed states is,
\[ |\langle 2, n-1 | e^{-i\hat{H}_n t} | 1, n \rangle|^2 = \frac{4n \Omega^2 \Delta^2}{\varpi_n^2} \sin^2 \frac{\varpi_n t}{2}. \]  
(15.30)
The temporal evolution follows with
\[ \hat{\rho}(t) = e^{-i\hat{H}_n t} \hat{\rho}(0) e^{i\hat{H}_n t} \equiv \mathcal{L}(t) \hat{\rho}(0). \]  
(15.31)
A genuine phenomenon observed in the Jaynes-Cummings model, the temporal disap-
pearance of any signatures of quantum coherence in the light field known as quantum
collapse and revival is studied in Exc. 15.2.4.1.

15.2.1 The classical and quantum limits

15.2.1.1 The limit of high laser intensities and resonant interaction

The classical limit is recovered for \( n \to \infty \), where a single photon makes no difference,
that is, we can treat the states \(|n\rangle\) and \(|n+1\rangle\) as equivalent. Then, we can approximate
the Hamiltonian of the system (15.24) by the trace of this same Hamiltonian taken
over the number of photons,
\[ \hat{H}_{semi} = \lim_{n \to \infty} \text{Tr}_{field} \hat{\rho} \hat{H} = \sum_m \langle m | \hat{\rho} \hat{H}_n | m \rangle \]  
(15.32)
This situation, as illustrated in Fig. 15.4, describes well the state of a laser as a
coherent state, \(|\alpha\rangle = \sum_n \frac{\alpha^n}{\sqrt{n!}} |n\rangle e^{-|\alpha|^2/2}\). For \( n \to \infty \), the uncertainty of the Poisson
distribution is small, \( \Delta n/\bar{n} = 1/\sqrt{n} \to 0 \), such that the light mode is characterized
by the average number of photons, and fluctuations are negligible. This allows us to
replace the Poisson distribution,
\[ P_n = |\langle n | \alpha \rangle|^2 = \delta_{n \bar{n}}, \]  
(15.33)
Now, in the case of a resonant interaction, \( \Delta = 0 \), the Jaynes-Cummings evolution is,
\[ e^{-i\hat{H}_n t} = \frac{1}{\sqrt{2}} e^{-i(\bar{n}-1/2)\omega t} \begin{pmatrix} \cos \frac{1}{2} \varpi_n t & t \sin \frac{1}{2} \varpi_n t \\ t \sin \frac{1}{2} \varpi_n t & \cos \frac{1}{2} \varpi_n t \end{pmatrix}, \]  
(15.34)
which is a result already obtained in Exc. 2.4.6.1.

Example 56 (Resonant \( \pi/2 \)-pulse): In this example, we consider resonant
\( \pi/2 \)-pulses, that is, \( \sqrt{\varpi_n t} t = \frac{1}{2} \pi \). The Jaynes-Cummings evolution now simplifies
to,
\[ e^{-i\hat{H}_n t} = \frac{1}{2} e^{-i(\bar{n}-1/2)\omega t} \begin{pmatrix} 1 & t \\ t & 1 \end{pmatrix}. \]  
(15.35)
For large $\bar{n}$, a resonant $\pi/2$-pulse does (ignoring irrelevant dynamical phases),
\[
\left(\begin{array} {|c|c|}
|2\rangle & |\bar{n} - 1\rangle \\
|1\rangle & |\bar{n}\rangle \\
\end{array}\right) \xrightarrow{\pi/2} \left(\begin{array} {|c|c|}
(|2\rangle + i|1\rangle) & |\bar{n} - 1\rangle \\
(i|2\rangle + |1\rangle) & |\bar{n}\rangle \\
\end{array}\right),
\]
that is, for a coherent field,
\[
\left(\begin{array} {|c|c|}
|2\rangle & |\alpha\rangle \\
|1\rangle & |\alpha\rangle \\
\end{array}\right) \xrightarrow{\pi/2} \left(\begin{array} {|c|c|}
(|2\rangle + i|1\rangle)|\alpha\rangle \\
(i|2\rangle + |1\rangle)|\alpha\rangle \\
\end{array}\right).
\]
Obviously, the structure of the field $|\alpha\rangle$ is not affected, and we recover the dynamics of a two-level atom excited by a resonant classical radiation as described by the Bloch equations (14.61).

![Figure 15.4: Atomic level scheme for the implementation of resonant interactions with classical radiation fields (on the lower transition) and dispersive interactions with quantum fields (on the upper transition).](image)

### 15.2.1.2 Dispersive interaction, the limit of large detunings

The dispersive Jaynes-Cummings dynamics can be implemented by irradiating a light field, which is sufficiently detuned to avoid Rayleigh scattering processes, as shown in Fig. 15.4. This interaction results in a phase shift of the atomic levels. For $|\Delta| \gg \sqrt{n}\Omega$ the Hamiltonian simplifies to,
\[
\hat{H}_n = \hat{H}_n^{(0)} + \hat{H}_n^{(1)} = \left(\begin{array} {|cc|}
(n - \frac{1}{2})\omega - \frac{\Delta}{2} & 0 \\
0 & (n - \frac{1}{2})\omega + \frac{\Delta}{2} \\
\end{array}\right) + \left(\begin{array} {|cc|}
0 & \frac{\Omega}{\sqrt{n}} \\
\frac{\Omega}{\sqrt{n}} & 0 \\
\end{array}\right).
\]
In the unperturbed case we have, $\hat{H}_n^{(0)}|\psi_{j,n}\rangle = E_{j,n}|\psi_{j,n}\rangle$, where the $n$-photon subspace is spanned by the basis $|j\rangle = (1 \ 0)$ and $(0 \ 1)$. In second order of perturbation,
\[
\langle\psi_{j,n}|\hat{H}_n|\psi_{j,n}\rangle = \langle j|\hat{H}_n^{(1)} + \hat{H}_n^{(2)}|j\rangle + \sum_{j \neq i} \frac{\langle j|\hat{H}_n^{(1)}|i\rangle\langle i|\hat{H}_n^{(1)}|j\rangle}{E_{j,n}^{(0)} - E_{i,n}^{(0)}} = \pm \frac{n\Omega^2}{4\Delta},
\]
where the upper sign holds for $|j\rangle = (1 \ 0)$. This result was already obtained in the Excs. 5.1.3.4 and 14.3.5.14. In matrix notation,
\[
\hat{H}_n^{(1)} \simeq \begin{pmatrix}
\frac{n\Omega^2}{4\Delta} & 0 \\
0 & -\frac{n\Omega^2}{4\Delta}
\end{pmatrix}.
\]
The temporal propagation operator (15.29) then simplifies to,
\[
e^{-i\hat{H}_n^{(1)}t} = \begin{pmatrix}
e^{in\Omega^2t/4\Delta} & 0 \\
0 & e^{-in\Omega^2t/4\Delta}
\end{pmatrix}.
\]
The fact that the ground and excited atomic states evolve with different phase factors is important, as we will show in the following example.

**Example 57 (Dispersive \( \pi \)-pulse):** As in the previous case, we consider a two-level atom subject to a coherent field, but now tuned out of resonance. Introducing the abbreviation \( \varphi \equiv \Omega^2 t / 4 \Delta \), the Jaynes-Cummings evolution is,

\[
e^{-i \hat{H}_{\text{int}}^{(1)} t} = \begin{pmatrix} e^{i \varphi} & 0 \\ 0 & e^{-i n \varphi} \end{pmatrix}.
\]

(15.42)

The fact that the phase shift \( n \varphi \) depends on the number of photons, and that it goes in opposite directions for the ground and excited states, is crucial. We have already studied in Exc. 14.5.5.6, that the dispersive interaction of the atom with a radiation field can phase-shift the Bloch vector. Now, we observe that in addition, it causes a phase shift of the probability amplitude of having \( n \) photons in the radiation field by a value proportional to \( n \), i.e. (ignoring irrelevant dynamical phases),

\[
\left( |2\rangle|n - 1\rangle \right)^{n \varphi} \propto \begin{pmatrix} e^{i n \varphi} |2\rangle|n - 1\rangle \\ e^{-i n \varphi} |1\rangle|n\rangle \end{pmatrix}.
\]

(15.43)

Applying this result to Glauber states,

\[
\left( |2\rangle|\alpha\rangle \right)^{n \varphi} \left( |2\rangle \sum_n \frac{a^n}{\sqrt{n!}} e^{i n \varphi} |n\rangle \right) \propto \left( |2\rangle|\alpha e^{i \varphi}\rangle \right).
\]

(15.44)

Apparentlv, the phase of the radiation field is shifted by a value \( \varphi \), which depends on the state of the atom.

We note here, that the dynamics studied in the last example provides a method of transferring coherence from an atomic superposition to a quantum correlation of a radiation field. All we have to do, is to bring the atom into a superposition of states \( |1\rangle + |2\rangle \), and the field will automatically evolve toward a Schrödinger cat state \( |\alpha e^{i \varphi}\rangle + |\alpha e^{-i \varphi}\rangle \). The transfer of quantum correlations between coupled degrees of freedom is one of the characteristics of the Jaynes-Cummings model. As examples we will study the phenomena of quantum collapse and revival in Exc. 15.2.4.2 and of vacuum Rabi splitting in 15.2.4.3.

### 15.2.1.3 Temporal evolution of the Bloch vector and the \( Q \)-function

In the limit of low laser intensities we must consider photonic distributions that are not necessarily coherent. The stationary solution of the Schrödinger equation consists of the dressed states \( |1, n\rangle \) and \( |2, n - 1\rangle \). If we now expand a general Jaynes-Cummings state in amplitudes \( c_{jn}(t) \),

\[
|\psi\rangle = \sum_n \left( c_{1,n} |1, n\rangle + c_{2,n-1} |2, n - 1\rangle \right)
\]

(15.45)

they will follow the Schrödinger equation,

\[
\frac{d}{dt} \begin{pmatrix} c_{2,n-1} \\ c_{1,n} \end{pmatrix} = \hat{H}_n \begin{pmatrix} c_{2,n-1} \\ c_{1,n} \end{pmatrix}.
\]

(15.46)
The evolution of the coefficients $c_{jn}$ completely describes the Jaynes-Cummings dynamics of the system through the formula (15.29). Obviously, the Jaynes-Cummings state is normalized because,

$$\langle \psi | \psi \rangle = \text{Tr} | \psi \rangle \langle \psi | = \sum_n (|c_{1,n}|^2 + |c_{2,n}|^2) = 1 .$$  \hspace{1cm} (15.47)

The expectation value for field observables $\hat{A}$ is,

$$\langle \psi | \hat{A} | \psi \rangle = \text{Tr} \hat{A} = \sum_{i,n} \langle i | \langle n | \psi \rangle \langle \psi | n \rangle | i \rangle = \sum_n A_n (|c_{1,n}|^2 + |c_{2,n}|^2) .$$  \hspace{1cm} (15.48)

The expectation value for the annihilation operator $\hat{a}$ is,

$$\langle \psi | \hat{a} | \psi \rangle = \sum_n \sqrt{n} (c_{1,n-1}^* c_{2,n} + c_{2,n-1}^* c_{1,n}) .$$  \hspace{1cm} (15.49)

To determine the internal state of the atom, we must trace over the light field. As dissipation processes are neglected, we get a pure state described by, $\hat{\rho} = |\psi \rangle \langle \psi |$. The populations and coherences are, therefore,

$$\rho_{ij} = \langle i | \text{Tr}_\text{field} \hat{\rho} | j \rangle = \langle i | \sum_n \langle n | \psi \rangle \langle \psi | n \rangle | j \rangle = \sum_n c_{i,n} c_{j,n}^* .$$  \hspace{1cm} (15.50)

The projection onto the atomic state is done by,

$$\langle j | \hat{\rho} | j \rangle = \sum_n c_{j,n} | j, n \rangle = \sum_{j,n} \frac{c_{j,n} | j, n \rangle}{\sum_m |c_{j,m}|^2} .$$  \hspace{1cm} (15.51)

With this, we can calculate the atomic Bloch vector, whose norm is interestingly NOT preserved, since,

$$|\hat{\rho}| = \left( \begin{array}{c} \sqrt{2} \text{Re} \rho_{12} \\ \sqrt{2} \text{Im} \rho_{12} \\ \rho_{22} - \rho_{11} \end{array} \right) = 2 |\rho_{12}|^2 - 2 \rho_{11} \rho_{22} = -2 \text{det} \hat{\rho}$$

$$= 2 \sum_n c_{1,n} c_{2,n}^* c_{2,n} - 2 \sum_n |c_{2,n}|^2 \sum_n |c_{1,n}|^2 \neq 1 .$$  \hspace{1cm} (15.52)

To determine the state of the light field, we must trace over the atomic state. For example, the probability amplitude of encountering the state $|\psi \rangle$ in $|n \rangle$ is,

$$\langle n | \psi \rangle = c_{1,n} |1 \rangle + c_{2,n} |2 \rangle ,$$  \hspace{1cm} (15.53)

such that,

$$p_n = \langle n | \text{Tr}_\text{atom} \hat{\rho} | n \rangle = \sum_{i=1,2} \langle i | \psi \rangle \langle \psi | i \rangle |n \rangle = |\langle n | \psi \rangle|^2 = |c_{1,n}|^2 + |c_{2,n}|^2 .$$  \hspace{1cm} (15.54)

To characterize the optical field separately from the atomic state, we can try, by a calculation similar to (15.48), to project the Jaynes-Cummings state onto a basis
of coherent states. Thus, the probability amplitude of encountering the state \(|\psi\rangle\) in \(|\alpha\rangle\) is,

\[
\langle \alpha | \psi \rangle = e^{-|\alpha|^2/2} \sum_n \frac{\alpha^n}{\sqrt{n!}} (c_{1,n}|1\rangle + c_{2,n}|2\rangle)
\]

such that,

\[
\pi Q(\alpha) \equiv \langle \alpha | \text{Tr}_{\text{atom}} \hat{\rho} | \alpha \rangle = e^{-|\alpha|^2} \left( \sum_n c_{1,n} \frac{\alpha^n}{\sqrt{n!}} \right)^2 + \sum_n c_{2,n} \frac{\alpha^n}{\sqrt{n!}} \right)^2 \right).
\]

We will derive this result in Exc. 15.2.4.4. This quantity, called \(Q\)-function, allows the illustration of the state in a coordinate system spanned by Re \(\alpha\) and Im \(\alpha\) [66]. It is generally easy to calculate, but does not exhibit much information, e.g., on interference phenomena caused by quantum correlations. In the following section, we will define other distribution functions, such as the Wigner function, which can also be evaluated from the Jaynes-Cummings coefficients [186].

![Figure 15.5](code)

Figure 15.5: (code) Evolution of the state during a Jaynes-Cummings type interaction: (a) Bloch vector, (b) time evolution of the coherence \(\rho_{12}\) showing the phenomenon of collapse and revival, (c) photon distribution, and (d) \(Q(\alpha)\) function.

The Jaynes-Cummings dynamics illustrated in Fig. 15.5 demonstrates the transfer of coherence between an atom and a light field. In Exc. 15.2.4.5 we study how to create, via a sequence of Ramsey pulses, a Schrödinger cat state in a light field.

### 15.2.2 Quantum correlations in light modes

Quantum correlations resulting in non-poissonian photon number distributions can be generated, for example, through a Jaynes-Cummings interaction of an atom with a light mode, as discussed in Sec. 15.2. Sometimes, it can be advantageous to represent these correlations in a coherent state basis. There are several representations, the most common ones being the coherent distribution functions \(Q\) and \(P\), and the Wigner function \(W\). Before calculating the quantum correlations produced by a Jaynes-Cummings interaction, we will discuss in this section the distribution functions for the some fundamental states, that is, the Fock and the Glauber state, the thermal state, and the Schrödinger cat state.
To define the coherent distribution functions, we need to introduce first the characteristic functions \( \chi_{N,S,A} \),

\[
\chi_N(\lambda) = \text{Tr} \hat{\rho} e^{\lambda \hat{a}^\dagger} e^{-\lambda \hat{a}}, \quad P = \mathcal{F}^{-1} \chi_N
\]
\[
\chi_S(\lambda) = \text{Tr} \hat{\rho} e^{\lambda \hat{a}^\dagger - \lambda \hat{a}^\dagger}, \quad W = \mathcal{F}^{-1} \chi_S
\]
\[
\chi_A(\lambda) = \text{Tr} \hat{\rho} e^{-\lambda \hat{a}} e^{-\lambda \hat{a}^\dagger}, \quad Q = \mathcal{F}^{-1} \chi_A
\]

Here, \( N \) denotes normal order, \( S \) symmetric order, and \( A \) antisymmetric order. Apparently, the distribution functions are related to each other. Using the Baker-Hausdorff formula (4.92) it is easy to show,

\[
e^{-|\lambda|^2/2} \chi_N(\lambda) = \chi_S(\lambda) = e^{|\lambda|^2/2} \chi_A(\lambda).
\]

Thus, \( Q \)-function corresponds to a smoothed Wigner function, which in turn corresponds to a smoothed \( P \)-function. The inverse complex Fourier transformation gives immediately \(^5\),

\[
Q = W \ast \left( \int \frac{2}{\pi} e^{-2|\lambda|^2} P \ast \left( \int \frac{2}{\pi} e^{-2|\lambda|^2} \right) \right) \ast \frac{2}{\pi} e^{-2|\lambda|^2} = P \ast \frac{1}{\pi} e^{-|\lambda|^2}.
\]

The distribution functions can be interpreted as follows: \( P(\alpha) \) is the probability of finding the coherent state \( |\alpha\rangle \) within the statistical mixture given by,

\[
\hat{\rho} = \int P(\alpha)|\alpha\rangle\langle\alpha| d^2\alpha
\]

and \( Q(\alpha) \) is the expectation value of the density operator:

\[
Q(\alpha) = \frac{1}{\pi} \langle\alpha|\hat{\rho}|\alpha\rangle.
\]

The various states that a light field can adopt can now be expressed either by photon number distribution in a Fock state basis, or by two-dimensional weighting functions \( P, Q, W \) in a coherent state basis. Here, are some examples for these representations.

### 15.2.2.1 Fock state in the coherent representation

On the number state basis \( |n\rangle \), the Fock state is characterized by,

\[
|n\rangle = (\hat{a}^\dagger)^n |0\rangle
\]
\[
\hat{\rho} = |n\rangle \langle n|
\]
\[
P_k = \delta_{nk}
\]
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Figure 15.6: (code) Q functions (first line) and Wigner function (second line) of a Glauber state (first column), a Fock state (second column), and a Schrödinger cat state (third column).

This state can be expanded on coherent states $|\alpha\rangle$ by following procedure. For large $n$ we first calculate the coherent distribution $P$-function,

$$P_{|n\rangle}(\alpha) = \delta^{(1)}(|\alpha| - \sqrt{n}),$$

(15.62)

because it allows us to derive the density matrix via the formula (15.59),

$$\hat{\rho}_{|n\rangle} = \int \delta^{(1)}(|\alpha| - \sqrt{n})|\alpha\rangle\langle\alpha|d^2\alpha = \int_{0}^{2\pi} \delta^{(1)}(|\alpha| - \sqrt{n})|\alpha\rangle\langle\alpha| |\alpha|^2 d|\alpha|d\varphi_{\alpha} = n \int_{0}^{2\pi} |\alpha\rangle\langle\alpha|d\varphi_{\alpha}.$$  

(15.63)

The coherent distribution $Q$-function becomes, inserting the density operator obtained in (15.63),

$$Q_{|n\rangle}(\alpha) = \frac{1}{\pi} \langle\alpha|\hat{\rho}_{|n\rangle}|\alpha\rangle = \frac{1}{\pi} \int_{0}^{2\pi} |\langle\alpha|\beta\rangle|^2 d\varphi_{\beta} = \frac{1}{\pi} n \int_{0}^{2\pi} e^{-|\alpha-|\beta|}e^{i\varphi_{\beta}} |\beta|^2 d\varphi_{\beta} \triangleq \frac{|\alpha|^2}{\pi n!} e^{-|\alpha|^2},$$  

(15.64)

and finally the Wigner function is,

$$W_{|n\rangle}(\alpha) = \frac{2}{\pi} e^{-2|\alpha|^2} (-1)^n \sum_{n=0}^{n_0} \left( \frac{n}{n} \right) (-4|\alpha|^2)^n \frac{n!}{n!}. $$

(15.65)
15.2.2.2 Representations of Glauber states

Vice versa, coherent states can be expanded on a Fock state basis by,

\[ |\alpha\rangle = e^{-|\alpha|^2/2} \sum_n \frac{\alpha^n}{\sqrt{n!}} |n\rangle \]
\[ \hat{\rho} = \sum_n |\alpha|^n e^{-|\alpha|^2/2} \frac{1}{n!} |n\rangle\langle n| \]  \hspace{1cm} (15.66)
\[ P_n = |\langle n|\alpha\rangle|^2 = e^{-|\alpha|^2} \frac{1}{n!} \]

The coherent distribution \( P\)-function is,

\[ P_{|\beta\rangle}(\alpha) = \delta^{(2)}(\alpha - \beta) \]  \hspace{1cm} (15.67)

the density matrix,

\[ \hat{\rho}_{|\beta\rangle} = \int \delta^{(2)}(\alpha - \beta) |\alpha\rangle\langle \alpha| d^2\alpha = |\beta\rangle\langle \beta| \]  \hspace{1cm} (15.68)

the coherent distribution \( Q\)-function becomes,

\[ Q_{|\beta\rangle}(\alpha) = \frac{1}{\pi} e^{-|\alpha - \beta|^2} \]  \hspace{1cm} (15.69)

and the Wigner function is,

\[ W_{|\beta\rangle}(\alpha) = 2 \frac{1}{\pi} e^{-2|\alpha - \beta|^2} \]  \hspace{1cm} (15.70)

**Example 58 (State of a laser):** Following \cite{?}, the correct state of a laser beam is not simply a coherent state, but rather,

\[ \hat{\rho} = \int |ae^{i\phi}\rangle\langle ae^{i\phi}| \frac{d\phi}{2\pi} . \]  \hspace{1cm} (15.71)

After averaging, this state can be written as a superposition of Fock states,

\[ \hat{\rho} = \sum_n P_n |n\rangle\langle n| , \]  \hspace{1cm} (15.72)

but without a specific phase,

\[ \hat{\rho} \neq \sum_{m,n} c_m^* c_n |m\rangle\langle n| . \]  \hspace{1cm} (15.73)

15.2.2.3 Thermal states

A light mode in a thermal mixture can not be represented by a pure state, but requires a density matrix,

\[ \hat{\rho}_{\text{therm}} = \sum_n \frac{\bar{n}^n}{(1 + \bar{n})^{1+n}} |n\rangle\langle n| \]  \hspace{1cm} (15.74)
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The coherent distribution $P$-function is,

$$P_{\text{therm}}(\alpha) = \frac{1}{\pi \bar{n}} e^{-|\alpha|^2 / \bar{n}} ,$$  \hspace{1cm} (15.75)

the density matrix,

$$\hat{\rho} = \frac{1}{\pi \bar{n}} \int e^{-|\alpha|^2 / \bar{n}} |\alpha\rangle \langle \alpha| d^2 \alpha ,$$  \hspace{1cm} (15.76)

the coherent distribution $Q$-function becomes,

$$Q_{\text{therm}}(\alpha) = \frac{1}{\pi (\bar{n} + 1)} e^{-|\alpha|^2 / (\bar{n}+1)} ,$$  \hspace{1cm} (15.77)

and the Wigner function is,

$$W_{\text{therm}}(\alpha) = \frac{1}{\pi (\bar{n} + 1/2)} e^{-|\alpha|^2 / (\bar{n}+1/2)} .$$  \hspace{1cm} (15.78)

15.2.2.4 Schrödinger cat states

Schrödinger cat states are correlated states of many particles (or quasi-particles). The expansion of the Schrödinger cat state on a Fock state basis yields,

$$|\psi_{\pm}\rangle = \sum_n \frac{1 \pm (-1)^n}{\sqrt{2}} |\alpha|^n e^{-|\alpha|^2 / n!} |n\rangle .$$  \hspace{1cm} (15.79)

The coherent distribution $P$-function is,

$$P_{|\beta_0\rangle|\beta_1\rangle}(\alpha) = \delta^{(2)}(\alpha - \beta_0) + \delta^{(2)}(\alpha - \beta_1) ,$$  \hspace{1cm} (15.80)

the density matrix,

$$\hat{\rho} = ,$$  \hspace{1cm} (15.81)

the coherent distribution $Q$-function becomes,

$$Q_{|\beta_0\rangle|\beta_1\rangle}(\alpha) = \frac{1}{\pi} e^{-|\alpha - \beta_0|^2 / 2} + \frac{1}{\pi} e^{-|\alpha - \beta_1|^2 / 2} .$$  \hspace{1cm} (15.82)

The normally ordered characteristic function is,

$$\chi_N(\lambda) = \langle \beta_0| e^{\lambda a^+} e^{-\lambda^* a} |\beta_1\rangle = e^{\lambda \beta_0^* - \lambda^* \beta_1} ,$$  \hspace{1cm} (15.83)

and the Wigner function is,

$$W(\alpha) = \frac{1}{\pi} \int \chi_S(\lambda) e^{\lambda^* a - \lambda a^*} d^2 \lambda$$

$$= \frac{1}{\pi} \int e^{-|\lambda|^2 / 2} e^{(\alpha - \beta_1) \lambda^* + (-\alpha + \beta_0) \lambda} d^2 \lambda = \frac{2}{\pi} e^{(\alpha^* - \beta_1^*)(\alpha - \beta_0)} .$$  \hspace{1cm} (15.84)

For $\beta_0 = \beta_1$ we recover the Glauber state,

$$\chi_N(\lambda) = (|\beta_0\rangle \pm |\beta_1\rangle) e^{\lambda a^+} e^{-\lambda^* a} (|\beta_1\rangle \pm |\beta_0\rangle) ,$$  \hspace{1cm} (15.85)
and
\[
W(\alpha) = \frac{e^{-2|\alpha - \beta|^2} + e^{-2|\alpha - \beta_1|^2} \pm 2\Re \left( e^{2\beta_1^* \beta_0} e^{-2(\alpha^* - \beta_1^*)(\alpha - \beta_0)} \right)}{\pi \left( 1 \pm \Re e^{2\beta_1 \beta_0} \right)}.
\]  \hspace{1cm} (15.86)

On the microscopic level, we have the example of the internal degrees of freedom of an atom, which may be in a superpositon state \(|\langle i|j \rangle| = \delta_{ij}\). On the other hand, the Schrödinger cat states discussed above occur in continuous Schrödinger fields with mesoscopic quantum superpositions \(|\langle \alpha|\beta \rangle| = e^{-|\alpha - \beta|}\).

At this point, we have to emphasize the fundamental difference between Schrödinger cats and superpositions of modes,
\[
|\psi\rangle = |\alpha\rangle + |\beta\rangle \quad \neq |\alpha|\beta\rangle \\
\rho = |\alpha\rangle \langle \alpha| + |\beta\rangle \langle \beta| + |\alpha\rangle \langle \beta| + |\beta\rangle \langle \alpha| \quad \neq |\alpha\beta\rangle \langle \alpha\beta| \\
W(\alpha) = \frac{1}{\pi} (e^{-2|\alpha - \alpha_0|^2} + e^{-2|\beta - \beta_0|^2} + \text{interference terms}) \neq \frac{1}{\pi} e^{-2|\alpha^* - \alpha_0|^2} \quad (15.87)
\]
Schrödinger cats exhibit interferences in phase space, whereas for mode superpositions, interferences only appear when a parameter is varied (e.g., the length of an interferometer arm).

Macroscopic quantum interferences (i.e. interferences that are detectable with macroscopic apparatuses, for example in heterodyne schemes) are named fuzzy Schrödinger cats, if the interfering states are conspicuously separated in phase space.

Schrödinger cat states are very sensitive to dissipation and easily converted into statistical mixtures. For example, \(|\alpha\rangle \pm | - \alpha\rangle\) contains only odd (even) photon numbers in the distribution function \(P_n\). After some time \(\sim \tau_{\text{cav}}/N\), the distribution is converted into a Poisson distribution. The higher the particle number \(N\), the faster the decoherence will be. Consequently, true macroscopic cat states have never been observed.

**15.2.2.5 The \(Q\)-, \(P\)- and \(W\)-function for Jaynes-Cummings cat states**

For the state \(|\psi\rangle = 2^{-1/2}(|\alpha\rangle + i|\beta\rangle)\), we have,
\[
\langle \psi|\hat{a}|\psi\rangle = \frac{1}{2} (\alpha + \beta) \quad \text{such that} \quad c_{1,n} = e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{2n!}} \quad \text{and} \quad c_{2,n} = ie^{-|\beta|^2/2} \frac{\beta^n}{\sqrt{2n!}}.
\]

And for the state \(|\psi\rangle = 2^{-1/2}(|\alpha\rangle + |\beta\rangle),
\[
\langle \psi|\hat{a}|\psi\rangle = \frac{1}{2} \left( \alpha + \beta + e^{-|\alpha|^2/2} - |\beta|^2/2 (\beta e^{-\gamma^*} \beta + \gamma e^{-\gamma^*}) \right).
\]

Be,
\[
|\psi\rangle = \frac{1}{\sqrt{2}} (|1\rangle|\beta\rangle + i|2\rangle|\gamma\rangle). \hspace{1cm} (15.88)
\]

Comparing with the JC coefficients it follows,
\[
\beta = \frac{1}{2} \sum_n \sqrt{n} c_{1,n}^* c_{1,n} \quad \text{and} \quad \frac{1}{2} \sum_n \sqrt{n} c_{2,n}^* c_{2,n}. \hspace{1cm} (15.89)
\]
The functions \(Q\), \(P\), and \(W\) for the usual Schrödinger cats are known. Now, just insert \(\beta\) and \(\gamma\).
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Example 59 (Wigner function for the Jaynes-Cummings dynamics): Other distribution functions are often used to characterize the state of a Heisenberg field. The Wigner function, for example, is defined as [186],

\[ W(\alpha) = \frac{1}{\pi} \int \chi_S(\lambda) e^{\alpha \lambda^* - \alpha^* \lambda} d^2\lambda \quad \text{where} \quad d^2\lambda = d\text{Re} \lambda \, d\text{Im} \lambda . \]

Here, the characteristic functions are given by,

\[ \chi_S(\lambda) = e^{-|\lambda|^2/2} \chi_N(\lambda) \quad \text{where} \quad \chi_N(\lambda) = \langle \psi | e^{\lambda \hat{a}^\dagger} e^{-\lambda^* \hat{a}} | \psi \rangle , \]

where we expanded \(|\psi\rangle = \sum_n c_{1,n} |1\rangle |n\rangle + c_{2,n-1} |2\rangle |n\rangle\). Now we calculate,

\[ \hat{a}^k |n\rangle = \sqrt{\frac{n!}{(n-k)!}} |n-k\rangle \]

and,

\[ e^{-\lambda^* \hat{a}} |n\rangle = \sum_k (\frac{-\lambda^*}{k})^k \frac{\hat{a}^k}{k!} |n\rangle = \sum_k (\frac{-\lambda^*}{k})^k \frac{1}{\sqrt{k!}} \binom{n}{k} |n-k\rangle , \]

and,

\[ \langle n | e^{\lambda \hat{a}^\dagger} e^{-\lambda^* \hat{a}} | n \rangle = \sum_{k=0}^n \frac{(-\lambda^*)^k}{\sqrt{k!} (m-n+k)!} \left( \frac{m}{k} \right) \left( \frac{m-n+k}{m-n} \right) \text{ if } m \geq n \]

\[ = \frac{\sqrt{\frac{n!}{m!}} \lambda^{m-n} \frac{1}{m} \sum_{k=0}^n \binom{m}{k} \frac{m-n}{k} \frac{(-|\lambda|^2)^k}{k!} \text{ Laguerre polynomial} \]

\[ = e^{-|\lambda|^2/2} u_{nm}(\lambda) \text{ if } m \geq n \quad \text{else, take } u_{mn}(\lambda^*) . \]

The normally-ordered characteristic function is now,

\[ \chi_S(\lambda) = \sum_{m,n} c_{1,m}^* c_{1,n} \langle m | e^{\lambda \hat{a}^\dagger} e^{-\lambda^* \hat{a}} | n \rangle + c_{2,m-1}^* c_{2,n-1} \langle m-1 | e^{\lambda \hat{a}^\dagger} e^{-\lambda^* \hat{a}} | n-1 \rangle \]

\[ = \sum_{m,n} (c_{1,m}^* c_{1,n} + c_{2,m}^* c_{2,n}) \sqrt{\frac{n!}{m!}} \lambda^{m-n} L_n^{m-n}(|\lambda|^2) . \]

and the symmetrically ordered characteristic function,

\[ \chi_S(\lambda) = \sum_{m,n} (c_{1,m}^* c_{1,n} + c_{2,m}^* c_{2,n}) u_{nm}(\lambda) . \]

We must distinguish two cases, because \( u_{nm}(\lambda) = u_{mn}(\lambda^*) = (-1)^{m-n} u_{mn}(\lambda^*) \),

\[ \chi_S(\lambda) = \sum_{m \geq n} (c_{1,m}^* c_{1,n} + c_{2,m}^* c_{2,n}) u_{nm}(\lambda) + \sum_{m < n} (c_{1,m}^* c_{1,n} + c_{2,m}^* c_{2,n}) u_{nm}(\lambda^*) \]

\[ = (|c_{10}|^2 + |c_{20}|) e^{-|\lambda|^2/2} + \sum_{m > n} \sqrt{\frac{n!}{m!}} e^{-|\lambda|^2/2} L_n^{m-n}(|\lambda|^2) \]

\[ \left( (c_{1,m}^* c_{1,n} + c_{2,m}^* c_{2,n}) \lambda^{m-n} + (c_{1,m}^* c_{1,n} + c_{2,m}^* c_{2,n}) (-\lambda^*)^{m-n} \right) . \]
The simulation flowchart is,

\[
\begin{align*}
\psi(t + dt) & \rightarrow e^{-i\hat{H}_{\text{eff}} dt} \psi(t)
\end{align*}
\]

The Fourier transform of \(u_{nm}(|\lambda|)\) instead of \(u_{nm}(\lambda)\) is,

\[
\int u_{nm}(|\lambda|) e^{i\lambda^* - i\lambda} d^2\lambda = \int u_{nm}(\frac{1}{2}|x_\lambda + ip_\lambda|) e^{ip_\lambda x_\lambda - ix_\lambda p_\lambda} dx_\lambda dp_\lambda \\
&= \frac{1}{i p_\alpha - x_\alpha} \left[ \int e^{ip_\alpha x_\lambda} u_{nm}(\frac{1}{2} x_\lambda) dx_\lambda - \int e^{-ix_\alpha p_\lambda} u_{nm}(\frac{1}{2} p_\lambda) dp_\lambda \right],
\]

and,

\[
\int e^{ip_\alpha x_\lambda} u_{nm}(\frac{x_\lambda}{2}) dx_\lambda = \sqrt{\frac{n!}{m!}} \int e^{-x_\lambda^2 / 2} x_\lambda^{m-n} L_n^m(x_\lambda) e^{ip_\alpha x_\lambda} dx_\lambda \\
&= \sqrt{\frac{n!}{m!}} \sqrt{\frac{\pi}{2}} \frac{1}{n!} (-1)^{m-n} e^{-p_\alpha^2 / 2} \text{He}_n(p_\alpha) \text{He}_m(p_\alpha).
\]

The Wigner function is now,

\[
W(\alpha) = \frac{1}{\pi^2} (c_{1,m} c_{1n} + c_{2,m} c_{2n}) \left[ \sum \frac{1}{\alpha} \sqrt{\frac{\pi}{2}} \sqrt{\frac{1}{n!m!}} (-1)^{m-n} e^{-p_\alpha^2 / 2} \text{He}_n(p_\alpha) \text{He}_m(p_\alpha) \right].
\]

### 15.2.3 The Jaynes-Cummings model with dissipation

Applying the numerical method of *quantum Monte Carlo wavefunction simulation* to the Jaynes-Cummings model, we write the effective Hamiltonian of the light field as [216],

\[
\hat{H}_{\text{eff}} = \omega \hat{a}^\dagger \hat{a} + \omega_0 \left( \hat{\sigma}^+ \hat{\sigma}^- - \frac{1}{2} \right) + \Omega \left( \hat{a} \hat{\sigma}^+ + \hat{a}^\dagger \hat{\sigma}^- \right) + \frac{i \Gamma}{2} \hat{\sigma}^+ \hat{\sigma}^-.
\]  

(15.90)

Or in matrix notation,

\[
H_{\text{eff}} = \begin{pmatrix}
-\frac{1}{2} \omega & 0 & 0 & \frac{\omega_0}{2} & \frac{\omega}{2} \\
0 & \frac{1}{2} \omega - \frac{i}{2} \Gamma & \frac{\omega_0}{2} & 0 & \frac{\omega}{2} \\
0 & \frac{\omega_0}{2} & \frac{\omega}{2} & \frac{\sqrt{2}}{2} \omega & \frac{\omega}{2} \\
\frac{\omega}{2} & \frac{\omega}{2} & \frac{\sqrt{2}}{2} \omega & 2 \omega - \frac{i}{2} \Gamma & 0 \\
0 & \frac{\omega}{2} & \frac{\omega}{2} & 0 & 2 \omega - \frac{i}{2} \Gamma
\end{pmatrix}
\]

(15.91)

The simulation flowchart is,

\[
\begin{array}{c}
\text{projection} \quad \text{dynamic evolution} \quad \text{renormalization}
\end{array}
\]

\[
\begin{array}{c}
|\psi\rangle \rightarrow |\psi(t + dt)\rangle = e^{-i\hat{H}_{\text{eff}} dt} |\psi\rangle \\
|\psi\rangle \rightarrow |\psi\rangle \\
\end{array}
\]

\[
\begin{array}{c}
\sum c_{1m} |m\rangle + c_{2n} |n\rangle \\
\sum c_{1m} |m\rangle + c_{2n} |n\rangle
\end{array}
\]

\[
\sum c_{1m} |m\rangle + c_{2n} |n\rangle
\]

\[
\begin{array}{c}
\text{yes} \quad \hat{\zeta} > \langle \psi(t+dt) \rangle \langle \psi(t+dt) \rangle \\
\text{no}
\end{array}
\]

\[
\begin{array}{c}
\text{random variable}
\end{array}
\]

\[
\begin{array}{c}
\text{random variable}
\end{array}
\]
Absorption or scattering of light causes the optical field to decay as $\alpha(t) \propto e^{-\kappa t/2}$. The projection (in component notation) is implemented by,

$$c'_{jn} \equiv \frac{1}{\sqrt{\sum_n (|c_{1n}|^2 + |c_{2n}|^2)}} c_{jn},$$

and the dynamical evolution by $c'_{jn} \equiv e^{-\kappa nt/2} c_{jn}$. We note, that the dissipation due to cavity losses can also be taken into account by a master equation. Do the Exc. 17.2.5.1.

### 15.2.4 Exercises

#### 15.2.4.1 Ex: The Jaynes-Cummings model

Consider the Jaynes-Cummings Hamiltonian.

a. Determine from the Schrödinger equation the system of differential equations for the temporal evolution of the coefficients $c_{2,n}(t)$ and $c_{1,n+1}(t)$ in the interaction picture within the rotating wave approximation (RWA).

b. Calculate the time evolution for the start condition $c_{2,n}(0) = 1$ and $c_{1,n+1}(0) = 0$ for the particular case $\omega = \omega_0$.

c. Generalize the result of item (a) for a multimode field, for which initially (i) all modes of field $k$ are empty $|0\rangle$ and (ii) the atom is in the excited state $|a\rangle$. Use the ansatz,

$$|\psi(t)\rangle = c_{2}(t)e^{-iE_2t/\hbar}|2,0\rangle + \sum_k c_{1,k}(t)e^{-i[E_1/\hbar+\omega_k]t}|1,1_k\rangle,$$

and determine the equations of motion for the amplitudes $c_2$ and $c_{1,k}$.

#### 15.2.4.2 Ex: Quantum collapse and revival in the Jaynes-Cummings model

Consider the Jaynes-Cummings Hamiltonian and show that the quantum coherence between the two atomic levels can disappear altogether for long periods and reappear later. Explain how this is possible.

#### 15.2.4.3 Ex: Vacuum Rabi splitting

Calculate the Autler-Townes splitting for an excited atom interacting with an empty cavity.

#### 15.2.4.4 Ex: The $Q$-function in a Jaynes-Cummings state

Calculate the $Q$-function for a Jaynes-Cummings state from its definition (15.56).

#### 15.2.4.5 Ex: Creation of quantum correlations in an optical mode

We will show in this exercise how, via coherent operations in a three-level system, we can create Schrödinger-type quantum-type correlations in an optical mode. In the system shown in Fig. 15.7 we imagine the lower transition excited by $\pi/2$-pulses of a classical resonant microwave radiation (as described by the operation (15.34)). The
upper transition is excited by quantum laser pulses tuned very far out of resonance, thus creating a dispersive dynamics (as described by the operation (15.34)). At time \( t = 0 \) the atom is in state \( |1\rangle \). Now, we apply the following pulse sequence: (i) a microwave pulse with \( \sqrt{\bar{n}} \Omega_{12} t = \pi/2 \), (ii) an optical pulse with \( \Omega_{23}^2 t/4 \Delta_{23} = \pi \), (iii) another microwave \( \pi/2 \)-pulse, and finally (iv) an optical pulse of light which is resonant with the transition \( |2\rangle - |3\rangle \) and projects the population of the atom into one of the states of the microwave transition. Describe the evolution of the state of the system during the sequence and determine the final state of the optical mode.

![Figure 15.7: (a) Level scheme and (b) pulse sequence.](image)

**15.2.4.6 Ex: Master equation derived from JC model Hamiltonian for two-level systems**

Write down the Liouvillian for a JC system in matrix form for a density operator defined like,

\[
(\cdots \rho_{11}^{n-1} \rho_{22}^n \rho_{12}^n \rho_{21}^n \rho_{11}^n \rho_{22}^{n+1} \cdots) .
\]

**15.3 Spontaneous emission and light scattering**

**15.3.1 Interaction of atoms with vacuum modes**

The Jaynes-Cummings Hamiltonian (15.10), discussed in Sec. 15.2, describes the purely coherent dynamics of a single immobile two-level atom interacting with a single cavity mode. The model is simple enough to allow for analytical solutions. However, it does not include processes of spontaneous emission, which can be understood as the interaction of the atom with the light modes of the vacuum. That is, we must extend the Hamiltonian,

\[
\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{field}} + \hat{H}_{\text{atom-field}} + \hat{H}_{\text{vacuum}} + \hat{H}_{\text{atom-vacuum}} .
\] (15.93)

The evolution of the system represented by the Hamiltonian (15.93) is described by a total density operator, \( \hat{\rho}_{\text{total}}(t) \), obeying the von Neumann equation,

\[
\frac{d\hat{\rho}_{\text{total}}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}_{\text{total}}] ,
\] (15.94)
which has the solution,

$$\hat{\rho}_{\text{total}}(t) = e^{-i\hat{H}t/\hbar} \hat{\rho}_{\text{total}}(0) e^{i\hat{H}t/\hbar} \equiv e^{-i\mathcal{L}t} \hat{\rho}_{\text{total}}(0).$$  (15.95)

Often, we are only interested in either the evolution of the light field, or the internal state of the atom. In these cases, we calculate the trace over all those degrees of freedom, which are we are NOT interested in,

$$\hat{\rho}_{\text{atom}} = \text{Tr}_{\text{light}} \hat{\rho}_{\text{total}} \quad \text{and} \quad \hat{\rho}_{\text{light}} = \text{Tr}_{\text{atom}} \hat{\rho}_{\text{total}}.$$  (15.96)

The procedure is the following. We begin choosing the initial state of the electromagnetic vacuum as the photonic vacuum \( \hat{\rho}_{\text{field}} = |\{0\}\rangle \langle \{0\}| \) and defining a projection operator onto this state, \( \hat{P}_{\text{...}} \equiv \hat{\rho}_{\text{field}}(0) \text{Tr}_{\text{field}} \text{...} = \hat{P}_{\text{...}}^2 \). Then we apply to the von Neumann equation the rotating wave, the Markov and the Born approximations. Finally, tracing over the vacuum field variables, we obtain after some calculations the Bloch-Lindbladt equation or master equation [491] for the atom interacting with the driving field. For a discussion of the validity of the Born-Markov approximation [441]. For the relation between the Markov approximation and the Fermi’s Golden Rule [7].

We emphasize that the Hamiltonian (15.93) describes the interaction of light with a single immobile atom at the most fundamental level. However, it excludes many-body effects introduced by quantum statistics or interatomic interactions (to be discussed in Chp. 26.8.4), as well as the center-of-mass motion of the atom and the impact of photonic recoil (to be discussed in Chp. 16.3.4).

In the following section we give a simplified derivation concentrating us on the situation of a single motionless atom, excited by a laser and emitting photons into the electromagnetic vacuum.

### 15.3.1.1 The spontaneous emission

Spontaneous emission can be understood as an energy diffusion process from a system with a restricted number of degrees of freedom into a large thermal bath. For example, although a two-dimensional Hilbert space is sufficient to describe a laser-driven two-level atom, this atom couples to a huge phase-space by spontaneously emitting photons into arbitrary directions. We account for his fact by including in the Hamiltonian not only the interaction of the atom with the incident laser (wavevector \( k_0 \), frequency \( \omega_{k_0} \), coupling force \( g_{k_0} \)), but also with the modes of the electromagnetic vacuum (wavevector \( k \), frequency \( \omega_k \), coupling force \( g_k \)). We will see, that with this Hamiltonian, we can derive, in a calculation is known as Weisskopf-Wigner theory, the Schrödinger equation for the amplitudes of the atomic levels (14.82) including spontaneous emission.

Denoting the frequency of the atomic resonance by \( \omega_a \), the Hamiltonian is,

\[
\hat{H} = \hbar g_{k_0} (\hat{\sigma}^- e^{-i\omega_a t} + \hat{\sigma}^+ e^{i\omega_a t}) \left( \hat{a}^\dagger_{k_0} e^{i\omega_0 t - ik_0 \cdot r} + \hat{a}_{k_0} e^{-i\omega_0 t + ik_0 \cdot r} \right) + \sum_k \hbar g_k (\hat{\sigma}^- e^{-i\omega_a t} + \hat{\sigma}^+ e^{i\omega_a t}) \left( \hat{a}^\dagger_k e^{i\omega_k t - ik \cdot r} + \hat{a}_k e^{-i\omega_k t + ik \cdot r} \right). 
\]

(15.97)

\( \Omega_0 \) is the Rabi frequency of the interaction between the atom and the pump mode (which, here, is treated as classical field), \( \hat{\sigma}^- \) is the atomic deexcitation operator, \( \hat{a}_k \) is
CHAPTER 15. ATOMS IN QUANTIZED RADIATION FIELDS

the annihilation operator of a photon, and \( g_k = \sqrt{\omega/(\hbar \varepsilon_0 V)} \) describes the coupling between the atom and a vacuum mode whose volume is \( V \). The atom has two states, the ground state \( |g\rangle \) and excited state \( |e\rangle \). Since we are considering only one atom fixed in space \(^6\), we can as well locate it at the origin \( r = 0 \). In addition, considering a high power incident laser, \( \hat{a}_{k0}|n_0\rangle_{k0} = \sqrt{n}|n_0 - 1\rangle_{k0} \simeq |n_0\rangle_{k0} \),

\[ (15.98) \]

\( \hat{a}_{k0} \) is approximately an observable proportional to the root of the intensity. As \( [\hat{a}_{k0}, \hat{a}_{k0}^\dagger] \simeq 0 \), we can disregard the quantum nature of the incident field and replace, \( \Omega_0 \equiv 2\sqrt{n_0}g_k \). Within the rotating wave approximation (RWA), the Hamiltonian becomes,

\[ \hat{H} = \frac{\hbar}{2}\Omega_0 \left[ \hat{\sigma}^+ \hat{a}_{k0}^\dagger e^{i\Delta_0 t} + h.c. \right] + \hbar \sum_k \left[ g_k \hat{\sigma}^+ \hat{a}_{k}^\dagger e^{i\Delta_k t} + h.c. \right], \]

\[ (15.99) \]

where we introduced the abbreviations,

\[ \Delta_0 \equiv \omega_0 - \omega_a \quad \text{and} \quad \Delta_k \equiv \omega_k - \omega_a. \]

\[ (15.100) \]

The general state of the system is given by,

\[ |\Psi(t)\rangle = \alpha(t)|0\rangle_a |0\rangle_k + \beta(t)|1\rangle_a |0\rangle_k + \sum_k \gamma_k(t)|0\rangle_a |1\rangle_k. \]

\[ (15.101) \]

The temporal evolution of the amplitudes is obtained by inserting the Hamiltonian (15.99) and the ansatz (15.101) into the Schrödinger equation,

\[ \frac{\partial}{\partial t} |\Psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\Psi(t)\rangle. \]

\[ (15.102) \]

Solve the Exc. 15.3.5.1.

We obtain,

\[ \dot{\alpha}(t) = -\frac{\hbar}{2} e^{i\Delta_0 t} \beta(t) \]

\[ \dot{\beta}(t) = -\frac{\hbar}{2} \alpha(t) e^{-i\Delta_0 t} - \sum_k i g_k \gamma_k(t) e^{-i\Delta_k t} \]

\[ \dot{\gamma}_k(t) = -i g_k e^{i\Delta_k t} \beta(t). \]

\[ (15.103) \]

\(^6\)We do not let the atom be accelerated by photonic recoil.
Now, we chose the initial conditions,

\[ \alpha(0) = 1 \quad \text{and} \quad \beta(0) = 0 \quad \text{and} \quad \gamma_k(0) = 0 \quad , \] (15.104)

we integrate the third equation,

\[ \gamma_k(t) = -ig_k \int_0^t e^{i\Delta_k t'} \beta(t') dt' \quad , \] (15.105)

and we substitute it in the second equation,

\[ \dot{\beta}(t) = -\frac{\Omega_0}{2} \alpha(t) e^{-i\Delta_0 t} - \sum_k g_k^2 \int_0^t e^{i\Delta_k(t' - t)} \beta(t') dt' \quad . \] (15.106)

### 15.3.1.2 The Markov approximation

For small systems (which is the case of a single atom), we can apply the Markov approximation\(^7\) claiming that the temporal variation of the amplitudes \(\beta(t')\) is slower than the evolution of the system given by \(e^{i(\omega_k - \omega_a) t}\) in the integro-differential equation, which is equivalent to an arbitrarily high-order equation. Hence, substituting \(\beta(t') \rightarrow \beta(t)\) into the integro-differential equation, we reduce it to a simple first-order differential equation. Redefining the integration variable, \(t'' \equiv t - t'\), we get,

\[ \frac{d}{dt} \beta(t) \simeq -\frac{\Omega_0}{2} \alpha(t) - \sum_k g_k^2 \beta(t) \pi \delta(\omega_k - \omega_a) \quad , \] (15.107)

We implement the Markov approximation by setting \(\beta(t - t'') \simeq \beta(t)\), and with \(\lim_{t \to \infty} \int_0^t e^{-i(\omega_k - \omega_a) t'} dt' = \pi \delta(\omega_k - \omega_a)\), and replacing \(\sum_k \rightarrow \frac{V}{(2\pi)^3} \int d^3 k\), we arrive at,

\[ \frac{d}{dt} \beta(t) \simeq -\frac{\Omega_0}{2} \alpha(t) - \sum_k g_k^2 \beta(t) \pi \delta(\omega_k - \omega_a) \quad , \] (15.108)

\[ = -\frac{\Omega_0}{2} \alpha(t) - \frac{V}{(2\pi)^3} \beta(t) \int g_k^2 \pi \delta(\omega_k - \omega_a) d^3 k \]

\[ = -\frac{\Omega_0}{2} \alpha(t) - \frac{V}{(2\pi)^3} \beta(t) \frac{4\pi g_k^2 \pi k_a^2}{c} = -\frac{\Omega_0}{2} \alpha(t) - \frac{\Gamma}{2} \beta(t) \quad . \]

In the last step we introduced, as an abbreviation, the spontaneous emission rate,

\[ \Gamma \equiv \frac{V}{\pi c} k_a^2 g_k^2 \quad . \] (15.109)

Finally,

\[ \frac{d}{dt} \alpha(t) = -\frac{\Omega_0}{2} \beta(t) \quad \text{and} \quad \frac{d}{dt} \beta(t) = -\frac{\Omega_0}{2} \alpha(t) - \frac{\Gamma}{2} \beta(t) \quad . \] (15.110)

\(^7\)The approximation does not necessarily hold for large clouds of atoms.
These are exactly the equations for the probability amplitudes (14.82) derived from the Schrödinger equation, only that now, the spontaneous emission term has been derived explicitly. Solve the Exc. 15.3.5.2.

Example 60 (Emission stimulated by vacuum fluctuations): Spontaneous emission can be regarded as an emission stimulated by vacuum fluctuations. To see this write down the resonant optical cross section of a driven two-level atom without degeneracies, \( \sigma_0 = \frac{\lambda}{2\pi} \), and the intensity of an incident laser field, \( I = cN\hbar\omega_0/V \), generating the Rabi frequency,

\[
\Omega^2 = \sigma_0 I \frac{\hbar\omega_a}{\hbar\omega_0} = \frac{2\pi c N}{k_a^2 V} \Gamma .
\]

(15.111)

Now, we assume that the field is, in fact, a vacuum mode containing only half a photon, \( N = 1/2 \), which corresponds to vacuum fluctuations in the mode \( k_a \). Then,

\[
\Omega^2_{1/2} = \frac{\pi c}{k_a^2 V} \Gamma = g^2 .
\]

(15.112)

15.3.2 Resonance fluorescence and (in-)coherent light scattering

The typical situation for a spectroscopy experiment is illustrated in Fig. 15.9: When a beam of light, understood as a plane wave, strikes an atom (or a cloud of many atoms), a part of the light is absorbed and reemitted into a direction indicated by a solid angle \( d\Omega \). Light scattering is, of course, a second order process involving two atomic transitions, one absorption and one emission.

Figure 15.9: (a) Geometry of a scattering experiment. (b) Spectral contributions of light scattered elastically and inelastically by a three-level atom.

Radiation can be absorbed or scattered by an atom in different ways, depending on whether the interaction is an elastic scattering or an inelastic scattering process, a coherent or incoherent, a spontaneous or (bosonically) stimulated process. These properties characterize many processes, in particular, resonance fluorescence (i.e. absorption and reemission), Rayleigh scattering, or Raman scattering. In the following, we will clarify this classification.
Every scattering process is either spontaneous or stimulated. Rayleigh scattering is elastic, that is, the kinetic energy of the scattering atom is the same, before and after the scattering process. In contrast, Raman scattering is inelastic. Spontaneous emission is due to the decay of population from an excited state, and spontaneous Rayleigh scattering is due to the decay of an induced dipole moment. Both spontaneous processes can be regarded as being stimulated by vacuum fluctuations.

15.3.2.1 Resonance fluorescence

When we introduced the second quantization (15.8) we learned that the field of light emitted by a radiator in the radiation zone \((\lambda \ll r)\) is, taking into account retardation \(^9\), given by,

\[
\langle \hat{E}_s^+(r, t) \rangle \propto \langle \hat{a}_s^\dagger \sigma^- \rangle \propto \bar{\rho}_{21} \quad \text{and} \quad \langle \hat{E}_s^-(r, t) \hat{E}_s^+(r, t) \rangle \propto \langle \hat{a}_s^\dagger \sigma^- \hat{a}_s^\dagger \sigma^+ \rangle \propto \rho_{22} .
\] (15.113)

Therefore, the electric field emitted by an atom and the intensity of scattered light are given by,

\[
\langle \hat{E}_s^+(r, t) \rangle = -\frac{e \omega_0^2 \hat{\epsilon} \cdot \vec{r}_{12}}{4\pi \varepsilon_0 c^2 r} \bar{\rho}_{21}(t - \frac{r}{c}) e^{-i \omega(t - r/c)}
\]

\[
\tilde{I}_s = \omega_0 \langle \hat{E}_s^-(r, t) \hat{E}_s^+(r, t) \rangle = \frac{\alpha \hbar \omega_0^4 |\hat{\epsilon} \cdot \vec{r}_{12}|^2}{4\pi c^2 r^2} \rho_{22}(t - \frac{r}{c})
\] (15.114)

with the definition of the Sommerfeld constant \(\alpha = e^2/4\pi \varepsilon_0 \hbar c\). We calculate the total flux of emitted photons,

\[
W_{fit}^{(sp)} = \int \frac{\tilde{I}_s r^2}{\hbar \omega_0} d\Omega = \frac{1}{\hbar \omega_0} \int \frac{\alpha \hbar \omega_0^4 |\vec{r}_{12}|^2 \cos^2 \theta}{4\pi c^2} \rho_{22}(t - \frac{r}{c}) \sin \theta d\theta d\phi
\] (15.115)

\[
= \frac{8\pi}{3h\omega_0} \frac{\alpha \hbar \omega_0^4 |\vec{r}_{12}|^2}{4\pi c^2} \rho_{22}(t - \frac{r}{c}) = \frac{2\alpha}{3c^2 \omega_0^3 |\vec{r}_{12}|^2} \rho_{22}(t - \frac{r}{c}) .
\]

The result coincides with the spontaneous emission rate \(\Gamma\) calculated in (13.37).

A differential scattering cross section can be defined by,

\[
\frac{d\sigma}{d\Omega} = \frac{\omega \tilde{I}_s r^2}{\omega_0 \tilde{I}_0} .
\] (15.116)

15.3.2.2 Coherently scattered light and saturation

The total intensity of the scattered light being \(\tilde{I}_s\), the fraction of the coherently scattered light is,

\[
\frac{\tilde{I}_s^{coh}}{\tilde{I}_s} = \frac{\langle \hat{E}_s^-(r, t) \hat{\hat{E}}_s^+(r, t) \rangle}{\langle \hat{E}_s^-(r, t) \hat{E}_s^+(r, t) \rangle} .
\] (15.117)

\(^8\)Classical theories of light scattering through the excitation of an electronic motion based on the models of Lorentz or Drude can be found in the script Electrodynamics. Although being classical, these model are useful for a deeper understanding of many aspects of Compton scattering, Thomson scattering, and Rayleigh scattering.

\(^9\)The classical version of this formula is can be found in the script Electrodynamics, Sec. 9.1.3, Eq. (8.41).
Inserting the expressions (15.114) and the stationary solution of the Bloch equations (14.86),
\[ \frac{I_s^\text{coh}}{I_s} = \left| \frac{\rho_{21}(\infty)}{\rho_{22}(\infty)} \right|^2 = \frac{1}{1 + s} = 1 - \frac{I_s^\text{incoh}}{I_s}. \]
That is, since the resonance fluorescence is proportional to the excited state population, \( S_{\text{tot}} \equiv \rho_{22}(\infty) \), the coherent and incoherent parts of the fluorescence are,
\[ S_{\text{coh}} = \left| \frac{\rho_{21}(\infty)}{\rho_{22}(\infty)} \right|^2 = \frac{s/2}{(1 + s)^2} \quad \text{and} \quad S_{\text{incoh}} = \rho_{22}(\infty) - \left| \frac{\rho_{21}(\infty)}{\rho_{22}(\infty)} \right|^2 = \frac{s^2/2}{(1 + s)^2}. \]
Hence, \( S_{\text{incoh}} = sS_{\text{coh}} \).

![Figure 15.10: (code) Elastic (red) versus inelastic scattering (blue).](image)

We note, that the integral of the fluorescence spectrum is,
\[ \int_{-\infty}^{\infty} \frac{\Omega^2}{4\Delta^2 + 2\Omega^2 + \Gamma^2} d\Delta = \frac{\pi}{2} \frac{\Omega^2}{\sqrt{2\Omega^2 + \Gamma^2}} \rightarrow \frac{\pi \Omega^2}{2\Gamma}. \]  

15.3.3 Correlation functions

The coherence properties of a light field \(^{10}\) are measured by \( n^{\text{th}} \) order correlation function,
\[ g^{(n)}(r_1, t_1, \ldots, r_{2n}, t_{2n}) \equiv \frac{\langle \hat{E}^-(r_1, t_1) \ldots \hat{E}^-(r_n, t_n) \hat{E}^+(r_{n+1}, t_{n+1}) \ldots \hat{E}^+(r_{2n}, t_{2n}) \rangle}{\langle \hat{E}^-(r_1, t_1) \hat{E}^+(r_1, t_1) \rangle \ldots \langle \hat{E}^-(r_{2n}, t_{2n}) \hat{E}^+(r_{2n}, t_{2n}) \rangle}. \]
Particularly important are the 1\(^{st}\) and 2\(^{nd}\) order correlation functions \( g^{(1)} \) and \( g^{(2)} \). Considering only temporal coherences, i.e. \( k_1 \parallel k_2 \) and \( (t_2 - \frac{2i\epsilon}{c}) - (t_1 - \frac{2i\epsilon}{c}) = \tau \), since \( \hat{E}(r, t) = \hat{E}(\omega t - k \cdot r) \), we can define (without loss of generality),
\[ g^{(1)}(\tau) \equiv \frac{\langle \hat{E}^-(t) \hat{E}^+(t + \tau) \rangle}{\langle \hat{E}^-(t) \hat{E}^+(t) \rangle} \quad \text{and} \quad g^{(2)}(\tau) \equiv \frac{\langle \hat{E}^-(t) \hat{E}^-(t + \tau) \hat{E}^+(t + \tau) \hat{E}^+(t) \rangle}{\langle \hat{E}^-(t) \hat{E}^+(t) \rangle^2}, \]

\(^{10}\)Or a matter wave.
where,

\[ \langle \cdots \rangle_t = \lim_{t \to \infty} \frac{1}{t} \int_0^t \cdots dt \]  \hspace{1cm} (15.123)

denotes the time average. Defining the intensity as \( \hat{I} = 2\varepsilon_0c\hat{E}^+\hat{E}^- \), the coherences become,

\[ g^{(1)}(\tau) \equiv \frac{2\varepsilon_0c}{\langle TN \hat{E}^-(t)\hat{E}^+(t+\tau) \rangle} \quad \text{and} \quad g^{(2)}(\tau) \equiv \left( \frac{2\varepsilon_0c}{\langle TN \hat{I}(t)\hat{I}(t+\tau) \rangle} \right) . \]  \hspace{1cm} (15.124)

The correlation functions must be calculated from the field operators simultaneously respecting \textit{time order} and \textit{normal order}. These functions are useful quantities to describe phenomena such as photon \textit{bunching} or to understand the fluorescence spectra or the scattering of light from correlated atoms. \( g^{(1)} \) measures the \textit{coherence} of a light field (how much it resembles a sine wave). \( g^{(2)} \) measures, for a given degree of coherence, the deviation of the light field from the quantum state that most closely approximates a classical light (how much it resembles a laser).

The correlation functions \( g^{(1)} \) and \( g^{(2)} \) are experimentally measured in \textit{Young’s experiment} and in the \textit{Hanbury-Brown-Twiss experiment}. The experimental schemes are explained in Figs. 15.11.

![Figure 15.11](image)

Figure 15.11: (a) Scheme of Young’s experiment. (b) Scheme of the experiment of Hanbury, Brown, and Twiss. Young’s experiment reveals the coherence of a field, that is, its ability to interfere. In contrast, the Hanbury-Brown-Twiss experiment reveals correlations between the (quasi-)particles constituting the field, that is, effects due to quantum statistics or interactions.

Coherence and chaos are contrary properties of light. They leave their imprint in the spectrum of the light or in the autocorrelation functions. The emission spectrum of a light source generally emerges as a combination of various physical effects: The active medium gives rise resonances and broadenings, a resonator containing the active medium imprints a modal structure, and the coupling to a thermal bath gives rise to a thermal distribution of the radiation energy according to

\[ P_n = e^{-\hbar\omega(n+1/2)/k_BT} / \sum_n e^{-\hbar\omega(n+1/2)/k_BT} . \]

15.3.3.1 Correlation functions for laser light

First-order coherent light satisfies \( |g^{(1)}(\tau)| = 1 \), incoherent light \( |g^{(1)}(\tau)| = 0 \), and for partially coherent light, we get intermediate values. Second-order coherent light satisfies \( g^{(2)}(-\tau) = g^{(2)}(\tau) \) and \( 1 \leq g^{(2)}(0) \leq \infty \) and \( 0 \leq g^{(2)}(\tau) \leq \infty \) and \( g^{(2)}(0) \geq g^{(2)}(\tau) \to \infty \). Let us now look at some specific cases, for which the correlation functions can be calculated.
With the definitions (15.122) it is easy to calculate the autocorrelation functions and the spectrum of a laser light field,

\[ E = e^{i \omega t} \]
\[ \Rightarrow g^{(1)}(\tau) = \int \frac{e^{-i \omega \tau} dt}{\int dt} = e^{-i \omega \tau} \]
\[ \Rightarrow \mathcal{F}[g^{(1)}(\tau)] = \delta(\Delta) \]
\[ g^{(2)}(\tau) = 1 \]

(15.125)

We see that the absolute values of the first and second-order coherences are constant, and that the spectrum is narrow like a \( \delta \)-function. For a laser subject to white phase noise (\( \zeta \) be a normally distributed random number) we have,

\[ E = e^{i [\omega t + \zeta(t)]} \]
\[ \Rightarrow g^{(1)}(\tau) = \int \frac{e^{-i [\omega \tau + \zeta(t+\tau) - \zeta(t)]} dt}{\int dt} = e^{(i \omega - \gamma) \tau} \]
\[ \Rightarrow \mathcal{F}[g^{(1)}(\tau)] = \frac{\gamma/\pi}{\Delta^2 + \gamma^2} \]
\[ g^{(2)}(\tau) = 1 \]

(15.127)

We see, that the first-order coherence decays exponentially, \( |g^{(1)}(\tau)| = e^{-\gamma \tau} \), such that the spectrum has a Lorentzian profile. This result has already been derived in Sec. 13.3.1 for the natural linewidth of a transition subject to spontaneous emission. We understand the connection by interpreting spontaneous emission as being induced by vacuum fluctuations, which do have a white noise spectrum, indeed.

### 15.3.3.2 Correlation functions with pressure broadening

In Sec. 14.4.2 we have already seen, that collision or pressure broadening can be treated by assuming that the light is emitted as a superposition of coherent waves all having the same frequency, \( E_n(t) = e^{i \omega t + i \phi_n(t)} \), but being randomly interrupted by phase jumps,

\[ \langle E^*(t)E(t+\tau) \rangle = \int \sum_n e^{-i \omega t - i \phi_n(t)} \sum_m e^{i \omega t + i \omega \tau + i \phi_m(t+\tau)} dt \]
\[ = e^{i \omega \tau} \sum_{n,m} \int e^{i \phi_m(t+\tau) - i \phi_n(t)} dt = N \langle E^*_n(t)E_m(t+\tau) \rangle \delta_{nm} . \]

(15.129)

The crossed terms \( n \neq m \) of this expressions vanish. The pressure broadening is homogeneous, but the fact that the wavepackets are scattered by different atoms results in a modified second-order coherence,

\[ \langle E^*_n(t)E_n(t+\tau) \rangle = e^{i \omega \tau} \sum_n \int e^{i \phi_n(t+\tau) - i \phi_n(t)} dt = e^{i \omega \tau} \int \tau p(\tau) d\tau . \]

(15.130)
The probability density of finding a coherent interval of duration $\tau$ is $p(\tau)d\tau = \gamma_c e^{-\gamma_c \tau} d\tau$, which finally gives,

$$p(\tau) d\tau = \gamma_c e^{-\gamma_c \tau} d\tau,$$

The spectrum is a Lorentzian with the full linewidth $\gamma' = \gamma + \gamma_c$.

Figure 15.12: (code) First and second-order correlation functions for (red) a laser, (cyan) a laser subject to phase noise, (blue) a laser subject to collision broadening, (magenta) chaotic light, and (green) spectrally filtered thermal light.

### 15.3.3.3 Correlation functions with thermal broadening

For light emitted by an ensemble of non-colliding atoms in thermal motion, we must allow for different frequencies, $E_n(t) = e^{i\omega_n t + i\phi_n}$, but time-independent phases,

$$\langle E^*(t)E(t + \tau) \rangle = \int \sum_n e^{-i\omega_n t - i\phi_n} \sum_m e^{i\omega_m t + i\omega_m \tau + i\phi_m} dt,$$

$$\sum_{n,m} \int e^{-i\omega_n t - i\phi_n + i\omega_m t + i\omega_m \tau + i\phi_m} dt = \sum_n e^{i\omega_n \tau}.$$

The crossed terms $n \neq m$ of this expressions vanish. **Doppler broadening** is inhomogeneous. Hence, the probability density for frequencies emitted by thermal atoms is
a Gaussian, \( p(\omega)d\omega = (2\pi\delta)^{-1/2}e^{-(\omega_n-\omega_0)^2/2\delta^2}d\omega \), such that,

**thermal ensemble**

\[
\langle E^*(t)E(t+\tau) \rangle = N(2\pi\delta)^{-1/2} \int e^{i\omega_n\tau}e^{-(\omega_n-\omega_0)^2/2\delta^2}d\omega_n,
\]

\[\Rightarrow g^{(1)}(\tau) = e^{i\omega \tau - \delta^2 \tau^2/2}, \]

\[\Rightarrow \mathcal{F}[g^{(1)}(\tau)] = \sqrt{\ln 2}\pi\delta e^{-\ln 2 \omega^2/\delta^2}, \]

\[g^{(2)}(\tau) = 1 + e^{-\delta^2 \tau^2/2}. \tag{15.135}\]

For a totally emission \textit{chaotic light},

**chaotic line**

\[
g^{(1)}(\tau) = \delta(0) \]

\[
\mathcal{F}[g^{(1)}(\tau)] = 1, \tag{15.137}
\]

\[g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|. \]

Mono-mode chaotic light can be seen as incoherent multi-mode light, where all modes except a single mode are filtered by a Fabry-Pérot etalon. This light is characterized by \(|g^{(1)}(\tau)| = 1\) and \(g^{(2)}(\tau) = 2\), despite the coherence length being \(\tau \to \infty\). Do the Excs. 15.3.5.3 to 15.3.5.5.

### 15.3.4 The spectrum of resonance fluorescence

The \textit{correlation functions} defined in (15.122) represent an interesting concept for describing resonance fluorescence and for phenomena such as \textit{antibunching} observed in resonance fluorescence.

#### 15.3.4.1 The Wiener-Khintchine theorem

When the time dependence of a wave is given by \(E(t)\), we call

\[
R_e(\tau) = \langle \hat{E}^*(t)\hat{E}(t+\tau) \rangle_t, \tag{15.138}
\]

the autocorrelation function and the power density

\[
S_e(\omega) = (\mathcal{F}R_e)(\omega) = |(\mathcal{F}E)(\omega)|^2, \tag{15.139}
\]

the \textit{spectrum}. This relation is called the \textit{Wiener-Khintchine theorem}. We may also consider the normalized quantities, dividing (15.138) and (15.139) by \(R_e(0) = \langle \hat{E}^*(t)\hat{E}(t) \rangle_t = \int_{-\infty}^{\infty} |(\mathcal{F}E)(\omega)|^2 d\omega = \int_{-\infty}^{\infty} S_e(\omega)d\omega\). We obtain,

\[
g^{(1)}(\tau) = \frac{R_e(\tau)}{R_e(0)} \quad \text{and} \quad F(\omega) = (\mathcal{F}g^{(1)})(\omega) = \frac{S_e(\omega)}{R_e(0)}. \tag{15.140}
\]
The last quantity is the line profile. As we see, to compute the spectra of resonance fluorescence, we only need to compute the correlation function \( g^{(1)} \), i.e. the amplitudes of the field \( \hat{E}(t) \), which in turn are related to the field operators (15.8). The field operators follow the solutions of the Bloch equation, which, being linear, have the following generic form,

\[
\rho_{ij}(t + \tau) = \sum_{k,l} \alpha_{ijkl}(\tau) \rho_{ij}(t) + \beta_{ij}(\tau) .
\]

The trace condition is satisfied, when \((i, j), (k, l) \neq (1, 1)\).

### 15.3.4.2 The quantum regression theorem

To be able to explore this relationship (15.141), needed to calculate the correlation functions, we have to invoke the so-called quantum regression theorem,

\[
\langle \hat{A}(t + \tau) \rangle = \sum_i \xi_i(\tau) \langle \hat{A}_i(t) \rangle \quad \Rightarrow \quad \langle \hat{B}(t) \hat{A}(t + \tau) \hat{C}(t) \rangle = \sum_i \xi_i(\tau) \langle \hat{B}(t) \hat{A}_i(t) \hat{C}(t) \rangle .
\]

(15.142)

Example 61 (Quantum regression applied to the Langevin equation): We have,

\[
\dot{A}_\mu = D_\mu(t) + F_\mu(t) \quad (15.143)
\]

\[
\langle F_\mu(t) F_\nu(t) \rangle = 2\langle D_{\mu\nu} \rangle \delta(t - t') .
\]

We know,

\[
\langle A_\mu(t) F_\nu(t) \rangle = \langle D_{\mu\nu} \rangle \quad \text{and} \quad \langle F_\mu(t) A_\nu(t) \rangle = \langle D_{\mu\nu} \rangle
\]

(15.144)

and the quantum regression theorem gives,

\[
\frac{d}{dt} \langle A_\mu(t) A_\nu(t') \rangle = \langle D_\mu(t) A_\nu(t') \rangle ,
\]

(15.145)

because if \( t' < t \), the term \( \langle F_\mu(t) A_\nu(t') \rangle \) vanishes for a Markovian process.

### 15.3.4.3 Bloch equation for a two-level system

The Fourier transform of the first-order coherence, \( g^{(1)}(\tau) = e^{-i\omega \tau} G(\tau) \), gives,

\[
F(\nu) = (\mathcal{F}g^{(1)})(\nu) = \mathcal{F}[e^{-i\omega \tau}] \ast \mathcal{F}[G(\tau)] = \delta(\nu - \omega) \ast \mathcal{F}[G(\tau)] = (\mathcal{F}G)(\nu - \omega) .
\]

(15.146)

Therefore, we can look at the unshifted spectrum, \( (\mathcal{F}G)(\nu) \). Since the fluorescence spectrum is determined by the first-order coherence, which depends on the field operators, which in turn depend on the atomic populations and coherences, we have to solve the Bloch equation.

For a two-level atom the Bloch equations, having been reduced by the normalization condition (14.148) are,

\[
\dot{\tilde{\rho}}_{\text{red}} = \mathcal{M}\tilde{\rho}_{\text{red}} + \mathbf{b} = \begin{pmatrix}
-\Gamma & -\frac{i}{2}\Omega & -\frac{i}{2}\Omega & -\frac{i}{2}\Omega \\
-i\Omega & -\Gamma - i\Delta & 0 & 0 \\
i\Omega & -\Gamma + i\Delta & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\rho_{22} \\
\rho_{12} \\
\rho_{21} \\
\end{pmatrix}
+ \begin{pmatrix}
0 \\
\frac{i}{2}\Omega \\
-\frac{i}{2}\Omega \\
\end{pmatrix}
\]

(15.147)
with the solution (14.150), that is, $\bar{\rho}(t + \tau) = e^{\mathcal{M}\tau} \bar{\rho}(t) + (1 - e^{\mathcal{M}\tau})\bar{\rho}(\infty)$ with $\bar{\rho}(\infty) = -\mathcal{M}^{-1}b$. This solution can be cast in the following form,

$$\rho_{kl}(t + \tau) = \sum_{(mn)} \alpha_{(kl)(mn)}(\tau)\rho_{mn}(t) + \beta_{(kl)}(\tau),$$

(15.148)

where $(mn), (kl) = (22), (12), (21)$ identifying,

$$\alpha_{(kl)(mn)}(\tau) = \begin{pmatrix} \alpha_{22,22} & \alpha_{12,22} & \alpha_{21,22} \\ \alpha_{22,12} & \alpha_{12,12} & \alpha_{21,12} \\ \alpha_{22,21} & \alpha_{12,21} & \alpha_{21,21} \end{pmatrix} \equiv \begin{pmatrix} (e^{\mathcal{L}\tau})_{11} & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} = e^{\mathcal{M}\tau}$$

(15.149)

$$\beta_{(kl)}(\tau) = \begin{pmatrix} \beta_{22} \\ \beta_{12} \\ \beta_{21} \end{pmatrix} \equiv \begin{pmatrix} -[(1 - e^{\mathcal{M}\tau})\mathcal{M}^{-1}b]_1 \\ \cdots \\ \cdots \end{pmatrix} = -(1 - e^{\mathcal{M}\tau})\mathcal{M}^{-1}b.$$

Using quantum operators in the interaction image, $|k\rangle\langle l| = \hat{\sigma}_{kl}$, we have,

$$\langle \hat{\sigma}_{12}(t)\rangle = \langle \hat{\sigma}_{21}^\dagger(t)\rangle = \rho_{12}(t)e^{i\omega_0 t} \quad \text{and} \quad \langle \hat{\sigma}_{22}(t)\rangle = \langle \hat{\sigma}_{12}(t)\hat{\sigma}_{21}(t)\rangle = \rho_{22}(t).$$

yielding,

$$\langle \hat{\sigma}_{kl}(t + \tau)\rangle = \sum_{(mn)} e^{(l-k)i\omega_0(t+\tau)}e^{(m-n)i\omega_0 t}\alpha_{(kl)(mn)}(\tau)\langle \hat{\sigma}_{mn}(t)\rangle + e^{(l-k)i\omega_0(t+\tau)}\beta_{(mn)}(\tau)\langle 1 \rangle.$$

(15.151)

15.3.4.4 Correlation functions

We now look at the radiation field, which is related to the dipole moment operator via,

$$\hat{E}^- = \gamma \hat{\sigma}_{21},$$

(15.152)

where $\gamma$ is simply a constant. Substituting this relation in the correlation functions (15.122) we obtain,

$$g^{(1)}(\tau) = \frac{\langle \hat{\sigma}_{21}(t)\hat{\sigma}_{12}(t + \tau)\rangle}{\langle \hat{\sigma}_{21}(t)\rangle} = \langle \hat{\sigma}_{21}(t)\hat{\sigma}_{12}(t + \tau)\rangle_{\langle \hat{\sigma}_{22}(t)\rangle}$$

(15.153)

$$g^{(2)}(\tau) = \frac{\langle \hat{\sigma}_{21}(t)\hat{\sigma}_{21}(t + \tau)\hat{\sigma}_{12}(t + \tau)\hat{\sigma}_{12}(t)\rangle}{\langle \hat{\sigma}_{21}(t)\hat{\sigma}_{12}(t)\rangle^2} = \langle \hat{\sigma}_{22}(t)\rangle^2 \langle \hat{\sigma}_{22}(t + \tau)\rangle.$$

Now we can calculate, letting $\xi_i(\tau) \equiv \alpha_{(12)(mn)}$, $\hat{C}(t) \equiv 1$, $e \hat{B}(t) \equiv \hat{\sigma}_{21}(t),$

$$g^{(1)}(\tau) = \frac{\sum_{(mn)} e^{i\omega_0(t+\tau)}e^{(m-n)i\omega_0 t}\alpha_{(12)(mn)}(\tau)\langle \hat{\sigma}_{21}(t)\hat{\sigma}_{mn}(t)\rangle + e^{i\omega_0(t+\tau)}\beta_{(12)}(\tau)\langle \hat{\sigma}_{21}(t)\rangle}{\langle \hat{\sigma}_{22}(t)\rangle}$$

(15.154)

$$g^{(2)}(\tau) = \frac{\sum_{(mn)} e^{(m-n)i\omega_0 t}\alpha_{(22)(mn)}(\tau)\langle \hat{\sigma}_{22}(t)\hat{\sigma}_{mn}(t)\rangle + \beta_{(22)}(\tau)\langle \hat{\sigma}_{22}(t)\rangle}{\langle \hat{\sigma}_{22}(t)\rangle^2}.$$
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Using $\hat{\sigma}_{21}\hat{\sigma}_{mn} = \hat{\sigma}_{2n}\delta_{m1}$,

$$
g^{(1)}(\tau) = e^{i\omega_0\tau}\frac{\alpha_{(1)(2)}(\tau)\langle \hat{\sigma}_{21}(t)\hat{\sigma}_{12}(t) \rangle + \beta_{(12)}(\tau)\langle e^{i\omega_0 t}\hat{\sigma}_{21}(t) \rangle}{\langle \hat{\sigma}_{22}(t) \rangle} \quad (15.155)$$

$$
g^{(2)}(\tau) = \frac{\alpha_{(22)(21)}(\tau)\langle e^{i\omega_0 t}\hat{\sigma}_{22}(t)\hat{\sigma}_{21}(t) \rangle + \alpha_{(22)(22)}(\tau)\langle \hat{\sigma}_{22}(t)\hat{\sigma}_{22}(t) \rangle + \beta_{(22)}(\tau)\langle \hat{\sigma}_{22}(t) \rangle}{\langle \hat{\sigma}_{22}(t) \rangle^2} \quad . (15.156)$$

Returning to the density operator and letting $t \to \infty$,

$$
g^{(1)}(\tau) = e^{i\omega_0\tau}\left[\alpha_{(1)(2)}(\tau) + \beta_{(12)}(\tau)\frac{\rho_{21}(\infty)}{\rho_{22}(\infty)}\right] \quad \text{and} \quad g^{(2)}(\tau) = e^{i\omega_0\tau}\frac{\beta_{(22)}(\tau)}{\rho_{22}(\infty)} \quad . (15.157)$$

These correlation functions can easily be calculated via a numerical resolution of the Bloch equations (15.147), as will be exercised in Exc. 15.3.5.6. Fig. 15.13 shows the correlation functions and the fluorescence spectrum derived by Fourier transform of the first-order correlation function (15.140).

The spectrum 15.13(d) exhibits three lines known as the Mollow triplet. Note that the spontaneous emission triplet is only observed in the presence of a driving laser, because it is the laser excitation which causes the splitting. Indeed, the splitting and the position of the lines are easily understood in the dressed states picture visualized in Fig. 15.1: The coupling of the two-level atom to a light field splits up the levels $|n\rangle$ and $|n+1\rangle$ by an amount corresponding to the Rabi frequency $\Omega$. Now, the transition from the two excited state $|n+1\rangle$ levels to the ground state $|n\rangle$ levels can occur on three different frequencies. In Exc. 15.3.5.7 we calculate the Mollow spectrum for a transition between one ground and three excited Zeeman states. Fig. 15.14 illustrates the various methods to detect the Mollow triplet.

15.3.4.5 Mollow spectrum from effective Hamiltonian

The Mollow triplet is easily understood in the dressed states picture. On the other hand, we know that (for classical light) the semi-classical picture is totally equivalent (its just a unitary transform of the dressed states picture). Developing a physical picture the Mollow triplet in the semi-classical framework may give us a deeper insight. Generally, the Mollow spectrum is anyhow calculated using the semi-classical Bloch equations, via the correlation function $g^{(1)}(\tau)$ and the Wiener-Khintchine theorem, but the on the way the physical intuition is lost.

For example, looking at the stationary solution of the Bloch equations (14.86), we see that $\bar{\rho}(\infty)$ is time-independent, so that we might be surprised to see correlations in time domain (and consequently a structured spectrum) at all. This surprise results from a common misconception that may arise considering the damping of $\bar{\rho}(t)$ predicted by the Bloch model, as illustrated e.g. in Fig. 14.2: It seems that the atoms
eventually cease oscillating between the ground and excited states. In most experiments, measurement are made on a large number of atoms and indeed the oscillations are damped.

In fact, however, every individual atom undergoes a complicated unpredictable trajectory alternating times of coherent evolution with spontaneous emission events (called quantum jumps). The damped behavior only results as an average over many such quantum trajectories. In this light, the reason for $g^{(1)}$-type correlations is a subtle interplay between coherently and incoherently scattered light: The spontaneous emission probability is amplitude-modulated with the Rabi frequency.

An alternative way to calculate the Mollow spectrum consists in solving the Schrödinger equation with the effective Hamiltonian, as done in Exc. 15.3.5.2 and 15.3.5.8. The results are shown in Fig. 15.15. While providing an intuitive picture of the origin of of the Mollow triplet a quantitatively correct treatment requires a Monte-Carlo wavefunction simulation [429] (see Sec. 17.1.2).

### 15.3.4.6 Weak excitation and the role of collisions

For the case of a weakly excited two-level atom, $|\Omega| \ll \Gamma$, we have analytic solutions (14.92) of the Bloch equation. We can then take the coefficients $\alpha_{ijkl}$ and $\beta_{ij}$ and
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Figure 15.14: Schemes for detecting the Mollow triplet: (a) Homodyning, (b) temporal correlation, (c) spectrum, (d) demodulation.

insert them into the correlation functions,
\[ g^{(1)}(\tau) = e^{-\omega \tau}, \]
\[ g^{(2)}(\tau) = 1 + e^{-2\gamma \tau} - 2 \cos \Delta \tau, \]
\[ F(\omega_s) = (\mathcal{F}g^{(1)})(\omega_s) = \delta(\omega_s - \omega). \]

These functions show that the spectrum is essentially composed of Rayleigh scattering at the frequency of the incident light. The \( \delta \)-shaped fluorescence spectrum shows, that the contribution of elastically scattered light dominates below saturation, which confirms the results (15.119) illustrated in Fig. 15.10. The light is 'antibunched' and, at higher \( \tau \) exhibits a damped oscillation around the value 1.

If pressure broadening is taken into account, the two-level Bloch equations are given by (14.86), where \( \gamma' = \gamma + \gamma_{coll} \) is the width of the collision-broadened line. Within this model and in the limit \( \Omega \ll \Gamma \), the resonance fluorescence spectrum is given by [382],
\[ F(\omega_s) = \frac{\gamma' - \Gamma}{\gamma'} \frac{\gamma'/\pi}{(\omega_0 - \omega_s)^2 + \gamma^2} + \frac{\Gamma}{\gamma'} \delta(\omega_s - \omega). \]

So, we find that, even at low intensities, a continuous spectrum due to inelastic scattering appears around the resonance frequency \( \omega_0 \) additionally to the elastic Rayleigh peak.

15.3.5 Exercises

15.3.5.1 Ex: Derivation of the rate equations for two-level atoms

Inserting the ansatz (15.101) into the Schrödinger equation, derive the equations of motion (15.103) for the wavefunction amplitudes.
Figure 15.15: (a) Time evolution of the norm of a decaying driven two-level atom. (b) Time evolution of the ground and excited state amplitudes. (c) First-order auto-correlation function, and (d) spectrum.

### 15.3.5.2 Ex: Non-hermitian time evolution

Study the time evolution $|\psi(t)\rangle = e^{-i\hat{H}_{eff}t/\hbar}|\psi(0)\rangle$ with the effective Hamiltonian,

$$\hat{H}_{eff} = \begin{pmatrix} 0 & \frac{\hbar}{2}\Omega \\ \frac{\hbar}{2}\Omega & -\frac{\hbar}{2}\Gamma \end{pmatrix}$$

starting from the initial condition $\langle 2|\psi(0)\rangle = 1$. Calculate the evolution of $|\psi(t)\rangle$ and the norm $\langle \psi(t)|\psi(t)\rangle$. Plot the time evolution of the norm for various ratios $\Omega/\Gamma$ and interpret the curves.

### 15.3.5.3 Ex: Phase modulation

a. Show that it is not possible to construct a periodic phase modulation function such that the signal has only two sidebands.

b. From $1 = |e^{iM \sin \Omega t}|^2$ derive a sum rule for the Bessel functions.

c. Discuss the difference of the spectra $\sum_{k=-\infty}^{\infty} J_k(M)e^{ik\Omega t}$ and $\sum_{k=-\infty}^{\infty} |J_k(M)|e^{ik\Omega t}$.

### 15.3.5.4 Ex: First-order correlation function of phase- and amplitude-modulated light

a. Calculate $g^{(1)}(\tau)$ for amplitude-modulated light: $E_{am}(t) = e^{i\omega t}(1 + M \cos \Omega t)$.

b. Calculate $g^{(1)}(\tau)$ for phase-modulated light: $E_{pm}(t) = e^{i\omega t+iM \cos \Omega t}$. 
c. Repeat the calculation (a) for exponentially decaying amplitude-modulated light: 
\[ E_{am}(t) = e^{-\gamma t} e^{\omega t} (1 + M \cos \Omega t) \].

15.3.5.5 Ex: Correlation functions for two light modes

Calculate \(|g^{(1)}(\tau)|\) for two interfering and non-interfering modes neglecting fluctuations.

15.3.5.6 Ex: Resonance fluorescence via Bloch equations

a. Derive the analytic solution of the Bloch equations for a resonantly driven two-level atom.
b. Calculate the first-order correlation function \(g^{(1)}(\tau)\) from the formula (15.157).
c. Derive the spectrum of resonance fluorescence.

15.3.5.7 Ex: Fluorescence spectrum of a four-level system

A more realistic transition, allowing for a vectorial nature of the radiation field, involves one ground and three excited Zeeman states (e.g. the strontium \(^{1}\text{S}_0 \rightarrow ^{1}\text{P}_1\) transition). In this case, the emitted light is,
\[ \hat{E}^-(t) = \hat{E}^-_{\sigma}(t) + \hat{E}^-_{\sigma}(t) + \hat{E}^-_{\sigma}(t) . \]
Calculate the first-order correlation function and the fluorescence spectrum of this transition.

15.3.5.8 Ex: Semi-classical picture of the Mollow triplet

Calculate the first-order correlation function from the solution of the Schrödinger equation with the effective Hamiltonian derived in Exc. 15.3.5.2.

15.3.5.9 Ex: Monte-Carlo simulation of the Mollow triplet

Implement a Monte-Carlo simulation of the Mollow triplet for a driven two-level atom according to [135, 429].

15.4 Light scattering from multi-level atoms

15.4.1 Quantum beats

The phenomenon of quantum beats is another simple example of effects beyond semi-classical theory, requiring a full second-quantized calculation. In semi-classical theory (SCT), there is an interference or beat note term for both V-type and \(\Lambda\)-type atoms, while in quantum electrodynamics (QED) only V-type atoms exhibits a beat term.

In the semi-classical picture, the state vector of electrons is [546],
\[ \psi(t) = c_1 e^{-i\omega_1 t}|1\rangle + c_2 e^{-i\omega_2 t}|2\rangle + c_3 e^{-i\omega_3 t}|3\rangle . \] (15.160)
Writing the non-vanishing dipole matrix elements as

\[ d_{12} = e \langle 1 | r | 2 \rangle, \quad d_{23} = e \langle 2 | r | 3 \rangle \]

a three-level atom has two microscopic oscillating dipoles,

\[ P(t) = d_{12} (c_1^* c_2) e^{i \omega_{12} t} + d_{23} (c_2^* c_3) e^{i \omega_{23} t} + c.c. . \] (15.161)

In the semi-classical picture, the radiated field will be a sum of these two terms,

\[ E^+ = E_1 e^{-i \omega_{12} t} + E_2 e^{-i \omega_{23} t} . \] (15.162)

This leads to an interference or beat note term in a square-law detector,

\[ |E^+|^2 = |E_{12}|^2 + |E_{23}|^2 + E_{12}^* E_{23} e^{i (\omega_{12} - \omega_{23}) t} + c.c. , \] (15.163)

regardless of whether state \(|2\rangle\) decays simultaneously to \(|1\rangle\) and \(|3\rangle\) or vice versa.

\[ \langle \psi_V(t) | \hat{E}_{12}^- (t) \hat{E}_{23}^+ (t) | \psi_V(t) \rangle \] and \[ \langle \psi_\Lambda(t) | \hat{E}_{12}^- (t) \hat{E}_{23}^+ (t) | \psi_\Lambda(t) \rangle \] (15.164)

for the \(\Lambda\) and the \(V\)-system, respectively. The state vector for each type of system is,

\[ |\psi_V(t)\rangle = \sum_{i=1,2,3} c_i |i, 0\rangle + c_1 |c, 1_{12}\rangle + c_2 |c, 1_{23}\rangle \] (15.165)

and,

\[ |\psi_\Lambda(t)\rangle = \sum_{i=1,2,3} c'_i |i, 0\rangle + c'_1 |b, 1_{12}\rangle + c'_2 |c, 1_{23}\rangle . \] (15.166)

The beat note term becomes,

\[ \langle \psi_V(t) | \hat{E}_{12}^- (t) \hat{E}_{23}^+ (t) | \psi_V(t) \rangle = \kappa (1_{12} 0_{23} | a_1^\dagger a_2 | 0_{12} 1_{23}) e^{i (\omega_{12} - \omega_{23}) t} \langle 3 | 3 \rangle \] (15.167)
for the V-system and
\[ \langle \psi_{\Lambda}(t) | \hat{E}_1^-(t) \hat{E}_2^+(t) | \psi_{\Lambda}(t) \rangle = \kappa' \langle 1_{12} 0_{23} | a_1^+ a_2 | 0_{12} 1_{23} \rangle e^{i(\omega_{12} - \omega_{23}) t} \langle 2 | 3 \rangle \] (15.168)

for the Λ-system. However, orthogonality of the eigenstates requires \( \langle 3 | 3 \rangle = 1 \) and \( \langle 2 | 3 \rangle = 0 \). Therefore, there is a quantum beat note term for V-type atoms, but not for Λ-type atoms.

This difference originates in quantum mechanical uncertainty. A V-type atom decays to state \( |3\rangle \) via the emission with \( \omega_{12} \) and \( \omega_{23} \). Since both transitions decayed to the same state, one cannot determine along which path each decayed, similar to Young’s double-slit experiment. However, Λ-type atoms decay to two different states. Therefore, in this case we can identify the path by the end product.

Quantum beat spectroscopy is a technique which allows for Doppler-free resolution provided the separation of the adjacent levels is less than the Doppler width. It consists in generating a coherently distributed population of two upper states, e.g. via a short laser pulse, and detecting the beat frequency.

### 15.4.2 Two-photon transitions

We will now apply the Kramers-Heisenberg formula (5.113) to photon scattering processes \( \omega \rightarrow \omega_s \). The states are then product states of atomic excitations and photonic modes \( |m, n, n_s\rangle \). In particular, the final state must take into account the mode into which light is scattered,

\[
\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \sum_{k_s} \left| \langle f, n - 1, 1 | \hat{H}^{(2)} | i, n, 0 \rangle \right|^2 + \frac{1}{\hbar} \sum_m \frac{\langle f, n - 1, 1 | \hat{H}^{(1)} | m \rangle \langle m | \hat{H}^{(1)} | i, n, 0 \rangle}{\omega_i - \omega_m} \right|^2 \delta(\omega_f - \omega_i).
\] (15.169)

The initial energy is \( \omega_i \rightarrow n\omega \), the final energy \( \omega_f \rightarrow (n - 1)\omega + \omega_s + \omega_f \), two intermediate states are possible, \( |m\rangle \rightarrow |m, n - 1, 0\rangle \) and \( |m\rangle \rightarrow |m, n, 1\rangle \) over which we must sum, that is \( \omega_m \rightarrow \omega_m + (n - 1)\omega \) and \( \omega_m \rightarrow \omega_m + n\omega + \omega_s \). They are illustrated by the Feynman diagrams in Fig. xx. Hence, and neglecting the non-linear contribution \( \hat{H}^{(2)} \),

\[
\frac{1}{\tau} = \frac{2\pi}{\hbar^3} \sum_f \sum_{k_s} \sum_m \frac{\langle f, n - 1, 1 | \hat{H}^{(1)} | m, n, 0 \rangle \langle m, n, 0 | \hat{H}^{(1)} | i, n, 0 \rangle}{\omega_m} \right|^2 \delta(\omega_f - \omega + \omega_s).
\] (15.170)

Evaluated far from resonance, \( \omega \gg \omega_m \), this result leads to Thomson and Compton scattering. Close to resonance the second term of the sum may neglected.

The matrix elements can be evaluated by the electric dipole Hamiltonian in second quantization,

\[
\frac{1}{\tau} = \frac{2\pi}{\hbar} \sum_{k_s} \sum_m \frac{\Omega_f m \Omega_{m i}}{\omega - \omega_m} \right|^2 \delta(\omega_f - \omega + \omega_s).
\] (15.171)
We convert the transition rate into a cross section via,
\[
\sum_k \to \frac{V}{(2\pi)^3} \int \int k_s^2 dks d\Omega = \frac{V}{(2\pi c)^3} \int \int \omega_s^2 d\omega_s d\Omega . \tag{15.172}
\]

15.4.2.1 Transition rates for \(n\)-photon processes

Equation (??) describes the spontaneous emission. It is adequate to move to a continuum of final states of the field. The sum over the final states includes a sum over the modes \(k\) and the polarizations \(\lambda\),
\[
\sum_f = \sum_k \sum_{\lambda} \to \frac{1}{\hbar^3} \int \int d^3p d^3r \sum_{\lambda} = \frac{V}{(2\pi c)^3} \int \Omega d\omega \omega^2 \sum_{\lambda} . \tag{15.173}
\]
We now insert for the matrix element (first term in ())) the cartesian multipole expansion (,) and obtain,
\[
\frac{1}{\tau} = \frac{2\pi \hbar^2}{\hbar^2} \sum_f \left| \langle f | - ie \sqrt{\frac{\hbar \omega}{2\varepsilon_0 V}} [\hat{\varepsilon} \cdot \hat{d}_E + ...]|i \rangle \right|^2 \delta(\omega - \omega_f) \sum_{\lambda} \tag{15.174}
\]
\[
\rightarrow \frac{2\pi \hbar^2}{\hbar^2} \frac{V}{(2\pi c)^3} \frac{e^2 \hbar \omega}{2\varepsilon_0 V} \omega^2 \sum_{\lambda} \int |\hat{\varepsilon} \cdot \langle g|d_E|e \rangle + i\hat{\varepsilon} \cdot \langle g|q_E|e \rangle \cdot \hat{k} + ...|^2 d\Omega .
\]
Finally, letting \(\sum_{\lambda} = 2\),
\[
\frac{1}{\tau} = \frac{\alpha \omega^3}{\pi c^2} \int |\hat{\varepsilon} \cdot \langle g|\text{multipole-tensor}|e \rangle \text{wavenumber-tensor}|^2 d\Omega . \tag{15.175}
\]
For example, for dipole radiation, letting \(\hat{\varepsilon} = \hat{\varepsilon}_z\),
\[
\frac{1}{\tau} = \frac{\alpha \omega^3}{\pi c^2} \int |\hat{\varepsilon} \cdot \langle g|d_E|e \rangle|^2 d\cos \theta d\phi \tag{15.176}
\]
\[
= \frac{\alpha \omega^3}{\pi c^2} |\langle g|d_E|e \rangle|^2 \int |\cos \theta|^2 d\cos \theta d\phi = \frac{4\alpha \omega^3}{3c^2} |\langle g|d_E|e \rangle|^2 .
\]

15.4.2.2 Absorption

In first order perturbation theory we have Fermi’s Golden rule,
\[
\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f |\langle f|\hat{H}_{int}|i \rangle|^2 \delta(\omega_f - \omega_i) . \tag{15.177}
\]
In the dipolar approximation, \(\hat{H}_{int} = -\hat{d} \cdot \hat{E}\), and separating the field and atomic degrees of freedom, \(|f\rangle = |N_f\rangle |A_f\rangle\), we get for absorption processes,
\[
\frac{1}{\tau} = \frac{2\pi \alpha^2}{\hbar^2} \sum_{N_f} |\langle N_f|\hat{E}^-|N_i \rangle \cdot \langle A_f|\hat{\varepsilon} \cdot \hat{d}|A_i \rangle|^2 \delta(\omega_f - \omega_i) . \tag{15.178}
\]
15.4. LIGHT SCATTERING FROM MULTI-LEVEL ATOMS

Generalizing to a statistical mixture of Fock states via \( \sum_{N_f,N_i} \langle N_i|\hat{E}^+|N_f\rangle p_i \langle N_f|\hat{E}^-|N_i\rangle = \text{Tr}(\hat{\rho}\hat{E}^+\hat{E}^-) \), we may also write,

\[
\frac{1}{\tau} = \frac{2\pi e^2}{\hbar^2} |M_{abs}|^2 \delta(\omega_f - \omega_i) \text{Tr}(\hat{\rho}\hat{E}^+\hat{E}^-), \tag{15.179}
\]

where

\[
|M_{abs}|^2 \equiv \langle A_f|\hat{\epsilon} \cdot \hat{d}|A_i\rangle. \tag{15.180}
\]

For an incoming photon \( \omega \), we get \( \omega_f = E_f \) and \( \omega_i = E_i + \omega \). See Fig. 15.17(a).

![Feynman graphs](image)

Figure 15.17: Feynman graphs for (a) absorption, (b) spontaneous emission, (c) stimulated emission, (d) two-photon absorption, (e) spontaneous Raman, (f) stimulated Raman, (g) spontaneous second harmonic generation, (h) and stimulated second harmonic generation.

15.4.2.3 Spontaneous and stimulated emission

In complete analogy to the absorption process, but now using the scattered field, \( \hat{H}_{int} = -\hat{d} \cdot \hat{E}_s \), we get for emission processes,

\[
\frac{1}{\tau} = \frac{2\pi e^2}{\hbar^2} |M_{em}|^2 \delta(\omega_f - \omega_i) \text{Tr}(\hat{\rho}\hat{E}_s^+\hat{E}_s^-), \tag{15.181}
\]

where

\[
|M_{em}|^2 \equiv \langle A_f|\hat{\epsilon}_s \cdot \hat{d}|A_i\rangle. \tag{15.182}
\]

For an outgoing photon \( \omega_s \), we get \( \omega_f = E_f + \omega_s \) and \( \omega_i = E_i \).

15.4.2.4 Two-photon absorption

In second order perturbation theory we have the Kramers-Heisenberg rule,

\[
\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \left| \sum_m \frac{\langle f|\hat{H}_{int}|m\rangle\langle m|\hat{H}_{int}|i\rangle}{\omega - \omega_m} \right|^2 \delta(\omega_f - \omega_i). \tag{15.183}
\]
In the dipolar approximation, $\hat{H}_{int} = -\mathbf{d} \cdot \hat{\mathbf{E}}_1 - \mathbf{d} \cdot \hat{\mathbf{E}}_2$, and separating the field and atomic degrees of freedom, $|f\rangle = |N_f\rangle |A_f\rangle$, we get for two-photon absorption processes,

$$\frac{1}{\tau} = \frac{2\pi e^4}{\hbar^4} \sum_{N_f} \sum_{N_m,A_m} \frac{\langle N_f| E_2^-|N_m\rangle \langle N_m| E_1^-|N_i\rangle \langle A_f| \hat{\mathbf{d}}|A_m\rangle \langle A_m| \hat{\mathbf{d}}|A_i\rangle}{\omega_1 - \omega_m}$$

$$+ \frac{\langle N_f| E_1^-|N_m\rangle \langle N_m| E_2^-|N_i\rangle \langle A_f| \hat{\mathbf{d}}|A_m\rangle \langle A_m| \hat{\mathbf{d}}|A_i\rangle}{\omega_2 - \omega_m} \delta(\omega_f - \omega_1 - \omega_2).$$

(15.184)

Generalizing to a statistical mixture of Fock states via $\sum_{N_f,N_i} p_i |\langle N_f| E_2^- E_1^- |N_i\rangle = \text{Tr} (\hat{\rho} E_1^+ E_2^+ E_1^- E_1^-)$, we may also write,

$$\frac{1}{\tau} = \frac{2\pi e^4}{\hbar^4} |M_{tpa}|^2 \delta(\omega_f - \omega_i) \text{Tr} (\hat{\rho} E_1^+ E_2^+ E_1^- E_1^-),$$

(15.185)

where

$$M_{tpa} \equiv \langle A_f| \hat{\mathbf{d}}|G(E_1 + \omega_1)\hat{\mathbf{d}}|A_i\rangle + \langle A_f| \hat{\mathbf{d}}|G(E_1 + \omega_2)\hat{\mathbf{d}}|A_i\rangle.$$  (15.186)

For two incoming photons $\omega$, we get $\omega_f = E_f$ and $\omega_i = E_i + \omega_1 + \omega_2$. Here, $G$ denotes the photon propagator,

$$G(\omega) = \sum_m \frac{|A_m\rangle \langle A_m|}{\omega - E_m}.$$  (15.187)

(a) \[\begin{array}{c}
\begin{array}{c}
\text{\textbf{k}} \\
H^{(1)} \\
i \\
f
\end{array}
\end{array}\]  

(b) \[\begin{array}{c}
\begin{array}{c}
\text{\textbf{k}} \\
H^{(1)} \\
i \\
f
\end{array}
\end{array}\]  

(e1) \[\begin{array}{c}
\begin{array}{c}
\text{\textbf{k}} \\
H^{(2)} \\
i \\
f
\end{array}
\end{array}\]  

(e2) \[\begin{array}{c}
\begin{array}{c}
\text{\textbf{k}} \\
H^{(1)} \\
i \\
m \\
f
\end{array}
\end{array}\]  

(e3) \[\begin{array}{c}
\begin{array}{c}
\text{\textbf{k}} \\
H^{(2)} \\
i \\
m \\
f
\end{array}
\end{array}\]  

Figure 15.18: Feynman graphs for (a) absorption, (b) spontaneous emission, (c) stimulated emission, (e)(i-iii) spontaneous Raman.

**15.4.2.5 Spontaneous and stimulated Raman process**

In complete analogy to the two-photon absorption process, but now using the incident and the scattered fields, $\hat{H}_{int} = -\mathbf{d} \cdot \hat{\mathbf{E}}_1 - \mathbf{d} \cdot \hat{\mathbf{E}}_s$, we get for spontaneous and stimulated Raman processes,

$$\frac{1}{\tau} = \frac{2\pi e^4}{\hbar^4} |M_{ram}|^2 \delta(\omega_f - \omega_i) \text{Tr} (\hat{\rho} E_1^+ E_s^- E_1^- E_1^-),$$

(15.188)
where
\[
M_{\text{ram}} \equiv \langle A_f | \hat{\epsilon}_s \cdot \hat{d}G(E_i + \omega_1) \hat{\epsilon}_1 \cdot \hat{d}|A_i \rangle + \langle A_f | \hat{\epsilon}_1 \cdot \hat{d}G(E_i - \omega_s) \hat{\epsilon}_s \cdot \hat{d}|A_i \rangle .
\]  
(15.189)

For an incoming photon \(\omega_1\) and a scattered photon \(\omega_s\), we get \(\omega_f = E_f + \omega_s\) and \(\omega_i = E_i + \omega_1\).

### 15.4.2.6 General \(n\)-photon processes

The transition probability in \(n\)-th order perturbation theory can be formulated in a general way as,
\[
\frac{1}{\tau} = \frac{2\pi e^2}{\hbar^2 n} |M_{fi}^{(n)}|^2 \delta(\omega_f - \omega_i) \text{Tr}(\hat{\rho}\hat{E}_1^{\pm}\hat{E}_2^{\pm}...\hat{E}_n^{\mp}\hat{E}_1^{\mp}) , 
\]
(15.190)

where
\[
M_{fi}(\omega_n, ..., \omega_1) \equiv \mathcal{S}_p \langle A_f | \hat{\epsilon}_n \hat{d}G(E_i \pm \omega_1 \pm ... \pm \omega_{n-2} \pm \omega_{n-1}) ... \hat{\epsilon}_{n-1} \hat{d}G(E_i \pm \omega_1 \pm ... \pm \omega_{n-2}) ... \hat{\epsilon}_1 \cdot \hat{d}G(E_i \pm \omega_1)|A_i \rangle .
\]  
(15.191)

The upper signs hold for absorbed photons (up to \(n\)), the lower for emitted photons, \(\omega_f = E_f + \omega_1 + ... + \omega_n\) and \(\omega_i = E_i + \omega_1 + ... + \omega_n\).

For \(n\)-photon processes, there are theoretically up to \(n + 1\) different types, each one with \(n!\) possible temporal sequences, which can be illustrated in Feynman graphs. Additionally, for every emitted photon can be either spontaneous or stimulated. The number of possible time sequences is reduced, if some absorbed or emitted photons have the same frequency by \(m!\) (if \(m\) is the number of identical photons).

For example there are \((3+1)\) different types of three-photon processes: 3 photons in, 2 photons in 1 out, 1 photon in 2 out, 3 photons out.

For example second harmonic generation: 3! possible time sequences, 2 processes, 2 equivalent photons = \(\frac{3!2}{2!}\) possible Feynman graphs.

### 15.4.3 Exercises

#### 15.4.3.1 Ex: Two-photon transitions in rubidium

Considering the following transitions of rubidium, \(5S_{1/2} - 5P_{1/2}\) at 795 nm with \(\Gamma_{795} = (2\pi) 6 \text{ MHz}\) linewidth \(5S_{1/2} - 5P_{3/2}\) at 780 nm with \(\Gamma_{780} = (2\pi) 6 \text{ MHz}\), and \(5P_{3/2} - 5D_{5/2}\) at 776 nm with \(\Gamma_{776} = (2\pi) 700 \text{ kHz}\) linewidth. Calculate the rate for resonant two-photon transitions from the ground state to the \(5D_{5/2}\) level without bothering about hyperfine splitting induced by a laser intensity of \(I = 1 \text{ mW/cm}^2\).

#### 15.4.3.2 Ex: Spin relaxation in a dipole trap

Consider a transition in a hypothetical atomic species without nuclear spin between two levels \(2S_{1/2}\) and \(2P_{1/2}\) driven far-off resonance. Calculate the spin relaxation rate as a function of the detuning.
**15.4.3.3  Ex: Rayleigh scattering and spin relaxation**

Derive the rates for Rayleigh scattering and spin relaxation for $^{87}\text{Rb}$ driven far-off resonance. **Help:** Determine the hyperfine structure of the D1 and D2 lines and calculate the transition rates between sublevels from the Kramers-Heisenberg formula.

**15.5  Beam splitting and quantum amplification**

The *beam splitter* is a general quantum device that *mixes two modes* represented by field operators $\hat{a}$ and $\hat{b}$ according to the Hamiltonian,

$$\hat{H} = \frac{\hbar}{2} \Omega (\hat{a} \hat{b}^\dagger + \hat{a}^\dagger \hat{b}) .$$

(15.192)

It can be described in the Schrödinger or the Heisenberg picture.

**15.5.1  The beam splitter in various representations**

**15.5.1.1  Schrödinger picture**

In the Schrödinger picture, if $|\psi_0\rangle = |\alpha_0\rangle |\beta_0\rangle$ is the state of the modes before the beam splitter, the Schrödinger equation, $i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$, gives us the state after the splitter via its solution,

$$|\psi(t)\rangle = e^{i\Omega t/2(\hat{a}^\dagger \hat{b} + \hat{a} \hat{b}^\dagger)} |\psi_0\rangle .$$

(15.193)

A 50% beam splitter corresponds to a $\Omega t = \pi/2$ pulse.

![Beam splitter diagram](image)

Figure 15.19: Beam splitter

**15.5.1.2  Heisenberg picture**

We can also describe the beam splitter in the Heisenberg picture. With the commutation rules,

$$[\hat{a}, \hat{a}^\dagger] = 1 = [\hat{b}, \hat{b}^\dagger] , \quad [\hat{a}, \hat{b}] = 0 ,$$

(15.194)

and the Heisenberg equations,

$$\dot{\hat{a}} = \frac{i}{\hbar} [\hat{H}, \hat{a}] = \frac{i}{2} \Omega [(\hat{a} \hat{b}^\dagger + \hat{a}^\dagger \hat{b})] , \quad \hat{a} = -\frac{1}{2} \Omega \hat{b}$$

(15.195)

$$\dot{\hat{b}} = \frac{i}{\hbar} [\hat{H}, \hat{b}] = \frac{i}{2} \Omega [(\hat{a} \hat{b}^\dagger + \hat{a}^\dagger \hat{b})] , \quad \hat{b} = -\frac{1}{2} \Omega \hat{a} ,$$
we calculate,
\[ \ddot{a} = -\frac{1}{4}\Omega^2\dot{a} \quad \text{and} \quad \ddot{b} = -\frac{1}{4}\Omega^2\dot{b}, \]
the solution of which is,
\[ \left( \begin{array}{c} \hat{a}(t) \\ \hat{b}(t) \end{array} \right) = \left( \begin{array}{cc} \cos \frac{1}{2}\Omega t & -i\sin \frac{1}{2}\Omega t \\ -i\sin \frac{1}{2}\Omega t & \cos \frac{1}{2}\Omega t \end{array} \right) \left( \begin{array}{c} \hat{a}_0 \\ \hat{b}_0 \end{array} \right). \]
Introducing the abbreviation \( \eta \equiv \cos^2(\Omega t/2) \), we can describe the evolution as,
\[ \left( \begin{array}{c} \hat{a}(t) \\ \hat{b}(t) \end{array} \right) = \left( \sqrt{\eta} - i\sqrt{1-\eta} \sqrt{\eta} \right) \left( \begin{array}{c} \hat{a}_0 \\ \hat{b}_0 \end{array} \right). \]
For a \( \Omega t = \pi/2 \) pulse, we get,
\[ \left( \begin{array}{c} \hat{a}(t) \\ \hat{b}(t) \end{array} \right) = \sqrt{\frac{1}{2}} \left( 1 - i \right) \left( \begin{array}{c} \hat{a}_0 \\ \hat{b}_0 \end{array} \right). \]
that each the reflected beam suffers a phase shift of \( \pi/2 \) \(^{11}\).

### 15.5.1.3 Glauber representation

In the Heisenberg picture, the wavefunctions of the quantum states (and hence the density operator and the Wigner function) remain unchanged during the evolution, i.e.,
\[ |\psi\rangle \equiv |\alpha\rangle|\beta\rangle = |\alpha_0\rangle|\beta_0\rangle \equiv |\psi_0\rangle, \]
\[ \rho_{|\psi\rangle} = \rho_{|\psi_0\rangle}, \]
\[ W_{|\psi\rangle}(\gamma) = W_{|\psi_0\rangle}(\gamma), \]
\[ P_{|\psi\rangle}(\gamma) = P_{|\psi_0\rangle}(\gamma), \]
\[ Q_{|\psi\rangle}(\gamma) = Q_{|\psi_0\rangle}(\gamma), \]
where the \( |\psi\rangle \) are arbitrary quantum states and the \( |\gamma\rangle \) are Glauber’s states. This means that two field modes mixed at a beam splitter do not interfere with phase space, i.e. do not develop quantum correlations. Of course, that would be too easy, indeed; we will soon see in Sec. 15.6, that we need to work a little harder to produce quantum correlations.

Defining a beam splitting operator in analogy to the displacement operator \( (4.93) \) as,
\[ \hat{B}(\theta) \equiv e^{\theta(\hat{a}^\dagger\hat{b} - \hat{a}\hat{b}^\dagger)} \]
we find,
\[ \hat{B}(\theta)^\dagger \hat{a} \hat{B}(\theta) = \hat{a} \cos \theta + \hat{b} \sin \theta \]
\[ \hat{B}(\theta)^\dagger \hat{b} \hat{B}(\theta) = -\hat{a} \sin \theta + \hat{b} \cos \theta \]
as will be shown in Exc. 15.5.6.3 \(^{12}\).

\(^{11}\)This fact is a consequence of time-reversal invariance at the beam splitter. We will see later that, in fact, only the beam reflected at the surface of an optically denser medium suffers a phase-shift of \( \pi \), while the beam reflected at an optically thinner medium does not suffer any phase shift.

\(^{12}\)Compare to the formulas \( (4.100), (15.243), \) and \( (15.268) \).
15.5.1.4 Fock representation

Alternatively, we can describe the beam splitter in the Fock representation. The Hamiltonian of the beam splitter couples two modes of harmonic oscillators. Expanding on a two-dimensional Fock basis via $|\psi\rangle \equiv (...,|n_a\rangle...|n_b\rangle|0\rangle...)$ we can gain more insight:

$$
\hat{H} = \frac{\hbar}{2} \Omega (\hat{a} \hat{b}^\dagger + \hat{a}^\dagger \hat{b})
= \frac{\hbar}{2} \sum_{n_a,n_b} \sqrt{n_a(n_b+1)|n_a-1,n_b+1\rangle\langle n_a,n_b| + \sqrt{(n_a+1)n_b}|n_a+1,n_b-1\rangle\langle n_a,n_b|}
= \sum_{n_a+n_b} \hat{H}_{a+b},
$$

where,

$$
\hat{H}_{a+b} = \frac{\hbar}{2} \Omega \begin{pmatrix}
0 & \sqrt{1n_b} \\
\sqrt{1n_b} & 0 & \sqrt{2(n_b-1)} \\
& \sqrt{2(n_b-1)} & \ddots \\
& & \ddots & \sqrt{n_a1} \\
& & & \sqrt{n_a1} & 0
\end{pmatrix}.
$$

The sub-spaces with $n_a + n_b + 1$ photons are completely degenerate, since $\text{det}(\lambda I_{a+b} - \hat{H}_{a+b}) = \lambda^{n_a+n_b+1} = 0$. The degeneracy is removed, when we introduce loss mechanisms into one of the modes. Thus, the Hamiltonian can be understood as a Dicke system with the multiplicity $\frac{1}{2}(n_a + n_b) = n_a + n_b + 1$. See also Exc. 15.5.6.1.

**Example 62 (Beam splitter with 0 or 1 photons):** As an example, we consider $n_a, n_b = 0, 1$. Then, in the basis $(|0,0\rangle |0,1\rangle |1,0\rangle |0,2\rangle |1,1\rangle |2,0\rangle ...)^t$ the matrix of the Hamiltonian becomes,

$$
\hat{H} = \frac{\hbar}{2} \Omega \begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & \sqrt{2} \\
0 & \sqrt{2} & 0
\end{pmatrix}.
$$

It is easily verified that the matrix of eigenvectors and the matrix of eigenvalues,

$$
U = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & -1 & 1 & 0 & 0 \\
0 & 1 & 1 & 0 & 0 \\
0 & 0 & 0 & -\frac{1}{2}\sqrt{2} & -1 \\
0 & 0 & 0 & 1 & \frac{1}{2}\sqrt{2}
\end{pmatrix}
$$

respectively $E = \frac{\hbar}{2} \Omega \begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & -2 & 0 \\
0 & 0 & 0 & 0 & 2
\end{pmatrix}$

satisfy $U^{-1}HU = E$. Hence,

$$
|\psi\rangle = U^{-1}e^{iEt}U|\psi_0\rangle,
$$

\text{13A more in-depth discussion is found in Ref. [375].}
and we find, that the state $|1, 1\rangle = (0 \ 0 \ 0 \ 0 \ 1 \ 0)^T$ is transformed into a superposition,

$$
\begin{pmatrix}
0 & 0 & 0 & 0 & 1 & 0
\end{pmatrix}^T \frac{1}{\sqrt{2}} \sin \Omega t \ \cos \Omega t \ \frac{1}{\sqrt{2}} \sin \Omega t ^T \Omega t = \frac{1}{\sqrt{2}} (|0, 2\rangle + |2, 0\rangle).
$$

Similarly, we find that the superposition state $\frac{1}{\sqrt{2}}(|1, 0\rangle + |0, 1\rangle) = (0 \ 1 \ -1 \ 0 \ 0 \ 0)^T$ is transformed into,

$$
e^{-\frac{i}{2} \Omega t} (0 \ 1 \ -1 \ 0 \ 0 \ 0)^T \Omega t = \frac{1}{\sqrt{2}} (|1, 0\rangle + |0, 1\rangle).
$$

### 15.5.2 Fock and Glauber states at a beam splitter

A beam splitter divides a Fock state containing $N$ photons into two Glauber states,

$$|\psi\rangle = \frac{1}{2^{N/2} \sqrt{N!}} (\hat{a}_1^\dagger + \hat{a}_2^\dagger)^N |0, 0\rangle = \frac{1}{2^{N/2} \sqrt{N!}} \sum_{n=0}^{N} \begin{pmatrix} N \\ n \end{pmatrix} (\hat{a}_1^\dagger)^n (\hat{a}_2^\dagger)^{N-n}|0, 0\rangle \quad (15.205)$$

$$= \frac{1}{2^{N/2}} \sum_{n=0}^{N} \sqrt{\begin{pmatrix} N \\ n \end{pmatrix}} |n, N-n\rangle = \sum_{n=0}^{N} \sqrt{\begin{pmatrix} N \\ n \end{pmatrix}} 0.5^n 0.5^{N-n} |n, N-n\rangle$$

$$\approx \sum_{n=0}^{N} \sqrt{\begin{pmatrix} N/2 \\ n \end{pmatrix}} \frac{e^{-N/2}}{n!} |n, N-n\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{N} \frac{\alpha^n}{\sqrt{n!}} |n, N-n\rangle,$$

approximating the binomial distribution by the Poisson distribution,

$$\begin{pmatrix} N \\ n \end{pmatrix} p^n (1-p)^{N-n} \xrightarrow{N \to \infty} \frac{(pN)^n}{n!} e^{-pN}.$$

and defining $\alpha \equiv N/2$. The normalization is $\langle \psi | \psi \rangle = 1$. The population in an individual mode is,

$$\langle \hat{n}_1 \rangle = \langle \psi | \hat{a}_1^\dagger \hat{a}_1 | \psi \rangle = \frac{1}{2^N} \langle m, N-m | \sum_{n,m=0}^{N} \sqrt{\begin{pmatrix} N \\ m \end{pmatrix}} \hat{a}_1^\dagger \hat{a}_1 \sqrt{\begin{pmatrix} N \\ n \end{pmatrix}} |n, N-n\rangle = \sum_{n=0}^{N} \begin{pmatrix} N \\ n \end{pmatrix} n = \frac{N}{2} \quad (15.207)$$

The result (15.205) shows that, ignoring one of the modes, the other mode automatically becomes a Glauber state.

Besides that,

$$\langle \hat{n}_1^2 \rangle = \frac{1}{2^N} \sum_{n=0}^{N} \begin{pmatrix} N \\ n \end{pmatrix} n^2 = \frac{N}{2^N} \sum_{n=0}^{N-1} \begin{pmatrix} N \\ n \end{pmatrix} (n+1) = \frac{N(N+1)}{4} \quad (15.208)$$

$$\langle \hat{n}_1 \hat{n}_2 \rangle = \frac{1}{2^N} \sum_{n=0}^{N} \sqrt{\begin{pmatrix} N \\ n \end{pmatrix}} n(N-n) = N \langle \hat{n}_1 \rangle - \langle \hat{n}_1^2 \rangle = \frac{N(N-1)}{4}.$$
The evolution of such a state is described by the von Neumann equation:

$$\dot{\hat{\rho}} = \frac{\sigma^2(\hat{n}_1 - \hat{n}_2)}{\langle \hat{n}_1 \rangle + \langle \hat{n}_2 \rangle} = \frac{\langle \hat{n}_1^2 - 2\hat{n}_1 \hat{n}_2 + \hat{n}_2^2 \rangle}{N} = \frac{2\langle \hat{n}_1^2 \rangle - 2\langle \hat{n}_1 \hat{n}_2 \rangle}{N} = 1.$$ (15.209)

The correlation functions at equal times are,

$$g_{11} = \frac{\langle \hat{a}_1^\dagger \hat{a}_1^\dagger \hat{a}_1 \hat{a}_1 \rangle}{\langle \hat{n}_1 \rangle^2} = 1$$

$$g_{12} = \frac{\langle \hat{a}_1^\dagger \hat{a}_2^\dagger \hat{a}_2 \hat{a}_1 \rangle}{\langle \hat{n}_1 \rangle \langle \hat{n}_2 \rangle} = 1$$

The Cauchy-Schwarz inequality and the quantum inequality are both met,

$$g_{12} \leq \sqrt{g_{11}g_{22}}$$

$$g_{12} \leq \sqrt{\left( g_{11} + \frac{1}{\langle \hat{n}_1 \rangle} \right) \left( g_{22} + \frac{1}{\langle \hat{n}_2 \rangle} \right)}$$

In comparison, a Glauber state is normally divided,

$$|\psi\rangle = |\alpha_1\rangle |\alpha_2\rangle = e^{-|\alpha_1|^2/2} \sum_n \frac{\alpha_1^n}{\sqrt{n!}} |n\rangle e^{-|\alpha_2|^2/2} \sum_m \frac{\alpha_2^m}{\sqrt{m!}} |m\rangle$$

$$= e^{-|\alpha_1|^2/2 - |\alpha_2|^2/2} \sum_{n,m} \frac{\alpha_1^n \alpha_2^m}{\sqrt{n!} \sqrt{m!}} |n\rangle |m\rangle.$$ (15.212)

**15.5.2.1 Density matrix representation**

The density matrix for a pure state is,

$$\hat{\rho} = |\psi\rangle \langle \psi| = \begin{pmatrix} |\langle \psi|1\rangle|^2 & \langle 1|\psi\rangle |\psi|2\rangle \\ \langle 2|\psi\rangle |\psi|1\rangle & |\langle \psi|2\rangle|^2 \end{pmatrix}.$$ (15.213)

The evolution of such a state is described by the von Neumann equation:

$$i\hbar \partial_t \hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)].$$ (15.214)

For the beam splitter we obtain,

$$\hat{\rho} = |\psi\rangle \langle \psi| = \begin{pmatrix} |\langle \psi|0,0\rangle|^2 & \langle 0,0|\psi\rangle |\psi|0,1\rangle & \langle 0,0|\psi\rangle |\psi|1,0\rangle \\ \langle 0,1|\psi\rangle |\psi|0,0\rangle & |\langle \psi|0,1\rangle|^2 & \langle 0,1|\psi\rangle |\psi|1,0\rangle \\ \langle 1,0|\psi\rangle |\psi|0,0\rangle & \langle 1,0|\psi\rangle |\psi|0,1\rangle & |\langle \psi|1,0\rangle|^2 \end{pmatrix}.$$ (15.215)

**Example 63 (Density matrix for the beam splitter with 0 or 1 photons):** For the case of the superposition states, $|\psi\rangle = \frac{1}{\sqrt{2}}(|0,1\rangle \pm |1,0\rangle)$,

$$\hat{\rho} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}.$$ (15.215)

Obviously, $\hat{\rho} = \hat{\rho}^2$. For the above superposition state, $\partial_t \hat{\rho}(t) = 0$. 

15.5.3 Shot noise

As any quantized degree of freedom, a light mode is subject to intrinsic quantum noise imposed by the Heisenberg uncertainty relation, as we have seen for the harmonic oscillator (4.105). The Heisenberg limit in the quadrature phases of a light field determines the shot noise in the intensity of the light beam. To measure this noise, we divide the laser beam by a beam splitter into two beams $\hat{a}$ and $\hat{b}$ and recombine them with a second beam splitter,

\[ \hat{c} = \frac{1}{\sqrt{2}}(\hat{a} + \hat{b}) \quad , \quad \hat{d} = \frac{1}{\sqrt{2}}(\hat{a} - \hat{b}) . \]  

(15.216)

Detected by photodetectors with the gain coefficient $g$, these two beams produce currents,

\[ \hat{I}_c = g\hat{c}^\dagger \hat{c} , \quad \hat{I}_d = g\hat{d}^\dagger \hat{d} . \]  

(15.217)

We add and subtract these currents,

\[ \hat{I}_+ \equiv \hat{I}_c + \hat{I}_d = g(\hat{a}^\dagger \hat{a} + \hat{b}^\dagger \hat{b}) \quad , \quad \hat{I}_- \equiv \hat{I}_c - \hat{I}_d = g(\hat{a}^\dagger \hat{b} + \hat{b}^\dagger \hat{a}) . \]  

(15.218)

and,

\[ \hat{I}_+^2 = g^2[\hat{n}_a^2 + \hat{n}_b^2 + 2\hat{n}_a\hat{n}_b] \quad , \quad \hat{I}_-^2 = g^2[(\hat{a}^\dagger \hat{b})^2 + (\hat{b}^\dagger \hat{a})^2 + \hat{a}^\dagger \hat{a} + \hat{b}^\dagger \hat{b} + \hat{a}^\dagger \hat{a} + \hat{b}^\dagger \hat{b}] . \]  

(15.219)

The expectation values are,

\[ \langle \hat{I}_+ \rangle = g\langle \hat{n}_a \rangle_a \quad , \quad \langle \hat{I}_+ \rangle = 0 \]  

(15.220)

\[ \langle \hat{I}_+^2 \rangle = g^2\langle (\hat{a}^\dagger \hat{a})^2 \rangle_a \quad , \quad \langle \hat{I}_-^2 \rangle = g^2\langle \hat{n}_a \rangle_a . \]  

Now, with the definition, $\langle (\Delta \hat{I})^2 \rangle \equiv \langle \hat{I}_+^2 \rangle - \langle \hat{I}_-^2 \rangle$, we get the intensity noise of the field,

\[ \langle \Delta \hat{I}_+^2 \rangle = \langle (\Delta \hat{I}_+)^2 \rangle = g^2\langle (\Delta \hat{n}_a)^2 \rangle , \]  

(15.221)

and the shot noise,

\[ \langle \Delta \hat{I}_-^2 \rangle = g^2I_a . \]  

(15.222)

Figure 15.20: Shot noise measurement.
15.5.4 Quantum amplifier

We will call in the following as *quantum signals* degrees of freedom subject to quantum noise. Typically a quantum signal will be a mode of an electric field, represented by an annihilation operator $\hat{a}$. Such a mode can be enhanced by *quantum amplifier*, which is a device amplifying quantum signals according to the rules of quantum mechanics. Examples include the active elements of lasers and optical parametric amplifiers. A quantum amplifier is characterized by its gain and its own intrinsic quantum noise, which are interdependent parameters; the higher the gain, the larger the uncertainty noise. In the case of lasers, the uncertainty corresponds to the amplified spontaneous emission of the active medium.

Quantum amplification is a unitary transformation $\hat{U}$, acting in an initial state $|\text{in}\rangle$ and producing (in the Schrödinger figure) the amplified state,

$$|\text{out}\rangle = \hat{U}|\text{in}\rangle.$$  

(15.223)

The amplification depends on the mean value $\langle \hat{a} \rangle$ of the annihilation operator and its dispersion $\langle \hat{a}^\dagger \hat{a} \rangle - \langle \hat{a}^\dagger \rangle \langle \hat{a} \rangle$. A coherent state is a state with minimal uncertainty; when the state is transformed, the uncertainty may increase. This increase can be interpreted as noise in the amplifier. The gain $G$ can be defined as follows:

$$G = \frac{\langle \hat{a} \rangle_{\text{out}}}{\langle \hat{a} \rangle_{\text{in}}}.$$  

(15.224)

The quantum amplifier can also be described in the Heisenberg picture; the changes are attributed to the amplification of the field operator. Thus, the evolution of the operator $\hat{a}_{\text{out}}$ is given by

$$\hat{a}_{\text{out}} = \hat{U}^\dagger \hat{a} \hat{U},$$  

(15.225)

while the state vector remains unchanged. The gain is then given by,

$$G = \frac{\langle \hat{a}_{\text{out}} \rangle_{\text{in}}}{\langle \hat{a} \rangle_{\text{in}}}.$$  

(15.226)

In general, the gain $G$ may be complex, and it may depend on the initial state. For laser applications, the amplification of coherent states is important. Therefore, it is usually assumed that the initial state is a coherent state characterized by a complex-valued initial parameter $\alpha$, such that $|\text{in}\rangle = |\alpha\rangle$. Even with such a restriction, the gain may depend on the amplitude or phase of the initial field.

In the following, the Heisenberg representation is used; all brackets are assumed to be evaluated with respect to the initial coherent state,

$$\text{noise} = \langle \hat{a}_{\text{out}}^\dagger \hat{a}_{\text{out}} \rangle - \langle \hat{a}_{\text{out}}^\dagger \rangle \langle \hat{a}_{\text{out}} \rangle - (\langle \hat{a}^\dagger \hat{a} \rangle - \langle \hat{a}^\dagger \rangle \langle \hat{a} \rangle).$$  

(15.227)

The expectation values are assumed to be evaluated with respect to the initial coherent state. This quantity characterizes the increase of the uncertainty of the field due to amplification. As the uncertainty of the field operator does not depend on its parameter, the quantity above shows how much output field differs from a coherent state.
15.5. Beam Splitting and Quantum Amplification

15.5.4.1 Linear phase-invariant amplifier

Linear phase-invariant amplifiers may be described as follows. Assume that the unitary operator $U$ amplifies in such a way that the input $\hat{a}$ and the output $\hat{a}_{\text{out}} = \hat{U}^\dagger \hat{a} \hat{U}$, are related by a linear equation,

$$\hat{a}_{\text{out}} = c \hat{a} + s \hat{b}^\dagger,$$

where $c$ and $s$ are c-numbers and $\hat{b}^\dagger$ is a creation operator characterizing the amplifier. Without loss of generality, it may be assumed that $c$ and $s$ are real. The commutator of the field operators is invariant under unitary transformation $U$:

$$[\hat{a}_{\text{out}}, \hat{a}_{\text{out}}^\dagger] = 1 = [\hat{a}, \hat{a}^\dagger],$$

$$[a_{\text{in}}, a_{\text{out}}^\dagger] = 0 = [a_{\text{out}}, a_{\text{in}}^\dagger].$$

(15.229)

From the unitarity of $U$, it follows that $\hat{b}$ satisfies the same commutation relations. The c-numbers are then $c^2 - s^2 = 1$. Hence, the phase-invariant amplifier acts by introducing an additional mode to the field, with a large amount of stored energy, behaving as a boson. Calculating the gain and the noise of this amplifier, one finds $G = c$, and

$$\text{noise} = c^2 - 1.$$

(15.230)

The coefficient $g = |G|^2$ is sometimes called the intensity amplification coefficient. The noise of the linear phase-invariant amplifier is given by $g - 1$. The gain can be dropped by splitting the beam; the estimate above gives the minimal possible noise of the linear phase-invariant amplifier. The linear amplifier has an advantage over the multi-mode amplifier: if several modes of a linear amplifier are amplified by the same factor, the noise in each mode is determined independently; that is, modes in a linear quantum amplifier are independent.

To obtain a large amplification coefficient with minimal noise, one may use homodyne detection, constructing a field state with known amplitude and phase, corresponding to the linear phase-invariant amplifier. The uncertainty principle sets the lower bound of quantum noise in an amplifier. In particular, the output of a laser system and the output of an optical generator are not coherent states.

The multiplicative amplifier $D$ also adds additive noise $F$. We have $DD^\dagger = 1$,

$$\begin{pmatrix} a_{\text{out}}^\dagger \\ a_{\text{out}} \end{pmatrix} = D \begin{pmatrix} a_{\text{in}}^\dagger \\ a_{\text{in}} \end{pmatrix} + \begin{pmatrix} F_1 \\ F_2 \end{pmatrix}.$$

(15.231)

15.5.5 Homodyne detection and inverse Radon transform

In the method of homodyne detection or phase-sensitive detection the signal is obtained by superposing the field mode of interest with a local oscillator with a relative phase $\theta$ at a beam splitter and a subtraction of the photo currents in the two ports of the interferometer:

$$\Delta \hat{J} = \hat{a}_t^\dagger \hat{a}_t - \hat{b}_t^\dagger \hat{b}_t$$

$$= (2\eta - 1)(\hat{a}_0^\dagger \hat{a}_0 + \hat{b}_0^\dagger \hat{b}_0) + 2\sqrt{(1 - \eta)\eta}(\hat{a}_0^\dagger \hat{a}_0 + \hat{b}_0^\dagger \hat{b}_0) \xrightarrow{\eta \to 1/2} \hat{a}_0^\dagger \hat{a}_0 + \hat{b}_0^\dagger \hat{b}_0.$$

(15.232)
If the local oscillator is a classical light field $\hat{b}_0 = \alpha_{LO} e^{-i\theta}$,

$$\Delta \hat{J} = |\alpha_{LO}|(\hat{a}_0 e^{-i\theta} + \hat{a}_0^\dagger e^{i\theta})$$

$$= \sqrt{2}|\alpha_{LO}| \hat{x}_\theta,$$

where the field mode is expressed by the Hermitian quadrature components $\hat{a}_0 = 2^{-1/2} \cdot (\hat{x}_\theta + i\hat{y}_\theta)$. The expectation value of $\Delta \hat{J}$ is afflicted with the Heisenberg uncertainty and can be expressed as the first moment of the Wigner function $W(\alpha)$:

$$\langle \psi | \Delta \hat{J} | \psi \rangle = \int W_{|\psi\rangle}(\alpha) \Delta \hat{J} d^2\alpha$$

$$= \sqrt{2}|\alpha_{LO}| \int W_{|\psi\rangle}(x_\theta, p_\theta) x_\theta dx_\theta dp_\theta = \sqrt{2}|\alpha_{LO}| \int_{-\infty}^{\infty} w_\theta(x_\theta) x_\theta dx_\theta .$$

Here, the distribution function integrated over a rotated quadrature component $p_\theta$ is given by,

$$w_\theta(x_\theta) \equiv \int_{-\infty}^{\infty} W_\theta(x_\theta, p_\theta) dp_\theta.$$

This is called the radon transform. The distribution function $w_\theta(p_\theta)$ as well as the Wigner function are normalized to 1. Multiple measurements of the expectation value $x_\theta \equiv \langle \psi | \hat{x}_\theta | \psi \rangle$ now yields a histogram $H_{|\psi\rangle}(x_\theta)$ reflecting, if normalized, $w_{|\psi\rangle}(x_\theta) = H_{|\psi\rangle}(x_\theta) / \int H_{|\psi\rangle}(x_\theta)$ exactly the distribution function.

Considering the finite detector efficiency [375] $w_\theta(x_\theta)$ must be generalized to a convolution with an apparatus function $\zeta(x)$:

$$w_\theta^{\text{real}}(\sqrt{\eta}x_\theta) = (w_\theta^{\text{ideal}} * \zeta) \quad \text{onde} \quad \zeta(x) = \frac{1}{\sqrt{\pi(1-\eta)}} e^{-\eta x^2/(1-\eta)} .$$

A finite detector efficiency degrades the contrast of the quantum interference structures.

With the procedure of optical homodyne tomography or quantum state endoscopy the Wigner function for e.g. a Schrödinger cat state can be reconstructed from a set of distribution functions $w_\theta(x_\theta) = \int W(\alpha e^{i\theta}) dp_\theta$ measured for various phases $\theta$ [375]. To do this the data set is exposed to an inverse radon transform:

$$W(\alpha) = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\pi} \int_{-\infty}^{\infty} w_\theta(x_\theta) |\zeta| e^{i\zeta [\text{Re}(2^{-1/2}\alpha e^{-i\theta}) - x_\theta]} dx_\theta dp_\theta d\zeta .$$

In contrast to the conventional homodyne detection, where the phase dependency of amplitude noise is recorded, the homodyne tomography allows the complete reconstruction of a quantum state through measurement of the distribution of the amplitude noise power,

$$P_s = \frac{\omega_s}{2\pi} \int_0^{\omega_s/2\pi} dt |\langle I(t) \rangle|^2$$

for various phases.

Alternatively, to the homodyne method, one may reconstruct the photon distribution in field modes from their temporal evolution [613]. Another method could be to use atoms as sensors for the quantum state of a light field in a Jaynes-Cummings type dynamics.
15.5.6 Exercises

15.5.6.1 Ex: Elitzur and Vaidman bomb tester

a. Write down the beam splitter Hamiltonian in the Fock representation for a the case of a single photon, diagonalize it, and determine the propagator $e^{iHt/\hbar}$ for a 50/50 beam splitter.

b. Based on the propagator derived in (a) draw an analogy between a Mach-Zehnder interferometer and a resonantly driven two-level system. Interpreting the interferometer as a qubit explain the Elitzur and Vaidman bomb testing problem. What is the probability

15.5.6.2 Ex: Beam splitter

Show that the beam-split transformation $\begin{pmatrix} c \\ d \end{pmatrix} = \begin{pmatrix} t & -r \\ r & t \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$ preserves the commutations relations and the photon number.

15.5.6.3 Ex: Beam splitter

Show that for $\hat{B} \equiv e^{i(\hat{a}^\dagger \hat{b}^\dagger - \hat{a}^\dagger \hat{b})}$ holds,

$$\hat{B} \hat{a} \hat{B}^\dagger = \hat{a} \cos \theta + \hat{b} \sin \theta \quad \text{and} \quad \hat{B} \hat{b} \hat{B}^\dagger = -\hat{a} \sin \theta + \hat{b} \cos \theta.$$ 

15.5.6.4 Ex: Beam splitter

Show that $\hat{B}|1,0\rangle = \cos \theta |1,0\rangle - \sin \theta |0,1\rangle$ and $\hat{B}|0,n\rangle = \sum_{k=0}^{\infty} \sqrt{\binom{n}{k}} \cos^k \theta \sin^{n-k} \theta |n-k,k\rangle$.

15.5.6.5 Ex: Beam splitter

Show that two photons with different polarizations hitting simultaneously opposite sides of a beam splitter behave like classical coins.

15.5.6.6 Ex: Beam splitter

Show that $\hat{B}|\psi^+\rangle = \frac{1}{\sqrt{2}} \left( \hat{b}_h^\dagger \hat{a}_h^\dagger - \hat{a}_v^\dagger \hat{b}_v^\dagger \right) |00\rangle$, $\hat{B}|\psi^-\rangle = \frac{1}{\sqrt{2}} \left( \hat{b}_h^\dagger \hat{a}_v^\dagger - \hat{a}_h^\dagger \hat{b}_v^\dagger \right) |00\rangle$, and $\hat{B}|\psi^+\rangle = \frac{1}{2} (|2_h0\rangle - |02_h\rangle \pm |2_v0\rangle \mp |02_v\rangle)$.

15.5.6.7 Ex: Beam splitter

Show that the Werner state $\rho_W = p|\psi^-\rangle\langle\psi^-| + (1-p)\frac{1}{4}$ where $0 \leq p \leq 1$ is entangled for $p > \frac{1}{3}$.
15.6 Coherent and squeezed states of light

15.6.1 Coherent states and the laser

The laser can be characterized as a quantum mechanical device generating classical (that is, coherent) light.

15.6.2 Squeezing operator

Let us consider a Hamiltonian of the following form,

\[ \hat{H}_{sqz} = \hbar \omega \hat{a}^\dagger \hat{a} + \frac{i \hbar \xi}{2} \hat{a}^{\dagger 2} + \frac{i \hbar \xi^*}{2} \hat{a}^2. \] (15.239)

leading to the equation of motion,

\[ \dot{\hat{a}} = -i \omega \hat{a} + 2g \hat{a}^\dagger. \] (15.240)

The non-linear i.e. quadratic appearance of the field operators suggests that the interaction should include correlation pair production, as is the case for parametric processes or four-wave mixing. We will see later that cavities are good for producing squeezing. However, the unused ports of the cavity let vacuum fluctuations come in, which partially overrule squeezing.

For now, we study, in analogy with the displacement operator (4.93), the propagator \( e^{-i\hat{H}_{sqz}t/\hbar} \), i.e the operator given by,

\[ \hat{S}(\xi) \equiv e^{\xi \hat{a}^{\dagger 2}/2 - \xi^* \hat{a}^2/2}, \] (15.241)

and which we will call the squeezing operator. In analogy with the calculation (4.94), using the commutation rules, it is possible to verify the unitarity of this operator [383] (see Exc. 15.6.7.1).

In particular, using the relationship (2.165) and the abbreviation \( \hat{A} \equiv \frac{\xi}{2} \hat{a}^{\dagger 2} - \frac{\xi^*}{2} \hat{a}^2 \), we can show [579] (see Exc. 15.6.7.2),

\[ \hat{S}^\dagger(\xi) \hat{a} \hat{S}(\xi) = e^{\xi \hat{a}^{\dagger 2}/2 - \xi^* \hat{a}^2/2} \]

\[ = \hat{a} + \xi \hat{a}^{\dagger} + \frac{1}{2!} \xi \xi^* \hat{a} + \frac{1}{3!} \xi \xi^* \xi \hat{a}^{\dagger} + \ldots = \hat{a} \cosh |\xi| + \frac{|\xi|}{\xi^*} \hat{a}^\dagger \sinh |\xi|, \]

and similarly for \( \hat{a}^{\dagger} \), such that with \( \xi \equiv r e^{i\varphi} \),

\[ \hat{S}^\dagger(\xi) \hat{a} \hat{S}(\xi) = \hat{a} \cosh r + e^{-i\varphi} \hat{a}^\dagger \sinh r \]

\[ \hat{S}^\dagger(\xi) \hat{a}^{\dagger} \hat{S}(\xi) = \hat{a}^\dagger \cosh r + e^{i\varphi} \hat{a} \sinh r \] (15.243)

The formulas (15.243) describe a Bogolubov transform.

The squeezing operator does not commute with the displacement operator. However, from (15.243) we an derive the following simple relation,

\[ \hat{S}(\xi) \hat{D}(\alpha) \neq \hat{D}(\alpha) \hat{S}(\xi) = \hat{S}(\xi) \hat{D}(\alpha \cosh r + \alpha^* e^{i\theta} \sin r). \] (15.244)
15.6. COHERENT AND SQUEEZED STATES OF LIGHT

Solve the Exc. 15.6.7.3.

Squeezed coherent states are generated by coherent displacement of a *squeezed vacuum*,

\[ |\alpha, \xi\rangle = \hat{S}(\xi)|0, \xi\rangle = \hat{D}(\alpha)\hat{S}(\xi)|0\rangle . \] (15.245)

On the other hand, from (15.244),

\[ \hat{D}(\alpha)\hat{S}(\xi)|0\rangle = \hat{S}(\xi)\hat{D}(\alpha \cosh r + \alpha^* e^{i\varphi} \sinh r)|0\rangle \]
\[ = \hat{S}(\xi)|\alpha \cosh r + \alpha^* e^{i\varphi} \sinh r\rangle . \] (15.246)

15.6.2.1 Single-mode Bogolubov transform

A pair of annihilation and creation operators satisfying the commutation relation \([\hat{a}, \hat{a}^\dagger] = 1\) can be converted into another pair of operators by a *Bogolubov transform*,

\[ \hat{b} \equiv u\hat{a} + v\hat{a}^\dagger , \quad \hat{b}^\dagger \equiv u^*\hat{a}^\dagger + v^*\hat{a} , \] (15.247)

for complex numbers \(u\) and \(v\). By postulating the same commutation relation for new operators, \([\hat{b}, \hat{b}^\dagger] = 1\), we immediately get the condition,

\[ |u|^2 - |v|^2 = 1 . \] (15.248)

Comparing with the hyperbolic identity \(\cosh^2 r - \sinh^2 r = 1\), we can parametrize the constants as,

\[ u = \cosh r \quad \text{and} \quad v = e^{i\varphi} \sinh r . \] (15.249)

This is interpreted as a linear symplectic transformation in phase space.

15.6.2.2 Squeezing of the uncertainty relation

The real and imaginary parts of the transformed operators, defined by \(\hat{b} = \hat{x}_b + i\hat{y}_b\), are Hermitian and satisfy the Heisenberg uncertainty relation (2.87),

\[ [\hat{x}_b, \hat{y}_b] = \frac{i}{2} \quad \text{and} \quad \Delta \hat{x}_b \Delta \hat{y}_b \geq \frac{1}{2} \langle [\hat{x}_b, \hat{y}_b]\rangle = \frac{1}{2} . \] (15.250)

However, let us take a look at the uncertainties separately. They relate to the Glauber mode via,

\[ \hat{x}_b = \frac{1}{2}(\hat{b} + \hat{b}^\dagger) = \frac{1}{2}(\hat{a} \cosh r + \hat{a}^\dagger e^{i\varphi} \sinh r) + \frac{1}{2}(\hat{a}^\dagger \cosh r + \hat{a} e^{-i\varphi} \sinh r) \]
\[ = \hat{x}_a \cosh r + \frac{1}{2} \sinh r(\hat{a}^\dagger e^{i\varphi} + \hat{a} e^{-i\varphi}) \xrightarrow{\varphi = 0} \hat{x}_a e^r \]
\[ \hat{y}_b = \frac{1}{2i}(\hat{b} - \hat{b}^\dagger) = \frac{1}{2i}(\hat{a} \cosh r + \hat{a}^\dagger e^{i\varphi} \sinh r) - \frac{1}{2i}(\hat{a}^\dagger \cosh r + \hat{a} e^{-i\varphi} \sinh r) \]
\[ = \hat{y}_a \cosh r + \frac{1}{2i} \sinh r(\hat{a}^\dagger e^{i\varphi} - \hat{a} e^{-i\varphi}) \xrightarrow{\varphi = 0} \hat{y}_a e^r . \]

The individual fluctuations are (assuming \(\varphi = 0\)),

\[ \Delta \hat{x}_b^2 = \langle \hat{x}_b^2 \rangle - \langle \hat{x}_b \rangle^2 = e^{2r} \left( \langle \hat{a}^2 \rangle - \langle \hat{a} \rangle^2 \right) \]
\[ = \frac{1}{4} e^{2r} \left( 1 + \langle \hat{a}^2 \rangle + \langle \hat{a}^\dagger \rangle^2 + 2\langle \hat{a}^\dagger \hat{a} \rangle - \langle \hat{a} \rangle^2 - \langle \hat{a}^\dagger \rangle^2 - 2\langle \hat{a}^\dagger \rangle \langle \hat{a} \rangle \right) . \] (15.252)
With \( \langle \hat{a} \rangle = 0 \),
\[
\Delta x_b^2 = e^{2r} \left( \frac{1}{2} \text{Re} \langle \hat{a}^2 \rangle + \frac{1}{4} + \frac{1}{2} \langle \hat{a}^\dagger \hat{a} \rangle \right) \quad (15.253)
\]
\[
\Delta y_b^2 = e^{-2r} \left( -\frac{1}{2} \text{Re} \langle \hat{a}^2 \rangle + \frac{1}{4} + \frac{1}{2} \langle \hat{a}^\dagger \hat{a} \rangle \right) .
\]

Looking at the coherent vacuum, \( \hat{a} |\alpha\rangle = 0 \), hence,
\[
\Delta x_b = \frac{1}{2} e^r \quad \text{and} \quad \Delta y_b = \frac{1}{2} e^{-r} ,
\] (15.254)
and the squeezed state is at the uncertainty minimum.

### 15.6.3 Coherence of squeezed states

The squeezed state contains non-classical quantum correlations, as we will show by calculating \( g^{(1)} \) and \( g^{(2)} \) for squeezed states,
\[
g^{(2)}(0) = \frac{\langle \hat{b}^\dagger \hat{b} \rangle \langle \hat{b}^\dagger \rangle}{\langle \hat{b} \rangle^2} = 1 + \frac{\cosh 2r}{\sinh^2 r} .
\] (15.255)

The distribution functions in the coherent representation are,
\[
P_{|\beta\rangle}(\alpha) =
\]
\[
\rho =
\]
\[
Q_{|\beta\rangle}(\alpha) = \frac{\text{sech} r}{\pi} e^{-\frac{(|\alpha|^2 + |\beta|^2) + (|\alpha^* \beta + \alpha \beta^*|)}{2}} \sech r \tan \theta
\]
\[
and,
\]
\[
W_{|\beta\rangle}(\alpha) = \frac{1}{2\pi} \exp(-\frac{(\alpha + \alpha^*)^2}{2e^{2r}} + \frac{(\alpha - \alpha^*)^2}{2e^{2r}}) .
\] (15.257)

### 15.6.4 Homodyne signature

Let us mix squeezed light \( \hat{b} \) with a local oscillator \( \hat{a} \) at a beamsplitter,
\[
\begin{pmatrix}
\hat{x} \\
\hat{y}
\end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 & -i \\
-i & 1
\end{pmatrix} \begin{pmatrix}
\hat{b} \\
\hat{a}
\end{pmatrix} .
\] (15.259)

The homodyne signal is,
\[
P_{\text{hody}} \propto \hat{x}^\dagger \hat{x} - \hat{y}^\dagger \hat{y}
\]
\[
= 2 |\alpha| \left( \hat{b}_r \sin \theta - \hat{b}_p \cos \theta \right)
\]
(15.260)
if the local oscillator can be considered as classical, \( \alpha = |\alpha| e^{i\theta} \). I.e. the phase of the local oscillator permits us to select either one of the quadrature components.
15.6. Photon numbers in squeezed states

The numbers of photons in the squeezed state is $\langle n|\alpha, \xi \rangle = \left( \frac{\zeta}{2} \right)^n \frac{1}{\sqrt{n! \cosh r}} e^{-\frac{1}{2}(|\alpha|^2 + |\alpha|^2)} H_n \left( \frac{\alpha + \alpha^* \zeta}{\sqrt{2\zeta}} \right)$, with the abbreviation $\zeta \equiv e^{i\theta} \tanh r$. For squeezed vacuum $\alpha = 0$, noting that $H_n(0) = (-2)^{n/2}(n-1)!!$ for even $n$ and $H_n(0) = 0$ for odd $n$, we find, $\langle n|0, \xi \rangle = \left( -\zeta \right)^n \frac{1}{\sqrt{n! \cosh r}}$ for even photon number. Odd photon numbers are excluded.

In the photon representation we can easily see that the squeezed vacuum is (unlike the coherent and the Fock vacuum) not empty, $\langle \alpha, \xi | \hat{n} | \alpha, \xi \rangle = |\alpha|^2 + \sinh^2 |\xi| \frac{\alpha^* 0}{\alpha}$ and $\Delta_{\alpha, \xi} \hat{n} = |\alpha| + 2 \cosh^2 |\xi| \frac{\alpha^* 0}{\alpha} 2 \cosh^2 |\xi| \sinh^2 |\xi|$. Squeezed vacuum contains contributions from many $|n\rangle$.

For the squeezed vacuum state the photon number distribution displays odd-even-oscillations. This can be explained by the mathematical form of the squeezing operator, that resembles the operator for two-photon generation and annihilation processes. Photons in a squeezed vacuum state are more likely to appear in pairs.

15.6.6 Multimode squeezing

Define, $\hat{b} = \mu \hat{a} + \nu \hat{c}^\dagger$. Again using $\mu^2 - \nu^2 = 1$, the standard commutation rules for $\hat{a}$ and $\hat{c}$ give, $[\hat{b}, \hat{b}^\dagger] = 1$ and $[\hat{b}_r, \hat{b}_p] = \frac{i}{2}$.

The individual variances read, $\Delta \hat{b}_r = \langle \hat{b}_r^2 \rangle - \langle \hat{b}_r \rangle^2 = \frac{1}{4} \left( (\hat{b} + \hat{b}^\dagger)^2 - \frac{1}{2} (\hat{b} + \hat{b}^\dagger)^2 \right) = \frac{1}{4} \left( (\mu \hat{a} + \mu \hat{a}^\dagger + \nu \hat{c} + \nu \hat{c}^\dagger)^2 \right) = \frac{1}{4} \mu^2 + \frac{1}{4} \nu^2 + \frac{1}{2} \mu^2 \langle \hat{a} \hat{a}^\dagger \rangle + \frac{1}{2} \nu^2 \langle \hat{c} \hat{c}^\dagger \rangle = \frac{1}{2} \mu \nu \left( \langle \hat{a} \hat{c} \rangle + \langle \hat{a}^\dagger \hat{c}^\dagger \rangle \right)$. using $\langle \hat{a} \rangle = \langle \hat{c} \rangle = \langle \hat{a}^\dagger \hat{c} \rangle = 0$.

Two-mode squeezing can exist even if the individual modes are not squeezed, $|r, \phi \rangle = \cosh^{-1} r \sum_n \tanh^n r e^{i n \phi} |r, \phi \rangle_a |r, \phi \rangle_b$. (15.267)
A two-mode squeezed vacuum state can be generated by the squeezing operator

$$\hat{S}(\xi) \equiv \exp \left( \frac{\xi^*}{2} \hat{a} \hat{b} - \frac{\xi}{2} \hat{a}^\dagger \hat{b}^\dagger \right).$$  \hfill (15.268)

Remember that the single-mode squeezing is obtained if $\hat{a} = \hat{b}$. In a number state base

$$|r, \phi\rangle = \frac{1}{\cosh r} \sum_n (\tanh r)^n e^{in\phi} |n\rangle_a |n\rangle_b .$$  \hfill (15.269)

Two-mode relative number squeezing parameter

$$\xi_{i,j} = \sigma^2 (n_i - \langle n_j \rangle) \langle n_i \rangle + \langle n_j \rangle .$$  \hfill (15.270)

### 15.6.7 Exercises

#### 15.6.7.1 Ex: Unitarity of the squeezing operator

Calculate $\langle \hat{E} \rangle$ and $\Delta \hat{E}$.

#### 15.6.7.2 Ex: Transformation by the squeezing operator

Demonstrate the relationship (15.242).

#### 15.6.7.3 Ex: Squeezed states

Squeezed states may be introduced by the application of the operator $\hat{S}(\xi) \equiv e^{\frac{\xi^*}{2} \hat{a}^2 - \frac{\xi}{2} \hat{a}^\dagger 2}$ on a Glauber state $|\alpha\rangle$, where $\xi$ is the squeezing parameter. Calculate $\langle \alpha, \xi | \hat{n} | \alpha, \xi \rangle$ and show with $\alpha \to 0$, that the squeezed vacuum is not empty.

#### 15.6.7.4 Ex: Studying the squeezing operator

Using the Baker-Campbell-Hausdorff braiding identity,

$$e^{\hat{a}} e^{\hat{b}} e^{-\hat{a}} = e^{\hat{b} + \frac{1}{2} [\hat{x}, \hat{y}] + \frac{3}{12} [\hat{x}, [\hat{x}, \hat{y}]] + \ldots}$$

evaluate the expression $e^{\hat{a}^2 / 2} e^{\hat{a}^2 / 2} e^{-\hat{a}^2 / 2}$.

#### 15.6.7.5 Ex: Link between entanglement and squeezing

Prove that, if $\hat{a}_1$ and $\hat{a}_2$ are EPR-entangled beams with respect to quadrature components, then beams $\hat{b}_{1,2} = \frac{1}{\sqrt{2}} (\hat{a}_1 \pm \hat{a}_2)$ are squeezed with respect to two orthogonal quadrature components and vice versa [500, 501, 385].

### 15.7 Photon counting statistics
Chapter 16

Atomic motion in electromagnetic fields

So far – and especially in Sec. 4.5.6– we analyzed the motion of quantum particles in potential landscapes without specifying the physical origin of the potentials. We know the gravitational force, which can be derived from the Earth’s homogeneous attraction,

$$ F = -\nabla V_{\text{grav}} = -\nabla (mgz) = -gm\hat{e}_z. \quad (16.1) $$

Another fundamental force comes from electromagnetism. We have already studied – mainly in Sec. 9.3.2– the reaction of the electronic shell in atoms subjected to applied electromagnetic fields.

In contrast, the present chapter is devoted to the motion of the atomic center-of-mass subject to forces resulting from interactions with electromagnetic fields. We will begin, in the first section, with electromagnetic forces of the Coulomb-Lorentz type acting on charges (e.g. ions), permanent electric dipoles (e.g. polar molecules), or permanent magnetic dipoles (e.g. paramagnetic atoms). Also, more complex situations will be discussed, such as the scattering of light by confined atoms, atoms interacting with optical cavities, and adiabatic potentials.

The second section will entirely be devoted to the forces exerted by light beams, in particular the radiation pressure and the optical dipole force, which are nowadays widely used in atomic cooling and trapping experiments. We will leave the issue of the application of these forces to Chp. 24.6.6 and concentrate here on the (semiclassical or quantum) derivation and the interpretation of the forces. In fact, to understanding optical forces acting on atoms, we need to consider their internal degrees of freedom.

Apart from the degrees of freedom related to their center-of-mass motion (kinetic or potential energy), many quantum objects are endowed with internal degrees of freedom, for example, the motion of electrons inside atoms or molecules. In the simplest case, the Hamiltonian of such a system is composed of an outer part, comprising the kinetic and the potential energy, and an inner part counting for the excitation energy $\hbar \omega_0$ of an internal state $|e\rangle$,

$$ \hat{H}_{\text{atm}} = \frac{p^2}{2m} + V(r) + \hbar \omega_0 |e\rangle \langle e|. \quad (16.2) $$

The time scale of the electronic motion is usually very rapid compared to the motion of the nucleus, where (almost) the entire mass of the atom is concentrated. Therefore,
the external (nuclear) dynamics decouples from the internal (electronic) one, which allows the separation of the total wavefunction in two parts,

\[ |\psi\rangle = |\psi\rangle_{ext} |\psi\rangle_{ele} , \tag{16.3} \]

where for a simple two-level atom, \( |\psi(t)\rangle_{ele} = c_g(t)|g\rangle + c_e(t)|e\rangle \), with the atomic ground state \( |g\rangle \) and the excited state \( |e\rangle \). The external states are eigenstates of the momentum in the case of a free particle, \( |\psi\rangle_{ext} = |p\rangle \). For particles confined in a potential the external states are the vibrational eigenstates, \( |\psi\rangle_{ext} = |n\rangle \). The temporal evolutions of the internal and external degrees of freedom are governed by independent Schrödinger equations. For cold atomic clouds the kinetic energy is much smaller than the excitation energy, which allows the separation of the energy scales. That is, the internal degrees of freedom are frozen in the ground state. Many phenomena, for example, Bose-Einstein condensation and the dynamics of condensates are described in this regime.

Figure 16.1: The internal degrees of freedom of cold atoms are thermally frozen.

Nevertheless, the fact that it is thermally frozen does not prevent the intentional excitation of the internal degree of freedom by irradiating electromagnetic fields tuned close to resonances and coupling electronic energy levels. In the case of coupling, the external and internal degrees of freedom must both be considered.

### 16.1 Electromagnetic forces

Obviously, in order to allow for forces acting on the atomic center-of-mass, the atomic Hamiltonian must contain terms depending on the center-of-mass coordinates:

\[ \mathbf{F} = -\langle \nabla \hat{H}_{int} \rangle . \tag{16.4} \]

We will see shortly that some of terms may be dissipative, other conservative.

The impact of electromagnetic fields on the internal dynamics of atoms has already been studied in the Chp. 9.3.2. Here, we will focus on the force on the center-of-mass exerted by the gradient of electromagnetic potentials, where the Hamiltonian in Eq. (16.4) of a charge interacting with electromagnetic fields is obtained in minimum coupling (9.11) by,

\[ \hat{H}_{int} = \frac{1}{2m}(-i\hbar\nabla - q\mathbf{A})^2 + q\Phi \simeq \frac{-\hbar^2}{2m} \nabla^2 + \frac{i\hbar}{m} \mathbf{A} \cdot \nabla + q\Phi . \tag{16.5} \]
From this formula we can, in principle, calculate all electromagnetic forces.

The coupling of external and internal degrees of freedom is mediated by the photonic recoil transferred to the atom during absorption and emission processes. That is, the feature that the interaction with light simultaneously *excites* the atom and *exerts a force* couples the degrees of freedom. This fact manifests itself in the Hamiltonian of the atom interacting with a light field by the appearance of terms joining operators acting on different degrees of freedom,

\[ \hat{H} = \hbar \omega \hat{a}^\dagger \hat{a} + \hat{H}_{\text{int}} + \hat{H}_{\text{atm}} \quad \text{where} \quad \hat{H}_{\text{int}} = \hbar \Omega(\hat{\mathbf{r}}) e^{i \mathbf{k} \cdot \hat{\mathbf{r}}} \hat{\sigma} + \text{c.c.} , \]

where \( \hat{\sigma} \equiv |g\rangle \langle e| \) and \( \hat{a} \equiv \sum_n |n\rangle \langle n+1| \) and \( \hbar \Omega(\hat{\mathbf{r}}) \equiv \mathbf{d}_{12} \cdot \mathbf{E} \) is the coupling constant or *Rabi frequency*. The Hamiltonian is that of the Jaynes-Cummings model, except that in addition to the field operators \( \hat{a} \) and the atom transition operators \( \hat{\sigma} \), appears an operator for the position of the atom \( \hat{\mathbf{r}} \), whose quantum features we have not taken very seriously so far. It appears in the Rabi frequency and also in the term \( e^{i \mathbf{k} \cdot \hat{\mathbf{r}}} \). Now, we must remember, that

\[ U_{\text{momentum}} = e^{-i \mathbf{k} \cdot \hat{\mathbf{r}}} = |\mathbf{p} + \hbar \mathbf{k}| \langle \mathbf{p} | \]

is the unitary operator of the photonic recoil in the absorption process. We shall shortly see, that it is precisely this term in the Hamiltonian that gives rise to all phenomena related to light forces on atoms.

The presence of the position operator in the Jaynes-Cummings Hamiltonian introduces a new degree of freedom. With no external potential (that is, the system is invariant to spatial translations), this degree of freedom is simply the atomic center-of-mass momentum, such that the new set of quantum numbers is \( |j,n,\mathbf{p}\rangle \).

Strictly speaking we have to span the whole Hilbert space by an external product,

\[ \hat{H}_{\text{ele}} \otimes \hat{H}_{\text{rad}} \otimes \hat{H}_{\text{ext}}. \]

16.1.1 Forces on charges and electric dipole moments

As shown in Eq. (9.8), the equations (16.4) and (16.5) (obviously) lead to Coulomb-Lorentz forces on charges and currents.

In atomic optics, the Coulomb-Lorentz force is used, for example, to accelerate or trap ions (see Sec. 24.5) and other electrically charged particles.

Atoms naturally do not exhibit *permanent electric dipole moments*, when they are not subject to external electric fields. In contrast, polar molecules (such as heteronuclear dimers), which have permanent electric dipole moments can have their motion be influenced by inhomogeneous electric fields (see Sec. 24.5.3).

16.1.2 Forces on magnetic dipole moments

Neutral atoms are insensitive to electric fields. But as we have already seen in Chp. 9.3.2, the orbital motion of the electrons corresponds to a circular current generating a permanent magnetic dipole moment \( \mathbf{\mu} \), which can interact with external magnetic fields. We have already shown in the calculation (9.15) and (9.19) that the interaction energy (16.5) can be written as,

\[ U = -\mathbf{\mu}_J \cdot \mathbf{B} = -\frac{g_J \mu_B}{\hbar} \mathbf{J} \cdot \mathbf{B} \rightarrow -\frac{g_J \mu_B}{\hbar} |\mathbf{J}| \cdot |\mathbf{B}| = -g_J \mu_B m_J B, \]

(16.8)
where the Landé factor is given by the formula (9.21),
\[
g_J = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}.
\] (16.9)

Here, \( J = L + S \) is the total angular momentum resulting from the coupling of the total angular orbital momentum and the total spin of all electrons. If the atom has a nuclear spin \( I \) other than zero, then \( F = J + I \) replaces \( J \) in Eq. (16.8), and the \( g \)-factor generalizes to (9.35) \(^1\),
\[
g_F \simeq g_J \frac{F(F + 1) + J(J + 1) - I(I + 1)}{2F(F + 1)}.
\] (16.10)

In Sec. 9.2 we used the formula (16.8) to calculate the Zeeman shift of internal energy levels. But, according to the formula (16.4), the interaction also generates a force acting on the center-of-mass of atom,
\[
f = -g_F \mu_B m_F \nabla B.
\] (16.11)

In case of absence of hyperfine structure we simply replace \( f \) by \( J \).

Obviously, force is conditioned by the existence of a gradient of the absolute value of the magnetic field. It was first used in the famous Stern-Gerlach experiment, which led to the discovery of the electron (see Sec. 3.3.3). In atomic optics (see Sec. 24.4), this force is widely used to create magnetic traps for cold atoms. Resolve the Excs. 9.2.8.2, 16.1.4.1, and 16.1.4.2.

### 16.1.3 Adiabatic potentials

Adiabatic potentials can be used to realize more complicated trapping geometries \([125]\). To study adiabatic potentials we consider the two-level system \( |\frac{1}{2}, \frac{1}{2}\rangle \leftrightarrow |\frac{1}{2}, -\frac{1}{2}\rangle \) coupled by an incident radiation (e.g. a radiofrequency). A generalization to multilevel systems \( F > \frac{1}{2} \) is simple. The dressed states Hamiltonian of our two-level system is a \( 2 \times 2 \) matrix,
\[
\hat{H}(z) = \begin{pmatrix}
\frac{1}{2} \mu_B g_F B(z) - \frac{1}{2} \hbar \omega & \frac{1}{2} \hbar \Omega \\
\frac{1}{2} \hbar \Omega & -\frac{1}{2} \mu_B g_F B(z) + \hbar \omega
\end{pmatrix}.
\] (16.12)

For simplicity, we assume a one-dimensional geometry, \( B = B(z) \), but we can easily generalize to three dimensions. The eigenvalues of \( \hat{H} \) are,
\[
E_{\pm}(z) = \pm \frac{1}{2} \sqrt{\hbar^2 \Omega^2 + [\mu_B g_F B(z) - \hbar \omega]^2}.
\] (16.13)

Sufficiently far from resonance, \( \hbar \Omega \ll |\mu_B g_F B(z) - \hbar \omega| \), we obtain,
\[
E_{\pm}(z) \approx \pm \frac{1}{2} |\mu_B g_F B(z) - \hbar \omega| + \frac{\hbar^2 \Omega^2}{4 |\mu_B g_F B(z) - \hbar \omega|},
\] (16.14)

\(^1\)Note that the formula only applies to weak fields. For strong fields the Zeeman unfolding changes to the Paschen-Back unfolding of the hyperfine structure.
where the second term can be interpreted as the dynamic Stark shift of the energy levels.

To illustrate the influence of the radiofrequency, we calculate the potential energy and the dressed states assuming a linear 1D magnetic field gradient $B(z) \equiv zb$. Fig. 16.2(a) illustrates the radiofrequency coupling and Fig. 16.2(b) the dressed states for two magnetic substates coupled by a radiofrequency. The minimum emerging in the upper curve of Fig. 16.2(a) may serve as a confinement potential. Using an rf-radiation composed by several frequencies, potential minima can be realized at several distances $z$. In Exc. 16.1.4.3 we calculate an example.

In the dressed states basis with the Hamiltonian (16.12), the force is calculated from,

$$ F(r) = \langle \hat{F}(r) \rangle = -\text{Tr}_{\text{atom, laser}} \hat{\rho} \nabla_r \hat{H} = -\sum_{n,j} \langle n,j| \hat{\rho} \nabla_r \hat{H} |j,n \rangle. \quad (16.15) $$

We consider only one dimension and disregard the degrees of freedom of the radiation field,

$$ F(z) = -\text{Tr}_{\text{atom, laser}} \hat{\rho} \partial_z \hat{H} $$

$$ = -\sum_j \langle j| \hat{\rho} \partial_z \left( \frac{\mu_B g_F B}{2} |1\rangle \langle 1| - \frac{\hbar \omega_F}{2} |2\rangle \langle 2| + \frac{\hbar \omega}{2} |2\rangle \langle 2| + \frac{\hbar \Omega}{2} e^{ikz} \hat{\sigma}^+ + c.c. \right) |j \rangle. \quad (16.16) $$

Here we neglect any possible position dependence of $\Omega,$

$$ F(z) = -\frac{1}{2} \mu_B g_F \partial_z B \sum_j \langle j| \hat{\rho} (|1\rangle \langle 1| - |2\rangle \langle 2|) |j \rangle = -\frac{1}{2} \mu_B g_F \partial_z B (\rho_{11} - \rho_{22}) \quad (16.17) $$

If the atoms enter the coupling area adiabatically, the populations of the adiabatic potentials will only depend on $z$. This is analogous to the adiabatic transfer via adiabatic sweeps or STIRAP pulse sequences. If the atoms are too fast, the populations also depend on history (i.e. the recent trajectory of the atoms), which can result in Landau-Zener transitions to other (possibly untrapped) states.
16.1.4 Exercises

16.1.4.1 Ex: The Stern-Gerlach effect

Consider initially motionless $^{87}\text{Rb}$ atoms trapped in a superposition of two the trappable Zeeman states $|F, m_F\rangle = |2, +2\rangle$ and $|1, -1\rangle$. Suddenly a magnetic gradient of $\partial_z B = 100 \, \text{G/cm}$ is applied for 2 ms. Calculate the spatial separation of the atoms being in either one of the two states after 10 ms of ballistic expansion.

16.1.4.2 Ex: Potential for magnetic trapping

Invent a potential for magnetic confinement.

16.1.4.3 Ex: Adiabatic potentials

An adiabatic potential can be used to create more complicated trapping potentials [125]. To study these potentials we consider a system of two Zeeman states $m = \frac{1}{2}$ coupled by a radiofrequency radiation $\hbar \omega$. The dressed states Hamiltonian of our two-level system is a $2 \times 2$ matrix,

$$\hat{H} = \begin{pmatrix} \frac{1}{2} \mu_B B - \frac{1}{2} \hbar \omega & \frac{1}{2} \hbar \Omega \\ \frac{1}{2} \hbar \Omega & -\frac{1}{2} \mu_B B + \frac{1}{2} \hbar \omega \end{pmatrix},$$

defining the energetic zero in the middle between the states. Now, assume that the magnetic field grows linearly along the axis $z$, $B(z) = z \partial_z B$, where $\partial_z B$ is the gradient. Also assume that the radiofrequency is tuned in resonance with the difference of the energies of the Zeeman states at some distance $z_0$ such that, $\hbar \omega = \mu_B z_0 \partial_z B$.

a. Calculate the eigenenergies of the coupled system as a function of $z$.
b. Expands eigenenergies around the position $z_0$.
c. What would be the oscillation frequency of the trapped atoms inside the adiabatic potential?
d. Expands the eigenenergies in $\hbar \Omega$ for locations away from resonance.

16.2 Optical forces

Light carries momentum, and the scattering of light by an object produces a force on that object. Although these properties of light are direct consequences of Maxwell’s classical theory of electromagnetism, they were only verified in 1933 by Frisch, who observed a very small transverse deviation ($3 \cdot 10^{-5} \, \text{rad}$) of an atomic sodium beam exposed to the light of a lamp. With the invention of the laser, it became easier to observe the light’s mechanical effects, because the more intense and highly directional laser light exerts much larger forces. Although these results sparked the interest in using light forces to control the motion of neutral atoms, the fundamental bases for understanding the physics of light forces were not developed before the late 1970s. Unequivocal experimental demonstrations of cooling and trapping of atoms were not performed before the mid-1980s. In this section we will discuss some fundamental aspects of light forces. Practical schemes used to cool and trap neutral atoms will be presented in Secs. 24.2 and 24.3.
The light force acting on an atom can be of two types: a spontaneous dissipative force and a conservative dipole force. The spontaneous force arises from the recoil experienced by an atom when it absorbs or emits a quantum of light. As we saw in Sec. 1.2.6, when an atom scatters light, the resonant scattering cross section can be written as in Eq. (1.73), $\sigma_{0a} = \frac{g_2 \lambda_0^2}{4\pi}$, where $\lambda_0$ is the resonant wavelength. In the optical region of the electromagnetic spectrum the wavelengths of light are of the order of several hundred nanometers, and the resonant cross sections for scattering become very large, ($\sim 10^{-9}$ cm$^2$). Each absorbed photon transfers a quantum of momentum $\hbar k$ to the atom in the direction of propagation. Spontaneous emission following an absorption process occurs in random directions and, hence, averaged over many absorption-emission cycles, it cancels to zero. Consequently, the total spontaneous force acts on the atom in the propagation direction of the light, as shown schematically in the diagram of Fig. 16.3. The saturated photon scattering rate via spontaneous emission (the reciprocal value of the excited state’s lifetime) sets the upper limit for the magnitude of the force. This force is called radiation pressure force.

The dipolar gradient force can be easily understood by considering light as a classical wave. It is simply the time-averaged force resulting from the interaction of the transition dipole –induced by the oscillating electric field of the light– with the gradient of the electric field amplitude. The strength of this gradient can be controlled, e.g. by focusing the light beam. By tuning the optical frequency below or above an atomic transition, we can control the sign of the force acting on the atom: Tuning the light below resonance attracts the atom to the center of the light beam, tuning it above resonance repels it. The dipole force is a stimulated process without energy exchange between the field and the atom. Photons are absorbed in one light mode and reappear by stimulated emission in another one. However, conservation of momentum requires that the change in the propagation direction of the scattered photons from an initial mode to a final mode leaves the atom with a recoil. Contrary to spontaneous force, there is, in principle, no upper limit for the magnitude of the dipole force, since it is a function of the field gradient only and the detuning.

Within the theory of electromagnetism we calculate radiative forces on charges via Maxwell’s stress tensor$^2$. The interaction of radiation with atoms having internal degrees of freedom exhibiting resonances can be treated qualitatively by the Lorentz model$^3$. In the following, we will show quantitative semi-classical and quantum calculations: The force of a light beam on an atom can be calculated in many different ways, each emphasizing a slightly different aspect: From the classical Lorentz force exerted on an atom by electromagnetic fields we can derive a semi-classical Fokker-Planck equation [578]. In Sec. 16.2.1 we will derive the two contributions (dipole force and radiative pressure) within a semi-classical theory [225]. Wineland et al. [634] chose as starting point the cross section for an elementary scattering process (Sec. 16.2.3). Dalibard et al. [136] developed a quantum theory using the dressed states representation (Sec. 16.2.2). And Cirac et al. [108] showed an approach based on the master equation (Sec. 16.2.3).

$^2$See script on Electrodynamics (2020), Sec. 6.2.3.

$^3$See script on Electrodynamics (2020), Sec. 7.2.4.
16.2.1 The dipolar gradient force and the radiation pressure force

To compute the forces of light on an atom, we describe the atom as a two-level system: A fundamental level $|1\rangle$ and an excited level $|2\rangle$ decaying to the fundamental level with the rate $\Gamma$. The energy difference between the levels is $\omega_0 \equiv E_2 - E_1$. The light with frequency $\omega$ is derived from a laser beam, which can be detuned from the atomic transition, $\Delta \equiv \omega - \omega_0$. To describe the interaction, we consider the part (16.6) of the total Hamiltonian describing the interaction [136]. Using the density operator $\hat{\rho}$, we can calculate the force that the light field exerts on the atom,

$$F(r) = (\hat{F}(r)) = -\text{Tr}_a \hat{\rho} \nabla_r H_{\text{int}}$$

$$= -\frac{1}{2}\hbar \sum_j \langle j | \hat{\rho} \nabla_r (\Omega(r) e^{i k r - i \Delta t} |2\rangle \langle 1| + \Omega(r) e^{-i k r + i \Delta t} |1\rangle \langle 2|) |j\rangle$$

$$= -\frac{1}{2}\hbar \nabla_r \Omega(r) \left( \langle 1 | \hat{\rho} e^{i k r - i \Delta t} |2\rangle + \langle 2 | \hat{\rho} e^{-i k r + i \Delta t} |1\rangle \right)$$

$$- \frac{i}{2}\hbar k \Omega(r) \left( \langle 1 | \hat{\rho} e^{i k r - i \Delta t} |2\rangle - \langle 2 | \hat{\rho} e^{-i k r + i \Delta t} |1\rangle \right).$$

Now, let the atom be at the position $r = 0$,

$$F(0) = -\frac{1}{2}\hbar \nabla_r \Omega(0) (\rho_{12} e^{-i \Delta t} + \rho_{21} e^{i \Delta t}) - \frac{i}{2}\hbar k \Omega(0) (\rho_{12} e^{i \Delta t} - \rho_{21} e^{-i \Delta t}).$$  \hspace{1cm} (16.19)

The quantities $\rho_{12} \equiv \langle 1 | \hat{\rho} |2\rangle = \rho_{21}$ are the coherences, which develop in a two-level system excited by a laser beam. Inserting the stationary solutions of the Bloch equations,

$$\rho_{22} = \frac{\Omega^2}{4\Delta^2 + 2\Omega^2 + \Gamma^2} \quad \text{and} \quad \rho_{12} = \frac{(2\Delta - i \Gamma) \Omega}{4\Delta^2 + 2\Omega^2 + \Gamma^2} e^{-i \Delta t}.$$  \hspace{1cm} (16.20)

we obtain

$$F(0) = -\frac{1}{2}\hbar \nabla_r \Omega \left( \frac{4\Delta \Omega}{4\Delta^2 + 2\Omega^2 + \Gamma^2} + \hbar k \frac{\Gamma \Omega^2}{4\Delta^2 + 2\Omega^2 + \Gamma^2} \right).$$  \hspace{1cm} (16.21)

With the definition of the cross section, $\sigma_a(\Delta) = \sigma_{a0} \frac{\Gamma^2}{4\Delta^2 + 4\Omega^2 + \Gamma^2}$,

$$F(0) = -\frac{1}{2}\hbar \Delta \nabla_r \ln \left( 1 + \frac{4\Omega^2}{4\Delta^2 + \Gamma^2} \right) + \hbar k \frac{\Omega^2 \sigma_a(\Delta)}{\Gamma \sigma_{a0}}.$$  \hspace{1cm} (16.22)

The resonant cross section for a 'classical' transition is $\sigma_{a0} = 3\lambda^2/2\pi$.

Apparently, the force comprises two contributions. The dipolar gradient force can be derived from a potential. It is proportional to the intensity gradient and can be interpreted as resulting from absorption processes immediately followed by self-stimulated emission. Near resonance it is dispersive. Far from resonance it can be approximated by,

$$F_{dp} = \nabla_r \left( -\hbar \frac{\Omega^2}{4\Delta^2 + \Gamma^2} \frac{|\Delta| \gg \Gamma}{\nabla_r \left( -\hbar \frac{\Omega^2}{4\Delta^2 + \Gamma^2} \right)}. \hspace{1cm} (16.23)$$

\footnote{The density operator consists of an inner part (atomic excitation) and a light part $\hat{\rho} = \hat{\rho}_{\text{atom}} \otimes \hat{\rho}_{\text{laser}}$, where the part of the motion $\hat{\rho}_{\text{motion}}$ was omitted, despite having an important role in atomic optics.}
The radiation pressure force is dissipative. Close to resonance it is absorbing. It is proportional to the phase gradient and the only force exerted by plane waves. It can be interpreted as resulting from absorption processes followed by spontaneous emission. With $\Omega^2 = \sigma_a(\Delta) \Gamma / \hbar \omega$ we get a formula,

$$F_{rp} = \hbar k \frac{I}{\hbar \omega} \sigma_a(\Delta) = \hbar k \gamma_{sc} \Delta,$$

which describes the force as a product of the number of photons in the incident beam, $I/\hbar \omega$, the absorption cross section, $\sigma_a(\Delta)$, and the recoil momentum per photon, $\hbar k$. $\gamma_{sc}$ is the scattering rate. The dipole gradient force (and the associated potential) is

$$F_{dp} = -\frac{\hbar \Delta}{6} \frac{1}{1 + s} \nabla s = \frac{\hbar \Delta}{6} \nabla \ln[1 + s] \quad \text{and} \quad F_{rp} = \frac{\hbar k \Gamma}{6} \frac{s}{1 + s}.$$

Eq. (16.26) shows that the radiation pressure force 'saturates' as $s$ increases, and is therefore limited by the spontaneous emission rate. The saturation parameter essentially describes the relative importance of terms appearing in the denominator

Figure 16.3: (a) An atom with mass $m$ and velocity $v_A$ moves to the right and absorbs a photon propagating to the left with momentum $\hbar k_L$. Center: An excited atom suffers a change of momentum $p_A = mv_A - k_L$. (b) The isotropic reemission of a photon results, averaged over many absorption-emission cycles, in a momentum change for the atom of $\langle p_A \rangle = mv_A - k_L$.

often used to spatially confine atoms, and the radiation pressure force is often used to cool them down. Note that we still need to correct Eqs. (16.23) and (16.24) to take into account the square of the average over the possible spatial orientations of the transition matrix element $d_{12}/3$.

The saturation parameter,

$$s = \frac{1}{2} \frac{\Omega^2}{\Delta^2 + \frac{1}{4} \Gamma^2},$$

allows to write the dipolar gradient force and the radiative pressure force as,

Eq. (16.26) shows that the radiation pressure force 'saturates' as $s$ increases, and is therefore limited by the spontaneous emission rate. The saturation parameter essentially describes the relative importance of terms appearing in the denominator.
of the line profile function for the light forces. The spontaneous emission rate is an intrinsic property of the atom, proportional to the square of the atomic transition dipole moment, whereas the square of the Rabi frequency is a function of the incident laser intensity. If \( s \ll 1 \), the spontaneous emission is fast compared to any stimulated process, and the light field is said to be weak. If \( s \gg 1 \), the Rabi oscillation is fast compared to spontaneous emission and the field is considered as strong. The line profile factor indicates a ‘power broadening’ by saturation of a factor of \( \sqrt{2} \). Note that the dipolar gradient force and potential, Eqs. (16.26), do not saturate when the intensity of the light field is increased. Usually \( F_{dp} \) and \( U_{dp} \) are used to manipulate and trap atoms in a laser beam tuned far away from resonance in order to avoid absorption.

Often, the transition moment can be oriented using circularly polarized light. In this case, all previous expressions for \( F_{dp} \), \( F_{rp} \), and \( U_{dp} \) should be multiplied by 3. From now on we will abandon the average over the orientations and only use \( d^2_{12} \) for the square of the transition dipole moment. Solve Excs. 16.2.5.1 and 16.2.5.2.

### 16.2.2 Semiclassical calculation of dipole force and radiative pressure

In quantum mechanics we calculate the force from the Heisenberg equation [225],

\[
\hat{F} = \frac{d}{dt} \hat{p} = i \frac{\hbar}{\hbar} [\hat{H}, \hat{p}] = -\nabla_r \hat{H}_{int} \ .
\] (16.27)

Thus, the force is given by the gradient of the interaction energy between the atom and the light field. Within the dipole approximation the interaction energy is given by \( d \cdot \vec{E}(r) \). The force is now,

\[
F(r) = \langle \hat{F}(r) \rangle = \langle \nabla_r [d \cdot \vec{E}(r)] \rangle = \langle (d \cdot \nabla_r)\vec{E}(r) \rangle - \langle d \times (\nabla_r \times \vec{E}(r)) \rangle \quad (16.28)
\]

\[
\equiv F_C(r) + F_L(r) \ .
\]

The first contribution can be interpreted as the Coulomb force acting on the electron performing rapid oscillations at the position \( r(t) = r_0 + e^{-1}P(r_0, t) \). The second term is the time-averaged Lorentz force acting on the oscillating electric dipolar moment [270, 273, 271],

\[
F_C = e \langle \vec{F} \rangle \quad \text{and} \quad F_L = -\langle d \times \partial_t \vec{B} \rangle = \langle \partial_t d \times \vec{B} \rangle \ .
\] (16.29)

The relation between the light-induced electric dipole moment and the polarizability, \( d = \alpha(\vec{E})\vec{E} \), where \( \alpha_{\nu\nu} \equiv \alpha_{\nu} + i\beta_{\nu} \) and \( E_{\nu} \equiv \sqrt{I_{\nu}}e^{i\psi_{\nu}} \), becomes,

\[
F = \sum_{\nu=1}^{3} \alpha_{\nu} \nabla I_{\nu} + 2 \sum_{\nu=1}^{3} \beta_{\nu} I_{\nu} \nabla \psi_{\nu} \ .
\] (16.30)

### 16.2.3 Force exerted by a quantized radiation field

Photons carry one unit of momentum \( p = \hbar k \), which they transfer to the atom during an absorption or emission process. That is, the light exerts a recoil on the atoms.
16.2. OPTICAL FORCES

Spontaneous emission couples to all radiative modes of the electromagnetic vacuum, $H_{cm-vacuum} = \sum_j H_{cm-laser}(k_j)$. We can trace over these variables and only keep those of the atom and the laser. Following Cirac et al. [634, 108], the randomness of the recoil by spontaneous emission is accounted for by,

$$\hat{\rho} \to \int_{4\pi \mathbb{R}^2} S(r)e^{ik\cdot r} \hat{\rho} e^{-ik\cdot r} d\Omega,$$

such that the Lindblad operator becomes,

$$L_{atom}\hat{\rho} = -\Gamma\{\hat{\sigma}^\dagger \hat{\sigma} \hat{\rho}(t) - \frac{\alpha}{4\pi} \int S(r) e^{ik\cdot r} \hat{\sigma} \hat{\rho}(t) \hat{\sigma}^\dagger e^{-ik\cdot r} d\Omega + \hat{\rho}(t) \hat{\sigma}^\dagger \hat{\sigma}\}$$

(16.32)

$$L_{cavity}\hat{\rho} = -\kappa\{\hat{a}^\dagger \hat{a} \hat{\rho}(t) - 2\hat{a} \hat{\rho}(t) \hat{a}^\dagger + \hat{\rho}(t) \hat{a}^\dagger \hat{a}\},$$

where $e^{\pm ik\cdot r} = \sum_p |p\mp ik\cdot r\rangle\langle p|$ and $S(r) = \frac{1}{2} (1 + (\frac{k\cdot r}{kr})^2)$ and $d\Omega = d\varphi d\cos \vartheta$. From this they calculate the force and establish a Fokker-Planck equation for the Wigner function.

16.2.4 Refraction of atoms by light and of light by atoms

Non-resonant light acts on the external degrees of freedom of atoms by a phase shift of the Broglie wave, $\exp[\frac{i\hbar}{\hbar} \int U(r,t) dt]$, and simultaneously on the internal degrees of freedom by a dynamic Stark shift or light shift of the energy levels by the value of $U(r)$. The Bloch vector defined by,

$$\rho \equiv \begin{pmatrix} \frac{1}{\sqrt{2}} c_p c_e^* \\ \frac{1}{\sqrt{2}} c_p^* c_e \\ |c_e|^2 - |c_g|^2 \end{pmatrix}$$

(16.33)

describes, under the influence of the dispersive interaction, a precession around the polar axis. This was discussed in Exc. 14.5.5.6. The Stark shift causes a rotation of $\hbar^{-1} U(r)t$. Simultaneously, the atom is subjected to a force, which corresponds to the gradient of the potential $-\nabla U(r)$, as illustrated in Fig. 16.4(a). We see that the phase shifts of the Broglie wave and the Bloch vector are equal. Finally, the light mode phase is also shifted by the same amount in an effect called refraction. That is, the internal, external, and optical degrees of freedom are entangled.

This fact has a practical use in atomic interferometers, because it is often easier to detect an interference of internal excitation states rather than of Broglie waves. Because of the entanglement, it is sufficient to measure one interference pattern to know the other one.

By local variations of the potential $U(r)$, e.g. induced by a focused laser beam, it is possible to manipulate a Broglie wavefront in the same way that, in classical optics, we manipulate the wavefront of a light beam by lenses or other objects, such as for instance, the refractive index represented by an atomic cloud near resonance, as illustrated in Fig. 16.4(b).

The orientation of the force depends on the light frequency as compared to the resonant frequency. The dipolar force attracts the atom to regions where the light field
CHAPTER 16. ATOMIC MOTION IN ELECTROMAGNETIC FIELDS

Figure 16.4: Diagram (a) shows product states and dressed states for blue detuning. Note that the population is in the upper level and that the atom is subject to a repulsive weak field seeking force when it enters the laser beam. Diagram (b) is similar, but for red detuning. The population is in the lower level and the atom is subject to an attractive high field seeking force.

is strong, when the frequency is tuned below $\omega_0$, and it attracts the atom to regions of weak fields, when tuned above $\omega_0$. Integration over the relevant spatial coordinates results in an effective potential or barrier to the atom. The qualitative behavior of the dipolar potential and its effect on the motion of atoms is easily visualized in the dressed states picture. Fig. 16.5 shows what happens when an atom enters a well defined region of an optical field, for example a focused laser beam.

Figure 16.5: Analogy between light optics and atomic optics.

Outside the atom-dipole coupling zone the expression $\hbar \Omega$ is despicable and the 'dressed states' are just the atom-field product states. When the atom enters the field, this expression becomes nonzero and the atom-field states combine to produce a set of dressed states. The energy levels of the product states 'repel' each other and approach the dressed states levels. Assuming that the laser is sufficiently detuned to maintain the absorption rate negligible, the population remains in the ground state. We see that blue (red) detuning leads to a repulsive (attractive) potential for atoms remaining in the grounded state. In addition, since $\hbar \Omega$ is directly proportional to the root of the laser intensity, an increase in that intensity (optical power per unit area) obviously amplifies the force on the atom ($\mathbf{F} \simeq \nabla R \Omega$).
16.3. PHOTONIC RECOIL ON FREE AND CONFINED ATOMS

16.2.5 Exercises

16.2.5.1 Ex: Dipole force for large detunings

Verify that in the limit of large detunings the dipole potential Eq. (16.22) tends to $\rightarrow \frac{\Omega^2}{4\Delta}$.

16.2.5.2 Ex: Radiation pressure

Calculate the radiation pressure force exerted on a strontium atom by a laser beam in plane wave geometry ($I = 10$ mW/cm$^2$) tuned 50 MHz below the resonance at 461 nm ($\Gamma/2\pi = 30.5$ MHz).

16.3 Photonic recoil on free and confined atoms

A trap confining the atomic motion can dramatically modify the way in which they interact with light. For instance, a trapping potential may alter the scattering rate, the scattering angle, and the transfer of photonic recoil. However, potentials do not exist in microscopic reality, not more than friction forces do. What exists, as we learn in electrodynamics, are electromagnetic fields exerting Coulomb and Lorentz forces. When we write down the Hamiltonian $\hat{H} = \frac{p^2}{2m} + V(r)$ in quantum mechanics, we already make an important approximation, because the potential $V(r)$ is an artifact obtained by tracing over all those degrees of freedom, which are necessary to generate a force field that can be approximated by a conservative potential.

In the great majority of situations, the approximation is very good. Problems may however arise, when the momentum conservation comes into play, which is the case e.g. of light scattering from ultracold atoms being accelerated by the photonic recoil and shifting the scattered light via the Doppler effect. We then have to address the issue of photonic recoil conserving (or not) the momentum.

Let us begin with a recapitulation of the classical picture of the scattering process applying the rules of energy and momentum conservation to the elastic collision between a free atom and a photon. This process is known as Compton scattering.

16.3.1 Recoil- and Doppler-shift in classical mechanics

In classical mechanics we speak of elastic scattering when no energy is transferred to internal degrees of freedom of the collision partners, so that kinetic energy and momentum stay conserved. This concept can be transferred to quantum particles (e.g. atoms) and photons. In elastic Compton scattering, if the atoms keep their initial internal excitation, the law of momentum conservation requires the transfer of photonic momentum to the scattering atom which, consequently, changes its kinetic energy. To compensate for this kinetic energy change, the frequency of the scattered light must change in order to preserve the total energy, as illustrated in Fig. 16.6(b).

We will calculate in the following the frequency distribution of the light scattered by an atom as a function of its initial velocity $p_1$, of the frequency $\omega_1$ of the incident light. The interaction also depends on other parameters, such as the geometry of the confinement potential and on cooperative effects (bosonic stimulation), but this will be discussed later.
light and of the scattering angle, that is, the angle between the modes $k_1$ and $k_2$. We begin by writing the laws of conservation of energy and momentum,

$$\hbar k_1 + p_1 = \hbar k_2 + p_2 \quad (16.34)$$

$$\hbar \omega_1 + \frac{p_1^2}{2m} = \hbar \omega_2 + \frac{p_2^2}{2m}.$$ 

Eliminating $p_2$ from the second equations, we obtain,

$$\hbar \omega_1 - \frac{\hbar^2 k_1^2}{2m} - \frac{\hbar k_1 \cdot p_1}{m} = \hbar \omega_2 + \frac{\hbar^2 k_2^2}{2m} - \frac{(\hbar k_1 + p_1) \cdot \hbar k_2}{m}.$$ 

(16.35)

The photonic recoils of the incident and of the scattered light are almost equal,

$$\omega_{rec} \equiv \frac{\hbar k_1^2}{2m} \simeq \frac{\hbar k_2^2}{2m},$$

(16.36)

such we can approximate,

$$\omega_2 - \omega_1 = \omega_1 \left[\frac{1 - \frac{\hbar \omega_1}{m c^2} - \frac{p_1 v_1}{m c} \cos \angle(k_1, p_1)}{1 - \frac{\hbar \omega_1}{m c^2} \cos \angle(k_1, k_2) - \frac{p_1 v_1}{m c} \cos \angle(p_1, k_2)}\right].$$

(16.37)

using $\omega_1 = c k_1$, or also,

$$\omega_2 - \omega_1 = \omega_1 \left[\frac{\frac{\hbar \omega_1}{m c^2} [1 + \cos(\vartheta_{in} - \vartheta_{out})] + \frac{p_1 v_1}{m c} (\cos \vartheta_{out} + \cos \vartheta_{in})}{1 - \frac{\hbar \omega_1}{m c^2} \cos(\vartheta_{in} - \vartheta_{out}) - \frac{p_1 v_1}{m c} \cos \vartheta_{out}}\right],$$

(16.38)

where we call the angles $\vartheta_{in} = \angle(k_1, p_1)$, $\vartheta_{out} = \angle(k_2, p_1)$, and $\vartheta = \vartheta_{in} - \vartheta_{out} = \angle(k_1, k_2)$. For non-relativistic velocities, the denominator is approximately 1:

$$\omega_2 - \omega_1 = 2 \omega_{rec} (-1 + \cos \vartheta) + k_1 v_1 (\cos \vartheta_{out} + \cos \vartheta_{in}),$$

(16.39)

with $p_1 = m v_1$. The first term describes the recoil shift and the second term the Doppler shift.

The second term vanishes for initially at resting atoms, $p_1 = 0$, and Eq. (16.39) simplifies to,

$$\omega_2 - \omega_1 = 2 \omega_{rec} (-1 + \cos \vartheta).$$

(16.40)
It also vanishes for atoms which have no velocity component in the scattering plane spanned by the wavevectors $k_1$ and $k_2$, that is $\vartheta_{\text{out}} = 180^\circ - \vartheta_{\text{in}}$ \footnote{This situation is often realized in Bragg scattering from optical lattices \cite{560, 562, 561}.}, for which case we get the maximum recoil shift,

$$\omega_2 - \omega_1 = -4\omega_{\text{rec}} . \quad (16.41)$$

The recoil shift is a consequence of momentum conservation.

The recoil shift is typically on the order of $\omega_2 - \omega_1 \approx (2\pi) 10$ kHz, which in many situations is negligible (e.g. when we deal with thermal atomic clouds), such that we can consider the scattering as elastic, i.e. the first term can be disregarded. Considering, for simplicity, only backscattering, $\cos \vartheta_{\text{out}} = \cos \vartheta_{\text{in}} = 1$, then Eq. (16.39) simplifies to,

$$\omega_2 - \omega_1 = 2k_1 v_1 . \quad (16.42)$$

Obviously, the frequency shift depends on the initial velocity through the Doppler shift $k_1 v_1$. In a thermal gas, the velocities are distributed according to the Maxwell-Boltzmann distribution. Therefore, Rayleigh scattering of light off a cloud of free thermal atoms is subject to Doppler broadening \footnote{This Doppler broadening is explored e.g. in RIR spectroscopy, where the momentum distribution in $p_1$ reveals as a frequency distribution $\Delta \omega = \omega_2 - \omega_1$ of Bragg-scattered light, which can be measured by beating with an irradiated idler mode, which can be chosen as being identical to $k_2$.}

16.3.2 Kicking a free atom

A conceptual difficulty arises from the incompatibility of scattering picture (generally described in homogeneous space with momentum conservation) and the trapping picture (when it is described in inhomogeneous space without momentum conservation). The difficulty can be avoided by separating the processes into a ‘kick’ followed by a harmonic oscillation, for which we have to calculate the time-dependence of the states and the observables. We will leave the discussion of such a scattering process to 16.3.3 and for the time being just focus on the time evolution of a harmonic oscillator that just received a kick.

By a ‘kicking’ an atom we denote a change of momentum within an arbitrarily short amount of time. The shorter the kick-time the larger is, according to Heisenberg’s uncertainty relation, the spectrum of possible kinetic energies that can be reached by the kick (see Sec. 5.4.3). However, the spectrum is restricted by the free-particle dispersion relation, as illustrated in Fig. 16.6(a).

The kick is not a realistic physical concept, as it corresponds to an infinitely strong and infinitely short force \footnote{which is what allows us to write down a potential}. In a microscopic scattering process it assumes an infinitely heavy collision partner, while we are more interested in photon scattering. Consequently, in this case the spectrum of reachable energies is determined by the frequency of the photon and the free-particle dispersion relation. We will now turn our attention to the (Compton-)scattering of light by free atoms.
16.3.3 Elastic light scattering from a single weakly or strongly confined atom

We mentioned in the last subsection that a scattering process is elastic when none of the collision partners changes its internal excitation energy. The situation becomes, however, more complex when one of the collision partners is confined in a potential, as we will show in the following.

16.3.3.1 Cooperativity in light scattering

In light scattering cooperativity means breaking of the isotropic symmetry for the angular distribution of scattered modes. In this sense, the anisotropic scattering from an atom confined in an anisotropic trap is cooperative. But there are other cooperative scattering effects messing with isotropy and shaping the density-of-states, like the Purcell effect in the presence of an optical cavity or a photonic band gap concentrating optical modes in a specific solid angles [265]. Another cooperative effect, which is observed in the presence of other atoms, has to do with bosonic stimulation by the optical output mode (as in Bragg scattering [560, 562, 561]) or the momentum sidemode (as in stimulated matter wave 4WM). These effects, which all need to be considered in calculations of the static structure factor ruling the scattering of light, are often strong enough to hide the role of an anisotropic trapping potential. In the following subsections we will disregard all these effects and concentrate on a single trapped atom.

The simple picture of Compton scattering presented in Sec. 16.3.1 holds for free atoms, whose dynamics is totally understood in terms of their internal electronic excitation ($\hat{H}_{ele}$), the kinetic energy of their center-of-mass ($\hat{H}_{cm} = \frac{\hat{p}^2}{2m}$), the radiation field ($\hat{H}_{rad}$) (which may be treated classically under the circumstances discussed here), and the coupling ($\hat{H}_{int}$) of all three degrees of freedom,

$$\hat{H}_{\text{free}} = \hat{H}_{ele} + \hat{H}_{cm} + \hat{H}_{rad} + \hat{H}_{int}.$$  \hspace{1cm} (16.43)

Transition probabilities are readily calculated using Fermi’s Golden rule, because the density-of-states distributions for the final radiation modes receiving the scattered photons (photonic density-of-states) and the recoil modes receiving the scattered atoms (phononic density-of-states) are white, that is, without resonances, and isotropic.

In the presence of an imposed trapping potential, an additional term appears in the Hamiltonian, which has the capacity of dramatically changing the scattering features,

$$\hat{H}_{cm} = \frac{\hat{p}^2}{2m} + \hat{V}_{\text{trap}}(\mathbf{r}).$$ \hspace{1cm} (16.44)

The confining potential may or may not depend on the internal state of the atom. For ions in a Paul trap it does not depend, but for atoms in magnetic traps it usually depends,

$$\hat{H}_{atom} = |g\rangle \langle g| + |e\rangle \langle e| (\hat{H}_{cm,e} + \hbar \omega_0)$$  \hspace{1cm} (16.45)

$$\hat{H}_{cm,j} = \frac{\hat{p}^2}{2m} + V_j(\mathbf{r}),$$
where $\omega_0$ is the frequency of the atomic transition. In the following, however, we will treat potentials that are independent of the internal atomic state.

### 16.3.3.2 Resolved sideband regime

As discussed in Sec. 14.4.5, incident light is absorbed by an atom harmonically oscillating in a trap with frequency $\omega_{trp}$ on a spectrum of discrete sidebands separated by $\omega_{trp}$ with amplitudes given by $J_n(kv_0/\omega_{trp})$. The modulation index $kv_0/\omega_{trp} = kx_0 = 2\pi x_0/\lambda$ corresponds to the Lamb-Dicke parameter. When the modulation amplitude is within the so-called **Lamb-Dicke regime**, $kv_0 \ll \omega_{trp}$, the first sidebands become smaller than the carrier, $J_1(kv_0/\omega_{trp}) < J_0(kv_0/\omega_{trp})$ and, therefore, do not contribute to the Doppler width of the frequency distribution. That is, the linear Doppler effect vanishes.

![Figure 16.7](image)

Figure 16.7: Absorption profile in the regimes of (a) weak binding ($\eta > 1$) for the cases of unresolved sidebands (blue curve) and resolved sidebands (red curve), and (b) strong binding (Lamb-Dicke regime $\eta < 1$) for the same cases as in (a).

The relative size of the characteristic frequencies $\omega_{rec}$, $\omega_{trp}$, and $\Gamma$ define characteristic regimes, as illustrated in the table.

<table>
<thead>
<tr>
<th>confinement</th>
<th>sidebands</th>
</tr>
</thead>
<tbody>
<tr>
<td>weak $\eta &gt; 1$</td>
<td>unresolved $\omega_{trp} &lt; 1$</td>
</tr>
<tr>
<td>strong $\eta &lt; 1$</td>
<td>resolved $\omega_{trp} &gt; 1$</td>
</tr>
</tbody>
</table>

### 16.3.3.3 The Mößbauer effect

The role of photonic recoil in the scattering of light by confined atoms has been unraveled by Mößbauer, who performed scattering experiments of $\gamma$-photons on a $^{57}$Fe crystal on a narrow transition of this isotope at 14 keV (0.086 nm). The linewidth of this transition, $\Gamma \approx (2\pi) 1 \text{ MHz}$, is much narrower than the recoil-shift, $\omega_{rec} \approx (2\pi) 500 \text{ MHz} \gg \Gamma$, so that we should expect the scattered light to be considerably recoil-shifted and Doppler-broadened. In fact, the recoil-shift should be so large, that scattered photons cannot be reabsorbed by other atoms on this transition being at rest. This is *not* what Mößbauer observed in his experiments. He found that scattered photons can be reused for subsequent scattering, which means that the scattering must be elastic.

The explanation for this unexpected observation is that, if the nucleus is embedded in a crystal, the vibrational frequencies, which are even higher than the photonic recoil
frequency, $\omega_{trp} \approx 2\pi \cdot 3$ THz, are unreachable. That is to say, we are in the resolved sidebands Lamb-Dicke regime, $\omega_{trp} \gg \omega_{rec} \gg \Gamma$. Here, the phonons corresponding to the vibrations cannot be excited, so that the recoil momentum must be absorbed by the whole lattice, whose entire mass is so large, that the photon frequency is not recoil-shifted by the scattering process. Hence, the first-order Doppler effect is avoided and the measured width of the transition is just the natural linewidth. Furthermore, the atom remains in the same vibrational state of their localizing potential. This is the Mößbauer effect.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$ for $^{57}$Fe</th>
<th>optical for $^{172}$Yb$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>photon energy</td>
<td>$\approx 14$ keV $\approx 4 \times 10^{15}$ Hz</td>
<td>$\approx 3$ eV $\approx 640$ THz</td>
</tr>
<tr>
<td>recoil</td>
<td>$\approx 2$ meV $\approx 500$ MHz $\approx 10^{-10}$</td>
<td>$\approx 20$ peV $\approx 5$ kHz $\approx 10^{-11}$</td>
</tr>
<tr>
<td>linewidth</td>
<td>$\approx 5$ neV $\approx 1$ MHz $\approx 2 \times 10^{-13}$</td>
<td>$\approx 5$ neV $\approx 1$ Hz $\approx 2 \times 10^{-15}$</td>
</tr>
<tr>
<td>lattice vibrations</td>
<td>$\approx 10$ meV $\approx 3$ THz</td>
<td>$\approx 3$ neV $\approx 1$ MHz</td>
</tr>
</tbody>
</table>

Table 16.1: Comparison of $\gamma$-radiation and the optical regime.

A similar effect can be observed with trapped atoms driven on very narrow transitions, as we will discuss in the following.

16.3.3.4 Coupling of internal and external motion by photonic recoil, tracing over the internal excitation

When discussing the transfer of momentum to a harmonic oscillator in 4.5.2, we did not say how the momentum shift could be realized in practice. As we have seen in the example of the Mößbauer effect, a possible way is via the photonic recoil received on a light scattering process. The coupling of the relevant degrees of freedom of the system induced by the absorption of a photon by an atom is accounted for by an additional interaction term $\hat{H}_{int}$ in the Hamiltonian. The relevant degrees of freedom are the electronic orbital $|i\rangle$, the vibrational state $|n\rangle$, and the number of photons $|N\rangle$ in the light mode, assumed to be a plane wave $\hat{E}(\mathbf{r},t) = E_0 \hat{e}_y e^{ik_z z - i\omega t}$. Neglecting the quantum nature of the light, we will disregard this degree of freedom in the following. Assuming that the trapping potential is the same for all electronic orbitals, as in (16.45), the total state can be expressed as a product state, $|n,i\rangle \equiv |i\rangle \otimes |n\rangle$. The interaction Hamiltonian,

$$
\hat{H}_{int} = \frac{\hbar \Omega}{2} (e^{i k z \hat{a}} |e\rangle \langle g| + e^{-i k z \hat{a}^\dagger} |g\rangle \langle e|) - |e\rangle \hbar \omega \langle e|,
$$

(16.46)
couples the dynamics on the internal transition, given by the Rabi frequency $\hbar \Omega \equiv \langle e|d_g |g\rangle \mathcal{E}_0$, with the absorption (or stimulated emission) of a photon $\hat{a}$, and the transfer of a recoil momentum. The last term comes from the transformation into the
interaction picture. With this our total Hamiltonian (16.45) becomes,

$$
\hat{H} = \hbar \omega_{trp}(\hat{b}^{\dagger} \hat{b} + \frac{1}{2}) + |e\rangle \langle e| \omega_0 - \omega + \frac{\hbar \Omega}{2} (e^{ik\hat{z}}|e\rangle \langle g| + e^{-ik\hat{z}}|g\rangle \langle e|) .
$$

(16.47)

So, vibrational states are only coupled via electronic transitions,

$$
\langle n, g | \hat{H} | 0, g \rangle = 0 \quad \text{and} \quad \langle n, e | \hat{H} | 0, g \rangle = \frac{1}{2} \hbar \Omega \langle n | e^{ik\hat{z}} | 0, g \rangle .
$$

(16.48)

Hence, we have to span the complete Hilbert space of all operators like $\hat{\sigma}^{\dagger} = \sum_n |n\rangle \langle n| \otimes |e\rangle \langle g|$. We can expand the system’s state into,

$$
|\psi(t)\rangle = \sum_{n=0}^{\infty} (c_{n,g}|n, g\rangle + c_{n,e}|n, e\rangle ,
$$

(16.49)

and insert it together with the Hamiltonian (16.47) into the Schrödinger equation. Projecting onto the states $\langle n, g |$ and $\langle n, e |$, we easily derive the following equations of motion,

$$
\frac{dc_{n,g}}{dt} = -i \omega_{trp}(n + \frac{1}{2}) c_{n,g} - \frac{i \Omega}{2} \sum_{m=0}^{\infty} c_{m,e} \langle n | e^{-ik\hat{z}} | m \rangle ,
$$

$$
\frac{dc_{n,e}}{dt} = -i \omega_{trp}(n + \frac{1}{2}) c_{n,e} - i(\omega_0 - \omega) c_{n,e} - \frac{i \Omega}{2} \sum_{m=0}^{\infty} c_{m,g} \langle n | e^{ik\hat{z}} | m \rangle .
$$

(16.50)

The fact that only terms proportional to $\langle n | e^{ik\hat{z}} | m \rangle$ contribute can be understood in terms of the Franck-Condon overlap between the vibrational states to be coupled. And the fact that the energy of the harmonic oscillator, and thus the effective detuning $\Delta_n \equiv \omega - \omega_0 - \omega_{trp}(n + \frac{1}{2})$, depend on the vibrational state couples the internal and the external dynamics.

Nevertheless, the off-diagonal coupling elements only contain the degrees of freedom of the harmonic oscillator.

### 16.3.3.5 Momentum kick by photonic recoil

We said earlier that a momentum kick can drive an atom from the vibrational ground state $|0\rangle$ into a coherent superposition of states $|\alpha\rangle$, except when the Lamb-Dicke parameter is very small. When the kick is realized via photonic recoil, e.g. when an electronically excited atom decays to the ground state, the frequency of the emitted photon depends on the final vibrational state of the atom. That is we expect a coherent superposition of light frequencies, which in the limit $\eta > 1$ generates a Doppler broadening and in the limit $\eta < 1$ stays unshifted as for elastic scattering.

\[\text{Note, that this Hamiltonian cannot be used to describe spontaneous emission. To do so, we need to allow for 3D systems and decay modes,}\]

$$
\hat{H} = \hbar \omega_{trp}|n\rangle \langle n| + \frac{1}{2} + \hbar(\omega_0 - \omega)|e\rangle \langle e| + \frac{\hbar \Omega}{2} (e^{-ik\hat{z}} |e\rangle \langle g| + e^{ik\hat{z}} |g\rangle \langle e|) + \hbar g \sum_{k_f} (e^{ik_f\hat{\sigma}^{\dagger} \hat{\sigma} + c.c.) + \hbar g |e\rangle \langle e| + \hbar \Omega (|e\rangle \langle g| + e^{i\hat{z}} |g\rangle \langle e|) .
$$

\[\text{Reference:}\]
Figure 16.8: (a) Absorption (1) and Rayleigh scattering (2) in a weakly confining trap, where the momentum must stay conserved. (b) Illustration of the regime $\omega_{\text{rec}} > \Gamma$, where the atom moves during the absorption process. (c) Absorption and Rayleigh scattering in a strongly confining trap.

Let us now consider a single confined atom and address the question of the absorption probability. In first-order perturbation, using the Hamiltonian (16.47), the transition rate for absorption of a photon incident in $z$-direction is given by Fermi’s Golden Rule,

$$
\frac{1}{\tau} = \frac{d}{dt} |\langle n, e | e^{i\hat{H}t/\hbar} | 0, g \rangle|^2 \simeq \frac{2\pi}{\hbar^2} |\langle n, e | \hat{H} | 0, g \rangle|^2
$$

(16.51)

$$
= \frac{2\pi}{\hbar^2} |\langle n, e | \hbar \Omega (e^{ik\hat{z}} \hat{\sigma}^\dagger + e^{-ik\hat{z}} \hat{\sigma}) | 0, g \rangle|^2 = \frac{\pi \Omega^2}{2} |\langle n, e | e^{ik\hat{z}} | 0, e \rangle|^2.
$$

Obviously, it is thus sufficient to calculate $\langle n | e^{ik\hat{z}} | 0 \rangle$, i.e. we can trace over the internal degrees of freedom. Using our previous results (4.114), we find with $\alpha = -ika_{\text{trp}}/\sqrt{2}$,

$$
\frac{1}{\tau} = \frac{\pi \Omega^2}{2} |\langle n | \alpha \rangle|^2 = \frac{\pi \Omega^2}{2} e^{-|\alpha|^2} |\alpha|^2 \frac{n!}{n!}.
$$

(16.52)

The interpretation of this result is that the absorption of a photon by an atom in state $|0, g\rangle$ transfers recoil by leaving the vibrational state of the atom in a coherent superposition state. Inversely, for the emission process from state $|0, e\rangle$ within the Lamb-Dicke regime, most of the time we will encounter the emitted photon at the resonance frequency $\omega_0$, and rarely at $\omega_0 - \omega_{\text{trp}}$. In any case, energy conservation is satisfied, since,

$$
\sum_n n\hbar \omega_{\text{trp}} |\langle n | \alpha \rangle|^2 = \sum_n n\hbar \omega_{\text{trp}} e^{-|\alpha|^2} \frac{|\alpha|^2 n}{n!} = \hbar \omega_{\text{trp}} |\alpha|^2 \sum_n ne^{-|\alpha|^2} \frac{|\alpha|^{2n-2}}{(n-1)!}
$$

$$
= \frac{\hbar^2 k^2}{2m} \langle \alpha | \alpha \rangle = \hbar \omega_{\text{rec}}.
$$

(16.53)

Thus energy and momentum conservation are automatically satisfied by the way the kick is implemented.
16.3.3.6 A single anisotropically trapped atom in first-order perturbation

Let us now consider a single atom (e.g. a trapped ion) confined in a three-dimensional anisotropic trap (e.g. strong confinement in one and weak confinement in the other direction) and address the question, whether the scattering will be anisotropic, as well.

We generalize the problem to three dimensions by allowing for quantized vibrational states in three dimensions, \( \hat{\sigma} = \sum_n |n\rangle \langle n| \otimes |e\rangle \langle g| \) with \( |n\rangle = |n_x, n_y, n_z\rangle \).

In first-order perturbation, using the Hamiltonian (16.47), the transition rate for absorption or emission is given by Fermi’s Golden Rule,

\[
\frac{1}{\tau} = \frac{d}{dt} |\langle n, e| e^{i\hat{H}t/\hbar} |0, g\rangle|^2 \approx \frac{2\pi}{\hbar^2} |\langle n, e| \frac{\hbar \Omega}{2} (e^{i\mathbf{k}\cdot \hat{r}} + e^{-i\mathbf{k}\cdot \hat{r}}) |0, g\rangle|^2
\]

\[
= \frac{\pi \Omega^2}{2} |\langle n_x, e| e^{i\mathbf{k}\cdot \hat{r}} |0, e\rangle \langle n_y, e| e^{i\mathbf{k}\cdot \hat{r}} |0, e\rangle \langle n_z, e| e^{i\mathbf{k}\cdot \hat{r}} |0, e\rangle|^2 .
\]

Obviously, it is thus sufficient to calculate \( \langle n_j| e^{i\mathbf{k}\cdot \hat{r}} |0\rangle \), i.e. we can trace over the internal degrees of freedom. Using our previous results (4.114), we find with \( \alpha_j = -ik_j \alpha_{\text{trp}, j}/\sqrt{2} \),

\[
\frac{1}{\tau} = \frac{\pi \Omega^2}{2} |\langle n_x| \alpha_x \rangle \langle n_y| \alpha_y \rangle \langle n_z| \alpha_z \rangle|^2 = \frac{\pi \Omega^2}{2} e^{-|\alpha_x|^2 - |\alpha_y|^2 - |\alpha_z|^2} \frac{|\alpha_{\text{trp}, y}\alpha_{\text{trp}, y} \alpha_{\text{trp}, z}|^2}{n_x! n_y! n_z!} .
\]

In Exc. 16.3.4.1 we calculate and illustrate the transition matrix elements \( \langle 0| e^{i\mathbf{k}\cdot \hat{r}} |0\rangle \) and \( \langle n| e^{i\mathbf{k}\cdot \hat{r}} |0\rangle \).

16.3.3.7 A single anisotropically trapped atom in second-order perturbation

To understand Rayleigh scattering, we need to go to second-order perturbation summing over all intermediate vibrational states according to the Kramers-Heisenberg formula,

\[
\frac{d\sigma}{d\Omega} = \frac{d}{dt} |\langle n, g, k_f| e^{i\hat{H}t/\hbar} |0, g, k_i\rangle|^2 \approx \frac{2\pi}{\hbar^2} |\langle n, g, k_f \rangle \sum_m \hat{H}^{(1)}|m, e\rangle \langle m, e| \hat{H}^{(1)} \rangle \omega_i - \omega_m |0, g, k_i\rangle|^2
\]

\[
= \frac{\pi \hbar^2 \Omega^4}{8} \sum_m E_i/\hbar + (0\omega_x + 0\omega_y + 0\omega_z + \frac{3}{2}) - E_m/\hbar - (m_x\omega_x + m_y\omega_y + m_z\omega_z + \frac{3}{2}) \]

\[
= \frac{\pi \hbar^2 \Omega^4}{8} \sum_{m_x, m_y, m_z} \frac{\langle n, k_f| e^{-i\mathbf{q}\cdot \hat{r}} |m\rangle \langle m| e^{i\mathbf{q}\cdot \hat{r}} |0, k_i\rangle}{(E_i - E_m)/\hbar - m_x\omega_x - m_y\omega_y - m_z\omega_z} \]

\[
= \frac{\pi \hbar^2 \Omega^4}{8} \sum_{m_x, m_y, m_z} \prod_{j=x,y,z} \frac{\langle n_j| e^{-i\mathbf{k}_j\cdot \hat{r}_j} |m_j\rangle \langle m_j| e^{i\mathbf{k}_j\cdot \hat{r}_j} |0\rangle}{(E_i - E_m)/\hbar - m_x\omega_{mx} - m_y\omega_{my} - m_z\omega_{mz}} \]

\]

(16.55)

The transition matrix elements can be calculated via (4.119). This expression represents (in the same time) the dynamic structure factor of the single trapped atom.
**Example 64 (Axial incidence):** Let us consider the particular case of Rayleigh scattering from the ground state of light incident in the direction \( \mathbf{k}_i \equiv k_{iz} \hat{\mathbf{e}}_z \). We can then simplify,

\[
\frac{d\sigma}{d\Omega} = \frac{\pi \hbar^2 \Omega^4}{8} \sum_{m_z} \left| \langle 0 | e^{-i k_{zf} \hat{\mathbf{e}}_z} | 0 \rangle \langle 0 | e^{-i k_{zf} \hat{\mathbf{e}}_z} | m_z \rangle \langle m_z | e^{i k_{iz} \hat{\mathbf{e}}_z} | 0 \rangle \right|^2 - m_z \omega_{trp}
\]

\[
= \frac{\pi \hbar^2 \Omega^4}{8} e^{-|\alpha_{xz}|^2 - |\alpha_{yz}|^2 - |\alpha_{zz}|^2} \sum_{m_z} \frac{1}{(E_m - E_i)/\hbar - m_z \omega_{trp, z}} \left| \sum_{m_z} \alpha_{m_z} \alpha_{0z}^* \right|^2
\]

\[
= \frac{\pi \hbar^2 \Omega^4}{8} e^{-(k_{f} \cdot a_{trp})^2 / 2 - (k_{i} \cdot a_{trp})^2 / 2} \sum_{m_z} \frac{1}{(E_m - E_i)/\hbar - m_z \omega_{trp, z}} \left| \sum_{m_z} \alpha_{m_z} \alpha_{0z}^* \right|^2 ,
\]

where \( a_{trp} \equiv (a_{trp, x} a_{trp, y} a_{trp, z}) \). Looking into scattering into transverse direction, \( k_{f, z} = 0 \), we get,

\[
\frac{d\sigma}{d\Omega} \parallel = \frac{\pi \hbar^2 \Omega^4}{8 |E_m - E_i|^2} e^{-k_{f, z}^2 a_{trp, z}^2 / 2 - k_{f, y}^2 a_{trp, y}^2 / 2 - k_{f, x}^2 a_{trp, x}^2 / 2} .
\]

Looking into backscattering, \( k_{f, z} = -k_{i, z} \),

\[
\frac{d\sigma}{d\Omega} \perp = \frac{\pi \hbar^2 \Omega^4}{8 |E_m - E_i|^2} e^{-k_{i, z}^2 a_{trp, z}^2} \sum_{m_z} \frac{1}{(E_m - E_i)/\hbar - m_z \omega_{trp, z}} \left| \sum_{m_z} \alpha_{m_z} \alpha_{0z}^* \right|^2 .
\]

we expect a spectrum with vibrational resonances.

**16.3.4 Exercises**

**16.3.4.1 Ex: Transition elements in anisotropic harmonic traps**

a. Calculate and illustrate \( \langle 0 | e^{-i k \cdot \hat{\mathbf{r}}} | 0 \rangle \) for an anisotropic trap with cylindrical symmetry.

b. Calculate \( \langle n | e^{-i k \cdot \hat{\mathbf{r}}} | 0 \rangle \) and \( \sum_{n_x, n_y, n_z} \langle n \rangle | e^{-i k \cdot \hat{\mathbf{r}}} | 0 \rangle \).

**16.3.4.2 Ex: Periodicity of a lattice**

Calculate \( e^{i a \hat{p}} e^{2 i k \hat{z}} e^{-i a \hat{p}} \).

**16.3.4.3 Ex: Energy commutators**

Calculate the commutator between the kinetic and the potential energy for (a) a harmonic oscillator and (b) a standing wave dipolar potential.
Chapter 17

Quantum measurement

Since its foundation, the theory of quantum mechanics was driven by the urge to clarify the relationship between the world and what we can learn about it, that is, between reality and the observer. Scientists such as Bohr, Heisenberg, Schrödinger, and Einstein defended controversial positions and struggled for the correct interpretation of quantum mechanics. The \textit{measurement process} is supposed to provide information about the world out there, but it is not clear whether this information can be complete and accurate, or whether there are limitations or hidden variables. Also, it was unclear, to what extent a measurement can be non-invasive or whether it would always perturb the phenomenon under investigation. The most important step in this question was the \textit{Copenhagen interpretation} formulated by Bohr, Heisenberg and Born in 1927 and elaborated later by von Neumann and Dirac. Although contested many times in the past, it’s essence still remains valid today.

In this chapter we will study the measurement process from the viewpoint quantum mechanics and discuss some seemingly paradoxical effects, that will allow us to deepen our understanding. Among them are the quantum jump, Schrödinger’s cat, the quantum Zeno effect, and the Einstein-Podolski-Rosen paradox.

17.1 The observer and the reality

According to the Copenhagen interpretation, theoretical predictions have a probabilistic character. However, this is not an expression of the imperfection of the theory, but of the intrinsically indeterministic character of quantum processes \footnote{Note that it is problematic to identify unpredictability and indeterminism. We may be unable to predict specific events, without having to assume that these events occur in a random manner.}. Moreover, the Copenhagen interpretation desists to attribute to objects of the quantum formalism, such as wavefunctions and operators, an immediate reality. Instead, the objects of the formalism only represent vehicles for a probabilistic prediction of the results of measurements. These results are \textit{only truly real} elements of quantum theory. It is obvious, that the quantum theory and its interpretations are of fundamental importance to the scientific view of the world and our concept of nature.

17.1.1 Schrödinger’s cat

In the microscopic world, the relationship between the sample and the observer is very delicate. And this delicacy is at the origin of quantum effects that seem paradoxical.
through our classical concept of the world. It is, thus, not surprising that one of the most fascinating areas of investigations is the interface between the classical and the quantum, the macroscopic and the microscopic worlds. For the pioneers of quantum mechanics the most important questions were of the type: 'How is it possible that a microscopic particle flies simultaneously through two slits?' Nowadays, we are accustomed to such paradoxes, and we simply accept the fact that we have to consider a particle as a wave. Nevertheless, we still do not understand very well, why the classical and the quantum world behave so differently. 'Why does quantum mechanics allow for quantum superpositions states, which are absolutely forbidden in classical physics?', 'Why are the fundamental laws of the quantum world invariant to the arrow of time, while the macroscopic world always evolves from the past to the future?, 'How can it be that quantum mechanics allows for effects having no cause, like spontaneous emission, while the everyday world seems to be deterministic?'

Quantum mechanics must, in some limit, clearly encompass classical physics. But in spite of Ehrenfest’s correspondence principle, this fact is far from being trivial. Some predictions of classical and quantum physics are fundamentally different and, in some cases, even contradictory. The famous Schrödinger cat states are the epitome of this fact: In one version of this paradox, a particle crosses a double slit. Behind one of the slits is a detector which, as soon as it registers a particle, actuates a device killing a cat. We know that in quantum reality the particle crosses both slits in a superposition state, so that the cat should be in a superposition state as well. Hence, quantum cats can be in a superposition of 'dead' and 'alive'.

We believe nowadays that the answers to the above questions are somehow buried in processes that destroy the quantum superposition of Schrödinger cats during the transition from the microscopic to the macroscopic world. However, the details of these quantum coherence destruction processes, called decoherence, are very compli-
17.1. THE OBSERVER AND THE REALITY

Figure 17.2: The measurement of a quantum system presupposes the interaction of the system with a reservoir, which disturbs its dynamics.

cated and the subject of serious efforts in contemporary research. It is one of the motivations for trying to create in laboratories the largest possible (quasi-macroscopic) quantum systems, bring them in Schrödinger cat-like superposition states and study their decoherence.\(^2\)

17.1.1.1 Quantum measurement

Every unperturbed system follows the Schrödinger equation. Once its Hamiltonian has been determined, the formal solution,

\[ |\psi\rangle = e^{-iHt/\hbar} |\psi_0\rangle , \]

allows to calculate the time evolution, that is, the trajectory of the wavefunction. The evolution is coherent and reversible in time.

Now, the process of measuring a pure quantum state includes –according the Copenhagen interpretation and as discussed in Sec. 2.2.7– two consecutive steps: In the first step, the interaction of the quantum sample with the measuring device (which from now on we will call meter) destroys all coherences and projects the pure state into a statistical mixture of eigenstates of the meter. Following von Neumann, the impact of the meter on the quantum system is so strong, that its coherent evolution is interrupted and it is projected onto the degree of freedom that the apparatus wants to measure, e.g. its position or its momentum, but not both in the same time. The projection transforms a pure quantum state \( |\psi\rangle \) into a statistical mixture \( \rho \) of eigenstates,

\[ \rho_{\text{sample}} = |\psi(t)\rangle\langle\psi(t)| \bowtie \rho_{\text{proj}} = \sum_k |\langle \psi | k \rangle|^2 |k\rangle\langle k| . \]

This process is irreversible, that is, it separates the past from the future. The projection is not described by the Schrödinger equation. Instead, the sudden reduction of the state must be postulated, as done by von Neumann’s famous axiom.

In a second step, the observer looks at the measuring device and confirms one of the possible results. Thus, he transforms the state into a eigenstate of the device \(^3\):

\[ \rho_{\text{proj}} \bowtie \rho_{\text{meter}} = |k\rangle\langle k| . \]

\(^2\)There are attempts to introduce the concept of the time arrow also in the microscopic world: 'In an isolated system, spontaneous processes occur in the direction of increasing entropy.' [420].

\(^3\)We note that, only if all commuting observables of the system are measured and acknowledged, \( \rho_{\text{meter}} \) becomes a pure state. Otherwise \( \rho_{\text{meter}} \) remains a partial mixture.
From this moment, we can again leave the quantum system alone until the next measure.

From the viewpoint of the quantum system, the evolution of the measurement process appears discontinuous, because it destroys all possible coherences between its states. In fact, the problem comes from the non-ideal behavior of the measuring device (symbolized by $|\uparrow\rangle$ before the measurement). An ideal non-invasive measurement would leave the quantum state $|\psi\rangle$ unchanged:

$$|\psi\rangle|\uparrow\rangle \xrightarrow{H} |\psi\rangle|\nearrow\rangle,$$

while the measuring device changes to a state ($|\nearrow\rangle$ after the measurement) indicating the current state of the system. However, this is normally impossible without previously established correlation between $|\psi\rangle$ and $|\uparrow\rangle$. In a real meter device, the coupling between $|\psi\rangle$ and $|\uparrow\rangle$ requires that the meter and the system to be non-orthogonal.

### 17.1.1.2 Measurement-induced decoherence

A more modern view of the quantum measurement is the following: When the outer world (called reservoir, observer or meter) reads a quantum system, it causes, due to this transfer of information, an irreversible demolition of coherence. Consequently, the density operator condenses to its diagonal. On the other hand, the system as a whole (including the sample and the reservoir) always evolves coherently according to the von Neumann equation with the Hamiltonian of everything $\hat{H}_{\text{all}}$:

$$\dot{\rho} = \frac{i}{\hbar} [\rho, \hat{H}_{\text{all}}].$$

If $\hat{H}_{\text{sample}}$ is the small quantum system under investigation, a complete description of the measurement process requires the inclusion of the observer, that is, the total Hamiltonian is,

$$\hat{H} = \hat{H}_{\text{sample}} \otimes \hat{H}_{\text{meter}} = \begin{pmatrix} \text{sample} & 0 \\ 0 & \text{meter} \end{pmatrix}.$$

Ideally, the system evolves independently without being disturbed by the meter. Unfortunately, this also means that the meter evolves independently, that is, it is not influenced by the system and thus does not provide information about the system. To allow a transfer of information, we need to couple the respective spaces by an interaction $\Omega$, such that,

$$\hat{H} = \begin{pmatrix} \text{sample} & \Omega \\ \Omega & \text{meter} \end{pmatrix}.$$

Tracing over all degrees of freedom of the universe except those of the quantum system, the von Neumann equation (17.5) turns into a master equation,

$$\dot{\rho}_{\text{sample}} = \frac{i}{\hbar} [\rho, \hat{H}_{\text{sample}}] + \mathcal{L}_{\text{reservoir}} \rho.$$

---

4See the discussion of the quantum non-demolition measurement.
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Figure 17.3: Spontaneous emission can be seen as a coupling of the system under investigation to an external meter, because it delivers information to the meter, even if only to tell us: 'The system was in an excited state, but now it’s in a ground state.'

Example 65 (Quantum measurement in a two-qubit system): To discuss this at an example, we consider the simplest imaginable system: Two two-level atoms, the first one representing the quantum system under investigation and the second the meter. We introduce the following basis:

\[
|1\rangle \equiv |\downarrow\rangle|\downarrow\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix},
|2\rangle \equiv |\uparrow\rangle|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix},
|3\rangle \equiv |\downarrow\rangle|\uparrow\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix},
|4\rangle \equiv |\uparrow\rangle|\uparrow\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.
\]

The Hamiltonian of independent atoms is,

\[
\hat{H} = |\downarrow\rangle\langle \downarrow| \otimes |\uparrow\rangle\langle \uparrow|.
\]

The discussion about the correct interpretation of the measurement process is still ongoing. Modern theories describe the state reduction in terms of quantum decoherence due to interactions of the system with the environment. Other interpretations involve decoherent histories or assume multiple worlds [464]. On the practical side, the current interest in quantum decoherence is motivated by the fact that this phenomenon may turn out to be the fundamental factor limiting the useful operation of quantum computers. Another interesting area where quantum mechanics meets classical physics is the phenomenon of quantum chaos.

17.1.2 The quantum jump

Obviously, the whole quantum measurement process, including the discontinuity of the state projection, could be fully understood within a grand model of the complete system, which would include the measuring device. In practice, this is illusory, because of the excessive number of degrees of freedom of the classical measuring device (e.g. a Schrödinger cat).

On the other hand, many characteristics of quantum measurement can be illustrated in a simple three-level atom with a weak transition representing the quantum sample and a strong transition representing the meter. The assertion defended in the following is, that this three-level system, called quantum amplifier, gives a deep
insight into what happens during the process of state reduction and, therefore, can be considered as paradigmatic for theories on quantum measurement.

To be able to discuss the dynamics of this system on a firmer ground, we will first introduce the quantum Monte Carlo wavefunction simulation method (MCWF).

17.1.2.1 Quantum Monte Carlo wavefunction simulation of a two-level system

The possible occurrence of spontaneous emission produces a dynamics called quantum trajectory, which can be described by a non-hermitian effective Hamiltonian,

\[
\hat{H}_{\text{eff}} = \hbar \Delta \sigma_z + \hbar \Omega \sigma^+ + \text{c.c.} - \frac{i}{2} \Gamma \sigma_z = \begin{pmatrix} 0 & \Omega \\ \Omega & \Delta - i \frac{\Gamma}{2} \end{pmatrix},
\]

(17.9)

aiming at including energy dissipation processes. The problem with this Hamiltonian is that, for being non-hermitian, \([\hat{H}_{\text{eff}}, \hat{H}_{\text{eff}}^\dagger] \neq 0\), it also generates a non-unitary dynamics, \(e^{-i\hat{H}_{\text{eff}}t} \neq e^{i\hat{H}_{\text{eff}}^\dagger t}\). This means that the mere possibility of spontaneous emission prevents the reversibility of the dynamics. We observe a temporal decrease of the norm \(\langle \psi(t) | \psi(t) \rangle\) indicating a loss of energy,

\[
\langle \psi | \psi \rangle = \langle \psi_0 | e^{-i\hat{H}t} e^{i\hat{H}t} | \psi_0 \rangle \longrightarrow e^{-\Gamma t}.
\]

(17.10)

The loss of normalization during the evolution, until the next quantum jump occurs, is due to the dissipation of energy toward the reservoir,

\[
\text{Tr } \rho_{\text{sample}} \to 0 \quad \text{while} \quad \text{Tr } \begin{pmatrix} \rho_{\text{sample}} & 0 \\ 0 & \rho_{\text{reserv}} \end{pmatrix} = 1,
\]

(17.11)

and represents a measure of the probability that an irreversible process has occurred during the evolution time.

Dissipative processes can be simulated by playing dices with random numbers \(\zeta\). We divide time into small intervals \(dt\) and propagate the wavefunction from \(\psi(t)\) to \(\psi(t + dt)\). After each interval we evaluate the probability \(p = 1 - \langle \psi(t) | \psi(t) \rangle\) accumulated during the time period \([0, t + dt]\) that a dissipative process (such as
spontaneous emission) has occurred. Now, we generate a random number $\zeta$, uniformly distributed between 0 and 1, which we compare to probability the probability $p$. In case, $\zeta > 1 - \langle \psi(t) | \psi(t) \rangle$, we conclude that there was no dissipative process, and we let the system proceed in peace, only renormalizing the wavefunction to compensate for the losses [297, 135]. Otherwise, if $\zeta < 1 - \langle \psi(t) | \psi(t) \rangle$, we conclude that there was a dissipative process, and the system is projected into the eigenstate $\psi_0$. This projection is abrupt and called quantum jump. Now, the evolution restarts from zero, ruled by the effective Hamiltonian. The simulation implemented via,

$$
|\psi(t)\rangle \sim |\psi(t + dt)\rangle \equiv \left( \frac{(1-i\hat{H}dt)|\psi(t+dt)\rangle}{\sqrt{\langle \psi(t)|\psi(t) \rangle}} \right) \text{ if } \zeta > 1 - \langle \psi(t) | \psi(t) \rangle
$$

This is the method called quantum Monte Carlo wavefunction simulation.

The effective two-level Hamiltonian (17.9) dissipates via spontaneous emission, which is included in the dynamics through the possibility for the system to suffer a state reduction. The modification of $|\psi(t)\rangle$ by non-observation of spontaneous emission, reduces the population of the state excited by $1 - \frac{1}{2} \Gamma dt$, while the ground state population remains unchanged. Every quantum jump projecting the system into the ground state constitutes a measurement, because it corresponds to a detected fluorescence photon.
17.1.2.2 Three-level systems: The epitome of quantum measurement

Let us now return to the mysterious interaction between the sample and the meter, which we want to unravel by comparing two possible procedures: 1. treating the sample and the meter separately and explain the extraction of information following the von Neumann postulate; 2. treating the sample and the meter by a global theory.

As said above, the inclusion of the meter in a global theory is, in general, difficult. For this reason, to perform the comparison, we choose the simplest imaginable system: the three-level system with two transitions connecting to a common ground state and excited by radiation fields. As shown in Fig. 17.6(a) this three-level system can be an atom with a strong transition and a weak transition, for example, the dipolar transition $S_{1/2} - P_{1/2}$ and the forbidden quadrupolar transition $S_{1/2} - D_{5/2}$ in a single Ba$^+$ ion. We will now name the 'strong transition' as meter and the 'weak transition' as sample and show that this system allows to study the von Neumann measurement process including the direct observation of quantum jumps\(^5\). At the same time, the system is simple enough for a complete theoretical description. In this sense, the three-level system becomes the epitome of a quantum measurement device.

We turn our attention to the three-level atom: Obviously, the atom will preferentially scatters photons on its strong dipolar transition. However, at times when the valence electron is 'shelved' in the metastable state excited by the quadrupole transition, no fluorescence can be observed on the strong transition.

![Figure 17.6: (a) Quantum measurement at the example of a three-level atom incorporating a weak (sample) transition and a strong (meter) transition. (b) Random Telegraph signal in the resonance fluorescence due to quantum jumps.](image)

Quantum jumps were experimentally observed in single trapped ions, whose lowest energies form a three-level systems [447, 528, 529, 53].

17.1.2.3 Quantum Monte-Carlo wavefunction simulation of the quantum amplifier

When both lasers driving the weak and the strong transition are irradiated simultaneously, the coherence on the weak transition is easily perturbed by the dynamics of the strong transition. To resolve this problem Dehmelt invented what he called the

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\(^5\)The observability of quantum jumps as manifestations of sudden state reductions has been the object of long-standing debates: 'If we have to go on with these damned quantum jumps, then I'm sorry that I ever got involved with quantum mechanics.' [539].
17.1. THE OBSERVER AND THE REALITY

**quantum amplifier.** The idea consists in alternately irradiating the *sample* laser (at stage $S - D$ in Fig. 17.7) and the *meter* laser (at stage $S - P$ in Fig. 17.7) ⁶.

The alternating irradiation of the lasers $S - D$ and $S - P$ can also be treated by the Monte Carlo quantum wavefunction simulation method (17.12) using the effective Hamiltonian,

$$
\hat{H}_{\text{eff}} = \begin{pmatrix}
0 & \frac{1}{2} \Omega_{sp} & \frac{1}{2} \Omega_{sd} \\
\frac{1}{2} \Omega_{sp} & -\Delta_{sp} - \frac{1}{2} \Gamma_{sp} & 0 \\
\frac{1}{2} \Omega_{sd} & 0 & -\Delta_{sd}
\end{pmatrix},
$$

(17.13)

where the Rabi frequencies $\Omega_{sd}$ and $\Omega_{sd}$ are switched on alternately.

In the simulation 17.7 the quantum jumps to the shelved metastable state $D_{5/2}$ appear as long periods without population in the $P_{1/2}$ level (first period $S - P$, where the population of $S_{1/2}$, illustrated by the red curve, gradually tends to 0 for long times). The reduction of the system to the shelved state actually occurs by *non-observation* of fluorescence on the strong transition. The projection needs a finite time, simply because we can not be sure whether the non-observation is actually due to shelving or the incidental absence of scattering events on the $S - P$ transition: After all, it is not predictable, when the next photon will be spontaneously emitted, even though the lifetime of the excited state is short. But for longer observation times it becomes increasingly unlikely that the absence of photons is *not* due to shelving. It is this unlikeliness, which lets the population rapidly converge towards the metastable state. In the second $S - P$ period, Fig. 17.7 shows fast transitions to the $P_{1/2}$ followed by sudden decays to the ground state. These processes correspond to photon absorption and spontaneous reemission by the strong transition. The succession of the photon scattering events is so fast, that the signal recorded by photodetectors appears as a continuous fluorescence. The sudden transitions between bright and dark periods shown in Fig. 17.6(b), which occur totally randomly, are interpreted as quantum jumps.

17.1.2.4 Comparison with Bloch equations and interpretation of quantum jumps

We already mentioned in Fig. 17.5, that a trajectory generated by a MCWF simulation (17.12) represents *one* possible evolution of the system. In Chp. 14.5.5 we got to know an alternative way of predicting the evolution of a system, based on density operator obeying a *master equation*, which in the context of atomic excitation levels is called Bloch equation. Comparing MCWF trajectories (red curves in Fig. 17.7) with Bloch vector evolutions (green curves) it becomes apparent, that the Bloch vector evolution does not produce quantum jumps, but is always smooth and continuous.

In most cases, our knowledge about the actual state of an atom comes from the collection of spontaneously emitted photons. The observation of a photon projects the atomic state into the ground state. However, this concept is not included in the

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⁶The absence of the 'meter' laser during the 'sample' stage avoids saturation broadening and light-shifts of the ground state. Since the ground state is shared by both transitions, its broadening would reduce the spectral overlap between the 'sample' transition and the driving laser and therefore the probability to excite the metastable level. This inhibition of the coherent dynamic by too strong or too frequent measurements is known as *quantum Zeno effect*: The more an observer tries to extract information from a system, the more he inhibits its evolution. We will discuss this effect in more detail in Sec. 28.5.2.1.
Bloch equations, as we just saw in Fig. 17.7. So, as it seems, we have to take back our statement, that the three-level Bloch equation describe the complete system, although they somehow contain spontaneous emission.

Let us go one step back and ask, where the Bloch equations came from. In fact, as we learned in Sec. 15.3 and will deepen in Sec. 17.2, they are derived from a von Neumann equation for the three-level system plus the degrees of freedom of the vacuum modes receiving the spontaneously emitted photons by tracing over the latter ones.

We will not be able to handle all degrees of freedom. However, we can generalize the Bloch equations in the following way [428, 657]. We project the total density operator $\rho_{AFR}$ of the atom plus the driving field plus the reservoir of vacuum modes into the subspace of the atom and the driving field consisting of exactly $n$ photons,

$$\rho^{(n)} = \text{Tr}_R (P^{(n)} \rho_{AFR}) ,$$

and derive, from the von Neumann equation, the master equation for the atomic state $\rho^{(n)}$ under the constraint of a fixed number of photons $n$ in the field. The master equation differs only in one term from the usual Bloch equations: The expression $\Gamma_{12}\rho^{(n)}_{22}$, which describes the spontaneous decay of the population of the excited state of the meter transition, is replaced by the expression $\Gamma_{12}\rho^{(n-1)}_{22}$:

$$\frac{d}{dt}\rho^{(n)} = (\mathcal{L}|1\rangle\Gamma_{12}\langle 2|)\rho^{(n)} + |1\rangle\Gamma_{12}\langle 2|\rho^{(n-1)} ,$$

(17.15)
17.1. THE OBSERVER AND THE REALITY

The substate with of \( n \) photons violates the trace condition, \( \sum_j \rho_{jj}^{(n)} \neq 1 \). The physical explanation for this is the following: While induced emission and absorption maintain the number of photons in the combined light-atom system (like in the Jaynes-Cummings model), spontaneous emission decreases the number of photons, leading to an irreversible loss of energy. The quantum jump observed in MCWF model corresponds, in the modified equations (17.15), to a collapse of the subspace described by \( \rho^{(n)} \) with the time constant \( \Gamma_{12} \) and a birth of another subspace \( \rho^{(n-1)} \), whose evolution is guided by another (analogous) Bloch equation, now for \( n-1 \) photons.

Each fluorescence detection at time \( t = 0 \) determines the initial condition for the future development of the system: \( \rho^{(n)}(0) = 0 \) and \( \rho^{(n-1)}(0) = |1\rangle\langle 1| \). The probability density \( c(t) \) for a new observation of spontaneous emission at time \( t \) with detection efficiency \( \eta \), or in other words, the histogram of the durations of dark periods in the fluorescence signal is related to the solution \( \rho^{(n)} \) of the homogeneous part of the equation (17.14) via,

\[
c(t) = \eta \Gamma_{12} \rho_{22}^{(n)}(t) = \eta \sum_{j=1}^{4} \frac{d}{dt} \rho_{jj}^{(n)}(t) ,
\]

(17.16)

The second step immediately follows from the homogeneous part of equation (17.15).

17.1.2.5 Kraus operator for position measurement

As a canonical example of a Kraus operator [35, 100] we take \( \hat{H} = \hat{x} \otimes \hat{p} \), where the position and the momentum satisfy the commutation relation, \( [\hat{x}, \hat{p}] = i \). The initial state of the ancilla be a Gaussian distribution,

\[
|\phi \rangle = \frac{1}{(2\pi\sigma^2)^{1/4}} \int dq' e^{-q'^2/4\sigma^2} |q' \rangle .
\]

(17.17)

The position wavefunction of the ancilla is,

\[
\phi(q) = \langle q | \phi \rangle = \frac{1}{(2\pi\sigma^2)^{1/4}} e^{-q^2/4\sigma^2} .
\]

(17.18)

The Kraus operators are (compared to the previous discussion, we now let \( \lambda = 1 \)),

\[
M(q) = \langle q | e^{-i\hat{x} \otimes \hat{p}} | \phi \rangle = \frac{1}{(2\pi\sigma^2)^{1/4}} e^{-(q-x)^2/4\sigma^2} ,
\]

(17.19)

since the operator \( e^{-i\hat{x} \otimes \hat{p}} \) makes a spatial translation when applied to the degree of freedom of the position. The corresponding POVM elements are,

\[
E(q) = M_q^\dagger M_q = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(q-x)^2/2\sigma^2} ,
\]

(17.20)

which obey \( \int dq E(q) = \mathbb{I} \).

Calculate \( \langle \psi_q | \psi_q \rangle = \langle \psi' | M(q)^\dagger M(q) | \psi' \rangle \).

Note that \( \lim_{\sigma \to 0} E(q) = |x = q \rangle \langle x = q| \). That is, in a particular limit, these operators converge to a strong measurement of position. For \( \sigma \to \infty \), we speak of weak measurement.

Another example would be the three-level atom of Dehmelt’s quantum amplifier.
17.1.3 Exercises

17.1.3.1 Ex: Dispersive quantum jumps

Consider a three-level system in V-configuration, as depicted in Fig. 14.6(b), with an unstable state \( |1\rangle \), a ground state \( |2\rangle \), and a metastable state \( |3\rangle \). Discuss whether the atom shelved in state \( |3\rangle \) is sensitive to light-shift and power broadened induced by a laser resonant to the \( |1\rangle \rightarrow |2\rangle \) transition. E.g. will power-broadening only effect the transition rate \( |1\rangle \rightarrow |3\rangle \) or also \( |3\rangle \rightarrow |1\rangle \)?

17.2 Open systems and the master equation

Let us now derive the master equation for an open quantum system. We assume that the environment (also called bath or reservoir) and the system under consideration are quantum systems in the sense that (1) the relevant degrees of freedom are completely characterized by state vectors (or density matrices), and (2) the temporal evolution of the total system is unitary \( U(t) = e^{-i\hat H t} \). The total Hamiltonian, \( \hat H = \hat H_{sys} + \hat H_{res} + V \) is assumed to be independent of time and consists of three parts, namely the Hamiltonian of the system \( \hat H_{sys} \), the Hamiltonian of the bath \( \hat H_{res} \), and the interaction \( V \) between the system and the bath. The purpose of the master equation is to find the dynamics of the system by tracing over all degrees of freedom of the bath. This is not always possible, and we will assume that the interaction \( V \) is sufficiently weak, so that perturbation theory is applicable.

In the interaction representation the evolution of the total density matrix \( \hat \rho_{tot} \) becomes,

\[
\frac{i\hbar}{\hbar} \frac{d\hat \rho_{tot}}{dt} = [\hat V(t), \hat \rho_{tot}] \quad . \tag{17.21}
\]

where \( \hat \rho_{tot}(t) \equiv U_0^\dagger \hat \rho_{tot} U_0 \) and \( \hat V(t) \equiv U_0^\dagger VU_0 \) and \( U_0 = e^{-(\hat H_{sys}+\hat H_{res})t/\hbar} \). This evolution is, for the time being, very general, and the solution can be formally written,

\[
\hat \rho_{tot}(t) = \hat \rho_{tot}(0) + \frac{1}{i\hbar} \int_0^t dt_1 [\hat V(t_1), \hat \rho_{tot}(t_1)] . \tag{17.22}
\]

Iterating once again:

\[
\hat \rho_{tot}(t) = \hat \rho_{tot}(0) + \frac{1}{i\hbar} \int_0^t dt_1 [\hat V(t_1), \hat \rho_{tot}(0)] + \frac{1}{(i\hbar)^2} \int_0^t dt_1 \int_0^{t_1} dt_2 [\hat V(t_1), [\hat V(t_2), \hat \rho_{tot}(t_2)] . \tag{17.23}
\]

In the following, we will call several approximations to simplify the calculations, in particular, the Born approximation, the assumption that the initial state is a product state and, later-on, the Markov approximation.

17.2.1 Born approximation for weak coupling

We will now assume the interaction \( \hat V \) to be weak. We can then expect that, repeating the iterative process, the series will converge and write the general solution as,

\[
\hat \rho_{tot}(t) = \hat \rho_{tot}(0) + \sum_{n \geq 1} \frac{1}{(i\hbar)^n} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n [\hat V(t_1), \ldots, [\hat V(t_n), \hat \rho_{tot}(0)] \quad . \tag{17.24}
\]
This way of terminating an iterative equation by \( \rho_{\text{tot}}(0) \) is generally known as the Born approximation. Here, we will just go to second order in \( \tilde{V} \). Tracing over the bath,

\[
\tilde{\rho}_{\text{sys}}(t) = \text{Tr}_{\text{res}} \tilde{\rho}_{\text{tot}}(t),
\]

we extract the density matrix for only the system,

\[
\tilde{\rho}_{\text{sys}}(t) = \tilde{\rho}_{\text{sys}}(0) + \frac{1}{i\hbar} \int_0^t dt_1 \text{Tr}_{\text{res}} [\tilde{V}(t_1), \tilde{\rho}_{\text{tot}}(0)]
\]

\[
+ \frac{1}{(i\hbar)^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \text{Tr}_{\text{res}} \left[ \tilde{V}(t_1), [\tilde{V}(t_2), \tilde{\rho}_{\text{tot}}(0)] \right].
\]

### 17.2.2 Assumption of an initial product state

Next, we need to make the quite important assumption, that the initial state between the system and the environment are not correlated, or mathematically speaking, they can be written as product states,

\[
\tilde{\rho}_{\text{tot}}(0) = \tilde{\rho}_{\text{sys}}(0) \otimes \rho_{\text{res}}(0).
\]

Another assumption, which is not essential but often valid, is that \( \text{Tr}_{\text{res}}[\tilde{V}(t_1), \tilde{\rho}_{\text{tot}}(0)] = 0 \). If this is the case, then the first-order term will vanish. In second order, we can write,

\[
\tilde{\rho}_{\text{sys}}(t) = e^{\mathcal{M}(t)} \tilde{\rho}_{\text{sys}}(0).
\]

where \( \mathcal{M}(t) \chi \equiv \frac{1}{(i\hbar)^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \text{Tr}_{\text{res}} \left[ \tilde{V}(t_1), [\tilde{V}(t_2), \chi \otimes \rho_{\text{res}}] \right] \),

is a superoperator acting on the operator density of the system. Taking the temporal derivative, we have the explicit master equation,

\[
\frac{d\tilde{\rho}_{\text{sys}}(t)}{dt} = \mathcal{L}\rho_{\text{sys}}(t) = \frac{d}{dt} \left( \mathcal{M}(t) \tilde{\rho}_{\text{sys}}(t) \right)
\]

\[
= \frac{1}{(i\hbar)^2} \int_0^t d\tau \text{Tr}_{\text{res}} \left[ \tilde{V}(t), [\tilde{V}(\tau), \tilde{\rho}_{\text{sys}}(t) \otimes \rho_{\text{res}}] \right].
\]

The superoperator \( \mathcal{L} \) is called Lindbladt operator.

### 17.2.3 Markov approximation for short memory

Here, we have to evaluate the terms involving the average with respect to the thermal bath, which is assumed to have a short memory, in the sense that the correlation time is very short. Mathematically,

\[
\int_0^t d\tau \text{Tr}_{\text{res}} \left( \tilde{V}(t)\tilde{V}(\tau)\rho_{\text{res}} \right) = \int_0^t d\tau \text{Tr}_{\text{res}} \left( \tilde{V}(t-\tau)\tilde{V}(0)\rho_{\text{res}} \right)
\]

\[
\simeq \int_0^\infty d\tau \text{Tr}_{\text{res}} \left( \tilde{V}(t-\tau)\tilde{V}(0)\rho_{\text{res}} \right).
\]

In other words, the two-point correlation function is significant only, when \( t \simeq \tau \), and it is valid to extend the upper bound to infinity. This is the Markov approximation.
17.2.4 Example: Damped harmonic quantum oscillator

As an example, we let us consider the master equation for the Brownian motion of a quantum harmonic oscillator. It can be written,

$$\frac{d\tilde{\rho}_{\text{sys}}}{dt} = \frac{1}{(\hbar)^2} \int_0^t d\tau \text{Tr}_{\text{res}} \left\{ \hat{\mathcal{V}}(t) \hat{\mathcal{V}}(\tau) \rho(\tau) - \hat{\mathcal{V}}(\tau) \tilde{\rho}_{\text{sys}}(t) \otimes \rho_{\text{res}}(\tau) \right\} .$$

(17.31)

The coupling of the system to the bath is assumed to be of the form,

$$\hat{\mathcal{V}} = \hbar \left( \hat{a} \hat{\Gamma}(t)e^{i\Omega t} + \hat{a}^{\dagger} \hat{\Gamma}(t)e^{-i\Omega t} \right) ,$$

(17.32)

where $\hat{\Gamma}(t) = \sum_k g_k \hat{b}_k e^{-i\Omega_k t}$, the bosonic operators $\hat{a}$ and $\hat{b}_k$ act, respectively, on the system (with the frequency $\Omega$) and the bath (with the frequency $\omega_k$). Here, $g_k$ characterizes the coupling force between the oscillators of the system and the bath. Hence,

$$\frac{d\tilde{\rho}_{\text{sys}}}{dt} = -\int_0^t d\tau \text{Tr}_{\text{res}} \left\{ \left( a^{\dagger} \hat{\Gamma}(t)e^{i\Omega t} + a \hat{\Gamma}(t)e^{-i\Omega t} \right) (a^{\dagger} \hat{\Gamma}(\tau)e^{i\Omega \tau} + a \hat{\Gamma}(\tau)e^{-i\Omega \tau}) \hat{\rho}(t) \otimes \rho_{\text{res}} - \left( a \hat{\Gamma}(t)e^{i\Omega t} + a^{\dagger} \hat{\Gamma}(t)e^{-i\Omega t} \right) \hat{\rho}(t) \otimes \rho_{\text{res}} (a^{\dagger} \hat{\Gamma}(\tau)e^{i\Omega \tau} + a \hat{\Gamma}(\tau)e^{-i\Omega \tau}) \right\} .$$

(17.33)

Let’s take a closer look at one of the terms,

$$T \equiv -\int_0^t d\tau \text{Tr}_{\text{res}} \{ a^{\dagger} \hat{\Gamma}(t)e^{i\Omega t} a \hat{\Gamma}(\tau)e^{-i\Omega \tau} \hat{\rho}(t) \otimes \rho_{\text{res}} \}$$

$$= -a^{\dagger} a \hat{\rho}(t) \int_0^t d\tau \langle \hat{\Gamma}(t) \hat{\Gamma}(\tau) \rangle_{\text{res}} e^{i\Omega t} e^{-i\Omega \tau} .$$

(17.34)

We will have to evaluate quantities such as

$$\text{Tr}_{\text{res}} \langle V(t)V(s) \rho_{\text{res}} \rangle = h^2 a^{\dagger} a \langle \hat{\Gamma}(t) \hat{\Gamma}(s) \rangle_{\text{res}} e^{i\Omega(t-s)} + h^2 a a^{\dagger} \langle \hat{\Gamma}(t) \hat{\Gamma}(s) \rangle_{\text{res}} e^{-i\Omega(t-s)} ,$$

(17.35)

where $\langle \hat{\Gamma}(t) \hat{\Gamma}(s) \rangle_{\text{res}} \equiv \text{Tr}_{\text{res}} [ \hat{\Gamma}(t) \hat{\Gamma}(s) \rho_{\text{res}} ]$, and for the thermal bath, $\langle b_j^{\dagger} b_k \rangle = \delta_{jk}(1+n_k)$ and $n_k = (e^{\beta \hbar \omega_k} - 1)^{-1}$. Hence,

$$T = -a^{\dagger} a \hat{\rho}(t) \sum_{j,k} g_j g_k \langle b_j^{\dagger} b_k \rangle_{\text{res}} \int_0^t d\tau e^{i(\omega_j t - \omega_k \tau)} e^{i\Omega(t-\tau)}$$

$$\simeq -a^{\dagger} a \hat{\rho}(t) \sum_k g_k^2 n_k \int_0^{\infty} d\tau e^{i(\omega_k - \Omega)(t-\tau)} .$$

(17.36)

Then we will have to use the relationship,

$$\int_0^{\infty} d\tau e^{\pm i\pi \tau} = \pi \delta(\varepsilon) \pm i PV ,$$

(17.37)

where $PV$ denotes Cauchy part of the principal value. These correspond to a ‘Lamb shift’ and a ‘Stark shift’ of the frequency, which are considered to be small in com-
17.3. REPEATED MEASUREMENTS

comparion to Ω and should be neglected here,

\[ T = -a^\dagger a\hat{\rho}(t) \sum_k g_k^2 \left( e^{\beta\hbar\omega_k} - 1 \right)^{-1} \int_0^\infty d\tau e^{i(\omega_k-\Omega)(t-\tau)} \]  
\[ = -a^\dagger a\hat{\rho}(t) \sum_k g_k^2 \left( e^{\beta\hbar\omega_k} - 1 \right)^{-1} \pi \delta(\omega_k - \Omega) \]
\[ = -a^\dagger a\hat{\rho}(t) \sum_k g_k^2 \left( e^{\beta\hbar\Omega} - 1 \right)^{-1} \pi = -\pi N a^\dagger a\hat{\rho}(t) \sum_k g_k^2 \delta(\omega_k - \Omega) = Naa^\dagger\hat{\rho}(t)\pi \frac{\gamma}{2}. \]

where \( N \equiv \left( e^{\beta\hbar\Omega} - 1 \right)^{-1} \). We define \( \frac{\gamma}{2} \equiv \sum_k g_k^2 \delta(\omega_k - \Omega) \). The procedure can be repeated for all terms in the master equation. We then obtain the master equation for a damped harmonic oscillator,

\[ \frac{d\hat{\rho}}{dt} = \frac{\gamma}{2} (N + 1) \left( 2a\hat{\rho} - a^\dagger a\hat{\rho} - \hat{\rho}a^\dagger a \right) - \frac{\gamma}{2} N \left( 2a^\dagger\hat{\rho}a - aa^\dagger\hat{\rho} - \hat{\rho}aa^\dagger \right). \]  
(17.39)

17.2.5 Exercises

17.2.5.1 Ex: Master equation for cavities

Be κ the loss rate for photons by transmission through the mirrors of a cavity. Show that the master equation gives,

\[ \frac{d\hat{\rho}}{dt} = \frac{\kappa}{2} (\bar{n} + 1) \left( 2\hat{a}\hat{\rho} - \hat{a}^\dagger\hat{a}\hat{\rho} - \hat{\rho}\hat{a}^\dagger\hat{a} \right) - \frac{\kappa}{2} \bar{n} \left( 2\hat{a}^\dagger\hat{\rho}\hat{a} - \hat{a}\hat{a}^\dagger\hat{\rho} - \hat{\rho}\hat{a}\hat{a}^\dagger \right), \]

where the density operator is defined by \( \rho \equiv \sum_{m,n} P_{m,n} |m\rangle\langle n| \) and \( \bar{n} \) is the number of thermal photons.

17.3 Repeated measurements

17.3.1 The quantum Zeno effect

A famous problem raised by the Greek philosopher (490-430 AC) Zeno goes like this: Achilles and a turtle organize a race. The arrogant Achilles leaves a 100-meter lead to the turtle. The race begins. Achilles soon covers the 100 meters, only to find out that meanwhile the turtle has advanced by 10 meters. He continues running to cover the 10 meters, only to find out that meanwhile the turtle has advanced by 1 meter, and so on. Interestingly, Zeno’s problem has a counterpart in quantum mechanics. Let us do the following Gedankenexperiment: A laser beam passes through a dense series of \( n \) polarizers, each one being rotated by an angle \( \frac{\pi}{2n} \) with respect to the preceding one. Each polarizer performs a local measurement of beam polarization. The result of this

\(^7\)In another version of his paradox, Zeno questions the possibility of motion at the example of a flying arrow: At any instant of time it occupies a space equal to its size. That is, at any particular moment of its flight, it is at rest, in a space that does not move. That is, any kind of motion is impossible. Nowadays, we know that this paradox is false, because time and motion are not discrete. But this can only be understood on the basis of infinitesimal calculus [424].
arrangement is that, in the limit of an infinitely dense series, the continuous measurement of the system completely governs its evolution and rotates the polarization by an angle of $\pi/2$.\(^8\)

In every version of the Zeno effect, the system is inhibited from evolving freely, because of too frequent measurements of its current state. Achilles would surely be able to overtake the turtle, if he did not always check on her to assess the remaining distance \(^9\).

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**Fig. 17.8:** Gráfico dos distintos tempos de um sistema instável.

The temporal evolution of the wavefunction of a system described by the Hamiltonian $\hat{H}$ is $|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi_0\rangle$. We can then calculate the amplitude and probability for the system to stay in the initial state,

$$\langle\psi_0|\psi(t)\rangle = \langle\psi_0|e^{-i\hat{H}t/\hbar}|\psi_0\rangle$$

and $P(t) = |\langle\psi_0|\psi(t)\rangle|^2$. \(17.40\)

For short times we can expand,

$$\langle\psi_0|\psi(\delta t)\rangle = |\psi_0\rangle - \frac{i}{\hbar}\hat{H}\delta t/\hbar|\psi_0\rangle - \frac{1}{2\hbar^2}\hat{H}^2\delta t^2|\psi_0\rangle + \ldots = |\psi_0\rangle + |\delta\psi\rangle,$$ \(17.41\)

such that,

$$\langle\psi_0|\psi(\delta t)\rangle \simeq 1 - \frac{i}{\hbar}\hat{H}\delta t - \frac{1}{2\hbar^2}\hat{H}^2\delta t^2$$

and $P(\delta t) \simeq 1 - \frac{1}{\hbar^2}(\langle\hat{H}^2\rangle_0 - \langle\hat{H}\rangle_0^2)\delta t^2$. \(17.42\)

In this way we can extract the Zeno time from the above equations, $\tau_Z = \hbar^2/\sqrt{\langle\hat{H}^2\rangle_0 - \langle\hat{H}\rangle_0^2}$. We now make $N$ successive von Neumann measurements within a time $t$, which leads to a measurement frequency of $\tau^{-1}$. The measurements are conceived as to verify, whether the system is still in its initial state, but each measurement projects our system back to its initial state, from where it has to start the transition process from scratch. Under these conditions, the population of the initial state will evolve like,

$$P^{(N)}(\tau) = P^{(N)}(t/N)^N.$$ \(17.43\)

---

\(^8\)An analogous experiment can be imagined by a series of Stern-Gerlach measurements of the spin of an atom.

\(^9\)The quantum Zeno effect was often used to justify the physical relevance of the state reduction postulate. It was shown, however, that this postulate is not essential for understanding the quantum Zeno effect [42]. The effect already follows directly from the Schrödinger equation and therefore has a purely dynamical nature. This shows that the projection is a purely mathematical construct without physical reality (see Sec. 17.1.2).
Fig. 17.9 shows the evolution for five measurements separated by time intervals $\tau$. In comparison with the evolution, when no measurements are taken (dashed line), the evolution with measurements inhibits the depletion of the initial state. Extrapolating the number of measurements to infinity, the probability (17.43) converges to 1,

$$\left[ 1 - \left( \frac{t}{N\tau_Z} \right)^2 \right]^N \xrightarrow{N \text{ large}} e^{-t^2/2n^2} \xrightarrow{N \to \infty} 1.$$  \hfill (17.44)

See Excs. 17.3.3.1 and 17.3.3.2.

Figure 17.9: Inhibition of the decay of a state by repeated measurements (here $N = 5$). The dashed (solid) line represents the survival probability with (without) measurements. The gray line represents an exponential interpolation function.

Suppression of the evolution of a quantum system due to the quantum Zeno effect was observed experimentally [308] using beryllium ions. Nevertheless, the discussion about the correct interpretation of this effect and its relationship to trivial power broadening is not closed. Some works have even proposed the possibility of an anti-Zeno effect [?, 8, 610], where observation would accelerate the evolution of the system. Currently the quantum Zeno effect is also studied for possible applications in metrology, computation, and quantum information [343].

When the quantum Zeno effect was proposed for the first time, it was considered a paradox: How could an unstable particle never decay, just by being continually observed? And what would happen to Schrödinger’s cat, whose live depends on state of the particle? Could we save it from its cruel fate just by observing it?

Another interesting question concerns the quantum nature of the quantum Zeno effect. Is it really non-classical? On one hand, the quantum Zeno effect supposes the complete reduction of the system to an eigenstate. However, we can imagine classical measurements that also reduce the state (such as the above-mentioned measurement of the polarization of a beam of light).
17.3.2 Quantum non-demolition measurement

17.3.3 Exercises

17.3.3.1 Ex: The quantum Zeno effect

Discuss the quantum Zeno effect at the example of a laser beam passing through a birefringent medium. Compare the situations without polarizers and with an infinite number of vertical polarizers.

17.3.3.2 Ex: The quantum Zeno effect

A two-level atom resonantly driven by a laser can be described by the Hamiltonian:

\[ H = \begin{pmatrix} 0 & \frac{1}{2} \Omega \\ \frac{1}{2} \Omega & 0 \end{pmatrix}. \]

The solution of the Schrödinger equation gives,

\[ |\psi(t)\rangle = e^{-it\hat{H}/\hbar} |\psi_0\rangle = \begin{pmatrix} \cos \frac{1}{2} \Omega t & \frac{i}{2} \sin \frac{1}{2} \Omega t \\ \frac{i}{2} \sin \frac{1}{2} \Omega t & \cos \frac{1}{2} \Omega t \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \]

provided the atom is initially in the ground state \(|\psi_0\rangle = (1 \ 0)\). A measurement of the ground state population can only be done by a projection of the wavefunction, that is, the measurement yields the result \(\|\langle 1|\psi(t)\rangle\|^2\). What is the final state of the atom,

a. when the ground state population is measured once after an evolution time of \(t = \pi/\Omega\);

b. when the ground state population is measured once after \(n\) time intervals \(t_n = \pi/n\Omega\);

c. when the ground state population is measured \(n\) times after evolution times of \(t_n = \pi/n\Omega\);

d. when \(n \to \infty\).

17.3.3.3 Ex: The quantum Zeno effect

Consider a system described by a time-independent Hamiltonian \(\hat{H}\).

a. Calculate the probability \(P(t)\) of the system to remain in its initial state \(|\Psi_0\rangle\) in the short time approximation, that is, considering until the second-order expression expansion term for the probability. Use the simplification:

\[ \tau_z = \frac{\hbar}{\sqrt{\langle \hat{H}^2 \rangle - (\langle \hat{H} \rangle)^2}}, \]

where the term \(\tau_z\) is called the Zeno time.

b. If \(N\) measurements are performed during a time \(t\), we have the time interval \(T = t/N\) between measurements. When a measurement is performed, the system is projected on the initial state and the temporal evolution must start from zero. Thus, after \(N\) measurements, the probability of the system remaining in the initial state is given by \([P(T)]^N\). Show that for an infinite number of measurements, \(N \to \infty\), the
system remains in the initial state without loss of probability: \( [P(T)]^N = 1 \). Interpret the result.
c. One of the simplest imaginable systems, a laser-driven two-level system executing Rabi oscillation, is described by the Hamiltonian:

\[
\hat{H} = \begin{pmatrix} 0 & \Omega \\ \Omega & 0 \end{pmatrix}.
\]

Find the expression for \( \tau_z \) as a function of the Rabi frequency \( \Omega \) for the initial state \((1 \ 0)^\dagger\).
d. Choosing the evolution time \( t = 0.01\tau_z \ll \tau_z \) and performing \( N = 5 \) measurements during this time interval, how likely is the system to remain in the initial state?
e. Let us now include a decay channel for the state \((0 \ 1)^\dagger\) with \( \Gamma = 4\gamma \), such as to simulate a system with continuous measurement. The system is initially prepared in the state \((1 \ 0)^\dagger\). If we now observe emission by decay, it means that the system left the initial state. We now have the effective Hamiltonian:

\[
\hat{H} = \begin{pmatrix} 0 & \Omega \\ \Omega & -2i\gamma \end{pmatrix}.
\]

For this system, the probability amplitude for the initial state is:

\[
\langle \Psi_0 | \Psi(t) \rangle = \frac{1}{2} \left( 1 + \frac{\gamma}{\Delta} \right) e^{-(\gamma-\Delta)t/\hbar} + \frac{1}{2} \left( 1 - \frac{\gamma}{\Delta} \right) e^{-(\gamma+\Delta)t/\hbar},
\]

with \( \Delta = \sqrt{\gamma^2 - \Omega^2} \). For a decay rate \( \gamma \ll \Omega \), calculate the probability that the system remains in the initial state. Interpret the result.

Formulas:

\[
e^x = 1 + x + \frac{x^2}{2} + O(x^3), \quad (1 - x)^N = 1 - Nx + O(x^2)
\]

\[
\cos^2(x) = 1 - x^2 + O(x^3), \quad \hat{H} = \begin{pmatrix} 0 & \Omega \\ \Omega & 0 \end{pmatrix} \rightarrow e^{-i\hat{H}t/\hbar} = \begin{pmatrix} \cos \frac{\Omega t}{\hbar} & -i \sin \frac{\Omega t}{\hbar} \\ -i \sin \frac{\Omega t}{\hbar} & \cos \frac{\Omega t}{\hbar} \end{pmatrix}.
\]

17.4 Welcher Weg information

17.4.1 The Elitzur and Vaidman bomb testing problem

Mixing the concepts of particles and waves we sometimes arrive at seemingly paradoxical conclusions. One example is Elitzur and Vaidman’s bomb testing problem. They imagined a Mach-Zehnder interferometer with the particularity that the reflecting mirror of one of the arms be connected to a device measuring the photonic recoil. That is, when a photon passes through this arm, the mirror undergoes a small acceleration, which is sufficient to activate an explosive bomb.

Now, we distinguish two cases: 1. The recoil detector does not work, i.e. the bomb is not armed. 2. The bomb is armed. We now adjust the interferometer in a way to produce destructive interference in one of the two interferometer output ports.
having sent many photons through the interferometer, we never saw any photons in the 'dark' port, we can be almost sure that the bomb is not operational.

In case the bomb is operational, the observation of a photonic recoil destroys the interference pattern at the interferometer outputs. It has to do so, because the exploding bomb informs us, in which arm the photon has passed. However, with an operational bomb the interference pattern is also destroyed, when the photon passes through the other arm, since the fact that the bomb didn’t explode tells us, that the photon went the other way.

The funny conclusion is now, that it may happen, that a photon traverses the interferometer in the arm that does not contain the bomb and exits through the 'dark port'. The probability of this happening is only 25%, but nevertheless the observation of a photon in the 'dark port' informs us that the pump is operative without ever having interacted with it.\(^{10}\)

### 17.5 Noisy measures

#### 17.5.1 Quantum projection noise

The intrinsic indeterminism of quantum mechanics has serious consequences for metrology. To show this, we consider the example of a system of two levels \(|1\rangle\) and \(|2\rangle\). This system can be in a superposition state \(|\psi\rangle\). The probability \(^{11}\) to find the system in one of the two states \(|i\rangle\) is \(p_i = \langle \hat{P}_i \rangle = |\langle \psi | i \rangle|^2\), where \(\hat{P}_i\) is the projection operator.

The result of a measurement of the population is afflicted by an inherent uncertainty expressed by the variance \((\Delta p_i)^2 = p_i(1 - p_i)\). In other words, the random projection of the system on the eigenstate basis induces a noise called quantum projection noise.\(^{12}\) This noise inhibits the determination of the probabilities \(p_i\) in a single measurement. On the other hand, by measuring populations on a sample of \(n\) atoms or by repeating the measurement \(n\) times with a single atom under identical conditions, we can reduce the uncertainty. The probability of finding an atom \(r\) times in the state \(|2\rangle\) is,

\[
P_{n,r,2} = \binom{n}{r} p_2^r (1 - p_2)^{n-r} .
\]

The expectation value and variance of this binomial distribution are \([307]\),

\[
\bar{r} = \sum_{r=0}^{n} r P_{n,r,2} = np_2 \quad , \quad (\Delta r)^2 = \sum_{r=0}^{n} (r - np_2)^2 P_{n,r,2} = np_2(1 - p_2) .
\]

Note that the standard deviation decreased with the number of atoms, \(\sigma = \Delta r / \bar{r} \sim 1/\sqrt{n}\).

Under the influence of a radiation field, the population of the two-level system (which we assume free of spontaneous emission) performs Rabi oscillations, \(\rho_{22}(t) = \)

---

\(^{10}\)See https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=6635

\(^{11}\)We adopt here the viewpoint of the Copenhagen interpretation of the quantum state reduction, but we note that a discussion based on statistical mixtures described by density matrices gives the same results.

\(^{12}\)Projection noise can be interpreted as shot noise. However, the optical shot noise in photodetectors is generated by the repartition of the field energy into discrete photons, the projection noise is the consequence of the discretization of the electronic excitation levels.
\( \frac{\Omega^2}{G^2} \sin^2 \frac{Gt}{2} \), where \( G = \sqrt{\Delta^2 + \Omega^2} \). The probability of finding the system in state \( |2\rangle \), therefore, varies in time, \( p_2(t) = \rho_{22}(t) \), and the binomial distribution (17.45) becomes,

\[
P_{n,r,2}(t) = \binom{n}{r} \left( \frac{\Omega}{G} \right)^{2n} \sin^{2r} \left( \frac{1}{2} Gt \right) \cos^{2n-2r} \left( \frac{1}{2} Gt \right) .
\] (17.47)

When we increase the number of measurements, \( n \to \infty \), this function condenses around a narrow peak at the position \( Gt = 2 \arcsin \sqrt{r/n} \). The width of the peak evolves like \( 2 \arccos \left( 2^{-1/2n} \right) \).

In summary, even for perfectly efficient population measurements (e.g. using the microwave-optical double resonance method) it is impossible to measure the probability \( p_2 \) with a single atom in a single experiment. As such an observation only admits two possible results, 'fluorescence observed' or 'fluorescence not observed', i.e. \( \rho_{22} = 1 \) or \( \rho_{22} = 0 \), a whole range of possible populations between 0 and 1 is excluded. Therefore, a single observation only provides 'partial' information, which can be gradually improved with each consecutive observation.

A presentation on this topic is available here (watch talk).

### 17.5.1.1 Ramsey experiments

The Ramsey experiment is basically equivalent to the Rabi experiment described above except for an additional rotation in configuration space allowing for the measurement of the phase precession of the coherence between the Ramsey pulses via population spectroscopy. The Ramsey fringes are approximated by \( p_2 = 0.5(1 + \cos((\omega - \omega_0)T)) \). The interesting magnitude is the frequency uncertainty,

\[
\Delta r = \frac{\sqrt{np_2(1-p_2)}}{n(\partial p_2/\partial \omega)} = \frac{1}{T\sqrt{n}} .
\] (17.48)

### 17.6 Topological phases

We consider a Hamiltonian \( \hat{H}(r(t)) \), which only depends implicitly on time, that is, via some time-dependent parameter \( R_I(t) \). Then the Hamiltonian evolves by developing a non-measurable dynamic phase and additionally accumulates a geometric phase (also called topological phase or Berry phase). This geometric phase, which depends on the trajectory, is adiabatically followed in parameter space,

\[
H|\psi(t)\rangle = i\hbar \partial_t|\psi(t)\rangle .
\] (17.49)

We assume that at any instant of time the system stays in an eigenstate \( |n(r)\rangle \),

\[
H|n(r)\rangle = E_n(r)|n(r)\rangle .
\] (17.50)

When \( \hat{H} \) follows the trajectory \( C : t \to r(t) \), then we see from,

\[
|\psi(t)\rangle = \exp \left[ -\frac{i}{\hbar} \int_0^t E_n(r(t'))dt' \right] \exp(i\gamma_n(C))|n(r(t))\rangle
\] (17.51)

that the phase \( \gamma_n : C \to \gamma_n(C) \) is not integrable. Berry showed that the system accumulates, after a complete cycle in the space of the parameters \( r(T) = r(0) \) and
|n(r(0))⟩ = |ψ(0)⟩ the phase,
\[ \gamma_n(C) = \int_C V_n(r) dS, \]
where,
\[ V_n(r) = \text{Im} \sum_{m \neq n} \frac{\langle n(r) | \nabla_r H(r) | m(r) \rangle \times \langle m(r) | \nabla_r H(r) | n(r) \rangle}{(E_m(r) - E_n(r))^2}. \]

We consider the example of a two-level system without decay described by the Bloch vector,
\[ H = \frac{1}{2} R \sigma = \begin{pmatrix} \text{Re} \Omega & \sigma_x \\ \text{Im} \Omega & \sigma_y \end{pmatrix}. \]

The parameters \( r \) change adiabatically. It is easy to see that,
\[ E_\pm = \pm R/2 \quad \text{and} \quad \nabla_r H = \sigma/2 \]
\[ V_n(r) = \text{Im} \frac{\langle n_\pm(r) | \nabla_r H(r) | n_\pm(r) \rangle \times \langle n_\mp(r) | \nabla_r H(r) | n_\pm(r) \rangle}{(E_+(r) - E_-(r))^2} = \pm \frac{r}{2R^3}. \]

The resulting geometric phase,
\[ \gamma_n(C) = \pm \int_C \frac{dS}{2R^2} = \pm \frac{\Omega(C)}{2}, \]
depends on the enclosed solid angle.

**Example 66 (Topological phase in a two-level system):** We consider the following state [499],
\[ n_\pm(r) = \cos \theta | g \rangle \pm e^{\pm i \phi} \sin \theta | e \rangle. \]

Now, we want to calculate the topological phase,
\[ \gamma_\pm = \oint_C i(n_\pm(r) | \nabla_r | n_\pm(r) \rangle d\mathbf{r}. \]

Applying the gradient in spherical coordinates,
\[ \nabla_r = \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} + \hat{e}_r \frac{\partial}{\partial r} \]
to the function \( |n_+\rangle \), we find,
\[ \nabla_r | n_+ (r) \rangle = -\hat{e}_\theta \frac{\sin \theta}{r} | g \rangle + \hat{e}_\phi \frac{e^{\pm i \phi}}{r} \cos \theta | e \rangle + \hat{e}_\phi \frac{e^{\pm i \phi}}{r} | e \rangle, \]
and,
\[ i \langle n_\pm(r) | \nabla_r | n_\pm(r) \rangle = i \hat{e}_\phi \frac{\sin \theta}{r}. \]

Finally,
\[ \gamma_+ = \oint_C \frac{-\sin \theta}{r} \hat{e}_\phi dR = \oint_C \frac{-\sin \theta}{r} r \sin \theta d\phi = \oint_C \sin^2 \theta d\phi dt. \]

The condition of adiabaticity is essential for emergence of topological phases. The system always remains in an eigenstate (fixed quantum numbers) when we vary parameters of the environment more slowly than all characteristic constants of the system, even when the Hamiltonian is time-dependent (variable eigenvalues).
17.6. TOPOLOGICAL PHASES

17.6.0.1 Generalization of the Berry following Aharonov

We will now drop the conditions imposed to the Hamiltonian with regard to its
adiabatic behavior and request that the state must be a eigenstate:

$$\hat{H}|\psi(t)\rangle = i\hbar \dot{\psi}(t) \ .$$

(17.57)

A process is cyclic, when there is a \( \tau \), such that,

$$|\psi(\tau)\rangle = e^{i[f(\tau) - f(0)]} |\psi(0)\rangle \ .$$

(17.58)

Defining the space of radii by

$$|\tilde{\psi}(t)\rangle = e^{-if(t)} |\psi(t)\rangle ,$$

(17.59) and from the Schrödinger equation we obtain,

$$f(t) - f(0) = -\frac{1}{\hbar} \int_0^t \langle \psi(t)|\hat{H}(t)|\psi(t)\rangle dt + \int_0^t \langle \tilde{\psi}(t)|i\frac{d}{dt}|\tilde{\psi}(t)\rangle \equiv \delta + \beta \ .$$

(17.60)

Therefore, in the space of radii we have a closed curve:

$$C : [0, \tau] \rightarrow \psi(t) \in \mathcal{H} \quad \downarrow e^{-if(t)} \quad C' : [0, \tau] \rightarrow \tilde{\psi}(t) \in \mathcal{P} \ .$$

The dynamic phase \( \delta \) can be zeroed by an appropriate choice of \( \hat{H}(t) \), but not the
topological phase \( \beta \). \( \beta \) does not depend on \( \hat{H}(t) \), but is a geometric property of the
curve, which projects \( \mathcal{H} \) onto \( \mathcal{P} \). In contrast to \( e^{i\beta} \), the phase \( \beta \) is only determined
modulo \( 2\pi n \).

17.6.0.2 Berry phase for two-level systems

Following [6] we consider the Hamiltonian,

$$\hat{H} = \hbar \left( \frac{\Delta}{2} \Omega \right) \ .$$

(17.62)

The solution of the Schrödinger equation is \( |\psi(t)\rangle e^{-i\hat{H}t/\hbar}|\psi(0)\rangle \). The eigenvalue matrix is,

$$\hat{E} = \frac{\hbar}{2} G \hat{\sigma}_z \quad \text{with} \quad G \equiv \sqrt{\Delta^2 + \Omega^2} \quad \text{and} \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ .$$

(17.63)

The total phase shift after a precession cycle is,

$$\phi = \frac{\hat{H}}{\hbar} t = \frac{1}{2} G t = \pi \ .$$

(17.64)

The dynamic phase is,

$$\delta = \frac{1}{\hbar} \int_0^{2\pi/G} \langle \psi(t)|\hat{H}|\psi(t)\rangle dt = \frac{1}{\hbar} \int_0^{2\pi/G} \langle e^{iGt/2}\psi(0)|\frac{\hbar}{2} G |e^{-iGt/2}\psi(0)\rangle dt \ .$$

(17.65)
Starting from the initial state \( \psi = \begin{pmatrix} \cos \theta \\ \imath \sin \theta \end{pmatrix} \),
\[
\delta = \frac{\hbar}{2} \int_0^{2\pi/G} (\cos^2 \theta - \sin^2 \theta) > dt = -\pi \cos \theta .
\] (17.66)

The geometric phase corresponds to the enclosed solid angle,
\[
\beta = \phi - \delta = \pi (1 - \cos \theta) = \frac{1}{2} \Omega(C) ,
\] (17.67)
although the atom is not in an eigenstate and has no adiabatic variation of the parameters.

The Berry phase can be measured in Ramsey experiments, as discussed in Exc. 17.6.2.1.

17.6.1 Aharonov-Bohm effect

A particular case for topological phases is the Aharonov-Bohm effect, which we will discuss in the following. The only observables of electromagnetism are the forces of Coulomb and Lorentz which, in the theory of electrodynamics, are described by electric and magnetic fields. Electromagnetic potentials can be introduced to simplify calculations, but they are not observables with a physical reality. In contrast, in quantum mechanics, electromagnetic potentials are more fundamental than electromagnetic fields. This is demonstrated by the Aharonov-Bohm effect.

![Diagram](image)

Figure 17.10: (a) Scheme for measuring the Aharonov-Bohm effect. (b) Aharonov-Casher effect: the electrodes \( \Phi \) do not produce electric fields inside the conductors; even so, one observes constructive or destructive interference at the output of the interferometer, depending on the applied potential.

The idea of this effect is schematized in Fig. 17.10. An electron beam is coherently divided into two arms (e.g. by a double slit) passing both sides of an infinitely extended and perfectly shielded solenoid. In this way the magnetic field \( \vec{B} \) vanishes in the region outside the solenoid, but there must exist nonetheless a potential vector \( \vec{A} \), because we observe on the screen an interference pattern of the two arms of the electronic interferometer. When pass a current through the solenoid, we observe a displacement of the interference pattern.

17.6.1.1 Aharonov-Bohm effect and gauge transformation

Let \( R \) and \( S \) be two disconnected spatial regions. Suppose that the electric and magnetic fields are kept zero in region \( R \). Then, it is classically impossible to measure
some change in the dynamics of a body confined to the region $R$ resulting from a change of the magnetic field confined to the region $S$. The Aharonov-Bohm effect shows that the opposite is true: Electrons in the magnetic field-free region $R$ do sense magnetic field fluxes in a region $S$, despite the regions $R$ and $S$ having no intersection!

In the classical theory of electromagnetism, in a region of empty space (except for electric charges and electric currents), the electric $\vec{E}(r,t)$ and magnetic fields $\vec{B}(r,t)$ are related to the electric charge $\rho(r,t)$ and current densities $j(r,t)$ according to the Maxwell equations. When we know for a spatial region the sources $\rho$ and $j$ and the boundary conditions that the fields $\vec{E}$ and $\vec{B}$ must fulfill, we can determine the fields as solutions of Maxwell’s system of partial differential equations.

In classical electrodynamics, observed from some inertial frame, the electromagnetic force $F_{em}$ acting on a point-like body with charge $q$, at position $r$, and with velocity $v$, is given by the Lorentz force:

$$ F_{em}(r(t), t) = q\vec{E}(r(t), t) + qv(t) \times \vec{B}(r(t), t). $$  (17.68)

Electrodynamic theory affirms the existence of two functions $\Phi(r, t)$ and $A(r, t)$, such that,

$$ \vec{B}(r, t) = \nabla \times A(r, t) \quad \text{and} \quad \vec{E}(r, t) = -\nabla \Phi(r, t) - \frac{\partial A(r, t)}{\partial t}. $$  (17.69)

Thus, we can use the equations (17.69) to rewrite the Maxwell equations.

The so-defined potentials $\Phi$ and $A$ are not unique, but any $\Phi$ and $A$ leading to the same fields $\vec{E}$ and $\vec{B}$, and thus to the same physics, are equivalent. We will, however, fix $\Phi$ and $A$ adopting an additional condition that must be obeyed, i.e. we will adopt a particular gauge. For the discussion of the Aharonov-Bohm effect, we will adopt the Lorentz gauge defined by,

$$ \nabla \cdot A(r, t) + \frac{1}{c^2} \frac{\partial \Phi(r, t)}{\partial t} = 0, $$  (17.70)

where $c$ is the propagation velocity of light in vacuum.

### 17.6.1.2 Equation for quantum particle exposed to a vector potential $A$

Assume a particle (without spin) of mass $m$ and charge $q$, whose wavefunction is confined to a region $R$ (connected by paths). We demand $\Phi = 0$ and $\vec{E} = \vec{B} = 0$, but we let $A \neq 0$, that is, $\nabla \times A(r, t) = 0$. Note that along with (17.69) this forces $A$ to be stationary. According to quantum mechanics the wavefunction $\Psi$ of the particle must obey the following Schrödinger equation:

$$ \frac{1}{2m} \left( \frac{\hbar}{i} \nabla - qA(r) \right)^2 \Psi(r, t) + V(r)\Psi(r, t) = i\hbar \frac{\partial \Psi(r, t)}{\partial t}. $$  (17.71)

In (17.71) the potential vector $A$ is present, even if $\phi$, $\vec{E}$, and $\vec{B}$ are kept zero throughout the region $R$.

Since the rotation $A$ vanishes in $R$, considering that the integral can be calculated for any path contained in $R$ that is deformable to a (arbitrarily chosen) point $O \in R$,
we can define the following scalar field:

\[ g(r) \equiv \frac{q}{\hbar} \int_0^r A(x) \cdot dx. \quad (17.72) \]

From (17.72) we have:

\[ \nabla g(r) = \frac{q}{\hbar} A(r). \quad (17.73) \]

Now, we have already shown in Sec. 2.5.3, that the wavefunction

\[ \psi(r, t) \equiv e^{-ig(r)} \Psi(r, t) \quad (17.74) \]

corresponds to the gauge transform (2.195) and, given the condition (2.194), satisfies the same Schrödinger equation as \( \Psi(r, t) \). We showed this explicitly in Exc. 17.6.2.2. Thus, the presence of a potential vector in the region \( R \), even in the absence of fields, causes a phase shift \( e^{ig(r)} \) of the wavefunction. An interesting issue studied in Exc. 17.6.2.3 is, whether this implies that the freedom of choice of the gauge field is lost.

**Example 67 (Observation of the Aharonov-Bohm effect):** Imagine an electron beam passing through a double-slit, as shown in Fig. 17.10(a). The electronic wavefunction diffracts through both slits, which produces an interference pattern on a subsequent screen. Now, just after the double-slit, in the shade of the region separating the two slits, we place an ideal infinitely long solenoid traversed on its axis by a constant, however, adjustable flux of magnetic field. The magnetic (and also the electric) field of the solenoid is confined to a region \( S \), and the confinement can be guaranteed, e.g. with layers of shielding materials, including superconductors. On the other hand, the wavefunctions of the electrons are manifestly zero in this \( S \) region. In the \( R \) region, where the electronic wavefunction may be non-zero, the fields are kept zero. \( R \) and \( S \) have no overlap, both \( R \) and \( S \) are separately connected by paths.

We will show that the flux of the magnetic field in \( S \) can be measured through the electronic dynamics in the region \( R \), although the electron is never in the region \( S \), but confined to the field-free region \( R \). This is the Aharonov-Bohm (magnetic) effect.

The field \( \vec{B} \) in the inner region of the solenoid is given by \((I \) is the electric current in the wire, \( N \) is the density of windings),

\[ \vec{B}(r, t) = \mu_0 I N \hat{e}_z. \]

Outside the solenoid, that is, for \( \rho > a \), we have,

\[ A(r, t) = \frac{\Phi_B}{2\pi \rho} \hat{e}_\phi, \]

where \( \Phi_B = \pi a^2 B(0, t) \) is the magnetic field flux \( \vec{B} \) through the cross section of the solenoid.

At a point \( r_{sim} \) of the screen, located in the plane of symmetry of the system, we calculate \( g(r_{sim}) \) from Eq. (17.72) for two different paths: both starting at the source and ending at the screen, but one going through the left slit, the other through the right slit:

\[ g(r_{sim}) = \frac{q}{\hbar} \int_0^{r_{sim}} A(x) \cdot dx = \frac{q\Phi_B}{2\pi \hbar} \int \left( \frac{1}{\rho} \right) \cdot (\rho \hat{e}_\phi d\phi) = \pm \frac{q\Phi_B}{2\hbar}. \]
17.6. TOPOLOGICAL PHASES

The + sign means that the integration was done in the sense parallel to $A$, and thus in the sense of $I$ in the solenoid. The sign - holds for the other integration path. The phase difference, at point $r_{sim}$, between these two paths will be:

$$\delta = \frac{q\Phi_B}{\hbar}.$$ 

That is, the phase difference (experimentally observable via a shift of the interference pattern) is directly proportional to the magnetic field flux $\mathbf{B}$, even though the wavefunction is zero in the region $S$, where the $\mathbf{B}$ field is confined.

Let us also imagine another situation: Instead of an electron source producing a beam, let us confine an electronic wavefunction on a closed path circling the solenoid at a distance $b$, but inside the region of $R$. That is, the electron follows a field line $BA \propto \hat{e}_\phi$. Then it can be shown, that the flow $\Phi_B$ removes the degeneracy of the energy levels of the electron:

$$E_n = \frac{\hbar^2}{2mb} \left( n - \frac{q\Phi_B}{2\pi\hbar} \right)^2,$$

with integer, that is, $n = 0, \pm 1, \pm 2, ...$ [236].

17.6.1.3 Generalizations of the Aharonov-Bohm effect

The Aharonov-Bohm effect can be generalized to the internal degrees of freedom of a single atom, that is, from real space to configuration space. Let us imagine a Mach-Zehnder interferometer, where one of the arms crosses a constant homogeneous field region. The corresponding Lorentz force $\mathbf{F} = \int d^3r \hat{\rho}(\mathbf{r})\mathbf{E}(\mathbf{r}) + j(\mathbf{r}) \times \mathbf{B}(\mathbf{r})$ vanishes, but the de Broglie wave undergoes a phase shift $\chi = \int H_{int} dt$:

<table>
<thead>
<tr>
<th>scalar potentials</th>
<th>vector potentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi = -\int e\phi dt$</td>
<td>$-\oint \mathbf{E} \cdot d\mathbf{r}$</td>
</tr>
<tr>
<td>$\nabla \phi = 0$</td>
<td>$\nabla \times \mathbf{A} = 0$</td>
</tr>
<tr>
<td>for $\text{e}^-$</td>
<td>$\text{e}^-,$ (ABE)</td>
</tr>
<tr>
<td>$-\int d \cdot \mathbf{E} dt$</td>
<td>$-\oint d \times \mathbf{B} dr$</td>
</tr>
<tr>
<td>$\nabla \times \mathbf{E} = \nabla \cdot \mathbf{E} = 0$</td>
<td>?</td>
</tr>
<tr>
<td>$\text{Mg, Yb}^+$</td>
<td>$\text{n, Yb}^+$</td>
</tr>
<tr>
<td>$-\int \hat{\mu} \cdot \mathbf{B} dt$</td>
<td>$-\oint \mu \times \mathbf{E} dr$</td>
</tr>
<tr>
<td>$\nabla \cdot \mathbf{B} = \nabla \cdot \mathbf{B} = 0$</td>
<td>$\text{n, Ca},$ (ACE)</td>
</tr>
</tbody>
</table>

**Example 68 (Topological phase in configuration space):** We consider a temporal Ramsey experiment with a single trapped ion by exciting a hyperfine transition. Between the pulses we apply a magnetic field for a time $t$. The accumulated phase will be $\phi = (\hat{\mu} \cdot \mathbf{B}/\hbar)t$. This phase corresponds to the precession of the dipole moment excited by the first Ramsey pulse. The phase can be interpreted in analogy to Aharonov-Bohm effect, considering that 1. the magnetic field is homogeneous, and 2. despite this fact still acts on the spin, not exerting a force, but causing a phase shift.

17.6.2 Exercises

17.6.2.1 Ex: Measurement of the Berry phase in a two-level system

Discuss how the Berry phase in a two-level system can be measured via a Ramsey experiment.
17.6.2.2 Ex: The Aharonov-Bohm effect as a gauge transform

Show explicitly that the wavefunction transformed by a gauge transformation (17.74) satisfies the Schrödinger equation.

17.6.2.3 Ex: Aharonov-Bohm effect and gauge transformation

The phase of the interference pattern in the Aharonov-Bohm effect is fixed by the magnetic flux through the solenoid. Does that mean, that we lose the freedom of choosing an arbitrary gauge potential?
Chapter 18

Entanglement and quantum gates

The concept of entanglement arose in quantum mechanics by Einstein, Podolski and Rosen’s famous Gedankenexperiment, today called the EPR paradox [185]. In his Gedankenexperiment, Einstein tried to prove the necessity of hidden variables for quantum mechanics to be a complete theory. Consequently, we begin this chapter by introducing the notion of entangled particles and recapitulating the discussion of the EPR paradox.

Since Feynman discovered the utility of entangled states for quantum computation [466, 111], this area of research exploded with thousands of theoretical researchers, but very few experimentalists, due to the enormous technical difficulties of creating and controlling these states. On the other side, states of entangled photons already play an important role in quantum cryptology [48]. And in the context of metrology, spin-squeezed correlated quantum states offer the possibility of quantum noise reduction in frequency standards [632].

Among the various systems proposed for the realization of entangled states and quantum computing gates we will only discuss one idea, which is based on the mutual coupling of atoms through a Jaynes-Cummings-like interaction mediated by an optical mode.

18.1 Quantum correlations and entanglement

18.1.1 The EPR paradox and GHZ states

Let us imagine two maximally correlated particles produced by a suitable source, which fly freely without interaction in opposite directions along the z-axis toward two detectors a and b. The particles have an internal degree of freedom (spin) \(|\pm\rangle_{a,b}\), which can be measured in various directions, for example, \(x\) or \(y\) by operators \(\hat{\sigma}^x_{a,b}\) or \(\hat{\sigma}^y_{a,b}\). Since the particles are completely entangled, the result of a measurement on the first particle \(\hat{\sigma}^x_a\) allows the prediction of the result of another measurement \(\hat{\sigma}^b_x\) performed on the second particle, and similarly for \(\hat{\sigma}^a_y\) and \(\hat{\sigma}^b_y\). Why is that?

The theory of hidden variables proposed by Einstein, Podolsky and Rosen [185] postulates, that the total state describing the two particles contains all information about the way, how the particles should behave at the detectors. The information was imprinted on each one of the two particle’s when they were created in the source,
i.e. the total state must be of the type,
\[
|\psi\rangle = \left( \frac{\pm a_x}{\pm \xi y} \right) .
\] (18.1)

We should read this notation as a decision table.

On the other hand, quantum mechanics postulates that the reduction of the wavepacket describing the particle at detector \(a\) decides \textit{spontaneously} on the result of the measurement at detector \(b\). This decision \textit{has no physical cause}. If the particles move with the speed of light, this decision is not restricted by \textit{local causality} \[268\]. The state can be given in the form,
\[
|\psi\rangle = |+a +b\rangle - |-a -b\rangle .
\] (18.2)

Which one of the two pictures is correct, the hidden variables assumption or quantum mechanics, can actually be tested by Wheeler’s \textit{delayed choice} experiment. It consists of using pairs of correlated photons emitted in different directions, where they are expected by photodetectors. Polarizers located in front of the detectors fix the quantization axis to \(\hat{e}_x\) or \(\hat{e}_y\), but the choice of the axis is made only after the photons were created by the source, in order to avoid possible backactions of the polarizers on the source \(^1\). Bell \[44\] found an inequality condition for the statistics of the results of repeated measurements, where the orientation of the polarizers is randomly varied. The experiment run by Aspect \[22, 21\] showed that the assumption of hidden variables violates \textit{local realism} and thus confirmed quantum mechanics as being a complete theory.

Here, we show a modified version of the EPR experiment proposed by Greenberger, Horne and Zeilinger (GHZ) based on the \textit{GHZ state} \[229\]. They imagined a source creating three correlated non-interacting spin 1/2 particles flying toward three Stern-Gerlach type magnetic detectors, which measure the spins in \(x\) or in \(y\)-direction. The correct state is either quantum, \(|\psi\rangle = |+\rangle - |-\rangle\) or contains hidden variables \(|\psi\rangle = (\pm \pm \pm)\). We know from quantum mechanics, that \(\hat{\sigma}_x |\pm\rangle_x = |\mp\rangle_x\) and \(i \hat{\sigma}_y |\pm\rangle_x = \mp |\mp\rangle_x\). From this follows,
\[
\hat{\sigma}_x^a \hat{\sigma}_x^b \hat{\sigma}_x^c |\psi\rangle = -|\psi\rangle ,
\] (18.3)

but also,
\[
\hat{\sigma}_x^a \hat{\sigma}_y^b \hat{\sigma}_y^c |\psi\rangle = |\psi\rangle ,
\] (18.4)
\[
\hat{\sigma}_y^a \hat{\sigma}_x^b \hat{\sigma}_y^c |\psi\rangle = |\psi\rangle ,
\]
\[
\hat{\sigma}_y^a \hat{\sigma}_y^b \hat{\sigma}_x^c |\psi\rangle = |\psi\rangle .
\]

Hidden variables in a state \(|\psi\rangle\) that is \textit{not a coherent superposition} should at least be able to predict how each particle will behave in its respective detector, when we

\(^1\) We note that first attempts to demonstrate wave-particle duality with single photons in dilute laser beams are not really conclusive, because the attenuation of a coherent state does \textit{NOT} result in a single photon states (non-classical Fock state). Even if on average only less than one photon is in the interferometer, this may still be a Glauber state. Nonetheless, real single photon experiments involving the deexcitation of individual atoms by emission of two photons, produced the same result.
measure each one of the two spin components. Eight combinations can satisfy the requirement (18.4):

\[
\begin{align*}
(\uparrow \uparrow \uparrow), & \quad (\uparrow \downarrow \downarrow),
(\downarrow \uparrow \downarrow), & \quad (\downarrow \downarrow \uparrow),
(\uparrow \downarrow \uparrow), & \quad (\downarrow \uparrow \downarrow),
(\downarrow \downarrow \downarrow), & \quad (\uparrow \uparrow \uparrow),
\end{align*}
\]

(18.5)

but none satisfies (18.3). Therefore, the EPR critique of quantum mechanics regarding non-locality and its incompleteness must be refuted.\(^2\)

18.1.2 Information entropy

According to von Neumann, we can define the von Neumann entropy, also called quantum information entropy as,

\[
S \equiv -\langle \log_2 \hat{\rho} \rangle = \text{Tr} (\hat{\rho} \log_2 \hat{\rho}) = -\sum_n \hat{\rho}_n \log_2 \hat{\rho}_n ,
\]

(18.6)

where \(\rho_n \equiv \langle n | \hat{\rho} | n \rangle\). For statistically independent systems the density operator is \(\hat{\rho} = \hat{\rho}_1 \otimes \hat{\rho}_2\) and the entropy is additive \(S = S_1 + S_2\). The entropy is observable, that is, independent of the basis and invariant with respect to unitary transformations. Therefore, \(\hat{\rho}\) can be diagonalized and can be assumed diagonal in the following examples. For \(N\) independent qubits the density operator \(\hat{\rho}^{(N)}\) and the entropy \(S^{(N)}\) are:

\[
\begin{align*}
\hat{\rho}^{(0)} &= |1\rangle \langle 1| , \quad S^{(0)} = 0 \text{ bit} \quad (18.7)
\hat{\rho}^{(1)} &= \frac{1}{2} (|1\rangle \langle 1| + |2\rangle \langle 2|) , \quad S^{(1)} = 1 \text{ bits}
\hat{\rho}^{(2)} &= \frac{1}{4} (|11\rangle \langle 11| + |12\rangle \langle 12| + |21\rangle \langle 21| + |22\rangle \langle 22|) , \quad S^{(2)} = 2 \text{ bits}
\hat{\rho}^{(N)} &= \frac{1}{2^N} (|11\ldots 1\rangle \langle 11\ldots 1| + \ldots) , \quad S^{(N)} = N \text{ bits} .
\end{align*}
\]

The set is canonical and the entropy maximal. On the other hand, if the states are entangled, the entropy is always less than \(S^{(N)} = N\) bits. For the state of maximally entangled spins, we have,

\[
\hat{\rho}_{\text{corr}}^{(N)} = \frac{1}{2^N} (|11\ldots 1\rangle \langle 11\ldots 1| + |22\ldots 2\rangle \langle 22\ldots 2|) , \quad S_{\text{corr}}^{(N)} = 1 \text{ bit} . \quad (18.8)
\]

Entropy is a measure for the degree of entanglement of a system. For a Dicke state \(|J, M\rangle\) the entropy is,

\[
S_{JM} = -\log_2 \left( \binom{2J}{J+M} \right). \quad (18.9)
\]

For beam splitters, the information entropy is calculated as follows: A Fock state

\(^2\text{Note that the coupling of different degrees of freedom is not an entanglement, but it is the condition for being able to generate entanglement}\)
\[ |N\rangle = |1\rangle^N \text{ divided by a beam splitter is described by}, \]
\[ 2^{-N/2} : (|1\rangle + |2\rangle)^N = 2^{-N/2} \sum_{n=0}^{N} \binom{N}{n} |1\rangle^{N-n} |2\rangle^n \]
\[ (18.10) \]
\[ \rho_{\text{split}}^{(N)} = \frac{1}{2^N} \sum_{n,m=0}^{N} \binom{N}{n} \binom{N}{m} |1\rangle^{N-n} |2\rangle^n \langle 1|^{N-m} \langle 2|^m \]
\[ \rho_{\text{split}}^{(N)} = \frac{1}{2^N} \sum_{n=0}^{N} \binom{N}{n} \binom{N}{n} |1\rangle^{N-n} |2\rangle^n \langle 1|^{N-n} \langle 2|^n \]

For the information entropy, we obtain,
\[ S_{\text{split}}^{(N)} = N + \frac{1}{2^N} \sum_{n=0}^{N} \binom{N}{n} \log_2 \left( \binom{N}{n} \right) . \]
\[ (18.11) \]

The division of a beam is an incoherent process in the sense that it increases the entropy. The process is irreversible. The divided beams can not be recombined by a coherent process. For example, an interferometer always has two output ports. However, the phase is preserved.

The quantum information content is defined by the deviation from maximum entropy,
\[ Q = S_{\text{max}} - S_{\text{actual}} . \]
\[ (18.12) \]

If the system is in a mixed state, the entropy measures deviations from a pure state behavior [37].

18.1.3 Exercises

18.1.3.1 Ex: Bell states

Show that the Bell states cannot be written as products of two states.

18.1.3.2 Ex: Bell states

Calculate the reduced density matrix corresponding to a Bell state and the corresponding entropy (linear and von Neumann).

18.1.3.3 Ex: Entanglement

Upon detecting the polarization of one photon in an entangled photon pair, the polarization of the other photon gets determined. Does this lead to a faster than light communication? Justify your answer. How would you demonstrate the no-cloning theorem from the assumption that relativistic causality should prevail.

18.1.3.4 Ex: Entanglement

Three photon are prepared in the state GHZ:
\[ |\psi\rangle = \frac{1}{\sqrt{3}} (|h\rangle_1 |h\rangle_2 |h\rangle_3 + |h\rangle_1 |h\rangle_2 |h\rangle_3) . \]
Show that, when the components of polarization are measured along the axes that have an angle of 45° with respect to the original axes, corresponding to the states, 

\[ |h'\rangle = \frac{1}{\sqrt{2}}(|h\rangle + |v\rangle) \quad (x = 1) \quad \text{and} \quad |v'\rangle = \frac{1}{\sqrt{2}}(|h\rangle - |v\rangle) \quad (x = -1), \]

one gets necessarily an even number of photons with vertical polarization \( v' \).

### 18.1.3.5 Ex: NOON state

A **NOON state** is a quantum-mechanical many-body entangled state:

\[
|\psi_{\text{NOON}}\rangle = |N\rangle_a |0\rangle_b + e^{iN\theta} |0\rangle_a |N\rangle_b \sqrt{2}, \tag{18.13}
\]

which represents a superposition of \( N \) particles in mode \( a \) with zero particles in mode \( b \), and vice versa. Usually, the particles are photons, but in principle any bosonic field can support NOON states.

Two-photon NOON states, where \( N = 2 \), can be created deterministically from two identical photons and a 50:50 beam splitter. This is called the Hong-Ou-Mandel effect in quantum optics. Three- and four-photon NOON states cannot be created deterministically from single-photon states, but they have been created probabilistically via post-selection using spontaneous parametric down-conversion.

### 18.2 Creation of quantum correlations

Since the experimental verification of **Bell’s inequality** [23] numerous ideas were proposed for the creation and application of correlated states in distant particles. Realistic proposals on how to create such states are often based on a Jaynes-Cummings type coupling between states of atomic excitation and the degrees of freedom of a harmonic oscillator. The Jaynes-Cummings dynamics has been extensively studied in micromasers, where the non-resonant interaction of an atomic transition with the TEM\(_{00}\) mode of a stored radiation field generates quantum coherences. In very high finesse cavities, light field states with sub-Poissonian photon statistics can be generated and stored for macroscopic times, and schemes for the creation of Fock states and Schrödinger cat states were proposed and tested. Furthermore, the electronic excitation states of atoms successively traversing a micromaser can be correlated under suitable conditions. The availability of fundamental techniques motivated proposals for the investigation of phenomena such as EPR correlations, quantum teleportation, and quantum switching [172]. On the other hand, quantum coherences are very fragile to dissipation and rapidly decay when exposed to perturbations.

Jaynes-Cummings type dynamics can also be realized with a single ion stored in a Paul trap, where the interaction of its mechanical motion with an electronic transition [66] can induce very stable quantum coherences in the vibrational degrees of freedom. Schrödinger cat states have already been demonstrated in this system [406], as well as fundamental parts of a quantum computer, the quantum **controlled not gate** [406] and the quantum **phase gate** [601]. A possible extension of these ideas is the collective Jaynes-Cummings interaction of a sample of ions with an optical field, where the vibrational degrees of freedom are coupled through Coulomb repulsion.
Such scenarios are close to the currently most realistic ideas of quantum computers [111].

In order to correlate particles, they must be able to exchange information, that is, they must interact. One method used on ions trapped in a linear Paul trap, where they form a straight chain, and also on neutral atoms trapped in a dual optical lattice, consists in letting them undergo \textit{controlled collisions} [314]. The conditional quantum operation proposed by Jaksch et al. is based on a conditional collisional phase shift, the condition being that the atoms are in a particular state of excitation. In a suggestive notation for the Bloch vector of a particle subject to a resonant radiation pulse, the interaction is described by,

\[
\begin{align*}
|\downarrow\rangle & \xrightarrow{\pi/2} |\downarrow\rangle + i|\uparrow\rangle, \\
|\uparrow\rangle & \xrightarrow{\pi/2} |\uparrow\rangle - i|\downarrow\rangle.
\end{align*}
\]

(18.14)

Jaksch demonstrated the following \textit{phase gate},

\[
\begin{align*}
\downarrow\downarrow & \rightarrow \downarrow\downarrow, \\
\uparrow\downarrow & \rightarrow -\downarrow\uparrow, \\
\downarrow\uparrow & \rightarrow \uparrow\downarrow, \\
\uparrow\uparrow & \rightarrow \uparrow\uparrow.
\end{align*}
\]

(18.15)

This gate is equivalent to the \textit{XOR} port for the qubits defined by $\downarrow$ and $\downarrow \pm \uparrow$, since,

\[
\begin{align*}
\downarrow (\downarrow \pm \uparrow) & \rightarrow \downarrow (\downarrow \pm \uparrow), \\
\uparrow (\downarrow \pm \uparrow) & \rightarrow \uparrow (\downarrow \pm \uparrow).
\end{align*}
\]

(18.16)

Alternative approaches to realizing quantum gates use dipole-dipole interactions [85], conditional Raman adiabatic passages by laser-induced excitation of interatomic dipole-dipole interactions [386], or interactions between permanent dipoles of atoms in Rydberg states [315] \(^3\)

In Sec. ?? we showed already that the Jaynes-Cummings model is able to perform coherent operations on a two-level system –which from now on we will call \textit{qubit}–, such as the \textit{population inversion} (NOT-gate) and the controlled dephasing of an excited dipole moment (phase gate). These operations are fundamental for applications in quantum information, however, we still lack essential ingredients allowing us to entangle states of two, three or more qubits in order to perform a \textit{quantum register} of \textit{qubits}. Once these register are realized, we must define coherent quantum operations called \textit{quantum gates}.

18.2.1 The Jaynes-Cummings model for 2 atoms and 1 light mode

In Sec. 15.2 we showed, how a Jaynes-Cummings interaction between an atom and a radiation field can exchange quantum correlations. It is reasonable to expect that, when we have two (or more) atoms interacting with the same radiation field, we can exchange correlations between atoms via the field. This would allow the implementation of entanglement protocols and quantum gates. We will disregard spontaneous processes, such that all couplings are then coherent and the processes reversible.

\(^3\)A system to create quantum correlations is the \textit{optical parametric oscillator} (OPO).
18.2. CREATION OF QUANTUM CORRELATIONS

In Sec. 2.3.8 we learned how to span a Hilbert space of various particles. We will now apply these notions in the scope of generalizing the Jaynes-Cummings model to two atoms interacting with the same optical mode, without spontaneous decay processes considered. The Hamiltonian of the system, which consists of two non-interacting atoms, both coupled in the same optical mode, is,

\[
\hat{H} = \omega \hat{a} \hat{a}^\dagger + \sum_{i=1,2} \omega_{0i} (\hat{\sigma}_i^+ \hat{\sigma}_i^- - \frac{1}{2}) + \sum_{i=1,2} \frac{1}{2} \Omega_i(t) (\hat{a} \hat{\sigma}_i^+ + \hat{a}^\dagger \hat{\sigma}_i^-). \tag{18.17}
\]

The suffix denotes the individual atoms. Note that the coupling constant \( \frac{1}{2} \Omega_i(t) \) can be considered as time dependent, which may be useful for modeling radiation pulse envelopes. In matrix representation the Hamiltonian acting on the subspace of \( n \) photons is,

\[
|\psi\rangle = \sum_n \left( \begin{array}{c} c_{22} n^{-1} \\
 c_{21} n \\
 c_{12} n \\
 c_{11} n + 1 \end{array} \right) |n\rangle \quad \text{where} \quad c_{ij} \equiv A_2 \langle j | A_1 \langle i | \langle n | \psi \rangle \tag{18.18}
\]

for example,

\[
|n\rangle |2\rangle_{A_1} |2\rangle_{A_2} = |n\rangle \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |n\rangle |2\rangle_{A_1} |1\rangle_{A_2} = |n\rangle \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad \text{etc.} .
\]

The atomic transition operators are generalized to,

\[
\hat{\sigma}^+_A = \sum_n |n\rangle \sigma^0 \langle n| = \sum_n |n\rangle \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \langle n| \tag{18.19}
\]

\[
\hat{\sigma}^+_A = \sum_n |n\rangle \sigma^\dagger \langle n| = \sum_n |n\rangle \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \langle n| \quad \text{etc.} .
\]

The Hamiltonian is, on this basis,

\[
\hat{H} = \sum_n |n\rangle \begin{pmatrix} n\omega - \frac{\omega_{01}}{2} - \frac{\omega_{02}}{2} \\
 n\omega - \frac{\omega_{01}}{2} + \frac{\omega_{02}}{2} \\
 n\omega + \frac{\omega_{01}}{2} - \frac{\omega_{02}}{2} \\
 n\omega + \frac{\omega_{01}}{2} + \frac{\omega_{02}}{2} \end{pmatrix} \langle n| 
\]

\[
+ \sum_n |n-1\rangle \sqrt{n} \begin{pmatrix} 0 \\
 \frac{\Omega_1}{2} \\
 \frac{\Omega_2}{2} \\
 0 \end{pmatrix} \langle n| + \sum_n |n + 1\rangle \sqrt{n+1} \begin{pmatrix} 0 \\
 \frac{\Omega_2}{2} \\
 \frac{1}{2} \Omega_1 \\
 0 \end{pmatrix} \langle n| . \tag{18.20}
\]
Now, we can rearrange the subspaces and finally get,

\[ \hat{H} = \sum_n |n\rangle \begin{pmatrix} (n-1)\omega + \frac{\omega_1}{2} + \frac{\omega_2}{2} & \frac{\Omega_1}{2}\sqrt{n} & \frac{\Omega_2}{2}\sqrt{n} \\ \frac{\Omega_1}{2}\sqrt{n} & n\omega - \frac{\omega_1}{2} + \frac{\omega_2}{2} & \frac{\Omega_2}{2}\sqrt{n+1} \\ \frac{\Omega_2}{2}\sqrt{n+1} & \frac{\Omega_2}{2}\sqrt{n+1} & (n+1)\omega - \frac{\omega_1}{2} - \frac{\omega_2}{2} \end{pmatrix} |n\rangle. \]

The density operator for the subspace is,

\[ \hat{\rho} = \begin{pmatrix} |n-1\rangle\langle 2|, A_1|2\rangle, A_2|2\rangle, A_1 \langle 2| & |n-1\rangle\langle 2|, A_1|2\rangle, A_2|2\rangle, A_1 \langle 1| & \ldots \\ |n\rangle\langle 1|, A_1|2\rangle, A_2|2\rangle, A_1 \langle 2| & \ldots \\ |n\rangle\langle 2|, A_1|1\rangle, A_2|2\rangle, A_1 \langle 2| & \ldots \\ |n+1\rangle\langle 1|, A_1|1\rangle, A_2|2\rangle, A_1 \langle 2| & \ldots \end{pmatrix}, \]

if the basis is again defined by equation (18.19).

### 18.2.1.1 Resonant excitation

To discuss the case of resonant excitation, \( \Delta_1 = \Delta_2 = 0 \), let us assume identical atoms, \( \omega_{01} = \omega_{02} \equiv \omega_0 \), and equal Rabi frequencies, \( \Omega_1 = \Omega_2 \equiv \Omega \). Assuming dipolarly forbidden strongly saturated transition, \( n = \alpha^2 \) for all \( n \), the Hamiltonian simplifies considerably,

\[ \hat{H}_n = \begin{pmatrix} n\omega & \frac{1}{2}\sqrt{\Omega} & \frac{1}{2}\sqrt{\Omega} \\ \frac{1}{2}\sqrt{\Omega} & n\omega & \frac{1}{2}\sqrt{\Omega} \\ \frac{1}{2}\sqrt{\Omega} & \frac{1}{2}\sqrt{\Omega} & n\omega \end{pmatrix}, \]

the eigenvalues can be calculated and the time evolution matrix becomes, using the abbreviation \( \varphi \equiv \sqrt{\Omega}t/2 \),

\[ e^{-i\hat{H}_n t} = e^{-i\hat{H}^{A1}_n t}e^{-i\hat{H}^{A2}_n t} = \begin{pmatrix} \cos^2 \varphi & i \sin \varphi \cos \varphi & i \sin \varphi \cos \varphi & -\sin^2 \varphi \\ i \sin \varphi \cos \varphi & \cos^2 \varphi & -\sin^2 \varphi & i \sin \varphi \cos \varphi \\ i \sin \varphi \cos \varphi & -\sin^2 \varphi & \cos^2 \varphi & i \sin \varphi \cos \varphi \\ -\sin^2 \varphi & i \sin \varphi \cos \varphi & i \sin \varphi \cos \varphi & \cos^2 \varphi \end{pmatrix}. \]

For a \( \pi \)-pulse, we get,

\[ e^{-i\hat{H}_n t} \frac{\pi}{2} \frac{1}{2} \begin{pmatrix} 1 & i & i & -1 \\ i & 1 & -1 & i \\ i & -1 & 1 & i \\ -1 & i & i & 1 \end{pmatrix}. \]

(18.24)

It is interesting to note that some superposition states completely separate from the optical mode,

\[ e^{-i\hat{H}_n t} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix} \quad \text{and} \quad e^{-i\hat{H}_n t} \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix}. \]

(18.25)
18.2. Creation of Quantum Correlations

18.2.1.2 Dispersive excitation

In the dispersive limit, \( \Delta_i \gg n_i^{1/2} / \Omega_i \), the dynamic evolution can be evaluated from a first order perturbative approach, analogous to the one already made for the standard JCM model. In this approach, the off-diagonal matrix elements (18.21) generate a light-shift of the energy levels appearing on the diagonal of the approximated matrix. Using the abbreviation \( \Lambda_i \equiv \Omega_i^2 / 4\Delta_i \), the temporal evolution matrix \( e^{-i\hat{H}_n t} \) can now be evaluated from,

\[
\hat{H}_n = -\frac{\Delta_1 + \Delta_2}{2} \mathbb{I}_4 + \begin{pmatrix}
n\Lambda_1 + n\Lambda_2 & -n\Lambda_1 + (n + 1)\Lambda_2 \\
(n + 1)\Lambda_1 - n\Lambda_2 & -(n + 1)\Lambda_1 - (n + 1)\Lambda_2
\end{pmatrix}.
\] (18.26)

We now assume that the light field only interacts with the upper level, as in the case of the dual resonance configuration studied in Exc. 15.2.4.3. This can be taken into account, neglecting those terms in the matrix (18.25) rotating with a positive Rabi frequency. Letting, moreover, \( \Delta_1 = \Delta_2 \) and \( \Omega_1 = \Omega_2 \), we obtain,

\[
\hat{H}^{(1)}_n = \begin{pmatrix} 0 & -n\Lambda \\
-n\Lambda & -2(n + 1)\Lambda
\end{pmatrix}.
\] (18.27)

Thus, the temporal evolution is,

\[
e^{-i\hat{H}_n t} = \begin{pmatrix} 1 & e^{-n\Lambda} \\
e^{-n\Lambda} & e^{-2(n+1)\Lambda}
\end{pmatrix}.
\] (18.28)

For \( \Lambda = \pi \),

\[
e^{-i\hat{H}_n t} \pi \rightarrow \begin{pmatrix} 1 & -1 \\
-1 & 1
\end{pmatrix}.
\] (18.29)

18.2.2 Bloch vector and the Q-function in the JC model with 2 atoms

Despite the more complex structure of the Hilbert space, the Bloch vectors of the individual atoms and the Q-function can be evaluated in analogy to Sec. ???. The vector de Bloch \( \vec{\rho} \) is,

\[
\vec{\rho}_{A1} = \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{2} \text{Re} \rho_{12(A1)} \\
\sqrt{2} \text{Im} \rho_{12(A1)} \\
(\rho_{22(A1)} - \rho_{11(A1)})
\end{pmatrix} \text{ where } \rho_{ij(A1)} = \text{Tr} |i\rangle_1 \langle j| \langle \psi| \langle \psi|.
\] (18.30)
In particular we have,

$$\rho_{12(A1)} = \sum_{i,j,n} 2 \langle j|1\langle i|1(2|\psi\rangle\langle \psi|n)i|1j\rangle_2$$

$$= \sum_{j,n} 2 \langle j|1(2|\psi\rangle\langle \psi|n)1j\rangle_2$$

$$= \sum_{n,m,m'} \langle n|(c_{2,1,m}|m' + 1|c_{1,1,m'+1} + c_{2,2,m}|m' - 1)\langle m'c_{1,2,m'})|n\rangle$$

$$= \sum_{n}(c_{1,1,n}c_{2,1,n} + c_{1,2,n}c_{2,2,n})$$.

Summarizing,

$$\rho_{12(Ai\neq A)} = \sum_{n}(c_{1,1,n}c_{j,i,n} + c_{i,j,n}c_{2,2,n})$$

$$\rho_{11(Ai\neq A)} = \sum_{n}(|c_{2,1,n}|^2 + |c_{i,j,n}|^2)$$

$$\rho_{22(Ai\neq A)} = \sum_{n}(|c_{j,i,n}|^2 + |c_{2,2,n}|^2).$$

(18.32)

The function $Q(\alpha)$ for the JC dynamics of 2 atoms is,

$$Q(\alpha) = \frac{1}{\pi}\langle\alpha|\hat{\rho}_{field}|\alpha\rangle$$

$$= \frac{1}{\pi}\langle\alpha|\sum_{i,j} 2 \langle j|1\langle i|\psi\rangle\langle \psi|i\rangle_1j\rangle_2|\alpha\rangle$$

$$= \frac{1}{\pi}\langle\alpha|\sum_{m,n}(c_{2,2,m-1}c_{2,2,n-1}|n - 1)\langle m - 1| + c_{1,2,m}c_{1,2,n}|n\rangle\langle m|$$

$$+ c_{2,1,n}c_{2,1,n}|n\rangle\langle m| + c_{1,1,m+1}c_{1,1,n+1}|n + 1\rangle\langle m + 1|)|\alpha\rangle$$

$$= e^{-|\alpha|^2}\left[\sum_{n} c_{2,2,n-1} \frac{\alpha^n}{\sqrt{n!}} + \sum_{n} c_{1,2,n} \frac{\alpha^n}{\sqrt{n!}} + \sum_{n} c_{2,1,n} \frac{\alpha^n}{\sqrt{n!}} + \sum_{n} c_{2,2,n+1} \frac{\alpha^n}{\sqrt{n!}}\right]^2.$$

(18.33)

18.2.3 Correlating atoms in the JCM model

The investigations of the last section can be applied to describe the transfer of quantum coherence from one atom to another. The size of our system is now increased by the additional degrees of freedom, provided by internal states of the second atom. A suitable basis was defined in equation (2.109). Now, we imagine the following Gedankenexperiment: Starting from the initial condition that two adjacent atoms are in their respective electronic ground states, we assume a microwave $\pi/2$-pulse to create simultaneously, but independently on both atoms, a superposition of the HFS levels. Then, a non-resonant optical $\pi$-pulse interacts with the upper HFS level of the first atom $|1\rangle_{A1}$, and afterward the second atom $|2\rangle_{A2}$. Instead of reducing the atomic states and preparing a Schrödinger cat state in the optical field, (as we did in Sec. 15.2), we now project the field state onto the coherent state $|\beta\rangle$ and leave the atoms in a correlated state. The total procedure can be resumed by tracing the
evolution of the whole state in the following suggestive way [26]:

\[
\begin{pmatrix}
0 \\
0 \\
0 \\
|\beta\rangle
\end{pmatrix}
\xrightarrow{\pi/2\;\text{microwave}}
\frac{1}{4}
\begin{pmatrix}
-1 \\
i \\
i \\
1
\end{pmatrix}
\begin{pmatrix}
|\beta\rangle \\
|\beta\rangle \\
-i|\beta\rangle \\
-i|\beta\rangle
\end{pmatrix}
\xrightarrow{\pi\;\text{opt+atom}1}
\frac{1}{4}
\begin{pmatrix}
|\beta\rangle \\
i|\beta\rangle \\
i|\beta\rangle \\
|\beta\rangle
\end{pmatrix}
\xrightarrow{\pi\;\text{opt+atom}2}
\frac{1}{4}
\begin{pmatrix}
|\beta\rangle \\
-i|\beta\rangle \\
-i|\beta\rangle \\
|\beta\rangle
\end{pmatrix}
\]

(18.34)

\[
\begin{pmatrix}
0 \\
0 \\
0 \\
|\beta\rangle
\end{pmatrix}
\xrightarrow{\pi/2\;\text{microwave}}
\frac{1}{4}
\begin{pmatrix}
1 \\
0 \\
0 \\
1
\end{pmatrix}
|\beta\rangle
+ \frac{1}{4}
\begin{pmatrix}
-1 \\
0 \\
0 \\
1
\end{pmatrix}
|\beta\rangle
\xrightarrow{\text{reduction}}
\frac{1}{2}
\begin{pmatrix}
-1 \\
0 \\
0 \\
1
\end{pmatrix}
|\beta\rangle
.
\]

If this procedure is extended to an arbitrary number of atoms, obviously all atoms being excited by the same optical mode before its projection in a coherent state \(|\beta\rangle\) are included in the entangled state,

\[
|\psi\rangle = \frac{1}{4}
\begin{pmatrix}
1 \\
1 \\
1 \\
1
\end{pmatrix}
|\beta\rangle
+ \frac{1}{4}
\begin{pmatrix}
-1 \\
0 \\
0 \\
1
\end{pmatrix}
|\beta\rangle
.
\]

(18.35)

Finally, the correlation of the spin orientation of the atoms must be probed with additional laser light fields, which are selectively irradiated onto the atoms and resonantly tuned to a rapidly decaying optical transition. The states correlated in this way show a relatively low order entanglement, the von Neumann information entropy only being \(S' = -\langle \log_2 \rho \rangle = N - 1\).

Figure 18.1: (code) Evolution of the state during a Jaynes-Cummings interaction with 2 atoms: (a) Bloch vector for the two atoms, (b) time evolution of the coherence \(\rho_{12}\) showing the phenomenon of collapse and revival, (c) distribution of photons, and (d) \(Q(\alpha)\)-function.

18.2.3.1 The XOR gate, treating the field phase as degree of freedom

We define the state,

\[
|\psi\rangle = \begin{pmatrix}
c_{+\alpha_{11}} & c_{+\alpha_{11}} & c_{+\alpha_{12}} & c_{+\alpha_{12}} & c_{-\alpha_{21}} & c_{-\alpha_{21}} & c_{-\alpha_{22}} & c_{-\alpha_{22}}
\end{pmatrix}^T.
\]

(18.36)
A dispersive $\pi$-pulse does,

$$
\begin{pmatrix}
1 \\
0 \\
-1 \\
0 \\
-i \\
-i \\
0
\end{pmatrix}
= \begin{pmatrix}
1 \\
-1 \\
1 \\
1 \\
-i \\
-i \\
1
\end{pmatrix}
\begin{pmatrix}
1 \\
0 \\
0 \\
0 \\
-1 \\
0 \\
0
\end{pmatrix}.
$$

(18.37)

A resonant $\pi/2$-pulse acting on the first atom only does,

$$
\begin{pmatrix}
1 \\
-i \\
i \\
-i \\
1 \\
-i \\
i
\end{pmatrix}
= \begin{pmatrix}
1 \\
i \\
1 \\
i \\
1 \\
i \\
i
\end{pmatrix}
\begin{pmatrix}
1 \\
0 \\
0 \\
0 \\
-1 \\
0 \\
0
\end{pmatrix}.
$$

(18.38)

By reducing the Glauber state $|\alpha\rangle$ we obtain, a posteriori, the unitary XOR gate,

$$
\begin{pmatrix}
1 \\
-1 \\
i \\
i \\
1 \\
i \\
-1
\end{pmatrix}
= \begin{pmatrix}
1 \\
1 \\
i \\
i \\
1 \\
i \\
i
\end{pmatrix}
\begin{pmatrix}
0 \\
-1 \\
0 \\
i \\
-1 \\
i \\
0
\end{pmatrix}.
$$

(18.39)

### 18.2.4 Dicke states

The Jaynes-Cummings Hamiltonian in the limit $\Delta_1 = \Delta_2$ and $\Omega_1 = \Omega_2$ (both atoms are inside the mode volume of the field and are indistinguishable) is given by (18.23). This matrix shows two identical and non-shifted eigenvalues at $\lambda = n\omega$,

$$
\det(H_n - \lambda I) = (n\omega - \lambda)^2[(n\omega - \lambda)^2 - \Delta^2 - n\Omega^2] = 0.
$$

(18.40)

The description of the dynamics can be simplified by reducing the order of the matrix by calculating the average of the lines 2 and 3,

$$
H_n = \begin{pmatrix}
n\omega - \Delta & \frac{1}{2}\sqrt{2n\Omega} \\
\frac{1}{2}\sqrt{2n\Omega} & n\omega \\
\frac{1}{2}\sqrt{2(n+1)\Omega} & \frac{1}{2}\sqrt{2(n+1)\Omega}
\end{pmatrix},
$$

since $c_{01} n = c_{10} n$, and opting for a new base defined by,

$$
|\psi\rangle = \sum_n \begin{pmatrix}
c_{11} n-1 \\
c_{01} n \\
c_{00} n+1
\end{pmatrix} |n\rangle.
$$

(18.41)
The new Hamiltonian has the same eigenvalues $\lambda = n\omega, n\omega \pm \omega_n$, but without degeneracies. If we assume furthermore that the excitation is resonant, $\Delta = 0$, with high intensity, $n = \beta^2$ for all $n$, our matrix becomes,

$$\hat{H}_n \approx \begin{pmatrix} \frac{1}{\sqrt{2}} \beta \omega & \frac{1}{\sqrt{2}} \beta \omega \\ \frac{1}{\sqrt{2}} \beta \omega & \frac{1}{\sqrt{2}} \beta \omega \end{pmatrix},$$

with the eigenvalue matrix,

$$E_n = U_n^\dagger \hat{H}_n U_n \approx \begin{pmatrix} \beta^2 \omega - \beta \Omega & \beta^2 \omega \\ \beta^2 \omega & \beta^2 \omega + \beta \Omega \end{pmatrix},$$

where

$$U_n \approx \frac{1}{2} \begin{pmatrix} -1 & \sqrt{2} \\ \sqrt{2} & 1 \end{pmatrix}.$$

With this we can derive the propagator,

$$e^{-i \hat{H}_n t} = \frac{1}{2} e^{-i \beta^2 t} \begin{pmatrix} 1 + \cos \beta \Omega t & -\sqrt{2} i \sin \beta \Omega t \\ -\sqrt{2} i \sin \beta \Omega t & 2 \cos \beta \Omega t \end{pmatrix} \begin{pmatrix} 1 + \cos \beta \Omega t & -\sqrt{2} i \sin \beta \Omega t \\ -\sqrt{2} i \sin \beta \Omega t & 1 + \cos \beta \Omega t \end{pmatrix} \Rightarrow e^{-i\pi/2} \frac{1}{2} e^{-i\pi/2 \beta \omega / \Omega} \begin{pmatrix} 1 & -\sqrt{2} i \\ -\sqrt{2} i & 1 \end{pmatrix}.$$

The generalization to three atoms,

$$\hat{H}_n \approx \begin{pmatrix} (n + \frac{1}{2}) \omega - \frac{1}{2} \Delta \\ \frac{1}{2} \sqrt{3n} \Omega \end{pmatrix}, \begin{pmatrix} (n + \frac{1}{2}) \omega - \frac{1}{2} \Delta \\ \frac{1}{2} \sqrt{3(n + 1)} \Omega \end{pmatrix}, \begin{pmatrix} (n + \frac{1}{2}) \omega + \frac{1}{2} \Delta \\ \frac{1}{2} \sqrt{3(n + 2)} \Omega \end{pmatrix},$$

or $N$ atoms is easy. We define $2J$ as the number of atoms, $M$ as the collective atomic spin, $n$ as the number of photons in the optical mode, and $S^\pm \equiv \sum_i \sigma_i^\pm$. The so-called Dicke state $|J, M, n\rangle$ basically consists of a set of $N$ indistinguishable spin-1/2 states ($\hbar \equiv 1$). We introduce a basis by,

$$|\psi\rangle = \sum_n \begin{pmatrix} |J, J, n\rangle \\ |J, -J, n + 2J\rangle \end{pmatrix}.$$ 

Obviously, we have [162],

$$\langle J, M - 1, n + 1 | \frac{1}{\sqrt{2}} \Omega a^+ \sigma^- | J, M, n \rangle = \frac{1}{2} \Omega \sqrt{n + 1 + \frac{1}{2} \sqrt{J(J + 1) - M(M + 1)}}.$$ 

The Dicke states $|JM\rangle$ follow the SU(2) algebra. With this, we can calculate the number of particles with spin up:

$$\hat{N}_\pm = \hat{j}_\pm \hat{j}_\mp - \hat{j}^2 \pm \hat{j}_z$$

$$\hat{N}_+ = \frac{1}{2} (\hat{N}_+ - \hat{N}_- + N + \hat{N}_+ + N) = \frac{1}{2} (\hat{N}_+ - \hat{N}_- + N) = \hat{j}_z + J. $$
In the thermodynamic limit, \( N \to \infty \), the operators can be replaced by:

\[
\hat{J}_x \xrightarrow{N \to \infty} \frac{1}{2} \hat{N} \cos \hat{\phi} \quad \text{and} \quad \hat{J}_y \xrightarrow{N \to \infty} \frac{1}{2} \hat{N} \sin \hat{\phi}.
\]

In this case, the operators commute \([\hat{J}_x, \hat{J}_y]\) \( \to 0 \).

### 18.2.5 Spin squeezing

Measuring the population of a coherently excited two-level system by projecting it onto an energy eigenstate introduces quantum projection noise. This noise is inherent to determination of the resonance frequency and can only be surpassed by spin squeezing [632]. The projection noise limit has been observed with ions [307, 299] and with atomic clouds [526]. The reduction of the noise by spin squeezing has been observed with ions [519], micromasers [496], and atomic clouds [251, 365]. Also, a weakly entangled state of two modes was observed for continuous spin variables [326].

### 18.2.6 The Jaynes-Cummings model for 1 atom and 2 radiation modes

The Hamiltonian for two modes \(|+\rangle\) and \(|-\rangle\) is (despising dissipation),

\[
\hat{H} = \omega_+ \hat{a}_+^{\dagger} \hat{a}_+ + \omega_- \hat{a}_-^{\dagger} \hat{a}_- + \omega_0 \left( \hat{\sigma}^{\dagger} \hat{\sigma} - \frac{1}{2} \right) + g_+(t) \hat{a}_+^{\dagger} \hat{\sigma}_+ e^{-i k x} + g_- (t) \hat{a}_-^{\dagger} \hat{\sigma}_- e^{-i k x} + c.c.
\]

In analogy with Sec. ??, letting \( \hat{a}_\pm = \sum_{n_\pm} |n_\pm - 1\rangle \langle n_\pm| \), we can express the Hamiltonian in matrix notation. The Hamiltonian decomposes into subdomains \( H_{n_+ + n_-} \), each one having \( n_+ + n_- \) photons and being of dimension \( \min(n_+, n_-) \):

\[
H_{n_+ + n_-} =
\begin{pmatrix}
\frac{(n_+ - 1) \omega_+ + n_- \omega_+ + n_+ \omega_-}{\sqrt{n_+}} & \frac{g_+}{\sqrt{n_+}} & \frac{g_-}{\sqrt{n_-}} & \frac{g_+}{\sqrt{n_+ + 1}} & \frac{g_-}{\sqrt{n_- + 1}} \\
\frac{g_+}{\sqrt{n_+}} & \frac{(n_+ - 1) \omega_+ + n_- \omega_+ + n_+ \omega_-}{\sqrt{n_-}} & \frac{g_-}{\sqrt{n_-}} & \frac{g_+}{\sqrt{n_+ + 1}} & \frac{g_-}{\sqrt{n_- + 1}} \\
\frac{g_-}{\sqrt{n_-}} & \frac{g_+}{\sqrt{n_-}} & \frac{(n_+ - 1) \omega_+ + n_- \omega_+ + n_+ \omega_-}{\sqrt{n_-}} & \frac{g_-}{\sqrt{n_- + 1}} & \frac{g_+}{\sqrt{n_+ + 1}} \\
\frac{g_+}{\sqrt{n_+ + 1}} & \frac{g_-}{\sqrt{n_- + 1}} & \frac{g_+}{\sqrt{n_+ + 1}} & \frac{(n_+ - 1) \omega_+ + n_- \omega_+ + n_+ \omega_-}{\sqrt{n_- + 1}} & \frac{g_-}{\sqrt{n_- + 1}} \\
\frac{g_-}{\sqrt{n_- + 1}} & \frac{g_+}{\sqrt{n_- + 1}} & \frac{g_-}{\sqrt{n_- + 1}} & \frac{g_+}{\sqrt{n_+ + 1}} & \frac{(n_+ - 1) \omega_+ + n_- \omega_+ + n_+ \omega_-}{\sqrt{n_- + 1}}
\end{pmatrix}.
\]

This simplifies when the interaction is dispersive. Using, \( \Lambda_\pm \equiv \Omega_\pm^2 / 4 \Delta_\pm \),

\[
H_{n_+ + n_-} =
\begin{pmatrix}
\cdots & n_+ \omega_+ + n_- \omega_- - \frac{\omega_0}{2} & n_+ \Lambda_+ + n_- \Lambda_- & 0 \\
\cdots & n_+ \omega_+ + (n_- - 1) \omega_- + \frac{\omega_0}{2} & n_+ \Lambda_+ & 0 & \cdots
\end{pmatrix}
\]
If only the upper level of the atom interacts with both light fields, all terms with negative light shift, $\Lambda_{\pm}$ disappear:

$$\hat{H}^{(1)}_{n_+ + n_-} = \begin{pmatrix} \cdots & n_+ \Lambda_+ + n_- \Lambda_- & 0 & 0 & \cdots \\ n_+ \Lambda_+ + n_- \Lambda_- & 0 & 1 & 0 & \cdots \end{pmatrix}.$$  \hspace{1cm} (18.52)

The subspaces $H^{(1)}_{n_+ + n_-}$ are orthogonal, we can choose the following basis $|\psi\rangle = \sum_{n_\pm} (c_n|n_+\rangle|n_-\rangle)$. The interaction with the two modes can be treated separately in time, $e^{-i\hat{H}^{(1)}_{n_+ + n_-} t} = e^{-i\hat{H}^{(1)}_{n_+ + 0} t} e^{-i\hat{H}^{(1)}_{0 + n_-} t}$.

### 18.3 Quantum gates

In *quantum information* we use the notions introduced in the preceding sections and formalize the calculation. In this section, we present a brief formal introduction to the field of *quantum computation with qubit matrices*. The formalism is abstract, but we may keep in mind a chain of entangled ions confined in a linear Paul trap. We will show how the electronic states of the ions are correlated to form a single collective state, and how quantum gates can be realized on such correlated particles. With three ions, an arbitrary quantum gate can be implemented, which includes and generalizes the three-bit Toffoli gate.

To construct a quantum gate, we need at least two qubits spanning a 4-dimensional Hilbert space, since $\mathcal{H}^2 \otimes \mathcal{H}^2$ and $\mathcal{H}^1 \otimes \mathcal{H}^1$ are isomorphic, that is,

$$|\varepsilon\rangle_1 |\mu\rangle_2 = (|1\rangle_1 + i|2\rangle_1)(|1\rangle_2 + i|2\rangle_2) = \begin{pmatrix} |1\rangle_1 |1\rangle_2 \\ i|1\rangle_1 |2\rangle_2 \\ i|2\rangle_1 |1\rangle_2 \\ -|2\rangle_1 |2\rangle_2 \end{pmatrix} \quad \triangleq |\varepsilon\rangle_1 |\mu\rangle_2.$$  \hspace{1cm} (18.53)

A presentation on the subject is available at (watch talk).

### 18.3.1 The qubit

As we have seen above, the two principle ways a light mode acts on a two-level system are the resonant interaction and the dispersive interaction. From the Jaynes-Cummings model (15.34) and (15.41),

$$R(\tau) \equiv \begin{pmatrix} \cos \frac{\pi}{2} \tau & i \sin \frac{\pi}{2} \tau \\ i \sin \frac{\pi}{2} \tau & \cos \frac{\pi}{2} \tau \end{pmatrix} \quad \tau \to 1 \implies \begin{pmatrix} i \\ 1 \end{pmatrix} \equiv \hat{R},$$

$$D(\tau) \equiv \begin{pmatrix} e^{i\pi \tau} & 0 \\ 0 & 1 \end{pmatrix} \quad \tau \to 1 \implies \begin{pmatrix} -1 \\ 1 \end{pmatrix} \equiv \hat{D}.$$  \hspace{1cm} (18.54)
For example, a resonant $\pi$-pulse corresponds to a *negation* in the Hilbert $\mathcal{H}^2$,

$$U = \ket{A}\bra{A} = \hat{R}. $$ (18.55)

A qubit in the Hilbert space $\mathcal{H}^2$ can be understood as a quantum superposition,

$$|\varepsilon\rangle = \alpha|0\rangle + i\beta|1\rangle = \begin{pmatrix} \alpha \\ i\beta \end{pmatrix}, $$ (18.56)

or represented by a classical truth table,

$$|A\rangle \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}, $$ (18.57)

The only difference is, that now the possible values are not restricted to the binaries 0 or 1, but can be anything between 0 and 1, provide the total wavefunction stays normalized.

### 18.3.2 Quantum gates of 2 qubits, the 'controlled NOT' gate

We can generalize the single-qubit algebra to arbitrary registers using the *direct sum* and the *external product* defined in (2.109) and (2.111),

$$|A\rangle \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}, $$ (18.58)

The most interesting two-qubit quantum gate is the 'controlled NOT' gate, which we will now discuss in detail. This gate is originally defined on $\mathcal{H}^2 \otimes \mathcal{H}^2$. The quantum operation is implemented by first going to the Hilbert space $\mathcal{H}^1 \otimes \mathcal{H}^4$, applying the unitary transform,

$$\hat{N} = \begin{pmatrix} \mathbb{I}_2 & \hat{R} \end{pmatrix}, $$ (18.59)

where $\hat{R}$ has been defined in Eq. (18.54), and finally returning to $\mathcal{H}^2 \otimes \mathcal{H}^2$:

$$\begin{pmatrix} |\varepsilon\rangle_1|\mu\rangle_2 \\ \delta_{\varepsilon=1}|\varepsilon\rangle_1|\mu\rangle_2 + \delta_{\varepsilon=2}|\varepsilon\rangle_1 \begin{pmatrix} 1 \\ i \end{pmatrix}^{\dagger} |\mu\rangle_2 \end{pmatrix} \triangleq |\varepsilon\rangle_1|\varepsilon\oplus\mu\rangle_2 \triangleq \begin{pmatrix} |1\rangle_1|1\rangle_2 \\ i|1\rangle_1|2\rangle_2 \\ i|2\rangle_1|1\rangle_2 \\ -|2\rangle_1|2\rangle_2 \end{pmatrix} \triangleq \begin{pmatrix} |1\rangle_1|1\rangle_2 \\ i|1\rangle_1|2\rangle_2 \\ i|2\rangle_1|1\rangle_2 \\ -|2\rangle_1|2\rangle_2 \end{pmatrix}. $$ (18.60)

Or, using a short hand notation we can express the *negation* in $\mathcal{H}^4$ by,

$$U = |A, B\rangle\langle A, B| = \mathbb{I} \otimes \hat{R}. $$ (18.61)
Another operation is the antivalence in $\mathcal{H}^4$

$$
\begin{align*}
|A, A \oplus B\rangle\langle A, B| &= \mathbb{I} \oplus \hat{R}, \\
U &= |B \oplus A, B\rangle\langle A, B| = S(\mathbb{I} \oplus \hat{R})S.
\end{align*}
$$

18.3.3 Quantum gates of 3 qubits

We now consider three qubits in $\mathcal{H}^8 \equiv \mathcal{H}^2 \otimes \mathcal{H}^2 \otimes \mathcal{H}^2$. The truth table has the shape,

<table>
<thead>
<tr>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

for example $|010\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$.

We choose $\hat{1}_8$ as the basis of $\mathcal{H}^8$. It is possible to show that all quantum logic gates can be reduced to a gate called the Toffoli gate,

$$
\begin{align*}
\mathcal{H}^8 & \xrightarrow{U} \mathcal{H}^8 \\
|A, B, C\rangle & \xrightarrow{U} |A, B, (A \cdot B) \oplus C\rangle \\
\hat{1}_8 & \xrightarrow{U} U.
\end{align*}
$$

The unitary transform implemented by a quantum gate can be understood as a permutation of the basis vectors in the truth table. We can generalize the permutation rules (2.115) to 3D Hilbert spaces $\mathcal{H}^2 \otimes \mathcal{H}^2 \otimes \mathcal{H}^2$, where $M \otimes N \otimes R = S_{12}(N \otimes M \otimes R)S_{12} = S_{23}(M \otimes R \otimes N)S_{23} = S_{13}(R \otimes N \otimes M)S_{13}$, with

$$
S_{ij} = \mathbb{I}(k_{ij}, k_{ij}), \quad \begin{cases}
    k_{12} = [1, 2, 5, 6, 3, 4, 7, 8] \\
    k_{23} = [1, 3, 2, 4, 5, 7, 6, 8] \\
    k_{13} = [1, 3, 5, 7, 2, 4, 6, 8]
\end{cases}
$$

We can also generate the transformation matrices $S_{23} = \mathbb{I} \otimes S$, $S_{13} = S \otimes \mathbb{I}$ and $S_{12} = S_{13}S_{23}$.

18.3.3.1 Fundamental quantum gates

Examples of fundamental three-qubits gates are, in short notation, the negation in $\mathcal{H}^8$,

$$
\begin{align*}
U &= |A, B, \bar{C}\rangle\langle A, B, C| = \mathbb{I} \otimes \mathbb{I} \otimes R, \\
U &= |A, \bar{B}, C\rangle\langle A, B, C| = \mathbb{I} \otimes R \otimes \mathbb{I}, \\
U &= |\bar{A}, B, C\rangle\langle A, B, C| = R \otimes \mathbb{I} \otimes \mathbb{I},
\end{align*}
$$
the antivalence,

\[
U = |A, B, B \oplus C\rangle \langle A, B, C| = I \otimes (I \oplus R) \equiv X
\]

\[
U = |A, B, A \oplus C\rangle \langle A, B, C| = S_{12}XS_{12}
\]

\[
U = |A, A \oplus B, C\rangle \langle A, B, C| = S_{12}S_{23}XS_{23}S_{12}
\]

\[
U = |A, C \oplus B, C\rangle \langle A, B, C| = S_{23}XS_{23}
\]

\[
U = |B \oplus A, B, C\rangle \langle A, B, C| = S_{13}XS_{13}
\]

\[
U = |C \oplus A, B, C\rangle \langle A, B, C| = S_{13}S_{23}XS_{23}S_{13}
\]

and the Toffoli gate,

\[
U = |A, B, (A \cdot B) \oplus C\rangle \langle A, B, C| = I \oplus I \oplus I \oplus R .
\]

### 18.3.4 Universal quantum gates

Letting \( R \equiv \begin{pmatrix} r_1 & r_2 \\ r_3 & r_4 \end{pmatrix} \), we get explicitly,

\[
X_{B \rightarrow C} = \begin{pmatrix} I & R \\ R & I \end{pmatrix}, \quad X_{A \rightarrow C} = \begin{pmatrix} I & R \\ R & I \end{pmatrix}, \quad X_{A \rightarrow B} = \begin{pmatrix} I & R \otimes I \\ R & I \end{pmatrix}.
\]

Specifying further \( R \equiv \begin{pmatrix} e^{i\alpha/2} \cos \theta/2 & -ie^{i(\alpha-\theta)/2} \sin \theta/2 \\ -ie^{i(\alpha+\theta)/2} \sin \theta/2 & e^{i\alpha/2} \cos \theta/2 \end{pmatrix} \), we explicitly obtain the universal Toffoli gate from,

\[
T = X_{B \rightarrow C}X_{A \rightarrow C}X_{A \rightarrow B}(\alpha = \theta = \pi)X_{B \rightarrow C}X_{A \rightarrow B}(\alpha = \theta = \pi)
\]

### 18.3.5 The quantum composer representation

See IBM Circuit Composer.
18.3.5.1 One qubit Hilbert space

The most fundamental gate can be written as,

\[ U_3(\theta, \phi, \lambda) = \begin{pmatrix} \cos \frac{\theta}{2} & -e^{i\lambda} \sin \frac{\theta}{2} \\ e^{i\phi} \sin \frac{\theta}{2} & e^{i\lambda+i\phi} \cos \frac{\theta}{2} \end{pmatrix}. \]  \tag{18.71}

Special cases are the Hadamard gate,

\[ H = U_3\left(\frac{\pi}{2}, 0, \pi\right) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \]  \tag{18.72}

and the phase gate,

\[ U_1(\phi) = U_3(0, \phi, 0) = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\phi} \end{pmatrix}. \]  \tag{18.73}

Phase rotations about particular angles are named \( Z = U_1(\pi) \), \( S = U_1\left(\frac{\pi}{2}\right) \), \( T = U_1\left(\frac{\pi}{4}\right) \).

18.3.5.2 Two qubit Hilbert space

Obviously, to perform quantum calculations, we need at least two qubits and operations acting simultaneous on both.

18.3.6 The field of quantum information

The possibility to experimentally control, manipulate and read out individual qubits and gave birth to a new field of physics in the past two decades now called quantum information. This fields includes the more specific areas of quantum processing (which itself splits into the subareas of quantum computing and quantum simulation), quantum communication, and quantum sensing. Let us begin spending a few words on quantum sensing.

18.3.6.1 Quantum sensing

A quantum sensor is a measurement device exploiting quantum correlations in the form of quantum superpositions or entanglement to improve the sensitivity and resolution. Typically its core is a single qubit (or an incoherent ensemble of qubits) whose superposition states (i) are sensitive to some environment parameter, (ii) can be manipulated in a controlled way, and (iii) can be read out.

A typical quantum sensor can be described by the generic Hamiltonian \[ \hat{H}(t) = \hat{H}_{qbit} + \hat{H}_{cntrl}(t) + \hat{H}_{int}(t), \]  \tag{18.74}

composed of a (known) internal Hamiltonian \( \hat{H}_{qbit} \), a control Hamiltonian \( \hat{H}_{cntrl} \) allowing to manipulate or tune the sensor, and a signal Hamiltonian \( \hat{H}_{int} \) allowing to pass information about the state of the system to the outside world.

Typically, the internal Hamiltonian is static and defines the energy eigenstates \( |0\rangle \) and \( |1\rangle \),

\[ \hat{H}_{qbit} = E_0 |0\rangle \langle 0| + E_1 |1\rangle \langle 1| . \]  \tag{18.75}
The qubit internal Hamiltonian may contain additional interactions, such as couplings to other qubits or time-dependent stochastic terms due to interactions with an environment.

Many quantum sensing protocols require to manipulate the qubit either before, during, or after the sensing process. This is achieved via a control Hamiltonian, which allows implementing a sequence of appropriate quantum gates, such as the Hadamard gate and or Pauli X and Y gates. These gates are nothing else than what, in the language of atom interferometry is known as $\pi/2$ or $\pi$-pulses around different axes. Advanced sensing schemes employing more than one sensor qubit may further require conditional gates, especially controlled-NOT gates to generate entanglement, swap gates to exploit memory qubits, and controlled phase shifts in quantum phase estimation. Finally, the control Hamiltonian can include control fields for systematically tuning the transition frequency $\hbar \omega_0 = E_1 - E_2$.

Finally, the signal Hamiltonian represents the coupling between the sensor qubit and a signal $V(t)$ to be measured. When the signal is weak (which is assumed here) $\hat{H}_{\text{int}}$ adds a small perturbation to the internal Hamiltonian. The signal Hamiltonian can then be separated into two qualitatively different contributions,

$$\hat{H}_{\text{int}} = \hat{H}_{\text{int},||} + \hat{H}_{\text{int},\perp},$$

where $\hat{H}_{\text{int},||}$ is the parallel (commuting) and $\hat{H}_{\text{int},\perp}$ the transverse (non-commuting) components, respectively. The two components can quite generally be captured by,

$$\hat{H}_{\text{int},||} = \frac{\gamma}{2} [\langle 1 | V(t) | 0 \rangle - \langle 0 | V(t) | 1 \rangle],$$

$$\hat{H}_{\text{int},\perp} = \frac{\gamma}{2} [V_{\perp}(t) | 1 \rangle \langle 0 | + V_{\perp}^*(t) | 0 \rangle \langle 1 |],$$

where $\gamma$ is the coupling or transduction parameter of the qubit to the signal $V(t)$. Examples of coupling parameters include the Zeeman shift parameter or the Stark shift parameter of electric dipoles in an electric field. The parallel and transverse components of a signal have distinctly different effects on the quantum sensor. A commuting perturbation $\hat{H}_{\text{int},||}$ leads to shifts of the energy levels and an associated change of the transition frequency $\omega_0$. A non-commuting perturbation $\hat{H}_{\text{int},\perp}$, by contrast, can induce transitions between levels, manifesting through an increased transition rate. Most often, this requires the signal to be time dependent (resonant with the transition) in order to have an appreciable effect on the quantum sensor.

An important class of signals are vector signal $V(t)$, in particular, those provided by electric or magnetic fields. The interaction between a vector signal and a qubit can be described by the signal Hamiltonian,

$$\hat{H}_{\text{int}} = \gamma \mathbf{V}(t) \cdot \mathbf{\sigma},$$

where $\mathbf{\sigma}$ is the vector of Pauli matrices (2.47). For a vector signal, the two signal functions $V_{||}(t)$ and $V_{\perp}(t)$ are,

$$V_{||}(t) = V_z(t)$$

$$V_{\perp}(t) = V_z(t) + iV_y(t),$$

where the $z$-direction is defined by the qubit’s quantization axis. The corresponding signal Hamiltonian is,

$$\hat{H}_V(t) = \gamma \hat{\sigma}_z \text{Re} V_{\perp}(t) + \gamma \hat{\sigma}_y \text{Im} V_{\perp}(t) + \gamma \hat{\sigma}_z V_{||}(t).$$
Example 69 (Holstein-Primakoff transformation): The Holstein-Primakoff transformation in quantum mechanics is a mapping to the spin operators from boson creation and annihilation operators, effectively truncating their infinite-dimensional Fock space to finite-dimensional subspaces. Let us consider a spin operator \( \hat{S} \) defined by its commutation behavior \( [\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z \) and characterized by its eigenvectors \( |s, m_s\rangle \),

\[
\hat{S}_x^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle, \quad \hat{S}_z^2|s, m_s\rangle = \hbar m_s|s, m_s\rangle, \quad (18.81)
\]

with the projection quantum number \( m_s = -s, -s+1, \ldots, s-1, s \). We consider a single particle of spin \( s \) and take the state \( |s, m_s = +s\rangle \) as a vacuum for a set of boson operators, and each subsequent state with lower projection quantum number as a boson excitation of the previous one,

\[
|s, s - n\rangle \mapsto \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle. \quad (18.82)
\]

Each additional boson then corresponds to a decrease of \( m_s \) in the spin projection. Thus, the spin raising and lowering operators \( \hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \) satisfying so that \( [\hat{S}_+, \hat{S}_-] = 2\hbar \hat{S}_z \) correspond to bosonic annihilation and creation operators, respectively. The precise relations between the operators must be chosen to ensure the correct commutation relations for the spin operators. The resulting Holstein-Primakoff transformation can be written as,

\[
\hat{S}_+ = \hbar \sqrt{2s} \sqrt{1 - \frac{\hat{a}^\dagger \hat{a}}{2s}} \hat{a}, \quad \hat{S}_- = \hbar \sqrt{2s} \sqrt{1 - \frac{\hat{a}^\dagger \hat{a}}{2s}} \hat{a}^\dagger, \quad \hat{S}_z = \hbar (s - \hat{a}^\dagger \hat{a}). \quad (18.83)
\]

The transformation is particularly useful in the case where \( s \) is large, when the square roots can be expanded as Taylor series, to give an expansion in decreasing powers of \( s \) [586, 9].

18.3.6.2 Quantum Fourier transform

The quantum Fourier transform (QFT) is a linear transformation on qubits and the quantum analogue of the inverse discrete Fourier transform. The quantum Fourier
transform is a part of many quantum algorithms, notably Shor’s algorithm for factor-
ing and computing the discrete logarithm or the quantum phase estimation algorithm
for estimating the eigenvalues of a unitary operator.

The quantum Fourier transform can be performed efficiently on a quantum com-
puter, with a particular decomposition into a product of simpler unitary matrices.
Using a simple decomposition, the discrete Fourier transform on 2
n
amplitudes can
be implemented as a quantum circuit consisting of only \( O(n^2) \) Hadamard gates and
controlled phase shift gates, where \( n \) is the number of qubits. This can be compared
with the classical discrete Fourier transform, which takes \( O(2^n) \) gates, which is ex-
ponentially more than in the classical case. However, the quantum Fourier transform
acts on a quantum state, whereas the classical Fourier transform acts on a vector, so
not every task that uses the classical Fourier transform can take advantage of this
exponential speedup.

The quantum Fourier transform is the classical discrete Fourier transform applied
to the vector of amplitudes of a quantum state, where we usually consider vectors of
length \( N = 2^n \). The classical Fourier transform acts on a vector \((x_0, x_1, \ldots, x_{N-1}) \in \mathbb{C}^N\) and maps it to the vector \((y_0, y_1, \ldots, y_{N-1}) \in \mathbb{C}^N\) according to the formula:

\[
y_k = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} x_n \omega_N^{kn},
\]

where \( k = 0, 1, \ldots, N-1 \) and \( \omega_N = e^{2\pi i/N} \) and \( \omega_N^n \) is an \( N \)th root of unity. The lower
sign holds for the inverse FT.

Similarly, the quantum Fourier transform acts on a quantum state \(|x\rangle = \sum_{i=0}^{N-1} x_i |i\rangle\)
and maps it to a quantum state \(\sum_{i=0}^{N-1} y_i |i\rangle\) according to the same formula (18.84).
In case that \(|x\rangle\) is a basis state, the quantum Fourier Transform can also be expressed
as the map,

\[
|x\rangle \mapsto \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} \omega_N^{x_k} |k\rangle .
\]

Equivalently, the quantum Fourier transform can be viewed as a unitary matrix (or
a quantum gate, similar to a Boolean logic gate for classical computers) acting on
quantum state vectors, where the unitary matrix is given by,

\[
F_N = \frac{1}{\sqrt{N}} \begin{pmatrix}
1 & 1 & 1 & 1 & \cdots & 1 \\
1 & \omega & \omega^2 & \omega^3 & \cdots & \omega^{N-1} \\
1 & \omega^2 & \omega^4 & \omega^6 & \cdots & \omega^{2(N-1)} \\
1 & \omega^3 & \omega^6 & \omega^9 & \cdots & \omega^{3(N-1)} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
1 & \omega^{N-1} & \omega^{2(N-1)} & \omega^{3(N-1)} & \cdots & \omega^{(N-1)(N-1)}
\end{pmatrix}
\]

where \( \omega = \omega_N \). Do the Exc. 18.3.7.5.

The QFT is unitary,

\[
FF^\dagger = I,
\]

(18.87)
and can be efficiently performed on a quantum computer. The quantum gates used in the circuit are the Hadamard gate and the controlled phase gate $R_m$,

$$H = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \quad \text{and} \quad R_m = \begin{pmatrix} 1 & 0 \\ 0 & e^{2\pi i/2^m} \end{pmatrix},$$

with $e^{2\pi i/2^m} = \omega(2^m)$ the primitive $2^m$-th root of unity. The circuit is composed of $H$ gates and the controlled version of $R_m$.

Figure 18.3: Quantum circuit for QFT with $n$ qubits (without rearranging the order of output states).

All quantum operations must be linear, so it suffices to describe the function on each one of the basis states and let the mixed states be defined by linearity. This is in contrast to how Fourier transforms are usually described. We normally describe Fourier transforms in terms of how the components of the results are calculated on an arbitrary input. This is how you would calculate the path integral or show BQP is in PP. But it is much simpler here (and in many cases) to just explain what happens to a specific arbitrary basis state, and the total result can be found by linearity.

The quantum Fourier transform can be approximately implemented for any $N$; however, the implementation for the case where $N$ is a power of 2 is much simpler. As already stated, we assume $N = 2^n$. We have the orthonormal basis consisting of the vectors $|0\rangle, \ldots, |2^n - 1\rangle$. The basis states enumerate all the possible states of the qubits, $|x\rangle = |x_1 x_2 \ldots x_n\rangle = |x_1\rangle \otimes |x_2\rangle \otimes \cdots \otimes |x_n\rangle$, where $|x_j\rangle$ indicates that qubit $j$ is in state $x_j$, with $x_j$ either 0 or 1. By convention, the basis state index $x$ orders the possible states of the qubits lexicographically, i.e. by converting from binary to decimal in this way:

$$x = x_1 2^{n-1} + x_2 2^{n-2} + \cdots + x_n 2^0.$$  \hspace{1cm} (18.89)

It is also useful to borrow fractional binary notation:

$$[0.x_1 \ldots x_m] = \sum_{k=1}^{m} x_k 2^{-k}.$$  \hspace{1cm} (18.90)

For instance, $[0.1] = \frac{1}{2}$ and $[0.11] = \frac{3}{4} + \frac{2}{8}$. With this notation, the action of
the quantum Fourier transform can be expressed in a compact manner:

\[
\text{QFT}([x_1 x_2 \ldots x_n]) = \frac{1}{\sqrt{N}} \left( |0\rangle + e^{2\pi i \sum_{j=0}^{n-1} x_j 2^{-j}} |1\rangle \right) \otimes \ldots \otimes \left( |0\rangle + e^{2\pi i \sum_{j=0}^{n-1} x_j 2^{-j}} |1\rangle \right),
\]

where we have used \([0.x_1 x_2 \ldots x_m] = [x_1 x_2 \ldots x_n]/2^m\). This can be seen by rewriting the formula for the Fourier transform in the binary expansion:

\[
\text{QFT}(|x\rangle) = \frac{1}{\sqrt{N}} \sum_{k=0}^{2^n-1} \omega_n^x |k\rangle = \ldots = \frac{1}{\sqrt{N}} \bigotimes_{j=1}^{n} \left( |0\rangle + \omega_n^{2^{-n-j}} |1\rangle \right).
\]

Now, we have,

\[
\omega_n^{2^{-n-j}} = e^{\frac{2\pi i}{2^n} x 2^{-j}} = e^{2\pi i (x 2^{-j})}.
\]

Let,

\[
f(j) = x 2^{-j} = 2^{-j} \sum_{r=1}^{n} x_r 2^{-r} = \sum_{r=1}^{n} x_r 2^{-j-r} = \sum_{r=1}^{n-j} x_r 2^{-j-r} + \sum_{r=n-j+1}^{n} x_r 2^{-j-r} = a(j) + b(j).
\]

then \(a(j) \in \mathbb{N}_0\), because \(2^{-j-r} \geq 0\), for \(n-j-r \geq 0\), and \(b(j) = 0.x_{n-j+1} x_{n-j+2} \ldots x_n\), thus the \(2\) becomes:

\[
e^{2\pi i f(j)} = e^{2\pi i (a(j)+b(j))} = e^{2\pi i a(j)} \cdot e^{2\pi i b(j)} = e^{2\pi i [0.x_{n-j+1} x_{n-j+2} \ldots x_n]},
\]

since \(e^{2\pi i a(j)} = 1\) for all \(j\). Then we can write:

\[
\text{QFT}([x_1 x_2 \ldots x_n]) = \frac{1}{\sqrt{N}} \bigotimes_{j=1}^{n} \left( |0\rangle + \omega_n^{2^{-n-j}} |1\rangle \right).
\]

To obtain this state from the circuit depicted above, a swap operations of the qubits must be performed to reverse their order. After the reversal, the \(n\)-th output qubit will be in a superposition state of \(|0\rangle\) and \(e^{2\pi i [0.x_1 \ldots x_n]} |1\rangle\), and similarly the other qubits before that (take a second look at the sketch of the circuit above).

In other words, the discrete Fourier transform, an operation on \(n\) qubits, can be factored into the tensor product of \(n\) single-qubit operations, suggesting it is easily represented as a quantum circuit (up to an order reversal of the output). In fact, each of those single-qubit operations can be implemented efficiently using a Hadamard gate and controlled phase gates. The first term requires one Hadamard gate and \((n-1)\) controlled phase gates, the next one requires a Hadamard gate and \((n-2)\) controlled phase gate, and each following term requires one fewer controlled phase gate. Summing up the number of gates, excluding the ones needed for the output
18.3. QUANTUM GATES

reversal, gives $n + (n - 1) + \cdots + 1 = n(n + 1)/2 = O(n^2)$ gates, which is quadratic polynomial in the number of qubits.

The QFT is useful in the simulation of Hamiltonian evolution governed by conjugate variables,

$$e^{-\hat{H}t/\hbar} \quad \text{where} \quad \hat{H} = \frac{\hat{p}^2}{2m} + \frac{m}{2} \omega^2 \hat{x}^2,$$

where, similar to the time-splitting spectral algorithm, we may replace differential operators,

$$\hat{p} = F^{-1} \hat{x} F.$$ (18.97)

18.3.7 Exercises

18.3.7.1 Ex: Quantum composer

Show that:

(a) \hspace{1cm} (b) \hspace{1cm} (c)

![Figure 18.4](image)

18.3.7.2 Ex: Beam splitter

Calculate the negativity corresponding to the entangled state that evolves from the initial two-atoms state $\alpha |gg\rangle + \beta |ee\rangle$, where $r$ and $e$ are the ground and excited state of each atom, respectively, and the evolution law for each atom is,

$$|g\rangle_S \otimes |0\rangle_E \rightarrow |g\rangle_S \otimes |0\rangle_E \sqrt{1 - p}|e\rangle_S \otimes |0\rangle_E \sqrt{p}|g\rangle_S \otimes |1\rangle_E \quad \text{with} \quad p = 1 - e^{-\Gamma t}.$$ (18.97)

Show that, if $|\beta| > |\alpha|$, entanglement vanishes for a finite time.

18.3.7.3 Ex: Classical addition of two qubits

Design a quantum algorithm for the classical addition of up to 8 qubits.
18.3.7.4 Ex: CARL simulation on a quantum computer

Try to recast the so-called CARL Hamiltonian,

\[ \hat{H} = U_0(\hat{a}_+ \hat{a}_- e^{-i k \hat{r}} + \hat{a}_+ \hat{a}_+ e^{i k \hat{r}}) \]

such that it can be simulated by a sequence of quantum gates.

18.3.7.5 Ex: CARL simulation on a quantum computer

Write down the QF transformation matrix for the case of \( N = 4 = 2^2 \) and phase \( \omega = \iota \).
Chapter 19

Nonlinear optics

The discipline of nonlinear optics studies phenomena that occur as a consequence of modifications of the optical properties of materials by the presence of light. Such modifications are appreciable only, when the interacting light is sufficiently intense, i.e. of the order of the interatomic electric field,

\[ E_{at} = \frac{e^2}{4\pi\varepsilon_0 a_B^2} \simeq 5.14 \cdot 10^{11} \text{ V/m} , \]  

(19.1)

which explains that nonlinear effects could only be studied properly after the advent of the laser.

In general, light-matter interaction is expressed through the relationship between the polarization induced in the medium, \( \tilde{P}(\omega) \), with the optical light field, \( \tilde{E}(\omega) \). In linear optics this relation can be expressed as,

\[ \tilde{P}(\omega) = \varepsilon_0 \chi(\omega) \tilde{E}(\omega) . \]  

(19.2)

But in the perturbative regime of non-linear optics this expression must be generalized to a series of powers of the electric field,

\[ \tilde{P}(\omega) = \varepsilon_0 \chi^{(1)}(\omega) \tilde{E}(\omega) + \chi^{(2)}(\omega) \tilde{E}^2(\omega) + \chi^{(3)}(\omega) \tilde{E}^3(\omega) + ... \]  

(19.3)

so that higher order polarization terms, \( P^{(n)}(\omega) = \varepsilon_0 \chi^{(n)}E^N(\omega) \), are considered. Therefore, the phenomena are non-linear in the sense that they depend non-linearly on the optical field applied to the material. In a more complete treatment, in terms of the optical properties of materials, \( \tilde{P} \) and \( \tilde{E} \) are vector fields and the electric susceptibility is a tensor. However, to simplify the treatment, we consider the fields as scalars and \( \chi^{(n)} \) as constants independent of the frequency \( \omega \).

Examples of non-linear optical phenomena are: parametric processes of sum and difference frequency generation, as shown in Fig. 19.1, optical parametric oscillation, and the dependence of the refractive index with the optical intensity. Examples of non-parametric processes are: multi-photonic absorption, stimulated Raman scattering, and saturated absorption. In the latter example, the absorption coefficient of the material decreases with increasing light intensity:

\[ \alpha = \frac{\alpha_0}{1 + I/I_s} . \]  

(19.4)

Saturated absorption is an example where a perturbative approach is not capable of providing good results, and its most reliable description is given by the approximation of a two-level quantum system.
It is also important to emphasize that parametric processes are those, in which the initial and final quantum states of a system are identical. Consequently, the population of an initial state can only be moved to a virtual state, different in energy by $\Delta E$, for a short time lapse limited by Heisenberg’s uncertainty principle ($\hbar/\Delta E$). Nonparametric processes are those involving population transfer between real energy levels, eigenstates of the system’s Hamiltonian. In terms of the electrical susceptibility of the medium, $\chi^{(n)}$ is a real quantity for parametric and an imaginary one for non-parametric processes.

19.1 The nonlinear optical susceptibility

The description of nonlinear optical phenomena can be approached from a variety of perspectives, most of which are semi-classical in the sense that the matter is treated quantum mechanically, while the electromagnetic radiation is treated classically. One possible description explores the wave nature of the radiation, using Maxwell’s equations to describe the generation of new spectral components by the nonlinear terms of the polarization. More generally, this description explains how different frequencies can be coupled through their nonlinear interaction with the material. It can be shown that the electromagnetic wave equation in the nonlinear regime is,

$$\nabla \tilde{E} - \frac{n^2}{c^2} \frac{\partial^2}{\partial t^2} \tilde{E} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2}{\partial t^2} \tilde{P},$$

such that $\tilde{P} = \tilde{P}^{(1)} + \tilde{P}^{nt}$. In this view, $\tilde{P}^{nt}$ acts as a source of frequencies, several of that are incident.

Although electromagnetic theory is capable of explaining several aspects of nonlinear optics, it is the quantum description that provides explicit expressions for nonlinear optical susceptibility. There are three main motivations for obtaining quantum expressions:

- They reveal a functional form of the nonlinear optical susceptibility and show how they depend on microscopic parameters of the material, such as transition dipole moments and atomic energy levels.
- They exhibit the intrinsic symmetries of nonlinear susceptibility.
They can be used to calculate numerically the values of nonlinear susceptibilities.

The numerical predictions of quantum theory for nonlinear optical susceptibilities are particularly accurate in the case of atomic vapors, because the atomic parameters of these are known with sufficient precision for the theory to provide reliable results.

Two quantum mechanical formalisms can be used for the calculation of nonlinear optical susceptibilities. Perturbation theory is used to make predictions on non-resonant systems, i.e. situations where the photon energy is much smaller than the energy separation between two eigenstates of the material. On the other hand, when the interactions are close to resonance, such that it becomes necessary to include relaxation processes, the state-density matrix formalism is used. Although this approach is more complex, it provides better results.

### 19.1.1 Non-linear optics in a two-level system approximation

We will now discuss the example of saturated absorbers, where a power series expansion does not converge, that is, a perturbative treatment of the impact of a light field on the system is not convenient. We recall in saturated absorbers the absorption coefficient depends on the intensity,

\[ I = 2n\varepsilon_0 c |E|^2, \]

of the applied optical field. The complexity induced by the non-perturbative treatment is partially reduced by the restriction to only two energy levels, because it eliminates the sum over all states appearing in the general expression of \( \chi^{(n)} \).

In a two-level system \( a \) and \( b \), abstaining from damping effects, the interaction with an optical field is described by the Hamiltonian \( \hat{H} = \hat{H}_0 + V(t) \), where \( \hat{H}_0 \) represents the energy of the pure states, \( E_a = \hbar \omega_a \) and \( E_b = \hbar \omega_b \), and \( V(t) \) is the interaction with light. Assuming that the interaction can be described by the electric dipole approximation, \( V(t) = -\mu \cdot \mathbf{E}(t) \), and that the states of the system have a well-defined parity, we obtain \( V_{aa} = V_{bb} = 0 \), since \( \mu_{aa} = \mu_{bb} = 0 \). Thus, the only non-zero elements of the interaction are \( V_{ba} \) and \( V_{ab} \), related by \( V_{ba} = V_{ab}^* = -\mu_{ba} \mathbf{E}(t) \).

The evolution of the density operator \( \rho \) of the two-level system is given by the following expression:

\[
\frac{d}{dt} \rho_{nm} = -i \frac{\hbar}{\hbar} [\hat{H}, \rho] = -\omega_{nm} \rho_{nm} - i \sum_n (V_{n\nu} \rho_{\nu m} - \rho_{n\nu} V_{\nu m}), \tag{19.6}
\]

such that \( \omega_{nm} = (E_n - E_m)/\hbar \) is the transition frequency.

Developing this equation of motion for the levels \( a \) and \( b \) we see that \( \rho_{aa} + \rho_{bb} \) is a conserved quantity, and since the diagonal elements \( \rho \) represent occupation probabilities of the states, a closed system must satisfy \( \rho_{aa} + \rho_{bb} = 1 \).

At this point the equation of motion can be generalized to include relaxation processes (see Fig. 19.2), such as the decay of the level \( b \) towards \( a \) with the rate \( \Gamma_{ba} = 1/T_1 \) and the transition linewidth \( \gamma_{ba} = 1/T_2 \).

In general, relaxation processes are introduced phenomenologically into the equations of motion,

\[
\frac{d}{dt} \rho_{bb} = -(i \omega_{ba} + \frac{1}{T_2}) \rho_{bb} + i \frac{\hbar}{\hbar} V_{ba} (\rho_{bb} - \rho_{aa}) \tag{19.7}
\]

\[
\frac{d}{dt} (\rho_{bb} - \rho_{aa}) = -\frac{(\rho_{bb} - \rho_{aa}) - (\rho_{bb} - \rho_{aa})^{eq}}{T_1} - 2i \frac{\hbar}{\hbar} (V_{ba} \rho_{ab} - \rho_{ba} V_{ab}),
\]

where \( \rho_{ab} \) and \( \rho_{ba} \) are the off-diagonal elements of the density matrix.
where we emphasized the population difference between the states, that relax from
the initial condition, \( \rho_{bb}(0) - \rho_{aa}(0) \), toward the equilibrium, \( (\rho_{bb} - \rho_{aa})^{eq} \), assuming
that in thermal equilibrium this term may differ from \(-1\) for a time of the order of
\( T_1 \).

Since the equations of motion can not be solved analytically for \( V_{ba} \), we apply the
so-called rotating wave approximation (RWA). In this approximation, assuming the
absence of external sources, \( \rho_{ba} \) evolves like \( e^{-i\omega_{ba}t} \) and \( e \), hence, \( \omega \) is approximately
equal to \( \omega_{ba} \). Therefore, the part of \( V_{ba} \) which oscillates like \( e^{-i\omega t} \) acts more efficiently
than \( e^{i\omega t} \) on the evolution of \( \rho_{ba} \):

\[
V_{ba} = -\mu_{ba}(Ee^{-i\omega t} + E^{*}e^{i\omega t}) \simeq -\mu_{ba}Ee^{-i\omega t}.
\]

(19.8)

It is also helpful to eliminate the transient solution from the equations of motion
and concentrate on the stationary solution. To do so, a slowly varying term is intro-
duced, \( \sigma(t)_{ba} = \rho(t)_{ba}e^{i\omega t} \), and the time derivatives are neglected (\( d/dt \simeq 0 \)). Solving
the equations algebraically, we obtain:

\[
\rho_{bb} - \rho_{aa} = \frac{(\rho_{bb} - \rho_{aa})^{eq}[1 + (\omega - \omega_{ba})^2T_2^2]}{1 + (\omega - \omega_{ba})^2T_2^2 + \frac{4}{\hbar^2}\mu_{ba}^2|E|^2T_1T_2}
+ \frac{4}{\hbar^2}\mu_{ba}^2|E|^2T_1T_2
\]

(19.9)

\[
\rho_{ba} = \sigma_{ba}e^{-i\omega t} = \frac{\mu_{ba}Ee^{-i\omega t}(\rho_{bb} - \rho_{aa})}{\hbar(\omega - \omega_{ba} + i/T_2)}.
\]

Finally, the polarization of the material is determined (\( \tilde{P}(t) = Pe^{-i\omega t} + c.c. \)), and
consequently its susceptibility (\( P = \varepsilon_0\chi E \)), through the density matrix formalism, as
a function of microscopic parameters of the medium,

\[
P(t) = NTr(\hat{\rho}\hat{\mu}) = N(\mu_{ab}\rho_{ab} + \mu_{ba}\rho_{ab})
\]

(19.10)

\[
\chi = [N(\rho_{bb} - \rho_{aa})^{eq}[\mu_{ba}^2T_2^2]}{\varepsilon_0\hbar} - \frac{\Delta T_2 - i}{1 + \Delta^2T_2^2 + \Omega^2T_1T_2},
\]

where \( \Omega = 2|\mu_{ba}||E|/\hbar \), is the frequency of Rabi and \( \Delta = \omega - \omega_{ba} \), is the detuning of
the optical field.

With this quantum formalism, the expressed susceptibility is complete, including
linear and non-linear effects. We show this by considering the absorption coefficient,
\( \alpha = \frac{\omega}{c \Im \chi} \), which is a directly observable quantity,

\[
\alpha(\Delta) = \frac{\alpha_0(0)}{1 + \Delta^2 T_2 \partial^2} \quad (19.11)
\]

\[
\alpha_0(0) = -\frac{\omega_{ba}}{c} \left[ N (\rho_{bb} - \rho_{aa})_{eq} |\mu_{ba}|^2 T_2 \right].
\]

We see that the equation describing absorption has the same functional form as Eq. (19.3), and that \( \alpha_0(0) \) relates the linear absorption coefficient to the quantum quantities of the two-level system. The tendency of the absorption to decrease when measured with intense optical fields is known as saturation. The situation is illustrated in Fig. 19.3.

![Graph showing real and imaginary part of susceptibility](image)

**Figure 19.3:** Real and imaginary part of susceptibility \( \chi \) (in units of \( \alpha_0c/\omega_{ba} \)).

Finally, the quantum expression for the susceptibility can be developed in a series of powers and compared with the first and third order terms:

\[
\chi^{(1)} = \left[ N (\rho_{bb} - \rho_{aa})_{eq} |\mu_{ba}|^2 T_2 \right] \frac{\Delta T_2 - i}{1 + \Delta^2 T_2^2} \quad (19.12)
\]

\[
\chi^{(3)} = -\frac{4}{3} N (\rho_{bb} - \rho_{aa})_{eq} |\mu_{ba}|^4 \frac{T_1 T_2^2}{\varepsilon_0 \hbar^3} \frac{\Delta T_2 - i}{1 + \Delta^2 T_2^2} \left( \frac{T_2}{\varepsilon_0 \hbar} \right)^2.
\]

As previously emphasized, the quantum formulation of nonlinear optics provides direct values for nonlinear terms and is more suitable close to resonance. For example, considering typical values for the transition \( 3s \rightarrow 3p \) in atomic sodium:
\( N = 10^{14} \text{ cm}^{-3}, (\rho_{bb} - \rho_{aa})^{eq} = -1, \mu_{ba} = 20 \times 10^{-29} \text{ Cm}, \Delta = 2\pi c(1 \text{ cm}^{-1}) = 6\pi \times 10^{10} \text{ rad/sec}, \text{ and } T_2/T_1 = 2. \) We obtain the value of \( \chi^{(3)} = 2.1 \times 10^{-16} \text{ m}^2/\text{V}^2, \) which is a higher value than that determined for non-resonant systems, but more accurate for systems close to resonance [79].

### 19.1.2 Hanle effect

The **Hanle effect** occurs when a magnetic and an optical field compete for the quantization axis. Imagine an atom irradiated by a laser from direction \( \mathbf{k} = k\hat{e}_x, \) linearly polarized \( \varepsilon = \hat{e}_y \) and subject to a magnetic field \( \mathbf{B} = B\hat{e}_z. \) The fluorescence is detected in direction \( \hat{e}_y \) through a linear polarizer [152].

If \( B = 0, \) no light is emitted into the detector since the dipole radiation pattern is a torus with symmetry axis \( \hat{e}_y. \) If \( B \) is now increased, the quantization axis is tilted and the torus slowly precesses about the \( \hat{e}_x \) axis. Plotting the time-averaged fluorescence as a function of the magnetic field \( B, \) we observe a **dark resonance**. These arguments are rather classical.

Quantum mechanically, Hanle resonances are easily calculated. The transition rates additionally depend on the relative orientation of the laser polarization and the magnetic field direction. This dependence is accounted for by decomposing the polarization vector into the coordinates defined by,

\[
\hat{e}_3 = \frac{\mathbf{B}}{B}, \quad \hat{e}_2 = \frac{\hat{e}_3 \times \hat{g}}{|\hat{e}_3 \times \hat{g}|}, \quad \hat{e}_1 = \frac{\hat{e}_2 \times \hat{e}_3}{|\hat{e}_2 \times \hat{e}_3|},
\]

where \( \hat{g} \) is an arbitrarily chosen direction, e.g. gravity. The relative amplitude of the transitions \( \Delta m_J = 0 \) is proportional to the projection of the polarization vector on the magnetic field axis \( \zeta_{e} = (\varepsilon \cdot \hat{e}_3)^2. \) To estimate the amplitude of the transitions \( \Delta m_J = \pm 1, \) we must project onto the coordinates,

\[
\hat{e}_\pm = \frac{1}{\sqrt{2}}(\hat{e}_1 \mp i\hat{e}_2),
\]

and we obtain \( \zeta_{e\pm} = (\varepsilon \cdot \hat{e}_\pm)^2. \)

### 19.1.3 Exercises

#### 19.1.3.1 Ex: Coherent trapping and dark states

Consider a three-level system \( a, b, \) and \( c \) in \( \Lambda \)-configuration interacting with two electromagnetic fields with frequencies \( \omega_1 \) and \( \omega_2, \) as shown in the figure. I.e. the two states of lower energy \( b \) and \( c \) are coupled with a more energetic state \( a. \) Assume that
the transition $|b\rangle \leftrightarrow |c\rangle$ is forbidden and that the Hamiltonian of the system has the form $\hat{H} = \hat{H}_0 + \hat{H}_I$, where,

$$\hat{H}_0 = \hbar \omega_a |a\rangle\langle a| + \hbar \omega_b |b\rangle\langle b| + \hbar \omega_c |c\rangle\langle c|$$

$$\hat{H}_I = -\frac{\hbar}{2} (\Omega_1 e^{-\omega_1 t} |a\rangle\langle b| + \Omega_1^* e^{\omega_1 t} |b\rangle\langle a|) - \frac{\hbar}{2} (\Omega_2 e^{-\omega_2 t} |a\rangle\langle c| + \Omega_2^* e^{\omega_2 t} |c\rangle\langle a|).$$

a. Assuming that the system’s state is described by $|\psi\rangle = K_a |a\rangle + K_b |b\rangle + K_c |c\rangle$ find the system of equations that describe the dynamics of probability amplitudes $K_i$ ($i = a, b, c$).

b. Rewrite the equations for the case where the frequencies of the applied fields are resonant (that is, $\omega_1 = \omega_a - \omega_b$ and $\omega_2 = \omega_a - \omega_c$). Simplify the system by writing in terms of the variables $u_k = C_k e^{i\omega_k t}$ ($k = a, b, c$).

c. Assuming the initial condition $|\psi(0)\rangle = (|b\rangle + |c\rangle)/\sqrt{2}$, solve the system of equations for the resonant case and interpret the result.

19.1.3.2 Ex: Hanle effect in Ca

Simulate the Hanle effect for the Ca 3-level system using optical Bloch equations.

19.2 Quantum interference

19.2.1 Brillouin scattering

Stimulated scattering of phonons is called stimulated Brillouin scattering (SBS). Like Raman-scattering (SRS) Brillouin-scattering is a limiting factor for the transmission efficiency in optical fibers. It is used in acousto-optic modulators (AOM). While SBS is based on the exchange of phonons between atoms bound in crystals, SRS is based on the exchange of phonons between atoms bound in molecules.

Raman-scattering (in a restricted historical sense) is very common technique of molecular spectroscopy. The process is Rayleigh-scattering at an electronic transition, but towards a different vibrational substate. Brillouin-scattering also involves the motional state of the scatterer, but its center-of-mass motion rather than some internal degree of freedom. It is also related to polariton scattering in solids, which produces optical phonons, rather than acoustic phonons.

If a strong electromagnetic field (pump laser) is irradiated into a medium (typically a crystal or a fluid) it produces a time-varying electrostrictive strain, which can be understood as the reaction force of particles dislocated from their equilibrium position. The strain is quantized into phonons and may drive a sound wave. This wave modulates the optical dielectric constant $\varepsilon$ and thus create a periodic polarization $\vec{P}$. This polarization may now interact with the incident electric field (pump laser $\omega_2, k_2, \vec{E}_2$). The resulting energy exchange can, under suitable circumstances, lead to simultaneous amplification of a probe wave ($\omega_2, k_2, \vec{E}_2$) and a sound wave ($\omega_s, k_s, u_s$).

Let us consider a 1D geometry, $k_j = k_j \hat{e}_z$ and $\vec{E}_j = E_j \hat{e}_z$. (More general geometries can be considered [649]). The pump field $E_2(t, z)$ causes a strain $\partial u_s/\partial z$ via longitudinal displacements $u_s(z, t)$ of test volumes. This strain produces a modulation of $\varepsilon$ by $\delta \varepsilon = -\gamma \partial u_s/\partial z$, where $\gamma$ is the strain coefficient (or coupling strength).
The modulation of the dielectric constant $\delta \varepsilon$ now modulates the interaction energy $\delta U = -\frac{1}{2} \delta \varepsilon E_2$, which exerts work $p \partial u_s / \partial z = \delta U$ against the pressure $p$. The pressure modulation creates a force $F = -\partial p / \partial z = \frac{1}{2} \gamma \partial E_2^2 / \partial z$. We can now set up a Fokker-Planck type force equation,

$$ \rho \frac{\partial^2 u_s}{\partial t^2} = \frac{\gamma}{2} \frac{\partial E_2^2}{\partial z} - \eta \frac{\partial u_s}{\partial t} + T \frac{\partial^2 u_s}{\partial z^2}, $$

where $\rho$ is the mass density, $T$ the elastic constant and $\eta$ acoustic dissipation. $v_s \equiv \omega_s / k_s = \sqrt{T/\rho}$ is the free propagation velocity of sound. Simultaneously we know that the light wave propagates like,

$$ \frac{\partial^2 E_j}{\partial z^2} + \frac{\mu \varepsilon}{\partial t^2} \frac{\partial^2 E_j}{\partial t^2} + \frac{\mu}{\partial t^2} \frac{\partial P_{NL,j}}{\partial t} = 0, $$

We insert the ansatz $E_j(t, z) = \frac{1}{2} E_{j0}(z) e^{i(\omega_j t - k_j z)} + \text{c.c.}$ and $u_s(t, z) = \frac{1}{2} u_{s0}(z) e^{i(\omega_s t - k_s z)} + \text{c.c.}$ first into the above equations. We use the approximations $k_s^2 u_s \gg d^2 u_s / d z^2 \ll k_s d u_s / d z$ and $|\partial (E_2 E_1^*) / \partial z| \ll |k_s E_2 E_1^*|$ and focus on the real parts. Assuming that the pump field $E_2$ is undepleted, stimulated Brillouin-scattering is described by the following set of equations,

$$ \frac{dE_1^*}{dz} = -\alpha \frac{\partial u_s}{\partial t} - \frac{k_1 k_s}{4 \varepsilon_1} E_2^* u_s, $$

$$ \frac{du_s}{dz} = -\frac{\eta}{2 \rho v_s} u_s - \frac{\gamma}{8 \rho v_s^2} E_2 E_1^*. $$

Here $\rho$ is the mass density, optical losses are described by $\alpha$, and $\eta$ is the dissipation constant for phonons. $\varepsilon_1 \approx \varepsilon_0$. The above equations describe exponential gain and threshold behavior for $E_1$ and $u_s$. For backscattering $k_1 k_2 = -k_1 k_2$ the rate of growth for the probe $E_1$ is influenced by the values of $E_1$ lying ahead in the direction $k_1$. This is by virtue of the sound beam propagating in opposite direction to $E_1$ and provides the positive feedback being at the origin of exponential gain.

The equations are reminiscent to the CARL equations. The difference is the nature of the mediating force field: The CARL force is mediated by photons. The mediation is thus instantaneous. Photons do not require a medium in order to propagate. In contrast, the Brillouin-gain is mediated by phonons. Phonons propagate through a gas by collisions. Sound needs a medium to propagate. In dilute gases where CARL is observed, collisions are totally negligible. Brillouin-scattering may lead to bunching, which propagates along $k_s$. But similar to water waves, which do not transport the water molecules, the bunching does not lead to a net transport of atoms.

Just like CARL and the superradiant Rayleigh scattering in BECs SBS can be understood as being mediated by dipole-dipole interactions (i.e. the exchange of real or virtual photons between atoms). In a BECs SBS can be interpreted as phonon-like excitations (smaller momentum transfer) due to dipole-dipole interactions [222], while CARL are particle-like excitations due to dipole-dipole interactions (the nature of scattered particles changes from recoiling atoms to phonons). Note that while ultralow temperatures are necessary, these effects are not base on superfluidity, i.e. binary collisions. Thus the speed of sound is not the Bogolubov sound. The question is whether quantum degeneracy plays a role.
19.3 Selective reflection spectroscopy

19.3.1 Fresnel’s formulas

The reflected light comes from interference of reflection at the interface and the gas polarization [450]. The reflection at the interface is given by the Fresnel formulae, the response of the gas polarization is labeled $S$,

$$
\tilde{E}_1^r(r) = E_0 \left( \frac{2nb}{n\beta+b} \sin \phi \right) \left( \frac{2nb}{n\beta+b} \cos \phi \right)
$$

and

$$
\tilde{E}_2^r(r) = E_0 \left( \frac{n\beta-b}{n\beta+b} \sin \phi \right) \left( \frac{n\beta-b}{n\beta+b} \cos \phi \right) + S \left( \frac{\beta^2-\alpha^2}{n\beta+b} \right) \left( \frac{1}{n\beta+b} \right). \tag{19.18}
$$

For small angles of incidence $\phi$ (partial reflection, no evanescent wave) $\beta = \sqrt{1 - n^2 \sin^2 \phi}$ is real. Then,

$$
S = \frac{i k}{\epsilon_0} \int_0^\infty dz_0 e^{i\beta k z_0} P_0(z_0), \tag{19.19}
$$

is the sum of the contributions of the polarizations at different places shifted by the displacement factor $e^{i\beta k z_0}$ away from the surface. In the evanescent case, $S$ is the Laplace transform of the polarization at different phases $k z_0$ yields the spectrum of the response arising from different penetration depths $i\beta$.

![Figure 19.4: Selective reflection.](image)

The polarization at a given location,

$$
\frac{1}{\epsilon_0 E_1} P_0(z) = \frac{\hbar \Omega}{T_1} \int d^3v W(v) e^{i\beta k z} \left[ \sigma_+(v, z/v_z) + \sigma_-(v, z/v_z) \right]. \tag{19.20}
$$

The Maxwell-Boltzmann velocity distribution $W(v) = (3/2\pi v_0^2)^{3/2} e^{-3v^2/2v_0^2}$ is normalized, where mean velocity $v_0 = \sqrt{k_B T/m}$. The definition of the Laplace transform is,

$$
\tilde{\sigma}_+(v, s) = \int_0^\infty dt e^{-st} \sigma_+(v, t). \tag{19.21}
$$

Solution of two-level Bloch equations,

$$
S \tilde{\sigma}_+(v, s) = \frac{i \Omega}{2} \frac{i (\Delta - kv) + \gamma + s}{(\Delta - kv)^2 + \frac{\gamma + s}{\tau + s} \Omega^2 + (\gamma + s)^2}. \tag{19.22}
$$
The steady-state simply follows from $\hat{\sigma}_+ (\mathbf{v}) = \lim_{s \to 0} s \hat{\sigma}_+ (\mathbf{v}, s)$. We chose $\Gamma = (2\pi)6 \text{ MHz}$ and $\gamma = \frac{1}{2} \Gamma$,

$$
\frac{S}{E_1} = -\frac{N\hbar \Omega}{2\beta I_1} \int d^3\mathbf{v} W(\mathbf{v}) \left[ \theta(v_z) (-2i\beta kv_z) \hat{\sigma}_+(\mathbf{v}, -2i\beta kv_z) + \theta(-v_z) \hat{\sigma}_+(\mathbf{v}) \right].
$$

(19.23)

### 19.3.2 Gas of two-level atoms

Plugging in the solution of the Bloch equations,

$$
\text{Re} \frac{S}{E_1} = -\frac{N\hbar \Omega}{2\beta I_1} \left( \frac{3}{2\pi v_0^2} \right)^{3/2} \text{Re} \int dv_x dv_y dv_z e^{-3v_z^2/(2v_0^2)} e^{-3v_x^2/(2v_0^2)} e^{-3v_y^2/(2v_0^2)} \times
$$

$$
\times \frac{i\Omega}{2} \left[ \theta(v_z) \frac{i(\Delta - k_x v_x - k_y v_y - k_z v_z + \gamma - 2i\beta kv_z)}{(\Delta - k_x v_x - k_y v_y - k_z v_z)^2 + \frac{\gamma^2}{\Gamma^2 - 2i\beta kv_z} \Omega^2 + (\gamma - 2i\beta kv_z)^2} + \theta(-v_z) \frac{i(\Delta - k_x v_x - k_y v_y - k_z v_z + \gamma)}{(\Delta - k_x v_x - k_y v_y - k_z v_z)^2 + \frac{\gamma^2}{\Gamma^2} \Omega^2 + \gamma^2} \right].
$$

(19.24)

For normal incidence $k_x = k_y = 0$, $k_z = k$, and $\beta = 1$ and neglecting collisions $\gamma = \frac{1}{2} \Gamma$,

$$
\text{Re} \frac{S}{E_1} = -\frac{N\hbar \Omega^2}{4I_1} \left( \frac{3}{2\pi v_0^2} \right)^{1/2} \int dv_z e^{-3v_z^2/(2v_0^2)} \times
$$

$$
\times \text{Re} \left[ \frac{-\Delta + 3kv_z + \frac{i}{2} \Gamma}{(\Delta - kv_z)^2 + \frac{\Gamma^2 - 2i\beta kv_z}{\Gamma^2} \Omega^2 + \left( \frac{1}{2} \Gamma - 2ikv_z \right)^2} \right. + \left. \frac{-\Delta + kv_z + \frac{i}{2} \Gamma}{(\Delta - kv_z)^2 + \frac{\Gamma^2}{\Gamma^2} \Omega^2 + \gamma^2} \right].
$$

(19.25)

Define a normalized function $\Phi = \frac{k^4 v_0}{N A} \text{Re} \frac{S}{E_1} = \frac{2\pi I_1 k v_0}{N M^2} \text{Re} \frac{S}{E_1}$,

$$
\Phi = -\sqrt{\frac{3\pi}{8}} \int dk v_z e^{-3v_z^2/(2v_0^2)} \text{Re} \left[ \frac{\theta(v_z) (-\Delta + 3kv_z + \frac{i}{2} \Gamma)}{(\Delta - kv_z)^2 + \frac{\Gamma^2 - 2i\beta kv_z}{\Gamma^2} \Omega^2 + \left( \frac{1}{2} \Gamma - 2ikv_z \right)^2} \right. + \left. \frac{-\Delta + k v_z + \frac{i}{2} \Gamma}{(\Delta - kv_z)^2 + \frac{\Gamma^2}{\Gamma^2} \Omega^2 + \gamma^2} \right].
$$

(19.26)
Figure 19.5: (code) Selective reflection profile.
Part IV

Collective Scattering of Light
Chapter 20

Cooperativity in light scattering

In Chp. 14.5.5 we discussed the interaction of light with individual atoms. In the practice of spectroscopy, however, we often work with ensembles of scatterers. Depending on their spatial distribution (e.g., disordered, quasi-continuous, periodic), their motion (hot gas or cold cloud), the possible existence of correlations between them, the presence of boundary conditions (e.g., free space, cavities, or photon bands), and finally, in case of degenerate quantum gases, of a possible bosonic stimulation of the scattering process, we expect new collective effects. In this chapter we will discuss several examples, in particular, localization effects induced by disorder, super- and subradiance, Bragg scattering, and the formation of forbidden photonic bands in periodic lattices. Phenomena leading to self-organization, such as the collective atomic recoil laser, will be discussed in Chp. 22.6.7.

This chapter starts with introducing as the main theoretical tools the structure factor and the coupled dipoles model. In Sec. 20.1 we will derive the formalism and learn, how to employ it to calculate, e.g., the spatial distribution of light scattered by an atomic cloud and the radiation pressure force on the atoms focusing on situations, where interatomic interactions induced by the incident light can be neglected. In Sec. 20.2 we will, disregarding the atomic’s cloud graininess and disorder, introduce the smooth density approximation and compare it to macroscopic Mie scattering. In Sec. 20.3 we will focus on cooperative effects inducing collective lineshifts and broadenings, such as the Lorentz-Lorenz and the Lamb shift. We will also discuss disorder-induced localization effects, super- and subradiance. In Sec. ?? we study
scattering from correlated atoms, and finally, in Sec. 20.2, we investigate Bragg scattering, i.e. scattering from periodically ordered atoms.

### 20.1 Theoretical tools and models

As mentioned above, the process of light scattering by an atomic cloud depends on several factors, many of which can be summarized by a quantity called the *structure factor*. This structure factor, obtained in perturbation theory, describes the probability for the light to be scattered into a particular direction as a function of the properties of the atomic cloud (spatial distribution, motion, etc.). The quantity is well suited for dealing with stationary situations.

On the other hand we have at our disposal a microscopic theory called the *coupled dipole model*. In this model we treat every individual atom as a dipole, which interacts with all other atoms by rescattering the incident light. The resolution of the Schrödinger equation allows, several approximations having been made, to calculate the dynamics of the system.

#### 20.1.1 The structure factor and definition of cooperativity

One way of characterizing the scattering process is by structure factor. The *static structure factor* is the normalized response of a system to a perturbation with the wave vector $\mathbf{q}$. It can be understood as the final density of states for the atom after the scattering process. In contrast, the *dynamic structure factor* also considers the final density of states for the emitted or scattered photon. That is, on one hand, the frequency and momentum of the photon must satisfy the Bragg condition. On the other hand, the density of available states can also be structured, for example, when the scattering process takes place inside a cavity.

In lowest-order perturbation theory (Fermi’s Golden Rule) we get the general expressions \[ \frac{d\sigma}{d\Omega_s d\omega} = \left( \frac{d\sigma}{d\Omega_s} \right) S(q, \omega), \] that is, the effective scattering cross section is reduced to the effective Rayleigh scattering cross section by an isolated atom times a geometric term called *dynamic structure factor*, \[ S(q, \omega) \equiv \frac{1}{2\pi} \int dt e^{i\omega t} \langle \hat{\rho}(\mathbf{q}, t) \hat{\rho}^\dagger(\mathbf{q}, 0) \rangle, \] where, \[ \hat{\rho}(\mathbf{q}, t) = \int_V \hat{n}(\mathbf{r}, t) e^{i\mathbf{q}\cdot\mathbf{r}} d^3r \] is Fourier transform of the atomic density. Thus, $S(q, \omega)$ is the Fourier transform of the density-density correlation function. On the other hand, $\int e^{i\omega t} d\omega = 2\pi \delta(t)$, and we calculate the *static structure factor*, \[ S(q) \equiv \int S(q, \omega) d\omega = \langle \hat{\rho}(\mathbf{q}, 0) \hat{\rho}^\dagger(\mathbf{q}, 0) \rangle. \]
In the equations (20.2) and (20.3) we have written the quantities $\hat{\rho}(\mathbf{q}, t)$ and $\hat{n}(\mathbf{r}, t)$ as operators, in order to take allow for the possibility, that the atomic ensemble is a quantum gas, i.e. a Bose-Einstein condensate characterized by a single wavefunction $\hat{\psi}(\mathbf{r}, t)$ normalized to the density distribution, $\hat{\rho}(\mathbf{r}, t) = \hat{\psi}^\dagger(\mathbf{r}, t)\hat{\psi}(\mathbf{r}, t)$. We shall return to this subject in Sec. 28.1.1. In the following, we will restrict ourselves to atoms localized in space with well-defined velocities and calculate the structure factor (i) for disordered clouds of atoms excited by the passage of a photon in Sec. 20.1.6 and (ii) for Bragg scattering by optical lattices in Sec. 20.4. In these cases, we find in the literature often another definition of the structure factor as the expectation value of the Fourier transform of the atomic density,

$$F(\mathbf{q}) = \langle \hat{\rho}(\mathbf{q}) \rangle ,$$

(20.5)

Thus, it describes the amplitude of the electric field of the scattered radiation. We study the structure factor for various atomic density distributions in Excs. 20.1.8.1 to 20.1.8.3.

**Example 70 (Structure factor of a discrete cloud):** In case of discrete clouds, $n(\mathbf{r}, t) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j)$, we can disregard the quantum nature of the operators. The relationship (20.3) immediately gives,

$$\rho(\mathbf{q}, t) = \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j(t)}$$

(20.6)

and the relationship (20.2),

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int dte^{i\omega t} \rho(\mathbf{q}, t)\rho^*(\mathbf{q}, 0) = \frac{1}{2\pi} \int dte^{i\omega t} \sum_{j,k} e^{i\mathbf{q}\cdot(\mathbf{r}_j(t) - \mathbf{r}_k(0))}.$$  

(20.7)

Assuming atoms fixed in space, $\mathbf{r}_j(t) = \mathbf{r}_j$,

$$S(\mathbf{q}, \omega) = \sum_{j,k} e^{i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)} \delta(\omega).$$

(20.8)

That is, without recoil the light must be scattered elastically.

**Cooperativity** is defined as any deviation of the structure factor from isotropy. For example, Bragg scattering and optical cavities are highly cooperative, because they favor scattering in particular directions.

20.1.2 The scalar coupled dipoles model

In the following, we develop the coupled dipoles model, within which we define the structure factor for light scattering by a cloud of scatterers making the following assumptions:

- The light is (mostly) treated as a scalar field. That is, we disregard effects due to the polarization of light and assume two-level atoms. Generalizations are shown in Sec. 20.4.4 [558, 402].

\(^1\text{Note that cooperativity does not request the atoms to interact and exists in the single scattering regime. In the multiple scattering regime other forms of collective phenomena, such as collective Lamb shifts emerge, as we will see later on.}\)
Atoms are supposed to be fixed in space. That is, we disregard the Doppler shift of moving atoms and the photonic recoil. Therefore, it will suffice to consider the static structure factor.

Atoms are initially uncorrelated and not degenerate. That means that we neglect effects such as bosonic stimulation or Fermi blocking\(^2\).

Be \(\omega_0\) the frequency of the incident light, \(\omega_a\) the frequency of the atomic resonance, and \(\omega\) the frequency of the scattered light. The Hamiltonian is nothing more than the generalization of (15.97) to several assumed atoms located at the positions \(r_j\),

\[
\hat{H} = \sum_{j=1}^{N} \hbar g_{k_0} (\hat{\sigma}_j e^{-i\omega_0 t} + \hat{\sigma}_j e^{i\omega_0 t})(\hat{a}_{k_0}^\dagger e^{i\omega_0 t - i\mathbf{k}_0 \cdot \mathbf{r}_j} + \hat{a}_{k_0} e^{-i\omega_0 t + i\mathbf{k}_0 \cdot \mathbf{r}_j}) + \sum_{k} \sum_{j=1}^{N} \hbar g_k (\hat{\sigma}_j e^{-i\omega_a t} + \hat{\sigma}_j e^{i\omega_a t})(\hat{a}_k^\dagger e^{i\omega_k t - i\mathbf{k} \cdot \mathbf{r}_j} + \hat{a}_k e^{-i\omega_k t + i\mathbf{k} \cdot \mathbf{r}_j}). \tag{20.9}
\]

Here, \(\Omega_0 = 2g_{k_0}\sqrt{n_0}\) is the Rabi frequency of the interaction between an atom and the incident light (which is treated as a classical field with \(n_0\) photons), \(\hat{\sigma}_j\) is the deexcitation operator for the \(j\)-th atom, \(\hat{a}_k\) is the photon annihilation operator, and \(g_k = d\sqrt{\omega/\hbar \epsilon_0 V_{ph}}\) describes the coupling between the atom and the vacuum modes the volume of which is \(V_{ph}\). The \(j\)-th atom has its lower and upper states denoted by \(|g_j\rangle\) and \(|e_j\rangle\), respectively. That is, we treat the atoms as simple two-level systems.

We also assume that all atoms are excited by the same unperturbed incident laser beam, thus neglecting their dephasing along the laser path or induced by near-field effects (which could arise for large spatial densities).

Within the rotating wave approximation (RWA) the Hamiltonian simplifies to,

\[
\hat{H} = \hbar \sum_{j=1}^{N} [g_{k_0} \hat{\sigma}_j \hat{a}_{k_0}^\dagger e^{i(\omega_0 - \omega_a)t - i\mathbf{k}_0 \cdot \mathbf{r}_j} + h.c.] + \hbar \sum_{j=1}^{N} \sum_{k} [g_k \hat{\sigma}_j \hat{a}_k^\dagger e^{i(\omega_k - \omega_a)t - i\mathbf{k} \cdot \mathbf{r}_j} + h.c.]. \tag{20.10}
\]

The RWA only considers energy-conserving terms in single-photon processes. But this is an artifact from the field quantization. Energy conservation can be warranted by considering multi-photon virtual processes, which as a whole, conserve energy. These terms appear in the full Hamiltonian, but are neglected in the RWA. While the RWA often is a good assumption in single atom quantum optics, this is frequently not the case for collective scattering. Here, we adopt the RWA to simplify the subsequent solution of the Schrödinger equation, but we will need to generalize the results obtained a posteriori, as shown in the discussion of Sec. 20.1.4.

We call \(|0\rangle_a = |g_1, \ldots, g_N\rangle\) the atomic ground state, \(|j\rangle_a = |g_1, \ldots, e_j, \ldots, g_N\rangle\) the state where only the atom \(j\) is excited, and we assume that the system is in a the

\(^2\)Spontaneous emission by an atom in a Fermi gas of temperature \(T = 0\) can not occur if the photon wave vector is inside the Fermi lake, \(q < k_F\).
superposition of states described by \(^3\),

\[
|\Psi(t)\rangle = \alpha(t)|0\rangle_a|n_0\rangle_{k_0}|0\rangle_k + \sum_{j=1}^{N} \beta_j(t)|j\rangle_a|n_0 - 1\rangle_{k_0}|0\rangle_k + \sum_k \gamma_k(t)|0\rangle_a|n_0 - 1\rangle_{k_0}|1\rangle_k .
\] (20.11)

With this ansatz we imply that at every instant of time, there can be at most only one excitation in the atomic cloud. The temporal evolution of the amplitudes is obtained by inserting the Hamiltonian and the ansatz into the Schrödinger equation, \(i\hbar \partial_t |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle\). Once the evolution of the amplitudes is calculated, we can determine the observables of the system, such as the radiative pressure force or the amplitudes of the scattered radiation fields or the fields inside the cloud.

**Figure 20.2**: Scheme of the interaction of a light beam with a sample of atoms.

**Example 71 (Interaction Hamiltonian in the rotating frame)**: The Hamiltonian in the rotating wave approximation is,

\[
\hat{H} = \hbar g \left( \sigma e^{-i\omega_0 t} + \sigma^\dagger e^{i\omega_0 t} \right) \left( \hat{a}^\dagger e^{i\Delta_0 t} + \hat{a} e^{-i\Delta_0 t} \right) \simeq \hbar g \left( \sigma \hat{a}^\dagger e^{i\Delta_0 t} + \sigma^\dagger \hat{a} e^{-i\Delta_0 t} \right).
\]

For the Pauli matrices we have the following rules,

\[
[\sigma_z, \sigma] = -\sigma \quad \text{and} \quad [\sigma_z, \sigma^\dagger] = \sigma^\dagger ,
\]

such that,

\[
[\sigma_z, \hat{H}] = \hbar g \left( -e^{i\Delta_0 t} \hat{a}^\dagger \sigma + e^{-i\Delta_0 t} \sigma \hat{a}^\dagger \right)
\]

\[
[\sigma_z, [\sigma_z, \hat{H}]] = \hbar g \left( e^{i\Delta_0 t} \hat{a}^\dagger \sigma + e^{-i\Delta_0 t} \sigma \hat{a}^\dagger \right) = \hat{H}
\]

\[
[\sigma_z, [\ldots [\sigma_z, \hat{H}]] \ldots ] = \hbar g \left[ (-1)^n e^{i\Delta_0 t} \hat{a}^\dagger \sigma + e^{-i\Delta_0 t} \sigma \hat{a}^\dagger \right] .
\]

\(^3\)This ansatz is well adapted to situations where the RWA holds. Otherwise, additional counter-rotating terms must be included [291].
Using the Baker-Haussdorff formula,
\[
e^{i \omega_0 t \hat{\sigma}_z} \hat{H} e^{-i \omega_0 t \hat{\sigma}_z} = \hat{H} + [i \omega_0 t \hat{\sigma}_z, \hat{H}] + \frac{1}{2!} [i \omega_0 t \hat{\sigma}_z, [i \omega_0 t \hat{\sigma}_z, \hat{H}]] + \ldots
\]
\[
= \hbar g \sum_{n=0}^{\infty} \frac{(-i \omega_0 t)^n}{n!} [(-1)^n e^{i \Delta_0 t \hat{a}^\dagger \hat{\sigma} + e^{-i \Delta_0 t \hat{a} \hat{\sigma}^\dagger}]
\]
\[
= \hbar g e^{i \Delta_0 t \hat{a}^\dagger \hat{\sigma}} \sum_{n=0}^{\infty} \frac{(-i \omega_0 t)^n}{n!} + \hbar g e^{-i \Delta_0 t \hat{a} \hat{\sigma}^\dagger} \sum_{n=0}^{\infty} \frac{(-i \omega_0 t)^n}{n!}
\]
\[
= \hbar g \left( e^{-i \omega_0 t \hat{a}^\dagger \hat{\sigma} + e^{i \omega_0 t \hat{a} \hat{\sigma}^\dagger} \right).
\]

20.1.2.1 Temporal evolution of the amplitudes

The time evolution of the amplitudes is obtained by inserting the Hamiltonian \( \hat{H} \) and the ansatz \( |\Psi(t)\rangle \) into the Schrödinger equation,
\[
\frac{\partial}{\partial t} |\Psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\Psi(t)\rangle \tag{20.12}
\]

one obtains with \( \Omega_0 = 2g_{k_0} \sqrt{n_0} = 2g_{k_0} \),
\[
\dot{\alpha}(t) = -i \frac{\Omega_0}{2} e^{i \Delta_0 t} \sum_{j=1}^{N} \beta_j(t) e^{-i k_0 \cdot r_j} \tag{20.13}
\]
\[
\dot{\beta}_j(t) = -i \frac{\Omega_0}{2} \alpha(t) e^{-i \Delta_0 t + i k_0 \cdot r_j} - \sum_k g_k \gamma_k(t) e^{-i \Delta_k t + i k \cdot r_j}
\]
\[
\dot{\gamma}_k(t) = -i g_k e^{i \Delta_k t} \sum_{j=1}^{N} \beta_j(t) e^{-i k \cdot r_j}.
\]

We set the initial conditions,
\[
\alpha(0) = 1 \quad , \quad \beta_j(t) = 0 \quad , \quad \gamma_k(t) = 0 \tag{20.14}
\]

For low excitation rate, we can set \( \alpha(t) \simeq 1 \). Integrating the third equation,
\[
\gamma_k(t) = -i g_k \sum_{j=1}^{N} e^{-i k \cdot r_j} \int_0^t e^{i \Delta_k t'} \beta_j(t') dt', \tag{20.15}
\]

and substituting it into the second equation,
\[
\dot{\beta}_j(t) = -i \frac{\Omega_0}{2} \alpha(t) e^{-i \Delta_0 t + i k_0 \cdot r_j} - \sum_k g_k^2 \sum_{m=1}^{N} e^{i k \cdot (r_j - r_m)} \int_0^t e^{i \Delta_k (t' - t)} \beta_m(t') dt'. \tag{20.16}
\]
20.1.3 The Markov approximation

For small systems, $R < \lambda$, we can make use of the Markov approximation, which holds when the collective decay time $t_{\text{decay}} < R/c$. Larger systems persist memory effects, which may lead to (Rabi) collective Rabi oscillations. In the Markov approximation given by $\beta_j(t') \simeq \beta_j(t)$ the integro-differential equation (which is equivalent to a differential equation of arbitrarily high order) reduces to a simple first order differential equation. Defining $\beta_j \equiv \tilde{\beta}_j e^{-\gamma_0 t + i t_0 \cdot r_j}$, we obtain,

$$\frac{d}{dt} \alpha(t) = -\frac{i \Omega_0}{2} \sum_{j=1}^{N} \beta_j(t)$$

$$\frac{d}{dt} \tilde{\beta}_j(t) = i \Delta_0 \tilde{\beta}_j(t) - \frac{\Omega_0^2}{4} \sum_{m=1}^{N} \int_{0}^{t} \tilde{\beta}_m(t') dt' - \sum_{k} g_k^2 \sum_{m=1}^{N} e^{i(k-k_0) \cdot (r_j - r_m)} \int_{0}^{t} e^{-i(\omega_k - \omega_0) t''} \tilde{\beta}_m(t - t'') dt'' ,$$

where we substituted $t'' = t - t'$ in the last integral. Now, using the Markov approximation $\tilde{\beta}_m(t - t'') \simeq \tilde{\beta}_m(t)$, with $\lim_{t \to \infty} \int_{0}^{t} e^{-i(\omega_k - \omega_0) t'} dt' = \pi \delta(\omega_k - \omega_0)$, and with the rate of spontaneous emission,

$$\Gamma \equiv \frac{V_{ph} k_0^2 g_{k_0}^2}{\pi c} ,$$

the third term becomes for the case $m = j$,

$$\sum_{k} g_k^2 \int_{0}^{t} e^{-i(\omega_k - \omega_0) t''} \tilde{\beta}_j(t - t'') dt'' \simeq \sum_{k} g_k^2 \tilde{\beta}_j(t) \pi \delta(\omega_k - \omega_0)$$

$$= \frac{V_{ph}}{(2\pi)^3} \tilde{\beta}_j(t) \int g^2_k \pi \delta(\omega_k - \omega_0) d^3k = \frac{V_{ph}}{(2\pi)^3} \tilde{\beta}_j(t) 4\pi g_{k_0}^2 k_0^2 \frac{1}{c} = \frac{\Gamma}{2} \tilde{\beta}_j(t) .$$

The third term becomes for the case $m \neq j$, evaluating the sum over the wavevectors by $\sum_{k} \rightarrow \frac{V_{ph}}{(2\pi)^3} \int d^3k$,

$$\sum_{k} g_k^2 \sum_{m \neq j}^{N} e^{i(k-k_0) \cdot (r_j - r_m)} \int_{0}^{t} e^{-i(\omega_k - \omega_0) t''} \tilde{\beta}_m(t - t'') dt''$$

$$\simeq \sum_{k} g_k^2 \sum_{m \neq j}^{N} e^{i(k-k_0) \cdot (r_j - r_m)} \tilde{\beta}_m(t) \pi \delta(\omega_k - \omega_0)$$

$$= \frac{V_{ph}}{(2\pi)^3} \sum_{m \neq j}^{N} \tilde{\beta}_m(t) \int g_k^2 e^{i(k-k_0) \cdot (r_j - r_m)} \pi \delta(\omega_k - \omega_0) d^3k = \frac{\Gamma}{2} \sum_{m \neq j}^{N} \gamma_{jm} \tilde{\beta}_m(t) ,$$

\footnote{Later on we will be particularly interested in so-called timed Dicke states characterized by $\tilde{\beta}_j = \tilde{\beta}$ independent on $j$.}
with
\[ \gamma_{jm} = \frac{2}{\Gamma} \frac{V_{ph}^2}{(2\pi)^3} \int_0^\infty \int_0^\infty \int_0^{2\pi} g_k^2 e^{i(\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{r}_j-\mathbf{r}_m)} \frac{\pi}{c} \delta(k-k_0)k^2 \sin \theta dk d\theta d\phi . \] (20.22)

Finally,
\[ \frac{d}{dt} \tilde{\beta}_j(t) = i\Delta_0 \tilde{\beta}_j(t) - \frac{\Omega_0^2}{4} \sum_{m=1}^N \int_0^t \tilde{\beta}_m(t') dt' - \frac{\Gamma}{2} \sum_{m=1}^N \gamma_{jm} \tilde{\beta}_m(t) , \] (20.23)

or
\[ \frac{d}{dt} \alpha(t) = -i \frac{\Omega_0}{2} \sum_{j=1}^N \tilde{\beta}_j(t) \] (20.24)
\[ \frac{d}{dt} \tilde{\beta}_j(t) = i\Delta_0 \tilde{\beta}_j(t) - \frac{\Omega_0}{2} \alpha(t) - \frac{\Gamma}{2} \sum_{m=1}^N \gamma_{jm} \tilde{\beta}_m(t) . \]

This means that the problem is reduced to finding the \( \gamma_{jm} \).
\[ \gamma_{jm} = \frac{2}{\Gamma} \frac{V_{ph}^2}{(2\pi)^3} \int_0^\infty \int_0^\infty \int_0^{2\pi} g_k^2 e^{i(\mathbf{k}-\mathbf{k}_0)\cdot(\mathbf{r}_j-\mathbf{r}_m)} \frac{\pi}{c} \delta(k-k_0)k^2 \sin \theta dk d\theta d\phi \] (20.25)
\[ = \frac{1}{\Gamma} g_k^2 \frac{V_{ph}^2}{4\pi^2 c} e^{-i\mathbf{k}_0\cdot(\mathbf{r}_j-\mathbf{r}_m)} \int_0^\infty \int_0^{2\pi} \int_{-1}^1 e^{ik|r_j-r_m| \cos \theta} d\cos \theta d\phi \delta(k-k_0)k^2 dk \]
\[ = \frac{1}{\Gamma} g_k^2 \frac{V_{ph}^2}{\pi c} e^{-i\mathbf{k}_0\cdot(\mathbf{r}_j-\mathbf{r}_m)} \int_0^\infty \frac{\sin k|r_j-r_m|}{k|r_j-r_m|} \delta(k-k_0)k^2 dk \]
\[ = e^{-i\mathbf{k}_0\cdot(\mathbf{r}_j-\mathbf{r}_m)} \frac{\sin k_0|r_j-r_m|}{k_0|r_j-r_m|} . \]

Isolating the self-decaying term and assuming low saturation, \( \alpha(t) = 1 \), we get,
\[ \dot{\tilde{\beta}}_j = \left( i\Delta_0 - \frac{\Gamma}{2} \right) \tilde{\beta}_j - \frac{i\Omega_0}{2} - \frac{\Gamma}{2} \sum_{m\neq j} \gamma_{jm} \tilde{\beta}_m . \] (20.26)

In Exc. 20.1.8.4 we will analyze the validity of the Markov approximation for typical cold atoms experiments.

20.1.4 General solution with exponential kernel, validity of the RWA

The RWA is valid for \( \max(\Omega, \Gamma_n) \ll \omega \),
\[ \int_0^t dt' e^{-i(\omega_k-\omega_0)t} \simeq \mathcal{P} \left( \frac{1}{\omega_k+\omega_0} \right) - i\mathcal{P} \left( \frac{1}{\omega_k-\omega_0} \right) + \pi \delta(\omega_k-\omega_0) . \] (20.27)

The whole expression leads to the exponential kernel, the first two terms are the cosine part, the third term is the sine part. The rotating wave approximation consists in neglecting the first term, i.e. it only concerns the cosine part of the kernel.
Within the RWA we got\(^5,^6\),
\[
\gamma_{jm} = e^{-i k_0 (r_j - r_m)} e^{i k_0 |r_j - r_m|} \frac{i \sin(k_0 |r_j - r_m|)}{i k_0 |r_j - r_m|} .
\]
(20.28)

Without the RWA we would have found [547, 542, 543, 588],
\[
\gamma_{jm} = e^{-i k_0 (r_j - r_m)} e^{i k_0 |r_j - r_m|} .
\]
(20.29)

There has been a controversy between Friedberg and Scully about the role of virtual photons (or \textit{collective Lamb-shift}) [206, 587, 207, 544]. These terms result from counterrotating terms in the rotating wave approximation. Scully assumes timed Dicke states in \textit{infinitely large} clouds and finds the contributions weak. Friedberg does a mode expansion of the cloud and finds that different modes decay at different velocities. This yields time-dependent radiation patterns, which can be temporarily larger in backward direction.

Normally, the RWA is a good approximation, when \(\Omega \ll \omega\). Deviations from this approximations lead e.g. to the Bloch-Siegert shift and important corrections for very far-detuned (quasi-electrostatic) optical trapping. The above requirement is not well satisfied for our experiment, since \(\Omega_N = \sqrt{N} \Omega \approx 1\ldots 10\) THz.

Be \(|b_1 b_2 ... a_j ... b_N\rangle\) the state with all atoms in the ground state except atom \(j\) being in the excited state. Hence, the cloud’s state is simply expressed by the wavefunction,
\[
\Psi_{\text{atom}}(t) = \sum_{j=1}^{N} \beta_j(t) |b_1 b_2 ... a_j ... b_N\rangle .
\]
(20.30)

For large \(\sigma\) the radiation pressure is independent on the choice of the kernel. In fact we may even set the kernel to 0. For small \(\sigma\) there appears a considerable deviation. Interestingly, the imaginary part of the kernel gets important for higher densities, even when the optical density is maintained, e.g. by compressing the cloud in \(z\)-direction. This means that the collective Lamb shift becomes more apparent is small compressed clouds. But we postpone a more thorough discussion to Sec. 20.3.

The analytic expansion into eigenmodes assumes the RWA. Hence, the numerics deviate from the analytics for small \(\sigma\) and large \(N\). Is it possible to generalize the expansion to the exponential kernel (see [588])? The authors also suggest that the scattered radiation be frequency-shifted due to the imaginary part of the kernel. This might be an interesting observable for experiments.

20.1.4.1 \textit{Low collective saturation}

Note that for low \textit{saturation}, \(\alpha(t) = 1\), the first term simply becomes \(-i \frac{\alpha}{2} \Omega_0\). Even though the single atom excitation rate may be small in case of large detuning, the \textit{collective} Rabi frequency \(\sqrt{N} \Omega\) can be large. The presence of many excitations in...
the cloud means, that higher Dicke states are populated. Then we may expect a complicated many-body dynamics, if decay into other states than the timed Dicke state is possible.

Even though the single atom excitation rate may be small in case of large detuning, the collective Rabi frequency $\sqrt{N}\Omega$ can be large. The presence of many excitations in the cloud means, that higher Dicke states are populated. Then we may expect a complicated many-body dynamics, if decay into other states than the timed Dicke state is possible.

The model we use (ground state + first excited state in the times Dicke basis) does not allow more than 1 photon for $N$ atoms. For such a model, neglecting saturation means 'much' less than 1 atom in the excited state, i.e. the probability of having the any atom in the excited state is less than 1. But having $N$ atoms, this means that each atoms should have a excited state population of much less than $1/N$. Including the saturation in the naive way, means that when this term $N\Omega^2_0$ is not negligible, than we will have less atoms in the first excited state of the timed Dicke basis, than if when we would neglect saturation. This is precisely why we call this saturation, we cannot take more atoms away from the ground state, because the system cannot absorb more than one photon. But when this term is not longer negligible, then in a cloud of $N$ atoms, this does not prevent us from taking atoms away from the ground state (we have $N$ atoms which each can take one photon). Either the term is negligible (and we could drop it) or we will try to keep its contribution (even at first order in $N\Omega^2_0$), but then we cannot neglect the possibility of having 2 atoms excited.

### 20.1.4.2 Steady-state solution

In steady-state the equations of the coupled dipoles model can be solved numerically for an arbitrary (ordered or disordered) cloud of immobile atoms located at positions $r_j$ illuminated by an electric field.

Assuming scalar light and the validity of the Markov approximation, and furthermore defining $\tilde{\beta}_j \equiv \beta_j e^{i\omega_0 r_j}$ and $\Omega_0(r_j) \equiv \Omega_0(r_j) e^{i\omega_0 r_j}$, and using the exponential kernel,

$$\tilde{\gamma}_{jm} = \frac{e^{i\omega_0 |r_j - r_m|}}{i\omega_0 |r_j - r_m|},$$  \hspace{1cm} (20.31)

the Eq. (20.26) for the atomic states reads,

$$\frac{d}{dt} \tilde{\beta}_j = \left( i\Delta_0 - \frac{\Gamma}{2} \right) \tilde{\beta}_j - \frac{i\Omega_0(r_j)}{2} - \frac{\Gamma}{2} \sum_{m \neq j} \tilde{\gamma}_{jm} \tilde{\beta}_m.$$  \hspace{1cm} (20.32)

Defining the matrix,

$$M_{jm} \equiv (i\Delta_0 - \frac{\Gamma}{2})\delta_{jm} - \frac{\Gamma}{2}(1 - \delta_{jm})\tilde{\gamma}_{jm} = \begin{pmatrix} (i\Delta_0 - \frac{\Gamma}{2}) & i\gamma_{12} \frac{\Gamma}{2} & \cdots \\ i\gamma_{21} \frac{\Gamma}{2} & (i\Delta_0 - \frac{\Gamma}{2}) & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix},$$  \hspace{1cm} (20.33)

we can rewrite Eq. (20.34) as,

$$\frac{d}{dt} \tilde{\beta}_j = \sum_m M_{jm} \tilde{\beta}_m - \frac{i}{2} \tilde{\Omega}_0(r_j).$$  \hspace{1cm} (20.34)
The steady-state solution of is simply obtained by \( \dot{\beta}_j = 0 \) [295, 97],

\[
M_{jm} \bar{\beta}_m(\infty) = \frac{i}{2} \tilde{\Omega}_0(r_j).
\]  

(20.35)

This equation can now be solved by the dipole moment amplitudes,

\[
\bar{\beta}_m(\infty) = (M_{jm})^{-1} \frac{i}{2} \bar{\Omega}_0(r_j),
\]  

(20.36)

where we use the exponential kernel,

\[
\gamma_{jm} = \frac{e^{i k_0 (|r_j - r_m| + \delta_{jm})}}{i k_0 (|r_j - r_m| + \delta_{jm})},
\]  

(20.37)

where the trick with the \( \delta_{jm} \)-symbol helps to remove divergences for equal atom positions.

In this form the solution is immediately suitable for numerical implementation of the coupled dipoles model, although in practice the number of atoms is limited to \( N < 10000 \) for ordinary PCs.

20.1.4.3 Limit of dilute clouds

Dilute clouds are characterized by a large interatomic distance \( k_0 |r_j - r_m| \gg 1 \). In this case, the non-diagonal elements of the kernel (20.33) quickly vanish, and the equations of motion (20.34) decouple to,

\[
\frac{d}{dt} \bar{\beta}_j = \left( i \Delta_0 - \frac{\Gamma}{2} \right) \bar{\beta}_j - \frac{i}{2} \bar{\Omega}_0(r_j).
\]  

(20.38)

20.1.4.4 Characterization of the atomic cloud in steady-state

Plot the spacial dependence of the phases of the atomic dipoles, \( \phi(r_j) = \text{Im} \left( \ln \bar{\beta}_j \right) \).

Figure 20.3: Phase delay in the excitation of the atomic dipoles (a) without rescattering (\( \gamma_{jm} = 0 \)) and (b) with rescattering.

20.1.4.5 Time-dependence

In order to calculate the time-dependence, we reconsider the equation (20.34) for the excitation amplitudes. Its solution is formally given by the sum of the general solution
of the homogeneous equation and a particular (e.g. the asymptotic) solution of the inhomogeneous equation,
\[
\bar{\beta}_j(t) = e^{M_jm^t} \bar{\beta}_m(0) + (\mathbb{I} - e^{M_jm^t}) \bar{\beta}_m(\infty).
\]  
(20.39)

Inserting the steady-state solution we finally get,
\[
\bar{\beta}_j(t) = e^{M_jm^t} \bar{\beta}_m(0) + (I - e^{M_jm^t}) \bar{\beta}_m(\infty) - \bar{\beta}_m(\infty) M_jm^t \bar{\beta}_m(0).
\]  
(20.40)

20.1.5 Calculation of light scattering in steady-state

To calculate the distribution of scattered light, we start from the Heisenberg equation for the field operator \[291\],
\[
d\hat{a}_k/dt = \frac{1}{ik} [\hat{a}_k, \hat{H}] = -ig_k e^{i(\omega_k - \omega_a)t} \sum_{j=1}^N \hat{\sigma}_j e^{-i\mathbf{k} \cdot \mathbf{r}_j}.
\]  
(20.41)

where the fast oscillating term proportional to \(e^{i(\omega_k + \omega_a)t}\) has been neglected. Now,
\[
\hat{\mathbf{E}}_{\text{sct}}(\mathbf{r}, t) = \sum_k \epsilon_k \hat{a}_k(t) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega_k)t},
\]  
(20.42)

where \(\epsilon_k = \sqrt{\hbar \omega_k/2\varepsilon_0 V_{ph}}\). Integrating Eq. (20.41) with \(\hat{a}_k(0) = 0\), inserting it in Eq. (20.42), and approximating the sum over the modes \(k\) by an integral, we obtain,
\[
\hat{\mathbf{E}}_{\text{sct}}(\mathbf{r}, t) = -\frac{V_{ph}}{8\pi^2} \sum_{j=1}^N \int_0^t dt' \hat{\sigma}_j(t-t') e^{i\omega_{at}} \int d^3k \epsilon_k \hat{g}_k e^{i(\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)) - ikc t'}. 
\]  
(20.43)

Introducing spherical coordinates, \(d^3k = d\kappa d\phi d\theta \sin \theta\), and integrating the angular part Eq. (20.43) becomes,
\[
\hat{\mathbf{E}}_{\text{sct}}(\mathbf{r}, t) = -\frac{V_{ph}}{4\pi^2} \sum_{j=1}^N \int_0^t dt' \hat{\sigma}_j(t-t') e^{i\omega_{at}} \times
\]  
(20.44)

\[
\times \int d\kappa \epsilon_k \hat{g}_k [ e^{-ikc(t-t')/c} - e^{-ikc(t+t')/c} ].
\]

Assuming the radiation spectrum centered around \(k \simeq k_0\), we approximate \(k \hat{\mathbf{E}}_k \hat{g}_k \simeq k_0 \hat{\mathbf{E}}_{k_0} \hat{g}_{k_0}\). Then, extending the lower limit of integration of \(k\) to \(-\infty\), we obtain for \(t < |\mathbf{r} - \mathbf{r}_j|/c\) [481, 382],
\[
\hat{\mathbf{E}}_{\text{sct}}(\mathbf{r}, t) \simeq -\frac{d\kappa^2}{4\pi \varepsilon_0} \sum_{j=1}^N \epsilon_{ik_0} |\mathbf{r} - \mathbf{r}_j| \hat{\sigma}_j(t - |\mathbf{r} - \mathbf{r}_j|/c).
\]  
(20.45)

where we may neglect the radiation retardation in the limit \(t \gg \sigma_R/c\). Using (20.19) and expressing the coupling strength,
\[
\hbar g_k = d\mathcal{E}_k \quad \text{with} \quad \mathcal{E}_k = \sqrt{\frac{\hbar \omega_k}{2\varepsilon_0 V_{ph}}}.
\]  
(20.46)
we get,

$$\hat{E}_{\text{sc}}(r,t) \simeq -\frac{i\hbar \Gamma}{2d} \sum_{j=1}^{N} \gamma_{oj}(r) \hat{\sigma}_j(t) ,$$

(20.47)

where we defined the abbreviation,

$$\gamma_{oj}(r) \equiv \frac{e^{ik_0|r-r_j|}}{i k_0 |r-r_j|} .$$

(20.48)

When applied on the state of Eq. (20.11), neglecting virtual transitions, it yields

$$\hat{E}_{\text{sc}} | \Psi \rangle = E_{\text{sc}} | g_1, \ldots, g_N \rangle ,$$

where \(E_{\text{sc}}\) is the electric field radiated by the excited atoms. Once the excitation amplitudes \(\beta_j(\infty)\) are known, the scattered light field and the total field can easily be calculated via [522],

$$E_{\text{sc}}(r) = \langle \hat{E}_{\text{sc}}(r) \rangle = -\frac{i\hbar \Gamma}{2d} \sum_{j=1}^{N} \gamma_{oj}(r) \beta_j(\infty) \quad \text{and} \quad E_{\text{tot}} = E_{\text{las}} + E_{\text{sc}} ,$$

(20.49)

**Example 72 (Light scattering from a Gaussian beam):** Fig. 20.4 shows an example of light scattering from an incident light field parametrized as a Gaussian beam, as shown in (??),

$$\hat{E}_{\text{las}}(r) = iE_0 \frac{w_0}{w(z)} e^{-r^2/w(z)^2+i[kz+zkr^2/2R(z)]-i\varphi(z)} = i \frac{\hbar}{d} \Omega_0(r) e^{ik_0 \cdot r} .$$

(20.50)

Note that, for the chosen parameters, the result does not depend on the interaction terms. I.e. we can as well set the kernel to 0.

Note, that the phase factor \(e^{ik_0 \cdot r}\) can either be attributed to the atomic dipole moments or to the field. Here, \(N = 125\) atoms are periodically arranged in a threedimensional cubic lattice.

---

**Figure 20.4:** (code) (a) Geometry of light scattering from a cubic lattice with lattice constant \(d = 100\, \text{nm}\). The light is irradiated from below and is partially reflected. (b) Intensity distribution of scattered light along the yellow plane.
20.1.6 Calculation of the steady-state radiation pressure force

Let us now calculate the radiative pressure force exerted by an incident beam of light \( \mathbf{k}_0 \) on an atom \( j \) located at position \( \mathbf{r}_j \) inside an atomic cloud, as illustrated in Fig. 20.2,

\[
\frac{d\hat{\mathbf{P}}_j}{dt} = \hat{\mathbf{F}}_j = -\nabla_{\mathbf{r}_j} \hat{H} .
\]  

(20.51)

Inserting the Hamiltonian in the RWA (20.10),

\[
\hat{\mathbf{F}}_j = i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \left[ \hat{\sigma}_j^\dagger \mathbf{a}_{\mathbf{k}_0}^\dagger e^{i(\omega_0 - \omega_u)t - i\mathbf{k}_0 \cdot \mathbf{r}_j} - h.c. \right] + \sum_k i\hbar \mathbf{k}_k \left[ \hat{\sigma}_j^\dagger \mathbf{a}_k^\dagger e^{i(\omega_k - \omega_u)t - i\mathbf{k} \cdot \mathbf{r}_j} - h.c. \right].
\]  

(20.52)

Introducing \( \Delta_0 = \omega_0 - \omega_u \), the expectation value of the force separates in two contributions,

\[
\langle \hat{\mathbf{F}}_j \rangle \equiv \mathbf{F}_{aj} + \mathbf{F}_{ej} = i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \left[ \alpha^*(t) \beta_j(t) e^{i\Delta_0 t - i\mathbf{k}_0 \cdot \mathbf{r}_j} - c.c. \right] + \sum_k i\hbar \mathbf{k}_k \left[ \beta_j(t) \gamma_k^*(t) e^{i(\omega_k - \omega_u)t - i\mathbf{k} \cdot \mathbf{r}_j} - c.c. \right] = i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \left[ \alpha^*(t) \tilde{\beta}_j(t) - c.c. \right] + \sum_k i\hbar \mathbf{k}_k \left[ \tilde{\beta}_j(t) e^{-i(\omega_0 - \omega_k)t + i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_j} \gamma_k^*(t) - c.c. \right],
\]  

(20.53)

where we reintroduced the abbreviation (20.17). In particular, the term \( m = j \) in the sum of \( \mathbf{F}_{ej} \) vanishes since \( \sum_k \mathbf{k} = 0 \). Substituting \( \gamma_k \) with equation (20.16),

\[
\mathbf{F}_{aj} + \mathbf{F}_{ej} = i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \left[ \alpha^*(t) \tilde{\beta}_j(t) - c.c. \right]
\]  

(20.54)

\[
- \sum_k \hbar \mathbf{k}_k \left[ \tilde{\beta}_j(t) e^{-i(\omega_0 - \omega_k)t + i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_j} \sum_m e^{i\mathbf{k} \cdot \mathbf{r}_m} \int_0^t e^{-i(\omega_k - \omega_u)t'} \tilde{\beta}_m^*(t') dt' - c.c. \right]
\]

\[
= -2i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \text{Im} \left[ \alpha^*(t) \tilde{\beta}_j(t) \right]
\]

and applying the Markov approximation (20.20),

\[
\mathbf{F}_{aj} + \mathbf{F}_{ej} = -2i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \text{Im} \left[ \alpha^*(t) \tilde{\beta}_j(t) \right]
\]  

(20.55)

\[
- \sum_k \hbar \mathbf{k}_k \sum_{m=1}^N \left[ \tilde{\beta}_j(t) e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot (\mathbf{r}_j - \mathbf{r}_m)} \int_0^t e^{i(\omega_0 - \omega_k)(t' - t)} \tilde{\beta}_m^*(t') dt' - c.c. \right],
\]

This is the expression for the force acting on an atom at the position \( \mathbf{r}_j \). Knowing the stationary excitation amplitudes \( \beta_j(\infty) \) and assuming \( \alpha(\infty) \simeq 1 \), the radiation pressure force can numerically be calculated. Remembering \( \Omega_0 = 2g_{\mathbf{k}_0} \) we get for the absorption force acting on atom \( j \),

\[
\mathbf{F}_{aj} = -2i\hbar \mathbf{k}_0 g_{\mathbf{k}_0} \text{Im} \left[ \tilde{\beta}_j(\infty) \right].
\]  

(20.56)
To evaluate the emission force acting on atom \( j \), for every atom \( m \) of the sum, we need to average over all possible scattering angles. To do so, we choose a reference frame in which the \( z \)-component of \( \mathbf{k} \) is directed along \( \hat{r}_{jm} = \frac{r_j - r_m}{|r_j - r_m|} \), that is,

\[
\mathbf{k} = \hat{e}_{x, jm} k \sin \theta_{jm} \cos \phi_{jm} + \hat{e}_{y, jm} k \sin \theta_{jm} \sin \phi_{jm} + \hat{r}_{jm} k \cos \theta_{jm},
\]

and evaluate the sum over the wavevectors by \( \sum_{\mathbf{k}} \rightarrow \frac{V_{ph}}{(2\pi)^3} \int d^3 k \),

\[
\mathbf{F}_{ej} = -\sum_{m=1}^{N} \beta_j(\infty) \beta^*_m(\infty) \frac{V_{ph} \pi}{(2\pi)^3 c} \int d\theta_{jm} d\phi_{jm} dk \ h k \left( \frac{\sin \theta_{jm} \cos \phi_{jm}}{\sin \theta_{jm} \sin \phi_{jm}} \right) \times (20.58)
\]

\[
\times g(k) \left[ e^{i(k_0 - k) \cdot (r_j - r_m)} \delta(k - k_0) k^2 \sin \theta_{jm} - c.c. \right.
\]

\[
= -\hbar k_0 \frac{\Gamma}{8\pi} \sum_{m=1}^{N} e^{i(k_0 \cdot (r_j - r_m))} \tilde{\beta}_j(\infty) \tilde{\beta}^*_m(\infty) \int_0^{\pi} \int_0^{2\pi} d\theta_{jm} d\phi_{jm} \left( \frac{\sin \theta_{jm} \cos \phi_{jm}}{\sin \theta_{jm} \sin \phi_{jm}} \right) \times (20.59)
\]

\[
\times e^{-i k_0 \cdot (r_j - r_m) \cos \theta_{jm} \sin \theta_{jm} - c.c.}
\]

remembering \( \Gamma = \frac{V_{ph} \pi^2 k_0^2 \hbar^2}{8\pi} \) from Eq. (20.19). The integrals over \( \phi_{jm} \) vanishes whereas the integral over \( \theta_{jm} \) becomes, using,

\[
\int_0^{\pi} d\theta \sin \theta \cos \theta e^{-i \alpha \cos \theta} = 2\frac{\alpha \cos \alpha - \sin \alpha}{\alpha^2} = -2i j_1(\alpha).
\]

we find,

\[
\mathbf{F}_{ej} = -\hbar k_0 \frac{\Gamma}{4} \sum_{m=1}^{N} e^{i k_0 \cdot (r_j - r_m)} \tilde{\beta}_j(\infty) \tilde{\beta}^*_m(\infty) \hat{r}_{jm} \times (20.60)
\]

\[
\times \int_0^{\pi} \cos \theta_{jm} \sin \theta_{jm} e^{-i k_0 \cdot (r_j - r_m) \cos \theta_{jm}} d\theta_{jm} - c.c.
\]

\[
= i \hbar k_0 \frac{\Gamma}{2} \sum_{m=1}^{N} e^{i k_0 \cdot (r_j - r_m)} \tilde{\beta}_j(\infty) \tilde{\beta}^*_m(\infty) \hat{r}_{jm} j_1(k |r_j - r_m|) - c.c.
\]

\[
= -i \hbar k_0 \frac{\Gamma}{2} \sum_{m=1}^{N} f_{jm} \tilde{\beta}_j(\infty) \tilde{\beta}^*_m(\infty) - c.c.,
\]

where we defined \( f_{jm} = j_1(k |r_j - r_m|) e^{i k_0 \cdot (r_j - r_m)} \hat{r}_{jm} \).

In summary we got,

\[
\begin{align*}
\mathbf{F}_{aj} &= -i \hbar k_0 \Omega \text{Im } \tilde{\beta}_j(\infty) \\
\mathbf{F}_{ej} &= -i \hbar k_0 \Gamma \sum_{m=1}^{N} f_{jm} \text{Im } [\tilde{\beta}_j(\infty) \tilde{\beta}^*_m(\infty)] .
\end{align*}
\]

\[7\]For exploitation in MATLAB we may express the spherical Bessel function by a Bessel function of the first kind: \( j_n(x) = \sqrt{\pi/2} x J_{n+1/2}(x) \).
The steady state absorption and the emission part of the radiation pressure force on the center of mass of the atomic cloud follow from,

\[ F_a = \frac{1}{N} \sum_j \langle \hat{F}_{aj} \rangle \quad \text{and} \quad F_e = \frac{1}{N} \sum_j \langle \hat{F}_{ej} \rangle . \]  

(20.63)

Figure 20.5: (code) Force distribution upon scattering of a photon by an atom of an spherical Gaussian cloud (a) without and (b) with rescattering according to Eqs. (20.63).

As long as the RWA and the Markov approximation are valid and only the lowest Dicke state is considered (no collective saturation), this simulation is supposed to be exact and contains all the physics including, e.g., multiple scattering. Fig. 20.5 shows a comparison of the cases when the off-diagonal components of the kernel (20.37) are present or not. Apparently, the presence of rescattering dramatically spoils the radiation pressure force, a phenomenon that we will extensively study in Secs. 20.1.7 and 20.2 [291, 292, 296, 474, 55, 293].

20.1.7 The structure factor of the 'timed' Dicke state

When a beam of light passes through an atomic cloud, its phase fronts will excite the atomic dipole moments as it traverses the cloud. That is, understanding the beam as a plane wave \( e^{i(k_0 \cdot r - \omega t)} \), the dipoles start to oscillate with relative phase delays \( e^{i k_0 \cdot (r_j - r_m)} \) depending on their position along the optical axis \( k_0 \). The resulting collective state has been termed timed Dicke state [545]. Assuming that this phase delay is the only parameter distinguishing two atoms, we may write with Eq. (20.17),

\[ \tilde{\beta}_j(t) = \beta_j(t) e^{i(\Delta_0 t - k_0 \cdot r_j)} \equiv \frac{1}{\sqrt{N}} \beta(t) , \]  

(20.64)

where \( \beta \) is the macroscopic dipole moment. Note, that the fact that \( \beta(t) \) does not depend on the atomic position does not imply a continuous density distribution. The atoms are still sitting at their positions \( r_j \); only are their dipole moments synchronized to the incident light wave.

The assumption of a timed Dicke state for the atomic cloud is, nevertheless, an approximation which is not always good [291]. For example, it neglects dispersive phase shifts of the excitation of the atomic dipole moments by the pump laser beam.
being delayed on its propagation due to its interaction with the atoms. If such phase shifts (and absorption as well) are radially inhomogeneous, this can lead to deformation of the pump laser beam’s phase front and thus to lensing. We will discuss this in Exc. 20.1.8.5 and in Sec. 20.2.

20.1.7.1 Structure factor for 'timed' Dicke states

We start again with the Eqs. (20.24) inserting the ansatz of timed Dicke states,

\[ \dot{\beta} = \frac{1}{N} \sum_{j=1}^{N} \dot{\beta}_j(t) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \frac{d}{dt} \tilde{\beta}_j(t) \]

\[ = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \left( i \Delta_0 \tilde{\beta}_j(t) - \frac{\Omega_0}{2} \alpha(t) - \frac{\Gamma}{2} \sum_{m=1}^{N} \gamma_{jm} \tilde{\beta}_m(t) \right) \]

\[ = \left( i \Delta_0 - \frac{\Gamma}{2} N s_N \right) \beta(t) - i \frac{\sqrt{N} \Omega_0}{2} \alpha(t) , \]

where we introduced the abbreviation,

\[ s_N = \frac{1}{N} \sum_{j,m=1}^{N} \gamma_{jm} . \]

Taking the kernel from (20.25), we get,

\[ s_N = \frac{1}{2N} \frac{2 V_{ph}}{\Gamma} \int_{\mathbb{R}^3} \frac{1}{N} \frac{1}{2} \sum_{j,m=1}^{N} e^{i(k-jk_{0}) \cdot (r_j-r_m)} \frac{\pi}{c} \delta(k-k_{0}) k^2 \sin \theta dk d\theta d\phi \]

\[ = \frac{1}{2N} \frac{2 V_{ph}}{\Gamma} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} g_k \frac{2N}{c} |S_{N}(k,\theta,\phi)|^2 \delta(k-k_{0}) k^2 \sin \theta dk d\theta d\phi \]

\[ = \frac{1}{4\pi} \int_{0}^{\pi} \int_{0}^{2\pi} |S_{N}(k_{0},\theta,\phi)|^2 \sin \theta d\theta d\phi , \]

introducing the normalized static structure factor,

\[ S_{N}(k) \equiv \rho(q) = \frac{1}{N} \sum_{j=1}^{N} e^{i(k-jk_{0}) \cdot r_j} , \]

where \( q = k - k_{0} \) and \( \rho(q) \) is the static structure factor defined in (20.3).

In steady state, \( \dot{\beta}(t) = 0 \), and disregarding saturation, \( \alpha(t) \approx 1 \), the solution of (20.65) reads,

\[ \beta(\infty) = \frac{\sqrt{N} \Omega_0}{2 \Delta_0 + i \Gamma N s_N} , \]

such that,

\[ |\beta(\infty)|^2 = \frac{N \Omega_0^2}{4 \Delta_0^2 + N^2 \Gamma^2 s_N^2} \]

\[ \text{Im} [\alpha(\infty) \beta^*(\infty)] = \frac{N^{3/2} \Omega_0 s_N}{4 \Delta_0^2 + N^2 \Gamma^2 s_N^2} . \]
The time-dependent solution is easily obtained as,

$$\beta(t) = \beta(0)e^{i(\Delta_n - \Gamma N_s / 2)t} + \beta(\infty). \quad (20.71)$$

The evolution of the cloud very much depends on the initial conditions, e.g. \(\beta_j(0) = 1\) for the uniformly excited symmetric state \(\beta_j(0) = e^{i k_0 \cdot r_j}\) for timed Dicke states.

In cylindrical coordinates the structure factor can be written,

$$S(k, \theta, \phi) = \frac{1}{N} \sum_{j=1}^{N} e^{i(kx_j \sin \theta \cos \phi + ky_j \sin \theta \cos \phi + (k \cos \theta - k_0) z_j)} . \quad (20.72)$$

It basically tells the angular distribution of the scattered light. Fig. 20.6 shows numerical calculations and analytical approximations of the structure factor for various shapes and sizes of the atomic cloud. Obviously, the radiation pattern very much depends on the size of the spherical cloud. For \(R < \lambda\) it is isotropic, for \(R > \lambda\) scattering mainly occurs in forward direction. Furthermore, if the cloud is ellipsoidal the radiation pattern is shifted into forward direction.

![Figure 20.6: Numerical calculation of \(S(k, \theta)\) according to (20.68) for 10^4 atomic positions \(r_j\) chosen by a random number generator. For the graphs (a-b) the cloud is homogeneous and spherical and has the sizes \(R = \lambda\) (red) and \(R = 10\lambda\) (blue). For the graphs (c-d) the cloud is Gaussian and spherical and has the same sizes as (a-b). For the graphs (d-e) the cloud is homogeneous and ellipsoidal with aspect ratio \(R_z / R_\rho = 3\) and has the same radial sizes as in (a-b).](image-url)
20.1.7.2 Time evolution of radiation modes

We are interested in the power emitted into the solid angle \( \Omega_k \), \( P(t) \propto |\gamma_k(t)|^2 \). For timed Dicke state (20.64) we get immediately from the equations of motion,

\[
\dot{\gamma}_k(t) = -ig_k e^{i\Delta_k t} \sum_{j=1}^{N} \beta_j(t) e^{-i\mathbf{k}_j \cdot \mathbf{r}_j} \tag{20.73}
\]

\[
= -ig_k e^{i(\Delta_k - \Delta_0) t} \frac{1}{\sqrt{N}} \beta(t) \sum_{j=1}^{N} e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_j} = -ig_k e^{i(\Delta_k - \Delta_0) t} \sqrt{N} S_N(k) .
\]

We see that the time-dependence factorizes from the structure factor, which is the only component containing an angular dependence. The same holds for symmetric Dicke states defined by \( |\beta_j| = |\beta_m| \).

![Figure 20.7](code) Time-dependent of (a) the dipole amplitudes and (b) the forces for \( \sigma = 1, \Delta_0 = 20\Gamma, \Omega_0 = 0.01\Gamma, \) and \( \eta = 1. \)

20.1.7.3 Light scattering in the ‘timed Dicke state’

The scalar electric field scattered by an arbitrary distribution of atoms has been calculated in (20.49). Substituting the stationary timed Dicke state (20.69), we get,

\[
\vec{E}_{sc} = \frac{i\hbar \Gamma}{2d} \frac{\sqrt{N} \Omega_0}{2\Delta_0 + i\Gamma N S_N} \sum_{j=1}^{N} e^{i\mathbf{k}_0 \cdot \mathbf{r}_j} \frac{e^{i\mathbf{k}_0 \cdot |\mathbf{r} - \mathbf{r}_j|}}{\sqrt{N} S_N(k)} .
\]

Note that the ‘timed Dicke’ state starts from the assumption of an infinitely extended plane wave incident light field. This excludes situations where the incident beam size is smaller than the cloud’s size.
20.1.7.4 Force in the 'timed Dicke state' on a particular atom in a cloud

The time-dependent expressions (20.56) for the forces in the coupled dipoles model can be further evaluated for timed Dicke states (20.64),

\[ F_{aj} + F_{ej} \]

\[ = - \frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) - \sum_k \hbar k g_k^2 N \sum_{m=1}^N \left[ e^{i(k_0-k) \cdot (r_j-r_m)} \frac{\pi}{c} \delta(k - k_0) |\beta(t)|^2 - \text{c.c.} \right] \]

\[ = - \frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) - \sum_k \hbar k g_k^2 \left[ S_N(k) e^{-i(k-k_0) \cdot r_j} \frac{\pi}{c} \delta(k - k_0) |\beta(t)|^2 - \text{c.c.} \right]. \]

Evaluating the sum over the wavevectors by \( \sum_k \rightarrow \frac{V_{ph}}{(2\pi)^3} \int d^3k \),

\[ F_{aj} + F_{ej} = - \frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) \]

\[ - |\beta(t)|^2 \frac{\Gamma}{8\pi \hbar k_0} \int_0^\pi \int_0^{2\pi} (\hat{e}_x \sin \theta \cos \phi + \hat{e}_y \sin \theta \sin \phi + \hat{e}_z k \cos \theta) [S_N(k, \theta, \phi) - \text{c.c.}] \sin \theta d\theta d\phi dk. \]

Let us consider an atom sitting on axis, \( r_j = 0 \), and use cylindrical coordinates, \( k_0 = k_0 \hat{e}_z \) and \( k = \hat{e}_z k \sin \theta \cos \phi + \hat{e}_y k \sin \theta \sin \phi + \hat{e}_z k \cos \theta \), and using the definition (20.19) of \( \Gamma \),

\[ F_{aj} + F_{ej} = - \frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \hat{e}_z \text{Im} \beta(t) \]

\[ - |\beta(t)|^2 \frac{\Gamma}{8\pi \hbar k_0} \int_0^\pi \int_0^{2\pi} (\hat{e}_z \sin \theta \cos \phi + \hat{e}_y \sin \theta \sin \phi + \hat{e}_z k \cos \theta) [S_N(k, \theta, \phi) - \text{c.c.}] \sin \theta d\theta d\phi dk. \]

Using the abbreviation,

\[ \tilde{f}_N \equiv \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} \text{Re} S_N(k_0, \theta, \phi) \sin \theta \cos \theta d\theta d\phi, \]

the z-component becomes,

\[ F_{zaj} + F_{zej} = - \frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) - |\beta(t)|^2 \frac{\Gamma}{\hbar k_0} \tilde{f}_N. \]

In steady state and normalizing to the standard radiation pressure,

\[ F_{z1j} = \frac{\Gamma}{\hbar k_0} \frac{\Omega_0^2}{4\Delta_0^2 + \Gamma^2} = \frac{\hbar k_0 \sigma(\Delta) I}{\hbar \omega}, \]

where \( \sigma(\Delta_0) \) is the optical cross section and \( I \) the intensity of the incident light, we can write,

\[ \frac{F_{zaj} + F_{zej}}{F_{z1j}} = \left( - \frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(\infty) - |\beta(\infty)|^2 \frac{\Gamma}{\hbar k_0} \tilde{f}_N \right) \frac{4\Delta_0^2 + \Gamma^2}{\Gamma \hbar k_0 \Omega_0^2}. \]

Finally, inserting the expression (20.69) for the dipole moment, we obtain for the timed Dicke state,

\[ \frac{F_{zaj} + F_{zej}}{F_{z1j}} = \frac{(2\Delta_0/\Gamma)^2 + 1}{(2\Delta_0/\Gamma)^2 + N^2 s_N^2} N(s_N - \tilde{f}_N). \]
using $\Omega_0 = 2g_{k_0}$.

The factors $s_N$ and $f_N$ can be calculated exactly, as will be done in Exc. 20.1.8.6,

\[
s_N = \frac{1}{N^2} \sum_{j,m=1}^{N} \frac{\sin(k_0|\mathbf{r}_j - \mathbf{r}_m|)}{k_0|\mathbf{r}_j - \mathbf{r}_m|} \cos[k_0(z_j - z_m)] \tag{20.83}
\]

\[
f_N = \sqrt{\frac{\pi}{2}} \frac{1}{N^2} \sum_{j,m=1}^{N} \frac{J_{3/2}(k_0|\mathbf{r}_j - \mathbf{r}_m|)}{(k_0|\mathbf{r}_j - \mathbf{r}_m|)^{3/2}} k_0(z_j - z_m) \sin[k_0(z_j - z_m)] .
\]

However, this is only practicable for atom numbers small enough for numerical simulations. For larger atom number we may use the analytic expressions including the disorder term [56].

### 20.1.7.5 Force on the center of mass of the cloud

The force acting on the center of mass of the atomic cloud is given by the average of the forces (20.76) sensed by particular atoms,

\[
\mathbf{F}_a + \mathbf{F}_e = \frac{1}{N} \sum_{j=1}^{N} (\mathbf{F}_{aj} + \mathbf{F}_{ej}) \tag{20.84}
\]

\[
= -\frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) - |\beta(t)|^2 \frac{V_{ph}}{(2\pi)^3} \int_{\mathbb{R}^3} h\hbar g_k \left[ S_N(k, \theta, \phi) \frac{1}{N} \sum_{j=1}^{N} e^{-i(k-k_0) \cdot \mathbf{r}_j} \delta(k-k_0) - c.c. \right] k^2 \sin \theta d\theta d\phi dk .
\]

Using cylindrical coordinates, $\mathbf{k}_0 = k_0 \hat{e}_z$ and $\mathbf{k} = \hat{e}_x k \sin \theta \cos \phi + \hat{e}_y k \sin \theta \sin \phi + \hat{e}_z k \cos \theta$, and the definition of $\Gamma$,

\[
\mathbf{F}_a + \mathbf{F}_e = -\frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \hat{e}_z g_{k_0} \text{Im} \beta(t) - |\beta(t)|^2 \frac{V_{ph}}{(2\pi)^3} \int_{\mathbb{R}^3} \hbar g_k \left[ S_N(k, \theta, \phi) \frac{1}{N} \sum_{j=1}^{N} e^{-i(k-k_0) \cdot \mathbf{r}_j} \delta(k-k_0) - c.c. \right] k^2 \sin \theta d\theta d\phi dk .
\]

\[
\mathbf{F}_a + \mathbf{F}_e = -\frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \hat{e}_z g_{k_0} \text{Im} \beta(t) - |\beta(t)|^2 \frac{V_{ph}}{(2\pi)^3} \int_{\mathbb{R}^3} \hbar g_k \left[ S_N(k, \theta, \phi) \frac{1}{N} \sum_{j=1}^{N} e^{-i(k-k_0) \cdot \mathbf{r}_j} \delta(k-k_0) - c.c. \right] k^2 \sin \theta d\theta d\phi dk .
\]

Using the abbreviation,

\[
f_N \equiv \frac{1}{4\pi} \int_{0}^{\pi} \int_{0}^{2\pi} |S_N(k_0, \theta, \phi)|^2 \sin \theta \cos \theta d\theta d\phi , \tag{20.86}
\]

we get for the $z$-component an analogous formula to (20.79),

\[
F_{za} + F_{ze} = -\frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) - |\beta(t)|^2 \frac{\Gamma}{8\pi} \hbar k_0 \int_{0}^{\pi} \int_{0}^{2\pi} 2|S_N(k, \theta, \phi)|^2 \sin \theta \cos \theta d\theta d\phi
\]

\[
= -\frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(t) - |\beta(t)|^2 \frac{\Gamma}{8\pi} \hbar k_0 f_N . \tag{20.87}
\]

In steady state and normalizing again to the standard radiation pressure (20.80),

\[
\frac{F_{za} + F_{ze}}{F_{z1}} = \left( -\frac{2\hbar k_0 g_{k_0}}{\sqrt{N}} \text{Im} \beta(\infty) - |\beta(\infty)|^2 \frac{\Gamma}{8\pi} \hbar k_0 f_N \right) \frac{4\Delta_0^2 + \Gamma^2}{\Gamma \hbar k_0 \Omega_0^2} . \tag{20.88}
\]
Finally, inserting the the expression (20.69) for the dipole moment, we obtain for the timed Dicke state,

\[
\frac{F_{za} + F_{ze}}{F_{z1}} = \frac{(2\Delta_0/\Gamma)^2 + 1}{(2\Delta_0/\Gamma)^2 + N^2s_N^2}N(s_N - f_N)
\]  

(20.89)

using \(\Omega_0 = 2g_{k0}\). Inserting the expressions (20.67) for \(s_N\) and (20.86) for \(f_N\), we may also write,

\[
\frac{F_{0a} + F_{0e}}{F_{z1}} = \frac{(2\Delta_0/\Gamma)^2 + 1}{(2\Delta_0/\Gamma)^2 + N^2s_N^2}N \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi |S_N(k, \theta, \phi)|^2 (1 - \cos \theta) \sin \theta d\theta d\phi.
\]

(20.90)

Let us assume in the following that the scattering of every single photon can be treated independently [543]. In particular, the density distribution may change between two scattering events. The force is something like the first moment of the structure factor. This makes it so adapted to measure fluctuation-induced deviations from the structure factor.

We want to compare this force to the force acting on a cloud of \(N\) uncorrelated scatterers, i.e. atoms receiving recoil from the pump photons but reemitting isotrop-

---

8Insert a clarifying discussion of what we said in the EPDJ and what we did not: We said there is a collective effect coming from the structure factor of the cloud. We did NOT say that interatomic interactions are essential...!
20.1. THEORETICAL TOOLS AND MODELS

\[ \langle F_{\text{unc}, z} \rangle = \frac{V_{ph}}{(2\pi)^3} \sigma(\Delta) \frac{l}{\hbar \omega} \hbar k_0 \int_0^\infty \int_0^\pi \int_0^{2\pi} |S_N(k, \theta, \phi)|^2 k^2 \sin \theta d\theta d\phi dk. \]  
(20.91)

For such a cloud the structure factor is \( S_N = N^{-1/2} \). Note that this is unlike \( N \) atoms in the Dicke limit, where \( S_N = 1 \).

A dense homogeneous cloud with \( S_N(k) \propto \delta(k - k) \) does not scatter light and experiences no force, \( \langle F_{\text{hom}} \rangle = 0 \). This is however not true any more in the limit of small extended clouds, where fluctuations introduce disorder. This can be shown by simulating a random atomic distribution \( r_j \) and integrating the resulting force over all possible \( k \). For simplicity we assume a very sharp momentum distribution, \( |k| = |k_0| \) or \( \frac{V_{ph}}{2\pi} \int_0^\infty k^2 dk = 1 \),

\[ \langle F_z \rangle = \sigma(\Delta) \frac{l}{\hbar \omega} k_0 (s_N - f_N). \]  
(20.92)

Finally to compare with experiment we evaluate the ratio,

\[ \frac{\langle F_z \rangle}{\langle F_{\text{unc}, z} \rangle} = 1 - \frac{f_N}{s_N}. \]  
(20.93)

We describe the cloud as being made of two fractions: An isotropically scattering fraction of \( N_0 = \sqrt{N} \) disordered atoms, whose structure factor is \( S_{\text{iso}}(k) = 1 \), and a forward scattering homogeneous cloud with structure factor \( S_{\text{hom}}(k) = \delta_{k_0, k} \). The surface integration of the total structure factor,

\[ S_N(k) = \frac{N_0}{N} S_{\text{iso}}(k) + \frac{N - N_0}{N} S_{\text{hom}}(k) = \frac{N_0}{N} + \frac{N - N_0}{N} \delta_{k_0, k} \approx \frac{N_0}{N}, \]  
(20.94)

yields the same \( N \)-dependence of the force,

\[ \frac{\langle F_z \rangle}{\langle F_{\text{iso}, z} \rangle} = \frac{1}{4\pi N^2} \int_0^\pi \int_0^{2\pi} |\sqrt{N}|^2 (1 - \cos \theta) \sin \theta d\theta d\phi = \frac{1}{N}. \]  
(20.95)

The interpretation is the following. In the experimentally realized situation, we are very far in the large cloud limit completely dominated by forward scattering, which means that if the cloud were homogeneous no radiation pressure force should be expected at all. However diffuse scattering from disordered atoms (or fluctuations) disturbs the forward scattering. It is this scattering which gives rise to radiation pressure.

There is an interesting analogy: Diffuse scattering not only inhibits forward scattering in homogeneous clouds, but also coherent backscattering from ordered structures. E.g. in optical lattices [561] it disturbs the detection of photonic band gaps. In an optical lattice the atoms are in the Dicke limit and do not absorb photonic recoil. Hence, no displacement due to radiation pressure is expected. However, diffuse scattering is observed as absorptive features in the spectra [57, 561].

The Bragg scattering is expressed by a periodic structure factor. A widely used approach to describe the impact of disordered atoms in lattices is to divide the cloud into a perfectly ordered part with density \( n_{fDW} \) and isotropically scattering part with density \( n(1 - f_{DW}) \) [561]. The factor \( f_{DW} \) is known as Debye-Waller factor. In Exc. 20.1.8.7 we try an alternative treatment of radiation pressure based on a Monte-Carlo simulation.
20.1.7.6 Cooperative scattering and single photon superradiance

A non-isotropic structure factor scattering light into a specific direction of space (e.g. the Bragg angle) at a rate scaling like $N^\alpha$ with $\alpha > 1$ needs several ‘cooperating’ particles. In this sense cooperation only means, that the particles be arranged in space in a particular way, i.e. in a lattice or in a particular bulk shape like a homogeneous sphere or a Gaussian cigar-shaped density distribution. It also immediately becomes clear that disorder ought to play a major role. However, cooperation goes further, since cooperative scattering can be observed in spontaneous emission of an atomic cloud being excited by just a single photon. Single-photon superradiance is the topic of the following sections.

For now let us state that a non-isotropic structure factor results in collective scattering. The density distribution (which is the Fourier transform of the structure factor) can adopt two extremes: A periodic lattice results in backscattering into specific directions, a homogeneous clouds shows nothing but forward scattering. Both situations are never perfectly realized, but are subject to density fluctuations (Debye-Waller factor in a lattice, radiation pressure in a homogeneous cloud).

A single photon on its trip through an atomic cloud successively excites the atomic dipole moment thus establishing a phase relation between potential radiators [179, 589, 544, 590]. One could think that the scattering process localizes atom and photon, i.e. only one atom scatters. However, we don’t know which atom scatters, and this introduces a correlation of the dipole moments along the propagation direction of the light beam.

While normally the radiation rate of a dilute cloud is $\propto N$, in the presence of coherent interactions it scales as $\propto N^2$. Coherent interactions are not conditioned to overlapping space functions of the atoms, i.e. it is not compulsory that the density be $n^{-1/3} > \lambda$. For example, scattering from ordered structures also scales as $\propto N^2$ [328]. However, the scattering will be dramatically different if $n^{-1/3} < \lambda$.

Spontaneous emission radiation pattern from uncorrelated scatterers only depend on the relative orientation of $\hat{\sigma}$ and $\vec{B}$, but not on the $\mathbf{k}$-vector of the incident light. This also holds for Dicke superradiance in the small cloud limit, but not for large clouds. Here forward scattering dominates.

We have seen in this section that, despite its simplicity, the coupled dipoles model has a large range of applications. It allows for a deeper understanding of known classical phenomena and, as we will study in Excs. 20.1.8.8 to 20.1.8.10 and in forthcoming sections, it allows to unravel new effects.
20.1.8 Exercises

20.1.8.1 Ex: Structure factor of a linear array
a. Based on the definition (20.1) compute the structure factor of a linear array of point-like scatterers.
b. Based on the definition (20.2) compute the structure factor of a linear array of 10 Gaussian density distributions.

20.1.8.2 Ex: Structure factor of a cloud
Based on the definition (20.1) compute the structure factor of (i) a slit, (ii) a pinhole, and (iii) a homogeneous spherical cloud.

20.1.8.3 Ex: Structure factor and Snell’s law
Calculate the structure factor for a light beam passing through a plane interface between two dielectrics.

20.1.8.4 Ex: Validity of Markov approximation
a. Calculate the single-atom scattering rate for a rubidium cloud of \( N = 10^6 \) atoms driven with \( P = 100 \text{ mW} \) laser power focused into a waist of \( w_0 = 100 \mu \text{m} \) and detuned by \( \Delta = (2 \pi) 100 \text{ GHz} \) from the \( D_2 \)-line at 780 nm [97].
b. Assume for the cloud a homogeneous spherical density distribution with radius \( R = 250/k_0 \). Based on Ref. [589] estimate whether the Markov approximation is valid.

20.1.8.5 Ex: Lensing by a dense atomic cloud with the coupled dipoles model
Simulate the pump laser phase shift and lensing by a small dense cloud by the coupled dipoles model for red and blue detuning. Discuss the influence of rescattering by removing artificially the off-diagonal terms from the scattering kernel. Discuss whether lensing is observed within the timed Dicke approximation.

20.1.8.6 Ex: Exact calculation of projected structure factors
Calculated the integrals (20.66), (20.78), and (20.86).

20.1.8.7 Ex: Monte-Carlo simulation of cooperative radiation pressure
In a regime of negligible interatomic interaction single photons are scattered by individual atoms, which thereby receive the entire photonic recoil. That is, the acceleration occurs in quantized steps, which can be easily resolved in experiments [304, 559] with Bose-Einstein condensates. In the absence of collective effects, we generally observe halo-shaped momentum distributions. Because of the recoil received upon absorption, the halos are centered at \( \hbar k \), and since the emission is generally isotropic, they have a radius of \( \hbar k \). On the other hand, as we have seen earlier, cooperative effects can suppression radiation pressure. In the following we try a different approach
based on a Monte-Carlo simulation with a Langevin force. 
This approach starts from the idea that it is possible to simulate the radiation 
pressure without explicit calculation of the force by treating the scattering process as a 
Langevin force. The simulation describes the scattering of single photons by individ-
ual atoms. Cooperativity is included 1. in the scattering rate, which is influenced by 
collective effects, 2. by weighing the probability for the direction \((\theta, \phi)\) into which the 
photons are scattered with the structure factor. The enhancement of the collective 
scattering rate corresponds to the rate of absorption part of the radiation pressure, 
\[^{9,10}\]
\[
\gamma_c = \frac{\gamma R}{F_{c,abs}} = \sigma_{opt}(\Delta_0) \frac{I}{\hbar \omega}, \quad \frac{4\Delta_0^2 + \Gamma^2}{4\Delta_0^2 + N^2\Gamma^2 s_N^2} N ,
\]
where \(s_N = N^{-1} + (2\sigma)^{-2}\). The structure factor is numerically calculated for a 
randomly distributed cloud.

**20.1.8.8 Ex: Super- and subradiance with two atoms**

Super- and subradiance have been observed in two ion crystals \([480, 161]\). In this 
exercise, we study this system in the framework of the coupled dipoles model.

a. Calculate the structure factor of this system.

b. Write down the equations of motion \((20.26)\) and solve them in steady-state.

**20.1.8.9 Ex: Signatures of subradiance**

Super- and subradiance are contained in the coupled dipoles model. Try to identify 
the presence of subradiant states via a reduced decay rate of \(\beta(t)\) starting from the 
timed Dicke state.

**20.1.8.10 Ex: Other applications of the coupled dipoles model**

Discuss whether the coupled dipoles model can be extended to provide a micro-
scopic description of gaseous metamaterials (negative refractive index) and the Goos-
Hänchen, Imbert-Fedorov, Spin-Hall, and Ewald-Oseen effects, and interference with 
a LO. Is it possible to check Ewald-Oseen’s theorem in media with negative refractive 
index?

**20.2 Continuous density distributions and Mie scat-
tering**

In the last sections we developed the coupled dipoles model describing light scattering 
from ensembles of individual microscopic particles by a set of equations of motion, 
in the simplest case, one for every atomic dipole. This limits the number of atoms

\[^{9}\text{Note that in reality the scattering of a photon converts the scattering atom into a coherent superposition of directions into which the atom might have scattered. This is of course not described by the simulation.}\]

\[^{10}\text{Although the atomic motion is frozen, it is not correct to say that the external degree of freedom is not involved in the collective dynamics, since the spatial atomic distribution shapes the structure factor.}\]
20.2. CONTINUOUS DENSITY DISTRIBUTIONS AND MIE SCATTERING

that can be considered in numerical simulations to a few 1000. On the other hand, most cold atom experiments nowadays are performed with $10^5$ to $10^9$ atoms. The following section are devoted to introducing concepts and approximations allowing us to understand light scattering from large atomic clouds.

The main step will consist in an approximation called smooth or continuous density approximation, where the discrete distribution of point-like scatterers is replaced by an inhomogeneous but smooth continuous density distribution characterized by a refraction index field $n_{rfr}(r)$. The interaction of this density distribution with light is then treated in the framework of Maxwell’s equations, i.e. inhomogeneities are treated as macroscopic boundary conditions to the electromagnetic fields. In the following we will term this regime as Mie scattering.

At first sight Rayleigh scattering from point-like particles and Mie scattering from extended objects are quite different phenomena. Rayleigh scattering exhibits resonances due to the internal structure of the particles, e.g. an atom. Mie scattering shows resonances induced by the boundary conditions the scattering objects impose to the field. On the other hand, from a microscopic viewpoint, any extended object (e.g. a dielectric sphere) is nothing but an assembly of microscopic scattering particles. The question we need to study is then whether a description of the diffraction from this object as the sum of the radiation patterns scattered from the individual constituent particles is correct; or in how far the graininess of the cloud’s density distribution and cooperative effects arising from the interaction between the individual particles play a role [97].

Interesting phenomena are expected in the transition regime between the limits of a dense bunch of individual scatterers and macroscopic dielectric objects. One of them is a strong modification of the radiation pressure force [295], which can conveniently be studied with atomic ensembles. The reason is that, in the smooth density approximation, the cloud can be understood as a macroscopic object characterized by a refraction index, which can be tuned over huge ranges by changing the cloud’s density and volume, or by tuning the frequency of the incident light exploiting the existence of atomic resonances. We will see in the following that it is possible to study radiation pressure with cold atoms in the Rayleigh-Debye-Gans limit of small phase-shifts, as well as in the Mie limit of large phase shifts [292]. Despite the absence of sharp boundaries for the atomic cloud, we predict the occurrence of Mie resonances, which could be detected experimentally [296].

20.2.1 Continuous density approximation

In light scattering experiments, disorder (or granularity) plays a role when the number of atoms projected onto a cross section perpendicular to the incident beam is small enough so that a light mode focused down to the diffraction limit (that is $\sim \lambda^2$) would be able to resolve and count the atoms. In other words, the stochastic fluctuations induced by the random positions of the atoms can be neglected when the total number of atoms $N$ is larger than the number of modes $\sim \sigma^2$ that fit into the cloud’s cross section, i.e. when the optical density is $b_0 = 3N/\sigma^2 \gg 1$. Under this hypothesis, the differential equation (20.26) for $\tilde{\beta}_j$ can be simplified by replacing the discrete sum
over atom positions by an integral over a density distribution \( \rho(r) \),

\[
\sum_{j=1}^{N} \rightarrow \int \rho(r') d^3r' \quad \text{and} \quad \tilde{\beta}_j(t) \rightarrow \tilde{\beta}(r', t).
\]

(20.96)

For example, the smoothed structure factor reads,

\[
S(k) = \frac{1}{N} \sum_{j=1}^{N} e^{i(k-k_0)r_j} = \frac{1}{N} \int d^3r' \rho(r') e^{i(k-k_0)r'}.
\]

(20.97)

In the Exc. 20.2.5.1 we calculate the structure factors for a homogeneous spherical cloud of radius \( R \) and for a Gaussian ellipsoidal cloud with the \textit{rms}-width \( \sigma_{\rho,z} \):

\[
S_{\text{homog.sphere}}(k) = \frac{3}{q^3R^3} (\sin qR - qR \cos qR)
\]

(20.98)

\[
S_{\text{gauss.ellipse}}(k) = e^{-\frac{1}{2}k^2\sigma^2_{\rho} \sin^2 \theta - \frac{1}{2} \sigma^2_{z}(k \cos \theta - k_0)^2}.
\]

The simulated structure factor (red curve in Figs. 20.10) agrees well with the analytical expression (green curve). Since small clouds have a larger fluctuations, the fact that the total force is a sum of intensities rather than amplitudes leads to a finite value at large scattering angles \( \theta \).

![Figure 20.10](code)

(a) The red curve shows a calculation of the structure factor: \( |S(k = k_0, \theta, \phi = 0)|^2 \) for 200 atoms randomly distributed in a homogeneous spherical cloud of size \( R = 10/k_0 \). The blue curve shows an average over 500 realizations of such a cloud according to \( \sum_{m=1}^{200} |S(k, \theta, \phi = 0)|^2 \). The black curve is an analytical calculation according to Eq. (20.98) [589].

(b) Same curves as in (a) but with a stretched y-axis.

In the continuous limit defined by (20.96) for the equations of motion (20.32) \(^{11}\),

\[
\dot{\tilde{\beta}}(r, t) = i \left( \Delta_0 + i \frac{\Gamma}{2} \right) \tilde{\beta}(r, t) - \frac{i}{2} \Omega_0 - \frac{\Gamma}{2} \int d^3r' \rho(r') \frac{\sin(k_0|\mathbf{r} - \mathbf{r}'|)}{k_0|\mathbf{r} - \mathbf{r}'|} \tilde{\beta}(r', t) e^{-ik_0 \cdot (\mathbf{r} - \mathbf{r}')}. \]

(20.99)

Transforming back to \( \beta_j \equiv \tilde{\beta} e^{ik_0 \cdot r} \), we obtain the fundamental equation for the dipolar excitation field,

\[
\dot{\beta}(r, t) = i \left( \Delta_0 + i \frac{\Gamma}{2} \right) \beta(r, t) - \frac{i\Omega_0}{2} e^{ik_0 \cdot r} - \frac{\Gamma}{2} \int d^3r' \rho(r') \frac{\sin(k_0|\mathbf{r} - \mathbf{r}'|)}{k_0|\mathbf{r} - \mathbf{r}'|} \beta(r', t).
\]

(20.100)

\(^{11}\)Note that the 'timed Dicke' assumption (20.64) has not been used here.
Example 73 (Connection between coupled dipoles model and Helmholtz equation): The steady-state solution of (20.100) can also be obtained from the Helmholtz equation of Maxwell’s theory [291, 292, 296], as shown in 12,

\[
[\nabla^2 + k_0^2 n_r^2(r)]\beta(r) = 0 \quad \text{defining} \quad n_r^2(r) = 1 - \frac{4\pi \rho(r)}{k_0^2(2\Delta_0/\Gamma + i)}.
\]

(20.101)

20.2.2 Simulations of the time evolution

We start from the second equation (20.18),

\[
\dot{\beta}_j(t) = \iota \Delta_0 \beta_j(t) - \frac{\Omega^2_0}{4} \sum_{m=1}^{N} \int_{0}^{t} \beta_m(t')dt' - \sum_{k} g_k^2 \sum_{m=1}^{N} e^{i(k-k_0)(r_j-r_m)} \int_{0}^{t} e^{-i(\omega_k-\omega_0)(t-t')} \beta_m(t')dt'.
\]

(20.102)

Substituting the timed Dicke state (20.64),

\[
\dot{\beta}(t) = \frac{1}{N} \sum_{j=1}^{N} \dot{\beta}(t) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} \dot{\beta}_j(t)
\]

(20.103)

\[
\dot{\beta}(t) = \iota \Delta_0 \beta(t) - \frac{N\Omega^2_0}{4} \int_{0}^{t} \beta(t')dt' - \frac{V_{ph}}{(2\pi)^3} \int d^3k \; g_k^2 N^2|S(k)|^2 \int_{0}^{t} e^{-i(\omega_k-\omega_0)(t-t')} \beta_m(t')dt',
\]

where we used \(\sum_{m=1}^{N} e^{i(k-k_0)(r_j-r_m)} = N^2|S(k)|^2\) from Eq. (20.67). Finally, at resonance and low saturation we may neglect the first two terms,

\[
\dot{\beta}(t) = -N \frac{V_{ph}}{(2\pi)^3} \int_{0}^{t} dt' \; \beta(t') \int_{0}^{\infty} \frac{dk}{2\pi} e^{i(\nu_k-\omega)(t-t')} |S(k,\theta)|^2 2\pi k^2 \sin \theta d\theta dk
\]

(20.104)

\[
= -N \frac{V_{ph}}{(2\pi)^3} g_k^2 \int_{0}^{t} dt' \beta(t') \int_{0}^{\infty} \frac{dk}{2\pi} e^{i(\nu_k-\omega)(t-t')} I(k) dk = -\Omega_N^2 \int_{0}^{t} dt' \beta(t') G(t-t'),
\]

with the collective Rabi frequency \(\Omega_N = \sqrt{N} g_k\) and the surface integrated structure factor,

\[
I(k) = \int_{0}^{2\pi} \int_{0}^{\pi} |S(k,\theta,\phi)|^2 \sin \theta d\theta d\phi,
\]

(20.105)

and

\[
G(\tau) = V_{ph} \frac{(2\pi)^3}{e^{-i\omega\tau} \int_{0}^{\infty} e^{i\nu_k \tau} I(k) dk},
\]

(20.106)

\(^{12}\text{See script on Electrodynamics (2020)Sec. 21.3.2.}\)
with $\omega = ck_0$ and $\nu_k = ck$. The integral $I(k)$ has been solved by Nicola for an ellipsoidal Gaussian density distribution. It is quite close to,

$$I(k) \simeq I(k_0) \simeq \sqrt{\frac{\pi}{2}} \frac{1}{k \sigma_z} e^{F^2/2} \left[ 1 - \text{erf} \left( \frac{F}{\sqrt{2}} \right) \right],$$

(20.107)

with the Fresnel number $F = k \sigma_r^2 / \sigma_z$.

![Figure 20.11](code) Averaging of the structure factor over the whole k-space.

### 20.2.2.1 Analytical method

To evaluate the above integro-differential equation, we use the rule for differentiating integrals with variable boundaries,

$$\frac{\partial}{\partial t} \int_{\phi(t)}^{\psi(t)} f(x,t)dx = \int_{\phi(t)}^{\psi(t)} \frac{\partial f(x,t)}{\partial t} dx + f(\psi(t),t)\psi'(t) - f(\phi(t),t)\phi'(t),$$

(20.108)

it is easy to show,

$$\frac{\partial}{\partial t} \int_{0}^{t} f(t')G(t-t')dt' = f(t)G(0) + \int_{0}^{t} f(t')\dot{G}(t-t')dt'$$

(20.109)

and to thusly evaluate the integral until $\frac{\partial^n}{\partial \tau^n} G(t-t')$ gets smooth enough to be neglected.

### 20.2.2.2 Numerical method

We can directly solve the integro-differential equation numerically using,

$$G(\tau) = \left[ 1 + \frac{3c}{4R^3} - \frac{c^3}{16R^3 \tau^3} \right] \Theta(3R - c\tau),$$

(20.110)

for a homogeneous spherical cloud and,

$$G(\tau) = \frac{k \sigma_r^2}{k \sigma_z^2 + ic\tau} e^{-(c\tau/\sigma_z)^2/2},$$

(20.111)

for an ellipsoidal Gaussian cloud. The iteration is done via,

$$\beta(t + dt) = \beta(t) - dt \int_{0}^{d} \beta(t')G(t-t')dt'.$$

(20.112)
The discretization is done via,

\[ t_{m+1} = t_m + dt \]  \hspace{1cm} (20.113)

\[ \beta_{m+1} = \beta_m - dt \sum_{m'} N g_k^2 \beta_{m'} G(t_m - t_{m'}) dt . \]

Figure 20.12: (code) Calculation of the time evolution of $\beta$ for a homogeneous spherical cloud. The parameters are $\lambda \simeq 780 \text{ nm}$ and $c/\Omega \simeq 30 \text{ cm}$ with $\Omega = \sqrt{N} g_k$ for typically $g_k \simeq 1 \text{ MHz}$ and $N \simeq 10^6$.

With the solution of the integro-differential equation $\beta(t)$, we can calculate the probability that atoms are excited \[ P(t) = |\beta(t)|^2 = \sum_j |\beta_j(t)|^2 = \int d^3 r |\beta(t,r)|^2 . \] (20.114)

**Example 74 (Solutions for a homogeneous spherical cloud):** For a homogeneous spherical cloud, we find three regimes characterized by the size of the cloud compared to the two length scales $\lambda$ and $c/\Omega$:

\[
\beta(t) = \beta(0) \begin{cases} 
e^{-NTt} & \text{for } R < \lambda \ll c/\Omega \\
e^{-2NTt/8(k_0 R)^2} & \text{for } \lambda < R \ll c/\Omega \ \\
\cos \Omega t e^{-3ct/8R} & \text{for } \lambda \ll c/\Omega < R
\end{cases}
\]

20.2.2.3 Complete numerical simulation

In order to be independent from initial conditions, we generate a random distribution $r_{j'}$ and solve the differential equation,

\[
\dot{\beta}_j(t) = -N g_k^2 \int_0^t dt' \frac{V_{ph}}{(2\pi)^3} \int d^3 k \frac{1}{N} \sum_{j'=1}^N \beta_{j'}(t') e^{i(\nu_k - \omega)(t-t') + ik(r_j - r_{j'})} .
\]  \hspace{1cm} (20.115)

\[ \overline{13} \text{Compare to Jaynes-Cummings model in a CQED environment: A single photon is coherently exchanged between the cavity and the atomic excitation, we get Rabi oscillations. Here, the atomic cloud is the cavity. We know that the Mollow triplet in the dressed states picture gives rise to an oscillating decay curve resembling that of Fig. 20.12. Does this curve also have an interpretation in terms of collective dressed states?} \]
We propagate the amplitudes in time via,

\[ \beta_j(t + dt) = \beta_j(t) - dt g_k^2 \left( \frac{V_{ph}}{(2\pi)^3} \int_0^t dt' \sum_{j' = 1}^N \beta_{j'}(t') \int_0^{\infty} k^2 e^{i(ck - \omega)(t - t')} I_{jj'}(k) dk \right), \]

(20.116)

where \( I_{jj'}(k) \equiv \frac{\pi}{V_{ph}} \int_0^{2\pi} e^{ik \left[ (x_j - x_{j'}) \sin \theta \cos \phi + (y_j - y_{j'}) \sin \theta \sin \phi + (z_j - z_{j'}) \cos \theta \right]} \sin \theta d\theta d\phi \), and discretize via,

\[ t_{m+1} = t_m + dt \]

(20.117)

\[ \beta_j(t_{m+1}) = \beta_j(t_m) - dt g_k^2 \sum_{m' = 1}^m \sum_{j' = 1}^N \beta_{j'}(t_{m'}) G_{jj'}(t_m - t_{m'}) , \]

with \( G_{jj'}(t_m - t_{m'}) = \frac{V_{ph}}{(2\pi)^3} \int_0^{\infty} k^2 e^{i(ck - \omega)(t_m - t_{m'})} I_{jj'}(k) dk \).

### 20.2.3 Radiation pressure force in macro- and microscopic scattering

As mentioned at the beginning of this section, scattering of light by an extended object such as an atomic ensemble or a dielectric sphere is fundamentally different from scattering at a point-like scatterer such as a single atom. On one hand, the finite size of the object leads to Mie scattering. On the other hand, the spatial distribution of the scatterers rules the degree of cooperativity. Homogeneous and periodic distributions tend to scatter cooperatively, whereas disorder suppresses cooperativity. In an atomic cloud, the amount of disorder can be tuned via the optical density seen by the incident light, and its role can be studied via the radiation pressure exerted by the light on the atomic cloud. We present an analytic expression for the radiation pressure valid for any numbers of atoms and arbitrary density distributions, which interpolates between the regimes of dominating disorder and dominating cooperativity. Furthermore, we present first experimental signatures of radiation pressure reduction due to cooperative scattering.

The radiation pressure exerted by a plane wave laser beam with frequency \( \omega_0 \) and wave vector \( k_0 = k_0 \hat{e}_z \) on a single two-level atom with resonance frequency \( \omega_a = \omega_0 - \Delta_0 \) is correctly described by the standard formula (20.80). Generalization to scattering by atomic ensembles and extended objects is only possible, if a number of effects is explicitly taken into account. The most important ones are named in the following.

a. **Cooperativity** and b. **disorder**: Cooperativity is the tendency of atoms located in the same area of space, forming regular structures or being forced by the mode structure of the environment (e.g. optical cavities) to scatter light synchronously into the same direction, as in the case of Dicke superradiance. While homogeneously or periodically distributed atoms concentrate the scattered light in specific solid angles by forward or Bragg scattering, randomly distributed atoms do not cooperate and scatter light isotropically. In this respect, cooperativity and disorder are antagonists. c. **Mie scattering and refraction**: The finite volume and the shape of the cloud represent an inhomogeneity at which light is scattered in a global way. As long as the optical density is low, the pump mode depletion is mainly due to the fact, that the atomic cloud distorts the phase front of the incident light. For high optical density, scattering
is predominantly absorptive. d. **Multiple scattering** and e. **resonance fluorescence**: Near resonance, multiple scattering leads to radiation trapping. Even off-resonance, inelastic scattering pumps resonant photons into the atomic cloud, which have a high probability to be reabsorbed. Taking account of all these effects, the real radiation pressure can differ by orders of magnitude from the naive prediction of the above formula.

For smooth density distributions $F_c$ is only limited by Mie scattering at the inhomogeneity represented by the *finite extend* of the atomic cloud [295]. The radiation pressure depends on the number of atoms $N$ in the volume, and the scaling $F_c(N)$ depends on the pump laser detuning and the radial cross section of the cloud. But small scale inhomogeneity *within the cloud*, i.e. disorder, can play an eminent role for collective scattering. This is the case, when the number of atoms is beyond a critical value, which mainly depends on the volume and shape of the cloud. In the following we will derive an analytic expression for the radiation pressure as a function of atom number, which interpolates between the regimes of dominating disorder (single-atom Rayleigh scattering) and dominating cooperativity (pure Mie scattering).

On the other hand, we point out, that we do not consider multiple scattering in our treatment. This is a good assumption far from resonance, where the scattering is predominantly Rayleigh scattering and inelastic scattering can safely be disregarded. In contrast, our extensions of single to multi-atom scattering are not valid near resonance.

The radiation pressure provides sensitive signatures for the impact of cooperativity and disorder. We describe an experiment measuring the displacement of cold atoms confined in a far-off resonance dipole trap and interpret our observations in terms of collective scattering.

### 20.2.3.1 Radiation pressure for timed Dicke states

As a first approach we will calculate the radiation pressure for a timed Dicke state from Eq. (20.89) by explicit analytical integration of the surface-integrated structure factors $s_\infty$ and $f_\infty$ in the smooth density limit (20.96) for an ellipsoidal Gaussian smooth density distribution, as shown in Exc. 20.2.5.2. In the spherical case, $\rho(\mathbf{r}) = \rho_0 e^{-r^2/2\bar{r}^2}$ with $\rho_0 = \frac{N}{(2\pi)^{3/2}\bar{r}^{3/2}}$, (20.118) and introducing $\sigma \equiv k\bar{r}$, we get,

$$s_\infty = \frac{1 - e^{-4\sigma^2}}{4\sigma^2} \xRightarrow{\sigma \gg 1} \frac{1}{4\sigma^2} \quad (20.119)$$

$$f_\infty = \frac{1}{4\sigma^2} \left[ 1 - \frac{1}{2\sigma^2} + \left( 1 + \frac{1}{2\sigma^2} \right) e^{-4\sigma^2} \right] \xRightarrow{\sigma \gg 1} s_\infty - 2s_\infty^2.$$  

Hence,

$$\frac{F_{za} + F_{ze}}{F_{z1}} = \frac{(2\Delta_0/\Gamma)^2 + 1}{(2\Delta_0/\Gamma)^2 + N^2 s_\infty^2} N(s_\infty - f_\infty).$$  

(20.120)

Note that the radiation pressure calculated from Eq. (20.120) also holds for elongated ellipsoidal Gaussian clouds characterized by an aspect ratio $\eta > 1$, even though the expressions for the surface-integrated structure factors become more complicated.
It is revealing to compare the smooth density expressions (20.120) with numerical simulations based on randomly generated atomic distributions from which the structure factor is directly from the sum (20.68). Interestingly, we find in certain parameter regimes (in particular at low atom numbers) considerable deviations between $s_N, f_N$ and $s_\infty, f_\infty$ and consequently between the numerical simulations and the analytic calculations of the radiation pressure. We attribute these deviations to disorder in the atomic cloud, which is not seen in the smooth density limit, but naturally incorporated in the numerical approach.

By comparison to numerical simulations [black solid lines and blue circles in Figs. 20.13(a)] we found that the surface-integrated structure factors in the presence of disorder are well described by [56],

$$s_N = \frac{1}{N} + s_\infty \quad \text{and} \quad f_N = f_\infty. \quad (20.121)$$

### 20.2.3.2 Cooperativity versus disorder

We expect disorder to play a dominant role, when the coarse graininess, which is related to the average distance between two atoms, $|r_i - r_j|$, can be resolved by the incident light. For the absorption process, this means that disorder gets important, when the number of spatial modes supported by the pump laser in a radial cross section of the atomic cloud,

$$N_{ca} = s_\infty^{-1} \simeq 4\sigma^2, \quad (20.122)$$

(for voluminous clouds) surpasses the number of atoms, $N < N_{ca}$. This is just the case, when the mean resonant optical density (for a ray passing through the center of the cloud $x = y = 0$) is larger than 1,

$$b_0 = \int_{-\infty}^{\infty} dz \rho(z)\sigma_{opt} = \frac{3N}{\sigma^2} = \frac{12N}{N_{ca}} > 1, \quad (20.123)$$

where $\sigma_{opt} = \frac{3\lambda^2}{2\pi}$ is the resonant optical cross section and $\rho(r)$ the spherical Gaussian density distribution (20.118). For the scattering process, the number of modes available for the reemitted light also counts. Hence, the critical number of atoms that can be resolved by light scattering is larger than $N_{ca}$:

$$N_{ce} = (s_\infty - f_\infty)^{-1} \simeq \frac{1}{2}(2\sigma)^4 = \frac{1}{2}N_{ca} \cdot \sigma^2. \quad (20.124)$$

In order to simplify the discussion, we neglect saturation, $\Omega_0 \to 0$. Using $\Delta_0 \gg \Gamma$ and defining a third characteristic atom number,

$$N_{cr} = \frac{2\Delta_0}{\Gamma s_\infty}, \quad (20.125)$$

Eq. (20.120) can be written,

$$\frac{F_c}{F_1} \simeq \frac{1 + N/N_{ce}}{1 + (N/N_{cr})^2}. \quad (20.126)$$

In the limit of very large detunings, $\Delta_0/\Gamma \gg \sigma^2 \gg 1$, the three introduced characteristic atom numbers introduced in Eqs. (20.122), (20.124) and (20.125) satisfy
20.2. CONTINUOUS DENSITY DISTRIBUTIONS AND MIE SCATTERING

Figure 20.13: (code) (a) Numerical evaluation of $s_N$ (blue circles) and $f_N$ (blue crosses) [97]. Analytical calculation of $s_N$ (black solid line) according to Eq. (20.121). Smooth density limit of $s_\infty$ (red solid line) and $f_\infty$ (green crosses). The cloud is assumed spherical, $\eta = 1$, and Gaussian with size $\sigma = 5$. (b) Numerical evaluation (blue circles) of the corresponding force ratio as a function of atom number $N$ for $\Delta_0 = (2\pi)2$ GHz and small collective saturation, $\sqrt{N\Omega_0} \ll \Delta_0$. Analytical calculation in the smooth density limit (green solid line) and according to Eq. (20.126) (black solid line). The magenta line traces the radiation pressure force resulting from pump photon absorption only.

$N_{ca} < N_{ce} < N_{cr}$, and we obtain the $N$-dependence of the radiation pressure depicted in Fig. 20.13.

In the regime $N < N_{ca}$, radiation pressure is dominated by the absorption process, $s_N \gg f_N$, because the emission is isotropic. The absorption radiation pressure exerted on a hypothetical smooth density distribution occupying the same volume as the atomic cloud [green line in Fig. 20.13] is dramatically reduced with respect to the single-atom radiation pressure (cyan dash-dotted line). However, disorder suppresses cooperativity and increases the radiation pressure up to the single-atom value. The novelty as compared to Ref. [543] is the fact that cooperativity and disorder not only influence the collective emission of a photon by an atomic cloud, but also the collective absorption of a photon from a pump laser beam.

Neglecting the photon reemission at higher atom numbers would result in an increase of radiation pressure in the regime $N_{ca} < N < N_{ce}$ (magenta line). However, in this regime, the emission process becomes increasingly important, $s_N \simeq f_N$, because the emission changes its radiation pattern from isotropic to forward scattering. Consequently, the radiation pressure is reduced with respect to its purely absorptive component. This regime is still ruled by disorder, so that the critical atom number for the impact of disorder on the absorption process, $N_{ca}$, has no impact. It does not even show up in the formula (20.126).

In the regime $N_{ce} < N < N_{cr}$, disorder steps back and cooperativity wins, so that the radiation pressure approaches the smooth density limit. Since in this regime, the smooth density radiation pressure depends on atom number like $\propto N$, as already shown in Ref. [295], we observe an increase of the radiation pressure beyond the single-atom value. This is only possible, because the collective enhancement of absorption (magenta line) rises as fast with $N$, as the collective enhancement of emission.

For even higher atom numbers, $N_{cr} < N$, the radiation pressure dramatically alters its $N$-dependency from $\propto N$ to $\propto N^{-1}$. This change of behavior is not caused by the interplay of cooperativity and disorder, but can be understood within the
framework of Mie scattering, as discussed in the next section.

**20.2.3.3 Rayleigh-Debye-Gans versus Mie scattering**

Radiation pressure is observed in many experiments, as it is the basis for optical cooling techniques (like magneto-optical traps) and limits the efficiency of resonant absorption imaging of cold atoms, because their acceleration leads to considerable Doppler-shifts. However, as stated before, the impact of disorder on radiation pressure can only be seen for large optical densities, \( b \gg 1 \), which may partially explain, why this effect has not been observed until two experiments explicitly searched for it \([56, 47]\) (see Fig. 20.14).

![Figure 20.14](image-url)  
Figure 20.14: (code) (a) Double-logarithmic plot of the measured (symbols) and calculated (lines) \( N \) dependence of the radiation pressure force. The red symbols and lines correspond to the detuning \( \Delta_0 = (2\pi)0.5 \text{ GHz} \) and the intensity \( I_0 = 95 \text{ mW/cm}^2 \). For the blue symbols and lines, \( \Delta_0 = (2\pi)4 \text{ GHz} \) and \( I_0 = 730 \text{ mW/cm}^2 \). The red (bottom) and blue (top) solid lines show calculations based on the full expression (20.120) without adjustable parameters. The red (bottom) and blue (top) dotted lines represent just the fraction of expression (20.120). The dash-dotted lines representing just the parentheses coincide for both values of \( \Delta_0 \) \([47]\).  

Depending on the parameter regime chosen, the measurements exhibited in Fig. 20.14 present data for reduced or enhanced radiation pressure for larger \( N \). As explained above, the reduction is understood as microscopic Rayleigh scattering at disordered atoms together with superradiant acceleration of the decay, while the enhancement is observed when the bulk cloud becomes so small and dense that it turns into an inhomogeneous dielectric sphere refracting and lensing incident light by macroscopic Mie scattering.

The question then remains why the radiation pressure, with increasing \( N \), after an initial rise the drops again. To answer this question we must have a look at the phase shift induced in the pump light by the cloud’s refraction index.. From calculations done in Secs. 1.2.7 and 24.6.1 we know that (below saturation) the optical density \( b \) and the phase shift \( \varphi \) are linked to the refraction index \( n_{rfr} \) and the optical scattering
cross section \( \sigma_{\text{opt}} \) via,

\[
\frac{ib}{2} + \varphi = \frac{\omega}{c} \int_{-\infty}^{\infty} [n_{rfr}(r) - 1] dz = \left( i - \frac{2\Delta_0}{\Gamma} \right) \sigma_{\text{opt}}(\Delta_0) \int_{-\infty}^{\infty} \rho(r) dz \tag{20.127}
\]

where \( \sigma_{\text{opt}}(\Delta_0) = \frac{2\pi}{k^2} \frac{\Gamma^2}{4\Delta_0^2 + \Gamma^2} \) and \( n_{rfr}(r) - 1 = -\frac{4\pi\rho(r)}{k^3(2\Delta_0/\Gamma + i)} \),

such that,

\[
\frac{b}{\sigma_{\text{opt}}(\Delta_0)} = -\sigma_{\text{opt}}(\Delta_0) \int_{-\infty}^{\infty} \rho(r) dz = b_0 \frac{\Gamma^2}{4\Delta_0^2 + \Gamma^2} \quad \text{and} \quad \varphi = \frac{2\Delta_0}{\Gamma} b \tag{20.128}
\]

Estimating coarsely \( k \int_{-\infty}^{\infty} [n_{rfr}(r) - 1] dz \simeq \sigma[n_{rfr}(r) - 1] \), where \( \sigma \equiv k\bar{r} \), we may simplify,

\[
\frac{ib}{2} + \varphi = \sigma[n_{rfr}(r) - 1] \tag{20.129}
\]

At high atom numbers (i.e. in the smooth density limit), the dependency of the radiation pressure on atom number (20.126) exhibits a maximum at \( N_{cr} \). For an atomic cloud with density \( n \) and the resonant optical density \( b_0 \), the characteristic atom number can be expressed in terms of the phase shift \( \varphi \) experienced by the pump laser beam on its path across the cloud. Absorption losses for the pump beam (e.g. resonance fluorescence, whose differential cross section contributes \( \sigma_{\text{opt}} \) to the total scattering cross section [382]) is completely negligible at large detunings. Only elastic Rayleigh scattering occurs, which in the smooth density limit of Mie scattering becomes pure diffraction (real part of the refraction index). We can than understand the atomic cloud as a non-absorbing dielectric sphere with a Gaussian index of refraction.

Rewriting Eq. (20.126) in terms of the refraction index,

\[
\frac{F_c}{F_1} \simeq \frac{N}{1 + (2\varphi)^2} \frac{2}{(2\sigma)^2} \tag{20.130}
\]

we see that, as long as \( \varphi < \frac{1}{2} \), the force increases linearly like \( \propto N \). The proportionality comes from the perfect (in the sense of not spoiled by disorder) cooperative enhancement of the scattering rate in the smooth density limit. The enhancement is only limited by the finite size \( \sigma \) of the cloud, which is accounted for in the second fraction. This regime, characterized by \( 14 \),

\[
\sigma[n_{rfr}(r) - 1] \ll 1 \tag{20.131}
\]

is termed the Rayleigh-Debye-Gans regime.

For larger phase shifts, \( \varphi > \frac{1}{2} \), refraction more and more distorts the wavefront of the pump beam, which spoils the pump mode depletion and hence reduces radiation pressure. Consequently, the radiation pressure decreases again like \( N^{-1} \). This is the Mie regime of scattering. The maximum is thus a pure diffraction effect, a so-called Mie resonance. It corresponds to the \( n_{rfr} \), where the Rayleigh-Debye-Gans scattering

\[^{14}\text{Note the necessity of another condition } [n_{rfr}(r) - 1] \ll 1 \text{ termed Born approximation, which demands that the incident wave be not appreciably reflected.}\]
approximation loses its validity according to (20.131). In Excs. 20.2.5.3 and 20.2.5.4 we study Mie and Rayleigh-Debye-Gans scattering, and in 20.2.5.5 we discuss the question is whether recoil is imparted to individual atoms or to the center-of-mass of the whole cloud.

In the limit of the approximations made, our formula correctly describes the radiation pressure force on extended objects. These objects can either be ensembles of scatterers like homogeneous, ordered or disordered atomic clouds of arbitrary shapes and volumes, or macroscopic objects like dielectric spheres. The formula thus represents a bridge between microscopic Rayleigh scattering and macroscopic Mie scattering. At very low atom numbers, the atomic cloud basically represents a randomly distributed bunch of scatterers, whose intrinsic disorder spoils cooperativity. The radiation pressure is then well described by the single-atom value. At large atom numbers, the atomic cloud forms a smooth density distribution characterized by an almost perfect a cooperativity, which is only limited by Mie scattering.

20.2.3.4 Light scattering in the continuous density approximation

The scalar electric field scattered by an arbitrary distribution of atoms has been calculated in (20.49). In the continuous density approximation (20.96), we get,

\[
\vec{E}_{\text{sc}}(\mathbf{r}) = -\frac{i\hbar \Gamma}{2d} \sum_{j=1}^{N} \frac{e^{ik_0|\mathbf{r}-\mathbf{r}_j|}}{ik_0|\mathbf{r}-\mathbf{r}_j|} \beta_j(\infty) \rightarrow -\frac{i\hbar \Gamma}{2d} \int d^3r' \rho(r') \frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{ik_0|\mathbf{r}-\mathbf{r}'|} \beta(r', \infty) .
\]

(20.132)

In particular, for a timed Dicke state,

\[
\vec{E}_{\text{sc}}(\mathbf{r}) = -\frac{i\hbar \Gamma \sqrt{N\Omega_0}}{2d(2\Delta_0 + i\Gamma Ns_N)} \sum_{j=1}^{N} \frac{e^{ik_0|\mathbf{r}-\mathbf{r}_j|}}{ik_0|\mathbf{r}-\mathbf{r}_j|} \rightarrow -\frac{i\hbar \Gamma \sqrt{N\Omega_0}}{2d(2\Delta_0 + i\Gamma (1 + Ns_\infty))} \int d^3r' \rho(r') \frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{ik_0|\mathbf{r}-\mathbf{r}'|} .
\]

(20.133)

20.2.4 Spherical harmonics expansion and generalized timed Dicke state

The results derived in (20.120) assumed the cloud to be in a timed Dicke state. As we have seen in Exc. 20.1.8.5, timed Dicke states do not account for pump laser phase shifts induced by the cloud’s refraction index. The timed Dicke states might work well for homogeneous cylinders, but not for ellipsoidal clouds, which we assume in our analytical treatments. Therefore, a better approach consists in expanding the cloud into spherical harmonics. Under the assumption that the cloud is radially symmetric, \(\rho(\mathbf{r}) = \rho(r)\), we get [291],

\[
\beta(r, \theta, t) = \sum_{n=0}^{\infty} \sqrt{\frac{2n+1}{4\pi}} \alpha_n(t) j_n(k_0r) P_n(\cos \theta) e^{-ik_0r \cos \theta} ,
\]

(20.134)

where the coefficients \(\alpha_n\) are the solutions of,

\[
\dot{\alpha}_n = \left[ i\Delta_0 - \frac{\Gamma}{2}(1 + \lambda_n) \right] [\alpha_n - \alpha_n(\infty)] ,
\]

(20.135)
In steady state,
\[ \alpha_n(\infty) = \frac{2n\sqrt{\pi(2n+1)\Omega_0}}{2\Delta_0 + i\Gamma(1 + \lambda_n)} , \]  
(20.136)

where,
\[ \lambda_n \equiv 4\pi \int_0^\infty \rho(r) j_n^2(k_0r) \]  
(20.137)
is the decay rate of eigenmode \( n \).

Inserting this into the steady-state solution (20.100) and integrating over the volume,
\[ \langle \beta_\infty \rangle \equiv \frac{2\pi}{N} \int_0^{2\pi} d\theta \sin \theta \int_0^\infty dr^2 \rho(r) \beta(r, \theta) = \frac{\Omega_0}{N} \sum_{n=0}^{\infty} \frac{(2n+1)\lambda_n}{2\Delta_0 + i\Gamma(1 + \lambda_n)} \]  
(20.138)

\[ \langle |\beta_\infty|^2 \rangle \equiv \frac{2\pi}{N} \int_0^{2\pi} d\theta \sin \theta \int_0^\infty dr^2 \rho(r) |\beta(r, \theta)|^2 = \frac{\Omega_0^2}{N} \sum_{n=0}^{\infty} \frac{(2n+1)\lambda_n}{4\Delta_0^2 + \Gamma^2(1 + \lambda_n)^2} . \]

**Example 75 (Spherical harmonics expansion for a Gaussian density distribution):** The density distribution determines the coefficients \( \lambda_n \). For a Gaussian distribution \( n(r) = N/[(2\pi)^{3/2}\sigma^3]e^{-r^2/2\sigma^2R} \) using the sine kernel,
\[ \lambda_n = N \sqrt{\frac{\pi}{2}} e^{-\sigma^2/2} I_{n+1/2}(\sigma^2) . \]

For a homogeneous sphere, \( n(r) = n_0 \), of radius \( \sigma = k_0R \), using the sine kernel ([588], Eq. (18)),
\[ \lambda_n = \frac{3N}{2} [j_n^2(\sigma) - j_{n-1}(\sigma)j_{n+1}(\sigma)] . \]

### 20.2.4.1 Expansion of the radiation pressure forces

This allows us to calculate the forces,
\[ F_a = -\hbar k_0 \Omega_0 \Gamma \text{Im} \langle \beta_\infty \rangle \]  
(20.139)
\[ F_e = -\hbar k_0 \Omega_0^2 \sum_{n=0}^{\infty} \frac{2(n+1)\lambda_n \lambda_{n+1}[4\Delta_0^2 + \Gamma^2(1 + \lambda_n)(1 + \lambda_{n+1})]}{[4\Delta_0^2 + \Gamma^2(1 + \lambda_n)(1 + \lambda_{n+1})]^2 + 4\Delta_0^2 \Gamma^2(\lambda_{n+1} - \lambda_n)^2} . \]

As seen in Fig. 20.15, the results obtained via the complete analytical formula (20.139) coincide with the fully numerical simulations according to formula (20.63). But both disagree with analytical and numerical results obtained within the timed Dicke state approximation.

It is possible to approximate the Bessel function \( I_{n+1/2}(\sigma^2) \) and to obtain analyt-
Figure 20.15: (a) Absorption, (b) emission, and (c) total force for a Gaussian cloud with the following parameters: $\sigma = 2$, $\Delta_0 = 10\Gamma$, $\Omega_0 = 0.001\Gamma$, and $\eta = 1$. The magenta dots show a fully numerical calculation for a randomly generated cloud according to formula (20.63). The red lines show a calculation according to the complete formula (20.139). The cyan dots show a calculation assuming timed Dicke states according to (20.82) via numerical calculation of the structure factor according to (20.83) for the same randomly generated cloud as for the full simulation. The blue lines are obtained within the timed Dicke state approximation with structure factors estimated from formula (20.120). (d-f) Same as (a-c) but with $\sigma = 0.2$.

The new formula works for $\sigma \gg 1$ and $\eta = 1$ [291],

\[
F_a = \frac{\Omega_0^2 \sigma^2}{\Gamma N} \ln \left( 1 + \frac{N^2 \Gamma^2 s_N}{\sigma^2 (4\Delta_0^2 + \Gamma^2)} \right) = \frac{\Omega_0^2}{4N\Gamma s_\infty} \ln \left( 1 + \frac{4N^2 \Gamma^2 s_\infty s_N}{4\Delta_0^2 + \Gamma^2} \right) \tag{20.140}
\]

\[
F_e = -F_a + \frac{\Omega_0^2 \sigma^2}{\Delta_0 N} \arctan \frac{\Delta \Gamma N}{\sigma^2 (4\Delta_0^2 + \Gamma^2 + \frac{\Gamma^2 N^2}{2\sigma^2})} = \frac{\Omega_0^2}{4N\Delta_0 s_\infty} \arctan \frac{4\Delta_0 \Gamma N s_\infty}{4\Delta_0^2 + \Gamma^2 + 2\Gamma^2 N s_\infty}
\]

\[
b_0 = \frac{3N}{\sigma^2}
\]

\[
s_N = \frac{1}{N} + s_\infty = \frac{1}{N} + \frac{1}{(2\sigma)^2}.
\]

### 20.2.4.2 Expansion of the scattered radiation intensity

The incident electric field is ...
The radiated electric field $\hat{E}^{(+)}(r,t)|\psi\rangle$ where $\hat{E}^{(+)}(r,t) = \sum_k \varepsilon_k \hat{a}_k e^{i\varepsilon_k r - i\omega_k t}$,

$$\hat{E}^{(+)}(r,t)|\psi\rangle = \sum_k \varepsilon_k \gamma_k(t) e^{i\varepsilon_k r - i\omega_k t}|0\rangle|1\rangle_k$$

(20.141)

$$\hat{E}^{(+)}(r,t)|\psi\rangle = -\frac{V_{ph}g_0\varepsilon_k 0}{4\pi\sqrt{N}} e^{-i\omega_0 t} \sum_{j=1}^N (e^{ik_0 r - i\omega_0 t} e^{-ik_0 |r - r_j|} - e^{-ik_0 |r - r_j|}).$$

We neglect the second term, which describes an incoming wave and go to smooth densities. We expand into spherical harmonics and obtain,

$$\hat{E}^{(+)}(r,t)|\psi\rangle = e^{-i\omega_0 t} \sum_{n=0}^{\infty} \frac{V_{ph}g_0\varepsilon_k 0}{c\sqrt{N}} \frac{\lambda_n}{2\Delta_0 + i\Gamma(1 + \lambda_n)} \Omega_0(2n+1) e^{i\varepsilon_n h^{(1)}_n(k_0r)} P_n(\cos \theta).$$

(20.142)

### 20.2.4.3 Mie resonances

It is an interesting question whether the maxima found in the curves of Fig. 20.15 can be associated with Mie resonances [68, 565, 49]. To show this we need to apply the formalism of Mie scattering to atomic clouds with the smooth density approximation, where it is described by a continuous refraction index, as studied in Ref. [292]. The Mie formalism had been developed for homogeneous spheres, which can be dielectric or absorptive. For more general refractive index distribution the formalism gets quickly cumbersome. Also Mie resonances are generally though of being conditioned to the existence of sharp boundaries.

The results of Ref. [292] surprisingly show that Mie resonances are expected for parabolic distributions of atoms, as is the case for example for Bose-Einstein condensates in the Thomas-Fermi limit. However, the spectra of Mie resonances exhibit much less structure. This is understood by the fact that ‘whispering galerly’ Mie resonances may live on the surface of a sphere whose refraction index drops quadratically to zero, while cavity type Mie resonances may not.

### 20.2.5 Exercises

#### 20.2.5.1 Ex: Structure factor of a homogeneous spherical and of a Gaussian ellipsoidal cloud

a. Calculate the structure factor of a homogeneous spherical cloud of radius $R$, and discuss the limits $qR < 1$ and $qR < 1$. Plot the structure factor as a function of $\theta$ for various radii $R$.

b. Calculate the structure factor of an ellipsoidal Gaussian cloud having the $rms$-widths $\sigma_z$ and $\sigma_r$, and discuss the limits $qR < 1$ and $qR < 1$. Plot the structure factor as a function of $\theta$ for various aspect ratios $\sigma_z/\sigma_r$.

---

15There is a treatment for parabolic radial variations [335].
20.2.5.2 Ex: Force coefficients of a homogeneous spherical and of a Gaussian ellipsoidal cloud

a. Calculate the force coefficients $s_N$, $\tilde{f}_N$, and $f_N$ from the Eqs. (20.66), Eqs. (20.78), and Eqs. (20.86), respectively, for a homogeneous spherical cloud of radius $R$.

b. Repeat the calculation of (a) for an ellipsoidal Gaussian cloud having the rms-widths $\sigma_z$ and $\sigma_r$.

20.2.5.3 Ex: RDG and Mie

Estimate whether it is possible to distinguish Rayleigh-Debye-Gans scattering from Mie scattering in strontium spectra.

20.2.5.4 Ex: Mie scattering from absorbing spheres

Calculate the force on a homogeneous dielectric sphere as a function of the absorptive and dispersive part of the refraction index [335].

20.2.5.5 Ex: Momentum halos and heating, is the recoil cooperative?

Discuss the question is whether recoil is imparted to individual atoms or to the center-of-mass of the whole cloud.

20.3 Scattering from disordered and dense clouds

20.3.0.1 Vectorial light

The procedure can be generalized to the vectorial case [557, 558, 402], where we get a similar steady-state solution as in (20.37),

$$\vec{\beta}_j = (M_{jm})^{-1} \hat{\epsilon} \frac{i}{2} \Omega_0(r_m),$$

(20.143)

only that the dipole moment amplitudes and the incident light field are now considered as vectors. The expression for the matrix $M_{jm}$ is the same as in (20.36). However, the vectorial kernel must be calculated in a different way. Using the abbreviations,

$$r_{jm} = r_j - r_m, \quad r_{jm} = |r_j - r_m| + \delta_{jm}, \quad c_{jm} = \frac{i}{k_0 r_{jm}} - \frac{1}{(k_0 r_{jm})^2},$$

(20.144)

the new vectorial kernel can be written,

$$\gamma_{jm}^{(3)} = \frac{3}{2} \gamma_{jm} \left(1 + c_{jm}\right) r_{jm}^2 \delta_{mn} - (1 + 3 c_{jm}) r_{jm} r_{jm}^\top,$$

(20.145)

The steady-state scattered light field and the total field are now,

$$\vec{E}_{scat}(r) = -\frac{i}{2} \sum_{j=1}^{N} \frac{3 \gamma_{oj}(r)}{2} \frac{(1 + c_{oj}(r)) k_0^2 |r_j - r_j|^2 \vec{\beta}_j - (1 + 3 c_{oj}(r)) (r_j - r_j) \cdot \vec{\beta}_j |r_j - r_j|^2}{|r_j - r_j|^2}.$$

(20.146)

A movie can be assisted at [watch movie].
20.3.0.2 Coherent backscattering

Shining coherent light on a homogeneous cloud, we expect no coherent scattering (exception made of multiple-atom scattering in backward direction, CBS and of fluctuations like speckle patterns). Like radiation trapping, coherent backscattering (CBS) is a manifestation of interference in multiple scattering. Just like photon echoes it is not due to interatomic correlations. While in radiation trapping this leads to an energy storage inside the atomic cloud connected to destructive interference of the radiation emitted to the cloud’s outside, when the coherent beam is reflected at a diffuse scattered, one observes speckle patterns. This holds as well for laser light reflection as for atomic wave reflections at a rough surface. See also (watch talk).

The coherent backscattering is an effect of constructive interference between two light scattering paths having the exact time-reversed single scattering sequence,

\[
I = \left| \sum_j \vec{E}_j e^{i\varphi_j} \right|^2 = \sum_j |\vec{E}_j|^2 + \sum_{j \neq k} \vec{E}_j \vec{E}_k^* e^{i(\varphi_j - \varphi_k)}. \tag{20.147}
\]

Only the second term makes speckles. However, the atomic motion smoothes out the speckle pattern in all directions. Only in the presence of correlations in the atomic positions they do not. E.g. in crystals or in the backscattering directions. Therefore, the constructive interference depends strongly on the backscattering angle \( \vartheta \). Fast atomic motion internal excitations can dynamically break the time-reversal symmetry of the scattering path, esp. when the laser is close to resonance and the phase delay per scattering process is long. Coherent backscattering is a weak form of Anderson localization (also strong localization) of light.

20.3.1 Exercises

20.3.1.1 Ex: The green flash

Discuss whether the 'green flash' at sunset could be due to superradiant extinction. It can last seconds because refraction sweeps the ray through the spectrum (see the movie Le rayon vert by Éric Rohmer).

20.3.1.2 Ex: Faraday effect with vectorial kernel in the coupled dipoles model

Try to simulate the pump laser phase shift and lensing by a small dense cloud by the coupled dipoles model for red and blue detuning. Discuss the influence of rescattering.

20.4 Scattering from periodic structures and photonic bands

Long-range spatial ordering can have a dramatic influence on the propagation of light and the cooperativity of scattering, as we have already pointed out in the introduction of the structure factor in Sec. 20.1.1. This is true for the scattering of electronic waves in crystals. But atomic gases can also be arranged in periodic luminous potentials.
generated by dipolar forces (introduced in Sec. 16.2.2) exerted by counterpropagating laser beams. Such potentials, called optical lattices, can be realized with various geometries in 1, 2 or 3 dimensions. See also (watch talk).

Periodic structures are usually probed by Bragg scattering. This procedure can be applied to atoms ordered in optical lattices \[57, 620, 560, 562\]: A test beam with wavevector \( k_{\text{brg}} \) and intensity \( I_{\text{brg}} \) is irradiated into the atomic cloud, and the power \( P_s \) of the first-order reflected beam by Bragg is detected under a solid angle \( \Omega_s \). Bragg diffraction is an interference effect of radiation patterns emitted by Rayleigh scattering from periodically aligned point-like antennas, the interference being constructive in only specified directions.

For optically dilute lattices, where multiple reflections can be neglected, the imaginary part of the atomic response is sufficient to describe Bragg reflection. For optically dense lattices, multiple reflections between consecutive atomic layers lead to interference phenomena between reflected and transmitted light fields and cause the emergence of frequency bands, inside which the propagation of light waves through the cloud is prohibited. These bands are known as forbidden photonic bands.

Photonic bands in optical lattices are interesting for several reasons:

1. They may facilitate the study of the phenomenon of Anderson localization. In fact, Anderson location of light in atomic gases requires very high densities or very large optical cross sections. Now, it is expected that, if the disorder is realized within periodic structures near the Bragg condition, the high density requirement is dramatically relaxed.

2. They modify the local density of states in a way to suppress spontaneous emission.

3. In optical lattices, unlike other systems, the scattering is very weak except when the light is tuned close to atomic resonances. Consequently, the expected forbidden bands are very narrow. This bears the advantage that we can adjust the optical density and tune the photon energy and the Bragg angle (i.e. the quasi-momentum) independently, which facilitates the mapping of the dispersion relation.

4. Crystals are always hampered by defects in the periodicity \[348\]. In latest-generation photonic crystals, the typical distance over which coherent light turns diffuse is limited to less than 20 \( \mu \)m. This limitation plays no role in optical lattices, where the delocalized photons rigorously guarantee perfect long-range order, even though the Debye-Waller factor may introduce local disorder.

Spectra of photonic bands in atomic clouds were detected experimentally \[535\] in one-dimensional structures. Most of the above mentioned effects require omnidirectional photonic bands, but this is technically very difficult, mainly because of the narrow linewidth of the atomic transitions. We will develop this point in the course of this section. We also mention the prediction of forbidden photon bands in Bose condensates \[397\].

A presentation on this subject is available here (watch talk).
20.4. SCATTERING FROM PERIODIC STRUCTURES AND PHOTONIC BANDS

20.4.1 Bragg scattering

We write the density in a periodic lattice as \[ n(r) = [n_0(r) \sum_{l,m,n} \delta(r - la - mb - nc)]s(r) \] ,

where \( s(r) \) is the density distribution in an elementary cell. We define the reciprocal lattice by,

\[ a^* \equiv \frac{b \times c}{V}, \quad b^* \equiv \frac{c \times a}{V}, \quad c^* \equiv \frac{a \times b}{V}, \quad V \equiv a(b \times c). \]

The Fourier transform of the density is,

\[ \rho(u) = \sum_{l,m,n} \rho_{hkl} \delta(u - la - mb - nc) * s(r) , \]

where the structure factor is,

\[ \rho_{hkl} = \int_0^{a,b,c} n(x,y,z) e^{2\pi i(hx/\alpha + ky/\beta + lz/\gamma)} dx dy dz = V \int_0^1 n(r) e^{2\pi i h \cdot r} dr , \]

with \( h \equiv (h,k,l) \) and \( r \equiv (x/a, y/b, z/c) \). The density is given by the inverse transformation,

\[ n(r) = V^{-1} \sum_{h,k,l} \rho_{hkl} e^{-2\pi i h \cdot r} s(r) . \]

We consider a wave being scattered from the direction \( k_0 \) towards the direction \( k_s \equiv k_0 + \Delta k \). The structure factor \( \rho \) describes the amplitude of the radiation field scattered by the lattice. If the density distribution is the same at all sites of the lattice,

\[ n(r) = n_1(r) \sum_{R} \delta^{(3)}(r - R) , \]

the structure factor becomes,

\[ \rho(\Delta k) = \sum_{m} e^{im\Delta k \cdot R} \int_V n_1(r) e^{i\Delta k \cdot r} d^3r . \]

**Example 76 (Elementary cell with gaussian distribution):** With the ansatz \( n_1(r) = n_0 e^{-r^2/\bar{r}^2} \), such that \( \int n_1(r) d^3r = n_0 (2\pi)^{3/2} \bar{r}^3 = N_1 \),

\[ \rho(\Delta k) = \sum_{m} e^{im\Delta k \cdot R} \int_V n_1(r) e^{i\Delta k \cdot r} d^3r \]

\[ = \frac{1 - e^{iN_s \Delta k \cdot R}}{1 - e^{i\Delta k \cdot R}} \times n_0 \int_V e^{-x^2/\bar{r}^2} e^{-y^2/\bar{r}^2} e^{-z^2/\bar{r}^2} e^{i\Delta k \cdot r} d^3r \]

\[ \approx N_s \delta(\Delta k - 2\pi/R)n_0 (2\pi)^{3/2} \bar{r}^3 e^{-6\Delta k^2 \bar{r}^2} = N \delta(\Delta k - 2\pi/R)e^{-6\Delta k^2 \bar{r}^2} . \]

\(^{16}\)This is similar to the square of the Bloch function defined in Sec. 6.1
20.4.1.1 Impact of disorder in one-dimensional lattices

A wave be incident on a lattice in the direction $k_0$ and scattered into the direction $k_s \equiv k_0 + \Delta k$. The structure factor $F_{hkl}$ describes the amplitude of radiation field scattered by the lattice,

$$\rho_{hkl} = \int_V \rho(r) e^{i\Delta k \cdot r} d^3 r .$$

(20.156)

Let the density distribution be,

$$n(r) = \sum_j \rho_j(r) \star \delta^{(3)}(r - r_j) = n_1(r) \star \sum_j \delta(r - j\hat{e}_z \lambda_{dip} \frac{\Delta k}{2}) ,$$

(20.157)

that is, for perfect periodicity, introducing the density distribution of a unit cell and a 1D lattice.

The Debye-Waller factor describes the diffusion of the density over the sites of the lattice due to the thermal motion,

$$\overline{\rho}_{hkl} = \int_V n_1(r) e^{i\Delta k \cdot r} d^3 r \sum_j e^{i(j\hat{e}_z \lambda_{dip} / 2 + u)\Delta k}$$

(20.158)

$$= \rho_{hkl} e^{iu\Delta k} ,$$

with

$$e^{iu\Delta k} \approx e^{-|G|^2 u^2 / 6} .$$

(20.159)

**Example 77 (Optical lattice):** The exponential distribution $e^{-6\Delta k^2 x^2}$ is called Debye-Waller factor and describes the smearing out of the population over the lattice due to the thermal motion of the atoms. The $\delta$-function sets the wavevector of emitted light. That is, the power of light is only emitted in particular directions given by the Bragg condition. Here, the solid angle $\Delta \Omega_s$ does not depend on the thermal distribution (as long as the atoms are within the Lamb-Dicke regime), but on the lattice size, which determines the goodness of the approximation of the Airy function (the sum in the above equation) by a Dirac $\delta$-function. The width of the Airy function for a lattice of size $w_0$ is approximately $\Delta k = 2\sqrt{3}/w_0$. With this the solid angle is,

$$\Delta \Omega_s = \frac{12}{k^2 w_0^2} .$$

(20.160)

We can also estimate the solid angle from the diameter $d$ of the Gaussian beam at a distance $x$ away from a scattering medium of size $w_0$,

$$d = w_0 \sqrt{1 + \left( \frac{\lambda x}{\pi w_0^2} \right)^2}$$

(20.161)

$$\Delta \Omega_s = \frac{\pi d^2}{x^2} = \frac{\lambda^2}{\pi w_0^2} = \frac{4\pi}{k^2 w_0^2} .$$

(20.161)

The power scattered into this solid angle is,

$$P_s = |A_s|^2 F^2 \Delta \Omega_s = |A_s|^2 e^{-2W} N^2 \Delta \Omega_s .$$

(20.162)
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It depends quadratically on the number of atoms. Strictly speaking, the derivation only applies to perfectly ordered lattices, i.e. all the lattice sites are equally occupied. Defects lead to diffuse scattering, i.e. a background of isotropically distributed power at the expense of Bragg scattering. The sharpness of the Bragg radiation distribution remains intact.

We parametrize the density in an optical 1D lattice as follows:

\[
\begin{align*}
    n_l(r) &= n_0 e^{(-x^2-y^2)/2\sigma_r^2} e^{-z^2/2\sigma_z^2} \\
    n_a(r) &= \sum_{m=1}^{N_s} \delta(r - mde_z) \ast n_l(r) = \sum_{m=1}^{N_s} n_l(r - mde_z).
\end{align*}
\]

We will show in Exc. 20.4.4.1, that the structure factor is then,

\[
S_{k_0}(k) = \frac{n_0}{N} e^{iNdq_z} \frac{1}{1 - e^{-iNdq_z} e^{-q_y^2\sigma_y^2/2} e^{-q_z^2\sigma_z^2/2}}.
\]

In Exc. 20.4.4.2 we derive the structure factor in spherical coordinates.

Some comments are needed:

1. The structure factor treatment assumes low optical density, which is not necessarily guaranteed when the laser is tuned close to a resonance [560].

2. As the structure factor is independent of the laser detuning, it will not reveal any spectral structure, such as a band-gap or dip due to diffuse scattering. Also, absorption is not incorporated into the model.

20.4.1.2 The structure factor and the Bragg condition

The reciprocal space, obtained by Fourier transformation of the periodic density distribution, also adopts the shape of a periodic lattice. The Bragg condition requires that the difference between the incident and emitted wavevectors, \( \Delta k \equiv k_s - k_i \), matches a vector of the reciprocal lattice, \( r_j = jG \). The Bragg condition is thus automatically incorporated into the structure factor (20.201).

\[
\begin{align*}
\text{(a)} & \quad \text{(b)} & \quad \text{(c)}
\end{align*}
\]

Figure 20.16: Several Bragg lattices.

With the lattice constant \( d = \frac{1}{2} \lambda_{\text{dip}} \) the interference is constructive when the difference of the paths of two beams reflected by different layers is a multiple of the wavelength,

\[
\frac{1}{2} \lambda_{\text{dip}} \cos \beta_i + \frac{1}{2} \lambda_{\text{dip}} \cos \beta_s = \lambda.
\]
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This is illustrated in Fig. 20.16(a). If the transverse distribution can be considered as homogeneous, as shown in Fig. 20.16(b), we have as second condition,

$$\beta_i = -\beta_s.$$  \hfill (20.166)

That is, the angles of incidence and reflection must be the same, as if we were dealing with a dielectric mirror. In contrast, if the transverse extent of the atomic layers gets smaller (until converging to the limit of a one-dimensional chain of point-scatterers, $G \equiv 2k_{dip}\hat{e}_z$), we return to the condition (20.165). In intermediate situations, illustrated in Fig. 20.16(c), and for $\lambda_{dip}\cos\beta_i \neq \lambda$ the reflection angle does not follow any of the relations (20.165) and (20.166).

20.4.1.3 Incoherent background

A finite size or defects in the periodic ordering of the atoms may lead to an isotropic background of Rayleigh-scattered light,

$$\frac{dP_s}{d\Omega_s} = |A_s|^2 \left[ e^{-2W}|F|^2 + N_1 N (1 - e^{-2W}) \right].$$  \hfill (20.167)

The amount of photons scattered into the same solid angle as the one of Bragg scattering is typically for 1D lattices,

$$\frac{(1 - e^{-2W})N_1 N}{e^{-2W}|F|^2} = (e^{2W} - 1) \frac{N_1}{N} \approx 0.002.$$  \hfill (20.168)

However, if we compare the total amount of coherently Bragg-scattered light, we obtain,

$$\frac{(1 - e^{-2W})N_1 N}{e^{-2W}|F|^2} \frac{4\pi}{d\Omega_s} \approx 2500.$$  \hfill (20.169)

20.4.2 Transfer matrices calculation 1D-lattices

For one-dimensional optical lattices, that is, when the atoms are trapped in a potential dipole generated by a stationary light wave, we may consider applying the transfer matrix formalism developed in Secs. 4.3. The premisses of this model are the homogeneity and the infinite extent of the cloud in a direction transverse to the optical axis.

We calculate the reflection coefficient $\beta$ of a classical polarizable sample as the optical density (depth) of a thin layer, $nd$, times the optical cross section $\sigma(\Delta)$,

$$\beta = nd \sigma(\Delta),$$  \hfill (20.170)

where the optical cross section can be expressed by the microscopic polarizability,

$$\sigma(\Delta) = \frac{6\pi}{k^2} \frac{-\Gamma^2}{4\Delta^2 + \Gamma^2} = \frac{6\pi}{k^2} \text{Im} \frac{-1}{2\Delta/\Gamma + i} = k \text{Im} \frac{\alpha_e}{\varepsilon_0}.$$  \hfill (20.171)
or macroscopic susceptibility \( \chi_e = \frac{n\alpha_e}{\varepsilon_0} \). With the notation introduced in Fig. 20.17 we find the equations relating the incident electric fields with the transmitted and reflected ones,

\[
E_+^+ = (1 + \imath \beta) E_0^+ + \imath \beta E_0^-, \quad (20.172)
\]

or in \( S \)-matrix notation,

\[
\begin{pmatrix} E_+^+ \\ E_0^- \end{pmatrix} = S_\beta \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix}, \quad (20.173)
\]

where

\[
S_\beta = \begin{pmatrix} \imath \beta & 1 + \imath \beta \\ 1 + \imath \beta & \imath \beta \end{pmatrix} = \begin{pmatrix} r & t \\ t & r \end{pmatrix}, \quad (20.174)
\]

and where we defined the coefficients

\[ t = 1 + \imath \beta \quad \text{and} \quad r = \imath \beta, \quad (20.175) \]

which satisfy \( |t|^2 - |r|^2 = 1 \). Recasting the problem into the \( T \)-matrix notation,

\[
\begin{pmatrix} E_+^+ \\ E_0^- \end{pmatrix} = T_\beta \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix}, \quad (20.176)
\]

where

\[
T_\beta = \frac{1}{1 + \imath \beta} \begin{pmatrix} 1 + 2 \imath \beta & \imath \beta \\ -\imath \beta & 1 \end{pmatrix} = \frac{1}{t} \begin{pmatrix} t^2 - r^2 & \imath r \\ \imath r & 1 \end{pmatrix}. \quad (20.177)
\]

We have \( \det T_\beta = 1 \). For weak reflection, \( \beta \ll 1 \),

\[
T_\beta \simeq \det \begin{pmatrix} 1 + \imath \beta & \imath \beta \\ -\imath \beta & 1 - \imath \beta \end{pmatrix}. \quad (20.178)
\]

We note that the employed model is classical, since we describe the gas by a sequence of layers, each characterized by a refractive index. Applying the transfer matrix model, we calculate how the incident and reflected light fields transform from one layer to another. The intrinsically 1D model allows to calculate the reflection, transmission, and absorption by the atomic lattice as a function of the incident laser frequency.

We still need to multiply with the transfer matrix describing the propagation of the incident beam through the layer,

\[
T_d = \begin{pmatrix} e^{\imath k d} & 0 \\ 0 & e^{-\imath k d} \end{pmatrix}, \quad (20.179)
\]

such that the transfer matrix for passing the beam through an atomic layer is,

\[
T = T_\beta T_d. \quad (20.180)
\]

\[\text{Note the difference from the calculation (21.83) made for the reflection coefficient of an atom in a cavity in Sec. 21.2.4, which gave,}\]

\[
\beta = \frac{k}{\pi w^2} \frac{\alpha_e}{\varepsilon_0} = \frac{6}{k^2 w^2} \frac{1}{2\Delta/T + i} = \frac{\sigma_0}{\pi w^2} \frac{1}{2\Delta/T + i}. \]


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For \( N_s \) layers we must obviously concatenate the matrices \( \mathcal{M}_{N_s} \). The reflection coefficient is now simply,

\[
r_{N_s} = \left( \frac{T_{N_s}}{\mathcal{M}_{N_s}} \right)_{12},
\]

and can be evaluated numerically or analytically [159]. If the incident beam hits the cloud under an angle, \( \mathbf{k} \cdot \mathbf{d} = kd \cos \theta = k_z d \), and furthermore, as shown in [160] Eq. (A10), the theory must be generalized by replacing,

\[
\beta \rightarrow \frac{\beta}{2} (\cos^{-1} \theta + \cos \theta).
\]

However, for \( \theta < 60^\circ \) the correction is small.

### 20.4.2.1 Limit of optically dilute clouds

For optically dilute clouds, \( r \ll 1 \), we expect standard Bragg scattering as described by equation (20.178),

\[
T = T_\beta T_d \simeq \begin{pmatrix} e^{i k_z d} & i \beta e^{-i k_z d} \\ -i \beta e^{i k_z d} & e^{-i k_z d} \end{pmatrix},
\]

with \( \mathbf{k} \cdot \mathbf{d} = kd \cos \theta = k_z d \). Near the Bragg angle we have \( \cos \theta \simeq \cos \theta_{brg} = \lambda_{sp} / \lambda_{dip} \) and near resonance we have \( 2\pi/k = \lambda \simeq \lambda_{sp} \), so that, with \( d = \lambda_{dip}/2 \), we obtain \( k_z d \simeq \pi \) and,

\[
T_{N_s} \simeq \begin{pmatrix} e^{i \pi} & i \beta e^{-i \pi} \\ -i \beta e^{i \pi} & e^{-i \pi} \end{pmatrix}^{N_s} = (-1)^{N_s} \begin{pmatrix} 1 & N_s i \beta \\ -N_s i \beta & 1 \end{pmatrix},
\]

which we will verify in Exc. 20.4.4.3. The total reflectivity being \( r_{N_s} \simeq N_s i \beta \), we get the reflection,

\[
|r_{N_s}|^2 \simeq \frac{N_s^2 \beta_{sp}^2 \Gamma_{sp}^2}{4 \Delta^2 + \Gamma_{sp}^2}.
\]

Thus, the profile of the reflection curve is Lorentzian.
20.4. LIMIT OF OPTICALLY DENSE CLOUDS

In order to obtain analytical expressions in the regime of dense clouds, we write the transfer matrix for a single layer, using the expressions (20.177) and (20.179), as follows [160],

\[ T = T_\beta T_d = \begin{pmatrix} (1 + i\beta)e^{ikd} & i\beta e^{-ikd} \\ -i\beta e^{ikd} & (1 - i\beta)e^{-ikd} \end{pmatrix}. \] (20.186)

Given that \( \det T = 1 \), the matrix represents a unitary transformation and the eigenvalues can be cast into the form \( e^{±i\phi} \). Letting,

\[ \cos \Theta \equiv \frac{1}{2} \text{Tr} \ T = \cos kzd - \beta \sin kzd, \] (20.187)

we can write the matrix,

\[ T = I \cos \Theta + iA \sin \Theta = e^{i\Theta A} \] (20.188)

with

\[ A = \frac{1}{\sin \Theta} \begin{pmatrix} \beta \cos kzd + \sin kzd & \beta e^{-ikzd} \\ -\beta e^{ikzd} & -\beta \cos kzd - \sin kzd \end{pmatrix}. \] (20.189)

The eigenvectors of \( T \), and therefore of each power of \( T \), are Bloch states of the periodic lattice. We verify in Exc. 20.4.4.4, that the following relationships are satisfied,

\[ \text{Tr} A = 0, \quad A^2 = 1, \quad \det A = 1. \] (20.190)

The eigenvalues of \( A \sin \Theta \) are \( \lambda_A ± 1 \). The eigenvalues of the transfer matrix are,

\[ \lambda = \cos kzd - \beta \sin kzd ± i\sqrt{1 - (\cos kzd - \beta \sin kzd)^2} = \cos \Theta ± i \sin \Theta \] (20.191)

\[ = e^{±i \arccos(\cos kzd - \beta \sin kzd)} = e^{±i\theta}. \]

This decomposition allows us to calculate the transfer matrix for a succession of \( \mu \) layers. We get,

\[ T_\mu = e^{i\mu\theta A} = I \cos(\mu \theta) + iA \sin(\mu \theta) \] (20.192)

\[ = I \cos \left( \mu \arccos(\cos kzd - \beta \sin kzd) \right) + iA \sin \left( \mu \arccos(\cos kzd - \beta \sin kzd) \right), \]

which gives us the reflection coefficient,

\[ r_\mu = \frac{(T_\mu)_{12}}{(T_\mu)_{22}} = \frac{i\sin(\mu \theta) T_{12}}{\cos(\mu \theta) + i\sin(\mu \theta) T_{22}} \] (20.193)

\[ = \frac{i\beta}{\sin \theta \cot(\mu \theta) - i \sin kzd - i \beta \cos kzd}. \]

This is the final result. Near the Bragg angle, \( \cos \theta \sim 1 \), we have,

\[ r_{N_s} = \frac{i\beta}{\sin \theta \cot(N_s \theta) - i \beta} \approx \frac{iN_s \zeta}{1 - iN_s \beta} \] (20.194)

\[ |r_{N_s}|^2 \approx \frac{N_s^2 \beta_{sp}^2 \Gamma_{sp}^2}{4\Delta^2 + (1 + n_s \beta_{sp}^2) \Gamma_{sp}^2}. \]

The intensity reflection profile, therefore, is a Lorentzian also in the limit of thick clouds. The additional condition for the occurrence of prohibited photonic bands is a large number of atomic layers, \( N_s \gg 1 \). We note that the model is an extension of the Kronig-Penney model introduced in Sec. 6.2.
20.4.2.3 Application of transfer matrices to real 1D optical lattices

The analytical treatment shown in the previous sections does not take account of possible lattice imperfections, since the atomic layers are assumed to be identical, infinitely thin, immobile and located at fixed periodic distances. Realistic optical lattices are different for several reasons:

1. Atomic clouds are not perfectly localized in ultra-thin layers, but distributed in a Gaussian way as a function of the cloud’s temperature. The Debye-Waller factor (20.158) describes the impact of this distribution on the Bragg model.

2. The atoms are in thermal motion causing an inhomogeneous Doppler shift and are affected by the photonic recoil received in each scattering process. This causes a broadening of the reflection profiles and decreases the interference capability.

3. The number of atoms per layer may vary. Also, the global extent of the cloud is not infinite, that is, we have $N_s$ layers filled with atoms with a gradual decrease at the confines of the cloud.

4. The atoms trapped in the optical potential are subjected to a dynamic Stark shift \(^{18}\) causing an inhomogeneous broadening of the atomic transition as well.

5. The periodicity of the lattice is slightly modified because the refractive index experienced by the laser beams creating the dipole potential locally depends on the atomic density concentrated in the lattice’s anti-nodes. The consequence is a local decrease of the lattice constant $d$ \(^{19}\).

All of the aforementioned imperfections may be included in a numerical treatment of the transfer matrices. For this we subdivide the atomic cloud into sufficiently thin sublayers, as shown in Fig. 20.17. Each sublayer, being characterized by its own 2D atomic density and its own shift from resonance, is described by an individual transfer matrix. The matrices are concatenated, and the reflection profile is computed, as shown in the expression (20.181) \(^{561}\). Fig. 20.18 shows a numerical calculation of a photonic band in a rubidium optical lattice. The experimental variables are the incidence angle $\theta$ of the probe laser and its tuning $\Delta$ from a transition $\lambda_{sp}$. $\Delta$ determines $\sigma$ and $\beta$ via the polarizability (20.170) \(^{20}\) and thus governs the propagation of light inside the layers. $\theta$ determines $k_z d$ and thus probes the periodicity between the layers.

Depending on the atomic density we can identify different behaviors \(^{21}\):
1. At the limit of thin lattices, we do not expect multiple scattering. The absorptive (imaginary) part of polarizability dominates, $\beta \approx \Im \beta$. Thus, the reflection coefficient is almost real, $re^{i\phi} \approx |r|$, the phase shifts are negligible, the profile of the reflection spectrum is symmetric. In this scheme, the interference of the radiation patterns of individual atoms is destructive in all directions, except under the Bragg angle. There are losses caused by scattering in non-paraxial modes. They are also due to elastic Rayleigh scattering but, because of the finite Debye-Waller factor, the radiation becomes diffuse and incoherent.

2. At the limit of thick lattices, we have multiple scattering. The (real) dispersive part of the polarizability is $\beta \approx \Re \beta$. Thus, absorption is suppressed, we observe large phase shifts and the reflection spectrum profile is asymmetric. Multiple beam interference gives rise to global scattering.

Physically, the set parameters consistent of the quasi-momentum and the energy of the Bloch wave, $(\Theta, \Delta)$, is more relevant because it allows analyzing the dispersion relation. We observe the existence of energies $\Delta$, where the real part of the quasi-momentum vanishes (modulo $\pi$). The 3D representation in Fig. 20.18(e) illustrates the occurrence of an avoided crossing due to the band gap at the edge of the Brillouin zone.

![Figure 20.18: Numerical calculation of a photonic band in a 1D optical lattice (wavelength $\Lambda_{dip} = 797$ nm) far-tuned from the rubidium D1 transition ($\lambda_{D1} = 795$ nm). The probe laser exciting the Bragg resonance is tuned close to the rubidium resonance at $\lambda_{sp} = 422$ nm. We assume atomic densities of $n = 4 \times 10^{11}$ cm$^{-3}$ and $N_s = 40000$ atomic layers. (a) Real and imaginary parts of the reflection index ($\alpha$ polarizability) as a function of detuning $\Delta$. (b,c) Real and imaginary parts of the quasi-momentum ($x$-axis) as a function of the detuning $\Delta$. (d,e) 2D and 3D representation of the reflection coefficient.

In fact, Bragg resonances can be understood in reciprocal space as reflections at the edges of the Brillouin zone. Through the angle of incidence of the injected light

\[22\text{We note, that } \Theta \text{ via the relation } (20.187) \text{ of the angle of incidence } \theta, \text{ but only weakly of the energy } \Delta.\]
beam, we adjust the quasi-momentum. The frequency of the light beam determines the energy. The forbidden photonic bands are caused by the formation of an energetic gap in the dispersion relation induced by the interaction of the atoms with the optical lattice.

### 20.4.2.4 Intensity distribution and LDOS within a lattice

The density matrix formalism (20.177) not only allows to calculate the overall reflectivity of the 1D optical lattice, but also the local intensity \( I \propto |E_a^+ + E_a^-|^2 \) at a point \( z = a \) inside the lattice[561].

To calculate this intensity we assume that the network is located between the points \( z = 0 \) and \( z = b \) of the optical axis with \( 0 < a < b \). The transfer through the entire structure is given by,

\[
\begin{pmatrix}
E_b^+ \\
E_b^-
\end{pmatrix} = \mathcal{T} \begin{pmatrix}
E_0^+ \\
E_0^-
\end{pmatrix}.
\]  

(20.195)

We use the boundary condition that, \( E_0^+ \) being preset, there is no reflection of light behind the last layer, i.e., \( E_b^- = 0 \). We obtain,

\[
E_0^- = -\frac{T_{21}}{T_{22}} E_0^+ \quad \text{and} \quad E_b^+ = \left( T_{11} - \frac{T_{12} T_{21}}{T_{22}} \right) E_0^+.
\]  

(20.196)

Now we separate the entire structure into two parts \( \mathcal{T} = \mathcal{T}^{(b)} \mathcal{T}^{(a)} \), such that the field between the two parts is,

\[
\begin{pmatrix}
E_1^+ \\
E_1^-
\end{pmatrix} = \mathcal{T}^{(a)} \begin{pmatrix}
1 \\
-T_{21}/T_{22}
\end{pmatrix} E_0^+.
\]  

(20.197)

The sum gives,

\[
E_1^+ + E_1^- = \left( T_{11}^{(a)} + T_{21}^{(a)} - \frac{T_{21}}{T_{22}} (T_{12}^{(a)} + T_{22}^{(a)}) \right) E_0^+.
\]  

(20.198)

Figure 20.19: (code) The intensity decreases exponentially over a infinite lattice. For a finite lattice (here \( N_s = 3000 \)), the intensity approaches a constant value at the end of the lattice. The graph shows in blue the intensity along the lattice, in red the exponential decay due to absorption in a homogeneous cloud (Lambert-Beer law), in green the hyperbolic decay following Ohm’s law and in cyan the transmission assuming a lattice of \( N \) layers.
20.4. SCATTERING FROM PERIODIC STRUCTURES AND PHOTONIC BANDS

The local density of states (LDOS) in a photonic band can be evaluated from [602, 218],

\[ N(\omega) = 2\omega \sum_k \delta(\omega^2 - \omega_k^2) \]  \hspace{1cm} (20.199)

William found out:

\[ k_{eff} = \frac{d\phi}{dz} \]  \hspace{1cm} (20.200)

with \( \phi = \arctan(\text{Im} E / \text{Re} E) \). The \( E \)-field between two layers can be calculated using transfer matrices. The density of the states is given as the derivative of the inverse function of the dispersion relation:

\[ N(\omega) = \frac{dk_{eff}(\omega)}{d\omega} \]  \hspace{1cm} (20.201)

20.4.2.5 Suppression of spontaneous emission in forbidden photonic bands

The decrease in the LDOS is equivalent to the suppression of spontaneous emission, that is, an excited atom located inside the lattice will not be able to emit its photon. This is the condition for a forbidden photonic band to be omnidimensional. Omnidirectional bands need three-dimensional lattices. Nevertheless, the reduction of the spontaneous emission rate has already been observed in [265, 637], which can be interpreted as 1D photonic crystals.

20.4.2.6 Impurities

The formula (20.198) allows the calculation of the impact of localized defects in numerical simulations. For example, it is instructive to look at the intensity profile along the structure in the presence of a localized lattice defect. In Fig. 20.20(c) we observe an intensity peak located at the 100-th atomic layer, exactly where the defect was introduced. This peak corresponds to a localized evanescent wave. Photons can not propagate freely through the lattice: they prefer to tunnel between lattice defects the rather than propagate by radiation.

The curves (a-b) of Fig. 20.20 illustrate how an empty photonic band fills up with localized states with well-defined energies when noise is added to the periodicity of the lattice. This situation is similar to that in semi-conductors doped by donor and acceptor states.

20.4.3 Photonic bands in the Bloch and the coupled dipoles models

The transfer matrix model is limited in several respects:

1. Firstly, being intrinsically 1D, the model does not apply to 2D or 3D lattices.

2. Also, it does not incorporate the possibility of transverse disorder or effects linked to the finite transverse extension of the atomic layers, for example, the limitation of the number of layers participating in multiple reflection ('walk-off') [562] or the impact of an imperfect mode matching [560].

23For the same reason, resonant dipole-dipole interactions are suppressed [364].
20.4.3.1 The Bloch model and forbidden electronic bands

The **Bloch model** is another model to describe 3D periodic systems [17]. It was introduced in Chp. 6.1.6 for 1D optical lattices. Its disadvantages are that it supposes infinite lattices and the absence of defects.

The Bloch model is commonly used to describe the scattering of electron waves in a solid, where the band gap originates from the Coulomb interaction of the electron with the atoms of the solid crystal. In contrast, in photonic crystals, the modes with high (low) frequency $\omega$ concentrate their energy in spatial regions with low (high) dielectric index $\epsilon$. Close to geometric (Mie) resonances this causes a repulsion in the density distribution of photonic states, and the opening of a gap separating high frequency bands (air bands) from low frequency bands.

In optical lattices the photons interact with the atomic resonances. Photons and electrons are distinguished by their different dispersion relations and by the fact that electronic waves are scalar and photonic waves are vectorial. The electrons of a crystal are bound to an energy surface and follow the lines of the dispersion relation without leaving the metal. In contrast, photons are usually injected into the structure, which gives an additional degree of freedom. Therefore, any point in the phase diagram can be reached and the dispersion relation only informs, where at which point the transmission is stronger.
20.4. SCATTERING FROM PERIODIC STRUCTURES AND PHOTONIC BANDS

<table>
<thead>
<tr>
<th>lattice structure</th>
<th>photonic crystal</th>
<th>metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>particles</td>
<td>atoms in a stationary wave</td>
<td>atoms in a crystal</td>
</tr>
<tr>
<td>equations of motion</td>
<td>photons</td>
<td>electrons in a metal</td>
</tr>
<tr>
<td>dispersion relation</td>
<td>Maxwell</td>
<td>Schrödinger</td>
</tr>
<tr>
<td>tune</td>
<td>$\hbar k/c$</td>
<td>$\hbar k^2/2m$</td>
</tr>
<tr>
<td>band gap origin</td>
<td>Bragg angle and frequency</td>
<td>voltage</td>
</tr>
<tr>
<td>band gap width</td>
<td>$\text{Im } \alpha$ absorption by atoms $&lt; \omega_0 - \omega_{\text{dip}}$</td>
<td>e$^-$ interacting with the atomic nuclei</td>
</tr>
</tbody>
</table>

Figure 20.21: Attempt of an artistic illustration of the isoenergetic surfaces for electrons in a metal (left), photons in a 3D optical lattice (center), and photons in a 1D optical lattice (right). The interaction of atoms with the lattice is much weaker than the interaction of electrons with the metal, except close to resonances. Therefore, photonic bands are much narrower than electronic bands.

20.4.4 Exercises

20.4.4.1 Ex: Factor structure of a 1D lattice
Calculate the structure factor of the density distribution (20.163) and the square $|S_{k_0}(k)|^2$.

20.4.4.2 Ex: Structure factor in spherical coordinates
Write the structure factor (20.163) in spherical coordinates.

20.4.4.3 Ex: Reflection in the dilute cloud limit
Verify the calculation (20.184).

20.4.4.4 Ex: Reflection in the dense cloud limit
Verify the representation (20.188).

20.4.4.5 Ex: Photonic band spectra
Plot the 1D-photonic band gap spectrum in a standing wave as a function of $\Delta_{pr}$ and $n$.

20.4.4.6 Ex: Intensity drop inside photonic bands
Plot the intensity of the probe on its passage through the 1D optical lattice.
20.4.4.7 **Ex: Intensity drop inside photonic bands in the presence of disorder**

Simulate the intensity of the probe on its passage through the 1D optical lattice in the presence of disorder.

20.4.4.8 **Ex: Photonic bands with sidebands**

Plot the intensity of the probe on its passage through the 1D optical lattice as a function of detuning in the presence of modulation sidebands.

20.4.4.9 **Ex: Photonic bands versus absorption**

Compare the signatures of band gaps with absorption.

20.4.4.10 **Ex: Structure of a diamond lattice**

A geometric configuration of point-like scatterers that can exhibit a broad omnidirectional photonic bandgap is the one of a diamond lattice [112, 527, 17]. In this exercise we will study such a diamond-shaped lattice.

a. Produce a geometric representation of the primitive cell and a Wigner-Seitz cell.

b. Study the optical lattice generated by the following configuration of incident lasers,

\[ k_0 = \frac{\pi}{a} (0, -2, -1), \quad k_1 = \frac{\pi}{a} (2, 0, 1), \quad k_2 = \frac{\pi}{a} (0, 2, -1), \quad k_3 = \frac{\pi}{a} (-2, 0, 1) \]

with \( k_{\text{laser}} = \omega_{\text{laser}}/c = \sqrt{5}\pi/a \).

c. Calculate the forbidden band according to [112, 527, 17].
Chapter 21

Coupling of atoms and optical cavities and the CQED regime

So far we have considered the coherent dynamics between atoms and radiation fields and extended the theory to take into account the dissipative coupling to the electromagnetic vacuum by spontaneous emission and atomic motion. The vacuum represents a homogeneous and isotropic reservoir characterized by a continuous white energy spectrum. The situation changes completely when we place the atom in an optical cavity which breaks the translational and rotational symmetries and imprints a resonance structure into the density of photonic states. Obviously, the cavity will profoundly change the atomic coupling to the electromagnetic vacuum, and hence the way in which the atom reacts to incident light, as much with respect to scattering as with respect to optical forces. The description of the impact of optical cavities on the interaction dynamics between atoms and light fields is the subject of the following chapters.

To identify the problem, we start constructing the Hamiltonian and decide which degrees of freedom should be treated as being quantized. Here, we only consider individual atoms (no collisions and no properties requiring symmetrization of their wavefunctions). The atoms can be free or trapped in external potentials, and they interact with quantized radiation fields. Both the atomic excitation and the radiation fields may decay.
21.1 Light fields in cavities without atoms

21.1.1 Quantum Langevin equation

21.1.1.1 Input-output theory for cavities

The coupling of a cavity mode $\hat{a}$ to the continuum of a heat bath $\hat{b}(\omega)$ is described by the Hamiltonian,

$$
\hat{H} = \hat{H}_{cav} + \hat{H}_{bth} + \hat{H}_{int}
$$

$$
\hat{H}_{cav} = \hbar \omega_0 \hat{a}^\dagger \hat{a}
$$

$$
\hat{H}_{bth} = \hbar \int_{-\infty}^{\infty} d\omega \hat{b}(\omega) \hat{b}(\omega)
$$

$$
\hat{H}_{int} = i\hbar \int_{-\infty}^{\infty} d\omega \kappa(\omega) [\hat{b}(\omega) \hat{a}^\dagger - \hat{a} \hat{b}(\omega)]
$$

with $[\hat{b}(\omega), \hat{b}(\omega')] = \delta(\omega - \omega')$. Note that the Hamiltonian of the system may have a more general form. According to the input-output theory [215, 119] we can derive the Langevin equation for an arbitrary system operator $\hat{\sigma}$,

$$
\dot{\hat{\sigma}} = -\frac{i}{\hbar} [\hat{\sigma}, \hat{H}_{cav}] - [\hat{\sigma}, \hat{a}] \left( \frac{\kappa}{2} \hat{a} + \sqrt{\kappa} \hat{b}_{in}(t) \right) + \left( \frac{\kappa}{2} \hat{a}^\dagger + \sqrt{\kappa} \hat{b}_{in}^\dagger(t) \right) [\hat{\sigma}, \hat{a}]
$$

$$
\dot{\hat{\sigma}} = -\frac{i}{\hbar} [\hat{\sigma}, \hat{H}_{cav}] - [\hat{\sigma}, \hat{a}^\dagger] \left( -\frac{\kappa}{2} \hat{a} + \sqrt{\kappa} \hat{b}_{out}(t) \right) + \left( -\frac{\kappa}{2} \hat{a}^\dagger + \sqrt{\kappa} \hat{b}_{out}^\dagger(t) \right) [\hat{\sigma}, \hat{a}].
$$

For example, we are interested in the dynamics of $\hat{\sigma} = \hat{a}$,

$$
\dot{\hat{a}} = (-i\omega_0 - \frac{\kappa}{2}) \hat{a} - \sqrt{\kappa} \hat{b}_{in}(t)
$$

$$
\dot{\hat{a}} = (-i\omega_0 + \frac{\kappa}{2}) \hat{a} - \sqrt{\kappa} \hat{b}_{out}(t).
$$

The above equations are not stochastic, since no assumption was made about the heat bath’s density operator. To derive from the Langevin equation a master equation, we assume a quantum Wiener process and trace the total density operator $\rho = \rho_{cav} \otimes \rho_{bth}$ over the bath’s degrees of freedom.
21.1. Light Fields in Cavities Without Atoms

21.1.1.2 Master Equation

We can fill the cavity with energy by pumping it with an external light field matched to the cavity mode,

\[ \hat{H}_{\text{int}} = i\hbar (\beta^* \hat{a} - \beta \hat{a}^\dagger) . \] (21.4)

Note that the propagator \( e^{-i\hat{H}_{\text{int}}/\hbar} \) corresponds to a coherent state displacement operator. The inevitable coupling of the cavity to the environment, \( \hat{H}_{\text{cavity-vacuum}} \), leads to irreversible losses. These losses can be described as spontaneous emission to the continuous vacuum. The irreversibility of the process is readily understood in terms of the phase space offered by the vacuum being much larger. In fact, whenever discrete states are coupled to a continuum, the equilibrium is very much on the side of the continuum, that is, discrete states decay. Since an optical cavity can be considered a temperature reservoir \( T \), where \( \bar{n} = \left(1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right)^{-1} \), the Lindbladt operator is,

\[ \mathcal{L}_{\text{cav}} \rho = \frac{\kappa}{2} (\bar{n} + 1)(2\hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} - \rho) + \frac{\kappa}{2} \bar{n}(2\hat{a}^\dagger \hat{a} - \hat{a}^\dagger \hat{a}^\dagger - \rho) \] (21.5)

We have already shown this in Exc. 17.2.5.1. The constants are the cavity decay rate \( \kappa \) and the pump rate \( \beta \). Note that at room temperature in the microwave regime, \( \bar{n} \) may be as large as a few hundred photons, whereas in the optical regime we may neglect the thermal excitation.

\[ \dot{\rho} = -i[\hat{H}, \rho] + \mathcal{L}_{\text{cav}} \rho , \] (21.6)

The expectation values are given by a quantum Langevin equation \[119\],

\[ \dot{\alpha} = \langle \dot{\hat{a}} \rangle = i[\{[\hat{H}, \hat{a}]\} - \kappa \langle \hat{a} \rangle] = (-\kappa - i\Delta) \alpha + \eta , \] (21.7)

The solution is easy to derive,

\[ \alpha(t) = \left( \alpha(0) - \frac{\eta}{\kappa + i\Delta} \right) e^{(-\kappa - i\Delta) t} + \frac{\eta}{\kappa + i\Delta} \] (21.8)

or, using the electric field normalized to the amplitude of the field generated by a single photon, \( E_{\text{cav}}^+ = E_1 \alpha \),

\[ E_{\text{cav}}(z, t) = \text{Re} \left[ E_1 e^{i(kz - \omega t)} \alpha(t) + E_1 e^{i(-kz - \omega t)} \alpha(t) \right] = 2E_1 \cos kz \text{ Re} \left[ e^{-i\omega t} \alpha(t) \right] \] (21.9)

This result is quite interesting, because the cavity begins to oscillate at its own frequency, before the pump dominates. Letting \( \eta = 0 \), we see that the cavity field decays with the time constant \( \kappa \) from the stationary situation. \( \kappa \) also corresponds to
the HWHM of the field intensity, $|\alpha(|\Delta_c| = \kappa)|^2 = \frac{1}{2}|\alpha(0)|^2$. Note, that the intensity decays as $2\kappa$, and the HWHM of the field amplitude is $|\alpha(|\Delta_c| = \sqrt{3}\kappa)| = \frac{1}{2}|\alpha(0)|$.

Frequently, we are interested in the response of the cavity to a pump beam $E^+_{\text{in}}$. For small angles, this reduces to, 

$$\alpha = \tan \theta \approx \frac{\Delta \alpha}{\kappa} \approx \frac{\Delta \phi}{\kappa}.$$ 

To better understand the behavior of the phase as a function of the pump beams, we analyze the interference of the two modes, which is, 

$$E^+_{\text{refl}}(t+dt) = E^+_{\text{refl}}(t) + dt \left[ \left( \eta + \frac{\eta^*}{\kappa + i\Delta_c} \right) E^+_{\text{cav}}(t) + \eta E^+_{\text{in}}(t) \right]. \quad (21.11)$$

It is already clear that we should expect a ringing with a fixed frequency $\Delta_c$. We will study this phenomenon in Exc. 21.1.4.1. In Exc. 21.1.4.2 we will show, how it is possible to empty an optical cavity in times shorter than $1/\kappa$.

### 21.1.1.3 Response of a ring cavity

In case of a ring cavity, equation (21.8) should be generalized to,

$$\alpha_\pm(t) = \left( \alpha_\pm(0) - \frac{\eta_\pm}{\kappa + i\Delta_c} \right) e^{(-\kappa - i\Delta_c) t} + \frac{\eta_\pm}{\kappa + i\Delta_c}. \quad (21.12)$$

To better understand the behavior of the phase as a function of the pump beams, we analyze the interference of the two modes, which is,

$$\alpha_+\alpha^*_- = \left( \alpha_+(0)\alpha^*_-(0) - \frac{\eta_+\alpha_+(0)}{\kappa - i\Delta_c} - \frac{\eta^*_-\alpha^*_-(0)}{\kappa + i\Delta_c} + \frac{\eta_+\eta^*_-}{\kappa^2 + \Delta_c^2} \right) e^{-2\kappa t} + \frac{\eta_+\eta^*_-}{\kappa^2 + \Delta_c^2} +$$

$$+ \left( \alpha_+(0)\frac{\eta^*_-}{\kappa + i\Delta_c} - \frac{\eta_+\eta^*_-}{\kappa^2 + \Delta_c^2} \right) e^{(-\kappa - i\Delta_c) t} + \frac{\eta^*_-}{\kappa + i\Delta_c} - \frac{\eta_+\eta^*_-}{\kappa^2 + \Delta_c^2} e^{(-\kappa + i\Delta_c) t}. \quad (21.13)$$

To simplify, we assume a symmetric pump, $\eta_\pm = \eta e^{\pm i\phi}$. We are interested in the reaction of the field’s phase to a sudden change of $\phi$. Now, we define the initial stationary conditions for $\phi = 0$, to be $\alpha_\pm(0) = \frac{\eta}{\kappa + i\Delta_c}$ and obtain,

$$\alpha_+\alpha^*_- = \frac{\eta^2}{\kappa^2 + \Delta_c^2} \left[ (1 - e^{i\phi})^2 e^{-2\kappa t} + e^{2i\phi} + 2e^{i\phi}(1 - e^{i\phi}) e^{-\kappa t} \cos \Delta_c t \right], \quad (21.14)$$

or in resonance,

$$\alpha_+\alpha^*_- = \frac{\eta^2}{\kappa^2} \left[ (1 - e^{-\kappa t}) e^{i\phi} + e^{-\kappa t} \right]^2. \quad (21.15)$$

This shows that the cavity phase adjusts exponentially to the pump:

$$\tan \theta = \frac{\Im \alpha_+\alpha^*_-}{\Re \alpha_+\alpha^*_-} = \frac{(1 - e^{-\kappa t})^2 \sin 2\phi + 2(1 - e^{-\kappa t}) e^{-\kappa t} \sin \phi}{(1 - e^{-\kappa t})^2 \cos 2\phi + 2(1 - e^{-\kappa t}) e^{-\kappa t} \cos \phi + e^{-2\kappa t}}. \quad (21.16)$$

For small angles, this reduces to,

$$\theta = 2\phi(1 - e^{-\kappa t}), \quad (21.17)$$
or \( \dot{\theta} \approx \kappa (2\phi - \theta) \) or \( \ddot{\theta} \approx -\kappa \dot{\theta} \). The pump represents a friction force for the phase. We also see that the phase adjustment requires a finite time \( \kappa^{-1} \). Out of resonance,

\[
\alpha_+ \alpha_-^* = \frac{\eta^2}{\Delta_c^2} \left[ 1 + 2(\epsilon^{2i\phi} - \epsilon^{i\phi})(1 - \cos \Delta_c t) \right] + ,
\]

such that,

\[
\tan \theta = \frac{2(\sin 2\phi - \sin \phi)(1 - \cos \Delta_c t)}{1 + 2(\cos 2\phi - \cos \phi)(1 - \cos \Delta_c t)} .
\]

For very small angles \( \phi \), This simplifies to \( \theta \approx 4\phi \sin^2 \frac{1}{2} \Delta_c t \).

### 21.1.1.4 Transfer function of a ring cavity

Now we want to investigate the transfer function of a ring cavity,

\[(\partial_t + \kappa + i\Delta_c)\alpha_\pm = \eta e^{\pm i\phi_0 \sin \omega t} .\]

The solution is,

\[
\alpha_\pm(t) = e^{(-\kappa - i\Delta_c)t} \left( \alpha_\pm(0) + \eta \int_0^T e^{(\kappa + i\Delta_c)\tau} \pm i\phi_0 \sin \omega_\tau d\tau \right) .
\]

For small amplitude oscillations, we can expand the pump term,

\[
\alpha_\pm(t) = e^{(-\kappa - i\Delta_c)t} \left( \alpha_\pm(0) + \eta \int_0^T \left( e^{(\kappa + i\Delta_c)\tau} \pm \frac{\phi_0}{\kappa} e^{(\kappa + i\Delta_c)\tau + i\omega \tau} \mp \frac{\phi_0}{\kappa} e^{(\kappa + i\Delta_c)\tau - i\omega \tau} \right) d\tau \right)
\]

\[
= e^{(-\kappa - i\Delta_c)t} \alpha_\pm(0) + \frac{1 - e^{(-\kappa - i\Delta_c)t}}{\kappa + i\Delta_c} \pm \frac{\phi_0}{\kappa} e^{i\omega t} - \frac{e^{(-\kappa - i\Delta_c)t}}{\kappa + i\Delta_c + i\omega} \mp \frac{\phi_0}{\kappa} e^{-i\omega t} - \frac{e^{(-\kappa - i\Delta_c)t}}{\kappa + i\Delta_c - i\omega}
\]

\[
= \frac{\eta}{\kappa} \mp i\phi_0 \eta \frac{\kappa \sin \omega t - \omega \cos \omega t + \omega e^{-\kappa t}}{\kappa^2 + \omega^2} .
\]

In the last two steps, we defined for simplicity, \( \alpha_\pm(0) = \frac{\eta}{\kappa + i\Delta_c} \) and \( \Delta_c = 0 \). After some initial transients, when \( t \gg \kappa^{-1} \), we can write,

\[
\alpha_\pm \alpha_-^* = \frac{\eta^2}{\kappa^2} + \phi_0^2 \eta^2 \left( \frac{\kappa \sin \omega t - \omega \cos \omega t}{\kappa^2 + \omega^2} \right)^2 ,
\]

\[
\alpha_\pm \alpha_+^* = \left( \frac{\eta}{\kappa} \pm i\phi_0 \eta \frac{\kappa \sin \omega t - \omega \cos \omega t}{\kappa^2 + \omega^2} \right)^2 ,
\]

giving,

\[
\theta = \arctan \frac{2\phi_0 (\kappa^2 + \omega^2) (\kappa^2 \sin \omega t - \kappa \omega \cos \omega t)}{(\kappa^2 + \omega^2)^2 - \phi_0^2 (\kappa^2 \sin \omega t - \kappa \omega \cos \omega t)^2} \approx 2\phi_0 \frac{\kappa^2 \sin \omega t - \kappa \omega \cos \omega t}{\kappa^2 + \omega^2} .
\]

At low frequencies, \( \omega \ll \kappa \), the phase of the cavity field goes as, \( \theta(\phi_0) \approx 2\phi_0 \sin \omega t \), and for high frequencies, \( \omega \gg \kappa \), as, \( \theta(\phi_0) \approx -2\phi_0 \frac{\kappa}{\omega} \cos \omega t \). Thus, we observe a low-pass behavior of the phase excursions with a cut-off frequency, \( \kappa^{-1} \):

\[
\theta_m \approx \frac{2\phi_0}{1 + \omega/\kappa} .
\]
21.1.2 Characterization of the bare cavity

We first consider a linear cavity of length $L$ pumped by a laser without any scatterer located inside the cavity. The cavity spectrum is an equidistant comb of eigenfrequencies separated by,\[
\delta_{\text{fsr}} \equiv \tau_{\text{rt}}^{-1} = \frac{c}{2L}.
\] (21.25)

The free spectral range $\delta_{\text{fsr}}$ is given in units of a real frequency. $\tau_{\text{rt}}^{-1}$ is the time for a photon to make a round trip in the cavity. The amplitude decay rate of the cavity,\[
\kappa = \tau_{\text{rt}}^{-1} = \frac{\pi \delta_{\text{fsr}}}{F}.
\] (21.26)

The intensity decay rate of the cavity, measured by ‘cavity ring-down’ is $2\kappa$. Note, that $\kappa$ is also the FWHM width of the intensity transmission spectrum $^1$.

Example 78 (Finesse of a cavity): For example, for a cavity of length $L = 10$ cm an intensity decay time of $\tau_{\text{int}} = 20$ $\mu$s is measured, and we want to evaluate the finesse. We begin calculating the free spectral range $\delta_{\text{fsr}} = c/2L \approx 1.5$ GHz. Since the cavity field decays like $E(t) = E_0 e^{-\kappa t}$ and the intensity like $I(t) = E_0^2 e^{-2\kappa t}$, we get $\kappa = 1/\tau_{\text{int}} = 1/2\tau_{\text{int}} \approx (2\pi)$ 4 kHz. Finally, the finesse is $F = \pi \delta_{\text{fsr}}/\kappa \approx 189000$.

For a cavity with a given geometry filled with a Gaussian mode of light with power $P$, the intensity is determined by Gaussian optics $^2$,
\[
I(r) = \frac{2P}{\pi w^2(z)} e^{-2\rho^2/w^2(z)} \quad \text{and} \quad w(z) = w_0 \sqrt{1 + \left(\frac{\lambda z}{\pi w_0^2}\right)^2}.
\] (21.27)

Defining the mode volume via $I(0)V_m \equiv \int I(r)dV$ and evaluating the spatial integral over the Gaussian mode along the cavity, we obtain,
\[
V_m = \frac{\pi}{4} L w_0^2.
\] (21.28)

Defining the amplitude of the electric field generated by a single photon via,
\[
I(r) = n\varepsilon_0 c E_1^2(r),
\] (21.29)

where $n$ is the number of photons in the cavity, we calculate for the energy stored in the cavity,
\[
\int \varepsilon_0 |\vec{E}_1(r)|^2 dV = \varepsilon_0 \int \frac{I(r)}{n\varepsilon_0 c} \rho d\rho d\phi dz = \frac{1}{nc} \int \frac{2P}{\pi w^2(z)} e^{-2\rho^2/w^2(z)} \rho d\rho d\phi dz = \frac{1}{nc} \frac{P}{2L} = \frac{1}{nc} \frac{nh\omega\delta_{\text{fsr}}}{2} L = \frac{\hbar \omega}{2}.
\] (21.30)

$^1$See script on Electrodynamics (2020), Sec. 7.3.5 and Exc. 7.3.6.15.$^2$See script on Electrodynamics (2020), Sec. 7.4.1 and Exc. 7.4.3.1.
Hence,

\[
|\vec{E}_1(0)| = \sqrt{\frac{I(0)}{n\varepsilon_0 c}} = \sqrt{\frac{1}{n\varepsilon_0 c} \frac{2P}{\pi w_0^2}} = \sqrt{\frac{1}{n\varepsilon_0 c} \frac{L\hbar\omega \delta_{fsr}}{2V_m}} = \sqrt{\frac{\hbar\omega}{2\varepsilon_0 V_m}}. \tag{21.31}
\]

Resolve Exc. 21.1.4.3.

The light power can now be expressed as,

\[
P = \frac{\pi w_0^2}{2} I(0) = \frac{2V_m}{L} n\varepsilon_0 c |\vec{E}_1(0)| = 2V_m \delta_{fsr} \frac{\hbar\omega}{2\varepsilon_0 V_m} = \delta_{fsr} \hbar \omega. \tag{21.32}
\]

We assume that the cavity is pumped by a laser beam. To estimate the pump rate, we assume that the power \( P_{input} \) be measured in transmission. The coefficient \( \eta \) for resonant pumping is related to the number \( n \) of photons inside the cavity,

\[
n = |\alpha|^2 = \frac{\eta^2}{\kappa^2}. \tag{21.33}
\]

The intracavity field is resonantly amplified by the finesse,

\[
\alpha = \frac{F}{\pi} \alpha_{input} = \frac{\delta_{fsr}}{\kappa} \alpha_{input}. \tag{21.34}
\]

This gives,

\[
\eta = \kappa \alpha = \kappa \sqrt{\frac{I}{\hbar \omega V_m}} = \delta_{fsr} \alpha_{input} = \delta_{fsr} \sqrt{\frac{I_{input}}{\hbar \omega V_m}}. \tag{21.35}
\]

In practice, the pump rate will depend on the quality of the phase matching of the Gaussian beams and the impedance matching (in case of partially absorbing mirrors).

### 21.1.3 Density of states in cavities

We first calculate the density of states \( \rho(\omega, \mathbf{k}) \) of an optical cavity. It is defined by,

\[
\int_\mathcal{R} \rho(\omega, \mathbf{k}) d\omega d\Omega = \frac{1}{(2\pi)^3} \int d^3x d^3k. \tag{21.36}
\]

For free space photons we calculate,

\[
4\pi \int \rho_{free}(\omega, \mathbf{k}) d\omega = \frac{V}{(2\pi)^3} \int k^2 \sin \theta d\theta d\phi dk = \frac{V k^3}{6\pi^2} = \frac{V \omega^3}{6\pi^2 c^3}, \tag{21.37}
\]

such that,

\[
\rho_{free}(\omega, \mathbf{k}) = \frac{V \omega^2}{(2\pi c)^3}. \tag{21.38}
\]
21.1.3.1 The role of cavity geometry

For light in a cavity, the density of states is modified, because it becomes frequency-dependent and anisotropic. The frequency dependence is expressed by the Airy formula,

\[
\mathcal{L}(\omega) = \frac{\sqrt{1 + (2F/\pi)^2}}{1 + (2F/\pi)^2 \sin^2 kL},
\]

(21.39)

and the anisotropy by,

\[
\mathcal{R}(k) = 1 \quad \text{for} \quad k \in \Omega_{cav},
\]

(21.40)

where \( \Omega_{cav} \) is the solid angle covered by the cavity mode. The formula,

\[
\rho_{cav}(\omega, k) = \rho_{free}(\omega, k)[1 - \mathcal{R}(k)] + \rho_{free}(\omega, k)\mathcal{L}(\omega)\mathcal{R}(k)
\]

(21.41)

expresses that the density of states is nothing more than the structure factor of the cavity.

For a confocal cavity the solid angle is easy to calculate [265, 266],

\[
\Omega_{cav,con} = 2 \int_0^{2\pi} \int_0^{\arcsin(2b/L)} \sin \theta d\theta d\phi = 4\pi \left( 1 - \sqrt{1 - \frac{4b^2}{L^2}} \right) \approx \frac{8\pi b^2}{L^2},
\]

(21.42)

where \( b \) is the clear aperture of the cavity mirrors. But for non-degenerate geometries the functions \( \mathcal{L} \) and \( \mathcal{R} \) depend on the order \( mn \) of the transverse gaussian modes:

\[
\mathcal{L}_{mn}(\omega) = \frac{\sqrt{1 + (2F/\pi)^2}}{1 + (2F/\pi)^2 \sin^2 (kL + \varphi_{mn})}
\]

and \( \mathcal{R}_{mn}(k) = 1 \quad \text{for} \quad k \in \Omega_{mn}, \]

where \( \varphi_{mn} \) is the frequency shift of the transverse modes.

21.1.3.2 Expansion into Gaussian modes

More correctly, \( k \in \Omega_{mn} \) means that we must weigh the density of states by the structure factor of the mode volume, which is nothing more than the Fourier transform of the mode function,

\[
\int_{k \in \Omega_{mn}} \cdots d^3k \rightarrow \int_{\mathbb{R}} \mathcal{F} \left[ \frac{u_{mn}(r)}{\hbar \omega} \right] \cdots d^3k,
\]

(21.43)

where,

\[
u_{mn}(r) = \hbar \omega \frac{w_0}{w} e^{-2(x^2+y^2)/w^2} H_m(\sqrt{2}x/w)^2 H_n(\sqrt{2}y/w)^2,
\]

(21.44)

with \( w = w(z) \) is the energy density distribution. The Hermite polynomials are the eigenfunctions of the Fourier transform,

\[
\mathcal{F}[e^{-x^2/2}H_n(x)] = (-i)^n e^{-k^2/2}H_n(k).
\]

(21.45)
Hence,

\[
\mathcal{F}\left[\frac{1}{\hbar \omega} u_{mn}(r)\right] = \frac{1}{\hbar \omega} \mathcal{F} \left[ e^{-2(x^2 + y^2)/w^2} H_m(\sqrt{2}x/w)^2 H_n(\sqrt{2}y/w)^2 \right]
\]

\[
= \frac{1}{\hbar \omega} \mathcal{F} \left[ e^{-2x^2/w^2} H_m(\sqrt{2}x/w)^2 \right] \mathcal{F} \left[ e^{-2y^2/w^2} H_n(\sqrt{2}y/w)^2 \right]
\]

\[
= \frac{1}{\hbar \omega} w_0 e^{-2k_x^2w^2} H_m(\sqrt{2}k_x w)^2 e^{-2k_y^2w^2} H_n(\sqrt{2}k_y w)^2
\]

\[
m,n=0 \rightarrow \frac{1}{\hbar \omega} w_0 e^{-2(k_x^2+k_y^2)w^2}.
\]

and

\[
\mathcal{R}_{mn}(k) = \int \mathcal{F} \left[ \frac{u_{mn}(r)}{h\omega} \right] d\left(\frac{tk_x}{k}\right) d\left(\frac{k_y}{k}\right)
\]

\[
= \frac{1}{\hbar \omega} w_0 \int_{m,n=0}^{\pi} \frac{\pi}{2k^2w^2} e^{-2k_x^2w^2} H_m(\sqrt{2}k_x w)^2 d\left(\frac{k_x}{k}\right) e^{-2k_y^2w^2} H_n(\sqrt{2}k_y w)^2 d\left(\frac{k_y}{k}\right)
\]

using \(P = \int I_{mn}(r)dxdy = \frac{1}{\pi} w^2 I_0\). This coincides with the intuition, that for the TEM\(_{00}\) mode, the aperture is simply the divergence angle of the Gaussian mode.

**Example 79 (Solid angle for confocal cavities):** For confocal cavities, we must add \(\sum_{mn} \mathcal{F} \left[ \frac{1}{\hbar \omega} u_{mn}(r) \right]\) up to a limit, where the maximum \(H_m(\sqrt{2}kw)\) is cut by the finite aperture of the mirrors of the cavity. Empirically, we find that \(H_n(\xi^2) e^{-\xi^2}\) has its maximum at \(\xi_{\text{max}} = 13.7 \cdot n^{1/2}\). From the condition \(u_{mn}(x,y,L) = 0\) for \(xy > a^2\), we obtain,

\[
x_{\text{max}} y_{\text{max}} < a^2
\]

\[
\left(13.7 \cdot n^{1/2}\right)^2 = \frac{\sqrt{2}x_{\text{max}} \sqrt{2}y_{\text{max}}}{w(L)} < \frac{2a^2}{w(L)^2} \rightarrow \frac{a^2 k_w^2}{2L^2},
\]

using \(w(L) = w_0 \sqrt{1 + (\frac{\lambda \ell}{\pi w_0^2})^2} \rightarrow \frac{\lambda \ell}{\pi w_0}\). Finally,

\[
\sum_{mn} \mathcal{F} \left[ \frac{1}{\hbar \omega} u_{mn}(r) \right] = \frac{\pi}{2k^2w^2} \sum_{13.7^2 m,n < a^2 k_w^2/2L^2} = \frac{\pi}{2k^2w^2} \frac{13.7^2}{13.7^2} \frac{a^2 k_w^2}{2L^2} = \frac{1}{13.7^2} \frac{\pi a^2}{4L^2}.
\]

### 21.1.4 Exercises

#### 21.1.4.1 Ex: Quick ullage of an optical cavity

Consider a linear cavity resonantly pumped by a laser beam until a stationary state is reached. Suddenly, the phase of the incident light is changed by 180°. Based on equation (21.8), analyze the evolution of the light field inside the cavity.

#### 21.1.4.2 Ex: Ringing of an optical cavity

Consider a linear cavity with resonant frequency \(\omega_c\) and the decay rate \(\kappa\) pumped by a laser beam whose frequency is swept linearly over a range \(\omega \in [-10\kappa, 10\kappa]\). Prepare a numerical simulation varying the time \(\Delta t\) of the sweep.
21.1.4.3  **Ex: Mode volume of a cavity**

a. Calculate the volume of a linear cavity of length $L = 10$ cm and mirrors with radius of curvature $\rho = 15$ cm.
b. Calculate the amplitude of the electric field created by a single photon at the point where the intensity is maximum.

21.1.4.4  **Ex: Cooperative amplification for a rubidium gas in a cavity**

Consider an non-degenerate cavity characterized by $\delta_{fsr} = 2$ GHz, $F = 80$, and $w_0 = 6$ $\mu$m. In order to benefit from the cooperativity of the cavity, the atoms must be within a volume axially delimited by the Rayleigh length and radially by the diameter of the mode near its waist.
a. Calculate the Rayleigh length for a wavelength of 780 nm and the mode volume.
b. For a given partial pressure of rubidium at room temperature of $p \approx 10^{-5}$ Pa, calculate the average number of atoms within the mode volume.
c. Of these atoms only those with an axial Doppler shift below $k v_z < \kappa$ emit resonantly into the cavity. Calculate the number of these atoms from the Maxwell-Boltzmann distribution.
d. Calculate the cooperative amplification of the emission rate into the cavity.

21.2  **Characterization of the interaction between atoms and cavities**

In this section we will introduce some parameters characterizing the interaction between atoms and cavities. In particular, we will relate the important notions of the cooperativity of several atoms and the structure factor for light scattering, with the cavity-to-free space scattering ratio, the finesse and the density-of-states of a cavity, simply by pointing out that a cavity multiplies the number of atoms interacting with a light modes by the number of its mirror images.

We will also interpret super- and sub-radiance as a modification of the structure factor by 'spontaneous stimulation', i.e. by 'cooperativity'.

21.2.1  **One atom in a cooperative environment**

Let us consider a laser-driven atom located at position $\mathbf{r}$ described by two of its eigenstates, a ground state $|g\rangle$ with lowest energy $(E_g = -\frac{1}{2}\hbar\omega_0)$ and long lifetime and an excited state $|e\rangle$ with highest energy $(E_e = +\frac{1}{2}\hbar\omega_0)$ coupled to $|g\rangle$. In presence of an external electromagnetic field, the Hamiltonian of the two atom-field system in the electric dipole approximation is,

$$\hat{H} = \hat{H}_{at} + \hat{H}_{int} + \hat{H}_{rad}$$

where $\hat{H}_{at} = \hbar\omega_0 \hat{\sigma}^z$,

$$\hat{H}_{rad} = \int_V \frac{1}{2} [\varepsilon_0 \hat{\mathbf{E}}(\mathbf{r}) + \mu_0^{-1} \hat{\mathbf{B}}(\mathbf{r})] d^3 r$$

$$\hat{H}_{int} = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r})$$

(21.48)
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are respectively the atomic Hamiltonian expressed by the Pauli matrices defined earlier, the electromagnetic field Hamiltonian, and the atom-field interaction Hamiltonian, where the electric dipole moment operator only contains non-diagonal dipole moment matrix elements, \( \mathbf{d} \equiv \langle e | \mathbf{d} | g \rangle \).

In the Coulomb-gauge, the electric and magnetic field operators are \( \hat{E}(\mathbf{r},t) = -\partial_t \mathbf{A}(\mathbf{r},t) \) and \( \hat{B}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t) \), respectively, where the quantized transverse vector potential is,

\[
\mathbf{A}(\mathbf{r},t) = \sum_\alpha \sqrt{\frac{\hbar}{2\omega_\alpha \varepsilon_0}} [\mathbf{u}_\alpha(\mathbf{r}) \hat{a}_\alpha(t) + \mathbf{u}_\alpha^*(\mathbf{r}) \hat{a}_\alpha^\dagger(t)] .
\]

Note that on one hand, the quantum properties of the electric and magnetic field operators are determined by the bosonic annihilation and creation operators, \( \hat{a}_\alpha(t) \) and \( \hat{a}_\alpha^\dagger(t) \), respectively, with usual commutation relations: \( [\hat{a}_\alpha(t), \hat{a}_\beta(t)] = 0 \) and \( [\hat{a}_\alpha(t), \hat{a}_\beta^\dagger(t)] = \delta_{\alpha\beta} \). On the other hand, the mode functions \( \mathbf{u}_\alpha(\mathbf{r}) \) are classical vector functions satisfying the vector Helmholtz equation and the transversality condition: \( \nabla^2 + k^2_\alpha \mathbf{u}_\alpha(\mathbf{r}) = 0 \) and \( \nabla \cdot \mathbf{u}_\alpha(\mathbf{r}) = 0 \), with \( k_\alpha = \omega_\alpha / c \) [421]. These classical functions are chosen to form an orthonormal set: \( \int_V \mathbf{u}_\alpha^*(\mathbf{r}) \cdot \mathbf{u}_\beta(\mathbf{r}) d^3r = \delta_{\alpha\beta} \). In free space, one has,

\[
\mathbf{u}_{k\lambda}^{\text{free}}(\mathbf{r}) = \frac{\hat{\epsilon}_\lambda}{\sqrt{V}} e^{i \mathbf{k} \cdot \mathbf{r}} ,
\]

where \( \hat{\epsilon}_\lambda \) is a polarization vector such that \( \mathbf{k} \cdot \hat{\epsilon}_\lambda = 0 \) and \( V \) is the photon quantization volume.

For weak-coupling between the atoms and the field, one has the contributions to the Hamiltonian,

\[
\hat{H}_{at} = \hbar \omega_0 \hat{\sigma}^z,
\]

\[
\hat{H}_{rad} = \sum_k \hbar \omega_k [\hat{a}_{k\lambda}^\dagger(t) \hat{a}_{k\lambda}(t) + \frac{1}{2}]
\]

\[
\hat{H}_{int} = -i\hbar \sum_{k,\lambda} (\hat{\sigma}^+ + \hat{\sigma}^-) [g_{k\lambda}(\mathbf{r}) \hat{a}_{k\lambda} - g_{k\lambda}^*(\mathbf{r}) \hat{a}_{k\lambda}^\dagger]
\]

and,

\[
g_{k\lambda}(\mathbf{r}) \equiv \sqrt{\frac{\omega_k}{2\varepsilon_0 \hbar}} \mathbf{d} \cdot \mathbf{u}_{k\lambda}(\mathbf{r})
\]

is a complex function associated with the coupling strength between the atom and the field.

By solving the Heisenberg equations of motion for the atomic and field operators within the Born and Markov approximations, one obtains the spontaneous emission rate on a transition \( |e\rangle \rightarrow |g\rangle \) of frequency \( \omega_0 \):

\[
\gamma^{rad}(\mathbf{r}) = 2\pi \sum_{k,\lambda} |g_{k\lambda}(\mathbf{r})|^2 \delta(\omega_k - \omega_0)
\]

which is the same result obtained by the Weisskopf-Wigner theory [421].

To evaluate the sum we need go to a continuous \( k \)-space via,

\[
\sum_{k,\lambda} \rightarrow \lim_{V \rightarrow \infty} \sum_{\lambda} \frac{V}{8\pi^3} \int d^3k .
\]
Hence, in free space, inserting the mode function (21.50),

$$\gamma^{rad}(r) = \frac{\pi \omega_0}{\varepsilon_0 \hbar} \sum_{k, \lambda} |d \cdot u_{k \lambda}(r)|^2 \delta(\omega_k - \omega_0)$$

(21.55)

$$= \frac{\hbar \omega_0}{8 \pi^2 \varepsilon_0 \hbar^2} \lim_{V \to \infty} \sum_{\lambda} \int d^3k |d \cdot \hat{\epsilon}_\lambda|^2 \delta(\omega_k - \omega_0)$$

$$= \lim_{V \to \infty} \sum_{\lambda} \int \frac{|d \cdot \hat{\epsilon}_\lambda|^2 \hat{\epsilon}_k^2}{\hbar^2} 2\pi \delta(\omega_k - \omega_0) \frac{V}{8 \pi^3 c} k^2 d\Omega_k d\omega_k$$

$$= \sum_{\lambda} \int \frac{|d \cdot \hat{\epsilon}_\lambda|^2 \hat{\epsilon}_k^2}{\hbar^2} 2\pi \delta(\omega_k - \omega_0) \rho(\omega_k, k) d\Omega_k d\omega_k,$$

with the density of states (21.38).

### 21.2.1.1 Two atoms

Let us now consider two excited atoms labeled by \( q = 1, 2 \), located at \( r_1 \) and \( r_2 \), and described by two of their eigenstates, \( \{|g_q\}, |e_q\rangle \). As usual, \( |g_q\rangle \) is the eigenstate with lowest energy (\( E_{g_q} = -\frac{1}{2} \hbar \omega_q \)) and longer lifetime, i.e. the ground state, whereas \( |e_q\rangle \) is the eigenstate with highest energy (\( E_{e_q} = +\frac{1}{2} \hbar \omega_q \)) coupled to \( |g_q\rangle \). In presence of an external electromagnetic field, the Hamiltonian of the two atom-field system in the electric dipole approximation is,

$$\hat{H} = \sum_{q=1,2} [\hat{H}_{at}^{(q)} + \hat{H}_{int}^{(q)}] + \hat{H}_{rad},$$

(21.56)

where \( \hat{H}_{at}^{(q)} \equiv \hbar \omega_q \hat{S}_q^z \) is the atomic Hamiltonian, with \( \hat{S}_q^z \equiv \frac{1}{2} \langle |e_q\rangle \langle e_q| - |g_q\rangle \langle g_q| \rangle \) being the energy operator of the \( q \)-th atom, and \( \hat{H}_{int}^{(q)} \equiv -\hat{d}_q \cdot \hat{\hat{\epsilon}}(r_q) \) is the atom-field interaction Hamiltonian. The electric dipole moment operator satisfies \( \langle e_q|\hat{d}_q|e_q\rangle = 0 = \langle g_q|\hat{d}_q|g_q\rangle \) and has non-vanishing off-diagonal elements, i.e. the eigenstates have no permanent dipole moment. We define the dipole-moment matrix element as \( d_q \equiv \langle e_q|\hat{d}_q|g_q\rangle \). The description of the field is identical to the case of one atom (21.49).

For weak-coupling between the atoms and the field, the interaction Hamiltonian becomes,

$$\hat{H}_{int} = -i\hbar \sum_{k, \lambda} \sum_{q=1,2} (\hat{S}_q^+ + \hat{S}_q^-) [g_{k \lambda}(r_q) \hat{a}_{k \lambda} - g^*_{k \lambda}(r_q) \hat{a}^+_{k \lambda}],$$

(21.57)

where \( \hat{S}_q^+ \equiv |e_q\rangle \langle g_q| \) and \( \hat{S}_q^- \equiv |g_q\rangle \langle e_q| \) are the electric dipole raising and lowering operators, respectively, and

$$g_{k \lambda}(r_q) \equiv \sqrt{\frac{\omega_k}{2\varepsilon_0 \hbar}} d_q \cdot u_{k \lambda}(r_q)$$

(21.58)

is a complex function associated with the coupling strength between the \( q \)-th atom and field. The dipole operators satisfy the well-known commutation and anti-commutation relations: \( [\hat{S}_q^+, \hat{S}_q^-] = 2\hat{S}_q^2 \delta_{qq'}, [\hat{S}_q^+, \hat{S}_q^+] = \pm \hat{S}_q^\pm \delta_{qq'}, \) and \( [\hat{S}_q^+, \hat{S}_q^-]_+ = 0 \) with \( (\hat{S}_q^\pm)^2 = 0 \).
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By solving the Heisenberg equations of motion for the atomic and field operators within the Born and Markov approximations, one obtains the spontaneous emission rate on a transition \( |e_q\rangle \rightarrow |g_q\rangle \) of frequency \( \omega_q \):

\[
\gamma^\text{rad}_q = \frac{2 \pi}{\varepsilon_0 \hbar} \sum_{k,\lambda} |d_q \cdot u_{k\lambda}(r_q)|^2 \delta(\omega_k - \omega_q),
\]

which is the same result obtained by the Weisskopf-Wigner theory [421]. In addition, due to the coupling between the atoms through the vacuum field, one also has the cross-damping spontaneous emission rate [10]:

\[
\gamma^\text{rad}_q(r_1, r_2) = \gamma^\text{rad}_q(r_2, r_1) = \frac{\pi \omega_0}{\varepsilon_0 \hbar} \sum_{k,\lambda} \text{Re} \left[ d_1 \cdot u_{k\lambda}(r_1) u_{k\lambda}^*(r_2) \cdot d_2^* \right] \delta(\omega_k - \omega_q),
\]

which shows explicitly the cooperative effect of the dipole-dipole interaction in the spontaneous emission rate.

21.2.2 Scattering from correlated atoms

Until now we disregarded the possibility that the atoms in the ensemble be correlated. In Sec. 15.1 we have shown how to describe the dynamics of a single two-level atom driven by a quantized electromagnetic field and embedded in an electromagnetic vacuum under the assumption that the driving field be a plane wave and the vacuum be isotropic. In the following, we want to relax these conditions. We proceed by generalizing Eq. (15.7) by replacing the plane wave \( e^{ik \cdot r} \) by a mode function \( u_k(r) \) and by allowing the coupling constant (15.16) \( g_k \) to depend on \( k \). Furthermore, we will extend the formalism to the presence of several atoms.

21.2.2.1 Master equation for two atoms

We have already introduced master equations for two- and three-level systems in Secs. 14.3.3 and 14.5.1. This concept can be extended to two coupled two-level systems [41],

\[
\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}_{\text{tot}}, \hat{\rho}] - \mathcal{L} \hat{\rho} \quad \text{with} \quad \mathcal{L} \hat{\rho} = \sum_{i,j=1}^{2} \gamma_{ij} (s_i^+ s_j^- \hat{\rho} + \hat{\rho} s_i^+ s_j^- - 2 s_i^- s_j^+ \hat{\rho} s_i^+),
\]

where the two spins operators are,

\[
\hat{s}_1^\pm \equiv \sigma^\pm \otimes \mathbb{I} \quad \text{and} \quad \hat{s}_2^\pm \equiv \mathbb{I} \otimes \sigma^\pm,
\]

that is, using (2.113),

\[
s_1^+ = (s_1^-)^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad s_2^+ = (s_2^-)^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}.
\]
The density operator is,
\[
\hat{\varrho} \equiv \hat{\rho}_1 \otimes \hat{\rho}_2 = \begin{pmatrix}
\rho_{1,gg}\rho_{2,gg} & \rho_{1,gg}\rho_{2,ge} & \rho_{1,gg}\rho_{2,ee} & \rho_{1,ge}\rho_{2,gg} & \rho_{1,ge}\rho_{2,ge} & \rho_{1,ge}\rho_{2,ee} \\
\rho_{1,gg}\rho_{2,eg} & \rho_{1,gg}\rho_{2,ee} & \rho_{1,ge}\rho_{2,eg} & \rho_{1,ge}\rho_{2,ee} & \rho_{1,ee}\rho_{2,gg} & \rho_{1,ee}\rho_{2,ge} \\
\rho_{1,eg}\rho_{2,gg} & \rho_{1,eg}\rho_{2,ge} & \rho_{1,ee}\rho_{2,gg} & \rho_{1,ee}\rho_{2,ge} & \rho_{1,ee}\rho_{2,eg} & \rho_{1,ee}\rho_{2,ee} \\
\rho_{1,eg}\rho_{2,eg} & \rho_{1,eg}\rho_{2,ee} & \rho_{1,ee}\rho_{2,eg} & \rho_{1,ee}\rho_{2,ee} & \rho_{2,gg} & \rho_{2,ge} \\
\rho_{1,eg}\rho_{2,eg} & \rho_{1,eg}\rho_{2,ee} & \rho_{1,ee}\rho_{2,eg} & \rho_{1,ee}\rho_{2,ee} & \rho_{2,gg} & \rho_{2,ge} \\
\rho_{1,eg}\rho_{2,eg} & \rho_{1,eg}\rho_{2,ee} & \rho_{1,ee}\rho_{2,eg} & \rho_{1,ee}\rho_{2,ee} & \rho_{2,gg} & \rho_{2,ge}
\end{pmatrix} .
\] (21.64)

Thus, we have 16 equations to describe the evolutions of the 16 components of the total density matrix \((\varrho_{ij})\).

### 21.2.3 Spontaneous emission in a cavity and cooperativity

The **cooperativity parameter** of a cavity is defined as the rate at which an atom emits into the volume of a cavity mode normalized to the rate at which it would scatter into free space,
\[
\Upsilon \equiv \frac{\Gamma_{cav}|\hat{\epsilon}_k|\in cav}{\Gamma_{free}}.
\] (21.65)

#### 21.2.3.1 Modification of the natural linewidth for the TEM\(_{00}\) cavity mode

In a cavity, spontaneous emission is strongly modified [265, 266, 267]. An atom interacting with a cavity will spontaneously emit into the cavity mode at an increased (reduced) rate, if the cavity is resonant (out of resonance). The natural width due to spontaneous decay and the line shift are calculated by integration over the coupling force between the atom and every available field mode,
\[
\Gamma = \int \int |\hat{d}_{eg} \cdot \epsilon_k|^2 \frac{\epsilon_k^2}{\hbar^2} 2\pi \delta(\omega - \omega_k)\rho(\omega_k, k) d\Omega_k d\omega_k
\]
\[
\Delta \omega = \sum_i \int \int |\hat{d}_{ei} \cdot \epsilon_k|^2 \frac{\epsilon_k^2}{\hbar^2} \omega_{ei} - \omega_k \rho(\omega_k, k) d\Omega_k d\omega_k
\] (21.66)

with the field amplitude per photon, \(|\hat{\epsilon}_k| = \sqrt{\frac{\hbar \omega_k}{2\varepsilon_0 V}}\). Inserting the number of modes per unit of frequency range and per unit of solid angle in free space \((\rho/V)\) is the density of states,
\[
\rho_{free}(\omega_k, k) = \frac{V\omega_k^2}{(2\pi)^3 c^3},
\]
and since in free space there is no preferred orientation, we obtain,
\[
\Gamma_{free} = \int_{\epsilon_k \in \mathbb{R}^3} \frac{d^2 \sin^2 \theta \hbar \omega_0}{\hbar^2} \frac{V\omega_0^2}{2\varepsilon_0 V (2\pi)^3 c^3} 2\pi \sin \theta d\theta d\phi = \frac{d^2 k^3}{3\pi \varepsilon_0 \hbar} .
\]
(21.68)

Since the solid angle of free space is restricted by the presence of the cavity,
\[
\Gamma_{free}|_{\epsilon_k \notin cav} = \Gamma_{free} \left[ 1 - \frac{3}{8\pi} \Omega_{cav} \right] .
\]
(21.69)

For \(k \in\) cavity the density of states is modulated by the Airy function,
\[
\rho_{cav}(\omega_k, k) = \rho_{free}(\omega_k, k) \mathcal{L}(\omega_k).
\]
The cavity breaks the isotropy, so the following is only valid for \( \mathbf{k} \perp \vec{B} \parallel \hat{e} \). Inserting the density of states of the cavity,

\[
\Gamma_{cav|\hat{e}k\in cav} = \int_{\hat{e}k\in cav} \frac{d^2 \sin^2 \theta}{\hbar^2} \frac{h\omega_0}{2\varepsilon_0 V} \mathcal{L}(\omega_0) \frac{V\omega_0^2}{(2\pi)^3 c^3} 2\pi \sin \theta d\theta d\phi
\]

Inserting the total density of states of the cavity and remaining free space (21.43) in the expression for the linewidth (21.66), we see that the modification of the linewidth is a sum,

\[
\Gamma_{cav} = \Gamma_{free|\hat{e}k\in cav} + \Gamma_{cav|\hat{e}k\in cav} = \Gamma_{free} \left[ 1 - \frac{3}{8\pi} \Omega_{cav} \right] + \Gamma_{free} \mathcal{L}(\omega_0) \frac{3}{8\pi} \Omega_{cav} = \Gamma_{free} \left[ 1 + (\mathcal{L}(\omega_0) - 1) \right] \left( 1 - \frac{3}{8\pi} \Omega_{cav} \right).
\]

The extremes are,

\[
\Gamma_{enh} = \Gamma_{free} \left( 1 + \frac{3}{4\pi^2} F \Omega_{cav} \right) \quad \text{and} \quad \Gamma_{inh} = \Gamma_{free} \left( 1 - \frac{3}{8\pi} \Omega_{cav} \right) \simeq \Gamma_{free}.
\]

For a small solid angle, we can expect a noticeable increase of the scattering into the cavity, but without inhibition of the total decay. The solid angle is calculated via,

\[
\Omega_{cav} = 2 \cdot \frac{\pi w(z)^2}{z^2} = 2 \cdot \frac{\pi w_0^2}{z^2} \left( 1 + \left( \frac{\lambda z}{\pi w_0^2} \right)^2 \right)^2 \rightarrow \frac{8\pi}{k^2 w_0^2}.
\]

The **cooperativity parameter** finally is,

\[
\Upsilon \equiv \frac{\Gamma_{cav|\hat{e}k\in cav}}{\Gamma_{free}} = \mathcal{L}(\omega_0) \frac{3}{8\pi} \Omega_{cav} = \sqrt{1 + \left( \frac{2F}{\pi} \right)^2} \frac{3}{8\pi} \Omega_{cav}
\]

\[
\simeq \frac{3F}{4\pi^2} \Omega_{cav} = \frac{\Gamma_{enh}}{\Gamma_{free}} - 1 = \frac{3F}{4\pi^2} \frac{8\pi}{k^2 w_0^2},
\]

that is,

\[
\Upsilon = \frac{F}{\pi} \frac{6}{k^2 w_0^2}.
\]

**Example 80**: For example, for a non-degenerate linear cavity with finesse \( F = 80000 \) and waist \( w_0 = 110 \mu m \), the cooperativity is weak, \( \eta \approx 0.2 \). In this sense, confocal or concentric cavities may present more favorable geometries [265, 266, 267].
21.2.3.2 Modification of the natural linewidth for confocal and concentric cavities

Using the solid angle of a confocal cavity (21.44), the cooperativity parameter is,

$$\eta \simeq \frac{3F}{4\pi^2} \Omega_{cav} = \frac{3F}{4\pi^2} \frac{8\pi b^2}{L^2}, \quad (21.76)$$

where $b$ is the clear aperture of the cavity mirrors. That is,

$$\Upsilon = \frac{F}{\pi} \frac{6b^2}{L^2}. \quad (21.77)$$

21.2.3.3 Scattered intensities

If the atoms are saturated by an incident laser, they scatter light into the cavity at a rate (apart from a factor $\frac{1}{2}$),

$$\Gamma_{cav}|_{\hat{e}_k \in cav} = \Gamma_{free} \mathcal{L}(\omega_0) \frac{3}{8\pi} \Omega_{cav}. \quad (21.78)$$

Without cavity the emission into the same solid angle is obtained via $F \to 0$,

$$\Gamma_{free}|_{\hat{e}_k \in cav} = \Gamma_{free} \frac{3}{8\pi} \Omega_{cav}. \quad (21.79)$$

With a resonant high finesse cavity the emission is obtained via $kL \to 0$,

$$\Gamma_{enh}|_{\hat{e}_k \in cav} = \Gamma_{free} \sqrt{1 + \left(\frac{2F}{\pi}\right)^3 \frac{3}{8\pi} \Omega_{cav}} = \eta \Gamma_{free}. \quad (21.80)$$

With a non-resonant cavity, the emission is obtained via $kL \to \pi/2$,

$$\Gamma_{inh}|_{\hat{e}_k \in cav} = \Gamma_{free} \sqrt{1 + \left(\frac{2F}{\pi}\right)^{-1} \frac{3}{8\pi} \Omega_{cav}} \simeq 0. \quad (21.81)$$

The scattering will fill the cavity with photons, until the leakage equalizes the pumping. When the balance is reached, $\Gamma_{cav}|_{\hat{e}_k \in cav}$ will also be the rate at which photons are emitted by the cavity mode. We calculate an example in Exc. 21.1.4.4.

21.2.4 Atom-field coupling force

21.2.4.1 The atomic dipole moment

The atom-field coupling constant, which is precisely HALF the single photon Rabi frequency, is,

$$g \equiv \frac{d\hat{\mathcal{E}}_1(0)}{\hbar} = \sqrt{\frac{3\pi \Gamma \omega}{2k^3 V_m}} = \sqrt{\frac{3\Gamma \delta_{fsr}}{k^2 w^2}}. \quad (21.82)$$

See also (watch talk).
21.2. CHARACTERIZATION OF THE INTERACTION BETWEEN ATOMS AND CAVITIES

Figure 21.2: (code) Spontaneous emission in a cavity with $F = 80000$ and $w_0 = 110 \mu m$, such that $\Upsilon = 0.2$. With $N_0 = 10^4$ saturated rubidium atoms, $P_j = 2 \times 10^{-14} W$, we expect a number of $T \frac{\hbar}{\omega} = 10^7 s^{-1}$ photons. (a) Cooperativity $\mathcal{L}(\omega)$ from Eq. (21.39) as a function of the detuning of the cavity. (b) Linewidth $\Gamma_{\text{cav}}$ from (21.71) and (c) frequency shift of the rubidium transition. (d) green: spontaneous emission into the cavity, and red: to the sides.

Figure 21.3: Relevant parameters for an atom interacting with a cavity.

21.2.4.2 Cooperativity in cavities

The detuning between an atomic resonance and the laser frequency is typically $\Delta_a = 2\pi \times 1000 \text{ GHz} \ (2 \text{ nm})$. The reflection coefficient for a single atom is,

$$\beta_{\Delta} = \left| \frac{k \cdot \text{Re} \alpha}{\epsilon_0} \right| = \frac{k}{\pi w^2} \frac{6\pi}{k^3} \frac{\Gamma}{2\Delta_a + i\Gamma} \approx \frac{6}{k^2 w^2} \frac{\Gamma}{2\Delta_a + i\Gamma} \approx \frac{6}{k^2 w^2} \frac{\Gamma}{2\Delta_a} \frac{\Gamma}{2\Delta_a + i\Gamma},$$

(21.83)

where $\alpha$ is the complex atomic polarization and $\Delta_a = \omega_{\text{dip}} - \omega_0$. The resonant reflection coefficient can be interpreted in terms of a phase shift that depends on the matching between the optical cross-section of the atom, $\sigma = 3\lambda^2/2\pi$, and the cross section of the optical mode $^{3}$,

$$\beta_0 = \frac{\sigma_0}{\pi w^2} = \frac{6}{k^2 w^2} = \frac{2g^2}{\delta_{\text{fsr}} \Gamma}.$$

(21.84)

The frequency shift accumulated during a round trip in the cavity $\delta_{\text{fsr}} \beta_0$ becomes

$^{3}$For our BEC ring cavity: $\beta_0 \approx 0.76$. 
noticeable, when it exceeds the linewidth of the cavity $\kappa$. From this condition, we obtain the optical depth for a single passage through the atomic sample multiplied by the finesse of the cavity, which is precisely the \textit{cooperativity parameter} \footnote{For our BEC ring cavity $\Upsilon \approx 0.2$.},

$$\eta \equiv \frac{\delta_{fsr} \beta_0}{\kappa} = \frac{F}{\pi} \frac{6}{k^2 w^2} = \frac{2g^2}{\kappa \Gamma}.$$  \hspace{1cm} (21.85)

The sensitivity to the atom number can be measured in terms of a \textit{critical atom number} $N_{\text{crit}}$, which the system can resolve. It goes to infinity as the resonant single atom reflection coefficient disappears, $\beta_0 \to 0$, and converges to zero when $\beta_0 \to 1$,

$$N_{\text{crit}} = \frac{4\pi}{F \beta_0} = \frac{4\pi k^2 w^2}{6F} = \frac{2\pi \Gamma\delta_{fsr} \beta_0}{F g^2} = \frac{2\kappa \Gamma}{g^2} = \frac{4}{\eta}.$$ \hspace{1cm} (21.86)

The total reflection coefficient is increased by the number of atoms $N$ and the number of photon round trips $F$ in the cavity, which gives out of resonance,

$$NF\beta_\Delta \approx NF \frac{6}{k^2 w^2} \frac{\Gamma}{2\Delta_a} = NF \frac{g^2 k V}{\Delta_a \omega \pi w^2} = NU_0 \frac{L}{c} F = \frac{NU_0}{\kappa},$$

where we introduced the 'light-shift' produced by a single off-resonant photon,

$$U_0 \approx \frac{g^2}{\Delta_a}$$ \hspace{1cm} (21.88)

and the Rayleigh scattering rate produced by a single photon,

$$\gamma_0 \approx \frac{g^2 \Gamma}{\Delta_a^2}.$$ \hspace{1cm} (21.89)

Using the dipole moment $d = \sqrt{3\pi \varepsilon_0 \hbar \Gamma / k^3}$ and defining the electric field amplitude per photon $E_1$ by the photon number $n$, the power $P$, and the intensity $I = \varepsilon_0 c n_{ph} E_1^2 = 2P/\pi w_0^2$, we calculate for the single-photon Rabi frequency (or atom-field coupling strength),

$$g = \frac{dE_1}{\hbar} = \sqrt{\frac{1}{\hbar^2} 3\pi \varepsilon_0 \hbar \Gamma} \frac{I}{\varepsilon_0 c n_{ph}} = \sqrt{1} \frac{3\pi \varepsilon_0 \hbar \Gamma}{\hbar^2} \frac{1}{k^3} \frac{1}{\varepsilon_0 c n_{ph} \pi w_0^2} = \sqrt{\frac{6}{k^2 w_0^2}} \frac{P}{\Delta_a} \frac{\Gamma \beta_\Delta}{n_{ph} \hbar \omega}.$$ \hspace{1cm} (21.90)

The single-photon light shift (or atom-atom coupling strength) is,

$$U_0 = \frac{g^2}{|\Delta_a|} = \frac{6}{k^2 w_0^2} \frac{\Gamma}{|\Delta_a|} \frac{P}{n_{ph} \hbar \omega} = \beta_\Delta \frac{P}{n_{ph} \hbar \omega},$$ \hspace{1cm} (21.91)

and the single-photon Rayleigh scattering rate,

$$\gamma_0 = \frac{g^2 \Gamma}{\Delta_a^2} = \frac{6}{k^2 w_0^2} \frac{\Gamma^2}{\Delta_a^2} \frac{P}{n_{ph} \hbar \omega}.$$ \hspace{1cm} (21.92)

In a cavity the flux $\delta_{fsr} = P/n_{ph} \hbar \omega$ is just the photon round trip rate (or free spectral range). $1/\delta_{fsr}$ is the time a photon interacts with an atom. In free space,
this does not make sense to me, because I don’t know how define the mode volume. I can however consider the interaction of a photon with an extended sample of length \( L \). In this case, a photon interacts with the sample for the time \( L/c \), so that,

\[
U_0 = \frac{g^2}{|\Delta_a|} = \frac{6}{k^2 w_0^2} \frac{\Gamma}{|\Delta_a|} \frac{c}{L} = \beta \Delta c \frac{c}{L},
\]

and

\[
\gamma_0 = \frac{g^2 \Gamma}{\Delta_a^2} = \frac{6}{k^2 w_0^2} \frac{\Gamma^2}{\Delta_a^2} \frac{c}{L}.
\]

This means, we can use the CARL equations derived for a ring cavity by just substituting \( \kappa = \delta \delta_{fsr} = c/L \), where \( L \) is now not the cavity but the sample length.

**21.2.4.3 Optical density**

Lambert-Beer’s law relates the amplitude of the field transmitted to the incident,

\[
\frac{E_t}{E_0} = \exp \left[ i \sigma (\Delta_a) \left( \frac{i}{2} - \frac{\Delta_a}{\Gamma} \right) \int_{-\infty}^{\infty} n(r) dz \right] = e^{-\alpha/2} e^{i \delta}.
\]

I.e. the field is shifted by an amount \( \delta \) and absorbed by an amount \( \alpha \). The exponent (called optical density) can be rewritten, if we assume that the atoms are homogeneously distributed over a cylinder with length \( L \) and radius \( \bar{r} = w_0 \),

\[
OD = i \sigma (\Delta_a) \left( \frac{i}{2} - \frac{\Delta_a}{\Gamma} \right) \int_{-\infty}^{\infty} n(r) dz = \sigma_0 \frac{\Gamma^2}{\Delta_a^2} \left( -\frac{1}{2} - \frac{i \Delta_a}{\Gamma} \right) \int_0^L \frac{N}{\pi r^2 L} dz = \frac{6N}{k^2 w_0^2} \frac{\Gamma^2}{\Delta_a^2} \left( -\frac{1}{2} - \frac{i \Delta_a}{\Gamma} \right)
\]

\[
= \frac{6N}{k^2 w_0^2} \left( -\frac{1}{2} \frac{\Gamma^2}{\Delta_a^2} - \frac{i \Gamma}{\Delta_a} \right) = N \frac{L}{c} (\gamma_0 - i U_0)
\]

Hence, the parameters \( N \gamma_0 \) and \( N U_0 \) that we use in our CARL simulations are nothing else that the optical density per photon lifetime \( \kappa = c/L \).

**21.2.4.4 Collective cooperativity**

While the strong coupling regime of the CQED requires \( \eta > 1 \) with a single atom, collective cooperativity is reached with \( N \) atoms if \( N \eta > 1 \) \[84, 120\]. In this case, the atomic ensemble couples to the mode like a single ’super-atom’, the coupling force being magnified to \( g_N = g_1 \sqrt{N} \). We have already obtained this result within the Jaynes-Cummings model for two indistinguishable atoms coupling to the same light mode and forming a *Dicke state* (see Sec. 18.2.4).

**21.2.4.5 Saturation parameter in cavities**

The *saturation parameter* for a single photon is given by,

\[
s = \frac{g^2}{\Gamma^2}.
\]
Therefore, the number of photons needed to saturate an atomic transition is,

\[ n_{\text{sat}} = \frac{\Gamma^2}{2g^2} = \frac{\Gamma}{\delta_{\text{fsr}}} \frac{k^2w^2}{6} = \frac{1}{2s} . \]  

(21.98)

We see, that there is a symmetry between \( N_{\text{cr}} \) and \( s \), that is, between \( N_{\text{cr}} \) and \( n_{\text{sat}} \). The regime \( N\eta > 1 \) denotes the collective behavior of \( N \) atoms in the same way as \( n_{\text{sat}} > 1 \) indicates saturation. While \( \eta \) depends only on the phase matching between the atomic antenna and the cavity, \( s \) also depends on the cavity mode volume and the natural decay rate.

### 21.2.4.6 Cavity resolution parameter

Comparing the photonic recoil, which is given by,

\[ \omega_{\text{rec}} = \frac{\hbar k^2}{2m} , \]  

(21.99)

with the resolution power of a cavity \( \kappa \), we can define the resolution parameter,

\[ r \equiv \frac{\omega_{\text{rec}}}{\kappa} . \]  

(21.100)

In Exc. 21.2.5.1 we compare the coupling force and other characteristic parameters for various combinations of atomic species and optical cavities. In Exc. 21.2.5.2 we calculate the number of photons in a cavity pumped in or out of resonance.

### 21.2.5 Exercises

#### 21.2.5.1 Ex: Characteristic parameters for various atom-cavity systems

Complete the following table calculating \( \kappa, V_m, \omega_r, g_1, \Upsilon, s \), and \( r \),

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>( \mathcal{F} )</th>
<th>( L )</th>
<th>( w_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 MHz</td>
<td>250000</td>
<td>100 ( \mu )m</td>
<td>20 ( \mu )m</td>
</tr>
<tr>
<td>6.8 kHz</td>
<td>250000</td>
<td>3 cm</td>
<td>70 ( \mu )m</td>
</tr>
</tbody>
</table>

#### 21.2.5.2 Ex: Number of photons in a cavity

a. How many photons are in the mode of a cavity with finesse \( F = 80000 \) (i) in resonance e (ii) out of resonance?

b. What power must be injected to produce 1 photon inside the cavity?

c. Resonant backscattering by the cavity mirrors can scatter photons into the reverse mode. Typically, \( P_-/P_+ \approx 0.005 \). Hence, \( n_{-\text{cav}} = 1.5 \times 10^7 \) and \( n_{\text{off}-\text{cav}} = 0.01 \). Using advanced techniques it is possible to reduce the number of backscattered photons by factor of \( > 20 \). Assuming that the losses due to backscattering are \( S = 1 \) ppm. Can the resonant backscattering by the mirrors destroy a BEC?

d. What is the amplitude of the CARL signal in terms of photons?
21.2.5.3 Ex: Lindblad term for two atoms
Write down explicitly the cooperative Lindblad term for two atoms.

21.2.5.4 Ex: Relationship between super- and subradiance and cooperativity
Seek an interpretation of super- and subradiance as a modification of the structure factor by cooperativity.

21.3 Noise analysis of Bragg scattering

21.4 Atoms interacting with surfaces
Chapter 22

Atomic motion in optical cavities

22.1 Cavity interacting with a single atom

Here, we consider atoms interacting with the modes of an optical cavity pumped by lasers. As we saw in the previous chapter, the density of the modes in a cavity is concentrated around the optical axis, such that a scatterer located within the mode emits preferentially within the cavity, where the light is recycled. Therefore, we can in many situations treat the system as one-dimensional.

In free space, as discussed in Chp. 16.3.4, the force of light has two components: the radiation pressure, which scatters photons isotropically into space, and the dipole force, which can be interpreted in terms of a redistribution of photons between light modes. In cavities, where the isotropic scattering is much reduced, radiative pressure can often be neglected. In contrast, if light is tuned away from atomic resonances, the atom will feel a dipole force originating from the backscattering of photons between counterpropagating modes.

22.1.1 Linear and ring cavities

We must distinguish two types of cavities with very different behaviors: The linear cavity or \textit{(Fabry-Pérot etalon)}, where counterpropagating modes form a single mode, and the ring cavity, where counterpropagating modes have independent photon budgets.

For a \textit{linear cavity}, boundary conditions imposed by the surfaces of the cavity mirrors determine the possible spatial mode functions, which are necessarily standing waves. The amplitudes of the electric field are in second quantization (15.8),

\[
\hat{E}(z,t) = \hat{E}^+(z,t)e^{-i\omega t} + \hat{E}^-(z,t)e^{i\omega t}
\]

with \[
\hat{E}^\pm(z,t) = E_1\hat{a}(t)e^{\pm k z} = (\hat{E}^-(z,t))^\dagger.
\]

with \[[\hat{a},\hat{a}^\dagger] = 1\]. With this we obtain, for a single atom coupled to the mode of the cavity pumped by a laser, within the dipolar approximation and the RWA \(^1\), the

\(^1\)For the transformation into the rotating frame see the derivation of (14.51).
following relevant contributions to the Hamiltonian ($\hbar = 1$),

$$
\hat{H}_{\text{atom}} = -\Delta_a \hat{\sigma}^+ \hat{\sigma}^- + \frac{\hat{p}^2}{2m}
$$

$$
\hat{H}_{\text{cav}} = -\Delta_c \hat{a}^\dagger \hat{a}
$$

$$
\hat{H}_{\text{atom-cav}} = g \hat{a}^\dagger \hat{\sigma}^- e^{-ik\hat{z}} + \text{h.c.}
$$

$$
\hat{H}_{\text{laser-cav}} = \eta \hat{a}^\dagger + \text{h.c.}
$$

neglecting the dynamics of the pump field, which is supposed to be classical, $\eta = \delta_{\text{fsr}}(\hat{a}_\text{in}^\dagger)$. Note that the propagator $e^{-i\hat{H}_{\text{laser-cav}}t}$ corresponds to a coherent state displacement operator. $\Delta_a$ is the detuning between the light and the atomic resonance, $\Delta_c$ between the light and cavity resonance and $g$ is the light-atom coupling force, also called the single-photon Rabi frequency. The first three contributions define the Jaynes-Cummings model. Do the Excs. 22.1.5.1 and 22.1.5.2.

For a ring cavity, we must distinguish the counterpropagating modes $\hat{a}_\pm$,

$$
\hat{E}^\pm(z,t) = E_1 \hat{a}_+(t) e^{ikz} + E_1 \hat{a}_-(t) e^{-ikz} = (\hat{E}^- (z,t))^\dagger.
$$

such that the total Hamiltonian $\hat{H}$ consists of the following parts

$$
\begin{align*}
\hat{H}_{\text{atom}} &= \hat{H}_{\text{electron}} + \hat{H}_{\text{motion}} = -\Delta_a \hat{\sigma}^+ \hat{\sigma}^- + \frac{\hat{p}^2}{2m} \\
\hat{H}_{\text{cav}} &= -\Delta_c \hat{a}_+^\dagger \hat{a}_+ - \Delta_c \hat{a}_-^\dagger \hat{a}_- \\
\hat{H}_{\text{atom-cav}} &= g \hat{a}_+^\dagger \hat{\sigma}^- e^{-ik\hat{z}} + \text{h.c.} + g \hat{a}_-^\dagger \hat{\sigma}^- e^{ik(\text{grz} + \text{h.c.})} \\
\hat{H}_{\text{laser-cav}} &= -\eta \hat{a}_+^\dagger (\hat{a}_+ - \hat{a}_+^\dagger) - \eta \hat{a}_-^\dagger (\hat{a}_- - \hat{a}_-^\dagger)
\end{align*}
$$

We identify the degrees of freedom of the system through the quantum observables appearing in the Hamiltonian: the counterpropagating modes of light with the amplitudes ($\hat{a}_\pm$), the internal degrees of freedom ($\hat{\sigma}^\pm$), and the spatial coordinates of the atom ($\hat{z}, \hat{p}$).

In contrast to linear cavities, ring cavities have the following particularities: 1. The phase of the standing wave is free to move; 2. the counterpropagating modes of the cavity have independent photon budgets, each backscattering event conserves momentum; 3. the backscattering acts on the phase of the standing wave. Atoms can be trapped by the dipole force within the cavity mode volume. The dipole force corresponds to a backscattering of photons between modes.

### 22.1.2 Eliminating spontaneous emission and cavity decay

In fact, there are more degrees of freedom involved in the dynamics of atoms moving in a laser-pumped ring cavity, because of the atoms may scatter light into directions other than the cavity modes by spontaneous emission, and the cavity modes may decay by transmission through the mirrors. Therefore, we need to treat the respective vacuum

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2Throughout this chapter we will sometimes emphasize the motional degree of freedom in green color, photonic states in blue, electronic excitation states in pink.
22.1. CAVITY INTERACTING WITH A SINGLE ATOM

Figure 22.1: Scheme of an atom interacting with a ring cavity showing the relevant degrees of freedom ($\hat{x}$, $\hat{p}$, $\hat{a}_\pm$) and the possible decay processes ($\kappa$, $\Gamma$) for the derivation of the field equations.

Field modes receiving the photons $\hat{a}_k$ and $\hat{a}_\omega$ quantum mechanically and include the respective Hamiltonians,

$$\hat{H}_{\text{atom-vac}} = \sum_k g_{\text{spont.vac}} \hat{a}_k^\dagger \hat{\sigma}^- e^{-i \hat{r} \hat{p}} + \text{h.c.}$$  \hspace{1cm} (22.5)

$$\hat{H}_{\text{cav-vac}} = \sum_\omega g_{\text{cav.vac}} \hat{a}_\omega^\dagger \hat{a}_\omega + \text{h.c.}$$  \hspace{1cm} (22.6)

in the description of the coupled dynamics. The total density operator, the Hamiltonian and the equation of motion are, consequently,

$$\hat{\rho} = \hat{\rho}_{\text{atom}} \otimes \hat{\rho}_{\text{electron}} \otimes \hat{\rho}_{\text{spont.vac}} \otimes \hat{\rho}_{\text{cav.vac}}$$  \hspace{1cm} (22.7)

$$\hat{H} = \hat{H}_{\text{motion}} + \hat{H}_{\text{electron}} + \hat{H}_{\text{cav}} + \hat{H}_{\text{atom-cav}} + \hat{H}_{\text{laser-cav}} + \hat{H}_{\text{atom-vac}} + \hat{H}_{\text{cav-vac}}$$

$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] .$$

With the inclusion of the vacuum field modes $\hat{a}_\omega$ and $\hat{a}_k$ the number of degrees of freedom to be treated literally explodes, and we have to find a way to eliminate them from the equation of motion. We do this by partially tracing the density operator over the vacuum field modes using the Weisskopf-Wigner theory,

$$\tilde{\hat{\rho}} \equiv \text{Tr}_{\text{spont.vac}} \text{Tr}_{\text{cav.vac}} \hat{\rho} = \hat{\rho}_{\text{atom}} \otimes \hat{\rho}_{\text{electron}} \otimes \hat{\rho}_{\text{cav}} .$$  \hspace{1cm} (22.8)

This allows us to reduce the Hamiltonian $\hat{H} = \hat{H} - \hat{H}_{\text{atom-vac}} - \hat{H}_{\text{cav-vac}}$. The price to pay is, that the equation of motion for this receives dissipative terms: The Liouville equation turns into a master equation with the following form,

$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}_{\text{atom-vac}} + \mathcal{L}_{\text{cav-vac,+}} + \mathcal{L}_{\text{cav-vac,-}}$$

$$\mathcal{L}_{\text{atom-vac}}(t) = -\gamma \{ \hat{\sigma}^+ \hat{\sigma}^- \hat{\rho}(t) - 2 \hat{\sigma}^- \hat{\rho}(t) \hat{\sigma}^+ + \hat{\rho}(t) \hat{\sigma}^+ \hat{\sigma}^- \} ,$$  \hspace{1cm} (22.9)

$$\mathcal{L}_{\text{cavity-vac,±}}(t) = -\kappa \{ \hat{a}_\pm^\dagger \hat{a}_\pm \hat{\rho}(t) - 2 \hat{a}_\pm \hat{\rho}(t) \hat{a}_\pm^\dagger + \hat{\rho}(t) \hat{a}_\pm^\dagger \hat{a}_\pm \}$$

where $\hat{H}$ is the Hamiltonian from (22.4). We see that each degree of freedom has its
own loss mechanism. \( \kappa \) for the finite transmission of the resonator mirrors [119, 215],\(^3\) \( \Gamma \) for the spontaneous emission, and \( \gamma_{frc} \), when we exert a frictional force on the atoms.

### 22.1.2.1 The problem with spontaneous emission in cavities

The above treatment still is incomplete, if we regard \( \dot{\rho} \) as the atomic Bloch vector. The reason is that we know what the dissipative Lindblad terms \( \dot{L}_{\text{spont. vac}} \dot{\rho} \) generated by spontaneous emission look like for the atomic excitation \( \dot{\rho}_{\text{atom}} \), but the Hamiltonian \( \hat{H}_{\text{atom-vac}} \) also contains the motional degree of freedom \( e^{-ik\mathbf{r}} \), which is intrinsically three-dimensional. That is, the dissipative terms also need to describe, how the motion diffuses in momentum space.

The inclusion of dissipative terms, however, is difficult, because unavoidable photonic recoil violates the supposed one-dimensionality of the atomic motion along the optical axis. Omnidirectional photonic recoil is also incompatible with the assumption that the momentum is quantized in multiples of \( 2\hbar k \) in the direction of the optical axis. And finally, if we consider degenerate matter waves, photonic recoil will eject atoms from a BEC. Even if, neglecting the emission process, we only consider absorption, we would need a quantization in multiples of \( 1\hbar k \) instead of \( 2\hbar k \). In the following, in order to keep the problem 1D, we will neglect momentum diffusion, i.e., we consider the simplified Hamiltonian \( \hat{H} \) and discard motional terms from the term \( \dot{L}_{\text{spont. vac}} \dot{\rho} \).

### 22.1.2.2 Quantum derivation of the CARL equations

To obtain the equations of motion we insert the Hamiltonian (22.4) into the equations for the field operators, for which the following commutation rules hold, \([\hat{a}_\pm, \hat{a}_\pm^\dagger] = 1\) and \([\hat{a}_\pm, \hat{a}_\pm^\dagger] = 0 = [\hat{a}_\pm, \hat{a}_\pm]\),

\[
\dot{\hat{a}}_+ = i[\hat{H}, \hat{a}_+] - \kappa \hat{a}_+
\]

\[= -i\Delta_c [\hat{a}_+^\dagger \hat{a}_+, \hat{a}_+] + ig e^{ik\hat{r}} \hat{\sigma} [\hat{a}_+^\dagger \hat{a}_+, \hat{a}_+] + ig e^{-ik\hat{r}} \hat{\sigma} [\hat{a}_+, \hat{a}_+^\dagger \hat{a}_+, \hat{a}_+] + \eta_+ [\hat{a}_+ - \hat{a}_+^\dagger, \hat{a}_+] - \kappa \hat{a}_+
\]

\[= (-\kappa + i\Delta_c) \hat{a}_+ - ig \hat{\sigma} e^{-ik\hat{r}} + \eta_+ ,
\]

and similarly for \( \hat{a}_- \). For the Pauli deexcitation matrix, using the following commutation rules, \([\hat{\sigma}^+, \hat{\sigma}^-] = \hat{\sigma} \) and \([\hat{\sigma}^-, \hat{\sigma}^-] = 0 \), we calculate,

\[
\dot{\hat{\sigma}}^- = i[\hat{H}, \hat{\sigma}^-] - \gamma \hat{\sigma}^-
\]

\[= -i\Delta_a [\hat{\sigma}^+ \hat{\sigma}^-, \hat{\sigma}^-] + ig e^{ik\hat{r}} \hat{\sigma}^+ \hat{\sigma}^- + ig e^{-ik\hat{r}} \hat{\sigma}^- \hat{\sigma}^- + \gamma \hat{\sigma}^-
\]

\[= (-\gamma + i\Delta_a) \hat{\sigma}^- + ig e^{ik\hat{r}} \hat{\sigma}^+ \hat{\sigma}^- + ig e^{-ik\hat{r}} \hat{\sigma}^- \hat{\sigma}^- .
\]

For the Pauli inversion matrix, using the following commutation rules, \([\hat{\sigma}^+ \hat{\sigma}^+, \hat{\sigma}^-] = 0 \) and \([\hat{\sigma}^+, \hat{\sigma}^-] = \pm 2\hat{\sigma} \), we calculate,

\[
\dot{\hat{\sigma}}_z = i[\hat{H}, \hat{\sigma}_z] - 2\gamma - 2\gamma \hat{\sigma}_z
\]

\[= ig e^{-ik\hat{r}} \hat{a}_+^\dagger [\hat{\sigma}^-, \hat{\sigma}_z] + 2ig e^{ik\hat{r}} \hat{a}_+ [\hat{\sigma}^+, \hat{\sigma}_z] + ig e^{ik\hat{r}} \hat{a}_+ [\hat{\sigma}^+, \hat{\sigma}_z] + ig e^{-ik\hat{r}} \hat{a}_- [\hat{\sigma}^-, \hat{\sigma}_z] - 2\gamma \hat{\sigma}_z
\]

\[= -2\gamma - 2\gamma \hat{\sigma}_z + 2ig e^{-ik\hat{r}} \hat{a}_+^\dagger \hat{\sigma}^- + 2ig e^{ik\hat{r}} \hat{a}_+ \hat{\sigma}^+ - 2ig e^{ik\hat{r}} \hat{a}_+ \hat{\sigma}^+ - 2ig e^{-ik\hat{r}} \hat{a}_- \hat{\sigma}^+ .
\]

\(^3\)Here, we only consider cavity decay into a zero temperature reservoir without quantum phase fluctuations.
Finally, we need to derive the equations governing the motion of atoms. For the position we obtain,

\[ \dot{z} = i [\hat{H}, \hat{z}] = i [\frac{\hat{p}^2}{2m}, \hat{z}] = \frac{1}{m} \hat{p}. \] (22.13)

In order to calculate the momentum, we need to do a small auxiliary calculation. With the commutator \([\hat{z}, \hat{p}] = i\) we derive,

\[
[z^n, \hat{p}] = i \frac{\delta z^n}{\delta \hat{z}} = n \hat{z}^{n-1}
\] (22.14)

\[ [e^{ik\hat{z}}, \hat{p}] = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} [\hat{z}^n, \hat{p}] = -k \sum_{n=0}^{\infty} \frac{(ik)^{n-1}}{(n-1)!} \hat{z}^{n-1} = -ke^{ik\hat{z}}, \]

and with this result,

\[ \dot{\hat{p}} = i [\hat{H}, \hat{p}] \]

\[ = ig \hat{a}^\dagger \hat{\sigma}^- [e^{-ik\hat{z}}, \hat{p}] + c.c. + ig \hat{a} \hat{\sigma}^- [e^{ik\hat{z}}, \hat{p}] + c.c. \]

\[ = -igk \hat{a}^\dagger \hat{\sigma}^- e^{-ik\hat{z}} + c.c. + igk \hat{a} \hat{\sigma}^- e^{ik\hat{z}} + c.c. \].

The quantum Langevin equations \([119]\) describing the dynamics of the internal and external degrees of freedom of the atom and the field are coupled,

\[
\begin{align*}
\dot{\hat{a}}_\pm &= (-\kappa + i \Delta_\varepsilon) \hat{a}_\pm - ig \hat{\sigma}^- e^{ik\hat{z}} + \eta_\pm \\
\dot{\hat{\sigma}}^- &= (-\gamma + i \Delta_a) \hat{\sigma}^- + ig(e^{ik\hat{z}} \hat{a}_+ + e^{-ik\hat{z}} \hat{a}_-) \hat{\sigma}_z \\
\dot{\hat{\sigma}}_z &= -2\gamma \hat{\sigma}_z + 2ig(e^{-ik\hat{z}} \hat{a}_+^\dagger + e^{ik\hat{z}} \hat{a}_-^\dagger) \hat{\sigma}^- - 2ig(e^{ik\hat{z}} \hat{a}_+ + e^{-ik\hat{z}} \hat{a}_-) \hat{\sigma}^+ \\
\dot{\hat{p}} &= \hat{p}/m \\
\dot{\hat{n}}_\pm &= i[\hat{H}, \hat{n}_\pm]
\end{align*}
\] (22.16)

We may also verify,

\[
\begin{align*}
\dot{\hat{n}}_+ &= i[\hat{H}, \hat{n}_+] \\
&= -i [\Delta_c \hat{a}_+^\dagger + g \hat{a}_+ \hat{\sigma}^- e^{-ik\hat{z}} + g \hat{a}_+ \hat{\sigma}^+ e^{ik\hat{z}} - \eta_+(\hat{a}_+ - \hat{a}_+^\dagger), \hat{n}_+] \\
&= (\eta_+ - ig e^{-ik\hat{z}} \hat{\sigma}^-) \hat{a}_+^\dagger + (\eta_+ + ig \hat{\sigma}^+ e^{ik\hat{z}}) \hat{a}_+, \nabla
\end{align*}
\] (22.17)

and hence conservation of momentum,

\[
[\hat{H}, \hbar k(\hat{n}_+ - \hat{n}_-) - \hat{p}] = \hbar k \eta_+ (\hat{a}_+^\dagger + \hat{a}_+) - \hbar k \eta_- (\hat{a}_-^\dagger + \hat{a}_-),
\] (22.18)

in the absence of pumping, \(\eta_+ = 0 = \eta_-\).

### 22.1.3 Adiabatic elimination of the excited state

Under certain conditions, however, the internal and external dynamics occur at very different time scales, which allows a decoupling of the differential equations \(^4\). When

\(^4\)In good cavity the limit the degrees of freedom of atomic excitation \(\hat{\sigma}^\pm\) drop out of the dynamics, in the bad cavity limit, the fields \(\hat{a}^\pm\) drop out of the dynamics.
the light fields are very detuned from atomic resonances, the internal dynamics of the atoms are very fast, that is, the internal state adapts very rapidly to the boundary conditions defined by the external state and the state of the light field. Therefore, the internal state has no separate dynamics of its own, and we can adiabatically eliminate the internal degrees of freedom. Thus, we can neglect correlations between degrees of freedom, \( \langle \hat{a}_z \hat{\sigma}^\pm \rangle = \langle \hat{a}_\pm \rangle \langle \hat{\sigma}^\pm \rangle \) etc. [468, 211].

We obtain the stationary solutions for \( t \to \infty \) in the same way as for the optical Bloch equations [see Eq. (14.86)], assuming in Eq. (22.16),

\[
\dot{\hat{\sigma}}^- = 0 = \dot{\hat{\sigma}}_z \tag{22.19}
\]

where \( \langle \hat{\sigma}^- \rangle = \rho_{21} \). Introducing the position-dependent Rabi frequency of the atom in the standing wave \(^5\),

\[
\hat{\Omega}(z) = 2g(e^{ikz} \hat{a}_+ + e^{-ikz} \hat{a}_-), \tag{22.20}
\]

we write,

\[
0 = (-\gamma + i\Delta_a)\hat{\sigma}^- + \frac{1}{2}i\hat{\Omega}\sigma_z \tag{22.21}
\]

\[
0 = -2\gamma - 2\gamma\hat{\sigma}_z + i\hat{\Omega}^\dagger\hat{\sigma}^- - i\hat{\Omega}\hat{\sigma}^+. \tag{22.22}
\]

These equations are solved by,

\[
\hat{\sigma}_z(\infty) = -\frac{2(\gamma^2 + \Delta_a^2)}{2(\gamma^2 + \Delta_a^2) + \Omega^\dagger\Omega} \tag{22.23}
\]

\[
\text{and} \quad \hat{\sigma}^-(\infty) = \frac{-i(\gamma + i\Delta_a)\hat{\Omega}}{2(\gamma^2 + \Delta_a^2) + \Omega^\dagger\Omega} \simeq \frac{-i(\gamma + i\Delta_a)}{2\Delta_a^2} \hat{\Omega}. \tag{22.24}
\]

Inserting the approximated expression for \( \hat{\sigma}^- \) into the equation of motion (22.16) for the light modes,

\[
\dot{\hat{a}}_\pm = (-\kappa + i\Delta_c)\hat{a}_\pm - ig\hat{\sigma}^-(\infty)e^{\mp ikz}\hat{a}_\pm + \eta_\pm \tag{22.25}
\]

\[
= (-\kappa + i\Delta_c - \frac{g^2\gamma}{\Delta_a^2} - \frac{ig^2}{\Delta_a})\hat{a}_\pm - \left(\frac{g^2\gamma}{\Delta_a^2} + \frac{ig^2}{\Delta_a}\right)e^{\mp ikz}\hat{a}_\pm + \eta_\pm, \tag{22.26}
\]

and for the atomic momentum,

\[
\dot{\hat{p}} = ig\hbar\hat{\sigma}^-(\infty)(\hat{a}_+ e^{-ikz} - \hat{a}_- e^{ikz}) - ig\hbar k\hat{\sigma}^+(\infty)(\hat{a}_+ e^{ikz} - \hat{a}_- e^{-ikz}) \tag{22.27}
\]

\[
= \frac{2\hbar k g^2}{\Delta_a^3}(\hat{a}_+^\dagger \hat{a}_+ - \hat{a}_-^\dagger \hat{a}_-) - \frac{2\hbar k g^2}{\Delta_a} (e^{2ikz}\hat{a}_+^\dagger \hat{a}_+ - e^{-2ikz}\hat{a}_+^\dagger \hat{a}_-). \tag{22.28}
\]

Defining the light-shift \( U_0 \) caused by only one photon and the scattering rate \( \gamma_0 \) by,

\[
U_0 = \frac{g^2}{\Delta_a} \quad \text{and} \quad \gamma_0 = \frac{\Gamma g^2}{\Delta_a^2}, \tag{22.29}
\]

\(^5\)Note that the factor of 2 ensure consistency with previous definitions of the Rabi frequency, such as in (15.22). Note also, that \([\hat{\Omega}, \hat{\Omega}^\dagger] = 8g^2 \neq 0\), but this is negligible when the fields are large enough to be considered as classical. On the other hand the quadratic terms \( \hat{\Omega}^\dagger\hat{\Omega} \) are negligible when they are small compared to \( \gamma^2 \) or \( \Delta_a^2 \).
with $\Gamma = 2\gamma$, we finally get a set of equations, where the internal degree of freedom of the atom has been eliminated,

$$
\begin{align*}
\hat{a}_\pm &= (\kappa - \gamma_0 + i\Delta_c - iU_0)\hat{a}_\pm - (\gamma_0 + iU_0)e^{\mp 2ikz}\hat{a}_\mp + \eta_\pm \\
\dot{\hat{p}} &= 2\hbar\kappa\gamma_0(\hat{a}_\uparrow \hat{a}_+ - \hat{a}_\uparrow \hat{a}_- + \eta_\pm)
\end{align*}
$$

(22.26)

### 22.1.3.1 Radiation pressure and the adiabatically approximated Hamiltonian

The impact of radiation pressure should be considered when the pumping laser is close to a resonance. Then $\gamma_0 \ll U_0$ is no longer satisfied [211], and we get one more term from the equation for the atomic force: $\propto \hbar\gamma_0(|\alpha_+|^2 - |\alpha_-|^2)$.

For the adiabatically approximated Hamiltonian we get immediately from (22.4) [409],

$$
\hat{H} = \frac{\hat{p}^2}{2m} + \sum_{\pm}(U_0 - \Delta_c)\hat{a}^\dagger_{\pm}\hat{a}_\pm + U_0(e^{-2ikz}\hat{a}^\dagger_+\hat{a}_- + e^{2ikz}\hat{a}_+\hat{a}^\dagger_-) - i\sum_{\pm}\eta_\pm(\hat{a}_\pm - \hat{a}^\dagger_\pm)
$$

(22.27)

as shown in Exc. 22.1.5.3. Note that dissipative terms are (naturally) absent from this Hamiltonian, so that it shall not be used for the description of radiation pressure. On the other hand, all coherent terms of the equations of motion can be derived from this Hamiltonian (22.27), and we can verify momentum conservation (22.18) and deduce transformation properties.

These equations, which we will call CARL equations for reasons that we will become clear in Sec. 22.3, describe the coupled dynamics of atoms being accelerated by the kick $e^{ikz}$ imparted by the photonic recoil received upon scattering a photon from one mode into the counterpropagating one. In the same time, the backscattering annihilates a photon $\hat{a}_\pm$ in one mode and creates a photon $\hat{a}^\dagger_\mp$ in the counterpropagating mode. From now on we will exclusively use the CARL equations.

Finally, let us summarize, how the operators act on states and observables of the coupled system, noting that the same transformation rules as for free and trapped atoms (4.108) also hold for the optical lattice,

$$
\begin{align*}
e^{ikz}|z\rangle &= |z\rangle, & e^{-ikz}\hat{z}e^{ikz} &= \hat{z} \\
e^{ikz}|p\rangle &= |p + \hbar k\rangle, & e^{-ikz}\hat{p}e^{ikz} &= \hat{p} + \hbar k \\
\hat{a}_\pm|\alpha\rangle &= \sqrt{\n\pm n - 1)|\alpha\pm n - 1\rangle, & e^{-ikz}\hat{H}(\hat{z}, \hat{p})e^{ikz} &= \hat{H}(\hat{z}, \hat{p} - \hbar k) \\
\hat{a}^\dagger_\pm|\alpha\rangle &= \sqrt{\n\pm n + 1)|\alpha\pm n + 1\rangle, & e^{-i\hat{p}/\hbar}\hat{H}(\hat{z}, \hat{p})e^{i\hat{p}/\hbar} &= \hat{H}(\hat{z} - \alpha, \hat{p})
\end{align*}
$$

(22.28)

The last relationship is verified in Exc. 22.1.5.4. For $ka = \pi$ the phase shift vanishes: $[e^{i\hat{p}/\hbar}, \hat{H}(\hat{z}, \hat{p})] = 0$.

The dynamics is given by the time evolutions,

$$
e^{-i\hbar\hat{H}_t}\hat{z}(0)e^{i\hbar\hat{H}_t}, \quad e^{-i\hbar\hat{p}(0)}e^{i\hbar\hat{H}_t}, \quad e^{-i\hbar\hat{n}(0)}e^{i\hbar\hat{H}_t}.
$$

(22.29)
In Exc. 22.1.5.5 we calculate the photon number superposition state resulting from a kick \( e^{i k \cdot \hat{z}} \).

### 22.1.4 Deriving the equations of motion

We have, in the previous sections, derived Heisenberg equations (22.16), respectively (22.26) which, together with the Schrödinger equation for the system’s state \( |\psi(t)\rangle \) or the master equation for the density operator \( \hat{\rho}(t) \) form an over-complete set. This section aims at providing a general recipe for choosing the right set of equations depending on two basic criteria for the nature of the degrees of freedom involved in the dynamics: (i) Do judge it necessary to treat the degree of freedom as quantum or may a classical description be sufficient; and (ii) Is the degree of freedom subject to dissipation (e.g. spontaneous emission of the electronic excitation, cavity decay of the field mode, or collisions messing up the center-of-mass motion), or not. The procedure, which will be applied throughout the remaining part of this chapter, leads to very different descriptions of the system depending on the specific parameter regime.

1. The procedure is generally applicable to coupled systems: We first need to identify all relevant degrees of freedom and set up the Hamiltonian, possibly eliminating irrelevant degrees of freedom, e.g. via adiabatic elimination or by tracing over them, if they contribute to dissipation. In the context of atoms coupled to a ring cavity, we assume our system to be in some state \(^6\)

\[
|\psi(t)\rangle = |r\rangle \otimes |\alpha_+\rangle \otimes |\alpha_-\rangle \otimes |i\rangle,
\]  

(22.30)

coupling the atomic motion, the light fields and the electronic excitation, although the electronic excitation \( |i\rangle \) is often eliminated adiabatically. The dissipative degrees of freedom related to vacuum modes leading to spontaneous emission and cavity decay, as well as collisions between moving atoms are traced away, but may be considered in the master equation for the density operator and in the Heisenberg equations, where the corresponding decay rates are added phenomenologically.

This first item has already been solved in the previous sections and led us to the Hamiltonian (22.4) and the corresponding Heisenberg equations (22.16), or the adiabatically approximated Hamiltonian (22.27) and the corresponding Heisenberg equations (22.26).

2. Now, we must decide which degrees of freedom \( B \) can be treated as classical. Typically, those are highly excited degrees of freedom (e.g. fast velocities of many photons in a mode). The corresponding operators can be substituted by their expectation value. Purely classical energy terms in the Hamiltonian can be ignored and removed. For the degrees of freedom \( \hat{A} \) we want to treat as quantum, we chose an appropriate common basis, which can be discrete \( \{|m\}\) where \( m \) is a complete set of quantum numbers. It can also be continuous \( \{|r\}\).

---

\(^6\)Throughout this chapter we will denote momentum states by the Greek letters \( |\mu\rangle \) or \( |\nu\rangle \). Photonic states will be labeled by the Latin letters \( |n\rangle \) or \( |m\rangle \). Electronic excitation states will be labeled by the Latin letters \( |i\rangle \) or \( |j\rangle \). Finally, expansion coefficients \( c_{\nu,i,n_+,n_-} \) of the state or of the density matrix elements will sometimes be emphasized in red.
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or a combination of both \(|r, m\rangle\). Now, we need to expand all operators on the chosen basis.

3. For the quantized degrees of freedom must now decide, whether they all evolve coherently or whether they are subject to dissipation. In the first case, perform steps A4 to A7, in the second case, perform steps B4 to B7.

A4. In the case of coherent dynamics, we expand the state \(|\psi(t)\rangle\) on the whole basis. For example, expanded on a partially continuous basis, the coupled atom-ring cavity state may read,

\[
|\psi(t)\rangle = \sum_{n_+, n_-} \int d^3r \ c_{n_+, n_-, i}(r, t) |r\rangle \otimes |n_+\rangle \otimes |n_-\rangle \otimes |i\rangle , \tag{22.31}
\]

where \(\langle r, \alpha_+, \alpha_-, i |\psi(t)\rangle = c_{n_+, n_-, i}(r, t)\) are the expansion coefficients depending on photon numbers \(n_{\pm}\) in the counterpropagating light modes, the electronic excitation state \(i\), and the atomic position \(r\) treated in terms of a continuous wavefunction in space \(^7\). When we want to treat the atomic motion as being quantized in discrete momentum states labeled by some integer number \(\mu\), we adopt the notation,

\[
|\psi(t)\rangle = \sum_{\nu, n_+, n_-} c_{\nu, n_+, n_-, i}(t) |\nu\rangle \otimes |n_+\rangle \otimes |n_-\rangle \otimes |i\rangle , \tag{22.32}
\]

where \(\langle \nu, \alpha_+, \alpha_-, i |\psi(t)\rangle = c_{\nu, n_+, n_-, i}(t)\) are the new expansion coefficients.

A5. Next, we write down the Schrödinger equation for the state \(|\psi(t)\rangle\), insert the expansion on the basis, and we derive a linear set of equation of motion for the expansion coefficients \(\dot{c}\{m\}(r)\). This set governs the dynamics of the quantum degrees of freedom.

A6. The dynamics of the classical degrees of freedom \(B\) is obtained by taking the expectation values of the Heisenberg equations. Here, we need to take care that the quantum degrees of freedom appearing in the Heisenberg equations are expressed by their expansions.

A7. The coupled set of equations for the expectation values of projectors of the system into a particular state, that is, \(\hat{c}_{\{m\}}(r)\) (respectively, \(\hat{c}_{\{m\}}(r)\)), and of observables \(B\) really represents all we need to describe the system dynamics and to simulate it numerically. Hack everything into your PC, pronto!

B4. In the case of dissipative dynamics, derive the master equation obeying commutation rules for all quantized degrees of freedom including the Lindblad terms and expand every quantized degrees of freedom on the common basis, we do the same expansions, but,

\[
\dot{\hat{\rho}}(t) = |\psi(t)\rangle \langle \psi(t) | . \tag{22.33}
\]

B5. Derive the linear set of equation of motion for the matrix elements \(\dot{\hat{c}}_{\{m\}, \{n\}}\).

\(^7\)Note that, in the absence of other quantum numbers, we rather use to write \(c(r) = \psi(r)\).
B6. Take the expectation values \( \text{Tr} \, \hat{\rho} \hat{B} \) of the Heisenberg equations for all degrees of freedom to be handled classical as expanding the quantized degrees of freedom on their basis.

B7. The coupled set of equations for \( \dot{\rho}_\{m\}, \{n\} \) and \( \hat{B} \) is sufficient to describe the dynamics of the system, hack everything into your PC, pronto!

Let us apply the procedure to the simplest case that the electronic excitation has been adiabatically eliminated and all remaining degrees of freedom can be treated classical. Then we do not require a Hamiltonian, nor the Schrödinger equation. We just take the expectation value of the Heisenberg equations (22.26) for all degrees of freedom which is easy to do, because there is no quantum state to be expanded: we just can replace the operators by \( c \)-numbers,

\[
\dot{\alpha}_\pm = \left( -\kappa + i \Delta_c - i U_0 \right) \alpha_\pm - i U_0 e^{\mp 2ikz} \alpha_\mp + \eta_\pm \\
\dot{\rho} = 2i \hbar k U_0 (e^{-2ikz} \alpha_+^\dagger \alpha_- - e^{2ikz} \alpha_+ \alpha_-^\dagger ) \tag{22.34}
\]

These totally classical equations, called CARL equations, will be studied in the subsequent sections, while a thorough discussion of partially quantized equations of motion is postponed to Sec. 22.5.

### 22.1.4.1 CARL as a beam splitter

Neglecting spontaneous emission, \( \gamma_0 = 0 \), cavity pumping, \( \eta = 0 \), cavity decay, \( \kappa = 0 \), and cavity detuning, \( \Delta_c = 0 \), the CARL equations in the adiabatic approximation can be derived from the following Hamiltonian,

\[
\hat{H} = \frac{\hat{p}^2}{2m} + \sum_{\pm} U_0 \hat{a}_\pm^\dagger \hat{a}_\pm + U_0 (e^{-2ikz} \hat{a}_+^\dagger \hat{a}_- + e^{2ikz} \hat{a}_+ \hat{a}_-^\dagger ) \tag{22.35}
\]

and read,

\[
\dot{\hat{a}}_\pm = -i U_0 \hat{a}_\pm - i U_0 e^{\mp 2ikz} \hat{a}_\mp \\
\dot{\hat{p}} = 2i \hbar k U_0 (e^{-2ikz} \hat{a}_+^\dagger \hat{a}_- - e^{2ikz} \hat{a}_+ \hat{a}_-^\dagger ) \tag{22.36}
\]

or with the substitution \( \hat{b}_\pm \equiv \hat{a}_\pm e^{iU_0 t} \),

\[
\dot{\hat{b}}_\pm = -i U_0 e^{\mp 2ikz} \hat{b}_\mp \\
\ddot{\hat{b}}_\pm = -U_0^2 \hat{b}_\pm - 2k \hat{z} U_0 e^{\mp 2ikz} \hat{b}_\mp \tag{22.37}
\]

we see that, if the motion weren’t a dynamic variable, \( \dot{z} = 0 \), the field amplitudes would just perform harmonic oscillations.

On the other hand, with the substitution \( \hat{c} \equiv \hat{a}_+ e^{ikz} + \hat{a}_- e^{-ikz} \), the complete Hamiltonian rephrased as,

\[
\hat{H} = \frac{\hat{p}^2}{2m} + U_0 \hat{c}^\dagger \hat{c} \tag{22.38}
\]

Here, we see that, if the motion described by \( (\hat{z}, \hat{p}) \) weren’t a dynamic variable, our system would simply be a harmonic oscillator vibrating with the frequency \( U_0 \).

---

8Provided we are allowed to commute the operators \( \hat{z} \) and \( \hat{a}_\pm \).
22.1.5 Exercises

22.1.5.1 Ex: Origin of quantum correlations
Derive the Hamiltonian (22.2) from the JCM Hamiltonian (15.22) transforming it into the co-rotating frame.

22.1.5.2 Ex: Linear pumping of a cavity mode
Study how the Hamiltonian $\hat{H}_{\text{pmp}} = \eta \hat{a}^\dagger - \eta \hat{a}$, describing linear pumping of a cavity mode, fills the cavity with photons in the absence of dissipation (see also (21.4)).

22.1.5.3 Ex: The adiabatically approximated Hamiltonian
a. Derive the adiabatically approximated Hamiltonian (22.27) from the total Hamiltonian (22.4).
b. Derive the CARL equations (22.26) directly from the adiabatically approximated Hamiltonian.
c. Show that, in the absence of pumping, the energy stored in the light fields is conserved separately from the mechanical energy of the atom.
d. Verify momentum conservation.

22.1.5.4 Ex: Periodicity of a lattice
Calculate $e^{i a^p} e^{2ikz} e^{-ia^p}$.

22.1.5.5 Ex: Periodicity of a lattice
Assume a symmetrically pumped ring cavity in equilibrium with an atom initially at rest. What photonic states are generated in the counterpropagating light modes, when the atom is kicked by an external force imparting a sudden recoil of $\hbar k_{ck}$.

22.2 Solutions for classical dynamics, cavity-cooling of atoms

For atoms much hotter than the recoil limit and macroscopic light intensities we may replace the quantum operators by complex numbers $z \equiv \hat{z}$, $\alpha_\pm \equiv \hat{a}_\pm$ and $\rho_{21} = \hat{\sigma}^-$. The classical equations of motion (22.34) for the coupled system of a single atom confined at the position $r = z$ of the dipolar potential of a ring cavity can be cast into the form,

$$
\begin{pmatrix}
\dot{\alpha}_+ \\
\dot{\alpha}_-
\end{pmatrix} =
\begin{pmatrix}
-\kappa - \gamma_0 + i(\Delta_c - U_0) & -(\gamma_0 + iU_0)e^{-2ikz} \\
-(\gamma_0 + iU_0)e^{2ikz} & -\kappa - \gamma_0 + i(\Delta_c - U_0)
\end{pmatrix}
\begin{pmatrix}
\alpha_+ \\
\alpha_-
\end{pmatrix}
+ \begin{pmatrix}
\eta_+ \\
\eta_-
\end{pmatrix},
$$

$$
\dot{p} = 2\hbar k_0 (\alpha_+ \alpha_+^* - \alpha_- \alpha_-^*) + 2\hbar kU_0 (\alpha_+^* \alpha_- e^{-2ikz} - \alpha_+ \alpha_-^* e^{2ikz})
$$

(22.39)

Recalling that $\alpha_\pm^*, \alpha_\pm$ is the number of photons in the respective mode, we can interpret this equation as a rate equation: The number of photons in a mode $\alpha_\pm$ changes by
CHAPTER 22. ATOMIC MOTION IN OPTICAL CAVITIES

photon losses at a rate $\kappa$ from resonator, or by gain due to backscattering from the counterpropagating mode, or by pumping with an external incident light field at rate $\eta_+$. The equations (22.39) completely describe our coupled atom-cavity system. They are totally classical and work for both, atoms and macroscopic particles.

22.2.1 Classical derivation of coupled atom-cavity equations

Since, the equations of motion (22.39) are obviously classical in all degrees of freedom, it is not surprising that they can be derived with entirely classical arguments. We consider a ring resonator with one coupling mirror ($r_{in}, t_{in}$) and a scatterer located within the mode volume of the resonator ($r_{\beta}, t_{\beta}$) = ($1 + i\beta, 1 + i\beta$), such that $r_{\beta}^2 + t_{\beta}^2 = 1$. The scatterer represents the backscattering of photons between the counter propagating modes of the resonator by the atoms. The incident field $E_{in}$ produces, in the cavity, field amplitudes of $\alpha_{\pm}$ for the co- and counterpropagating waves. As in (22.1) and (22.3), we normalize the amplitudes by the numbers of photons $n_{\pm} = |\alpha_{\pm}|^2$. After a turn $\tau$ through the mode volume we have in the position of the coupling mirror the field

\[
\begin{align*}
\alpha_+(t + \tau) &= r_{in}(1 + i\beta)e^{ikL}\alpha_+(t) + i\beta r_{in}^2 e^{2ikL-2ikz}\alpha_-(t) + t_{in}\alpha_{in}^+(t) \\
\alpha_-(t + \tau) &= r_{in}(1 + i\beta)e^{ikL}\alpha_+(t) + i\beta e^{2ikz}\alpha_+(t) + t_{in}(1 + i\beta)e^{ikL}\alpha_{in}^-(t) .
\end{align*}
\]

$L$ is the total length of the annular cavity. Obviously, we have $kL = \omega/\delta$. In the vicinity of a resonance we have, $\Delta_c \ll \delta$, and the quantity $\omega/\delta$ is almost integer, $\omega \approx 2\pi n\delta - \Delta_c$, such that we can expand the exponential, $e^{ikL} = 1 - i\Delta_c/\delta$. Thus, we obtain,

\[
\begin{align*}
\tau \dot{\alpha}_+ &= -\left[1 - r_{in}(1 + i\beta)e^{ikL}\right]\alpha_+ + i\beta r_{in}^2 e^{2ikz}\alpha_- + t_{in}\alpha_{in}^+ \\
\tau \dot{\alpha}_- &= -\left[1 - r_{in}(1 + i\beta)e^{ikL}\right]\alpha_- + i\beta e^{2ikz}\alpha_+ + t_{in}(1 + i\beta)\alpha_{in}^- .
\end{align*}
\]

We now connect the transmission of the coupling mirror $t_{in}$ with the decay constant $\kappa$ assuming that the light can only leave the cavity through this mirror. We define,

\[
\kappa \equiv \frac{T}{\tau} \tag{22.42}
\]

as the part of the light lost during one round trip. Thus, $t_{in}^2 = \sqrt{T} \approx \sqrt{\pi/F} = \sqrt{\kappa/\delta}$. Besides that, $t_{in}$ is very small, such that,

\[
t_{in}^2 = 1 - t_{in}^2 \approx 2(1 - r_{in}) . \tag{22.43}
\]

Thus, the first factor is,

\[
\begin{align*}
\delta \left[1 - r_{in}(1 + i\beta)e^{ikL}\right] &\approx \delta - \delta \left(1 - t_{in}^2/2\right)(1 + i\beta)(1 + i\Delta_c/\delta) \\
&\approx \kappa/2 + i\beta - i\Delta_c \approx -\kappa/2 .
\end{align*}
\]

It gives the cavity losses for the two modes at one round trip. We assume here that losses can only occur via the coupling mirror. However, all losses can be included in a single appropriate $\kappa$. There are usually other losses due to scattering on the surface of
the mirrors or absorption by the atoms. Finally, we obtain for weak atomic reflection and in resonance, that is, for $\beta \ll \kappa$ and $\Delta c = 0$ the system of equations,

$$\begin{align*}
\dot{\alpha}_+ &= -\kappa \alpha_+ + i \delta \beta (1 - t_{in}^2) e^{-2ikz} \alpha_- + \sqrt{\kappa \delta} \alpha_{in}^+ \\
\dot{\alpha}_- &= -\kappa \alpha_- + i \delta e^{2ikz} \alpha_+ + (1 + i \beta) \sqrt{\kappa \delta} \alpha_{in}^-
\end{align*}$$

(22.45)

To calculate the value of $\beta$, we need the reflection coefficient of a single atom. It depends on the polarizability,$$
\eta_{\alpha} = \frac{k}{\pi w^2} \frac{\alpha_{pol}}{\varepsilon_0} = \left( \frac{\sigma_0}{\pi w^2} \frac{\Gamma}{2\Delta_a} \right).
$$

(22.46)

The optical potential to which the atom is exposed is,$$
\phi = \frac{I \alpha_{pol}}{2c} \frac{\varepsilon_0}{\varepsilon_0},
$$

(22.47)

where we write the intensity of light as,$$
I = 2\varepsilon_0 c E_1^2 |\alpha_+ e^{ikZ} + \alpha_- e^{-ikZ}|.
$$

(22.48)

We normalize once more to the field generated by a single photon, $E_1 = \sqrt{\hbar \omega/2\varepsilon_0 V_m}$ with the mode volume, $V_m = \frac{\pi}{2} L w^2$. On the other hand, the potential can be determined directly through the Rabi frequency,$$
\phi(r) = \frac{\hbar \Omega(r)^2}{4\Delta_a},
$$

(22.49)

The Rabi frequency $\Omega(r)^2 = 4g^2 |\alpha_+ e^{ikZ} + \alpha_- e^{-ikZ}|^2$ is normalized to the frequency of Rabi generated by a photon $g$. Introducing the frequency shift (light-shift) by photon, $U_0 = \frac{g^2}{\Delta_a}$, we can also write,$$
\phi(r) = \hbar U_0 |\alpha_+ e^{ikZ} + \alpha_- e^{-ikZ}|^2.
$$

(22.50)

A comparison of the above equations gives,$$
\eta_{\alpha} = \frac{i U_0}{\delta}.
$$

(22.51)

With an atom in the resonator, we have,$$
\beta = \frac{i U_0}{\delta}.
$$

(22.52)

We define for convenience, $\eta_{\pm} = \sqrt{\kappa \delta} \alpha_{\pm}^{in}$ and we suppose, that $t_{in} \ll 1$, $r_{\beta} \ll 1$ and $\beta \ll 1$. This ultimately leads to the result,$$
\dot{\alpha}_\pm = -\kappa \alpha_\pm - i U_0 e^{\mp 2ikz} \alpha_\mp + \eta_{\pm}.
$$

(22.53)

The atom at position $z$ feels the classical potential of the stationary light wave, and therefore the dipole force,$$
F = -\nabla \phi = -\hbar U_0 \nabla Z = 2i U_0 |\alpha_+ e^{ikZ} + \alpha_- e^{-ikZ}|^2.
$$

(22.54)

Consequently, the dynamics of the scatterer is given by,$$
m \ddot{z} = -2i \hbar k U_0 (\alpha_+ \alpha_-^* e^{2ikz} - \alpha_+^* \alpha_- e^{-2ikz}).
$$

(22.55)
22.2.2 Solutions for forced atomic motion

The equations (22.39) treat the coordinates of the atom as dynamic variables influenced by the amplitudes and phases of the light fields. But we can also consider the coordinates being fixed by imposed boundary conditions. This situation occurs, for example, for very heavy scatterers, as in the case of imperfections on the surfaces of the mirrors of the cavity. Such imperfections can scatter light both out of the cavity and into the reverse mode. In laser gyroscopes this backscattering may induce a locking of counterpropagating modes and hamper their proper operation.

22.2.2.1 Stationary solutions and spectra

Considering the atom fixed in space, \( \dot{x} = 0 = \dot{p} \), we can concentrate on solving the equations of motion (22.39) only for the fields. As a first approach, we look for stationary solutions, being aware that they do not always exist, as we will see later in the discussion of the proper CARL effect. In the Exc. 22.2.3.1 we derive the stationary solutions of the equations:

\[
\alpha_{\pm}(\infty) = \eta_{\pm} \frac{\chi - iU_\gamma \xi_{\pm}^1}{\chi^2 + U_\gamma^2}. \quad (22.56)
\]

With the abbreviations,

\[
\chi \equiv \kappa + \gamma_0 - i(\Delta_c - U_0) \quad , \quad \xi \equiv e^{-2ikz} \frac{\eta_-}{\eta_+} \quad , \quad U_\gamma \equiv U_0 - i\gamma_0 \quad (22.57)
\]

the stationary solution can be written,

\[
\alpha_{\pm}(\infty) = \eta_{\pm} \frac{\chi - iU_\gamma \xi_{\pm}^1}{\chi^2 + U_\gamma^2}. \quad (22.58)
\]

We note that a phase shift \( \phi \) in the pump fields only shifts the phase of the quantity \( \xi = e^{-2ikz - 2i\phi} \frac{\eta_-}{\eta_+} \).

22.2.2.2 Splitting of the cavity resonance

The equation (22.39) can be written as follows,

\[
\dot{\alpha} = W\alpha + i\eta, \quad (22.59)
\]

where \( \alpha \) and \( \eta \) regroup the amplitudes \( \alpha_{\pm} \) and \( \eta_{\pm} \). This equation takes the form of a Schrödinger equation, where,

\[
W \equiv \begin{pmatrix} U_0 - \Delta_c - i(\kappa + \gamma_0) & (U_0 - i\gamma_0)e^{-2ikz} \\ (U_0 - i\gamma_0)e^{2ikz} & U_0 - \Delta_c - i(\kappa + \gamma_0) \end{pmatrix} \quad (22.60)
\]

would be the Hamiltonian describing the coupling between counterpropagating modes. The eigenvalues of this matrix are,

\[
W^{(1,2)} = 2(U_0 - i\gamma_0) - \Delta_c - i\kappa, \quad -\Delta_c - i\kappa. \quad (22.61)
\]
This *normal mode splitting* of the cavity results from the coupling of the two cavity modes $\hat{a}_+^{\dagger}\hat{a}_-$. Obviously, the energies and widths of the eigenvalues do not depend neither on the pump intensities $\eta_\pm$ nor the z-position of the atom. On the other hand, the spectral behavior of $\alpha_\pm$, and hence the observable quantities, such as the transmission

$$T_\pm \equiv \left| \frac{\kappa \alpha_\pm}{\eta_\pm} \right|^2$$ (22.62)

depend on these parameters. In the Exc. 22.2.3.2 we will calculate the spectrum by the condition $0 = \frac{\partial}{\partial \Delta_c} \alpha_\pm(\infty)$.

In the following, we will discuss two relevant cases: unidirectional pumping and symmetrical pumping.

### 22.2.2.3 Unidirectional pumping

For unilateral pumping, $\eta_- = 0$, the equation (22.58) simplifies to,

$$\alpha_+(\infty) = \eta_+ \frac{\chi}{\chi^2 + U_0^2} \quad \text{and} \quad \alpha_-(\infty) = \eta_+ \frac{iU_0 e^{2ikz}}{\chi^2 + U_0^2}.$$ (22.63)

These formulas show that, for weak coupling, $U_0 \ll \kappa$, the counterpropagating mode receives little light. On the other side, for strong coupling (or very high finesse) and $\Delta_c = 0$, the intensity is equally distributed, $|\alpha_+|^2 = |\alpha_-|^2 = \frac{\eta_+^2}{2\kappa}$.

We calculate the splitting of normal modes in Exc. 22.2.3.3.

The counterpropagating modes form, by interference, a standing light wave giving rise to a dipole potential in the form of a one-dimensional optical lattice. Defining the phase $\theta$ through,

$$\alpha_+ \equiv |\alpha_+| \quad \text{and} \quad \alpha_- \equiv |\alpha_-| e^{-i\theta},$$ (22.64)

we verify by the equations (22.1) and (22.3),

$$E^+(z, t) = E_1 |\alpha_+(t)| e^{ikz} + E_1 |\alpha_-(t)| e^{-i\theta(t)} e^{-ikz},$$ (22.65)

and,

$$\frac{1}{2e_0E_1^2} t(z, t) = \frac{1}{E_1^2} E^+(z, t) E^-(z, t) = |\alpha_+(t)|^2 + |\alpha_-(t)|^2 + 2|\alpha_+(t)||\alpha_-(t)| \cos(2kz + \theta).$$ (22.66)

That is, the phase indicates the positions of the potential maxima. Inserting the stationary solution for unilateral pumping (22.63), we derive the expression,

$$\tan \theta = \frac{\text{Im} \alpha_+(\infty) \alpha_+^{\star}(\infty)}{\text{Re} \alpha_+(\infty) \alpha_+^{\star}(\infty)} = \frac{\text{Im} \chi e^{-2ikz}}{\text{Re} \chi e^{-2ikz}} = \frac{\kappa \cos 2kz + (U_0 - \Delta_c) \sin 2kz}{\kappa \sin 2kz - (U_0 - \Delta_c) \cos 2kz},$$ (22.67)

The splitting is not exactly the *vacuum Rabi splitting*, which occurs when the excitation can not be eliminated adiabatically. The vacuum Rabi splitting results from the Jaynes-Cummings [593, 130] and is caused by the coupling of internal and external states $\hat{a}^{\dagger}\hat{\sigma}$.

This observation explains why perturbing effects such as backscattering from mirrors imperfections are dramatically magnified when the finesse is high. 

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9 The splitting is not exactly the *vacuum Rabi splitting*, which occurs when the excitation can not be eliminated adiabatically. The vacuum Rabi splitting results from the Jaynes-Cummings [593, 130] and is caused by the coupling of internal and external states $\hat{a}^{\dagger}\hat{\sigma}$.

10 This observation explains why perturbing effects such as backscattering from mirrors imperfections are dramatically magnified when the finesse is high.
Or in other words, the phase of light determines the equilibrium position of the atom (or vice versa). Two cases are interesting: (i) For $\Delta_c = 0$ and $U_0 \gg \kappa$ the condition (22.67) turns into $\tan \theta = -\tan 2kx$. In this case, the phase of the backscattered field adjusts in such a way, that the atom stays at the valleys of the anti-nodes. (ii) For $\Delta_c = U_0$ (or alternatively, when $\kappa \gg U_0, \Delta_c$) the condition (22.67) turns into $\tan \theta = -\tan(2kx + \frac{\pi}{2})$, such that the atom is at half height of the potential slope, exactly at the position, where it is able to backscatter the maximum of photons from the pumped mode $\alpha_+$ to the mode $\alpha_-$. 

Figure 22.2: (code) (columns 1 and 2) Steady state field values according to (22.56) for bidirectional pumping with a single scatterer located at $\phi$. (columns 3 and 4) Same for unidirectional pumping. Here the location of the scatterer does not matter.

**Example 81 (Resonant case):** Assuming that the cavity is in resonance, $\Delta_c = 0$, and pumped in a single direction, $\eta_- = 0$, neglecting spontaneous emission, $\gamma_0 = 0$, and assuming low backscattering rates, $U_s \ll \kappa$, 

$$
\alpha_+(\infty) \simeq \frac{\eta_+}{\kappa} \quad \text{and} \quad |\alpha_- (\infty)| = \frac{U_s}{\kappa} |\alpha_+(\infty)| .
$$

Looking at short times, we find that the dynamics of the unpumped mode is delayed, since,

$$
\dot{\alpha}_+(0) \simeq \eta_+ \quad \text{and} \quad \dot{\alpha}_-(0) \simeq -iU_s \alpha_+ e^{-2\kappa x},
$$

giving,

$$
\alpha_+(0) \simeq \eta_+ t \quad \text{and} \quad \alpha_-(0) \simeq -iU_s \eta_+ \frac{t^2}{2} e^{-2\kappa x} .
$$

The complete solution of the equations (22.39) with unidirectional pumping, $\eta_- = 0$, will be derived in Exc. 22.2.3.4.
22.2. Solutions for Classical Dynamics, Cavity-Cooling of Atoms

22.2.2.4 Symmetric pumping

Now, we assume equal intensities for the pumps, $\eta_\pm(t) = \eta e^{\pm i \phi(t)}$, such that $\xi = e^{-2 i k z - i \phi}$. Then, equation (22.58) simplifies to,

$$\alpha_\pm(\infty) = \eta_\pm \frac{\chi - i \eta \xi_\pm}{\chi^2 + \eta^2} = \eta \frac{\chi - i \eta U_0 e^{\mp 2 i k z \mp i \phi}}{\chi^2 + \eta^2 U_0^2}.$$  (22.68)

The potential is calculated in the same way as in (22.66). The coherences are,

$$\alpha_\pm(\infty) \alpha^*_\pm(\infty) = \eta^2 \frac{(\kappa + i \Delta_c + 2 U_0 e^{\pm ikz} \sin k z)(\kappa - i \Delta_c + 2 U_0 e^{\mp ikz} \sin k z)}{(\kappa^2 + 2 U_0 \Delta_c - \Delta_c^2 + i \kappa^2 (U_0 - \Delta_c)^2)}$$  (22.69)

$$e^{\pm 2 i k z} = \frac{\alpha_\pm \alpha^*_\pm}{|\alpha_\pm \alpha^*_\pm|^2}$$

such that the relative phase of the counter-propagating waves adjusts itself to,

$$\tan \theta = \frac{\text{Im} \alpha_+(\infty) \alpha^*_+(\infty)}{\text{Re} \alpha_+(\infty) \alpha^*_+(\infty)} = \frac{\kappa^2 \sin 2 \phi + 4 U_0^2 \sin^2(k z + \phi) \sin 2 k z}{\kappa^2 \cos 2 \phi - 4 U_0^2 \sin^2(k z + \phi) \cos 2 k z}.$$  (22.70)

The quantity $\eta^2 / \kappa^2$ denotes the number of intracavity photons. According to the formula (22.70), for a weak atom-field coupling, $U_0 \ll \kappa$, the phase adjusts itself to the external pumps, $\theta \rightarrow 2 \phi$, while for strong coupling, it adjusts to the position of the atom, $\theta \rightarrow 2 k z$.

Example 82 (‘Pulling’ of the optical mode by the atom): We study the case $U_0 \simeq \kappa$ considering $\gamma_0 = 0 = \Delta_c$ and a particular external phase [212], $\phi = \pi / 2$,

$$\alpha_\pm(\infty) = \pm \eta \frac{\kappa + i U_0 \pm U_0 e^{\pm 2 i k z}}{\kappa^2 + 2 i \kappa U_0}$$  (22.71)

$$\theta(\infty) = \arctan \frac{-4 U_0^2 \cos^2 k z \sin 2 k z}{\kappa^2 + 4 U_0^2 \cos^2 k z \cos 2 k z} \simeq \arctan \frac{-8 U_0^2}{\kappa^2 + 4 U_0^2 k z},$$

expanding the last formula around $k z = 0$. Fig. 22.3 shows how, with the increase in the coupling force between the field and the atoms, $U_0$, the phase tends to lock to the atomic position. However, the phase imposed by the external pump competes for this privilege. Curiously, this is independent of laser power, but depends only on the ratio between $U_0$ and $\kappa$.

22.2.2.5 Time-dependent solution without pump

To calculate the homogeneous time-dependent solution of the equation of motion of the ring cavity with $\eta_\pm = 0$, we solve the Schrödinger equation (22.59) the way we learned in quantum mechanics. We start by diagonalizing the matrix (22.60),

$$W = \begin{pmatrix} U_0 - i \kappa & U_0 e^{-2 i k z} \\ U_0 e^{2 i k z} & U_0 - i \kappa \end{pmatrix}$$  (22.72)

$$= \begin{pmatrix} e^{-2 i k z} & -e^{-2 i k z} \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 2 U_0 - i \kappa & 0 \\ 0 & -i \kappa \end{pmatrix} \begin{pmatrix} e^{-2 i k z} & -e^{-2 i k z} \\ 1 & 1 \end{pmatrix}^{-1} = U E W U^{-1},$$
where $E_W$ is the matrix of eigenvalues and $U$ a unitary transformation. So,

$$\bar{\alpha} = e^{-iWt} \bar{\alpha}_0 = U e^{-iE_Wt} U^{-1} \bar{\alpha}_0$$

(22.73)

We’ll see an alternative calculation in Exc. 22.2.3.5. We calculate the coherence by,

$$\alpha_+^+ (t) \alpha_-^* (t) = e^{-2\kappa t} \left[ (\alpha_0^+ + \alpha_0^-) \cos^2 U_0 t + e^{-2\kappa z} \sin^2 U_0 t \right] + \frac{1}{2} (\alpha_0^2 - \alpha_0^-) t e^{-2\kappa z} \sin 2U_0 t$$

(22.74)

making the transition to the Lamb-Dicke regime by $z \to 0$. The phase of the standing wave is,

$$\tan \theta = \frac{\text{Im} \alpha_+^+ (t) \alpha_-^* (t)}{\text{Re} \alpha_+^+ (t) \alpha_-^* (t)} \xrightarrow{z \to 0} \frac{\alpha_0^2 - \alpha_0^-}{2\alpha_0^+ + \alpha_0^-} \sin 2U_0 t .$$

(22.75)

We see that, in resonance and without pumping, the field adjusts its phase to the atom and also decays with the rate $\kappa$, while the atom redistributes the photons between modes with the (Rabi-)frequency $2U_0$. The formula (22.75) does not show any damping of the phase dynamics in the Lamb-Dicke regime. Thus, in the absence of pumping, the cavity dissipation reduces only the field amplitudes, but does not damp the adjustment of the phase to the atomic position.

### 22.2.2.6 Time-dependent solution with fixed pump

To find the complete solution of the inhomogeneous Schrödinger equation (22.59), we first calculate the stationary solution,

$$\bar{\alpha}(\infty) = -iW^{-1} \bar{\eta} .$$

(22.76)

This particular solution of the inhomogeneous equation, added to the general solution of the homogeneous equation, gives the general solution of the inhomogeneous Schrödinger equation,

$$\bar{\alpha}(t) = e^{-iWt} \bar{\alpha}(0) + (1 - e^{-iWt}) \bar{\alpha}(\infty) .$$

(22.77)
We derive and analyze this solution in the Exc. 22.2.3.6.

### 22.2.2.7 Forced atomic vibration (inhomogeneous time-dependent solution)

We now assume, that the atom is forced to vibrate by an external force. The vibration is described by,

\[ k_z = k_{z0} \sin \omega t \].

We consider fast oscillations with frequency, \( \omega \gtrsim k v = \omega k_{z0} \gg \kappa \), and small excursions, \( 1 \gtrsim k_{z0} \). In this (Lamb-Dicke) regime the Bessel-expansion yields \( e^{\pm 2ik_{z0} \sin \omega t} = \sum_n J_n(\pm 2k_{z0})e^{in\omega t} \simeq J_0(2k_{z0}) \pm 2iJ_1(2k_{z0}) \sin \omega t \simeq 1 \pm 2ik_{z0} \sin \omega t \). The differential equation for the cavity-field (22.27) can then be written:

\[ \dot{\alpha}_\pm = (L - 2ix \sin \omega t)\alpha_\pm + \eta_\pm , \]  

where,

\[ L = \begin{pmatrix} -\kappa - iU_0 & -iU_0J_0 \\ -iU_0J_0 & -\kappa - iU_0 \end{pmatrix} \quad \text{and} \quad X = \begin{pmatrix} 0 & -iU_0J_1 \\ iU_0J_1 & 0 \end{pmatrix} . \]  

We insert the ansatz \( \alpha_\pm = \sum_n a_\pm^{(n)} e^{in\omega t} \), where \( a_\pm^{(0)} = 0 \), into the equation and project onto the basis \( e^{in\omega t} \):

\[ in\omega \sum_n a_\pm^{(n)} e^{in\omega t} = (L - X(e^{i\omega t} - e^{-i\omega t})) \sum_n a_\pm^{(n)} e^{in\omega t} + \eta_\pm \]  

\[ \Rightarrow (L - in\omega)\alpha_\pm^{(n)} + X(\alpha_\pm^{(n+1)} - \alpha_\pm^{(n-1)}) = -\eta_\pm \delta_{n0} . \]  

We define operators \( S^{\dagger}_n \) by \( a_\pm^{(n+1)} = S^{\dagger}_n a_\pm^{(n)} \) for \( n \geq 0 \) and \( a_\pm^{(n-1)} = S^{\dagger}_n a_\pm^{(n)} \) for \( n \leq 0 \) and obtain,

\[ [L - in\omega + X(S^{\dagger}_n - S_n^\dagger)] \alpha_\pm^{(n)} = -\eta_\pm \delta_{n0} . \]  

For \( n = 0 \), we get,

\[ \alpha_\pm(\infty) = \alpha_\pm^{(0)} = - \left[ L + X(S^{\dagger}_0 - S_0^\dagger) \right]^{-1} \eta_\pm . \]  

If we substitute in equation (22.81) \( \alpha_\pm^{(n)} = S^{\dagger}_{n-1} a_\pm^{(n-1)} = S^{\dagger}_{n+1} a_\pm^{(n+1)} \), we get for \( n \gtrsim 0 \),

\[ S^{\dagger}_{n-1} = [L - in\omega + XS^{\dagger}_n]^{-1} X \quad \text{and} \quad S^{\dagger}_{n+1} = [L - in\omega - XS^{\dagger}_n]^{-1} X . \]  

By recursive substitution of the lower into the upper equation, the stationary solution can now be written by means of continued fractions,

\[ S^{\dagger}_0 = \frac{1}{L - in\omega \pm \frac{1}{L - 2in\omega \pm X}} X . \]  

\( \alpha_\pm(\infty) \) gives us the stationary solution of the differential equation, time-averaged over an oscillation period.
If we are deep in the Lamb-Dicke regime, we need only consider the first order of the continued fractions. We set \( S_0^{\uparrow\downarrow} = 1 \) and obtain the simplified equations,

\[
S_0^{\uparrow 0} = \left[ L - i\omega + X \right]^{-1} X \quad \text{and} \quad S_0^{\downarrow} = \left[ L - i\omega - X \right]^{-1} X \tag{22.86}
\]

\[
\alpha_{\pm}^{(0)} = -\left[ L + X \left( S_0^{\uparrow 0} - S_0^{\downarrow}\right) \right]^{-1} \eta_{\pm}
\]

\[
\alpha_{\pm}^{(1)} = S_0^{\uparrow 0} \alpha_{\pm}^{(0)} \quad \text{and} \quad \alpha_{\pm}^{(-1)} = S_0^{\downarrow 0} \alpha_{\pm}^{(0)} .
\]

Explicitly,

\[
S_0^{\uparrow \downarrow} = \frac{U_0 k z_0}{(\kappa + iU_0 + i\omega)^2 + U_0^2 (1 - k^2 x_0^2)} \begin{pmatrix}
- U_0 (1 \pm k z_0) & i(\kappa + iU_0 + i\omega) \\
- i(\kappa + iU_0 + i\omega) & -U_0 (-1 \pm k z_0)
\end{pmatrix}
\]

\[
S_0^{\uparrow} - S_0^{\downarrow} = \frac{-2U_0^2 k^2 x_0^2}{(\kappa + iU_0 + i\omega)^2 + U_0^2 (1 - k^2 x_0^2)} \mathbb{I} \tag{22.87}
\]

\[
\alpha_{\pm} = \alpha_{\pm}^{(0)} + \alpha_{\pm}^{(1)} e^{i\omega t} + \alpha_{\pm}^{(-1)} e^{-i\omega t} = - \left[ 1 + S_0^{\uparrow 0} e^{i\omega t} + S_0^{\downarrow 0} e^{-i\omega t} \right] \left[ L + X (S_0^{\uparrow 0} - S_0^{\downarrow 0}) \right]^{-1} \eta_{\pm} .
\]

The Fig. 22.4 shows how the phase of the cavity behaves in time for various atom-field coupling constants.

![Figure 22.4](image-url)

**Figure 22.4**: (code) Photon number and phase shift of the cavity in response to a modulated atomic position. \( \kappa = 2\pi \times 20 \) kHz, \( \omega = 1.5\kappa \), \( U_0 = 0.10\kappa \), \( \eta_{\pm} = 10\kappa \).

It is interesting to study the oscillatory response of the cavity-field to a forced atomic vibration, because it yields information about the cavity backaction. In fact, as shown above, the vibrating atom imprints sidebands to the intracavity refractive index [525, 5]. The sidebands appear in the cavity transmission spectrum. A more sophisticated method to detect the backaction could be to watch the response in the beat signal to a periodic modulation of the incoupled fields with a vibrating atom,

\[
\dot{x}_{\pm} = (-\kappa - iU_0) x_{\pm} - iU_0 e^{\mp 2\kappa k z_0 \sin \omega t} x_{\mp} + \eta e^{\pm i\phi_0 \sin \omega t} . \tag{22.88}
\]
We would expect a clear signature for resonance, $\omega_\phi = \omega$. The sidebands of the modulated pump would be coupled in, if they coincide. Instead of monitoring the cavity field, we could search the signature of the backaction in the atomic response. We will come back to this, when we discuss collective effects and the frequency shift of the center-of-mass motion.

**Example 83 (Locking of the pump laser):** In practice the resonant frequency of a cavity fluctuates due to ambient noise. Hence, it is easier, experimentally, to lock the pump laser on a cavity mode, e.g. using the Pound-Drever-Hall method. This means,

$$\alpha_+ = \frac{\eta_+}{\kappa}.$$  

In the presence of atoms, however, the resonant frequency can be shifted due to the refractive index of the atomic cloud [188]. Moreover, the shift depends on the atomic bunching and consequently varies during the dynamics of the CARL. The way the locking circuit works, is to continuously adjust the detuning between the laser and the cavity $\Delta_c$ (defined for the empty cavity) such as to maximize the amplitude of the field $|\alpha_+|$ and, hence, the transmission of the cavity filled with atoms. The dynamics of the detuning must be incorporated by an additional equation modeling the action of locking. Now that we know the effect, which an ideal lock should have, we can apply the boundary condition (22.89) and eliminate the pump mode $\alpha_+$ from the dynamics of the system. That is, the following equations are usually sufficient to describe the CARL:

$$\dot{\alpha}_- = (-\kappa + i\Delta_c - iU_0)\alpha_- - iU_0 e^{-2ikz} \alpha_+ + \eta_-.$$  

$$m\ddot{x} = -U_0 \nabla |\alpha_+ u_+ + \alpha_- u_- + \beta_- u_\beta|^2,$$

The frequency offset of the cavity resonances caused by the atom, $U_0$, can exceed the width of the cavity $\kappa$. From equation (22.27) we know, neglecting $\gamma = 0$,

$$|\alpha_+(\infty)|^2 = \frac{\chi \chi^*}{(\chi^2 + U_0^2)(\chi^*2 + U_0^2)} \eta_+^2.$$  

The maxima of $|\alpha_+(\infty)|^2$ as a function of $\Delta_c$ give the shifted resonances of the modes.

**22.2.2.8 Locking on transverse modes**

We already mentioned that as the CARL accelerates, the frequency of the light which is backscattered to the probe shifts to the red until it escapes from the resonant mode. What happens if we provide another resonant mode that can receive photons? We will show in the following calculation, that CARL simply picks up the closest mode to dump the photons. The starting point is generalized CARL equations to accommodate a second reverse mode labeled $\beta_-,$

$$\dot{\alpha}_+ = - (\kappa - i\Delta_c)\alpha_+ - iU_0 (u_+^* u_+ \alpha_+ + u_-^* u_- \alpha_- + u_\beta^* u_\beta \beta_-) + \eta_+$$  

$$\dot{\alpha}_- = - (\kappa - i\Delta_c)\alpha_- - iU_0 (u_-^* u_- \alpha_- + u_+^* u_+ \alpha_+ + u_\beta^* u_\beta \beta_-)$$  

$$\dot{\beta}_- = - (\kappa - i\Delta_\beta)\beta_- - iU_0 (u_\beta^* u_\beta \beta_- + u_\beta^* u_+ \alpha_+ + u_\beta^* u_- \alpha_-)$$  

$$m\ddot{x} = -U_0 \nabla |\alpha_+ u_+ + \alpha_- u_- + \beta_- u_\beta|^2,$$
com \( u_\pm = e^{\pm ikz} \) e \( u_\beta = e^{-ik_\beta x} \). We obtain,

\[
\dot{\alpha}_+ = -i(k - i\Delta_c + iNU_0)\alpha_+ - iU_0e^{-2ikz}\alpha_- - iU_1e^{-i(k+k_\beta)x}\beta_+ + \eta_+ \tag{22.92}
\]

\[
\dot{\alpha}_- = -(k - i\Delta_c + iNU_0)\alpha_- - iU_0e^{2ikz}\alpha_+ - iU_1e^{i(k-k_\beta)x}\beta_-
\]

\[
\dot{\beta}_- = -(k - i\Delta_\beta + iNU_1)\beta_- - iU_1e^{i(k+k_\beta)x}\alpha_+ - iU_1e^{-i(k-k_\beta)x}\beta_-
\]

\[
m\ddot{x} = -U_0(2ke^{2ikz}\alpha^*\alpha_+ - 2ke^{-2ikz}\alpha^*_+\alpha_-)
\]

\[
- U_1(i(k + k_\beta)e^{i(k+k_\beta)x}\beta^*_+\alpha_+ - i(k + k_\beta)e^{-i(k+k_\beta)x}\alpha^*_+\beta_-)
\]

\[
- U_1(i(k - k_\beta)e^{i(k-k_\beta)x}\alpha^*_+\beta_- - i(k - k_\beta)e^{-i(k-k_\beta)x}\beta^*_+\alpha_-)
\]

Note that \( k - k_\beta \approx 0 \) e \( k + k_\beta \approx 2k \). The result of the simulation is displayed in Fig. 22.5.

![Figure 22.5](image)

**Figure 22.5:** (code) The CARL locks to other modes of the cavity.

### 22.2.3 Exercises

#### 22.2.3.1 Ex: Stationary solution of the equations of motion

Derive the stationary solution of the equations of motion (22.39).

#### 22.2.3.2 Ex: Normal mode spectrum

Derive the normal mode spectrum of ring cavity pumped in one direction by applying the condition \( 0 = \partial_{\Delta_c} \alpha_\pm(\infty) \) to the stationary solution (22.58).

#### 22.2.3.3 Ex: Normal mode splitting

Assuming one-way pumping, \( \eta_- = 0 \), calculate the transmission of the cavity as a function of the detunings \( \Delta_a \) and \( \Delta_c \) and the number of atoms.

#### 22.2.3.4 Ex: Ring cavity pumped in one direction

Derive the complete solution of the equations (22.39).
22.3. **CARL: THE COLLECTIVE ATOMIC RECOIL LASER**

The collective atomic recoil laser (CARL) was first predicted in 1994 [72] as an atomic analog of FEL. The idea consists of a monochromatic homogeneous beam of moving two-level atoms (all atoms have the same velocity), a strong counterpropagating pump laser beam and a weak copropagating probe beam tuned to the blue side of the resonance. The lasers form a standing light wave that moves in the same direction as the atoms. Atoms that are faster than the velocity of the standing wave are rejected by the maxima of the dipolar potential created by the standing wave and feel a repulsive force. Atoms that are slower than the standing wave velocity are pushed by the dipole potential maxima and feel an accelerating force. These forces can be interpreted as backscattering of photons from the pump wave into the probe wave. This redistribution of energy amplifies the contrast of the stationary wave, which in turn amplifies the backscattering efficiency, etc. Therefore, the CARL converts kinetic energy into coherent radiation (or more precisely, into an increase of the energy difference between probe and pump) mediated by atomic bunching. It is a self-amplifying mechanism. The CARL signature is a transient exponential amplification for the incident probe, which defines the frequency of the 'CARL laser'.

The first experimental realization of CARL used an annular cavity [362].

### 22.3.1 Solutions for many mobile atoms

The preceding sections dealt with a single atom in a ring cavity. The most interesting part of the dynamics, however, only emerge in the presence of several atoms, because their motion can be become correlated via their simultaneous interaction with the...
same two counter-propagating modes of the cavity, as illustrated in the following movie (watch movie). A talk on CARL can be assisted at (watch talk).

### 22.3.1.1 Simulation of the dynamics for many perfectly bunched atoms

In experiment we generally deal with many atoms, which means that we have to extend the equations of motion (22.27) to \( N \) atoms via \( z \rightarrow z_j \) and \( p \rightarrow p_j \), where \( j = 1, N \). This will be done in the next chapter. Here, we will assume for simplicity, that the atoms are perfectly bunched, \( z_j = z \) and \( p_j = p \). This means that we only need to consider a single equation of motion for the atoms. However, their coupling to the cavity modes is \( N \) times stronger, which means that we have to substitute \( U_0 \rightarrow U_N \equiv NU_0 \) in the equation of motion for the cavity fields.

In general, the equations can not be solved analytically, especially when the pump
varies over time. Then we have to iterate numerically the equations,

\[ \alpha_\pm (t + dt) = \alpha_\pm(t) + dt \left[ -(\kappa + iNU_0 - i\Delta_c)\alpha_\pm - iNU_0e^{\mp 2ikz}\alpha_\mp + \eta(t) \right] \]  
\[ z(t + dt) = z + dt \frac{1}{m}p \]  
\[ p(t + dt) = p - dt 2\hbar kU_0(\alpha_+\alpha_-^*e^{2ikz} - \alpha_-\alpha_+^*e^{-2ikz}) . \]

The kinetic and potential energies are

\[ E_{kin} = \frac{p^2}{2m} , \quad E_{pot} = U_0I = U_0|\alpha_+e^{ikz} + \alpha_-e^{-ikz}|^2 . \]

### 22.3.1.2 Analytic approximations for one-sided pumping

Analytical solutions only exist in particular cases. However, they allow a better understanding of the dynamics. So let’s consider some limiting cases. In Exc. 22.2.3.6 we determine the steady state of an atom interacting with the modes of a unidirectionally pumped annular cavity. In Exc. 22.2.3.7 we calculate the stationary position of the atom in a unidirectionally pumped ring cavity. In Exc. 22.2.3.8 we derive motion equations for the 'intensities' \( \alpha_\pm\alpha_\mp^* \) and 'coherences' \( \alpha_\pm\alpha_\mp^* \).

When only one atom is in the cavity or when the atoms are perfectly bunched together, it is possible to derive analytical solutions. Particularly interesting is the following situation: We pump the cavity from one side. The pump is supposed to be dominant and locked to a resonance, such that we can neglect the feedback of the system on the pump, that is, we can assume, \( \alpha_+ = \eta/\kappa \). Using the abbreviations \( \chi \equiv \kappa + iU_0 - i\Delta_c \) and the photon recoil shift \[ \omega_{rec} = \frac{\hbar k^2}{2m} , \] the equations (22.27) then become,

\[ \dot{\alpha}_- = -\chi\alpha_- - iU_N\alpha_+e^{2ikz} \]  
\[ k\dot{v} = 4\omega_{rec}U_0\alpha_+(\alpha_-e^{-2ikz} - \alpha_-^*e^{2ikz}) . \]

We consider the stationary case (22.27). Doing the ansatz,

\[ \alpha_- \equiv \beta e^{2ikx} \quad \text{where} \quad \dot{\beta} = 0 \]

we assume that the atom and the standing wave have the same velocity, that is, they move in phase. We obtain as solution,

\[ \beta = -\frac{iU_N\alpha_+}{\kappa + 2ikv} , \quad k\dot{v} = 8\omega_{rec}U_0^2\alpha_+^2 \frac{2\kappa}{\kappa^2 + 4k^2\omega^2} . \]

If \( \kappa \ll 2kv \), then the differential equation is approximately solved by,

\( (kv)^3 = 3\xi U_0^2\alpha_+^2 t . \)

\[ ^{11} \text{Note, that there is also a radial motion of the atom coupled to the axial movement. The coupling happens, because the axial motion influences the number of intracavity photons of the radiation field which, in turn, determines the depth of the dipole potential.} \]
This means that the CARL frequency, that is, the frequency difference between the emitted probe wave and the incident light, increases temporarily. The frequency corresponds to the double Doppler shift. As the frequency of the probe light gradually shifts away from the cavity resonance, the probe light finally stops being amplified, and the amplitude of the probe field decreases: CARL is only a transient phenomenon. In fact, the behavior described by the equation (22.98) was observed in experiments [361].

### 22.3.1.3 Optical instability in ring cavities

We have until now concentrated on the regime of weak coupling, \(NU_0 < 1\). If the pump laser is tuned closer to resonance, or if the number of atoms is increased, so that \(NU_0 > 1\), we observe instabilities in the coupled atom-field dynamics, which critically depend on the pump intensities [446]. Imagine a sample of atoms trapped in an optical lattice formed by a symmetrically pumped ring cavity, \(\eta^+ = \eta^-\). The system is stationary, the atoms are confined at the antinodes of the standing wave, the light fields are equal in strength, \(\alpha^+ = \alpha^-\). At time \(t = 0\) we suddenly reduce the pump rate \(\eta^-\) of the non-stabilized mode by only a few percent. The response of the system observed in experiment [446] is to completely break down the field \(\alpha^-\). The disappearance of the standing wave ejects most atoms and reduces \(NU_0\), until the coupling gets so weak that the dynamics is essentially governed by the injected fields. The system recovers a stationary state, with much less atoms.

![Figure 22.8](image-url)

**Figure 22.8:** (code) Dynamics simulated with equations (22.39). At time \(\kappa t = 0\) the pump rate \(\eta^-\) is reduced by 1%. After a certain time that depends on \(NU_0\), the standing wave breaks down ejecting atoms from the mode volume. Here, we simulate this via an artificial linear trap loss process setting in at time \(\kappa t = 15\). As a result of the diminishing \(NU_0\) the standing wave recovers.

The physical explanation for the instability is reminiscent to the CARL behavior described in previous sections. Because atom-field coupling is strong, a small imbalance of the injected beam intensities is sufficient to displace the atoms to a location, where the light which they scatter into the reverse direction interferes destructively with the injected light. A simple argument explains, why the standing wave is attracted towards a position where it gets unstable. We treat the imbalance \(\eta^+ > \eta^-\) as if it was due to a scatterer fixed in space inside the mode volume sitting on an edge of the standing wave (corresponding to a \(\pi/4\) phase shift), such that it only scatters light from \(\alpha^+\) into \(\alpha^-\), but not the other way round. Whether the phase of
the standing wave adjusts itself to that of pump field or such that the scatterer sits at
the bottom of the potential well depends on the ratio of the coupling to the external
field (given by $\kappa$) and to the scatterer (given by $U_0$). If $U_0$ is stronger, the field is
pulled towards the scatterer dragging along the atoms which are free to move. The
stationary situation is therefore a displacement of the standing wave and the atoms
by $\lambda/4$, which is just the position where the cavity field $\alpha_-$ and the injected field
$\alpha_-^{(in)}$ are out of phase. The injected light is not transmitted through the cavity any
more.

Note that the instability occurs in a plane wave situation, there is no need to
consider the transversal motion. Furthermore, it is a single-atom effect, since we
assume perfect bunching. We may therefore consider a single atom strongly coupled to
the cavity and use the set of equations (22.39). In the undepleted pump approximation
we assume $\dot{\alpha}_+ = 0$, and if the atom adiabatically follows the dynamics of the potential
valley, $\dot{x} = 0$, so that,

$$0 = -\chi \alpha_+ - iU_0 \sqrt{\frac{\alpha_+ \alpha_+^*}{\alpha_+^2 \alpha_-}} \alpha_- + \eta_+ , \quad (22.100)$$

$$\dot{\alpha}_- = -\chi \alpha_- - iU_0 \sqrt{\frac{\alpha_- \alpha_-^*}{\alpha_-^2 \alpha_+}} \alpha_+ + \eta_- .$$

The first equation yields,

$$\alpha_+ = \frac{\eta_+}{\chi + iU_0 |\alpha_-|} , \quad (22.101)$$

$$|\alpha_+| \approx \frac{\eta_+}{\chi} \left(1 - \frac{U_0^2}{2\eta_+^2} |\alpha_-|^2\right) .$$

Plugging this result into the second equation and assuming the laser on resonance,
$\Delta_c = NU_0$, so that we may replace $\chi$ by $\kappa$, we get,

$$\dot{\alpha}_- \approx -\kappa \alpha_- - \frac{iU_0 \eta_+}{\kappa} \alpha_-^* \frac{\alpha_-}{|\alpha_-|} + \frac{iU_0^3}{2\kappa \eta_+} |\alpha_-| \alpha_-^* + \eta_- . \quad (22.102)$$

This equation describes optical bistability.

### 22.3.2 Phononic coupling of atoms mediated by a ring cavity

Phonons can be understood as vibrational excitations of quantum particles (atoms)
in quantized traps. When atoms are interconnected in vibrational lattices, phonons
can be transferred and shared between atoms. Due to the particularity of the
ring cavity of conserving the photonic momentum at each backscattering event, the
photonic momentum can be understood as a phononic excitation, propagating in one
dimension along the optical axis of the cavity.

We now consider a symmetrically pumped ring cavity [212]. The atoms are very
cold and deep in the Lamb-Dicke regime. Using blue-detuned light the atoms will

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12 This is similar to the situation in micromasers, where several atoms can share a single photon.
be trapped at the nodes of the standing wave, \( k z_n = \pi/2 + \varepsilon_n \), where \( \varepsilon_n \) are small displacements. Hence, we may expand,

\[
e^{\mp 2i k z_n} \simeq -(1 \mp 2i \varepsilon_n) \ . \tag{22.103}
\]

With the abbreviation \( \chi \equiv \kappa - i(\Delta_c - N U_0) \) and defining the center-of-mass of the small displacements, \( \varepsilon_{cm} = \frac{1}{N} \sum_n \varepsilon_n \), the equation for the two field modes are,

\[
\dot{\alpha}_\pm \simeq -\chi \alpha_\pm + i N U_0 (\mp 2i \varepsilon_0) \alpha_\mp + \eta . \tag{22.104}
\]

Neglecting the impact of the atom on the amplitudes of the fields, we may derive the steady-state solution,

\[
\alpha_\pm = \frac{\eta \chi + i N U_0 (1 \mp 2i \varepsilon_{cm})}{\chi^2 + N^2 U_0^2} . \tag{22.105}
\]

As shown in (22.29) the normalized field intensity can be written as,

\[
\frac{1}{2 e_0 c \epsilon_0^2} \epsilon(z, t) = |\alpha_+|^2 + |\alpha_-|^2 + 2|\alpha_+||\alpha_-| \cos(2kz + 2\theta) , \tag{22.106}
\]

provided the field amplitudes are expressed by,

\[
\alpha_\pm = |\alpha_\pm| e^{\pm i \theta} \text{ such that } \alpha_+\alpha_-^* = |\alpha_+||\alpha_-| e^{2i \theta} \text{ and } \tan 2\theta = \frac{\text{Im } \alpha_+\alpha_-^*}{\text{Re } \alpha_+\alpha_-^*} . \tag{22.107}
\]

Now,

\[
\tan 2\theta = \frac{\text{Im } [\chi + i N U_0 (1 - 2i \varepsilon_{cm})][\chi^* - i N U_0 (1 - 2i \varepsilon_{cm})]}{\text{Re } [\chi + i N U_0 (1 - 2i \varepsilon_{cm})][\chi^* - i N U_0 (1 - 2i \varepsilon_{cm})]} \tag{22.108}
\]

\[
= 4 N U_0 \varepsilon \frac{-\Delta_c + 2 N U_0}{-\kappa^2 - \Delta_c^2 + 4 \Delta_c N U_0 - 4 N^2 U_0^2 + 4 N^2 U_0^2 \varepsilon^2} \simeq \frac{4 N U_0 (\Delta_c - 2 N U_0)}{\kappa^2 + (\Delta_c - 2 N U_0)^2 \varepsilon} . \tag{22.109}
\]

An atom in this optical potential feels the dipolar force,

\[
m \ddot{z}_n = [-\hbar U_0 \partial_z I]_{z=z_n} = 4 \hbar k U_0 |\alpha_+||\alpha_-| \sin(2kz_n + 2\theta) \tag{22.109}
\]

\[
= 4 \hbar k U_0 \eta^2 \frac{|(\chi + i N U_0)^2 - 4 N^2 U_0^2 \varepsilon_{cm}|}{|\chi^2 + N^2 U_0^2|^2} \sin \left( 2kz_n + \frac{2 N U_0 (\Delta_c - 2 N U_0) 2 \varepsilon_n}{\kappa^2 + (\Delta_c - 2 N U_0)^2 \varepsilon} \right) \equiv \frac{m}{2k} \omega^2 \sin(2kz_n - 2\mu_\varepsilon_n) , \tag{22.109}
\]

where,

\[
m \omega^2 \equiv \frac{8 \hbar k U_0 \eta^2}{\kappa^2 + 4 U_0^2} \text{ and } \mu_N \equiv \frac{2 N U_0 |2 N U_0 - \Delta_c|}{\kappa^2 + (2 N U_0 - \Delta_c)^2} . \tag{22.110}
\]

Expanding this equation around the nodes we readily obtain,

\[
\ddot{e}_n + \omega^2 \mu_N \ddot{e}_n \simeq \mu_N \varepsilon_{cm} = \frac{\mu_N}{N} \sum_m \varepsilon_m , \tag{22.111}
\]
which describes the force on a single atom. Note that the harmonic force, \( \omega^2 \varepsilon_n \), on the atom is continuously fed by the center-of-mass force, \( \omega^2 \mu N \varepsilon_{cm} \). The above equation can be rewritten as,

\[
\begin{pmatrix}
\ddot{\varepsilon}_1 \\
\dot{\varepsilon}_1 \\
\ddot{\varepsilon}_2 \\
\dot{\varepsilon}_2
\end{pmatrix} =
\begin{pmatrix}
0 & -\omega^2 (1 - \frac{\mu N}{N}) & 0 & -\omega^2 \frac{\mu N}{N} \\
1 & 0 & 0 & 0 \\
0 & -\omega^2 \frac{\mu N}{N} & 0 & -\omega^2 (1 - \frac{\mu N}{N}) \\
0 & 0 & 1 & 0
\end{pmatrix}
\begin{pmatrix}
\varepsilon_1 \\
\dot{\varepsilon}_1 \\
\varepsilon_2 \\
\dot{\varepsilon}_2
\end{pmatrix}.
\] (22.112)

The eigenvalues of the matrix are \( e = i \omega, i \omega \sqrt{1 - \frac{\mu N}{N}} \). Therefore, we expect, in addition to the secular frequency \( \omega \), a second oscillation frequency,

\[
\omega_{cm} = \omega \sqrt{1 - \frac{\mu N}{N}}.
\] (22.113)

We find splitting in the strong coupling regime, \( g > \Gamma \), but we consider the weak coupling regime, \( g < \Gamma \), to implement the phononic coupling.

### 22.3.2.1 Probing the phonon spectrum

To probe the phonon spectrum, we can measure (or simulate) the oscillation of a single atom \( x_m(t) \) in the presence of several atoms. The Fourier spectrum of the oscillation should reveal the frequency components of the center-of-mass motion \( Z(t) \) and the relative motion. This is actually observed and discussed earlier.

An alternative method for observing normal modes would be to excite an atomic motion and look for a resonant enhancement of the vibration amplitude near the secular frequency, \( \omega_\phi \approx \omega_{cm}, \omega_0 \). For an empty cavity, we expect a low-pass behavior as discussed in Sec. 21.1.1: The modulation frequencies \( \omega_\phi \gg \kappa \) are not transformed into phase oscillations \( \theta \). However, if the atomic motion can act back on the field, then we expect a resonant enhancement. The atomic vibration can be excited by an external force, for example, by RIR resonances, superimposed on the field gradient of the cavity,

\[
\dot{p} = 2 \hbar k U_0 (\alpha_+^* \alpha_- e^{-2ikz} - \alpha_+ \alpha_-^* e^{2ikz}) + F_{rir} \sin \omega_\phi t,
\] (22.114)

or by modulating the pump field,

\[
\eta(t) = \eta e^{\pm \phi_0} \sin \omega_\phi t.
\] (22.115)

Fig. 22.9(a,b) shows a typical resonance curve obtained by plotting the maximum transfer of energy to the atoms as a function of the modulation frequency of the phase of the pump field.

Fig. 22.9(c,d) shows the same typical resonance curve, but taken here the atoms were subjected to a periodic external force. The phase does show a dispersive frequency-dependence \( \theta(\omega) \) if \( \eta \approx \kappa \). If the pumping is too strong, \( \eta \gg \kappa \), the phase does not exhibit any resonant enhancement. Even though the phase-oscillations are suppressed as \( \omega_\phi \) is increased, the atomic center-of-mass motion is excited, when the secular resonance, \( \omega_\phi = \omega_{cm} \), is met. The other modes \( \omega_0 \) are not excited. Also the power-imbalance of the beams \( |\alpha_+|^2 - |\alpha_-|^2 \) always has a strong resonant enhancement.
CHAPTER 22. ATOMIC MOTION IN OPTICAL CAVITIES

Figure 22.9: (code) The experimental parameters are \( N = 10, U_0 = -0.05, \gamma_0 \ll \kappa, \Delta_c = 2U_0, \eta = 10\kappa = \kappa\alpha_\pm(0), \omega_{rec} = 0.13, \phi_0 = 0.1, p_\omega = 10^{-4} \). The calculated secular frequencies are \( \omega = 3.22\kappa, \sqrt{1-\mu} = 3.21\kappa, \omega\sqrt{1-\mu_N} = 2.28\kappa, \omega\sqrt{1-\mu_1\sqrt{1-\mu}} = 2.27\kappa \).

The simulations have been done for the two situations that 1. the laser was not locked to the cavity resonance, but fixed to \( \Delta_c = 0 \), and 2. the laser was locked to the cavity resonance, which means \( \Delta_c = (1 + N^{-1}|\sum_m e^{-ikz_m}|)NU_0 \approx 2NU_0 \). This second case is shown in the blue curves in Figs. 22.9(a) to (d). The simulation exactly reproduces the expected deviation of the resonance frequency \( \omega_{cm} \) from the secular frequency \( \omega_0 \) (22.113). Obviously, at \( \Delta_c \approx 2NU_0 \) the shift of the CoM mode can not be observed via its resonant enhancement. We can excite the CoM, but at the unshifted frequency \( \omega_0 \). At \( \Delta_c \approx 0 \) where the shift occurs, we can not lock the laser.\(^{13}\)

**Example 84 (Two-coupled atoms):** Here we rewrite the field equations for two atoms in center-of-mass coordinates,

\[
Z = \frac{z_1 + z_2}{2} \quad \text{and} \quad z = z_2 - z_1,
\]

finding,

\[
\dot{\alpha}_\pm = (-\kappa + i\Delta_c - 2iU_0)\alpha_\pm - 2iU_0\alpha_\mp e^{\mp 2ikZ} \cos kz + \eta.
\]

**Example 85 (Feasibility analysis):** In order to make some realistic estimates, we choose a reasonably deep potential well \( U \simeq k_B 200 \, \mu K \). This implies a secular frequency on the order of \( \omega_0 = \sqrt{2U/mk^2} \simeq 12\kappa \approx 2\pi \times 250 \, \text{kHz} \). With \( N = 10^6 \) trapped atoms, we want to reach \( NU_0 \approx \kappa \), that is, \( U_0 = 10^{-6}\kappa \). With a given

\(^{13}\)It would also be interesting to calculate the resonance maxima as a function of \( \omega \) to see if the finite cavity bandwidth has an influence on atomic response!
22.3. CARL: THE COLLECTIVE ATOMIC RECOIL LASER

\( g = 20\kappa \), this requires detunings \( \Delta_a = g^2/U_0 \simeq 4 \times 10^3 \kappa = 2\pi \times 80 \) THz. Using \( \varepsilon = 0.26 \), the intracavity photon number should be \( \eta/\kappa = \omega_0/\sqrt{8\varepsilon U_0} \simeq 10^3 \), which gives an intensity of \( I = \frac{\eta^2 c \omega}{\kappa^2 V_{\text{mode}}} \simeq 7600 \) W/cm² and a power of \( P = \frac{\pi^2 w_v w_h \eta}{2} \simeq 2.3 \) W. This easily achievable with the cavity enhancement factor.

22.3.2.2 Phononic quantum gates

The normal mode coupling can be used to create quantum entanglement. A suggested procedure to correlate two atoms \( |m\rangle \) and \( |n\rangle \) is shown in Fig. 22.10 [272].

Figure 22.10: Scheme for entanglement in a ring-cavity.

The truth table reads,

\[
\begin{align*}
|g_m\rangle|g_n\rangle|0\rangle & \quad |g_m\rangle|g_n\rangle|0\rangle & \quad |g_m\rangle|g_n\rangle|0\rangle & \quad |g_m\rangle|g_n\rangle|0\rangle \\
|g_m\rangle|e_n\rangle|0\rangle & \quad |g_m\rangle|e_n\rangle|0\rangle & \quad |g_m\rangle|e_n\rangle|0\rangle & \quad |g_m\rangle|e_n\rangle|0\rangle \\
|e_m\rangle|g_n\rangle|0\rangle & \quad -i|g_m\rangle|g_n\rangle|1\rangle & \quad +i|g_m\rangle|e_n\rangle|1\rangle \\
|e_m\rangle|e_n\rangle|0\rangle & \quad -i|g_m\rangle|e_n\rangle|1\rangle & \quad -|e_m\rangle|e_n\rangle|0\rangle \\
\end{align*}
\]

In a new basis defined by \( |x_m\rangle|\pm_n\rangle \equiv \frac{1}{\sqrt{2}}(|g_n\rangle \pm |e_n\rangle) \) the above operation corresponds to a Controlled NOT gate. And if \( |x_m\rangle \) is initially in a superposition state, the states \( |x_m\rangle \) and \( |\pm_n\rangle \) end up entangled.

22.3.3 Collective effects

To understand the dynamics of CARL we must understand how atomic ensembles commonly interact with light modes. Let us first consider two atoms: The generalization of the fundamental equations (22.39) to two atoms is,

\[
\begin{align*}
\dot{\alpha}_+ &= -\kappa \alpha_+ - i U_0 e^{-2ikz_1} \alpha_- - i U_0 e^{-2ikz_2} \alpha_+ + \eta_+ \\
\dot{\alpha}_- &= -\kappa \alpha_- - i U_0 e^{2ikz_1} \alpha_+ - i U_0 e^{2ikz_2} \alpha_-.
\end{align*}
\]

The equations decouple to \( e^{-2ikz_1} = e^{-2ikz_2 - i\pi} \), such that the impact of the atoms on the light modes vanishes. This situation can be generalized to \( N \) atoms, for which
the fundamental equations (22.39) are generalized to,

\[
\dot{\alpha}_\pm = (-\kappa - iNU_0)\alpha_\pm - iU_0 \sum_{m=1}^N e^{\pm 2ikz_m} \alpha_\pm + \eta_\pm
\]
\[
\dot{p}_m = -2\hbar k U_0 (\alpha_+ e^{2ikz_m} - \alpha_- e^{-2ikz_m})
\]

If the quantity,

\[
b \equiv \frac{1}{N} \sum_j e^{-2ikz_j} \neq 0,
\]

called bunching parameter vanishes, it means that the atomic density distribution is homogeneous. So, the phases of randomly scattered photons destructively interfere, and the impact of the scatterers on the light modes cancels out.

On the other side, when atoms accumulate in the antinodes of the standing wave, it increases the contrast of it can spread more efficiently collectively by Bragg scattering. The particularity of the CARL is that during the temporal evolution the bunching process can amplify itself leading to an exponential growth of the counterpropagant mode, accompanied by an increasingly pronounced self-bunching.

**Example 86 (Universal scaling):** Our formula describing CARL,

\[
\dot{\alpha}_- = -iU_0 \eta_+ \sum_j e^{2ikz_j} - \chi \alpha_-
\]
\[
k\dot{v}_j = -4\omega_{\text{rec}} U_0 \eta_+ \left( \frac{\alpha_- e^{-2ikz_j} - \alpha_+^* e^{2ikz_j}}{\chi} \right) - \gamma_{\text{fric}} k v_j,
\]

where \( \chi = \kappa + iNU_0 - i\Delta_c \), can be rewritten in terms of a universal 'scaling' if we define,

\[
\tau = 4\omega_{\text{rec}} \rho t \quad \text{and} \quad \gamma = \frac{\gamma_{\text{fric}}}{4\omega_{\text{rec}} \rho}
\]
\[
\theta_j = 2kz_j \quad \text{and} \quad P_j = \frac{2kv_j}{4\omega_{\text{rec}} \rho}
\]
\[
A = \frac{i|\chi|}{\chi^* \sqrt{\rho N}} \alpha_- \quad \text{and} \quad \bar{\chi} = \frac{\chi}{4\omega_{\text{rec}} \rho}.
\]

We obtain,

\[
\mathbf{A} = \frac{1}{N} \sum_j e^{i\theta_j} - \bar{\chi} A
\]
\[
\mathbf{\dot{P}} = P_j \quad \text{and} \quad \mathbf{P}_j = -2(A^* e^{-i\theta_j} + A e^{i\theta_j}) - \bar{\gamma} P_j
\]

provided that the universal scaling parameter \( \rho \) is set to,

\[
\rho = \left( \frac{NU_0^2 \eta_+^2}{8\omega_{\text{rec}}^2 |\chi|^2} \right)^{1/3}
\]

The meaning of the \( \rho \) parameter can be gathered by rewriting it in terms of the number of photons of the pump \( |\alpha_+|^2 = \eta_+^2/\kappa^2 \) and the depth of the dipolar potential \( U_d = U_0 |\alpha_+|^2 \),

\[
\rho^3 = \frac{N U_d^2}{\alpha_+^4 \omega_{\text{rec}}^2}
\]
The \( \rho \) parameter therefore indicates the number of atoms per photon and the ratio between the depth of the dipolar trap and the photonic recoil energy. In Exc. 22.3.4.1 we calculate the gain spectrum of the CARL, when the atoms are subjected to an additional harmonic potential.

**Example 87 (Curiosities: Atomic transport around mirrors):** Displacement of the atomic cloud in a unidirectionally pumped ring-cavity. The left and right image in Fig. 22.11 are taken for different pumping directions \( \alpha \). The upper cloud shows atoms trapped in the main focus of the ring-cavity. The lower traces stem from atoms transported from the focus passed the mirrors \( T_1 \) and \( T_2 \) towards the incoupling mirror located at the place where the lower traces intersect. The lower trace are imaged twice, because the imaging beam is reflected from the incoupling mirror surface, before it is sent to a photodiode.

![Figure 22.11: (code) Displacement of the atomic cloud in a unidirectionally pumped ring-cavity. The left and right images are taken for different pumping directions \( \alpha \). The upper cloud shows atoms trapped in the main focus of the ring-cavity. The lower traces stem from atoms transported from the focus passed the mirrors \( T_1 \) and \( T_2 \) towards the incoupling mirror located at the place where the lower traces intersect. The lower trace are imaged twice, because the imaging beam is reflected from the incoupling mirror surface, before it is sent to a photodiode.](image)

### 22.3.4 Exercises

**22.3.4.1 Ex: CARL in a harmonic potential**

Extend the CARL dynamics by an additional harmonic potential for the atoms and study the steady state gain as a function of cavity detuning \( \Delta_c \).

**22.3.4.2 Ex: Filling and drainage of a ring cavity with one fixed atom**

Calculate by simulation of the classical CARL equation, how a laser-pumped ring cavity fills and looses photons in the presence of a single immobile atom.

**22.3.4.3 Ex: Coupled motion of Rb and Cs atoms in a ring-cavity**

Find out by simulation of the classical CARL equation, whether the motion of a Rb atom and a Cs atom can be coupled to the same mode of a ring cavity.
22.3.4.4 Ex: Inertially moving atom in a ring-cavity
Illustrate by simulation of the classical CARL equation, how an inertially moving single atom pushes the wave formed by two counterpropagating modes of a ring cavity.

22.3.4.5 Ex: Normal switch-off CARL
Do a simulation of the classical CARL equation suddenly switching off one of the two lasers pumping counterpropagating modes of a ring cavity.

22.3.4.6 Ex: Impact of an external friction force
Illustrate by simulation of the classical CARL equation, how friction (e.g. induced by an optical molasses) influences the motion of an atom interacting with two counterpropagating modes of a ring cavity.

22.3.4.7 Ex: Impact of various perturbations
Illustrate by simulation of the classical CARL equations how (a) radiation pressure, (b) mirror backscattering, (c) an external harmonic trapping potential, and (d) a phase-drifting pump laser influence the dynamics of an atom interacting with two counterpropagating modes of a ring cavity.

22.3.4.8 Ex: Cavity cooling in a ring cavity
Study cavity cooling in a ring cavity as a function of (a) friction and (b) detuning.

22.3.4.9 Ex: Motion of atoms in a ring-cavity
Discuss whether CARL can be observed without a ring-cavity.

22.3.4.10 Ex: Further studies on CARL
a. Illustrate by simulation of the classical CARL equations the Doppler shift of the accelerated atom by calculating the FFT of the interference signal $|\alpha_+ - \alpha_-|^2$.
b. Illustrate by simulation of the classical CARL equations
c. Illustrate by simulation of the classical CARL equations the Doppler shift of the accelerated atom by calculating the shape of the RIR signal.
d. Cavity emission spectrum as a function of detuning.

22.3.4.11 Ex: Motion of atoms in a ring-cavity including internal states
Motion of atoms in a ring-cavity, including internal states.

22.4 Phenomena related to CARL
The collective atomic recoil laser (CARL) unifies the principles of the FEL and LWI. Assume two-level atoms in their ground state moving against the pump beam $k_2$. An (at first) weak probe beam $k_1$ which is blue detuned with respect to $k_2$ builds
22.4. PHENOMENA RELATED TO CARL

a together with \(k_2\) a standing wave fraction moving in direction \(v\). This fraction gives rise to a moving dipole potential \(V(r)\) and a light force on the atoms. If the moving standing wave is slower than the atoms (and the light frequency detuning from the atomic resonance is suitable), the atoms fall into the potential valleys by rescattering photons from the pump into the probe wave. This way they amplify the probe (they push the ponderomotive wave like the FEL), deepen the light potential valleys, are therefore further focused, etc. We get a self-amplifying avalanche and feedback. In this process, the kinetic energy of the atoms is transformed into laser light. Or to resume: Collective recoil with self-bundeling produced by cooperative Compton-scattering generates coherent laser light [72].

The following notes first discuss the basic equations of motion in the limit of very far detuning, where the internal dynamics can be adiabatically eliminated. Then we turn our attention to some characteristic features of CARL.

22.4.1 Recoil-induced resonances

The recoil-induced resonances (RIR) can be explained in two complementary pictures [127]. In the Raman picture, an atomic transition stimulates Raman transitions between momentum states of the free atom without influencing the atomic excitation (the atom remains in a dark state) \(\rho_{\text{atom}} \otimes |p + 2\hbar k|\). Absorption \(\Delta > 0\) or amplification \(\Delta > 0\) of the probe field \(k_2\) by the pump field \(k_p\) is a result of the population imbalance. However, it is not an excitation imbalance (compare LWI) \(\rho_{\text{atom}} \otimes |p + 2\hbar k| \langle p + 2\hbar k| - \rho_{\text{atom}} \otimes |p\rangle |p\rangle\). In the Rayleigh picture the RIRs are an effect of coherent backward Bragg scattering of the probe wave at the phase-lag between the induced light-shift grating and the atomic density grating resulting from the periodic optical potential.

22.4.1.1 RIR-spectroscopy

Two laser beams 1 and 2 having each two different frequencies \(\omega - \Delta \omega/2\) and \(\omega + \Delta \omega/2\) are irradiated from two different directions enclosing a small angle \(\theta\) into the atomic trap,

\[
E(r, t) = E_1 + E_2
= E^{(0)} \left[ \cos (k_1 \cdot r - (\omega - \frac{1}{2}\Delta \omega)t) + \cos (k_2 \cdot r - (\omega + \frac{1}{2}\Delta \omega)t) \right]
\approx 2E^{(0)} \cos (K \cdot r - \omega t) \cos \left( \frac{1}{2}q \cdot r - \frac{1}{2}\Delta \omega t \right),
\]

where \(q \equiv k_2 - k_1\) and \(K \equiv \frac{1}{2}(k_2 + k_1).\) The cycle-averaged intensities are \(I_i(t) = 2|E_i|^2 = 4\varepsilon_0 c E^{(0)} \cos \left( \frac{1}{2}q \cdot r - \frac{1}{2}\Delta \omega t \right).\) Atoms coherently interacting with the light fields (which are tuned far from any atomic resonance) can redistribute the photons between the optical modes in a nearly-degenerate four-wave mixing process (4WM) thus modifying the amplitudes \(E_i^{(0)}\) so that a signal occurs.

From symmetry considerations, it is easy to see that a homogeneous density distribution (along \(q\)) of the motionless atoms does not give rise to a signal, neither. So let us assume that the atoms be bunched inside an optical grating according to some periodic distribution \(n(z) = n_0 \sin^2 k_\lambda z,\) but disregard their kinetics. The signals then
generalize to,

\[ E_1(z, t) = E_1 + \beta n(z) \chi^{(3)} (E_1 + E_2) E_1 E_2 E_1 + \beta n(z) \chi^{(3)} (E_1 + E_2) E_1 E_2 E_1 \]

\[ = E_1 + \beta n(z) \chi^{(3)} \left( 2E^{(0)} \cos \left( \frac{1}{2} qz - \frac{1}{2} \Delta \omega t \right) \right) E_1 E_2 E_1 \]

(22.126)

and analogous for \( E_2(z, t) \). Or following Lambert-Beer [357],

\[ I_1(x, z, t) = |E_1|^2 \exp \left( 2i \frac{\pi}{\lambda} \int \chi^{(3)} \left( 2E^{(0)} \cos \left( \frac{1}{2} qz - \frac{1}{2} \Delta \omega t \right) \right) dy \right) \]  

\[ = |E_1|^2 \exp \left( 2i \frac{\pi}{\lambda} \int n(x, y, z) dy \right) \]

\[ = |E_1|^2 \exp \left( 2i \frac{\pi}{\lambda} n_0 \sin^2 k \lambda z \right) \]

\[ I_1(t) = \int I_1(x, z, t) dx dz . \]

Regarding the momentum transfer, the 4WM process can be interpreted as Bragg scattering at the atoms at one of the two counterpropagating standing waves. We develop the theory of Bragg scattering in Sec. 28.2.

### 22.4.1.2 Temperature measurements via RIR

Temperature measurement are usually carried out by the time-of-flight method followed by absorption imaging. Alternatively, one can perform spectroscopy of RIR resonances. In the latter case, we detect intensity variations in a probe laser beam, i.e. the polarisation of the sample under the influence of all irradiated laser beams. In Sec. 13.3.6, we have seen that \( \alpha \propto \text{Im} \chi \propto \text{Im} P \propto \text{Im} \rho_{12} \). It is thus sufficient to calculate the atomic coherences, if necessary including the motional states of the
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atoms. Calculated by \[246\]

\[ W(t) = \frac{\pi}{2} \frac{\Omega_1 \Omega_2}{\Delta} \sqrt{\frac{m v}{k_B T}} \left[ \frac{\partial}{\partial v} e^{-mv^2/2k_B T} \right]_{v=\Delta \omega(t)/q} . \quad (22.128) \]

22.4.1.3 RIR-spectroscopy on trapped atoms

In the case of free particles, the Raman beams interact for every detuning with a different velocity class of atoms. The atoms are almost not disturbed. In the case of trapped atoms, a coherence can be excited, and since the atoms periodically change their velocity, be read out or reexcited at a later time. The same atom can thus interact with the Raman beams at different times/detunings. If the trap is a standing wave, the situation is complicated by the fact that there are two overlapping gratings: The standing wave and the Raman grating. However, if the trap is much deeper than the Raman grating the atoms can be considered as localized.

The signature of atomic oscillation is a modulation in the RIR signal with the periodicity of the secular frequency \[356, 492\]. Let us consider a standing-wave dipole-trap with \( \omega_z = 2\pi \times 700 \) kHz, \( \omega_r = 2\pi \times 1 \) kHz and \( U_{dip} = h \times 30 \) MHz = 4000 \( \times 2\epsilon = 45\omega_z = 2100\omega_z \). The 100 µK cold atoms are therefore deep inside at the bottom of trap. This implies that the atomic energy levels are sharp and equally distant, and that the transitions are degenerate upon coupling by Raman-beams. If we apply a scan of \( \pm 2\pi \times 300 \) kHz, we will not excite the longitudinal motion. But the radial motion can be excited. As seen earlier the absorption signal is \( \alpha \propto \text{Im} \rho_{12} \). What happens to the coherence, if the radiation is swept across a resonance depends on the scanning speed. If the scan is slow, we expect \( \alpha \propto \text{Im} \rho_{12}(\infty) \). We should be able to resolve the resonances \[246, 245, 247\] as peaks at \( \pm \omega_r, \pm 2\omega_r, \ldots \). In contrast, if the scan is fast, as long as \( \Delta_c \) is far from resonance, the population of the excited level \( \rho_{22} \) is just too small and nothing happens. When \( \Delta_c \) passes through 0, the coherence \( \rho_{12} \) is excited, and can now be driven by the laser even when \( \Delta_c \) is tuned far away. The coherence precesses faster and faster.

Let us compare to the situation of a laser swept across an electric dipole resonance. In analogy to the cavity response in reflection to a laser scanned across an eigenfrequency, we might expect a ringing coming from interference of the radiating electric dipole (which has been induced while the laser was close to resonance) with the original laser frequency. The radiated electric field is proportional to the excited state population. If we allow for a change of the input field, for example \( \Delta_c(t) \), the Bloch-equations must be numerically integrated,

\[
\rho(t + dt) = \rho(t) + dt \ M \rho(t) .
\]

It is already clear that we should expect a ringing with exactly the time-dependent frequency \( \Delta_c(t) \). Fig. 22.13 shows

This simple mathematical model only assumes a resonance with a given width and a frequency-scanned oscillator. The physical nature of the resonance and the level splitting are not specified and the formalism should be applicable to a variety of situations. A ringing is, in fact, observed for RIR scans, if the scanning speed is too fast, in particular for atoms trapped in optical lattices. Ringing can also be generated in classical harmonic oscillators and laser-driven two-level systems as we will see in Exc. 28.5.4.1.
22.4.1.4 RIR versus CARL

The dynamics is characterized by backaction of the atomic motion onto the cavity field. In this respect there is a connection to RIR resonances in the limit investigated by [357]. While normal RIR is the action of the atomic motion on light fields, they demonstrate that in the same time the Raman-lattice influences the atomic motion. The coherence is limited by the time the photon spends in the sample (similar to the limitation of superradiant Rayleigh scattering, without photonic recycling by a ring-cavity). Real backaction in the sense of coherent interdependence of the photonic and the kinetic degrees of freedom requires recycling of the photons.

22.4.2 FEL: the free electron laser

Normal lasers work by an inversion in the internal degrees of freedom, that is, bound electrons are excited to energetically higher orbitals, from where they can decay by emitting monochromatic light of well-defined frequency. Because, the free electron laser (FEL) works with beams of free electrons, they are tunable over wide frequency ranges. They have much higher efficiencies above 65%.

The principle is the following: Relativistic electrons are guided through an undulator, which is a device producing a magnetic field with periodically alternating polarization. Here, the electrons are subjected to a Lorentz force, $\mathbf{F} = -e\mathbf{v} \times \mathbf{B}$, forcing the electrons to oscillate with the periodicity of the undulator field. This corresponds to a dipole moment interacting with the incident light field. The transverse velocity of the electrons within the magnetic field of an incident light produces a Lorentz force in the axial direction called ponderomotive force. This force accelerates the electrons when they are a bit slower than the ponderomotive wave. Otherwise the electrons are decelerated. In the second case, the energy of the electrons is transmitted to the light field, which leads to a bunching of the atoms. Because it is a parametric process, there is a continuous energy flow between the field and the motion of the $e^{-}$ (analogous to parametric Raman cooling). Thus, the FEL converts the kinetic energy of the electron beam into laser radiation. The inversion in a FEL can be interpreted as a relative displacement of the probability distributions for absorption and emission.
of photons in momentum space,

\[ W_{\text{abs}}(\Delta) = \text{sinc}^2 \frac{1}{2}(\Delta + \varepsilon/2) \]

\[ W_{\text{abs}}(\Delta) = \text{sinc}^2 \frac{1}{2}(\Delta - \varepsilon/2) , \]

where \( \varepsilon = \hbar k^2/2m_e \). The gain is a convolution of the difference of the above distribution with the momentum distribution of the electrons [541].

There various kinds of FELs. In stimulated Compton FELs, described by the shown Feynman graphs, the electrons are scattered by virtual (momentum transfer without energy transfer) photons of the wiggler. In Bremsstrahlungs FEL, the electrons are scattered at a static field. Virtual photons of the static field are scattered at the electrons, who then emit Bremsstrahlung an change their propagation direction. In Raman FELs very dense electron beams produce charge density oscillations, which provides an additional effect. Free Electron Lasers already have a wide range of application ranging from biology and medicine to lithography and material science.

### 22.4.3 CARL in an ion storage ring

Bonifacio et al. [73] suggested to study collective atomic recoil lasing (CARL) with relativistic atoms. They found that using very fast atoms it should, in principle, be possible to get large CARL frequency shifts and much higher power enhancement factors than observed in free-electron lasers (FEL). Relativistic atomic velocities can be achieved in heavy ion accelerators such as the GSI heavy ion accelerator in Darmstadt and TSR ion storage ring in Heidelberg. Therefore the question arises, if CARL could be an alternative way to produce very energetic and intense UV radiation in concurrence to the FEL. In fact, CARL-based systems may prove more powerful and versatile as their electronic counterparts: Cooling techniques based on electron beams or on hybrid optical-radiofrequency friction forces are able to cool the ionic beams down to mK temperatures.

The CARL which has been predicted ten years ago by Bonifacio et al. [72], has recently been observed with cold atoms stored in a high-finesse ring cavity [362, 609]. This proof of principle, now may motivate a deeper study of the figure of merit of a relativistic CARL. This short note, however, shows that a relativistic CARL is still, in my opinion, far from being realizable.
22.4.4 Matter wave superradiance

There is a close relationship between CARL and the phenomenon of matter wave superradiance (or superradiant Rayleigh scattering) [71, 521], which will be discussed in the following sections.

In 1999 the group of W. Ketterle at the MIT made a surprising observation, when it illuminated an elongated Bose-Einstein condensate with a short linearly polarized laser pulse traversing the condensate perpendicularly to the long axis [304]. Instead of producing radiation with a dipole pattern, as we might expect for a polarized atomic cloud undergoing Rayleigh scattering, they observed emission of directional light bursts along the symmetry axis of the condensate. They also observed that some of the atoms were accelerated at angles of 45°. And these atoms could emit other generations of atoms at angles of 45°.

![Figure 22.15: (code) Flight-of-time measurement of the atomic momentum distribution after matter wave superradiance.](image)

The phenomenon was explained as follows. Let us imagine a first photon scattered by an atom into the direction of the long axis of the condensate. This atom will be accelerated by the photonic recoil in a direction of 135° with respect to the direction of the photon, and it will interfere with the rest of the condensate thus generating a standing matter wave of oriented in such a way, that the following photons are scattered into the same direction as the first one via Bragg scattering. This reinforces the contrast of the matter wave, etc.. We obtain an exponential gain of photons in the mode defined by the first scattered photon, as well as of the mode receiving the scattered matter wave. As the path of the gain is longer along the long axis of the condensate, this mode is favored. That is, the condensate can be considered as a cavity embracing the solid angle $\Omega_{\text{sol}}$.

The Rayleigh scattering rate for a single atom is,

$$ R_1 = \sin^2 \theta \sigma(\Delta_a) \frac{I}{\hbar \omega} \frac{3 \Omega_{\text{sol}}}{8 \pi}, $$

(22.131)

where $\theta$ is the angle between the polarization of the incident laser (intensity $I$) and the direction into which the light is scattered. The cross-section is $\sigma(\Delta_a) = \sigma_0 \frac{\Gamma^2}{4 \Delta^2 + 4 \Gamma^2 + 1}$, where $\sigma_0 = 3 \frac{\lambda^2}{2\pi}$. Now, for the set of atoms, the superradiant scattering rate is not only amplified by the number of condensed atoms, $N$, but also by the number of atoms, $N_r$, already being in the mode receiving scattered atoms,

$$ R_{sr} = R_1 N \frac{N_r + 1}{2}. $$

(22.132)
This is the *superradiance matter wave*.

### 22.4.5 Exercises

#### 22.4.5.1 Ex: Good and bad cavity regime

What are the characteristics distinguishing the good from the bad cavity limit.

#### 22.4.5.2 Ex: Ringing in resonant systems

In this exercise we study ringing in (a) an excited classical harmonic oscillator and (b) in a laser-driven two-level system.

### 22.5 Quantization of the atomic motion in cavities

At the beginning of this chapter we set up the complete Hamiltonian of the coupled atom-cavity system. Then tracing over dissipative degrees of freedom, we derived the master equation or derived the Heisenberg equations for the operators appearing in the remaining Hamiltonian quantum mechanically. But then for CARL we restricted to a classical treatment of the motion, as well as of the cavity modes.

Resuming the discussion started in Sec. 22.1.4 we will, in the remaining sections of this chapter, analyze effects due to the quantization of degrees of freedom represented by operators.

#### 22.5.1 Quantum description of the motion

Concretely, let us analyze again the situation of a single atom interacting with a ring cavity. We assume validity of the adiabatic elimination of the internal atomic excitation and want to treat the light fields as classical. In contrast, the atomic motion is considered as quantum:

\[
|\psi\rangle = |z\rangle_{\text{motion}} \otimes |\alpha^+\rangle \otimes |\alpha^-\rangle \text{ classical} \otimes |i\rangle_{\text{electron}} \xrightarrow{\text{adiab.elim.}} |z\rangle .
\]

(22.133)

Since the motion, being the only quantum degree of freedom, is not subject to dissipation, we may use the Schrödinger equation in addition to Heisenberg equations for the light fields. Then, following the procedure outlined in Sec. 22.1.4, with \( z \) being the only quantum number, we find that the system is completely described by the dynamics of the expansion coefficients,

\[
\frac{i}{\hbar} \frac{d}{dt} \langle z|\psi(t)\rangle = \langle z|\hat{H}|\psi(t)\rangle
\]

(22.134)

\[
\dot{\alpha}_\pm = \langle z|\{\hat{H}, \hat{a}_\pm\} - \kappa \hat{a}_\pm |z\rangle .
\]

(22.135)

Plugging in the Hamiltonian (22.27), we obtain the Schrödinger equation for the particle’s motional wavefunction \(^{14}\),

\[
\frac{i}{\hbar} \frac{d}{dt} \langle z|\psi(t)\rangle = \frac{p^2}{2m} \langle z|\psi(t)\rangle - iU_0 \langle z|\hat{a}_+^\dagger \hat{a}_- e^{-2ikz} + \hat{a}_+ \hat{a}_-^\dagger e^{2ikz}|\psi(t)\rangle ,
\]

(22.135)

\(^{14}\)Terms of the Hamiltonian (22.27) which do not depend on \( z \) or \( p \) have been ignored, as they can be removed from the Schrödinger equation by a simple unitary transformation. Note that this can be done even though these terms depend on the field amplitudes \( \alpha_{\pm} \).
and the Heisenberg equations for the light fields,

\[ \dot{a}_\pm = \langle z | - \kappa a_\pm + iU_0 e^{\mp 2ikz} \hat{a}_\mp + \eta_\pm | z \rangle \]

\[ = -\kappa a_\pm + iU_0 \alpha_\mp \int d^3r |\psi(t)\rangle \langle \psi(t)| e^{\mp 2ikz} |z\rangle + \eta_\pm \]

\[ = -\kappa a_\pm + iU_0 \alpha_\mp \int d^3r |\psi(z, t)|^2 e^{\mp 2ikz} + \eta_\pm . \]

In summary,

\[ \dot{\psi}(z) = -\frac{1}{2m} \frac{d^2}{dz^2} \psi(z) - iU_0 \left( \alpha_+ \alpha_- e^{-2ikz} + \alpha_+ \alpha_-^* e^{2ikz} \right) \psi(z) \]

\[ \dot{a}_\pm = -\kappa a_\pm + iU_0 \alpha_\mp \int d^3r |\psi(z)|^2 e^{\mp 2ikz} + \eta_\pm \]

These are the new CARL equations that should be used in cases when the particle is slower than the recoil velocity, in which its motion must be described as a propagating matter wave. Note, that under this form, the equations can easily be generalized to apply to macroscopic wavefunctions such as a Bose-Einstein condensate.

The expectation value of the particle’s position is then calculated via,

\[ z(t) = \langle \psi(0) | \dot{z}(t) | \psi(0) \rangle = \langle \psi(0) e^{-i\hat{H}t} | \dot{z} | e^{i\hat{H}t} | \psi(0) \rangle \]

\[ = \langle \psi(t) | \dot{z} | \psi(t) \rangle = \int \langle \psi(t) | z \rangle \langle z \dot{z} z' \rangle (z' | \psi(t) \rangle d\dot{z}' = \int |z| |\psi(t, z)|^2 d\dot{z} . \]

We can verify that the expectation value of the particle’s position satisfies the classical equation of motion,

\[ m\ddot{z} = \langle \psi(t) | \dot{p} | \psi(t) \rangle = 2\hbar k U_0 \left( \alpha_+^* \alpha_- |\psi(t)| e^{-2ikz} |\psi(t)\rangle - \dot{a}_+ \dot{a}_-^* \langle \psi(t)| e^{2ikz} |\psi(t)\rangle \right) \]

\[ = 2\hbar k U_0 \left( \alpha_+^* \alpha_- e^{-2ik\dot{z}} \dot{|\psi(t)|} - \dot{a}_+ \dot{a}_-^* e^{2ik\dot{z}} \dot{|\psi(t)|} \right) \]

\[ = 2\hbar k U_0 \left( \alpha_+^* \alpha_- e^{-2ik\dot{z}} - \dot{a}_+ \dot{a}_-^* e^{2ik\dot{z}} \right) . \]

**22.5.1.1 About the origin of quantized motion**

The quantization of the light field into photons is, as discussed in Chp. 15.6.7, an intrinsic property of light. In contrast, the quantization of atomic motion is less obvious, because the atoms are not confined in a trapping potential. The reason for it lies in the monochromaticity of the driving laser fields and the one-dimensional geometry of the system, which allow us to write the recoil operator (2.187) or (4.111) as,

\[ e^{2ik\dot{z}} = \int |p + 2\hbar k\rangle \langle p| dp . \]

Inserting it into the interaction part of the CARL Hamiltonian,

\[ \hat{H}_{int} = U_0 (e^{-2ik\dot{z}} \dot{a}_+ \dot{a}_- + e^{2ik\dot{z}} \dot{a}_+ \dot{a}_-^* ) , \]

\[ \hat{H}_{int} = U_0 (e^{-2ik\dot{z}} \dot{a}_+ \dot{a}_- + e^{2ik\dot{z}} \dot{a}_+ \dot{a}_-^* ) , \]
the Schrödinger equation for the expanded wavefunction

$$|\psi\rangle = \int c(p)|p\rangle dp$$  \hfill (22.142)

yields,

$$i\hbar \frac{d}{dt} \langle p|\psi\rangle = U_0 \hat{a}_+^\dagger \hat{a}_- \langle p|e^{-2ikz}\psi\rangle + U_0 \hat{a}_+ \hat{a}_+^\dagger \langle p|e^{2ikz}\psi\rangle$$  \hfill (22.143)

$$= i\hbar \frac{d}{dt} c(p) = U_0 [\hat{a}_+^\dagger \hat{a}_- c(p + 2\hbar k) + \hat{a}_+ \hat{a}_+^\dagger c(p - 2\hbar k)] .$$

That is, if the initial momentum distribution is narrow, $\Delta p \ll 2\hbar k$, and if CARL-induced recoil due to backscattering of photons between counterpropagating modes is the only force acting on the atoms, the momentum of the atoms can only adopt discrete values in units of $2\hbar k$, as if the atomic velocity were quantized. That is, the quantization of the field is, in some way, imprinted on the distribution of the atomic moment, so that we may as well use a discrete notation,

$$|\psi\rangle = \sum \nu c_\nu |\nu\rangle ,$$  \hfill (22.144)

such that,

$$i\hbar \frac{d}{dt} c_\nu = U_0 \hat{a}_+^\dagger \hat{a}_- c_{\nu+1} + U_0 \hat{a}_+ \hat{a}_+^\dagger c_{\nu-1} .$$  \hfill (22.145)

**Example 88 (Analogy to the Bose-Hubbard Hamiltonian):** Interestingly the CARL Hamiltonian with quantized motion (22.141) has, in momentum space, a similar shape as the 1D Bose-Hubbard Hamiltonian in position space,

$$\hat{H} = \sum \nu \hbar \omega_{\text{rec}} \nu^2 + U_0 \sum \nu \left( |\nu - 1\rangle \langle \nu | \hat{a}_+^\dagger \hat{a}_- + |\nu + 1\rangle \langle \nu | \hat{a}_+ \hat{a}_+^\dagger \right)$$

$$= \hbar \omega_{\text{rec}} \sum \nu^2 + U_0 \hat{a}_+^\dagger \hat{a}_- \sum \nu \hat{A}_{\nu+1}^\dagger \hat{A}_\nu + U_0 \hat{a}_+ \hat{a}_+^\dagger \sum \nu \hat{A}_\nu \hat{A}_{\nu+1} .$$

Now, it is important to understand that the statement that photonic recoil is quantized does not mean that the dipolar optical force can only be transmitted in units of $2\hbar k$, as if the force needed to accumulate a certain amount of energy before it makes a sudden transition to a different momentum state. Rather, the probability to find an initially resting atom subject to a force in the momentum state $2\hbar k$ gradually increases with time. The atom gradually evolves into a coherent superposition of states $|0\rangle + |2\hbar k\rangle + |4\hbar k\rangle + ..$, and only when we measure the momentum distribution will it have to decide in which state it ended up. The expectation value of the center-of-mass momentum linearly, as long as the force is constant. A slide show on the quantized CARL can be viewed at (watch talk).

### 22.5.2 Discretization of the momentum states

We will now assume that, for the physical reasons described above, the motional state of the atom can only exist with momenta corresponding to multiples of twice the photonic recoil.
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22.5.2.1 Schrödinger equation approach

We basically repeat the treatment of Sec. 22.5.1, but now expanding the motion on a discrete basis of momenta labeled by an integer number \( \nu \),

\[
|\psi\rangle = |\nu\rangle_{\text{motion}} \otimes |\alpha_+\rangle \otimes |\alpha_-\rangle^{\text{classical}} \otimes |j\rangle_{\text{electron}} \otimes |p\rangle_{\text{adiab.elim.}} \rightarrow |\nu\rangle .
\] (22.146)

Applying the recipe detailed at the beginning of Sec. 22.5, we write down the same Schrödinger equation as in (22.135) \(^\text{15}\), but now projecting on \( |\nu\rangle \) rather than on \( |z\rangle \) and inserting the expansion (22.144) and,

\[
e^{2\imath k \hat{\xi}} = \sum_{\nu} |\nu + 1\rangle \langle \nu| \quad \text{and} \quad \hat{p} = \sum_{\nu} \nu \hbar \hat{\kappa} |\nu\rangle \langle \nu| .
\] (22.147)

We get,

\[
\langle \nu| i\hbar \frac{d}{dt} \sum_{\nu''} c_{\nu''} |\nu''\rangle = |\nu\rangle \sum_{\nu'} \left( \frac{(\nu' \hbar \kappa)^2}{2m} |\nu'\rangle \langle \nu'| + U_0 \left( \sum_{\nu'} |\nu' - 1\rangle \langle \nu' | \hat{a}_+^\dagger \hat{a}_- + \sum_{\nu'} |\nu' + 1\rangle \langle \nu' | \hat{a}_+ \hat{a}_-^\dagger \right) .
\] (22.148)

And from the Heisenberg equation (22.16) for light modes,

\[
\langle \psi| \hat{a}_\pm |\psi\rangle = \langle \psi| (-\kappa + i \Delta_c - i \nu U_0) \hat{a}_\pm - i U_0 \hat{a}_\mp \hat{a}_\pm^\dagger \hat{a}_\mp^\dagger + \eta_\pm |\psi\rangle ,
\] (22.149)

we get,

\[
\sum_{\nu',\nu''} \langle \nu'| c_{\nu''} \hat{a}_\pm c_{\nu'} |\nu''\rangle = \sum_{\nu',\nu''} \langle \nu'| c_{\nu''} ((-\kappa + i \Delta_c - i \nu U_0) \hat{a}_\pm - i U_0 |\nu + 1\rangle \langle \nu | \hat{a}_\mp^\dagger \eta_\pm c_{\nu'} |\nu''\rangle .
\] (22.150)

Finally,

\[
\dot{c}_\nu = -i \omega_{\text{rec}} \nu^2 c_{\nu} - i U_0 \left( \alpha_+^* \alpha_- c_{\nu + 1} + \alpha_+ \alpha_-^* c_{\nu - 1} \right) ,
\]

\[
\dot{a}_\pm = (-\kappa + i \Delta_c - i \nu U_0) a_\pm - i U_0 \alpha_\mp \sum_{\nu} c_{\nu \mp 1}^* c_{\nu} + \eta_\pm .
\] (22.151)

22.5.2.2 Master equation approach

As in the situation under study the motion is the only quantum degree of freedom and not subject to dissipation, a master equation approach is useless, and we will show it here only for completeness.

In 22.5.6.1 we show a derivation obtained by directly inserting the adiabatically simplified Hamiltonian (22.27) into the Liouville equation (22.9). The result is,

\[
\dot{\rho}_{\mu,\nu} = i(\nu - \mu) [ (\nu + \mu) \omega_{\text{rec}} - \Delta_c ] \rho_{\mu,\nu} + i \nu U_0 \left( \alpha_+^* \alpha_- (\rho_{\mu,\nu - 1} - \rho_{\mu + 1,\nu}) + \alpha_+ \alpha_-^* (\rho_{\mu,\nu + 1} - \rho_{\mu - 1,\nu}) \right) .
\] (22.152)

\[15\]Here again, as done in Sec. 22.5.1, we ignore terms of the Hamiltonian (22.27) which do not depend on \( z \) or \( p \).
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22.5.3 Quantized motion with many particles

The Hamiltonian (22.135) holds for a single atom. If clouds of thermal atoms are considered, we may switch to a classical description of the motion, as done in Sec. 22.2. In the case of very cold (below the recoil limit) but still independent atoms, we may assume that they all are coherently distributed over the same momentum states. We may then apply a unique momentum state expansion for all atoms, as shown in the subsequent section.

If on the other hand quantum statistics play a role, then we need to replace the wavefunction in the Schrödinger equation (22.135) by field operators, as done in Sec. 28.5. In the following sections, we will restrict to single atoms that can be in a coherent superposition of momentum states or many atoms in a matter wave that can be treated as a $c$-number, e.g. a Bose-condensate without fluctuations.

22.5.3.1 Modal expansion of the motion of many independent atoms in the adiabatic approximation for one-sided pumping

Our starting point is the quantum version of the CARL equations (22.26), where we neglect spontaneous emission, $\gamma_0 = 0$. Setting $\alpha_+ = \eta_+ / \kappa$ and $\eta_- = 0$ we get,

\[
\begin{align*}
\dot{\hat{a}}^- &= \left( -\kappa + i\Delta_c - iU_0 \right) \hat{a}^- - iU_0 \frac{\eta_+}{\kappa} e^{-2ik\hat{z}_j} , \\
m\ddot{\hat{z}}_j &= 2\hbar k U_0 \left( \hat{a}_+^+ \hat{a}^- e^{-2ik\hat{z}_j} - \hat{a}^+_+ e^{2ik\hat{z}_j} \right)
\end{align*}
\] (22.153)

For this case, the total momentum is a constant of motion for $N$ atoms is,

\[
[\hat{H}, 2\hbar k \hat{a}_-^- + \sum_{j=1}^{N} \hat{p}_j] = 0 .
\] (22.154)

To treat the motion as being quantized we define a base $|\nu\rangle_j$,

\[
\hat{p}_j |\nu\rangle_j = 2\hbar k v |\nu\rangle_j \quad \text{and} \quad |\psi(z_j)\rangle = \sum_\nu c_{j,\nu} |\nu\rangle_j ,
\] (22.155)

and calculate the expected value of the equations (22.153) regarding the atomic motion,

\[
\begin{align*}
\frac{d\hat{a}^-}{dt} &= -i\Delta_c \hat{a}^- - iU_0 \frac{\eta_+}{\kappa} \sum_j \langle \psi(z_j) | e^{-2ik\hat{z}_j} | \psi(z_j) \rangle - \kappa \hat{a}^- \quad (22.156) \\
&= -i\Delta_c \hat{a}^- - iU_0 \frac{\eta_+}{\kappa} \sum_{j,\mu,\nu} c_{j,\mu}^* c_{j,\nu} \langle \mu | e^{-2ik\hat{z}_j} | \nu \rangle_j - \kappa \hat{a}^- \\
&= -i\Delta_c \hat{a}^- - iU_0 \frac{\eta_+}{\kappa} \sum_{j,\nu} c_{j,\nu}^* c_{j,\nu+1} - \kappa \hat{a}^- .
\end{align*}
\]

In addition, the Schrödinger equation $i\hbar \frac{d|\psi(z_j)\rangle}{dt} = \hat{H} |\psi(z_j)\rangle$ yields,

\[
\begin{align*}
\hbar \sum_\nu \frac{d c_{j,\nu}}{dt} |\nu\rangle_j &= \sum_\nu \frac{1}{2m} p_j^2 c_{j,\nu} |\nu\rangle_j + \frac{\hbar \Delta_c}{N} \hat{a}_+^+ \hat{a}^- + \sum_\nu c_j(\nu) |\nu\rangle_j \\
&+ \hbar U_0 \eta \sum_\nu (\hat{a}_-^- e^{-2ik\hat{z}_j} + \hat{a}_-^- e^{2ik\hat{z}_j}) c_{j,\nu} |\nu\rangle_j .
\end{align*}
\] (22.157)
Projecting on $j|\mu|$, we obtain [115],

\[
\dot{c}_{j,\mu} = -\imath \omega_r \mu^2 c_{j,\mu} - i \frac{\Delta_c}{N} \hat{a}_- c_{j,\mu} - i U_0 \eta \hat{a}_-^{\dagger} c_{j,\mu + 1} + a_- c_{j,\mu - 1} ,
\]

\[
d\hat{a}_- / dt = N U_0 \eta \sum_\nu c_{j,\nu}^{\dagger} c_{j,\nu + 1} - (\kappa_c + \imath \Delta_c) \hat{a} .
\] (22.158)

where $\omega_r = \hbar k^2 / 2m$. The equations (22.158) can be used for numerical simulations [505].

Figure 22.16: Probe light and 'bunching' when the temperature is raised.

22.5.3.2 Equations for the density matrix

The equations (22.158) allow to calculate the derivatives of the density matrix given by,

\[
\varrho_{\mu,\nu} = e^{-\imath (\mu - \nu) \Delta_c t} \frac{1}{N} \sum_j c_j^{\dagger} (\mu) c_j (\nu) ,
\] (22.159)

yielding,

\[
\frac{d \varrho_{\mu,\nu}}{dt} = e^{-\imath (\mu - \nu) \Delta_c t} N^{-1} \sum_j \left( \dot{c}_{j,\mu} c_{j,\nu}^{\dagger} + c_{j,\mu}^{\dagger} \dot{c}_{j,\nu} - \Delta_c c_{j,\mu}^{\dagger} c_{j,\nu} (\mu - \nu) \right)
\]

\[
= e^{-\imath (\mu - \nu) \Delta_c t} N^{-1} \sum_j \left[ \imath [\omega_r (\mu^2 - \nu^2) - \Delta_c t (\mu - \nu)] c_{j,\mu}^{\dagger} c_{j,\nu} +
\right.

\left. + \imath U_0 \eta \left[ a c_{j,\mu + 1}^{\dagger} c_{j,\nu} - a c_{j,\mu}^{\dagger} c_{j,\nu - 1} + \hat{a}_-^{\dagger} c_{j,\mu - 1} c_{j,\nu} - \hat{a}_- c_{j,\mu}^{\dagger} c_{j,\nu + 1} \right] \right] .
\] (22.160)

Introducing $\tilde{a} \equiv a e^{\imath \Delta_c t}$ we finally obtain,

\[
\frac{d \varrho_{\mu,\nu}}{dt} = \imath (\mu - \nu) [\omega_r (\mu + \nu) - \Delta_c] \varrho_{\mu,\nu} + \imath U_0 \eta \left[ \tilde{a} (\varrho_{\mu + 1,\nu} - \varrho_{\mu,\nu - 1}) + \tilde{a}_-^{\dagger} (\varrho_{\mu - 1,\nu} - \varrho_{\mu,\nu + 1}) \right] .
\] (22.161)

These are the CARL equations for the density matrix. In 22.5.6.1 we show an alternative derivation obtained by directly inserting the adiabatically simplified Hamiltonian (22.27) into the Liouville equation (22.9).
We note, that $\sum_\nu \rho_{\nu,\nu+1}$ is the 'bunching' and that $\rho_{\mu,\nu} = \rho_{\nu,\mu}$. The average moment is given by $\langle p \rangle = \sum_\nu \nu \rho_{\nu,\nu}$. In the Figs. 22.17 and 22.18 we show simulations in the semi-classical regimes $\rho \gg 1$ in the 'bad-cavity' limit, $\kappa > 1$, and the 'good-cavity' limit $\kappa \ll 1$.

![Figure 22.17: Simulation of the CARL equation (22.158) in the superradiant, semi-classical, 'bad-cavity' regime for $\kappa_c = 4$, $\rho = 4$, $\Delta_c = 0$.](image)

![Figure 22.18: Simulation of the CARL equation (22.158) in the superradiant, semi-classical, 'good-cavity' regime for $\kappa_c = 0.02$, $\rho = 4$, $\Delta_c = 0$.](image)

Here are some movies illustrating the quantum CARL dynamics, simulated using the momentum state expansion (watch movie) and (watch movie). The following dynamics were calculated via direct integration of the Schrödinger equation without momentum state expansion: Bloch oscillations (watch movie), CARL dynamics (watch movie), and joint Bloch and CARL dynamics (watch movie). See also (watch talk).

### 22.5.4 Approximation for a bimodal momentum distribution

We observe that in the quantum regime the momentum distribution of the matter wave is bimodal, that is, only two momentum states are simultaneously populated. This justifies a simplification of the equations (22.161), assuming that at a given time, atoms must either be in a specific state $|\mu \rangle _j$ or in a superposition of this state is an
adjacent state $|\mu-1\rangle$. Hence,

$$\frac{d\rho_{\mu,\mu}}{dt} = -iU_0\eta(\hat{a}\rho_{\mu,\mu-1} - \hat{a}^\dagger\rho_{\mu-1,\mu}) = -\frac{d\rho_{\mu-1,\mu-1}}{dt}$$

$$\frac{d\rho_{\mu-1,\mu}}{dt} = -i[(2\mu-1)\omega_r - \Delta_c]\rho_{\mu-1,\mu} + iU_0\eta\hat{a}(\rho_{\mu,\mu} - \rho_{\mu-1,\mu-1})$$

$$\frac{d\hat{a}}{dt} = -iNU_0\eta\rho_{\mu-1,\mu} - \kappa_c\hat{a}.$$  

Introducing the coherence $S_\mu = \rho_{\mu-1,\mu}$ and the inversion $W_\mu = \rho_{\mu,\mu} - \rho_{\mu-1,\mu-1}$ and postulating the normalization $1 = \rho_{\mu,\mu} + \rho_{\mu-1,\mu-1},$

$$\frac{dW_\mu}{dt} = -2iU_0\eta(\hat{a}S_\mu^* - \hat{a}^\dagger S_\mu)$$

$$\frac{dS_\mu}{dt} = -i[(2\mu-1)\omega_r - \Delta_c]S_\mu + iU_0\eta\hat{a}W_\mu$$

$$\frac{d\hat{a}}{dt} = -iNU_0\eta S_\mu - \kappa_c\hat{a}.$$  

22.5.4.1 Linearization and stability analysis

We assume that the atoms are initially 'bunched' in a specific state $|\mu\rangle$. Only adjacent momentum states are coupled,

$$\frac{d\rho_{\mu+1,\mu}}{dt} = i[\omega_r(2\mu + 1) - \Delta_c]\rho_{\mu+1,\mu} + iU_0\eta\hat{a}(\rho_{\mu,\mu} - \rho_{\mu+1,\mu+1})$$

$$\frac{d\rho_{\mu-1,\mu}}{dt} = -i[\omega_r(2\mu - 1) - \Delta_c]\rho_{\mu-1,\mu} + iU_0\eta\hat{a}(\rho_{\mu,\mu} - \rho_{\mu-1,\mu-1})$$

$$\frac{d\hat{a}}{dt} = -iNU_0\eta(\rho_{\mu+1,\mu} + \rho_{\mu-1,\mu}) - \kappa_c\hat{a}.$$  

Conjugate the upper equation and build the sum and difference, $B_\mu \equiv \rho_{\mu,\mu+1} + \rho_{\mu-1,\mu}$ and $D_\mu \equiv \rho_{\mu,\mu+1} - \rho_{\mu-1,\mu},$

$$\frac{dB_\mu}{dt} = i(\Delta_c - 2\mu\omega_r)B_\mu - \omega_r D_\mu + iU_0\eta\hat{a}(\rho_{\mu+1,\mu+1} - \rho_{\mu-1,\mu-1})$$

$$\frac{dD_\mu}{dt} = i(\Delta_c - 2\mu\omega_r)D_\mu - \omega_r B_\mu - 2iU_0\eta\hat{a} + iU_0\eta\hat{a}(\rho_{\mu+1,\mu+1} - 2\rho_{\mu,\mu} + \rho_{\mu-1,\mu-1})$$

$$\frac{d\hat{a}}{dt} = -iNU_0\eta B_\mu - \kappa_c\hat{a}.$$  

Use $\rho_{\mu,\mu} \approx 1$ and abbreviate $\delta_\mu \equiv 2r\omega_r - \Delta_c,$

$$\frac{dB_\mu}{dt} = -i\delta_\mu B_\mu - \omega_r D_\mu$$

$$\frac{dD_\mu}{dt} = -\omega_r B_\mu - i\delta_\mu D_\mu - 2iU_0\eta\hat{a}$$

$$\frac{d\hat{a}}{dt} = -iNU_0\eta B_\mu - \kappa_c\hat{a}.$$
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Seeking solution proportional to \( x \equiv \bar{x}e^{i(\lambda - \delta_\mu)t} \),

\[
\begin{align*}
\bar{i}\lambda B_\mu &= -i\omega_\mu D_\mu \\
\bar{i}\lambda D_\mu &= -i\omega_\mu B_\mu - 2iU_\mu \eta \bar{a} \\
\bar{i}(\lambda - \delta_\mu)\bar{a} &= -iNU_0\eta B_\mu - \kappa_c \bar{a}.
\end{align*}
\]

Abbreviating \( \Lambda_m \equiv \delta_m + i\kappa_c \), the characteristic equation is,

\[
\det \begin{pmatrix}
\lambda & \omega_r & 0 \\
\omega_r & \lambda & 2U_0\eta \\
NU_0\eta & 0 & \lambda - \Lambda_\mu
\end{pmatrix} = \lambda^3 - \Lambda_\mu \lambda^2 - \omega_r^2\lambda + \omega_r^2 \Lambda_\mu + 2NU_0^2\eta^2\omega_r = 0 .
\] (22.168)

The gain is given by the imaginary part of \( \lambda \). We have exponential amplification if \( \text{Im} \lambda < 0 \). Hence, we search for solution with the lowest imaginary value.

**Figure 22.19**: (code) Gain dependence on \( \rho \) and \( \kappa \).

### 22.5.4.2 Universal scaling

To simplify the formulae simplify, we rescale them. We start from Eq. (22.161) and use the substitution for universal scaling,

\[
\begin{align*}
\theta_j &\equiv 2kz_j & \bar{\theta}_j &\equiv 2kv_j/\rho \omega_r, \\
\tau &\equiv \rho \omega_r t & \kappa &\equiv \kappa_c/\omega_r \rho \\
\bar{\lambda} &\equiv \lambda/\omega_r \rho & \bar{\delta}_\mu &\equiv \delta_\mu/\omega_r \rho = 2\mu/\rho + \Delta_c/\omega_r \rho \\
\bar{A} &\equiv (2/N\rho)^{1/2} \bar{a} & \eta U_\mu &\equiv \sqrt{\rho^3 \omega_r^2}/2N .
\end{align*}
\] (22.169)
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This reproduces the Bonifacio notation,
\[
\tilde{\lambda} \tilde{B}_\mu + \rho^{-1} \tilde{D}_\mu = 0
\]
\[
\tilde{\lambda} \tilde{D}_\mu + \rho^{-1} \tilde{B}_\mu + \rho \tilde{A} = 0
\]
\[(\tilde{\lambda} - \delta_\mu - i\kappa) \tilde{A} + \tilde{B}_\mu = 0 .\]

Skipping the bars, the characteristic equation reads,
\[
\det \begin{pmatrix}
\lambda & \rho^{-1} & 0 \\
\rho^{-1} & \lambda & \rho \\
1 & 0 & \lambda - \delta_\mu - i\kappa
\end{pmatrix} = (\lambda - \delta_\mu - i\kappa)(\lambda^2 - \rho^{-2}) + 1 = 0 .
\]

(22.171)

Let us first discuss the semiclassical limit, \( \rho \gg 1 \). In the good-cavity regime, \( \kappa \simeq 0 \), we may neglect the recoil shift, \( 2 m \omega_r \to 0 \), so that \( \Lambda = \Delta_c \). The gain is largest when \( \Delta_c \to 0 \). The characteristic equation reduces to \( \lambda^3 = -1 \), yielding the solutions \( \lambda = 1, \frac{1}{2}(1 \pm i\sqrt{3}) \). Hence, the gain \( G = -\text{Im} \lambda \), is
\[
G = \frac{1}{2} \omega_r \rho \sqrt{3}
\]
\[
\Delta \omega_G \simeq \omega_r \rho \gg \kappa_c, \omega_r .
\]

The gain bandwidth \( \Delta \omega_G \) being much larger than the recoil frequency, the Bragg condition for scattering between different momentum states is approximately fulfilled for a large number of initial momenta. I.e. although the momentum transfer is quantized, \( \Delta_c = n \omega_r \), the atoms can be accelerated to high velocities. From Eq. (22.170)(a) we see \( |\tilde{D}_\mu/\tilde{B}_\mu| = \rho |\tilde{\lambda}| \gg 1 \), i.e. \( g_{\mu,\mu+1} \simeq g_{\mu-1,\mu} \).

In the superradiant regime, \( \kappa > 1 \), of the semiclassical limit the characteristic equation reduces to \( \lambda^2 = -i/\kappa \), i.e. \( \lambda = \pm (1 - i)/\sqrt{2\kappa} \).\(^{16}\) Hence, the gain is,
\[
G = \frac{1}{2} \omega_r \rho \sqrt{2/\kappa}
\]
\[
\Delta \omega_G \simeq \kappa_c = \omega_r \rho \kappa \gg \omega_r .
\]

In fact, the relative gain bandwidth is on the order of \( \Delta \omega_G/\omega_r \simeq \rho \propto (n N U_O^2)^{1/3} \). Since recoil can be neglected we can have absorption or emission. The gain results from the difference bewteen the average rates of both.

Now we turn to the quantum limit, \( \rho < 1 \). In the good-cavity regime, \( \kappa \simeq 0 \), \( \lambda = \rho^{-1} + \frac{1}{2} (\delta_m - \rho^{-1}) - \frac{1}{2} \sqrt{(\delta_m - \rho^{-1})^2 - 2 \rho} \). Hence, the gain is,
\[
G = \frac{1}{2} \omega_r \rho \text{Im} \sqrt{(\delta_m - \rho^{-1})^2 - 2 \rho} \simeq \frac{1}{2} \omega_r \rho \sqrt{2 \rho}
\]
\[
\Delta \omega_G = \omega_r \rho^{3/2} < \omega_r .
\]

In fact, the relative gain bandwidth is on the order of \( \Delta \omega_G/\omega_r \simeq \rho^{3/2} \propto \sqrt{n N U_O^2} \). Here recoil plays a role so that we have emission without absorption. Gain results exclusively from emission. From Eq. ((22.170)a) we see \( |\tilde{D}_m/\tilde{B}_m| = \rho |\tilde{\lambda}| \simeq 1 \), i.e. \( g_{m,m+1} \ll g_{m-1,m} \).

\(^{16}\)The assertion \( \text{Re} \lambda \ll \kappa \) used to simplify the characteristic equation is compatible with the solution.
In the superradiant regime, $\kappa > 1$, of the quantum limit, $\lambda = \rho^{-1} + \frac{\rho}{2}[(\delta_m - \rho^{-1}) + i\kappa]^{-1}$. Hence,

$$G = \frac{1}{2} \omega_r \rho \frac{\rho \kappa}{(\delta_m - \rho^{-1})^2 + \kappa^2} \approx \frac{1}{2} \omega_r \rho^2 \kappa$$

(22.175)

$$\Delta \omega_G = \kappa c > \omega_r \rho .$$

The various regimes may be summarized in the following phase diagram. We will see later, that each region produces qualitatively different solutions of the full (non-linearized) equations.

22.5.5 Quantization of the atomic motion without adiabatic elimination

So far we have discussed the quantization of the atomic motion in the CARL equations, which were obtained by adiabatic elimination of the electronically excited state. In the following, we will quantize the motion directly in the equations of motion (22.16) for the observables and in the Liouville equation for the density operator. We quantize the atomic motion along the optical $z$-axis simply by assuming that, in this direction, the momentum only exists in multiples of $\hbar k$, and organize up the Hilbert space like this,

$|\psi\rangle = |\nu\rangle_{motion} \otimes |i\rangle_{electron} \otimes |n\rangle_- \otimes |n\rangle_- \rightarrow |\nu, i\rangle ,

(22.176)

that is, skipping the quantum number counting the photons, we will treat the light fields classically, $\hat{a}_\pm = \alpha_\pm$,

$$\hat{p} = \sum_\nu \nu \hbar k |\nu \rangle \langle \nu | \otimes \mathbb{I}$$

$$e^{-i k \hat{z}} = \sum_\nu |\nu \rangle \langle \nu | \otimes \mathbb{I}$$

$$\hat{\sigma}^+ = \mathbb{I} \otimes |2\rangle \langle 1|$$

$$\hat{\rho} = |\psi\rangle \langle \psi| = \sum_{\mu,\nu,i,j} c^*_{\mu,i} c_{\nu,j} |\mu\rangle \langle \nu| \otimes |i\rangle \langle j|$$

(22.177)
where in the last equation we defined \( c_{\nu,j} = \langle p,j|\psi(t)\rangle = \langle \nu \hbar k,j|\psi(t)\rangle = \langle \nu,j|\psi(t)\rangle \), such that,

\[
\rho_{\mu,\nu;i,j} \equiv \langle \mu,i|\hat{\rho}|\nu,j\rangle = c_{\mu,i}^* c_{\nu,j}.
\]

Adopting the short notation \(|\nu\rangle \equiv |\nu \hbar k\rangle\) we can write the state of the system,

\[
|\psi(t)\rangle = \sum_{\nu} c_{\nu,1}|\nu \hbar k, 1\rangle + c_{\nu,2}|\nu \hbar k, 2\rangle
\]

(22.179)

\[
\langle \psi(t)|\hat{p}|\psi(t)\rangle = \hbar k \sum_{\nu} \nu (|c_{\nu,1}|^2 + |c_{\nu,2}|^2)
\]

\[
\langle \psi(t)|e^{\pm ik\hat{z}}|\psi(t)\rangle = \sum_{\nu} (c_{\nu,1,1}^* c_{\nu,1} + c_{\nu,1,2}^* c_{\nu,2})
\]

\[
\langle \psi(t)|\hat{a}^\dagger|\psi(t)\rangle = \alpha \sum_{\nu} (|c_{\nu,1}|^2 + |c_{\nu,2}|^2) = \alpha
\]

\[
\langle \psi(t)|\hat{\sigma}^\pm|\psi(t)\rangle = \sum_{\nu} c_{\nu,1}^* c_{\nu,2}
\]

\[
\langle \psi(t)|\hat{\sigma}_z|\psi(t)\rangle = \sum_{\nu} (|c_{\nu,2}|^2 - |c_{\nu,1}|^2).
\]

To describe the dynamics of the system we could use the Schrödinger equation, but the Hamiltonian (22.4) does not contain spontaneous emission nor cavity decay. So, let us employ the equations of motion (22.16), which were derived from a master equation. The equation of motion for the field yields,

\[
\dot{\alpha}_{\pm} = \langle \psi(t)|\hat{a}_{\pm}|\psi(t)\rangle = \langle \psi(t)|(-\kappa + i\Delta_c)\hat{a}_{\pm} - ig\hat{\sigma}^\mp e^{\pm ik\hat{z}} + \eta_{\pm}|\psi(t)\rangle
\]

(22.180)

\[
= (-\kappa + i\Delta_c)\alpha_{\pm} + \eta_{\pm} - ig \sum_{\nu} c_{\nu,1,1}^* c_{\nu,2}
\]

\[
= (-\kappa + i\Delta_c)\alpha_{\pm} + \eta_{\pm} - ig \sum_{\nu} \rho_{\nu,1,\nu,1,2}.
\]

For the atomic motion we get,

\[
\dot{x} = \langle \psi(t)|\hat{x}|\psi(t)\rangle = \frac{1}{m} \langle \psi(t)|\hat{p}|\psi(t)\rangle = \frac{\nu \hbar k}{m},
\]

(22.181)
and

\[ \dot{\rho} = \langle \psi(t) | \dot{\rho} | \psi(t) \rangle \]  
\[ = \langle \psi(t) | i \hbar \dot{\rho} - \delta \cdot \dot{\rho} + \rho \delta \cdot \sigma^+ \cdot \sigma^- \rangle | \psi(t) \rangle \]  
\[ = \sum_{\nu} i \hbar \kappa (\alpha^+ \sigma^-_{\nu-1,1} \sigma^+_{\nu,1} - \alpha^- \sigma^+_{\nu+1,1} \sigma^-_{\nu,1} - \alpha^+ \sigma^-_{\nu-1,1} \sigma^+_{\nu,1} - \alpha^- \sigma^+_{\nu+1,1} \sigma^-_{\nu,1}) \]

22.5. QUANTIZATION OF THE ATOMIC MOTION IN CAVITIES

22.5.5.1 Maxwell-Bloch equations without adiabatic elimination

Analogously to the treatment in Sec. 14.2.1, we will now derive the master equation without adiabatic elimination of the excited state (in this case called Maxwell-Bloch equations from the Liouville equation [first line of Eq. (22.9)] using the Hamiltonian (22.4). The coherent part is,

\[ \dot{\rho}_{\mu,\nu;i,j} \equiv \langle \mu, i | \dot{\rho} | \nu, j \rangle = -i \langle \mu, i | [\hat{H}, \rho] | \nu, j \rangle \]  
\[ = -i \sum_{\rho, u} \rho_{\mu,\nu;i,j} \rho_{\rho,\nu;i,j} + i \sum_{\rho, u} \rho_{\rho,\nu;i,j} \rho_{\mu,\nu;i,j} \]

\[ = -i \left[ \frac{i \hbar}{2m} \Delta \delta \cdot \Delta (-\varepsilon^2 + \varepsilon^2) \right] \rho_{\mu,\nu;i,j} \]

\[ + i \left[ \frac{i \hbar}{2m} \Delta \delta \cdot \Delta (-\varepsilon^2 + \varepsilon^2) \right] \rho_{\mu,\nu;i,j} \]

\[ + i \left[ \frac{i \hbar}{2m} \Delta \delta \cdot \Delta (-\varepsilon^2 + \varepsilon^2) \right] \rho_{\mu,\nu;i,j} \]

The incoherent part comprises the spontaneous decay [second line of Eq. (22.9)],

\[ \langle \mu, i | L_{\text{atom-vac}} | \nu, j \rangle = -\gamma \langle \mu, i | \hat{\sigma} \cdot \hat{\sigma} - 2 \hat{\sigma} \cdot \hat{\rho} \hat{\sigma}^+ \rangle | \nu, j \rangle \]  
\[ = -\gamma \sum_{\mu, u} \rho_{\mu,\nu;i,j} \rho_{\mu,\nu;i,j} + 2\gamma \sum_{\rho, u} \rho_{\rho,\nu;i,j} \rho_{\rho,\nu;i,j} \]

\[ = -\gamma \left[ \delta_{\rho,\nu;i,j} - 2 \delta_{\rho,\nu;i,j} \right] \]

and the cavity decay [third line of Eq. (22.9)],

\[ \langle \mu, i | L_{\text{cavity-vac},+} | \nu, j \rangle = -\kappa \langle \mu, i | \hat{a}^+ \hat{a}^\dagger + \hat{a}^\dagger \hat{a} | \nu, j \rangle = 0 \]  

(22.185)
Finally, using the definition of the recoil shift $\omega_{\text{rec}} = \hbar k^2 / 2m$ we get,

$$
\begin{align*}
\dot{\rho}_{\mu,\nu;1,1} &= i(\nu^2 - \mu^2)\omega_{\text{rec}}\rho_{\mu,\nu;1,1} + 2\gamma\rho_{\mu,\nu;2,2} \\
+ &\hbar g \left[ -\alpha^*_{\mu} \rho_{\mu+1,\nu;2,1} + \alpha_+ \rho_{\mu,\nu+1;2,1} - \alpha^*_+ \rho_{\mu-1,\nu;2,1} + \alpha - \rho_{\mu,\nu-1;2,1} \right] \\
\dot{\rho}_{\mu,\nu;1,2} &= [i(\nu^2 - \mu^2)\omega_{\text{rec}} - \hbar \Delta_a] \rho_{\mu,\nu;1,2} - \gamma \rho_{\mu,\nu;1,2} \\
+ &\hbar g \left[ \alpha^*_{+} \rho_{\mu,\nu-1;1,1} - \alpha^*_{\mu} \rho_{\mu+1,\nu;2,2} + \alpha^*_+ \rho_{\mu,\nu+1;1,1} - \alpha^* \rho_{\mu-1,\nu;2,2} \right] \\
\dot{\rho}_{\mu,\nu;2,1} &= [i(\nu^2 - \mu^2)\omega_{\text{rec}} + \hbar \Delta_a] \rho_{\mu,\nu;2,1} - \gamma \rho_{\mu,\nu;2,1} \\
- &\hbar g \left[ \alpha_+ \rho_{\mu-1,\nu;1,1} - \alpha^* \rho_{\mu,\nu+1;2,2} + \alpha \rho_{\mu+1,\nu-1;1,1} - \alpha^* \rho_{\mu,\nu+1;2,2} \right] \\
\dot{\rho}_{\mu,\nu;2,2} &= i(\nu^2 - \mu^2)\omega_{\text{rec}}\rho_{\mu,\nu;2,2} - 2\gamma\rho_{\mu,\nu;2,2} \\
+ &\hbar g \left[ \alpha^*_{-} \rho_{\mu,\nu-1;2,1} - \alpha_+ \rho_{\mu-1,\nu;1,1} + \alpha^* \rho_{\mu,\nu+1;2,2} - \alpha \rho_{\mu+1,\nu-1;2,1} \right] \rho_{\mu,\nu;2,2} \\
\dot{\alpha}_\pm &= (-\kappa + i\Delta_a)\alpha_\pm + \eta_\pm - ig \sum_{\nu} \rho_{\nu+1,\nu;1,2}
\end{align*}
$$

We note $\hat{\rho}_{\mu,\nu;2,1} = \hat{\rho}^*_{\nu,\mu;1,2}$.

The equations (22.186) form a set a equations to describe the quantized CARL without adiabatic elimination. And as shown in the derivation of the CARL equations (22.26), they contain radiation pressure. In Exc. 22.5.6.2 we study the quantized CARL Maxwell-Bloch equations without adiabatic elimination of the excited state for a three-level system.

### 22.5.6 Exercises

#### 22.5.6.1 Ex: Alternative derivation of the Maxwell-Bloch with adiabatic elimination

Derive the directly from the Liouville equation (22.9) using the Hamiltonian (22.27) in adiabatic elimination.

#### 22.5.6.2 Ex: Maxwell-Bloch equations without adiabatic elimination

Derive the Maxwell-Bloch equations for a three-level system coupled to a ring cavity without adiabatic elimination, but with quantized motion.

#### 22.5.6.3 Ex: Linearized quantum CARL

Analyze the quantum CARL according to [477].

### 22.6 Quantized light interacting with atoms moving in cavities

Cavity QED has been studied extensively in the context of the Jaynes-Cummings model in Sec. 15.2 and of cooperative scattering in Sec. 21.1.2, however, without addressing the issue of atomic motion which, via photonic recoil, inevitably influences the dynamics. We also started a discussion on the role of photonic recoil in Sec. 16.3,
which will be continued in the following sections in the context of ring cavities,
\[
\dot{c}_{n_n,i} = i \frac{d}{dt} \langle r, \alpha_+, \alpha_-, i | \psi(t) \rangle = \langle r, \alpha_+, \alpha_-, i | \hat{H} | \psi(t) \rangle
\]
\[
\dot{\alpha}_\pm = \langle \psi(t) | \hat{a}_\pm | \psi(t) \rangle = \langle \psi(t) | [\hat{H}, \hat{a}_\pm] - \kappa \hat{a}_\pm | \psi(t) \rangle.
\]

Concretely, we will be using the Hamiltonian (22.27), obtained after adiabatic elimination of the excited state.

### 22.6.1 QED in ring cavities

Macroscopic high-finesse ring cavities interacting with a cloud of cold atoms allowed to enter the regime of strong collective coupling. However, new interesting aspects arise from the regime of strong coupling on the level of individual atoms.

Today's research projects on cold atoms in cavities are essential divided into two classes, each class realizing an opposite regime: Cavity quantum electrodynamics (CQED) experiments as they are done by the groups of Rempe [363] and Kimble use microcavities having mode volumes so small that few photons give rise to macroscopic field strength. In such cavities the atom-field coupling is made to exceed all other decay rates. The other regime is that of cavity-cooling mainly investigated by Vuletic at the MIT and, in the case of ring cavities, of the collective atomic recoil laser (CARL) realized in the Tübingen research group. In this second regime the cavities are so large that the light fields can be considered as classical.

An interesting question is, whether the two regimes can be married to realize a system, where collective effects and entanglement between optical and atomic modes can be observed. The central idea is not to increase the coupling strength by reducing the mode volume, but to reduce the decay rates, in particular the natural linewidth of the atomic transition by choosing an atomic species that can be laser-cooled on a narrow intercombination line.

#### Example 89 (CQED by reducing the ring cavity mode volume):

Technically a ring cavity design with \((w, L, F) = (30 \mu m, 4 \text{ cm}, 200000)\) is feasible. This is enough to get below the critical atom number, but this is not sufficient to get into the CQED regime. Reducing \(\Gamma\) seems unavoidable.

The isotope \(^{88}\text{Sr}\) posses a narrow transition which can be used for optical cooling. The following table compares the various systems, i.e. a CQED example taken from Rempe, the macroscopic ring cavity with rubidium used in our Tübingen CARL experiments and a cavity tuned close to the strontium intercombination line.

<table>
<thead>
<tr>
<th>experiment</th>
<th>Rempe, Rb</th>
<th>Tübingen, Rb</th>
<th>São Carlos, Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma)</td>
<td>((2\pi)6 \text{ MHz})</td>
<td>((2\pi)6 \text{ MHz})</td>
<td>((2\pi)7.6 \text{ kHz})</td>
</tr>
<tr>
<td>(F)</td>
<td>440000</td>
<td>80000</td>
<td>200000</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>((2\pi)0.7 \text{ MHz})</td>
<td>((2\pi)22 \text{ kHz})</td>
<td>((2\pi)19 \text{ kHz})</td>
</tr>
<tr>
<td>(w)</td>
<td>29 (\mu)m</td>
<td>100 (\mu)m</td>
<td>30 (\mu)m</td>
</tr>
<tr>
<td>(L)</td>
<td>500 (\mu)m</td>
<td>8.5 cm</td>
<td>4 cm</td>
</tr>
<tr>
<td>(g)</td>
<td>((2\pi)1 \text{ MHz})</td>
<td>((2\pi)88 \text{ kHz})</td>
<td>((2\pi)13 \text{ kHz})</td>
</tr>
<tr>
<td>(N_{\text{crit}})</td>
<td>0.5</td>
<td>34</td>
<td>1.6</td>
</tr>
<tr>
<td>(n_{\text{sat}})</td>
<td>1.1</td>
<td>2312</td>
<td>0.16</td>
</tr>
</tbody>
</table>

With \(N = 10^4\) the cooperativity parameter \(N/N_{\text{crit}}\) is in all cases well above 1.
22.6.2 Description of quantized light fields in cavities

In order to calculate the evolution of photon distributions in the counter-propagating modes $\hat{a}_\pm$ of a ring cavity, we develop CARL in a Fock basis. For simplicity, we first consider the motion of a single atom as classical and fixed (i.e. not as a degree of freedom), and we apply the adiabatic approximation. I.e. we have only two quantized degrees of freedom, which we organize like,

$$|\psi\rangle = |\nu\rangle_{\text{motion}} \otimes |\hat{\psi}\rangle_{\text{electron}} \otimes |n\rangle_+ \otimes |n\rangle_- \rightarrow |n_+,n_-\rangle ,$$  \hspace{1cm} (22.188)

Expanding the fields into Fock states,

$$|\psi\rangle = \sum_{n_+,n_-} c_{n_+,n_-} |n_+,n_-\rangle ,$$  \hspace{1cm} (22.189)

the field operators and the density matrix read,

$$\hat{a}_+ = \sum_{n_+} \sqrt{n_+} |n_+ - 1\rangle \langle n_+| \otimes I = \sum_{n_+,n_-} \sqrt{n_+} |n_+ - 1, n_-\rangle \langle n_+, n_-|$$  \hspace{1cm} (22.190)

$$\hat{a}_- = I \otimes \sum_{n_-} \sqrt{n_-} |n_- - 1\rangle \langle n_-| = \sum_{n_+,n_-} \sqrt{n_-} |n_+ - 1, n_-\rangle \langle n_+, n_-|$$

$$\hat{\rho} = |\psi\rangle \langle \psi| = \sum_{m_+,m_-} c_{m_+,m_-}^* c_{n_+,n_-} |m_+,m_-\rangle \langle n_+, n_-| .$$

Figure 22.22: (a) Bragg scattering at a 1D optical lattice. (b) Same as in (a), but now the optical lattice is generated by the mode of an optical ring cavity.

Note that the master equation using the Lindblad operator traces over the reservoir. Hence, the master equation only treats the cavity modes, but does not allow predictions on the quantum behavior of outcoupled fields. In order to describe e.g. quantum correlations in output field, one needs an input-output theory [119, 215].
In the case of classical motion quantum light fields,

$$\dot{c}_{n+,n-} = i(\Delta_c - U_0)(n_+ + n_-) c_{n+,n-} $$
$$- iU_0 \left( e^{-2i k z} \sqrt{n_+ + 1} c_{n+1,n_-} - e^{2i k z} \sqrt{n_- + 1} c_{n_+,n_-+1} \right)$$
$$- \eta_+ \left( \sqrt{n_+ + 1} c_{n_+,n_-} - \sqrt{n_-} c_{n_+,n_-+1} \right)$$
$$- \eta_- \left( \sqrt{n_+ + 1} c_{n_+,n_-+1} - \sqrt{n_-} c_{n_+,n_-} \right)$$

$$\hat{z} = 2\hbar k U_0 \sum_{n_+,n_-} \left( e^{-2i k z} \sqrt{n_+ + 1} n_- c_{n+1,n_-+1} c_{n_+,n_-} \right)$$
$$- e^{2i k z} \sqrt{n_- + 1} c_{n_+,n_-+1} c_{n_+,n_-+1} \right)$$

(22.191)

22.6.3 Photon backscattering for fixed atomic position

To tackle the problem of quantized light field we first assume an atom fixed in space, that is, we completely disregard the motional degree of freedom by setting $\hat{p} = 0$ and restricting to the Hamiltonian,

$$\hat{H} = \sum_{\pm} \omega_{\pm} \hat{a}_{\pm}^\dagger \hat{a}_{\pm} - \eta_{\pm} (\hat{a}_{\pm} - \hat{a}_{\pm}^\dagger) + U_0 (\hat{a}_{\pm}^\dagger \hat{a}_{\pm} e^{-2i k z} + \hat{a}_{\pm}^\dagger \hat{a}_{\pm} e^{2i k z}) .$$

(22.192)

In Exc. 22.6.7.1 we show how to cast the Hamiltonian into a matrix form using an appropriate basis already used in the discussion of the beam splitter in the photon representation in Sec. 15.5.1.

In Exc. 22.6.7.2(a) we derive the equations of motion for the components $c_{n_+,n_-}$ of the state vector from the Schrödinger equation cavity decay. In Exc. 22.6.7.3(a) we derive the equations of motion for the components $\rho_{m_+,m_-} = \langle m_+, m_- | \hat{\rho} | n_+, n_- \rangle$ of the density operator. Simulations performed based on these equations of motion are shown in Fig. 22.23).

The simulations reveal a number of interesting facts:

- The field amplitudes $|\alpha_{\pm}|^2$ execute oscillations due to CARL coupling, but with preserved Poissonian shape of the photon number distributions.

- When simulations are done with initial Fock states, they eventually relax to a Glauber state.

- The mean photon numbers and the atomic coordinates evolve in a continuous way.

These observations are not surprising, once we understood the backscattering as a linear coupling between the modes being mediated by a beam splitter Hamiltonian of type (15.201)\textsuperscript{17},

$$\hat{H}_{int} = U_0 (\hat{a}_{\pm}^\dagger \hat{a}_{-} e^{-2i k z} + \hat{a}_{+}^\dagger \hat{a}_{-} e^{2i k z}) ,$$

(22.193)

\textsuperscript{17}Which itself represents a generalized displacement operator,

$$\hat{H}_{int} \simeq U_0 (\alpha_+^* e^{-2i k z} \hat{a}_- + \alpha_- e^{2i k z} \hat{a}_+^\dagger) \equiv \hbar \beta^* \hat{a}_- - \hbar \beta \hat{a}_+^\dagger ,$$
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Figure 22.23: (code) Time-evolution of CARL with one classical atom and two quantized field modes. (a) Photon number distributions of two modes after some evolution time \( t \). (b) Time-evolution of the mean photon number; at time \( t = 10 \), the atom is suddenly displaced. (c) Time-evolution of the (classical) atomic trajectory.

for which we found the relationship (15.202),

\[
e^{-i\hat{H}_{\text{int}}t}\hat{a}_\pm e^{i\hat{H}_{\text{int}}t} = \hat{a}_\pm \cos U_0 t \pm \hat{a}_x e^{\mp 2i\kappa z} \sin U_0 t.
\]

This means, that we expect (for a fixed location \( z \) of the atom) an oscillatory behavior of the field amplitudes \( |\alpha\pm|^2 \) and also of the phase (encoded in \( \alpha_+^*\alpha_- \)), but no modification of the coherent photon statistics. On the contrary, as shown in Sec. 15.5.1, a beam splitter tends to transform sub-Poissonian states into Poissonian ones. In fact, CARL is nothing else than a movable beam splitter.

Non-linearity may come into play, if photonic recoil is included, i.e. if the atomic motion itself becomes a degree of freedom. This is the next step of our problem, that needs to be solved.

### 22.6.4 Quantized light fields and quantized recoil

The simulations of the preceding section show that the CARL Hamiltonian (22.193), despite the appearance of photon creation and annihilation operator, does not request recoil to be quantized: If an arbitrary momentum kick of the atom can be absorbed by the light fields, then an arbitrary dipole force can be transmitted to the atomic momentum! The momentum conservation law (22.18) does not imply quantization of photonic recoil. The question is now, how to conceal this fact with the observation of discrete momentum sidemodes [559]. We have seen earlier, that the quantization of the motion is transferred from the quantized photon fields via the operator (22.140) to the atom: An initially resting atom can only adopt motional states with momenta equal to a multiple of \( 2\hbar k \).

We will now take the quantization of the atomic momentum for granted and study quantized light modes coupled by recoiling atoms, we extend our Hilbert space like,

\[
|\psi\rangle = |\nu\rangle_{\text{motion}} \otimes |i\rangle_{\text{electron adiab.elim.}} \otimes |n\rangle_+ \otimes |n\rangle_- \rightarrow |\nu, n_+, n_-\rangle,
\]

since defining \( \beta \equiv \frac{U_0}{\hbar} \alpha_+ e^{2i\kappa z} \), we find,

\[
B(\beta t) = e^{-i\hat{H}_{\text{int}}t/\hbar} = e^{\beta^* t\hat{a}_- \beta t\hat{a}_-^\dagger}.
\]
Expanding the motion and fields\textsuperscript{18},
\[
|\psi\rangle = \sum_{\nu,n_+,n_-} c_{\nu,n_+,n_-} |\nu,n_+,n_-\rangle ,
\] (22.196)

the momentum kick operator reads,
\[
e^{-2i k\hat{z}} \otimes 1 \otimes 1 = \sum_{\nu} |\nu h\rangle\langle \nu h| \otimes |2 h\nu,h,\nu\rangle\langle \nu,h,\nu| .
\] (22.197)

The equations of motions derived in Exc. 22.6.7.2 from the Schrödinger equation are now generalized to,
\[
\dot{c}_{\nu,n_+,n_-} = i(\Delta c - U_0)(n_+ - n_- c_{\nu,n_+,n_-}
\]
\[= - i U_0 \left( \sqrt{n_+ (n_+ + 1) c_{\nu-1,n_+,n_-} - 1} - \sqrt{(n_+ + 1) n_- c_{\nu+1,n_+,n_-}} \right) .
\]
\[= \eta_+ \left( \sqrt{n_+ + 1} c_{\nu,n_+,n_-} + \sqrt{n_- c_{\nu,n_-,n_-}} \right) - \eta_- \left( \sqrt{n_- + 1} c_{\nu,n_+,n_-} - \sqrt{n_- c_{\nu,n_-,n_-}} \right)
\] (22.198)

Note that the general shape of fully quantized Schrödinger equations looks like,
\[
\dot{c}_{\nu,n_+,n_-} = \nu(\Delta c - U_0)(n_+ - n_- c_{\nu,n_+,n_-}
\]
\[= 2 \hbar k U_0 \left( c_{\nu,n_+,n_-} - \sqrt{n_+ (n_+ + 1)} c_{\nu-1,n_+,n_-} - 1 - \sqrt{n_- c_{\nu+1,n_+,n_-}} \right) .
\] (22.199)

Note the fact, which is important for computation, that the dimension of the Hilbert space increases a lot, that is like dim$\nu \cdot$dim$n_+ \cdot$dim$n_-$, where $\nu, n_\pm$ are the numbers of states considered.

\textsuperscript{18}Note the fact, which is important for computation, that the dimension of the Hilbert space increases a lot, that is like dim$\nu \cdot$dim$n_+ \cdot$dim$n_-$, where $\nu, n_\pm$ are the numbers of states considered.
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Note that, in contrast to CARL equations, the fully quantized equations (22.198) are linear. That is, it is the ‘classization’\(^\text{19}\) of the degrees of freedom which introduces the non-linearities, which are typical for CARL, e.g. the feedback introduced by classical light fields. The process of ‘classization’ corresponds to tracing over degrees of freedom, which we want to treat classically and thus remove from the Hamiltonian.

22.6.4.1 Calculation of observables

Once the time evolution of the coefficients \(c_{\nu,n_+,n_-}(t)\) has been determined by solving the differential equation (22.198) we can calculate the observables in the following way. The probability distribution for photon numbers in the mode \(\alpha_+\) is given by,

\[
P_{n_+}(t) = \langle \psi(t) | \mathbb{I} \otimes |n_+\rangle \langle n_+ | \mathbb{I} | \psi(t) \rangle = \sum_{\nu,n_-} \langle \nu, n_+, n_- | \nu, n_+, n_- \rangle = \sum_{\nu,n_-} |c_{\nu,n_+,n_-}(t)|^2 ,
\]

the mean photon number by,

\[
\langle \hat{n}_+(t) \rangle = |\alpha_+(t)|^2 = \sum_{n_+} n_+ P_{n_+}(t) = \sum_{\nu,n_+,n_-} n_+ |c_{\nu,n_+,n_-}(t)|^2 ,
\]

and similarly for \(\alpha_-\). The probability distribution for momentum states is given by,

\[
P_\nu(t) = \sum_{n_+,n_-} |c_{\nu,n_+,n_-}(t)|^2 ,
\]

the mean momentum by,

\[
\langle \hat{p}(t) \rangle = \sum_{\nu,n_+,n_-} \nu \hbar k |c_{\nu,n_+,n_-}(t)|^2 ,
\]

the mechanical kinetic energy by,

\[
E_{\text{kin}}(t) = \frac{\langle \hat{p}^2 \rangle}{2m} = \sum_{\nu,n_+,n_-} \frac{(\nu \hbar k)^2}{2m} |c_{\nu,n_+,n_-}(t)|^2 = \sum_{\nu,n_+,n_-} \nu^2 \hbar \omega_{\text{rec}} |c_{\nu,n_+,n_-}(t)|^2 ,
\]

and the potential energy by,

\[
E_{\text{pot}}(t) = \hbar U_0 \langle e^{-2i k \hat{z} \hat{a}_{\dagger}^+ \hat{a}_{-} - 2i k \hat{z} \hat{a}_{\dagger} \hat{a}_{-}^+} \rangle = \hbar U_0 \sum_{\nu,n_+,n_-} \left( c_{\nu+1,n_+,+1,n_-1}^* c_{\nu,n_+,n_-} \sqrt{(n_+ + 1)n_-} 
+ c_{\nu,n_+,-1,n_-1}^* c_{\nu,n_+,n_-} \sqrt{n_+(n_- + 1)} \right) .
\]

With this we can check conservation of the total photon number,

\[
\langle \hat{n}_+(t) \rangle + \langle \hat{n}_-(t) \rangle = \text{const} ,
\]

\(^\text{19}\)As opposed to the term quantization.
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of the mechanical energy,

$$E_{\text{kin}}(t) + E_{\text{pot}}(t) = \text{const} \quad (22.210)$$

and of total linear momentum,

$$\hbar k[\langle \hat{n}_+(t) \rangle - \langle \hat{n}_-(t) \rangle] - \langle \hat{p}(t) \rangle = \text{const} \quad (22.211)$$

22.6.4.2 Master equation for CQED with atomic recoil in the adiabatic approximation

Using the Hamiltonian (22.27) or (22.135), the expansion of the recoil operator (22.140), the expansion of the photon field operators (22.190), and the matrix representation of the density operator (14.16), that is,

$$\hat{\rho} = \sum_{\mu, \nu; m_+, n_+; m_-, n_-} |\mu, m_+, m_-\rangle \rho_{\mu, \nu; m_+, n_+; m_-, n_-} \langle \nu, n_+, n_-| \quad (22.212)$$

the master equation (22.9) becomes,

$$\langle \mu, m_+, m_- | [\hat{H}, \hat{\rho}] | \nu, n_+, n_- \rangle = -i \langle \mu, m_+, m_- | \rho [\hat{H}, \hat{\rho}] | \nu, n_+, n_- \rangle + \mathcal{L}_{\text{cavity-vac}, \pm \hat{\rho}} \quad (22.213)$$

with the coherent contributions,

$$\langle \mu, m_+, m_- | \rho [\hat{H}, \hat{\rho}] | \nu, n_+, n_- \rangle = \omega_{\text{rec}}(2m^2 - \nu^2) \rho_{\mu, \nu; m_+, n_+; m_-, n_-} \quad (22.214)$$

$$\langle \mu, m_+, m_- | [-i\eta_+ (\hat{a}_+ - \hat{a}_+^\dagger), \hat{\rho}] | \nu, n_+, n_- \rangle = (U_0 - \Delta_c) n_{\pm \rho_{\mu, \nu; m_+, n_+; m_-, n_-}} \quad (22.215)$$

$$\langle \mu, m_+, m_- | [-i\eta_- (\hat{a}_- - \hat{a}_-^\dagger), \hat{\rho}] | \nu, n_+, n_- \rangle = (U_0 e^{-i\hat{q}_z \hat{a}_- \hat{a}_+^\dagger} - 1) \rho_{\mu, \nu; m_+, n_+; m_-, n_-} \quad (22.216)$$
and the incoherent contributions,

\[
\langle \mu, m_+, m_- | - \kappa [ \hat{a}^\dagger_+ \hat{a}_+ \hat{\rho} - 2 \hat{a}_- \hat{\rho} \hat{a}^\dagger_+ + \hat{\rho} \hat{a}^\dagger_+ \hat{a}_+ ] | \nu, n_+, n_- \rangle = -\kappa \left( m_+ \rho_{\mu,\nu; m_+, n_+; m_- n_-} + n_+ \rho_{\mu,\nu; m_+, n_+; m_- n_-} - 2 \sqrt{(m_+ + 1)(n_+ + 1)} \rho_{\mu,\nu; m_+, n_+; m_- n_- + 1} \right)
\]

\[
\langle \mu, m_+, m_- | - \kappa [ \hat{a}^\dagger_- \hat{a}_- \hat{\rho} - 2 \hat{a}_+ \hat{\rho} \hat{a}^\dagger_- + \hat{\rho} \hat{a}^\dagger_- \hat{a}_- ] | \nu, n_-, n_- \rangle = -\kappa \left( m_- \rho_{\mu,\nu; m_+, n_+; m_- n_-} + n_- \rho_{\mu,\nu; m_+, n_+; m_- n_-} - 2 \sqrt{(m_- + 1)(n_- + 1)} \rho_{\mu,\nu; m_+, n_+; m_- n_- + 1} \right)
\]

Figure 22.24: (code) Time-evolution of CARL with one classical atom and two quantized field modes. (a) Photon number distributions of two modes after some evolution time \( t \). (b) Time-evolution of the mean photon number; at time \( t = 10 \), the atom is suddenly displaced. (c) Time-evolution of the (classical) atomic trajectory.

22.6.5 Kicking and forcing an atom in a ring cavity

The question we want to elucidate here is, how a coupled atom-ring cavity system reacts to a kick transferring an arbitrary amount of momentum to the atom. We studied a similar question when studying the kicking of a harmonic oscillator in Sec. 4.5.2, however, the situation is quite different now because, in contrast to the harmonic oscillator, the motion of an atom subject to CARL dynamics is not localized and, hence, not quantized. That is, an arbitrarily kicked atom is not bound to join one of those momentum states it would populate when kicked by photonic recoil. Hence, a momentum state expansion like (22.144) is not appropriate, so that we have to go a step back and consider the Hamiltonian (22.27) again.
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22.6.5.1 Kicking

Let us first describe the kick as an incoherent disruptive one time event transforming operators, the Hamiltonian and the system’s state like,

$$A \rightarrow e^{-i\hat{q}\hat{z}} \hat{A} e^{i\hat{q}\hat{z}}, \quad |\psi\rangle \rightarrow e^{i\hat{q}\hat{z}} |\psi\rangle \quad (22.216)$$

and in particular,

$$H \rightarrow e^{-i\hat{q}\hat{z}} \hat{H} e^{i\hat{q}\hat{z}} = \hat{H}(\hat{z}, \hat{p} - \hat{h}q) \quad , \quad \langle p|\psi\rangle \rightarrow \langle p|e^{i\hat{q}\hat{z}}|\psi\rangle = \langle p - \hat{h}q|\psi\rangle \quad (22.217)$$

The Schrödinger equation tells us the system’s evolution during the force,

$$\frac{i\hbar}{dt} \langle p|\psi\rangle = \frac{\hat{p}^2}{2m} + U_0 \left( \langle p|e^{-2i\hat{k}z}|\psi\rangle \hat{a}_+^\dagger \hat{a}_- + \langle p|e^{2i\hat{k}z}|\psi\rangle \hat{a}_+ \hat{a}_-^\dagger \right) + mg\hat{z} \quad . \quad (22.218)$$

We note that this equations contains CARL feedback via the simultaneous presence of $\hat{z}$ and $\hat{p}$. If we want to disregard the CARL force (assuming, for example, that the motion is totally imposed by an external force, as done in Sec. 22.2.2 in order to focus on the behavior of the light fields), we must not project the Schrödinger equation on $\langle p|$ but treat the motional degree of freedom as classical.

22.6.5.2 Forcing

Let us now describe the kick as a force $F(t) = mg\theta(t)$ being switched on at a given time, but being constant afterward,

$$H = \frac{\hat{p}^2}{2m} + U_0 \left( e^{-2i\hat{k}z} \hat{a}_+^\dagger \hat{a}_- + e^{2i\hat{k}z} \hat{a}_+ \hat{a}_-^\dagger \right) + mg\hat{z} \quad . \quad (22.219)$$

We note that with (2.152) the Hamiltonian transformed into the accelerated frame reads,

$$\hat{H} \rightarrow e^{-im\hat{g}\hat{z}t/\hbar} \hat{H} e^{im\hat{g}\hat{z}t/\hbar} + i\hbar \left( \frac{d}{dt} e^{im\hat{g}\hat{z}t/\hbar} \right)^\dagger e^{im\hat{g}\hat{z}t/\hbar} = \hat{H}(\hat{z}, \hat{p} - mgt) - mg\hat{z}$$

$$= \frac{(\hat{p} - mgt)^2}{2m} + U_0 \left( e^{-2i\hat{k}z} \hat{a}_+^\dagger \hat{a}_- + e^{2i\hat{k}z} \hat{a}_+ \hat{a}_-^\dagger \right) \quad . \quad (22.220)$$

The Schrödinger equation for the transformed wavefunction $|\tilde{\psi}\rangle = |\psi\rangle e^{im\hat{g}\hat{z}t/\hbar}$, which tells us the system’s evolution during the force,

$$i\hbar \frac{d}{dt} \langle p|\tilde{\psi}\rangle = \frac{(p - mgt)^2}{2m} \langle p|\tilde{\psi}\rangle + U_0 \left( \langle p|e^{-2i\hat{k}z}|\tilde{\psi}\rangle \hat{a}_+^\dagger \hat{a}_- + \langle p|e^{2i\hat{k}z}|\tilde{\psi}\rangle \hat{a}_+ \hat{a}_-^\dagger \right) \quad , \quad (22.221)$$

has a similar shape to Eq. (22.218).

22.6.5.3 Vibrating

Another option might be to additionally confine the atom in a harmonic potential [648],

$$\hat{H} = \frac{\hat{p}^2}{2m} + U_0 \left( e^{-2i\hat{k}z} \hat{a}_+^\dagger \hat{a}_- + e^{2i\hat{k}z} \hat{a}_+ \hat{a}_-^\dagger \right) + \frac{m}{2} \omega^2 \hat{z}^2 \quad \quad (22.222)$$

$$= \hbar \omega (\hat{A}^\dagger \hat{A} + \frac{1}{2}) + U_0 \left[ D^\dagger (\alpha) \hat{a}_+^\dagger \hat{a}_- + D(\alpha) \hat{a}_+ \hat{a}_-^\dagger \right] \quad , \quad (22.222)$$
where $D(\alpha) \equiv e^{\alpha \hat{A} \dagger - \alpha^* \hat{A}}$ with $\alpha \equiv \frac{2\hbar k a_{ho}}{\sqrt{2}}$.

22.6.5.4 Quantized equations of motion

In both cases, ‘kicking’ and ‘forcing’, we may discretize momentum space, although in the latter case we need to transform back into the lab frame after having solved the Schrödinger equation (22.198).

22.6.6 Quantum correlations

Superradiant or CARL scattering exist due to a correlation of subsequent scattering events. In the quantum regime, the emergence of quantum correlations, such as entanglement and squeezing is to be expected as a consequence of CARL dynamics [432, 475, 490, 482, 483, 603, 116, 117, 118]. The advantage of doing CARL with BECs is the possibility to exploit the instability in the good-cavity regime to parametrically amplify optical and matter waves, manipulate matter wave coherence properties and generate entanglement.

For the description of the dynamics of the fields, i.e. the momentum sidemodes and the cavity modes, a first-quantized treatment of the atomic motion [477] would be sufficient. All information can be extracted from a numerical simulation of the quantum CARL equations. However, here we are also interested in quantum correlations. Hence, in a first-quantized treatment of the atomic motion, the coefficients $\hat{c}_n$ must be treated as field operators. Alternatively, we derive the basic equations rigorously from a second-quantized treatment.

22.6.6.1 Generation of squeezing and entanglement via CARL

An experiment by [493] produces squeezing in transmission of a cavity resonantly interacting with single atoms. The effect was induced by vacuum Rabi-splitting. In our case we have a ring cavity, we operate far from equilibrium, we have classical Stark splitting. Hence, we may expect squeezing and entanglement from the CARL dynamics.

Figure 22.25: Production and detection of squeezing.

Differences between entanglement and correlation (correlations involve time or space coordinates $g(\tau)$, particles correlate across space and time, coherence).

Bragg scattering of light at an atomic grating (or simply the splitting of light at a beam splitter) is an irreversible process (see Sec. 15.5). CARL can be interpreted in
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In terms of Bragg scattering of light at an atomic grating, which is generated itself by the Bragg scattering. Hence, the scattering of early photons influences the scattering of late photons, i.e. the scattering processes get correlated, the dynamics gets a history. The correlation between subsequent scattering processes is what preserves the coherence in CARL and superradiant Rayleigh scattering.

It is now interesting to ask how this classical correlations will behave in the quantum regime, i.e. upon 1. quantization of the motion of individual atoms and upon 2. quantization of atomic particle field. Following [432, 431, 434, 433, 475, 476, 482, 483], non-classical correlations such as entanglement of matter wave modes, and entanglement between matter-wave and optical modes is expected.

22.6.6.2 Quantum non demolition measurements with CARL

According to [483], a ring cavity could lend itself to quantum non demolition measurements. They consider our ring cavity being pumped from both sides through an incoupling mirror. A so-called pump mode is injected with a $p$-polarized light field, and a probe mode with a $s$-polarized light field. The light of the probe mode leaking through a mirror gives information about the atoms (e.g. via the refraction index). The counterpropagating pump light gives access to higher-order moments of the atom distribution.

The problem is that the effect is based on photon exchange between the modes, and those are orthogonally polarized. Even more problematic is that, in practice, the modes have different frequencies. Other work on this subject has been done by [28, 183, 409, 410, 103].

22.6.7 Exercises

22.6.7.1 Ex: Analogy between CARL and two-atom Dicke states

a. Write the Hamiltonian (22.192) in matrix form using the basis,

$$\psi_k = \{|0,0\rangle, |0,1\rangle, |1,0\rangle, |0,2\rangle, |1,1\rangle, |2,0\rangle, \ldots\} .$$

b. Now restrict to the finite number of states $\psi_k = \{|0,0\rangle, |0,1\rangle, |1,0\rangle, |1,1\rangle\}$ and discuss the analogy between CARL and two-atom Dicke states.

22.6.7.2 Ex: Cavity QED with Schrödinger equation

Assume a symmetrically pumped ring cavity in equilibrium with an atom at a fixed position.

a. Derive the equations of motion for the components for the probability amplitudes in a Fock state basis.

b. Express the possible initial states $|\alpha_+, \alpha_-\rangle$, $|\alpha_+, n_-\rangle$, and $|n_+, n_-\rangle$ in the Fock state basis. How to calculate the photon distribution $p_{n_+}$, the amplitudes of field modes $\alpha_\pm$, and the atom’s position and momentum at later times of the evolution?

22.6.7.3 Ex: Cavity QED with density matrix

Assume a symmetrically pumped ring cavity in equilibrium with an atom at a fixed position.
a. Derive the equations of motion for the components of the density operator.
b. Write down the density operator describing two decoupled Glauber states? How to retrieve the Fock state populations from the density operator?
c. Now, assume that the atom can move. What will be the evolution of the motional state?

22.6.7.4  **Ex: Photon number and momentum conservation**

a. Calculate the evolution under CARL interaction, $e^{-iH_{\text{carl}}t} \hat{n}_\pm e^{iH_{\text{carl}}t}$, of the photon numbers in each mode and show that the total photon number is conserved.
b. Assuming conservation of total momentum calculate the evolution of the atomic momentum.

22.6.7.5  **Ex: Self-synchronization of Bloch oscillations**

Study the Bloch-CARL dynamics for the case of a sinusoidally modulated CARL pump light intensity. Choose as the modulation frequency the expected Bloch oscillation frequency and a variable phase delay.

22.6.7.6  **Ex: Self-synchronization of Bloch oscillations**

Study the dynamics of the counterpropagating light modes of a ring cavity in the presence of an atom whose position is periodically modulated with a given frequency. Use the method of continued fractions to obtain analytical results.
Chapter 23

Statistical and thermodynamic approaches to CARL

The CARL phenomenon introduced in the previous chapter raises a variety of questions, such as: How does it compare to an ordinary laser? Is there a phase transition? Of what kind would be this transition (in the Ehrenfest or Landau classification scheme)? What are the coherence properties (measured by correlation functions)? How do these properties depend on the random motion (temperature) of the atoms? These issues will be addressed in this chapter and in the later chapter within the models of Langevin, Fokker-Planck, Vlasov, and Kuramoto.

23.1 The Langevin model

23.1.1 CARL with damping

We saw in the previous chapter that CARL is a transient phenomenon, the atoms and the phase of the light wave being continuously accelerated. However, it is possible to force stationary behavior by providing additional friction for the atoms. Such friction can be carried out by an optical molasses (see Sec. 24.2.1) characterized by a friction coefficient $\gamma_{frc}$. The friction force can be added to the CARL equations of motion (22.96),

$$\dot{\alpha} = -\kappa \alpha - iU_0 \alpha + \sum_m e^{2ikz_m}$$

$$4i\omega_{rec} U_0 \alpha + (\alpha e^{-2ikz} - \alpha^* e^{2ikz}) - \gamma_{frc} kv_n .$$

Now, the balance of forces happens at a well-defined atomic velocity, which incidentally corresponds to a well-defined CARL frequency. Assuming perfect ‘bunching’ $e^{2ikz_m} = e^{2ikz}$, and balanced forces, $\dot{v}_m = 0 e \alpha_- = \beta e^{2ikz}$ with $\beta = 0$, we obtain for $\kappa \ll 2kv$,

$$\alpha_- = \frac{-iNU_0 \alpha + e^{2ikz}}{\kappa + 2ikv}$$

$$(kv)^3 = \frac{2\omega_{rec} \kappa NU_0^2 \alpha^2}{\gamma_{frc}} .$$
Optical molasses obviously are subject to a cooling limit coming from the random scattering of photons. As a consequence, atoms follow a random walk in the momentum space, which leads to the diffusion and heating of atoms and impedes the bunching of atoms. It also turns out that a minimal grouping is required to initialize CARL. Therefore, there is a threshold behavior as a function of the equilibrium temperature of the molasses,

$$
\dot{\alpha}_- = -\kappa \alpha_- - i U_0 \alpha_+ \sum_m e^{2ikz_m} \\
kv_n = 4i\omega_{rec} U_0 \alpha_+ (\alpha_- e^{-2ikz_n} - \alpha^* e^{2ikz_n}) - \gamma_{frc} kv_n + \xi_n(t) 
$$

The equation corresponds to a Langevin equation, where the stochastic term $\xi_n(t)$ describes white noise. We can simulate this equation by a Runge-Kutta method, where the atoms are continually exposed to random momentum changes. For $N$ atoms we need to solve $2N + 2$ Langevin equations to describe the dynamics of all degrees of freedom. The Langevin equations are associated to so-called Fokker-Planck equations \[609, 507, 317, 608\]. These describe the temporal evolution of the atomic density along the optical $x$-axis. With these equations we replace the $2N$ trajectories of individual particles by a one-dimensional field $P(x,t)$. The Vlasov equation represents a different approach: Here we assume that the equilibrium between cooling and heating is achieved by a continuous thermalization process described by a single rate $\gamma_{th}$ \footnote{Through a linearization of the CARL equations, the cavity dissipation itself is found to exert a friction force to the atoms \[262, 212\]. This implies the existence of diffusion and a finite equilibrium temperature even at if the atoms are initially at $T = 0$.}.

### 23.1.1.1 Characterization of an optical molasses

Optical molasses is discussed in Sec. 24.2.1. In Exc. 24.2.5.1 we will show how, through a linearization of the radiative pressure force, we arrive at the following approximation,

$$
F = -\gamma_{frc} \mathbf{v} \quad \text{with} \quad \gamma_{frc} \simeq -\sqrt{3}h k^2 s(1 + s)^{-3/2}, 
$$

Figure 23.1: Scheme of the ring cavity.
where \( s = I/I_s \) is the saturation parameter. This formula estimates the maximum friction force, when the lasers are tuned close to an atomic resonance\(^2\).

A more fundamental problem is the interdependence of the molasses friction and the CARL. In fact, because the dipole potential influences the detuning of the molasses beams by light-shifting the \( D_2 \) line, the \( \gamma_{th} \) coefficient depends on \( \Delta_a \) and \( \eta_+ \) (the reverse field \(|\alpha_-|\) may be neglected). The threshold equations must then be solved in a self consistent way. It might however be possible to determine \( \gamma_{th} \) only slightly above threshold, where the modification is small, \( \gamma_{th} \approx \gamma_{th}^{(\text{thresh})} \).

### 23.1.2 Fluctuation-dissipation theorem

Trajectories of ensembles of particles subject to friction and stochastic forces can be described by *Langevin equations*. The friction and the diffusion forces are related by the *fluctuation-dissipation theorem*. This theorem states that, for a thermal sample of atoms whose coordinates \( \theta_n \) follow,

\[
\ddot{\theta}_n = -\gamma_{frc} \dot{\theta}_n + \xi_n(t) ,
\]

the Langevin force \( \xi(t) \) fluctuates stochastically with,

\[
\langle \xi_n(t) \rangle = 0 \quad \text{and} \quad \langle \xi_n(t) \xi_m(t + \tau) \rangle = 2\gamma_{frc}^2 D T \delta_{mn} \delta(\tau) .
\]

Here, the *diffusion coefficient*,

\[
D_T = \frac{\sigma^2}{\gamma_{frc}}
\]

is related to the width of the Maxwell-Boltzmann velocity distribution,

\[
\sigma = 2k \sqrt{\frac{k_B T}{m}} .
\]

### 23.1.2 Langevin simulations

The Langevin equations of CARL can be simulated, including the random term of the Langevin force, using the *Runge-Kutta method* [287]. The procedure consists in propagating a general first order differential equation,

\[
\dot{x} = f(x) + g(t) ,
\]

subject to a deterministic force \( f \) and a stochastic noise \( g \) satisfying,

\[
\langle g(t) \rangle = 0 \quad \text{and} \quad \langle g(t)g(t') \rangle = 2D \delta(t - t')
\]

\(^2\)We note that atomic species exhibiting a hyperfine structure in the ground state are subject to cooling phenomena called 'polarization gradient cooling', which can cause much higher friction coefficients.

We also note that, when the molasses is applied to atoms confined to a potential, the atomic levels can be displaced (e.g., by light-shift or the Zeeman effect). This causes an inhomogeneous effective detuning of the laser beams generating the molasses.
as follows,

\[
x(dt) = x_0 + \frac{1}{2} dt [f(x_0) + f(\tilde{x})] + \zeta (2Ddt)^{1/2},
\]

where \( \zeta \) is a random variable distributed according to a normal (Gaussian) distribution normalized as \(^3\),

\[
\langle \zeta \rangle = 0 \quad \text{and} \quad \langle \zeta^2 \rangle = 1.
\]

### 23.1.2.1 Langevin simulation in the adiabatic approximation

Now, we apply this method to the CARL subject to an optical molasses. Making the adiabatic approximation \( \ddot{\theta}_n = 0 \), the starting point is,

\[
\dot{\alpha}_\perp = -\kappa \alpha_\perp - i U_0 \alpha_\perp \sum_m e^{i\theta_m} \equiv B(\alpha_\perp, \theta_n)
\]

\[
\dot{\theta}_n = \frac{8i \omega_{rec} U_0 \alpha_\perp}{\gamma_{frc}} (\alpha_- e^{i\theta_n} - \alpha^*_e e^{i\theta_n}) + \frac{\xi_n(t)}{\gamma_{frc}} \equiv F(\alpha_\perp, \theta_n) + \frac{\xi_n(t)}{\gamma_{frc}}
\]

In order to apply the Runge-Kutta method (23.11), we identify the variables and functions,

\[
x(t) \equiv \begin{pmatrix} \alpha_\perp(t) \\ \theta_n(t) \end{pmatrix}, \quad f(x) \equiv \begin{pmatrix} B(\alpha_\perp, \theta_n) \\ F(\alpha_\perp, \theta_n) \end{pmatrix}, \quad g(t) \equiv \begin{pmatrix} 0 \\ \xi_n(t)/\gamma_{frc} \end{pmatrix},
\]

such that,

\[
\tilde{x} = \begin{pmatrix} \tilde{\alpha}_\perp \\ \tilde{\theta}_n \end{pmatrix} = \begin{pmatrix} \alpha_\perp(0) \\ \theta_n(0) \end{pmatrix} + dt \begin{pmatrix} B(\alpha_\perp(0), \theta_n(0)) \\ F(\alpha_\perp(0), \theta_n(0)) \end{pmatrix} + \begin{pmatrix} 0 \\ \zeta_n \sqrt{2D\gamma_{frc}} dt \end{pmatrix}
\]

and

\[
x(dt) = \begin{pmatrix} \alpha_\perp(dt) \\ \theta_n(dt) \end{pmatrix} \equiv \begin{pmatrix} \alpha_\perp(0) \\ \theta_n(0) \end{pmatrix} + \frac{dt}{2} \left[ \begin{pmatrix} B(\alpha_\perp(0), \theta_n(0)) \\ F(\alpha_\perp(0), \theta_n(0)) \end{pmatrix} + \begin{pmatrix} B(\tilde{\alpha}_\perp, \tilde{\theta}_n) \\ F(\tilde{\alpha}_\perp, \tilde{\theta}_n) \end{pmatrix} \right] + \begin{pmatrix} 0 \\ \zeta_n \sqrt{2D\gamma_{frc}} dt \end{pmatrix}.
\]

The Langevin equation can be used to simulate the temporal evolution of CARL. Fig. 23.2 shows a simulation of the frequency and amplitude of the CARL based on prescription (23.11).

\(^3\)The MATLAB random number generator satisfies this requirement: \( \langle \zeta_n \rangle \triangleq \text{sum}(\text{randn}(1, N))/N = 0 \) and \( \langle \zeta^2_n \rangle \triangleq \text{sum}(\text{randn}(1, N) \cdot \text{randn}(1, N))/N = 1.\)
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\[ N = 100000 \]
\[ \kappa / 2\pi = 550 \text{ kHz} \]
\[ \omega_{\text{rec}} / 2\pi = 4.8 \text{ kHz} \]
\[ \eta = 200 \text{ ns}^{-1} \]
\[ U_0 \equiv g_1^2 / \Delta a = (2\pi)^{-0.5} \text{ Hz} \]
\[ NU_0 / \kappa = -0.091 \]
\[ \gamma_{\text{frc}} = 1200000 \text{ s}^{-1} \]
\[ T_{\text{mol}} = 1000 \mu \text{K} \]

\[ \left| \alpha^- \right|^2 \] (a) \hspace{1cm} \[ |\alpha_+ + \alpha^-|^2 \] (b) \hspace{1cm} \[ b = \sum_m e^{i\theta_m} \] (c)

\[ p_{\text{cm}} \sqrt{\phi} \] (d) \hspace{1cm} \[ \rho / \hbar k \] (e)

Figure 23.2: (code) Time evolution with phase transition of the viscous CARL in the adiabatic approximation. Shown are (a) the number of photons in the probe mode, (b) the beat signal, (c) the bunching, (d) the phase of the standing wave and the position of the center-of-mass of the cloud, and (e) the dipole potential calculated from (22.22) with the atomic distribution.

23.1.2.2 Langevin simulation of the full dynamics

Without adiabatic approximation, the starting point is,

\[ \dot{\alpha} = \kappa \alpha - i U_0 \alpha \sum_m e^{i\theta_m} \]
\[ \dot{\theta}_n = V_n \]
\[ \dot{V}_n = 8i \omega_{\text{rec}} U_0 \alpha \alpha^* e^{-i\theta_n} - \alpha^* e^{i\theta_n} - \gamma_{\text{frc}} V_n + \xi_n(t) \]

In order to apply the Runge-Kutta method (23.11), we identify the variables and functions,

\[ x(t) \equiv \begin{pmatrix} \alpha_-(t) \\ \theta_n(t) \\ V_n(t) \end{pmatrix}, \quad f(x) \equiv \begin{pmatrix} B(\alpha_-, \theta_n) \\ V_n \\ F(\alpha_-, \theta_n, V_n) \end{pmatrix}, \quad g(t) \equiv \begin{pmatrix} 0 \\ 0 \\ \xi_n(t) \end{pmatrix} \]

(23.17) (23.18)
such that,

$$\dot{x} = \begin{pmatrix} \ddot{\alpha}_- \\ \dot{\theta}_n \\ \dot{V}_n \end{pmatrix} \equiv \begin{pmatrix} \alpha_-(0) \\ \theta_n(0) \\ V_n(0) \end{pmatrix} + dt \begin{pmatrix} B(\alpha_-(0), \theta_n(0)) \\ V_n(0) \\ F(\alpha_-(0), \theta_n(0), V_n(0)) \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \zeta_n \sqrt{2\gamma_{frc}^2 DT dt} \end{pmatrix}$$

(23.19)

and

$$x(dt) = \begin{pmatrix} \alpha_- (dt) \\ \theta_n(dt) \\ V_n(dt) \end{pmatrix} = \begin{pmatrix} \alpha_-(0) \\ \theta_n(0) \\ V_n(0) \end{pmatrix} + dt \begin{pmatrix} B(\alpha_-(0), \theta_n(0)) \\ V_n(0) \\ F(\alpha_-(0), \theta_n(0), V_n(0)) \end{pmatrix}$$

(23.20)

$$+ \begin{pmatrix} B(\ddot{\alpha}_-, \dot{\theta}_n) \\ \dot{V}_n \\ F(\ddot{\alpha}_-, \dot{\theta}_n, \dot{V}_n) \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \zeta_n \sqrt{2\gamma_{frc}^2 DT dt} \end{pmatrix}.$$

Figure 23.3: (code) Time evolution of the complete dynamics of the viscous CARL with phase transition. Same parameters as in Fig. 23.2. Shown are (a) the number of photons in the probe mode, (b) the beat signal, (c) the bunching, (d) the phase of the standing wave and the position of the center-of-mass of the cloud, and (e) the dipole potential calculated from (22.22) with the atomic distribution.
23.2. THE FOKKER-PLANCK AND THE VLASOV MODEL

23.1.3 Exercises

23.1.3.1 Ex: Viscous CARL

Assuming a perfect 'bunching', \( e^{2ikz} = e^{2ik_\alpha} \), \( e^{\alpha} \equiv \beta e^{2ik_\alpha} \) with \( \dot{\beta} = 0 \) and \( \ddot{z} = 0 \) derive the equations (23.2).

23.1.3.2 Ex: Langevin simulations

Langevin simulations

23.2 The Fokker-Planck and the Vlasov model

The Fokker-Planck equation for a density distribution \( Q(r, t) \),

\[
\frac{dQ}{dt} + Q \nabla \cdot v = D \nabla^2 Q ,
\]
represents a generalization of the continuity equation, since with \( \frac{d}{dt} \equiv \frac{\partial}{\partial t} + v \cdot \nabla \), we obtain,

\[
\frac{\partial Q}{\partial t} = -\nabla \cdot (vQ) + D \nabla^2 Q .
\]

If \( \rho \) is a local density, it the continuity equation reads,

\[
\frac{d\rho}{dt} + \rho \nabla \cdot v = 0 .
\]

Knowing,

\[
\frac{d}{dt} \equiv \frac{\partial}{\partial t} + v \cdot \nabla ,
\]
we obtain,

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho v) .
\]

The Fokker-Planck equation is just a generalization to include a diffusion process,

\[
\frac{d\rho}{dt} + \rho \nabla v = D_x \frac{\partial^2 \rho}{\partial x^2} ,
\]

or

\[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho v) + D_x \frac{\partial^2 \rho}{\partial x^2} .
\]

23.2.1 Thermalization in the Fokker-Planck equation

We now apply the Fokker-Planck equation to the density distribution (23.13) of an atomic cloud subjected to the CARL force [609, 507]. As CARL is a one-dimensional process, we can use \( \nabla \rightarrow \partial \theta \) and replace the velocity field \( v \rightarrow \dot{\theta} \):

\[
\dot{\alpha}_- = -\kappa \alpha_- - iNU_0 \alpha_+ b \\
\frac{\partial Q}{\partial t} = \frac{8i\omega_{rec} U_0 \alpha_+}{\gamma_{frc}} \frac{\partial}{\partial \theta} \left[ (\alpha_- e^{-i\theta} - \alpha_+ e^{i\theta})Q \right] + D_\theta \frac{\partial^2 Q}{\partial \theta^2} .
\]
The position diffusion coefficient can be estimated by,

$$D_\theta = \frac{\langle k^2 v^2 \rangle}{\gamma_{frc}}.$$  (23.29)

The normalization and the 'bunching' $|b|$ are given by,

$$1 = \int_0^{2\pi} Q(\theta, t)d\theta, \quad b \equiv \int_0^{2\pi} Q(\theta, t)e^{-i\theta}d\theta.$$  (23.30)

To simulate the equations (23.28) we expand the distribution function in spatial harmonics [507],

$$Q(\theta, t) = \sum_{\nu} Q_{\nu}(t)e^{i\nu\theta}.$$  (23.31)

In this expansion the normalization and the bunching become,

$$Q_0 = \frac{1}{2\pi}, \quad |b| = 2\pi|Q_1|,$$  (23.32)

and the equations (23.28) immediately yield,

$$\dot{\alpha}_- = -2\pi iNU_0\alpha_+Q_1 - \kappa\alpha_-$$

$$\frac{dQ_{\nu}}{dt} = \frac{8\omega_{frc}U_0\alpha_+}{\gamma_{frc}}\nu(\alpha_-Q_{\nu+1} + \alpha^*_Q_{\nu-1}) - \nu^2D_\theta Q_{\nu}.$$  (23.33)

We will derive the results (23.32) and (23.33) in Exc. 23.2.5.1. Also,

$$kv = \frac{d}{dt}\arctan \frac{\text{Im} \alpha_-}{\text{Re} \alpha_-},$$  (23.34)

and,

$$\langle \dot{\theta} \rangle = \int_0^{2\pi} \dot{Q}(\theta, t)d\theta = \sum_{\nu} \dot{Q}_{\nu}(t) \int_0^{2\pi} e^{i\nu\theta}d\theta$$

$$= \sum_{\nu} \frac{8\omega_{frc}U_0\alpha_+}{\gamma_{frc}}\nu(\alpha_-Q_{\nu+1} + \alpha^*_Q_{\nu-1}) \delta_{\nu0} = \frac{16\omega_{frc}U_0\alpha_+}{\gamma_{frc}}\text{Re}(\alpha_-Q_1^*) \delta_{\nu0}.$$  (23.35)

These equations can be easily simulated. Matlab simulations of the Fokker-Planck equation, shown in Fig. 23.4, reproduce quantitatively the curves previously obtained by simulations of the Langevin equations.

### 23.2.2 Bistability and instability of the viscous CARL

The threshold can be found by simulating the Fokker-Planck equation while varying a control parameter (pumping power, temperature, number of atoms) sufficiently slowly, that the system always remains in a steady state. Fig. 23.5 shows the behavior of the CARL, while the pump power is linearly reduced and then linearly increased at different velocities. We observe a bistability that slightly depends on the speed of the ramp. The behavior of the mass-center velocity $kv_{cm}$ and the phase of the standing wave, $\dot{\phi}$, are different [506].

\[\text{\textsuperscript{4}}\text{We can expect a second phase transition when the pump power exceeds a critical value, because for } N U_0 > \kappa, \text{ the CARL becomes unstable again: It will unlock from the self-determined frequency}\]
23.2. THE FOKKER-PLANCK AND THE VLASOV MODEL

\[ N = 100000 \]
\[ \kappa / 2\pi = 550 \text{ kHz} \]
\[ \omega_{\text{rec}} / 2\pi = 4.8 \text{ kHz} \]
\[ \eta = 200 \text{ ns}^{-1} \]
\[ U_0 \equiv g_0^2 / \Delta_0 = (2\pi) \cdot 0.5 \text{ Hz} \]
\[ NU_0 / \kappa s = -0.091 \]
\[ \gamma_{frc} = 1200000 \text{ s}^{-1} \]
\[ T_{\text{mol}} = 1000 \mu K \]

Figure 23.4: (code) Temporal evolution of the complete dynamics with phase transition of the viscous CARL. The same parameters as in Fig. 23.2. Shown are (a) the number of photons in the probe mode, (b) the beat signal, (c) the bunching, (d) the phase of the standing wave and the position of the center-of-mass of the cloud, and (e) the atomic density distribution.

23.2.3 Thermalization in the Vlasov equation

The basic equations describing our ring-cavity filled with atoms are [362],

\[
\begin{align*}
\dot{\alpha}_- &= \kappa \alpha_- - iU_0 \alpha_+ \sum_m e^{i\theta_m} \\
\dot{\theta}_n &= V_n \\
\dot{V}_n &= 8i\omega_{\text{rec}}U_0 \alpha_+ (\alpha_- e^{-i\theta_n} - \alpha^* e^{i\theta_n}) - \gamma_{frc} (V_n - V_n^{(0)})
\end{align*}
\]

if we assume the pump mode to be stationary \( \alpha_+/ = \eta_+ / \kappa^{-1} \) and define the atomic bunching parameter by \( b = \frac{1}{N} \sum_j e^{2ikx_j} \). A non-zero steady-state temperature is reached, if we allow the steady-state velocities of the atoms \( v_j^{(0)} \) to be different for all atoms and distributed according to a Maxwell-Gaussian velocity distribution. The assumption of a common steady-state velocity for all atoms obviously results in perfect bunching and cooling to \( T = 0 \).

Let us introduce a local phase space density of the atomic cloud \( Q(x, p, t) \) as a two-dimensional field in phase space. The time-evolution of this quantity is given by

and start to oscillate strongly. However, this effect is not described by the equations used for the simulation, which suppose an adiabatic elimination of the inertia.
the so-called Vlasov equation (or collisionless Boltzmann equation),

\[ 0 = \partial_t Q + v \partial_x Q + F \partial_p Q + \gamma_{th} (Q - Q_0) , \tag{23.37} \]

where \( v \) and \( F \) are the center-of-mass velocity and force taken from equation (23.36) without the friction term. According to this equation the atomic cloud tends to a stationary distribution \( Q_0 \) as time goes on. Following Bonifacio et al. [74] and Javaloyes [318, 319, 320], we replace the friction term by an additional (Vlasov) equation:

\[
\begin{align*}
\dot{\alpha}_- &= -i N U_0 \alpha_+ b - \kappa \alpha_- \\
\dot{\theta} &= \omega_{rec} V \\
\dot{V} &= i U_0 \alpha_+ (\alpha_- e^{-i\theta} - \alpha^*_+ e^{i\theta}) \\
0 &= \partial_t Q + \dot{\theta} \partial_\theta Q + \dot{\theta} \partial_\varrho Q + \gamma_{frc} (Q - Q_0) 
\end{align*}
\tag{23.38}
\]

The bunching parameter can now be rewritten in terms of

\[
b = \int_0^{2\pi} d\theta \int_{-\infty}^{\infty} d\varrho \; Q(\theta, \varrho, t) \; e^{2i\theta} . \tag{23.39}
\]

The equilibrium distribution is chosen to be a homogeneous cloud with a Maxwell-Boltzmann velocity distribution,

\[
Q_0 = \frac{1}{2\pi} \sqrt{\frac{\sigma}{\pi}} e^{-\sigma \varrho^2} , \tag{23.40}
\]

where \( \sigma \equiv \hbar \omega_{rec} / k_B T \) with \( \omega_{rec} \equiv \hbar k^2 / 2m \) such that \( \int_0^{2\pi} d\theta \int_{-\infty}^{\infty} Q_0 d\varrho = 1 \). We now perform a linear stability analysis. We expand \( Q \) around the steady state, \( Q(\theta, \varrho, t) = Q_0(\varrho) + Q_1(\theta, \varrho, t) \) and retain to first order,

\[
0 = \partial_t Q_1 + \dot{\theta} \partial_\theta Q_1 + \dot{\theta} \partial_\varrho Q_0 + \gamma_{th} Q_1 . \tag{23.41}
\]

Now we look for a time-dependent particular solution by inserting the ansatz,

\[
\begin{align*}
\alpha_- (t) &= \beta_- e^{i\lambda t} \quad \text{with} \quad \dot{\beta}_- = 0 \\
Q_1(\theta, \varrho, t) &= H_1(\varrho) e^{-2i\theta} e^{i\lambda t} + c.c.
\end{align*}
\tag{23.42}
\]

Figure 23.5: Bistability of CARL near the threshold when the power is ramped at different paces.
where $i\lambda \equiv \lambda_g + i\lambda_\omega$ into the field equation (23.38)a, the first order expansion of the Vlasov equation (23.41) (only retaining co-rotating terms) and into the expression for bunching (23.39). This ansatz accounts for the fact that, in steady state, we expect a fixed CARL frequency $\nu$ and a spatially modulated density distribution of the atoms. The set of equations becomes,

$$q_i\lambda\beta_- = -\kappa\beta_- - iNU_0\tilde{\eta}_+ e^{-i\lambda t}$$

$$0 = i\lambda H_1(\varrho) - 4i\omega_{rec}\varrho H_1(\varrho) + iU_0\tilde{\eta}_+ \beta_- \partial_\varrho Q_0 + \gamma_{th} H_1(\varrho)$$

$$b = \int_0^{2\pi} d\theta \int_{-\infty}^{\infty} d\varrho H_1(\varrho)e^{i\lambda t}.$$  

With the definition,

$$\Gamma(\sigma, \gamma_{th}, i\lambda) \equiv \int_{-\infty}^{\infty} d\varrho \frac{\partial_\varrho Q_0}{i\lambda - 4i\omega_{rec}\varrho + \gamma_{th}}$$

$$= -\int_{-\infty}^{\infty} \frac{d\varrho}{(i\lambda - 4i\omega_{rec}\varrho + \gamma_{th})^2},$$

the solution of the above set of equations is,

$$H_1(\varrho) = \frac{-iU_0\tilde{\eta}_+ \beta_- \partial_\varrho Q_0}{i\xi - 4i\omega_{rec}\varrho + \gamma_{th}}$$

$$b = -e^{i\xi t}iU_0\tilde{\eta}_+ \beta_- 2\pi \Gamma(\sigma, \gamma_{th}, i\lambda)$$

$$0 = [\kappa + i\lambda + NU_0^2\tilde{\eta}_+^2 2\pi \Gamma(\sigma, \gamma_{th}, i\lambda)] \beta_-.$$  

### 23.2.4 Calculation of the threshold

The bifurcation where the reverse field crosses the threshold to lasing occurs at $\lambda_g = 0$. We divide the field equation in real and imaginary parts,

$$\kappa + NU_0^2\tilde{\eta}_+^2 2\pi \text{Re} \Gamma(\sigma, \gamma, i\lambda_\omega) = 0$$

$$\nu + NU_0^2\tilde{\eta}_+^2 2\pi \text{Im} \Gamma(\sigma, \gamma, i\lambda_\omega) = 0.$$  

Now the condition $\lambda_\omega \text{Re} \Gamma(\sigma, \gamma_{th}, i\lambda_\omega) = \kappa \text{Im} \Gamma(\sigma, \gamma_{th}, i\lambda_\omega)$ leads to,

$$\int_{-\infty}^{\infty} \frac{d\varrho g e^{-\sigma g^2}(\kappa \lambda_\omega - 2\kappa \varepsilon \varrho + \lambda_\omega \gamma_{th})}{(\lambda_\omega - 2\varepsilon \varrho)^2 + \gamma_{th}^2} = 0.$$  

The values $\lambda_\omega$ where this integral is zero are inserted into one of the equations (23.46). Finally,

$$\tilde{\eta}_+^2 = -\frac{1}{NU_0^2 2\pi \text{Re} \kappa \Gamma(\sigma, \gamma_{th}, i\lambda_\omega)},$$

is the expression for the pump power threshold as a function of temperature $\sigma$, friction $\gamma_{th}$, cavity damping $\kappa$ and coupling constant $U_0$. The intracavity CARL power is,

$$P_+ = \hbar \omega \delta \tilde{\eta}_+^2.$$  

(23.49)
\( \lambda_\omega \) is the associated CARL frequency, i.e. the frequency difference between probe and pump.

The final equations show that the threshold power drops as \( NU_0^2 \) increases. To see the dependencies of the threshold power on \( T \) and \( \gamma_{th} \), we have to evaluation of the integral (23.47). Fig. 23.6 shows a numerical evaluation of Eqs. (23.47),(23.48) and (23.49) for finite \( T \) and \( \gamma_{th} \).

![Figure 23.6: Intracavity threshold power as a function of temperature and friction coefficient. The coupling strength is set to \( U_0 = -10^{-7} \), the atom number is \( N = 10^6 \).](image)

Apparently, the threshold pump power drops with vanishing friction and with low temperatures. For typical experimental situations, \( T \approx 100 \mu K \) and \( \gamma_{th} \approx 10\kappa \), we expect threshold powers on the order of about \( P_+ = 1 \) W, corresponding to \( P_+^{(out)} = 4 \mu W \) leaking out of the cavity.

### 23.2.5 Exercises

#### 23.2.5.1 Ex: Fokker-Planck equations

Derive the equations (23.32) and (23.33) from (23.30) and (23.28) applying the expansion (23.31).

### 23.3 The Kuramoto model

Ripples on a dusty street driven by cars, rapids in a river arising spontaneously or behind an obstacle, wind blowing over a water surface spontaneously creating waves. Imagine a photon wind blowing over an atomic sea. Just like for water waves friction hinders boundless acceleration. The analogies are wind-molasses-friction, water-atoms, wind-acceleration-field, gravitation-dipole-force. The phenomenon is closely related to the dissipative structure. See also (watch talk) and (watch talk).

Our system has the advantage over macroscopic systems, that the hypothesis of uniform coupling is exactly satisfied, because the coupling medium, i.e. the light fields
are delocalized within the cavity mode. In contrast, rapids develop exclusively behind
the perturbation. There are no delay times effects and no spatial constraints due to
a finite size of the individual oscillators.

The viscous CARL system is representative for of the vast class of Kuramoto
systems [584] introduced in Sec. ?? This can be seen most appropriately by rewriting
the CARL equations in terms of phase and amplitude of individual atoms. Another
approach is via the Fokker-Planck equation, for which there already exists a Kuramoto
equivalence.

Why is it interesting to investigate yet another coupled oscillator system? Our
CARL is fully classical, although we deal with microscopic particle, such as atoms and
photons. However, our system bears the possibility of being transferred to quantum
situations, and thus to study the coupling of large ensembles of quantum oscillators.
Furthermore, the coupling mechanism is well understood and controllable by experi-
ment. Because the coupling goes through the standing wave fraction, it depends on
the atom number and the coupling strength independently. Furthermore, the tunable
friction force (temperature) corresponds to a variable width of the distribution of the
oscillator frequencies, which we can manipulate in-situ and on-line.

Another realization of the Kuramoto model would be atoms in a ring cavity stand-
ing wave. Cold trapped atoms have the same oscillation frequencies. And thus do
not need to synchronize. For hot atoms, however, the oscillation period depends on
their kinetic energy.

The equation for the phases of the atoms is similar to the Kuramoto model [320],
\[
\dot{\theta}_n = \frac{K}{N} \sum_m \sin(\theta_n - \theta_m) - \xi_n(t).
\] (23.50)

The CARL equations which describes the dynamics of an ensemble of mean-
field coupled oscillators, belong to the class of Kuramoto systems [319]. The main
differences are: a Dirac-like distribution of eigenfrequencies and a mean-field self-
consistently provided by a dynamical equation. Hence, in contrast to the original
Kuramoto model, where the collective oscillation frequency is just the mean of the
individual frequencies, the CARL frequency is self-determined and depends also on
control parameters. This phenomenon is known from other systems like rhythmic ap-
plause, which only takes place by a reduction of the individual frequencies of clapping
hands, towards a resonance. For this to happen the mean-field must self-adjust while
the individual oscillators synchronize, e.g. the noise produce by the audience must
adjust to the average desire of the audience to produce a satisfying level of noise.

In [628] is stated: ‘The essence of the problem is the competition between the
intrinsic disorder (i.e. noise and diffusion) and the dynamical coupling strength. In
the Kuramoto model, the disorder enters via the distribution of natural frequencies,
while the effective coupling strength is set by the parameter combination $K \cos \alpha_j$.’

### 23.3.1 Phase formalism of CARL

The starting point is the CARL equations (22.118). We make ansatz,
\[
\alpha_+ \equiv \alpha_1, \quad \alpha_- \equiv \alpha_2 e^{i\phi}, \quad \eta_+ \equiv \eta_1, \quad \eta_- \equiv \eta_2 e^{i\Delta},
\] (23.51)
where the quantities with numeric suffixes are real, such that,

\[ |\alpha_+ + \alpha_-|^2 = \alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \phi . \]  

(23.52)

By this ansatz we assume that a pumping laser is locked to the mode \( \alpha_+ \) of the ring cavity, such that the phases of the fields \( \alpha_+ \) and \( \eta_+ \) are equal and, without loss of generality, zero. On the other hand, the phase \( \phi \) of the probe mode is a dynamic variable. Inserting the ansatz into the equations (22.118) we obtain,

\[ \dot{\alpha}_1 = -(\kappa + iNU_0 - i\Delta_c)\alpha_1 - iU_0 \sum_n e^{-i\theta_n + i\phi}\alpha_2 + \eta_1 , \]  

(23.53)

\[ \dot{\alpha}_2 + i\dot{\phi}\alpha_2 = -(\kappa + iNU_0 - i\Delta_c)\alpha_2 - iU_0 \sum_n e^{i\theta_n - i\phi}\alpha_1 + \eta_2 e^{i\Delta - i\phi} , \]

\[ \ddot{\theta}_n = 16\omega_{rec}U_0\alpha_1\alpha_2 \sin(\theta_n - \phi) . \]  

Eliminating \( \Delta_c \), we can substitute the third and fourth equations for,

\[ \dot{\phi} = NU_0 \left( \frac{\alpha_2}{\alpha_1} - \frac{\alpha_1}{\alpha_2} \right) \sum_n \cos(\theta_n - \phi) - \frac{\eta_2}{\alpha_2} \sin(\phi - \Delta) . \]  

(23.55)

Defining the 'bunching' parameter,

\[ b \equiv |b|e^{i\psi} \equiv N^{-1} \sum_n e^{i\theta_n} , \]  

(23.56)

we finally obtain, in the presence of friction and dissipation,

\[
\begin{align*}
\dot{\alpha}_1 &= -\kappa\alpha_1 - NU_0\alpha_2 |b| \sin(\psi - \phi) + \eta_1 \\
\dot{\alpha}_2 &= -\kappa\alpha_2 + NU_0\alpha_1 |b| \sin(\psi - \phi) + \eta_2 \cos(\phi - \Delta) \\
\dot{\phi} &= NU_0 \left( \frac{\alpha_2}{\alpha_1} - \frac{\alpha_1}{\alpha_2} \right) |b| \cos(\psi - \phi) - \frac{\eta_2}{\alpha_2} \sin(\phi - \Delta) \\
\ddot{\theta}_n &= 16\omega_{rec}U_0\alpha_1\alpha_2 \sin(\theta_n - \phi) - \gamma_{frc}\dot{\theta}_n + \xi_n
\end{align*}
\]  

(23.57)

A particularly interesting case is that of unidirectional pumping, \( \eta_2 = 0 \). Assuming that the pump mode be not affected, \( \dot{\alpha}_1 = 0 \), and that the probe mode be weak,
23.3. THE KURAMOTO MODEL

\( \alpha_1 \gg \alpha_2 \), and making the adiabatic approximation, \( \ddot{\theta}_n = 0 \), of the atomic motion, we obtain,

\[
\begin{align*}
\dot{\alpha}_2 &= -\kappa \alpha_2 + NU_0 \alpha_1 |b| \sin (\psi - \phi) \\
\dot{\phi} &\approx -\frac{NU_0 \alpha_1}{\alpha_2} |b| \cos (\psi - \phi) \\
\dot{\theta}_n &= \frac{\xi_n}{\gamma_{fr}} + \frac{16 \omega_{rec} U_0 \alpha_1 \alpha_2}{\gamma_{fr}} |b| \sin (\theta_n - \phi)
\end{align*}
\]

(23.58)

We note that the equation for the phases of the atoms is similar to the Kuramoto equation (23.50).

23.3.2 Relationship between CARL and Kuramoto

The viscous CARL described by the formulas (23.58) corresponds to the Kuramoto model \([584]\). Defining \( \theta_n \equiv 2kx_n \) as the position of the \( n^{th} \) atom, we assume the pump laser to be in resonance and write \( \alpha_+ \equiv \eta_+ / \kappa \) \([362]\). The diffusion in the momentum space is a process that limits the temperature in optical molasses.

We start from the Langevin equations (23.13). In addition, we assume that the standing wave propagates at a constant velocity, which is to say that for a strong viscous damping, the system quickly finds a steady state. This condition is formulated by \( |\alpha_-| = 0 \) and \( \dot{\alpha}_- = i \omega_{ca} \alpha_- \) with constant velocity \( \omega_{ca} \), which may be different from the velocity of the center of mass \( kv \). We note that this assumption can introduce a considerable error, when used to describe temporal phase transitions, since, as shown by simulations of the complete dynamics (23.17), the mode \( \alpha_- \) exhibits a transient behavior, as well. We obtain from the first Eq. (23.13),

\[
\alpha_- = -\frac{iU_0 \alpha_+}{i \omega_{ca} + \kappa} \sum_m e^{i \theta_m} .
\]

(23.59)

Substituting Eq. (23.59) into the second equation (23.13),

\[
\begin{align*}
\dot{\theta}_n &= \frac{\xi_n}{\gamma_{fr}} + \frac{8 \omega_{rec} NU_0^2 \alpha_+^2}{\gamma_{fr}} \frac{1}{N} \sum_m \left( \frac{e^{i \theta_m - i \theta_n}}{i \omega_{ca} + \kappa} + \frac{e^{-i \theta_m + i \theta_n}}{-i \omega_{ca} + \kappa} \right) \\
&= \frac{\xi_n}{\gamma_{fr}} + \frac{16 \omega_{rec} NU_0^2 \alpha_+^2}{\gamma_{fr}(\omega_{ca}^2 + \kappa^2)} \frac{1}{N} \sum_m \left[ \kappa \cos (\theta_m - \theta_n) + \omega_{ca} \sin (\theta_m - \theta_n) \right] .
\end{align*}
\]

(23.60)

Defining the order parameter,

\[
b \equiv |b| e^{i \psi} \equiv \frac{1}{N} \sum_m e^{i \theta_m} ,
\]

(23.61)

which also implies,

\[
|b| \sin (\psi - \theta_n) = \frac{1}{N} \sum_m \sin (\theta_m - \theta_n) ,
\]

(23.62)

we can write Eq. (23.62) as,

\[
\dot{\theta}_n = \frac{\xi_n}{\gamma_{fr}} + \frac{8 \omega_{rec} NU_0^2 \alpha_+^2 \kappa}{\gamma_{fr}(\omega_{ca}^2 + \kappa^2)} |b| \left[ \cos (\psi - \theta_n) + \frac{\omega_{ca}}{\kappa} \sin (\psi - \theta_n) \right] .
\]

(23.63)
In the 'good cavity' limit, $\kappa \ll \omega$, using \( (2kv)^3 = 8\varepsilon NU_0^2 \alpha_+^2 \kappa / \gamma_{fr} \) and additionally assuming small amplitude oscillations, $\psi \approx \theta_n$, that is, good 'bunching',

$$
\dot{\theta}_n \approx \frac{\xi_n}{\gamma_{fr}} + \frac{(2kv)^3}{\omega_2^2} |b| + \frac{(2kv)^3}{\kappa \omega_2} |b| \sin(\psi - \theta_n) .
$$

This shows that in the limit of perfect 'bunching' $\omega_{ca} = 2kv$ must be satisfied. If really $\kappa \ll \omega$ is valid, we can despise the cosine. Introducing the Kuramoto coupling constant,

$$
K = \frac{16\omega_{rec}NU_0^2 \alpha_+^2 \omega_{ca}}{\gamma_{fr}(\omega_2^2 + \kappa^2)} \approx \frac{1}{\kappa} \left( \frac{16\omega_{rec}NU_0^2 \alpha_+^2 \kappa}{\gamma_{fr}} \right)^{2/3} = \left( \frac{4\omega_{rec} \rho}{4\kappa \gamma_{fr}} \right)^{1/3},
$$

using $2\varepsilon \rho = (4\varepsilon NU_0^2 \alpha_+^2)^{1/3}$, Eq. (23.63) is precisely the one used by the Kuramoto model of $N$ coupled harmonic oscillators synchronizing over time,

$$
\dot{\theta}_n \approx \frac{\xi_n}{\gamma_{fr}} + \frac{\kappa K}{\omega_{ca}} |b| + K |b| \sin(\psi - \theta_n) .
$$

Oscillators with $\omega_n \leq K |b|$ are locked. For a reasonable 'bunching' this is satisfied in the 'good cavity' limit.

### 23.3.2.1 Kuramoto model with inertial effects

It is possible to incorporate inertial effects into the Kuramoto model [1]: allowing for $\ddot{\theta}_n \neq 0$, but still assuming $\dot{d}_1 |\alpha_-| = 0$ and $\dot{\alpha}_- = i\omega \alpha_-$, the equation (23.60) becomes,

$$
\ddot{\theta}_n = -\gamma_{fr} \dot{\theta}_n + \xi_n + \frac{16\omega_{rec}NU_0^2 \alpha_+^2}{\omega_2^2 + \kappa^2} \frac{1}{N} \sum_m [\kappa \cos(\theta_m - \theta_n) + \omega \sin(\theta_m - \theta_n)] \quad (23.67)
$$

$$
= -\gamma_{fr} \dot{\theta}_n + \xi_n + \frac{\kappa}{\omega} K |b| \cos(\psi - \theta_n) + K |b| \sin(\psi - \theta_n) .
$$

### 23.3.3 Fokker-Planck equation

Let us write the Kuramoto equation including stochastic noise,

$$
\dot{\theta}_n = \omega + K |b| \sin(\psi - \theta_n) + \xi_n(t) ,
$$

(23.68)

define the order parameter,

$$
b = |b| e^{i\psi} ,
$$

(23.69)

and the Langevin-force $\langle \xi_n(t) \rangle = 0$ and $\langle \xi_n(t) \xi_m(\tau) \rangle = 2D \delta_{ij} \delta(t - \tau)$.

The Fokker-Planck equation associated to Eq. (23.68) reads,

$$
\frac{\partial \rho}{\partial t} = -\frac{\partial \rho}{\partial \theta} \left[ \omega + K |b| \sin(\psi - \theta) \right] + D \frac{\partial^2 \rho}{\partial \theta^2} ,
$$

(23.70)

where $D = \sigma^2 / \gamma_{fr}$. Inserting $\rho(\theta, t) \equiv \sum_\nu \rho_\nu(t) e^{i\nu \theta}$,

$$
\frac{\partial \rho_\nu}{\partial t} = -(\nu^2 D + i\nu \omega) \rho_\nu + \frac{1}{2} \nu K (b^* \rho_{\nu-1} - b \rho_{\nu+1}) ,
$$

(23.71)
especially,
\[ \int_0^{2\pi} \rho(\theta, t) d\theta = 1 \quad \Rightarrow \quad \rho_0 = \frac{1}{2\pi}, \]  
(23.72)
and we defined the bunching as \(|b|\), where,
\[ b \equiv \int_0^{2\pi} \rho(\theta, t) e^{-i\theta} d\theta \quad \Rightarrow \quad b \equiv 2\pi \rho_1. \]  
(23.73)

### 23.3.3.1 Laser-type equation for CARL

Defining the displacement of the \( n \)th atomic oscillator as,
\[ E_n \equiv e^{i\theta_n}, \]  
(23.74)
we can rewrite the second equation (23.13) as,
\[ \dot{E}_n = \frac{i\xi_n}{\gamma_{fr}} E_n - \frac{8\omega_{rec} U_0}{\gamma_{fr}} (\alpha_- - \alpha^*_n E_n^2). \]  
(23.75)

Substituting \( \alpha_- \) by the integral of the first equation (23.13),
\[ \dot{E}_n = \frac{i\xi_n}{\gamma_{fr}} E_n + \frac{8\omega_{rec} iNU_0^2}{\gamma_{fr}} \left( \int b e^{-\kappa(t-t')} dt' + E_n^2 \int b^* e^{-\kappa(t-t')} dt' \right). \]  
(23.76)
In the limit \( e^{-\kappa(t-t')} = \kappa^{-1}\delta(t-t') \) we obtain an equation similar to that of an ordinary laser,
\[ \dot{E}_n = \frac{i\xi_n}{\gamma_{fr}} E_n + \frac{8\omega_{rec} iNU_0^2}{\gamma_{fr}} \frac{\alpha^2_+}{\kappa} (b + b^* E_n^2) \]  
(23.77)
\[ = \frac{i\xi_n}{\gamma_{fr}} E_n + \frac{8\omega_{rec} iNU_0^2}{\gamma_{fr}} \frac{\alpha^2_+}{\kappa} \left( \sum_m E_m + \sum_m E_m^* E_n^2 \right). \]

### 23.3.4 Exercises

#### 23.3.4.1 Ex: Kuramoto simulations

Implement the Kuramoto model with pendulum clocks.

### 23.4 Thermodynamics of the CARL process

There is an analogy between the laser threshold and a second-order phase transition [546], p. 341 ff: ‘... The usual treatment of laser behavior is a self-consistent field theory. In the laser analysis each atom develops a radiating dipole in an electromagnetic field due to (i.e. emitted by) all the other atoms. The radiation field produced by an ensemble of radiating atoms is then calculated in a self-consistent fashion. (...This) suggests the identification of the laser electric field as the variable corresponding to the (...) order parameter and the atomic population inversion as that corresponding to the temperature.’
Note that numerical simulations revealed that in certain regimes the CARL corresponds to a first-order phase transition: At high temperatures the probe to pump power diagram shows bistability [318] and [506].

The correspondence between CARL and a common laser is illustrated by the table below. A number of questions arise from the analogy:

<table>
<thead>
<tr>
<th>Control Parameter</th>
<th>Ferromagnet</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Parameter</td>
<td>External Magnetic Field ( H )</td>
<td>Pump Intensity ( S )</td>
</tr>
<tr>
<td>Order Parameter</td>
<td>Magnetization</td>
<td>Electric Field</td>
</tr>
<tr>
<td>Probability Density</td>
<td>( P(M) \propto e^{-F(M)/k_BT} )</td>
<td>( P)-representation</td>
</tr>
<tr>
<td>Thermodynamic Free Energy</td>
<td>( F = F(T, H) )</td>
<td>( G(x, y) )</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>( C(T) = \frac{\partial E(T)}{\partial T} )</td>
<td>?</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CARL Atoms</th>
<th>CARL Light</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Parameter</td>
<td>Pump Intensity ( \eta )</td>
</tr>
<tr>
<td>Equilibrium Parameter</td>
<td>Temperature ( T )</td>
</tr>
<tr>
<td>Order Parameter</td>
<td>Bunching</td>
</tr>
<tr>
<td>Probability Density</td>
<td>?</td>
</tr>
<tr>
<td>Thermodynamic Free Energy</td>
<td>?</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>?</td>
</tr>
</tbody>
</table>

### 23.4.1 CARL as a Laser

Why is CARL a laser? What is the basic difference between CARL and an AOM or a moving Bragg mirror? CARL is essentially based on exponential self-amplification. This self-amplification is in fact observed in our switch-off experiment [362]. But a laser is normally understood as a steady-state system. For CARL to find to a steady-state we have to insert friction forces.

Gordon rewrites the CARL as a common laser: He generalizes the linear stability analysis (previous Sec.) and retains the lowest-order nonlinearity. The Fokker-Planck equations read:

\[
\frac{dB_n}{d\tau} = in(aB_{n-1} + a^*B_{n+1}) - n^2DB_n
\]

\[
\frac{da}{d\tau} = B_1 - \kappa a
\]
with $B_0 = 1$ and $B_{-n} = B_n^*$. Linearization means $B_{n>1} = 0$,

\[
\frac{dB_1}{d\tau} = ia - DB_1
\]

or,

\[
\frac{d^2a}{d\tau^2} + (\kappa + D) \frac{da}{d\tau} + (\kappa D - i)a = 0
\]

\[
\frac{d^2B_1}{d\tau^2} + (\kappa + D) \frac{dB_1}{d\tau} + (\kappa D - i)B_1 = 0
\]

The determinant is,

\[
\det \begin{pmatrix} -D - \lambda & i \\ 1 & -\kappa - \lambda \end{pmatrix} = (D + \lambda)(\kappa + \lambda) - i = 0
\]

Including the lowest-order nonlinear term means $B_{n>2} = 0$,

\[
\frac{dB_2}{d\tau} = 2iaB_1 - 4DB_2
\]

\[
\frac{dB_1}{d\tau} = ia + ia^*B_2 - DB_1
\]

\[
\frac{da}{d\tau} = B_1 - \kappa a
\]

Assuming $dB_2/d\tau = 0$,

\[
\frac{dB_1}{d\tau} = ia - \left( \frac{|a|^2}{2D} + D \right) B_1
\]

\[
\frac{da}{d\tau} = B_1 - \kappa a
\]

or,

\[
\frac{d^2B_1}{d\tau^2} + (\kappa + D) \frac{dB_1}{d\tau} + (\kappa D - i)B_1 = -\frac{1}{2D} \left( \frac{d}{d\tau} + \kappa \right) |a|^2 B_1
\]

\[
= -(K_1|a|^2 - K_2|a|^4) B_1
\]

\[
\frac{d^2a}{d\tau^2} + (\kappa + D) \frac{da}{d\tau} + (\kappa D - i)a = -\frac{|a|^2}{2D} \left( \frac{d}{d\tau} + \kappa \right) a
\]

substitute $a(\tau) = A(\tau)e^{\lambda \tau}$ and Eq. (xx),

\[
e^{\lambda \tau} \left( \frac{d^2}{d\tau^2} + 2\lambda \frac{d}{d\tau} + \lambda^2 \right) A + e^{\lambda \tau} \left( (\kappa + D) \frac{d}{d\tau} + (\kappa + D)\lambda \right) A - (\lambda^2 + D\lambda + \kappa\lambda)e^{\lambda \tau} A
\]

\[
= -\frac{|e^{\lambda \tau} A|^2}{2D} \left( e^{\lambda \tau} \frac{dA}{d\tau} + \lambda e^{\lambda \tau} A + \kappa e^{\lambda \tau} A \right)
\]
neglect \(d^2A/d\tau^2\) and \(|A|^2dA/d\tau\),

\[e^{\lambda \tau} 2\lambda \frac{dA}{d\tau} + e^{\lambda \tau} (\kappa + D) \frac{dA}{d\tau} = -\frac{|e^{\lambda \tau} A|^2}{2D} \left( \lambda e^{\lambda \tau} A + \kappa e^{\lambda \tau} A \right)\]  (23.86)

substitute back \(a(\tau) = A(\tau)e^{\lambda \tau}\),

\[\frac{da}{d\tau} = \lambda a - \frac{\lambda + \kappa}{2D(2\lambda + \kappa + D)} |a|^2a\]  (23.87)

or,

\[\frac{d|a|^2}{d\tau} = 2|a|^2 \text{Re} \lambda - 2|a|^4 \text{Re} \lambda\]  (23.88)

in steady-state,

\[0 = \lambda a - C|a|^2a\]  (23.89)

![Figure 23.7: (code) Laser crossing the threshold.](image)

According to A. Politi a general laser theory exists, there is no point in repeating this for CARL. The analogy is there and evident.

### 23.4.1.1 CARL as a ferromagnet

A similar treatment with \(a(\tau) = A(\tau)e^{\lambda \tau}\) and \(B_1(\tau) = \beta(\tau)e^{\lambda \tau}\) and \(d^2\beta/d\tau^2 = 0\) and \(|A|^2d\beta/d\tau = 0\) and \(\beta d|A|^2/d\tau = 0\) results in,

\[\frac{dB_1}{d\tau} = \lambda B_1 - \frac{2\lambda + \lambda^* + \kappa}{2D(2\lambda + \kappa + D)} |a|^2B_1\]  (23.90)

\[= \lambda B_1 - \tilde{C}|a|^2B_1\]

i.e. the instability comes from the field and it drives the bunching.
23.4.2 Out-of-equilibrium thermodynamics

Strictly speaking the above analogy is flawed. In particular the analogy between CARL bunching and ferromagnetic ordering is not good. While the ferromagnetic ordering occurs as a thermodynamic phase transition, the CARL bunching is driven by a dissipative force, which triggers spatio-temporal instabilities. Therefore viscous CARL occurs far from thermodynamic equilibrium. This may point towards an interpretation of CARL bunching as a dissipative structure along the lines traced by Prigogine, who showed that non-equilibrium may be a source of order.

On the other hand, the laser itself is a system operating far from thermal equilibrium, since it requires a pump to emit steady-state radiation. Perhaps a comparison with estruturas de Bénard is better than with ferromagnets. Bénard structures occur as spontaneous breaking of translational symmetry, just like CARL. One could say that the periodicity of CARL is predefined by the pump laser wavelength, and thus not surprising. However, the size of the periodic structures is always fixed by boundary conditions in a more or less complicated way. For example, the size of the Bénard structures is fixed by the viscosity, the provided amount of heat, etc., the wavelength of surface waves can be calculated from first principles, i.e. the Navier-Stokes equations and the continuity equation for given boundary conditions. The symmetry breaking resides in the exact place, where the Bénard structure develops. It is the phase, which is broken, just like for CARL.

The Kuramoto model and the Weiss model of ferromagnetism are both mean field theories [552]. Despite the fundamental difference that ferromagnetism is a thermodynamic feature and Kuramoto a nonequilibrium phenomenon, they are far-reaching analogies. The role of temperature in ferromagnetism is played by external noise in Kuramoto. CARL is clearly a dissipative structure: It survives only as long as energy is fed to the system.

23.4.2.1 Finite and infinite temperature reservoirs

The phase transition is ruled by a competition of dissipation and diffusion. If the reservoir has zero temperature $\gamma_{\text{fric}} \neq 0$ but $D = \sigma^2/\gamma_{\text{fric}} = 0$, i.e. we have dissipation without diffusion. In this case, we do not expect a threshold behavior. The Lindblad operator for coupling to a finite-temperature reservoir is something like $\mathcal{L} \approx \kappa (\bar{n} + 1) \{\text{emission}\} + \kappa \bar{n} \{\text{absorption}\} + \eta \{\text{phase noise}\}$, where $\bar{n}$ is the mean photon number at thermal equilibrium with a given temperature $T \propto \bar{n}/(\bar{n}+1)$. The interpretation in terms of dissipation without diffusion is correct according to A. Buchleitner. There are three kinds of noises: 0 temperature noise for $\bar{n} \to 0$, $\infty$ temperature noise for $\bar{n} \approx \bar{n}+1$ and phase noise. Thus for $T = 0$ the energy flux goes only from the system to the reservoir. At $T > 0$ entropy may go from the reservoir to the system. The system reaches its cooling limit when the temperatures of the system and the reservoir are balanced.

But how to explain Doppler cooling or cavity-cooling? The electromagnetic vacuum is an effective $T = 0$ reservoir, but the cooling is nevertheless limited by the spontaneous decay width or the cavity linewidth, resp.. Why does coupling to a zero-temperature reservoir not cool down to zero? Apparently, the coupling is afflicted by vacuum noise. This permits coupling of degrees of freedom having different temperatures without reaching a temperature equilibrium. Examples are the limit of
cavity-cooling to the cavity decay width or simply Doppler-cooling by spontaneous emission.

Interprete damping as scattering into continuum!

23.5 Coherent properties of CARL

In Ref. [361] we have demonstrated collective interaction of atoms with light fields and how the application of friction via optical molasses can lead to stationary CARL radiation at a self-determined frequency. In the papers [507, 609] we have demonstrated that the molasses also lead to diffusion resulting in a threshold behavior and in atomic self-organization at finite temperatures. An interesting question is whether the temperature not only determines the collective behavior, but also the deviation from it. The temperature being related to the amount of random walk on top of the center-of-mass motion, we may wonder whether the viscous CARL radiation bears a signature of the atomic temperature not only in the self-determined CARL frequency, but also in the laser emission bandwidth. It is conceivable that the autocorrelation functions and the emission spectrum of the CARL are influenced by the fact that the atoms experience a random walk in momentum space due to the diffusion in the optical molasses.

In this subtext we will attempt an analytical approach, present numerical simulations and discuss how to access to the informations experimentally. The Fokker-Planck approach described in Refs. [507, 609] is particularly well adapted to calculating collective variables. In contrast the simulation of the Langevin equation conveniently gives access to the noise properties.

23.5.1 Analytical derivation of the coherence

Our starting point are the Langevin equations (23.13) [507, 609] in the adiabatic limit, \( \dot{\theta}_n = 0 \). The Langevin noise force is uncorrelated,

\[
\langle \xi^*_n(t)\xi_m(t+\tau) \rangle \equiv \lim_{T \to \infty} \frac{1}{T} \int_0^T \xi^*_n(t)\xi_m(t+\tau) d\tau = 2D\dot{\theta}_m \delta_{mn} \delta(\tau),
\]

where the momentum diffusion coefficient \( D\dot{\theta} = \gamma_f \sigma^2 \) is proportional to the atoms' equilibrium temperature, which is related to the Maxwell-Gaussian velocity spread by \( \sigma = 2k\sqrt{k_B T/m} \). In contrast, the trajectories of the atoms are not, because all atoms are motionally coupled by the fields, so that the noise imparted to one atom is sensed by all others. Therefore the relationship (23.92) certainly does not hold for the atomic positions,

\[
\langle \theta^*_n(t)\theta_m(t+\tau) \rangle \sim \delta_{mn} \delta(\tau).
\]

23.5.1.1 Single atom

So, let us first concentrate on a single atom coupled to the cavity fields. If its velocity only fluctuates a little around a mean value \( \omega_{ca} \), we may write \( \dot{\theta}(t) \equiv \omega_{ca} t + \varphi(t) \). The randomized position has a Gaussian statistics leading to a Brownian motion described
by a Wiener-Levy stochastic process: \( \langle \varphi(t) \rangle = 0 \) and \( \langle \varphi(t) \varphi(t + \tau) \rangle = D_\theta(2t + \tau - |\tau|) \) ([546], p. 344),

\[
R_\theta(\tau) = \langle [\omega_{ca} + \dot{\varphi}(t)][\omega_{ca} + \dot{\varphi}(t + \tau)] \rangle = \langle \dot{\varphi}(t) \dot{\varphi}(t + \tau) \rangle = 2D_\theta \delta(\tau), \tag{23.93}
\]

where \( D_\theta = \sigma^2/\gamma_{fr} \) is the position diffusion coefficient. Note that deterministic parts are removed from the function in order to satisfy \( \langle \dot{\varphi}(t) \rangle = 0 \). In that case the spectral density of fluctuations of the atomic phase is constant,

\[
S_\theta(f) = \int_{-\infty}^{\infty} R_\theta(\tau) e^{-2\pi if\tau} d\tau = 2D_\theta. \tag{23.94}
\]

Note that \( S_\theta(f) = f^2S_\theta(f) \). The variance of the fluctuations for white noise is or,

\[
\sigma^2_\theta(\tau) = \langle \dot{\varphi}(t)^2 \rangle = \frac{D_\theta}{\tau}. \tag{23.95}
\]

Under the assumption \( \dot{\alpha} = i\omega_{ca} \alpha \) and introducing the abbreviation \( \alpha_0 \equiv -iU_0\alpha_+/(\kappa + i\omega_{ca}) \), the first equation (23.13) takes the form \( \alpha_- = \alpha_0e^{i\theta} \) such that the autocorrelation function of the field amplitude reads,

\[
R_\alpha(\tau) \equiv \langle \alpha^*_+(t)\alpha_-(t + \tau) \rangle = |\alpha_0|^2 \langle e^{i[\theta(t + \tau) - \theta(t)]} \rangle = |\alpha_0|^2 e^{i\omega_{ca}\tau} \langle e^{i\tau\dot{\varphi}(t)} \rangle. \tag{23.96}
\]

In the case of a Gaussian distribution for the noise amplitude with \( \dot{\varphi}(t) = \dot{\varphi}(-t) \), we have \( \langle \dot{\varphi}^{2k-1} \rangle / (2k - 1)! = 0 \) and \( \langle \dot{\varphi}^{2k} \rangle / (2k)! = \langle \dot{\varphi}^2 \rangle^k / k! \) [139, ?, 187],

\[
\langle e^{i\tau\dot{\varphi}(t)} \rangle = \sum_k \frac{i^k \langle \dot{\varphi}(t)^k \rangle}{k!} = \sum_k \frac{i^{2k} \langle \dot{\varphi}^2(t)^{2k} \rangle}{(2k)!} = \sum_k \frac{(-1)^k \langle \dot{\varphi}(t)^2 \rangle^k}{k!} = e^{-\frac{1}{2}\tau^2 \langle \dot{\varphi}(t)^2 \rangle}. \tag{23.97}
\]

Apparently, noise mainly affects the field’s phase and not its amplitude. Note that the first-order coherence is just the normalized autocorrelation \( g^{(1)}(\tau) \equiv R_\alpha(\tau)/R_\alpha(0) \),

\[
g^{(1)}(\tau) = e^{i\omega_{ca}\tau} e^{-\omega_{ca}^2 \sigma^2_\theta^2/2} = e^{i\omega_{ca}\tau} e^{-D_\theta|\tau|/2}. \tag{23.98}
\]

The power spectral density is a Lorentzian,

\[
S_\alpha(\omega) = |\alpha_0|^2 \int_{-\infty}^{\infty} R_\alpha(\tau) e^{-i\omega\tau} d\tau \tag{23.99}
= \frac{|\alpha_0|^2 D_\theta^2}{(\omega - \omega_{ca})^2 + D_\theta^2}.
\]

The CARL emission bandwidth is thus \( \frac{1}{2}D_\theta \). The above results show that the CARL laser bandwidth increases linearly with temperature and reduces with the friction force. In our experiment we have \( \gamma_{fr} = 5\kappa \) and \( \sigma = 10\kappa \), so that \( D_\theta = \sigma^2/\gamma_{fr} = 20\kappa \). The CARL bandwidth is extremely large as compared to the CARL frequency \( \omega_{ca} = 5\kappa \). The reason is that we only considered a single atom. The impact of several atoms will partially compensate and reduce the linewidth.
CHAPTER 23. STATISTICAL AND THERMODYNAMIC APPROACHES TO CARL

23.5.1.2 Many atoms, hand-waving

In order to account for the combined effect of many atoms, we reconsider the Eq. (23.13). If \( \dot{\alpha}_- = i\omega \alpha_ - \), we may write it like,

\[ \alpha_- = \alpha_0 \sum_m e^{i\theta_m}, \]  

(23.100)

\[ \dot{\theta}_n = \frac{4\varepsilon U_0 \alpha_+ \alpha_0}{\gamma f_r} \sum_m \left( e^{i\theta_m - i\theta_n} + e^{-i\theta_m + i\theta_n} \right) + \frac{\xi_n}{\gamma f_r}. \]

The light mode \( \alpha_- \) appears to be a superposition of coherent waves having the same frequencies, \( \alpha_m(t) = \alpha_0 e^{i\omega \alpha t + i\varphi_m(t)} \), but interrupted by random phase jumps. We may thus try an analogous argumentation as for pressure broadening,

\[ \langle \alpha_-^* (t) \alpha_- (t + \tau) \rangle = |\alpha_0|^2 \int \sum_n e^{-i\omega \alpha t - i\varphi_n(t)} \sum_m e^{i\omega \alpha t + i\varphi_m(t + \tau)} dt \]

\[ = |\alpha_0|^2 e^{i\omega \alpha \tau} \sum_{n,m} \int e^{i\varphi_m(t + \tau) - i\varphi_n(t)} dt = N \langle \alpha_-^* (t) \alpha_m (t + \tau) \rangle \delta_{nm}. \]

Cross-terms vanish, the autocorrelation function is just the sum of the single-atom components. However, while we may view the noise impact of the atoms as coming from a single atom, the rate of the phase jumps is much higher, than for a single atom. For one atom the probability density for encountering a coherent intervall of length \( \tau \) is given by \( p_1(\tau)d\tau = \frac{1}{4} D_\theta e^{-D_\theta |\tau|/2} \) [382]. Thus,

\[ \langle \alpha_1^* (t) \alpha_1 (t + \tau) \rangle = |\alpha_0|^2 e^{i\omega \alpha \tau} e^{-D_\theta |\tau|/2} = |\alpha_0|^2 e^{i\omega \alpha \tau} \int_\tau^\infty p_1(\tau')d\tau'. \]  

(23.101)

For \( N \) atoms we expect a probability density for encountering a coherent intervall of length \( \tau \),

\[ p_N(\tau)d\tau = p_1(\tau/N)d\tau = \frac{D_\theta}{2\sqrt{N}} e^{-D_\theta |\tau|/2\sqrt{N}} d\tau, \]

(23.102)

such that \( \int_0^\infty p_N(\tau')d\tau' = 1 \). However this remains to prove. Thus,

\[ g_N^{(1)}(\tau) = e^{i\omega \alpha \tau} \int_\tau^\infty p_N(\tau')d\tau' = e^{i\omega \alpha \tau - D_\theta |\tau|/2\sqrt{N}}. \]  

(23.103)

The second-order correlation function is,

\[ g_N^{(2)}(\tau) = 1 + |g_N^{(1)}(\tau)|^2. \]  

(23.104)

The laser bandwidth is accordingly reduced by,

\[ D_N = \frac{D_\theta}{\sqrt{N}}. \]  

(23.105)

Fig. 23.8 shows the dependencies of the correlation functions on \( N \) and \( T \). For \( N = 10^6 \) atoms the CARL bandwidth becomes \( \beta_N = 0.01\kappa \), which is already well below any mechanical noise. The linewidth reduction with increasing atom numbers is quantitatively supported by numerical simulations (see below).
23.5. COHERENT PROPERTIES OF CARL

![Figure 23.8](code) First and second-order correlation functions. The solid and dotted lines in (a) and (b) are calculated for $N = 1$ and $N = 100$, resp.. The solid and dotted lines in (c) and (d) are calculated for $T = 100 \mu K$ and $T = 300 \mu K$, resp..

### 23.5.1.3 Many atoms, formal

In order to account for the combined effect of many atoms, we reconsider the Eq. (??). If $\dot{\alpha}_- = i\omega_{ca} \alpha_-$, we get,

$$\alpha_- = - \frac{iU_0 \alpha_+}{\kappa + i\omega_{ca}} \sum_m e^{i\theta_m},$$

$$\dot{\theta}_n = \frac{4\varepsilon U_0^2 \alpha_+^2}{\gamma_{fr} (\kappa + i\omega_{ca})} \sum_m \left( e^{i\theta_m - i\theta_n} + e^{-i\theta_m + i\theta_n} \right) + \frac{\xi_n}{\gamma_{fr}}.$$

The autocorrelation is then,

$$R_\alpha(\tau) \equiv \langle \alpha_-^\dagger(t) \alpha_- (t + \tau) \rangle = \frac{U_0^2 \alpha_+^2}{\kappa^2 + \omega_{ca}^2} \sum_{n,m} \langle e^{i\theta_n(t+\tau) - i\theta_m(t)} \rangle$$

$$= |\alpha_0|^2 e^{i\omega_{ca} \tau} \sum_{n,m} \langle e^{i\varphi_n(t+\tau) - i\varphi_m(t)} \rangle = |\alpha_0|^2 e^{i\omega_{ca} \tau} \sum_{n,m,k} \frac{i^k}{k!} \langle [\varphi_n(t+\tau) - \varphi_m(t)]^k \rangle$$

$$= |\alpha_0|^2 e^{i\omega_{ca} \tau} \sum_{n,m,k} \frac{i^k}{k!} \sum_{j=0}^k \sum_{j=0}^k \sum_{j=0}^k \langle [\varphi_n(t+\tau)]^j \varphi_m(t)^{k-j} \rangle.$$

The main role of cavity-induced interparticle correlations is to self-consistently establish a constant center-of-mass motion $\omega_{ca}$. We may, to first order, neglect the possibility that the coupling correlates the noise, since the noise is imprinted from the
outside, i.e. the molasses. Therefore, \( \langle \varphi_n(t + \tau) \varphi_m(t) \rangle \propto \delta_{nm} \),

\[
\langle \varphi_n(t + \tau)^2 \varphi_m(t)^{k-j} \rangle = \sum_{\text{all pairs}} \langle \varphi_n(t + \tau)^2 \rangle^{j/2} \langle \varphi_m(t)^2 \rangle^{k/2-j/2} 
\]

(23.108)

\[
= \frac{j!}{2^{j/2}(j/2)!} \frac{(k-j)!}{2^{(k-j)/2}(k/2-j/2)!} \langle \varphi_n(t + \tau)^2 \rangle^{j/2} \langle \varphi_m(t)^2 \rangle^{k/2-j/2}
\]

so that,

\[
R_\alpha(\tau) = |\alpha_0|^2 e^{i\omega_{ca}\tau} \sum_{n,m,k} \frac{i^k k!}{k!} \sum_{j=0}^{k} \left( \begin{array}{c} k \\ j \end{array} \right) \frac{j!}{2^{j/2}(j/2)!} \frac{(k-j)!}{2^{(k-j)/2}(k/2-j/2)!} \langle \varphi_n(t + \tau)^2 \rangle^{j/2} \langle \varphi_m(t)^2 \rangle^{k/2-j/2} 
\]

(23.109)

where \( j \) and \( k \) are even,

\[
R_\alpha(\tau) = |\alpha_0|^2 e^{i\omega_{ca}\tau} \sum_{n,m,k} \frac{1}{(k/2)!} \sum_{j=0}^{k/2} \left( \begin{array}{c} k/2 \\ j/2 \end{array} \right) \langle \varphi_n(t + \tau)^2 \rangle^{j/2} \langle \varphi_m(t)^2 \rangle^{k/2-j/2} 
\]

(23.110)

\[
= |\alpha_0|^2 e^{i\omega_{ca}\tau} \sum_n e^{-\frac{1}{2}} \langle \varphi_n(t+\tau)^2 \rangle \sum_m e^{-\frac{1}{2}} \langle \varphi_m(t)^2 \rangle = |\alpha_0|^2 N^2 e^{i\omega_{ca}\tau} e^{-\frac{1}{2}} \langle \varphi_n(t+\tau)^2 \rangle e^{-\frac{1}{2}} \langle \varphi_n(t)^2 \rangle .
\]

23.5.1.4 Memory effects

Relax adiabaticity, \( \dot{\alpha}_- \neq i\omega_{ca}\alpha_- \), substitute \( \beta = e^{\kappa t} \alpha_- \),

\[
\dot{\beta} = \frac{4\varepsilon iU_0 \alpha_+}{\gamma_f r} \left( \beta e^{-i\theta - \kappa t} - \beta^* e^{i\theta - \kappa t} \right) + \frac{\xi}{\gamma_f r},
\]

(23.111)

\[
\beta = -iU_0 \alpha_+ \int^t e^{i\theta + \kappa t'} dt' .
\]

so that,

\[
R_\alpha(\tau) \equiv \langle \alpha_-^*(t) \alpha_- (t + \tau) \rangle = \langle e^{-\kappa t} \beta^*(t) e^{-\kappa t - \kappa \tau} \beta(t + \tau) \rangle 
\]

(23.112)

\[
= e^{-\kappa \tau} \langle e^{-2\kappa t} \beta^*(t) \beta(t + \tau) \rangle 
\]

\[
= U_0^2 \alpha_+^2 e^{-\kappa \tau} \int^t \int^{t+\tau} e^{i\theta(t''') - i\theta(t')} e^{i\theta(t') + \kappa t' + \kappa \tau'' - 2\kappa t'' dt'' dt'} dt'' dt' 
\]

\[
= U_0^2 \alpha_+^2 e^{-\kappa \tau} \int^t \int^{t+\tau} e^{i\omega_{ca} t'' - i\omega_{ca} t' + i\varphi(t''') - i\varphi(t') - i\varphi(t') + \kappa t' + \kappa \tau'' - 2\kappa t'' dt'' dt'} dt'' dt' .
\]

Using the representation of half the \( \delta \)-distribution \( \int^t e^{i(\omega_{ca} + \kappa) t'} dt' = \delta_{1/2} = \lim_{\tau \to 0} \frac{1}{\tau + i\omega_{ca}} \).

23.5.1.5 Schawlow-Townes limit for CARL

The ultimate limit for the spectral purity of a perfectly stable laser oscillator is the Schawlow-Townes limit [531]. The origin of this limitation is the discrete nature of the light field. Similarly to quantum projection noise, which is caused by the discretisation
of atomic energy levels, the optical shot-noise registered in photodetectors arises from the discrete repartition of electromagnetic energy in photons. With a laser power $P$, a cavity bandwidth $\kappa$ and an interrogation time $\tau$, the Allan variance [?] and the linewidth of a Schawlow-Townes limited laser are given by,

$$\sigma_{ST}(\tau) = \frac{1}{\omega/\kappa} \frac{1}{\sqrt{(P/\hbar \omega) \tau}}$$

$$\beta = \frac{\kappa^2 \hbar \omega}{P}.$$  

In the case of CARL, using $P = \delta \hbar \omega |\alpha_-|^2$ the variance is $\sigma_{ST}^2(\tau) = \kappa/\tau \omega \delta |\alpha_-|^2 \approx 10^{-20} \text{s/} \tau$. The shot-noise which limits the CARL is not the one of the CARL light itself, but the random momentum kicks imparted by molasses-cooled atoms. The CARL linewidth is $\beta = \kappa^2/\delta |\alpha_-|^2 = 10^{-14} \kappa$.

The time-lap between two scattering events for a single atom be distributed according to $p_1(\tau) d\tau = \gamma e^{-\gamma \tau} d\tau$. What is the waiting time distribution for two atoms [532]? Schenzle related the waiting time distribution to the autocorrelation function $g^{(2)}(\tau)$.

Fig. 23.9: Simulated time-dependence of the (a) beat and the (b) intensity signals. Calculated (c) first and second-order correlation functions. The temperature was set to $T = 100 \mu\text{K}$ and the atom number to $N = 40$.

Fig. 23.10 shows spectra of the CARL frequency obtained by Fourier-transforming the autocorrelation function of a Langevin-simulated trajectory of the CARL frequency. The width results from thermal fluctuations in the atomic motion induced by momentum diffusion in the molasses. It is clearly visible that the width is reduced when the atom number is increased, thus confirming Eq. (23.105).
23.5.2 Measuring the coherence properties

We may also attempt to verify the predictions in experiment. Our signals are the beams transmitted through the cavity mirrors.

23.5.2.1 Homodyne signal

Ideally in order to get the full information on the first-order coherence, we should record both the in-phase and the quadrature component of the field $\alpha_- = \text{Re}\alpha_- + i\text{Im}\alpha_-$ by homodyning it with the local oscillator $\alpha_+$. Thus we need to use both ports of the beamsplitter: For the in-phase component we get,

$$P_{\text{hod}}^{(ph)} \propto b^\dagger b - c^\dagger c$$

$$= |\alpha_+ \sqrt{\eta} + \alpha_- \sqrt{1 - \eta}|^2 - |\alpha_- \sqrt{1 - \eta} - \alpha_+ \sqrt{\eta}|^2$$

$$= (1 - 2\eta)(|\alpha_-|^2 - |\alpha_+|^2) + 4\sqrt{\eta} - \eta^2 \alpha_+ \text{Re} \alpha_- .$$

For a 50% beamsplitter the offsets disappear, $P_{\text{hod}}^{(ph)} \propto 2\alpha_+ \text{Re} \alpha_-$, which means that the homodyne signal is insensitive to intensity noise in the individual ports. Similarly we obtain for the quadrature component,

$$P_{\text{hod}}^{(qu)} \propto |\alpha_+ \sqrt{\eta} + i\alpha_- \sqrt{1 - \eta}|^2 - |\alpha_- \sqrt{1 - \eta} - i\alpha_+ \sqrt{\eta}|^2$$

$$= -2\alpha_+ \text{Im} \alpha_- .$$

By mounting a piezo on one of the mirrors in the homodyne loop, we can influence which quadrature component to map. Is there a way how to get $\text{Im} \alpha_-$ and $\text{Re} \alpha_-$ simultaneously?

Knowing $\alpha_-$ we can calculate the first order coherence,

$$g^{(1)}(\tau) \equiv \frac{\langle \alpha^*(t)\alpha(t + \tau) \rangle}{\langle \alpha^*(t)\alpha(t) \rangle} = \frac{\int \alpha^*(t)\alpha(t + \tau) dt}{\int \alpha^2(t) dt} , \quad (23.116)$$
23.5. COHERENT PROPERTIES OF CARL

23.5.1 Second-Order Coherence

The second-order coherence,
\[ g^{(2)}(\tau) = \frac{\langle \alpha^*(t)\alpha^*(t+\tau)\alpha(t+\tau)\alpha(t) \rangle}{\langle \alpha^*(t)\alpha(t) \rangle^2} \]
\[ = \frac{\int P_-(t)P_-(t+\tau)dt}{\int P_-(t)dt} , \]
and the emission spectrum (power spectral density),
\[ F(\omega) = \frac{1}{\pi} \text{Re} \int g^{(1)}(\tau)e^{i\omega \tau}d\tau . \]

All these quantities can be evaluated from numerical simulations of the Langevin equations.

23.5.2 Real Signals

What we record in experiment is the probe field power \( P_{\text{probe}} \) and only one quadrature component of the beat between the probe and the pump. The probe signal is simply,
\[ P_- \propto |\alpha_-|^2 . \]

So it may be used directly for the intensity correlation function (23.117) analogous to Hanbury-Brown-Twiss.

The beat signal is obtained in a Young type experiment,
\[ P_\text{beat} \propto |\alpha_+ \pm \alpha_-|^2 = |\alpha_+|^2 + |\alpha_-|^2 \pm 2\alpha_+\text{Re }\alpha_- , \]

because we may assume \( \alpha_+ \) real. Obviously, the beat signal oscillates between the limits \( \pm 2\alpha_+|\alpha_-| \). Currently, we only use one port of the beamsplitter. Thus we miss information on the other quadrature phase. The question arises now, how to calculate the spectrum if only the real part of the field \( \text{Re }\alpha \) is known. The interesting quantity is \( |g^{(1)}(\tau)| \), because it contains the information on the photon statistics. This function is smooth (it does not oscillate) and should in our case describe an exponential decay (23.98). Fortunately, from numerical calculation it seems that \( |g^{(1)}(\tau)| \) is just the convolution of \( \langle \text{Re }\alpha(t)\text{Re }\alpha(t+\tau) \rangle / \langle \text{Re }^2 \alpha(t) \rangle \), so that we may recover the informations. For the spectrum, which is calculated from the complex quantity \( g^{(1)}(\tau) \) the question is more delicate. It comes down to asking if,
\[ F(\omega) \propto \text{Re} \int \langle \text{Re }\alpha(t)\text{Re }\alpha(t+\tau) \rangle e^{i\omega \tau}d\tau \]
23.5.2.3 Preliminary experimental observations

Technical noise may overrule the thermal noise just like in ordinary lasers. This situation may change if atom numbers are low, so that we have bad statistics, or if the collective force is strong enough to correlate the noise.

The spectral width may also be limited by the finite time window \( t \in [-\frac{1}{2}t_0, \frac{1}{2}t_0] \), which is taken for computing the spectrum. Even a perfect harmonic oscillation \( \alpha_-(t) = \alpha_- e^{i\omega_{ca} t} \) will then have a finite bandwidth,

\[
F_{\alpha_-}(\omega) = F[\alpha_- e^{i\omega_{ca} t}] \ast F[\chi[-t_0/2,t_0/2](t)]
= \alpha_- \delta(\omega - \omega_{ca}) \ast \sqrt{\frac{2}{\pi}} \frac{\sin \frac{1}{2}\omega t_0}{\omega}
= \alpha_- \sqrt{\frac{2}{\pi}} \frac{\sin \frac{1}{2}(\omega - \omega_{ca})t_0}{(\omega - \omega_{ca})}
\]  

(23.122)

The spectrum \( S_{\alpha_-}(\omega) = |F_{\alpha_-}(\omega)|^2 \) has a bandwidth of \( \beta = 5.6/t_0 \). For example an oscillation observed for a period 100 times longer than the cavity decay time, \( t_0 = 100/\kappa \), the bandwidth will be \( \beta = 0.056\kappa \). Simulations are based on the Langevin equation.

![Figure 23.12: (code) Measured trajectories (a) and (b) and correlation functions (c) and (d) of the CARL laser. The coupling constant was \( NU_0 = -0.1 \).](image)

23.5.3 Exercises

23.5.3.1 Ex: Autocorrelation functions
Figure 23.13: Spectrum of the CARL calculated from the first-order correlation function in Fig. ??(c). The coupling constant was $NU_0 = -0.1\kappa$. 
Part V

Atom Optics
Chapter 24

Manipulation of atomic gases

The field of atom optics deals with the motion of atoms and its control by technical tools. At high velocities with no external forces, the atoms follow straight paths, similar to light beams in classical optics. At low speeds, they propagate as waves, similarly to wave optics in Maxwell’s theory of electrodynamics. The term atom optics emphasizes the analogy and the duality in the behavior of microscopic particles.

The duality principle is one of the fundamental ideas of quantum mechanics. The appearance of an object as a wave or as a particle depends on the situation in which it is observed. While the wave nature of light was well established in classical physics since a long time, Louis de Broglie was the first in 1924 to apply the duality principle also to massive particles and to predict that particles, under certain conditions, behave like waves whose wavelengths increase as their velocity decreases. Each particle (or sample of particles) is delocalized along a distance corresponding to the ’de Broglie wavelength’. This feature of the matter was soon discovered experimentally in electron beams and is still used today in commercial devices, for example in electron microscopes.

The laser was discovered in 1956. In a laser, light particles are forced to oscillate synchronously, that is, coherently. By analogy, we can raise the question whether a similar phenomenon can occur with massive particles, and whether it is possible to construct an atom laser. Such a device would emit coherent matter waves just as the laser emits coherent light. When a gas is cooled to very low temperatures, the Broglie waves of the atoms become very long and, if the gas is sufficiently dense, eventually overlap. If the gas consists of a single species of bosonic particles with all atoms being in the same quantum state, their Broglie waves interfere constructively thus and form a huge wave of coherent matter. This matter wave is described by a single wavefunction exhibiting long range order and having a single phase. If this wavefunction is formed inside a trap, all atoms accumulate in its ground state. Thus, we obtain a pure quantum state of many bodies in the kinetic degree of freedom. The transition of a gas from individual atoms to a degenerate mesoscopic many-body quantum state occurs as a phase transition named Bose-Einstein condensation (BEC) as a homage to Bose and Einstein who predicted the effect already in 1924 [77, 184].

The experimental verification of Bose and Einstein’s prediction was for a long time a cherished dream of many physicists. On the one hand, several phenomena have been related to BEC in the past, for example, the phenomenon of superfluidity in liquid helium and superconductivity. On the other hand, these strongly interacting

\[1\] In particular, for very cold atoms whose internal excitation occurs on a very different energy scale, the corresponding degree freedom is frozen and does not influence the kinetics.
systems are not pure enough to clearly identify the role of BEC. In 1995, however, Bose-Einstein condensation of weakly interacting confined atomic gases was achieved in several laboratories [12, 143, 83, 256]. This success gave rise to a revolution in atom optics documented in an enormous amount of theoretical and experimental work. While initial work focused on the equilibrium thermodynamics of condensates near the phase transition, very soon the dynamic response of condensates to perturbations was the subject of in-depth investigations, followed by the study of superfluid characteristics, quantum transport phenomena, the interaction of condensates with light, of condensed gas mixtures [445, 577], and the behavior of condensates in periodic potentials. To name only a few landmarks, we mention the creation of vortices [400, 388] and quantum turbulence [275], the realization of various types of atom lasers [413, 11, 63, 250] and atom interferometers with condensates [253, 355], the coherent amplification of matter waves [304, 358, 306, 155], the creation of the Mott insulating states in optical lattices [230], the study of condensates in reduced dimensions [437], the Anderson localization of atomic matter waves [101, 504], the observation of Feshbach type collision resonances [294, 303, 611] and Efimov states [359, 38], the creation of homonuclear molecular [231, 325, 129, 658, 646, 276] and heteronuclear condensates [458] and degenerate Fermi gases [149], the observation of BCS type pairing [284, 232], the observation of matter wave superradiance [304] and the interaction of condensates with optical cavities [559, 96] and with surfaces [47].

It is clearly unthinkable to discuss all matters in this course. Let us, however, give a basic and practical introduction to atomic optics with condensates. The course begins in this chapter with a presentation of the most important experimental techniques for cooling, trapping, manipulating and detecting atomic gases. The knowledge of these techniques will allow for a better understanding of how it is possible to generate and analyze all the effects mentioned above. Chp. 26.8.4 introduces the phenomenon of Bose-Einstein condensation and the following chapters focus on the thermodynamic, superfluid, coherent and dielectric properties of condensates.

The incomparable success of atomic optics has been rewarded with 20 nobel prices in the last 25 years (Dehmelt, Paul, Ramsey, Cohen-Tannoudji, Chu, Phillips, Cornell, Wieman, Ketterle, Hänisch, Glauber, Hall, Wineland, Haroche, Ahskin)

![Temperature scale](image-url)

In this chapter we review the basic techniques of Atomic Optics, emphasizing the cooling, trapping and measurement of cold atomic gases. See also (watch talk) and (watch talk).

24.1 The atomic motion

24.1.1 The atom as a matter wave

We have already emphasized that atomic optics deals with the motion of atoms in a gas, that is, we are interested only in the external degrees of freedom of the atoms. To describe the motion of a free massive particle in one dimension, we write the Hamiltonian,

\[ \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}. \]  

Therefore, the general solution of the stationary Schrödinger equation,

\[ \hat{H}\psi(x) = E\psi(x), \]  

is,

\[ \psi(x) = Ae^{ikx} + Be^{-ikx} \quad \text{with} \quad k = \sqrt{\frac{2mE}{\hbar^2}}. \]  

Note, that the wavefunctions \( e^{ikx} \) are not quadratically integrable. On the other hand, they do not represent real physical systems. In practice, we need to consider wavepackets or specify a finite volume for the particle.

Note also that the eigenvalue spectrum of is continuous. To warrant the interpretation of the wavefunction as a probability density we will require quadratic integrability, \( \int |\psi|^2 d^3r = 1 \). This means that the wavefunction can not be infinite in a finite volume, but it can be infinite in an infinitely small volume.

The description of the atomic motion by a wave equation emphasizes the fact that microscopic particles have wave properties with each atom corresponding to a velocity-dependent de Broglie wave,

\[ \lambda_{dB} = \frac{h}{p}, \]  

which describes the coherence length of the atom.

24.1.1.1 Characteristic velocities

The behavior of an atom described by the Schrödinger equation depends very much on its kinetic energy. At high velocities (or short de Broglie waves), it will behave like a classical particle with a well-defined trajectory. At low velocities (or long de Broglie waves), it will propagate like a wave and exhibit phenomena such as diffraction.
and interference. Therefore, it is important to highlight some characteristic velocity regimes.

Most optical cooling techniques are based on the removal of kinetic energy upon light scattering on electronic transitions. It is, therefore, interesting to compare the kinetic energy (or temperature) of an ensemble of atoms with the width $\Gamma$ of the transition. The *Doppler limit* is given by (see Exc. 24.1.4.1),

$$k_B T_D = \frac{\hbar}{2} \Gamma.$$  \hspace{1cm} (24.5)

We can also compare the kinetic energy with the energy transferred to an atom by the absorption of a single photon. The *photonic recoil* energy is given by,

$$k_B T_{rec} = \frac{\hbar^2 k^2}{2m}.$$  \hspace{1cm} (24.6)

Atomic clouds with temperatures around $T_D = 100..1000 \mu K$ are called *cold*. Clouds with temperatures around $T_{rec} = 100..1000 nK$ are called *ultracold*.

In most atomic optical experiments we do not work with individual atoms (or ions), but with relatively dilute ensembles of atoms, called *clouds*. In general, clouds can not be described by a single wavefunction. Either we describe every atom by a separate and independent wavefunction (which only works when the atoms do not interact), or we describe the cloud by probability distributions (such as the *density matrix*). Let us now consider a thermal cloud. The *Maxwell-Boltzmann distribution* of velocities is,

$$g(v) = \sqrt{\frac{m}{2\pi k_B T}}^3 e^{-m v^2/2k_B T}.$$  \hspace{1cm} (24.7)

This distribution is normalized, $\int g(v) d^3v = \int_0^\infty 4\pi v^2 g(v) dv = 1$. Average velocity is now

$$\bar{v} = \int v g(v) dv = \sqrt{\frac{k_B T}{m}}.$$  \hspace{1cm} (24.8)

![Figure 24.2: (code) Maxwell-Boltzmann distribution.](image)

We define the *thermal de Broglie wavelength* of an atomic ensemble as,

$$\lambda_{therm} \equiv \frac{\hbar}{m\bar{v}} = \sqrt{\frac{2\pi \hbar^2}{mk_B T}}.$$  \hspace{1cm} (24.9)
24.1. THE ATOMIC MOTION

It represents an average over the de Broglie wavelengths of all atoms of the sample. When a dense gas is sufficiently dense, so that this quantity exceeds the average distance between atoms,

\[
\rho \equiv n \lambda_{\text{therm}}^3 > 1 ,
\]

(24.10)

where \( n \) is the atomic density, we enter a new regime, where the Maxwell-Boltzmann law ceases to be valid. Since \( \lambda_{\text{therm}} \propto T^{-1/2} \), this regime corresponds to low temperatures. The quantity \( \rho \) is called phase space density. A phase space density approaching 1 means an increased probability of finding more than one atom per elementary phase space cell. We then enter the regime of quantum degeneracy, where the Boltzmann statistics must be replaced by the Bose-Einstein statistics, in the case of bosons, or the Fermi-Dirac statistics, in the case of fermions. We will deepen the discussion of quantum statistics of ideal gases in Chp. 25.2.11. From the condition \( n \lambda_{\text{therm}}^3 \simeq 1 \), we obtain

\[
k_B T_c = \frac{1}{m} \left( \frac{2\pi \hbar}{\lambda_{\text{therm}}} \right)^2 = \left( \frac{2\pi \hbar}{m} \right)^2 \frac{n^{2/3}}{m} .
\]

(24.11)

24.1.2 Localized atoms

To avoid perturbative influence of the environment on the atoms, they are often trapped in potentials, which suspend them in a volume distant from massive walls. The Hamiltonian of a trapped atoms is,

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) .
\]

(24.12)

As the wavefunction is now localized, the spectrum of possible energies organizes into discrete levels, and the atoms are allocated in populations of these levels.

Often, a 3D potential can be written in the form,

\[
U(x, y, z) = U_x(x) + U_y(y) + U_z(z) .
\]

(24.13)

This is the case, for example, of a rectangular well characterized by \( U_x(x) = U_y(y) = U_z(z) = U_0/3 \) inside the well. The relationship (24.13) also holds for a harmonic potential,

\[
U(r) = \frac{m}{2} \left( \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2 \right) .
\]

(24.14)

In these cases, a product ansatz for the wavefunction is generally useful,

\[
\psi(r) = \psi_x(x)\psi_y(y)\psi_z(z) ,
\]

(24.15)

since its insertion into the Schrödinger equation,

\[
-\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) + U_x(x) + U_y(y) + U_z(z) \psi_x(x)\psi_y(y)\psi_z(z)
\]

(24.16)

separates it into three independent one-dimensional equations,

\[
-\frac{\hbar^2}{2m} \frac{\psi''_x(x)}{\psi_x(x)} + U_x(x) = \text{const.} \equiv E_x ,
\]

(24.17)
and similarly for \( y \) and \( z \). Since \( E = E_x + E_y + E_z \), we can have the same energy for different combinations of \( E_x, E_y \) and \( E_z \). That is, multidimensional systems are often degenerate.

### 24.1.3 Density-of-states of a trapping potential

The way an atomic cloud accommodates itself inside a trapping potential is governed by the density of available states. To calculate this density, we consider the Hamiltonian \( H(\mathbf{r}, p) = \frac{\hbar^2 k^2}{2m} + U(\mathbf{r}) \). For a cylindrical harmonic oscillator we write,

\[
U(\mathbf{r}) = \frac{m}{2} \omega_r^2 r^2 + \frac{m}{2} \omega_z^2 z^2 \quad \text{where} \quad r^2 = x^2 + y^2,
\]

or \( U(x) = \frac{m}{2} \omega_x^2 \rho^2 \), where \( \rho^2 = x^2 + y^2 + \lambda^2 z^2 \) with \( \lambda = \omega_z/\omega_r \). We define \( \bar{\omega} = (\omega_r^2 \omega_z)^{1/3} = \lambda^{1/3} \omega_r \). The single-particle levels of this Hamiltonian are, \( \epsilon_{n_x n_y n_z} = \hbar \omega_x n_x + \hbar \omega_y n_y + \hbar \omega_z n_z \), where the \( n_j \) are integer numbers.

![Figure 24.3](code) (a) The figure shows two dimensions of a Ioffe-Pritchard type magnetic trapping potential (characterized by being approximately linear at large distances from the center and harmonic near the center). (b) Harmonic approximation (most experimentally feasible potentials are approximately harmonic near the center). (c) One-dimensional cut through the potential of (a,b). (d) Density of states for a harmonic (dotted line) and a Ioffe-Pritchard type potential (solid line).

We now introduce the density of states \( \eta(\epsilon) \) for an arbitrary potential via,

\[
\int \eta(\epsilon) d\epsilon \equiv \frac{1}{(2\pi)^3} \int d^3 r d^3 k = \frac{(2m)^{3/2}}{(2\pi)^2 \hbar^3} \int d^3 r \int d\epsilon \sqrt{\epsilon - U(\mathbf{r})}.
\]
For the cylindrical harmonic trap defined in (24.18), we find with a little help from Dr. Bronstein [87],
\[
\eta(\epsilon) = \left(\frac{2m}{(2\pi)^2 \hbar^3}\right)^{3/2} \int d^3 r \sqrt{\epsilon - \frac{m}{2} \omega^2 r^2} \tag{24.20}
\]
\[
= \frac{1}{(2\pi)^2 (\hbar \omega)^3} \int_{-1}^{1} d\tilde{x} \int_{-\sqrt{1-\tilde{x}^2}}^{\sqrt{1-\tilde{x}^2}} d\tilde{y} \int_{-\sqrt{1-\tilde{x}^2-\tilde{y}^2}}^{\sqrt{1-\tilde{x}^2-\tilde{y}^2}} d\tilde{z} \sqrt{\epsilon}.
\]

The resolution of the integral gives,
\[
\eta(\epsilon) = \frac{\epsilon^2}{2(h\omega)^3} \quad \text{(harmonic potential)}. \tag{24.21}
\]

Another example is the box potential. In this case we can simply obtain,
\[
\eta(\epsilon) = \left(\frac{2m}{(2\pi)^2 \hbar^3}\right)^{3/2} \int_V d^3 r \sqrt{\epsilon} = \left(\frac{2m}{(2\pi)^2 \hbar^3}\right)^{3/2} V \sqrt{\epsilon} \quad \text{(box potential)}. \tag{24.22}
\]

A generalization is discussed in the Exc. 24.1.4.2.

### 24.1.4 Exercises

#### 24.1.4.1 Ex: Fundamental temperature limits

Calculate the Doppler limit, the recoil limit, and the threshold to quantum degeneracy for an atomic cloud of density \( n = 10^{14} \text{ cm}^{-3} \) for the sodium \( \text{D}_2 \) transition (\( \lambda = 590 \text{ nm}, \Gamma/2\pi = 10 \text{ MHz} \)) and the rubidium \( \text{D}_2 \) transition (\( \lambda = 780 \text{ nm}, \Gamma/2\pi = 6 \text{ MHz} \)).

#### 24.1.4.2 Ex: Density of states for non-harmonic potentials

Calculate the density of states for non-harmonic potentials, \( \hat{H} = \frac{\hbar^2 \mathbf{k}^2}{2m} + \left| \frac{x}{2x} \right|^p + \left| \frac{y}{2y} \right|^q \) using Ref. [29]. Apply the result to a quadrupolar potential.

### 24.2 Optical cooling

As discussed in Sec. 16.2, the force exerted by a light field on an atom can be of two types: a dissipative force arising called radiation pressure, which is often used for optical cooling purposes, and a conservative dipolar force which often serves for the engineering of optical trapping potentials. Both applications of optical forces will be detailed in the following sections.

#### 24.2.1 Optical molasses

In the Doppler cooling model, we treat the phenomenology of optical forces quantitatively by considering the amplitude, phase and frequency of a classical field interacting
with the dipole of an atomic transition in a two-level atom. From Eq. (16.24) and previous definitions of $\Omega$ and $\Omega_{sat}$, and with the intensity $I \propto E_0^2$, we can write the saturation parameter,

$$s = \frac{I}{I_{sat}} = \frac{\Omega^2}{\Omega_{sat}^2} = \frac{\Omega^2}{\Gamma^2/2},$$

(24.23)

and

$$F_{rp} = \frac{\hbar k \Gamma}{2} \frac{s}{(2\Delta/\Gamma)^2 + 1 + s}.$$  \hspace{1cm} (24.24)

Now, if we consider an atom propagating in $+z$ direction with the velocity $v_z$ counterpropagating to a light wave detuned by $\Delta$ from the resonance, the total detuning will be

$$\Delta \rightarrow \Delta + k v_z.$$

(24.25)

where the term $k v_z$ is the Doppler shift. The force $F_\perp$ acting on the atom will be in the direction opposite to the motion. In general,

$$F_\pm = \pm \frac{\hbar k \Gamma}{2} \frac{s}{(2\Delta \mp k v_z/\Gamma)^2 + 1 + s}.$$  \hspace{1cm} (24.26)

Supposing now, that we have two light fields propagating in directions $\pm z$, the total force will be $F = F_+ + F_-$. If $k v_z$ is small compared to $\Gamma$ and $\Delta$, we find through a Taylor expansion,

$$F_z \simeq 4\hbar k s \frac{k v_z (2\Delta/\Gamma)}{[1 + s + (2\Delta/\Gamma)^2]^2}.$$  \hspace{1cm} (24.27)

This expression shows that, if the detuning $\Delta$ is negative (that is, on the red side of the resonance), then the cooling force will oppose the motion and be proportional to the atomic velocity. Fig. 24.4 shows this restoring dissipative force as a function of $v_z$ at a detuning $\Delta = -\Gamma$ with $I = I_{sat}/2$. The one-dimensional motion of the atom, subject to a restoring force which is proportional to the atomic velocity, is that of a damped harmonic oscillator. The proportionality factor,

$$\alpha_d = s \frac{-4k^2(2\Delta/\Gamma)}{1 + s + (2\Delta/\Gamma)^2}$$  \hspace{1cm} (24.28)

is just the friction coefficient.

However, the atom will not cool down indefinitely. At some point, the Doppler cooling rate will be balanced by the heating rate coming from the momentum fluctuations of the atom absorbing and remitting photons. The Doppler cooling limit is given by,

$$k_B T = h \frac{\Gamma}{2}.$$  \hspace{1cm} (24.29)

This limit is generally, for alkaline atoms, on the order of dozens of micro-Kelvin. In the early years of cooling and trapping, the Doppler limit was thought to be a real physical barrier. But in 1988, several groups have shown that, in fact, atoms could be cooled well below the Doppler limit. The effect arises in atoms, whose ground state exhibits a hyperfine structure. We will show simplified one-dimensional models for sub-Doppler cooling in the next section. Resolve the Excs. 24.2.5.1 and 24.2.5.2.
24.2. OPTICAL COOLING

![Figure 24.4: Doppler force due to one-dimensional radiative pressure as a function of atomic velocity along the z-axis for red detuning $\Delta = -\Gamma$ at a light intensity of $I = 2I_{\text{sat}}$. The solid line shows the exact expression for the restoring force [Eq (24.26)]. The broken line shows the approximate linear expression of the velocity dependence according to Eq. (24.27).](image)

24.2.2 Sub-Doppler cooling

It turns out that atoms with a hyperfine structure in the ground state can be cooled below the Doppler limit (24.5). To explain this unexpected observation, models involving a slow motion of the atoms in polarization gradients of a standing light wave have been invoked. The phenomenon is now known as polarization gradient cooling.

Two principal mechanisms for cooling atoms to temperatures below the Doppler limit are based on spatial polarization gradients. These two mechanisms, however, invoke very different physical processes and are distinct by the spatial dependence of the light polarization. A key point is that these sub-Doppler mechanisms only work on atoms with multiple ground state levels. Two parameters, the friction coefficient and the capture velocity, determine the importance of these cooling processes. In this section we compare the expressions for these quantities in the sub-Doppler regime to those found by the conventional one-dimensional Doppler cooling model for optical molasses.

24.2.2.1 Lin $\perp$ lin molasses

In the first case, two counterpropagating light waves with orthogonal linear polarizations form a standing wave. This configuration is familiarly called lin-perp-lin. Fig. 24.5 illustrates the change of polarization every period of $\lambda/8$ from linear to circular to linear again, but rotated by $90^\circ$, and so on [137]. Along the same distance, the light-atom coupling produces a periodic energy shift (light-shift) of the ground state Zeeman levels. To illustrate the cooling mechanism, we assume the simplest case, a transition $J_g = \frac{1}{2} \rightarrow J_e = \frac{3}{2}$. As shown in Fig. 24.5 an atom moving through the region $z \simeq \lambda/8$, where the polarization is $\sigma_-$, will see its population pumped to $J_g = -\frac{1}{2}$. In addition, the Clebsch-Gordan coefficients that control the dipolar coupling of the $J_e = \frac{3}{2}$ require that the $J_g = -\frac{1}{2}$ couples to $\sigma_-$ with a force three times larger than the $J_g = +\frac{1}{2}$ does. The difference of the coupling forces leads to the light-shift between the two fundamental states shown in Fig. 24.5. As the atom
continues to move toward $+z$, the relative coupling forces are reversed near $3\lambda/8$, where the polarization is essentially $\sigma_+$. Thus, the relative energy levels of the two hyperfine fundamental states oscillate 'out of phase' when the atom moves through the standing wave.

The fundamental idea is that the optical pumping rate, which always redistributes population to the lower hyperfine level, delays the light-shift of the atom moving through the field. The result is a 'Sisyphus effect', where the atom spends most of its time in sub-levels climbing a potential hill and thus converting kinetic energy into potential energy. This accumulated potential energy is subsequently dissipated by spontaneous emission to the electromagnetic modes of the vacuum. Simultaneously, the spontaneous emission transfers the population back to the lower one of two ground state levels. The lower diagram of Fig. 24.5 illustrates the phase delay of optical pumping. For this cooling mechanism to work, the optical pumping time, which is controlled by the intensity of the light, must be sufficiently slow to give the atom enough time to climb a noticeable part of the light-shift potential. This time essentially depends on the speed of the atom. As the atom is moving slowly, having previously been cooled by the Doppler mechanism, the light field must be weak in order to decrease the optical pumping rate. Interestingly, this physical picture combines the conservative dipole optical force, whose spatial integral gives rise to the mounts and valleys of the potential on which the atom moves, and the irreversible dissipation of energy by spontaneous emission, which is necessary for any type of cooling.

We can obtain simple expressions for the friction coefficient and the capture velocity after some definitions. As in the Doppler cooling model we define the friction coefficient $\alpha_{lpl}$ as the proportionality constant between the force $F$ and the atomic velocity $v$,

$$ F = -\alpha_{lpl}v. $$ (24.30)
We assume that the light field is tuned to the red of the transition $J_g - J_e$,

$$\Delta = \omega - \omega_0,$$  \hspace{1cm} (24.31)

and we denote the light-shifts of the levels $J_g = \pm \frac{1}{2}$ as $\Delta_\pm$, respectively. At the position $z = \lambda/8$, we find $\Delta_- = 3\Delta_+$ and at $z = 3\lambda/8$, $\Delta_+ = 3\Delta_-$. As the applied field is tuned to red, all $\Delta_\pm$ have negative values. Now, for the cooling mechanism to be efficient, the optical pumping time $\tau_p$ should be similar to the time needed for an atom with velocity $v$ to move from the bottom to the top of the potential, $\frac{\lambda}{4}$,

$$\tau_p = \frac{\lambda/4}{v}$$  \hspace{1cm} (24.32)

or

$$\Gamma' \approx kv,$$  \hspace{1cm} (24.33)

where $\Gamma' = 1/\tau_p$ and $\lambda/4 \simeq 1/k$. Now, the energy $W$ dissipated during a cycle of escalation and spontaneous emission is essentially the average energy difference between the light-shifted ground states, $\Delta_{ls} \equiv \Delta_+ + \Delta_-$, that is $W \approx -\hbar \Delta_{ls}$. Therefore, the rate for energy dissipation is,

$$\frac{dW}{dt} = \Gamma' \hbar \Delta_{ls}.$$  \hspace{1cm} (24.34)

At the same time, every temporal energy change of a system can always be expressed as $\frac{dW}{dt} = F \cdot v$. Therefore, in this one-dimensional model, considering Eq. (24.31), we can write,

$$\frac{dW}{dt} = -\alpha_{lp} v^2 = -\Gamma' \hbar \Delta_{ls},$$  \hspace{1cm} (24.35)

such that with (24.33),

$$\alpha_{lp} = -\frac{\Gamma' \hbar \Delta_{ls}}{v^2} \approx -k v \frac{\hbar \Delta_{ls}}{v^2} \approx -\frac{\hbar k^2 \Delta_{ls}}{\Gamma' \lambda}.$$  \hspace{1cm} (24.36)

Note that since $\Delta < 0$, $\alpha_{lp}$ is a positive quantity. Also note, that for large detunings, ($\Delta \gg \Gamma$) Eq. (16.23) gives,

$$\frac{U}{\hbar} = \frac{\Delta_{ls}}{4} = \frac{\Omega^2}{4\Delta}.$$  \hspace{1cm} (24.37)

It is also true that for light-shifts, which are large compared to the natural width of ground state ($\Delta_{ls} \gg \Gamma'$), and for large red detunings ($\Delta \gtrsim 4\Gamma$),

$$\frac{\Gamma}{\Gamma'} \approx \frac{\Delta^2}{4\Omega^2}. $$  \hspace{1cm} (24.38)

Therefore, the sub-Doppler friction coefficient can also be written,

$$\alpha_{lp} = -\frac{\hbar k^2 \Delta}{4\Gamma}.$$  \hspace{1cm} (24.39)

Eq. (24.39) makes two remarkable predictions: Firstly, in the ‘lin-perp-lin’ configuration the sub-Doppler friction coefficient can be a large number in comparison to $\alpha_d$. Note that from Eq. (24.28), with $I \lesssim I_{sat}$ and $\Delta \gg \Gamma$,

$$\alpha_d \simeq \hbar k^2 \left( \frac{\Gamma}{\Delta} \right)^3,$$  \hspace{1cm} (24.40)
and

\[ \frac{\alpha_{lpl}}{\alpha_d} \simeq \left( \frac{\Delta}{\Gamma} \right)^4. \]

(24.41)

Secondly, \( \alpha_{lpl} \) is independent of the intensity of the applied field. This last result is different from the friction coefficient, which is proportional to the field intensity up to until saturation (see Eq. (24.28)). However, although \( \alpha_{lpl} \) seems impressive, the range of atomic velocities where it can operate is constrained by the condition,

\[ \Gamma' \simeq kv. \]

(24.42)

The ratio of the capture velocities for sub-Doppler versus Doppler cooling is therefore only,

\[ \frac{v_{lpl}}{v_d} \simeq \frac{4\Delta t_s}{\Delta}. \]

(24.43)

Fig. 24.6 graphically illustrates the comparison between the Doppler and the ‘lin-perp-lin’ sub-Doppler cooling mechanisms. The dramatic difference of the capture ranges is evident. Note also that the slopes of the curves give the friction coefficients and that, within the capture range, the slope is much steeper for the sub-Doppler mechanism.

\[ \text{Figure 24.6: Comparison of slopes, amplitudes, and capture ranges for Doppler and Sisyphus cooling.} \]

\[ 24.2.2.2 \quad \sigma^+ - \sigma^- \text{ molasses} \]

The second mechanism operates with two counterpropagating light beams, which are circularly polarized in opposite directions. When the two counterpropagating beams have the same amplitude, the resulting polarization is always linear and orthogonal to the propagation axis, but the tip of the polarization vector traces a helix with a periodicity of \( \lambda \) [see Fig. 24.7(b)]. The physics of this sub-Doppler mechanism does not involve hill-climbing nor spontaneous emission, but an imbalance of the photon scattering rates by the two counterpropagating light waves as the atom moves along the \( z \)-axis. This imbalance leads to a velocity-dependent force counteracting the
atom displacement. The essential factor leading to the different scattering rates is the creation of a population orientation along the z-axis between the sub-levels of the atomic ground state. The more populated sub-levels scatter more photons. Now, considering the energy level diagram (see Fig. 24.5) and the symmetry of the Clebsch-Gordan coefficients, it is evident that transitions $J_g = \frac{1}{2} \leftrightarrow J_e = \frac{3}{2}$ coupled by linearly polarized light can not produce an orientation of the population in the ground state. In fact, the simplest system exhibiting this effect is $J_g = 1 \leftrightarrow J_e = 2$. A measure for this orientation is the magnitude of the matrix element $\langle J_z \rangle$ between the sublevels $J_{gs} = \pm 1$. For an atom at rest at the position $z = 0$ interacting with the light polarized along the y-direction, the light-shifts $\Delta_0$ and $\Delta_\pm$ of the three sub-levels of the ground state would be,

$$\Delta_{+1} = \Delta_{-1} = \frac{3}{2} \Delta_0 ,$$  \hspace{1cm} (24.44)$$

and the stationary populations would be $4/17$, $4/17$ e $9/17$, respectively. Obviously, linearly polarized light does not produce a stationary orientation, $\langle J_z \rangle_s = 0$. But when the atom begins to move along the z-axis with velocity $v$, it sees a linear polarization precessing about the axis of propagation at an angle $\varphi = k z = -kv t$. This precession gives rise to a new term in the Hamiltonian, $V = kv J_z$. Furthermore, when we transform to a rotating coordinate system, the eigenfunctions of the Hamiltonian of the atom moving in this new 'inertial' system become linear combinations of the basis functions of the resting atom. The expectation value of the stationary orientation operator $J_z$, is now zero in the inertial system [137],

$$\langle J_z \rangle = \frac{40 \hbar k v}{17 \Delta_0} = \hbar (\Pi_+ - \Pi_-) .$$  \hspace{1cm} (24.45)$$

Figure 24.7: Polarization as a function of position (in units of a wavelength) for the $\sigma^+ - \sigma^-$ standing wave configuration.

Note that, as the expectation value of the orientation is nonzero only when the atom moves. In Eq. (24.45) we denote the populations of the sub-levels $|\pm>\,$ as $\Pi_{\pm}$, and we interpret nonzero matrix elements as a direct measure of the population difference between the ground state levels $|\pm>\,$. Note that, since $\Delta_0$ is negative (red
tuning), the Eq. (24.45) tells us, that the population $\Pi_{-}$ is larger than $\Pi_{+}$. Now, when an atom traveling in $+z$ direction is exposed to two light waves with polarizations $\sigma_{\mp}$ propagating in the $\mp z$ directions, the preponderance of population in the state $|\mp\rangle$ will result in a higher scattering rate from the wave propagating in $-z$ direction. Therefore, the atom will be subject to a total force opposite to its movement and proportional to its velocity. The differential scattering rate is,

$$
\frac{40}{17} \frac{k v}{\Delta_0} \Gamma^\prime.
$$

(24.46)

With a quantized momentum of $\hbar k$ transferred at each scattering event, the total force is,

$$
F = \frac{40}{17} \frac{\hbar k^2 v \Gamma^\prime}{\Delta_0}.
$$

(24.47)

The friction coefficient $\alpha_{cp}$ is,

$$
\alpha_{cp} = -\frac{40}{17} \frac{\hbar k^2 \Gamma^\prime}{\Delta_0},
$$

(24.48)

which is a positive quantity, since $\Delta_0$ is negative for red detuning. Comparing $\alpha_{cp}$ with $\alpha_{lpl}$ we see, that $\alpha_{cp}$ must be much smaller, because we always assumed that the light shifts $\Delta$ are much larger than the linewidths $\Gamma^\prime$. However, the heating rate due to fluctuations of the recoil is also much lower. Thus, the minimum temperatures that can be reached with the two sub-Doppler mechanisms are comparable.

Although the Doppler cooling mechanism also depends on an imbalance of scattering from counterpropagating light waves, in this case the imbalance comes from the fact that the Doppler shift experienced by the moving atoms leads to different probabilities for photon scattering. For the sub-Doppler mechanism the scattering probabilities from the two light waves are the same, but the ground state populations are not. The state with the largest population suffers the highest scattering rate.

### 24.2.3 Raman cooling

#### 24.2.3.1 Optical cooling of confined particles

It is also possible to cool ions confined in a trap [633]. The direction of their motion and their velocity change periodically with the secular frequencies $\zeta_r$ und $\zeta_z$. For optical cooling it is sufficient to irradiate a single red-detuned running-wave light field: In a real ion trap the cylindrical symmetry cannot be realized with absolute precision so that we get different secular frequencies $\zeta_x \neq \zeta_y \neq \zeta_z$ and a coupling of the degrees of freedom for all directions of space. The cooling of the ionic motion in a single direction results in a cooling of the motion in the other directions.

In the rest system of an ion oscillating in a harmonic trap the Doppler-shift of the laser frequency changes periodically: $v(t) = v_0 \cos \zeta_r z t$. The ion absorbs therefore in its rest system the light on a withb of sidebands whose distance and strength depend on the oscillation frequency and amplitude. The absorption profile of a transition in such a harmonically vibrating ion follows as a convolution of the Lorentz profile $\mathcal{L}_\Gamma$, describing the naturally broadened resonance, with a function $\mathcal{S}$, describing the
splitting of the absorption profile into sidebands [309]:

\[ A(\Delta) = (L_\Gamma \star S)(\Delta) \quad , \quad S(\Delta) = \sum_n J_n(\mathbf{k} \cdot \mathbf{v}_0 / \zeta_{r,z})^2 \delta(\Delta - n\zeta_{r,z}) . \] (24.49)

\( J_n \) denotes the Bessel function of \( n^{\text{th}} \) order. In essence, the system is governed by three time-constants: The natural decay width of the cooling transition \( \Gamma \) is a measure for the innerratomic time scale, since it determines the average duration of absorption-emissions cycles. The secular frequencies \( \zeta_{r,z} \) determine the time scales for changes in the external degrees of freedom, i.e. for changes of the ion’s location and velocity. The Doppler-shift \( k\mathbf{v}_0 \) of the resonance frequency in the return point of the ion motion finally, is a measure for the kinetic energy of the ion.

The relative importance of these three characteristic frequencies reveal the state of the ion in the trap. The modulation index \( k\mathbf{v}_0 / \zeta_{r,z} \) decides on the height and the number of sidebands in the excitation spectrum. The better the ion has been cooled, the smaller the modulation index and the smaller the height and number of sidebands. The kinetic energy of the ion is,

\[ E_{\text{kin}} = \frac{1}{2} m v_0^2 = \frac{1}{2} m \zeta_{r,z} x_0^2 . \] (24.50)

The modulation index \( k\mathbf{v}_0 / \zeta_{r,z} = kx_0 = 2\pi x_0 / \lambda \) is also called Lamb-Dicke parameter. By cooling the der Lamb-Dicke parameter is so much reduced and the ion is so well localized that its motional sidebands are smaller than the wavelength of the exciting light. It then is in the so-called Lamb-Dicke regime \( x_0 \ll \lambda \) and has so small motional sidebands that they do not contribute to the line shape and do not influence the line width. Therefore the linear Doppler effect vanishes.

The quantity \( \zeta_{r,z} / \Gamma \) defines the resolution of the sidebands. If the resolution is poor, we talk about weak confinement, else about strong confinement. Therefore the same ion can be weakly confined with respect to an allowed transition and strongly confined with respect to a forbidden transition. The cooling processes in the two cases of strong and weak trapping must be described differently. At weak confinement the oscillation frequency \( \zeta_{r,z} \) is so slow that many absorption-emission cycles with the time constant \( \Gamma^{-1} \) can occur during one oscillation period. Cooling process and cooling limit are approximately the same as for free particles and are described by Doppler cooling.

### 24.2.3.2 Raman sideband cooling

In the case of strong confinement for the description of the cooling process we must consider the quantization of the motional energy in the harmonic potential. The two levels coupled by the narrow transition split into vibrational sublevels \( |n_{r,z}\rangle \), which are populated in thermal equilibrium according to the Bose-Einstein distribution and have the kinetic energies \( E_{\text{kin}} \),

\[ n_{r,z} = \frac{1}{e^{\hbar \zeta_{r,z} / k_BT} - 1} \quad \text{and} \quad E_{\text{kin}} = \hbar \zeta_{r,z} (n_{r,z} + \frac{1}{2}) . \] (24.51)

To perform the so-called optical cooling sideband cooling [633] the laser is tuned to the first lower sideband. The laser light is then scattered in a Raman-Anti-Stokes
process at the excited electronic state with a vibrational quantum number lower by 1 \( |e, n_{r,z} - 1\rangle \). The subsequent spontaneous decay occurs most probably to the same vibrational substate of the ground state \( |g, n_{r,z} - 1\rangle \). The net effect of such a scattering process therefore is a transition to the next lower vibrational quantum number. The zero point energy of the ion in the trapping potential cannot be underscored by cooling, \( E_{\text{kin}} > \frac{1}{2} \hbar \omega_{r,z} \) (for the Yb\(^{+}\) ion it is \( E_{\text{kin}} > 2 \text{ neV} \)). However, the uncertainty of the kinetic energy, and the temperature \( T \) given by (24.51) have no lower limit [163].

At every absorption process, free particles carry away the momentum of the photons \( \hbar \kappa \). The recoil of a free Yb\(^{+}\) ion corresponds to the frequency shift \( \varepsilon / 2 \pi = 5.3 \text{ kHz} \). On a narrow transition, it yields a resonance at the frequency \( \varepsilon \). For trapped ions, this is not the case, because the momentum is absorbed by the whole trap (see analogy to the Mößbauer effect).

24.2.3.3 Stimulated Raman sideband cooling

We may use two lasers detuned far from resonance to couple two vibrational states. However, additional dissipation by optical pumping is still required.

Numerous schemes have been tested to cool neutral atoms in optical lattices. For the schemes to work, the ion should be already in the Lamb-Dicke regime. Otherwise, transitions with transfer of higher vibrational quantum numbers \( n_{r,z} \) are possible during spontaneous emission. The Lamb-Dicke limit is set by \( k_{\tau} < 1 \), or,

\[
\langle n \rangle = \frac{m \omega_{\text{trap}}}{2 \hbar k^2}.
\]

This means that higher trap frequencies ease the required temperature at which sideband cooling can start to work.

24.2.4 Adiabatic cooling of an optical lattice

Adiabatic cooling by [334] in 1D. Defining the lattice constant \( Q_0 \), the Boltzmann factor \( f_B \equiv e^{-\hbar \omega / k_B T} \), the initial thermal population \( \pi_n = (1 - f_B) f_B^n \), the recoil energy \( E_{\text{rec}} = \hbar^2 k^2 / 2m \),

\[
\frac{k_B T}{2} = \sum_n \frac{\pi_n}{h Q_0} \int_{(n+1)^{\text{th}} \text{Bloch band}} \frac{p^2}{2m} dp = 2 \sum_n \frac{\pi_n}{h Q_0} \int_{n \hbar Q_0 / 2}^{(n+1) \hbar Q_0 / 2} \frac{p^2}{2m} dp
\]

\[
= 2 E_{\text{rec}} \left( \frac{Q_0}{k} \right)^2 \sum_{n=0}^{\infty} \frac{3n^2 + 3n + 1}{24} = E_{\text{rec}} \left( \frac{Q_0}{k} \right)^2 \frac{1 + 4f_B + f_B^2}{12(1 - f_B)^2}.
\]

Furthermore,

\[
f_B = \frac{\bar{n}}{1 + \bar{n}} \quad \iff \quad \bar{n} = \frac{f_B}{1 - f_B}.
\]

24.2.5 Exercises

24.2.5.1 Ex: Optical molasses

Optical molasses are created (in one dimension) by two beams counterpropagating lasers tuned to red of an atomic transition. Each of the laser beams exerts on the
atoms the radiative pressure force \( F_\pm = \hbar k \frac{\Gamma}{2(\Delta \pm k\nu)/\Gamma} s \). \( \Delta \) is the detuning of the laser, \( \nu \) is the velocity of an atom.

a. Show that for small velocities (\( |k\nu| \ll \Gamma \) and \( \Delta \leq \Gamma \)) the optical molasses can be understood as a friction force and calculate the friction coefficient.

b. Heating processes caused by spontaneous emission limit the minimum temperature that can be reached in optical molasses. Calculate the laser tuning, where the temperature reaches its minimum value and specify the cooling limit.

**Help:** Suppose a one-dimensional molasses and assume, that the spontaneous emission only happens along this dimension. The heating rate follows from the scattering rate \( R \) through \( (\frac{dE}{dt})_{\text{heat}} = \frac{dt}{dt} \left( \frac{\langle p^2 \rangle}{2m} \right) = \hbar k^2 \frac{\Gamma^2}{2m} 2R \), the cooling rate follows from \( (\frac{dE}{dt})_{\text{cool}} = Fv \).

### 24.2.5.2 Ex: Atomic fountain

In atomic fountains atoms are accelerated upward by a 'moving optical molasses'. After the molasses has been switched off, they perform a ballistic flight in the Earth gravitational field. The moving molasses is generated by two pairs of counterpropagating laser beams intersecting at right angle and oriented both at an angle of 45° with respect to gravity. The upgoing beams are tuned to the blue, and the counterpropagating downgoing beams have the same detuning to the red side of the atomic resonance (\( \lambda = 780 \text{ nm} \)). Supposing that the resonator is close to the position of the molasses and has with negligible length, what should be the detuning in order to achieve 1 s time period between the two passages of the atoms through the microwave resonator?

### 24.3 Optical and magneto-optical traps

#### 24.3.1 The magneto-optical trap

An apparently fatal obstacle to the confinement of particles by optical forces is Earnshaw’s optical theorem. This theorem states that, if a force is proportional to the light intensity, its divergence must be zero because the divergence of the Poynting vector expressing the directional flux of intensity is zero inside a volume without sources nor sinks of radiation. The absence of divergence precludes the possibility of a restoring force to the interior at all places of a closed surface [19]. However, Earnshaw’s optical theorem can be bypassed by a clever trick. The internal degrees of freedom of the atom (i.e., its electronic energy levels) can change the proportionality between the force and the Poynting vector in a position-dependent manner, such that the optical Earnshaw’s theorem does not apply. Spatial confinement is then possible using the radiative pressure force generated by counterpropagating light beams. The most common trap configuration is based on a radial magnetic field gradient produced by a quadrupolar field and three pairs of counterpropagating circularly polarized laser beams tuned to the red of an atomic transition and intersecting at right angles at the point where the field is zero. This **magneto-optical trap (MOT)** uses the position-dependent Zeeman shift of the electronic levels as the atom moves in the radially increasing magnetic field. The use of circularly polarized light which is red-detuned by about \( \Gamma \) results in a spatially varying transition probability, whose effect is to
produce a restoring force that pulls the atom back to the origin. To understand better how the trapping scheme works, we consider a two-level atom with a transition \( J = 0 \rightarrow J = 1 \) moving along the z-direction. We apply a magnetic field \( B(z) \) growing linearly with the distance from the origin. The Zeeman shifts of the electronic levels depend on the position,

\[
\Delta_B = \frac{\mu_B g_F m_F}{\hbar} \frac{dB}{dz} z \equiv \partial \omega_{\text{zeem}} z ,
\]

see Fig. 24.8. We also apply counterpropagating laser beams along the directions \( \pm z \) with circular polarizations of opposite signs and tuned to the red of the atomic transition. It is clear from Fig. 24.8 that an atom moving in \( \pm z \) direction will scatter \( \sigma^\pm \) type photons at a faster rate than \( \sigma^\mp \) type photons, because the Zeeman effect will pull the \( \Delta m_J = \mp 1 \) transition closer to the laser frequency. The expression for the radiation pressure force extends Eq. (24.26) to include the Doppler effect \( kv_z \) and the Zeeman effect,

\[
F_{\pm z} = -\frac{\hbar k}{2} \Gamma \frac{2\Omega^2}{4(\Delta \pm kv_z \pm \partial \omega_{\text{zeem}} z)^2 + 2\Omega^2 + \Gamma^2} .
\]

(24.56)

The atom will, therefore, feel a restoring force which pushes it back to the origin. If the laser beams are red-detuned by an amount \( \Delta = -\Gamma \), the Doppler shift of the atomic motion introduces velocity-depending term to the restoring force, such that for small displacements and velocities the total restoring force can be expressed by the sum of a term which is linear in the velocity and a term which is linear in the displacement,

\[
F_{\text{MOT}} = F_{1z} + F_{2z} = -\alpha \dot{z} - \kappa z .
\]

(24.57)

From Eq. (24.57) we can derive the equation of motion of a damped harmonic oscillator with mass \( m \),

\[
\ddot{z} + \frac{2\alpha}{m} \dot{z} + \frac{\kappa}{m} z = 0 .
\]

(24.58)
The damping constant $\alpha$ and the spring constant $\kappa$ can be written compactly in terms of atomic parameters and the field as,

$$\kappa = \frac{16\hbar k \Omega^2 \Delta \partial_{z} \omega_{zeem}}{4\Delta^2 + 2 \cdot 6\Omega^2 + \Gamma^2}.$$  

(24.59)

and

$$\alpha = \kappa \frac{k}{\partial_{z} \omega_{zeem}}.$$  

(24.60)

Typical conditions for MOT are $\Omega = \Gamma/2$, $\Delta = -\Gamma$. For typical MOTs,

$$\alpha \simeq 2 \cdot 10^{-22} \text{ Ns/m} \quad \text{and} \quad \kappa \simeq 3.7 \cdot 10^{-19} \text{ N/m}.$$  

(24.61)

We can also estimate the curvature of the MOT,

$$\omega = \sqrt{\frac{\kappa}{m}} \simeq (2\pi) \cdot 200 \text{ Hz}.$$  

(24.62)

Solve Exc. 24.3.3.1 and 24.3.3.2.

MOTs are realized with current-carrying coils in anti-Helmholtz configuration which generates a quadrupolar geometry potential. Near the center, the magnetic field and its absolute value are well approximated by,

$$\mathbf{B} = q \begin{pmatrix} x \\ y \\ -2z \end{pmatrix} \quad \text{and} \quad |\mathbf{B}| = qB\sqrt{r^2 + 4z^2},$$  

(24.63)

with $r^2 = x^2 + y^2$ and the gradient $q \equiv \partial_r B$ is a constant, which depends only on the geometry of the coils and the current in them. Thus, the extension of the above results to three dimensions is simple if we consider the fact that the gradient of the quadrupolar field in the $z$-direction is twice the gradient in the radial directions $x$ and $y$, such that $\kappa_z = 2\kappa_x = 2\kappa_y$. The damping term, which proportional to the velocity, implies that the kinetic energy $E$ is dissipated from the atom (or a cloud of atoms) as,

$$E/E_0 = e^{-2\alpha t/m},$$  

(24.64)

where $m$ is the atomic mass and $E_0$ the kinetic energy at the beginning of the cooling process. Therefore, the dissipative force term cools the atomic cloud and, at the same time, combines with the position-dependent term to confine it. The time constant for the damping,

$$\tau = \frac{m}{2\alpha}$$  

(24.65)

is typically dozens of microseconds. It is important to keep in mind that a MOT is anisotropic, since the restoring force is proportional to the anisotropic field gradients. Because of its dissipative non-conservative nature, it is is more accurate to characterize a MOT by the maximum capture rate, rather than by a 'potential depth'.

In early experiments MOTs were loaded from a decelerated atomic beam. Later it was shown, that the low-velocity tail of the Maxwell-Boltzmann distribution provides a sufficient amount of atoms that can be captured by a MOT, so that it can be loaded directly from an atomic vapor at room temperature. Now many groups in the world use these assemblies for applications ranging from precision spectroscopy to the optical control of reactive collisions; the MOT has become the working horse of atom optics.
24.3.1.1 Density in a MOT

A typical MOT captures up to a billion atoms in a volume of a few \(1 \text{ mm}^3\) resulting in densities of \(\sim 10^{10} \text{ cm}^{-3}\). Although a MOT works as a versatile and robust 'reaction cell' for many applications, the frequencies of the light beams must be tuned close to atomic transitions, which bears the disadvantage that a considerable fraction of atoms remains in excited states. This fact is at the origin of two processes limiting the density of a MOT: (1) losses of trapped atoms by collisions and (2) repulsive forces between the atoms caused by reabsorption of photons scattered within the cloud. Collisonal losses arise from two sources: (i) hot atoms of the residual gas inside the chamber can elastically collide with cold atoms and kick them out of the MOT, and (ii) cold atoms in excited states can undergo inelastic binary collisions. ‘Photon-induced repulsion’ or *radiation trapping* arises when a trapped atom spontaneously emits a photon, which is then reabsorbed by other atoms. If the optical density of the cloud is high, it can take a long time for the photon to find its way out \(^2\). Since any photon exchange between two atoms will increase their relative momentum by \(2\hbar k\), this leads to a repulsive force, which is proportional to the absorption cross section for the incident light beam. When this repulsive force balances the confining force exerted by the MOT, any increase in the number of trapped atoms augments its size, but its density.

24.3.1.2 Dark SPOT

In order to overcome the ‘radiation trapping’ effect, the atoms can be optically pumped into a ‘dark’ hyperfine level of the ground state that does not interact with the MOT light. In a conventional MOT one usually employs an auxiliary light beam called ‘repumper’, copropagating with the MOT beams, but tuned to another transition between hyperfine levels of the ground and excited states. The repumper recycles the population leaking out of the (not perfectly) cyclic MOT transition. As an example, Fig. 24.10 shows the MOT and repumper transitions for sodium.

In contrast to this conventional MOT, the scheme known as the *dark spontaneous force optical trap* (dark SPOT), passes the repumping beam through a glass plate the center of which is obstructed by a small circular disk. The shadow of this disk is projected into the center of the trap in such a way that the atoms in the center are not repumped back into the cyclic transition, but spend most of their time (\(\sim 99\%\)) in ‘dark’ hyperfine levels. While the cooling and confinement force continue to operate

\(^2\)E.g. a photon at the center of the sun will take thousands of years to get out.
on the periphery of MOT, its center does not feel any radiation pressure. Dark SPOTs are able to increase the density of a trapped cloud by almost two orders of magnitude.

![Hyperfine structure in sodium atoms showing the usual cooling, pumping, and repumping transitions.](image)

**Figure 24.10:** Hyperfine structure in sodium atoms showing the usual cooling, pumping, and repumping transitions.

### 24.3.2 Optical dipole traps

When temporal variations are to be applied to a confinement potential, magnetic fields are not the best choice, because they are slow and of limited spatial resolution. On the other side, laser beams can be varied quickly and in localized well. The dipole force exerted by a far-detuned laser beam can be derived from the gradient of the Rabi frequency \( \mathbf{F} = -\nabla (\mathbf{d} \cdot \mathbf{E}) \). Hence, it can be derived from an optical potential, which can be used for trapping. The force may be attractive (toward the intensity maximum) or repulsive.

Compared to MOTs, optical traps (*far off-resonance optical trap*, FORT) are tuned far away from resonances, where the population in excited states is insignificant and spontaneous forces are absent. Note from Eq. (16.21), that spontaneous forces fall off with the square of the detuning while the potential derived from the dipolar force only decreases linearly with the detuning. The off-resonant optical density is negligible, so that radiation trapping is not an issue. The most simple FORT consists of a single focussed, linearly polarized gaussian laser beam tuned far to the red of an atomic resonance. For large detunings and strong field gradients the Eqs. (16.23) and Eqs. (16.24) become [237]³,

\[
U(\mathbf{r}) \simeq \frac{\hbar \Omega(\mathbf{r})^2}{4\Delta} = \frac{3\pi c^2}{2\omega_0^3} \frac{\Gamma}{\Delta} I(\mathbf{r}) \quad \text{and} \quad \hbar \gamma_{scf}(\mathbf{r}) \simeq \frac{\sigma_a(\Delta)}{\omega} \frac{I(\mathbf{r})}{\omega} = \frac{3\pi c^2}{2\omega_0^3} \left( \frac{\Gamma}{\Delta} \right)^2 I(\mathbf{r}),
\]

using the Rabi frequency \( \hbar \Omega = \mathbf{d} \mathbf{E} \), the dipole moment \( \mathbf{d} = \sqrt{3\pi \varepsilon_0 \hbar \Gamma/k^3} \), and the intensity \( I = \frac{\varepsilon_0 c |\mathbf{E}|^2}{2} \). This shows that the potential becomes directly proportional to the light intensity and inversely proportional to the detuning. Therefore, at large detuning but very high intensity, the depth of the FORT can be maintained, although

³Jürgen Bosse claims that the dipole trap formula given in [237] is wrong!
the atoms do not absorb photons. Important advantages of FORTs as compared to MOTs are: (1) high densities ($\sim 10^{12}$ cm$^{-3}$) and (2) a well-defined polarization axis along which the atoms can be aligned or oriented (polarization of the spins).

Since lasers beams can easily be manipulated in position, intensity, and frequency, they can realize a large wide variety of possible geometries. For example, with a focused laser beam, one may influence the local density of a condensate and stir it around by moving the position of the laser beam. Strongly focussed laser beams are often used for transporting or manipulating microscopic objects in arrangements called optical tweezers. And with standing light waves, it is possible to form periodic optical lattices in one, two or three dimensions (see Sec. 27.4.2).

24.3.2.1 Spin relaxation

When the atomic ground state has a hyperfine structure, another relaxation mechanism can be observed: Near-resonance Raman scattering can induce transitions between hyperfine states causing a population redistribution of between Zeeman sub-states called spin relaxation. In magnetic traps, this can lead to losses, because not all Zeeman substates are trapped.

The rate of an arbitrary scattering process starting from an initial state $|F, m\rangle$ through several possible excited states $|F'_j, m'_j\rangle$ to a final state $|F''m''\rangle$ is, according to the formula of Kramers-Heisenberg [419],

$$
\gamma_{Fm\rightarrow F'm'} \propto \left| \sum_j \frac{\alpha_{Fm\rightarrow F'm'}^{(F'_j m'_j)}}{\Delta F'_j m'_j} \right|^2.
$$

(24.67)

Far from resonance the scattering decreases as $\Delta^2$ for Rayleigh scattering, $Fm = F'm'$. Raman scattering, $Fm \neq F'm'$, is further suppressed by destructive interference of the different scattering paths.

In the case of rubidium, we calculate,

$$
\gamma_{spin} = \frac{3c^2 \omega^4}{8\pi} \frac{70}{81} \Gamma^2 \left( \frac{1}{\omega D_1} \right)^3 \frac{1}{\Delta D_1} - \left( \frac{1}{\omega D_2} \right)^3 \frac{1}{\Delta D_2} \right|^2 \frac{I_0}{\hbar \omega}.
$$

(24.68)

24.3.2.2 Potential of a Gaussian beam

The far-off resonance optical trap (FORT) is an example of an optical trap based on dipole forces [237]. The intensity distribution of a gaussian beam with a diameter of $w_0$ at its waist is $^4$,

$$
I(r) = \frac{2P}{\pi w_0^2} e^{(-2x^2 -2y^2)/w_0^2} e^{-z^2/z_R^2},
$$

(24.69)

where $P_{cav}$ is the total power of the beam and $z_R \equiv \pi w_0^2/\lambda_{dip}$ the Rayleigh length at a given wavelength $\lambda_{dip}$. The dipolar potential is given by (24.66). Using the potential depth,

$$
U_0 \equiv \frac{3\pi c^2 \Gamma}{2\omega_0^3} \frac{2P}{\Delta \pi w_0^2} < 0,
$$

(24.70)

$^4$See script on Electrodynamics (2020).
we can approach the potential near its center, that is, near the optical axis, \( r \ll \frac{1}{2}w_0 \), and within the range of the Rayleigh length, \( z \ll \pi w_0^2/\lambda \), by a harmonic potential \(^5\),

\[
U(r) \simeq U_0 e^{-2x^2-2y^2/w_0^2} e^{-z^2/z_R^2} \simeq U_0 \left( 1 - \frac{2x^2 + 2y^2}{w_0^2} - \frac{z^2}{z_R^2} \right) \quad (24.71)
\]

\[
\equiv U_0 + \frac{m}{2} \omega_r^2 r^2 + \frac{m}{2} \omega_z^2 z^2 \equiv k_B T \left( \frac{U_0}{k_B T} + \frac{r^2}{2\bar{r}^2} + \frac{z^2}{2\bar{z}^2} \right) .
\]

This leads to the equivalences,

\[
\begin{align*}
\omega_r &= \frac{2}{w_0} \sqrt{\frac{U_0}{m}} \quad \text{and} \quad \omega_z &= \frac{\sqrt{2}}{z_R} \sqrt{\frac{U_0}{m}} \\
\bar{r} &= \frac{w_0}{2} \sqrt{\frac{k_B T}{U_0}} \quad \text{and} \quad \bar{z} &= \frac{z_R}{\sqrt{2}} \sqrt{\frac{k_B T}{U_0}}
\end{align*}
\]

(24.72)

Solve Excs. 24.3.3.3 and 24.3.3.4.

**Example 90 (Dipole trap for rubidium):** The formulas (24.66) hold for a two-level system. In case of the \( D_1 \)- and \( D_2 \)-lines of rubidium, we must consider all contributions weighted by the respective detunings,

\[
U_0 \equiv \sigma_0 \frac{\hbar \Gamma}{4} \left( \frac{1}{\Delta D_1} + \frac{g_{D2}/g_{D1}}{\Delta D_2} \right) I_0 \frac{\hbar}{\omega} \simeq \frac{3\hbar \pi c^2}{2\omega^2} \frac{\Gamma}{\Delta \hbar \omega} ,
\]

where \( g_{D2}/g_{D1} = 2 \).

Similarly, the spontaneous emission rate is,

\[
\gamma_{sct} \simeq \frac{\pi c^2 \Gamma^2}{2\omega^2} \left( \frac{1}{\Delta^2 D_1} + \frac{g_{D2}/g_{D1}}{\Delta^2 D_2} \right) I_0 \frac{\hbar}{\omega} .
\]

The spontaneous emission rate decays faster with detuning than the potential depth. Thus, heating can be avoided by working at large detunings and providing higher laser intensities. Defining the recoil temperature by,

\[
T_{rec} = \frac{\hbar^2 k^2}{k_B m} ,
\]

the heating rate is [237],

\[
\dot{T} = \frac{1}{3} T_{rec} \gamma_{sct} = \frac{\hbar^2 k^2}{3m k_B} \gamma_{sct} .
\]

\(^5\)The diameter of a Gaussian beam can be characterized in several ways,

\[
\bar{r}_{1/\sqrt{\pi} \text{-radius}} = \frac{\bar{r}_{1/e^2 \text{-radius}}}{\sqrt{2}} = \sqrt{2} \bar{r}_{1/e^2 \text{-radius}} = \frac{\bar{r}_{1/2 \text{-radius}}}{2 \ln 2} ,
\]

and \( \bar{r}_{\text{rms}} \equiv \bar{r}_{1/\sqrt{\pi} \text{-diam}} \) and \( \bar{r}_{\text{hwhm}} \equiv \bar{r}_{1/2 \text{-diam}} \) and \( \bar{r}_{\text{diam}} = 2\bar{r}_{\text{radius}} \).
24.3.2.3 Trapping in standing light waves

If both counterpropagating modes are pumped at different powers, \( P_\pm \), the intensity distribution is,

\[
I(\mathbf{r}) = \frac{2}{\pi w_0^2} e^{(-2x^2 - 2y^2)/w_0^2} e^{-z^2/z_R^2} \left| \sqrt{P_+} e^{ikz} + \sqrt{P_-} e^{-ikz} \right|^2.
\]  

(24.73)

The potential depth is,

\[
U_0 = \frac{3\pi c^2 \Gamma}{2\omega_0^3} \frac{2(\sqrt{P_+} + \sqrt{P_-})^2}{\Delta} < 0.
\]  

(24.74)

Therefore, within the Rayleigh length, the potential is,

\[
U(\mathbf{r}) \approx U_0 e^{(-2x^2 - 2y^2)/w_0^2} \frac{P_+ + P_- + 2\sqrt{P_+ P_-} \cos kz}{P_+ + P_- + 2\sqrt{P_+ P_-}}.
\]  

(24.75)

Letting the powers be equal,

\[
U(\mathbf{r}) \xrightarrow{P_+ = P_-} U_0 e^{(-2x^2 - 2y^2)/w_0^2} \frac{P_+ + P_- + 2\sqrt{P_+ P_-} \sin^2 \frac{Kz}{2}}{P_+ + P_- + 2\sqrt{P_+ P_-}}.
\]  

(24.76)

This leads to the identities,

\[
\begin{align*}
\omega_r &= \frac{2}{w_0} \sqrt{\frac{U_0}{m}} \quad \text{and} \quad \omega_z = \frac{k}{2} \sqrt{\frac{U_0}{2m}}
\end{align*}
\]  

(24.77)
24.3. **OPTICAL AND MAGNETO-OPTICAL TRAPS**

Solve the Excs. 24.3.3.5 and 24.3.3.6.

### 24.3.3 Exercises

#### 24.3.3.1 Ex: Linearization of the MOT

Derive the friction coefficient and the spring constant for a MOT.

#### 24.3.3.2 Ex: Design of a Zeeman slower

In this exercise we will design a 'decreasing field Zeeman slower' for strontium (see also Exc. 14.4.6.3).

a. Calculate the mean velocity of atoms in a strontium gas heated to 500°C. What is the Doppler shift for an atom moving at this velocity at the cooling transition at \( \lambda = 461 \text{ nm} \) (linewidth 30.5 MHz)?

b. Assuming you want to decelerate a fraction of 20% of the atoms flying in a particular direction, to what frequency should a counterpropagating laser (intensity \( I = 20 \text{ mW/cm}^2 \)) be tuned in order to slow down the atoms?

c. Suppose the strontium atoms were always in resonance with the counterpropagating laser light while being decelerated. What would be the evolution of their Doppler shift along their trajectory (supposed to be on a straight line antiparallel to the laser beam).

d. In order to maintain the laser always in resonance we need to compensate for the diminishing Doppler shift along the atomic trajectory. This can be done exploiting the Zeeman shift induced by a magnetic field. We will now design a magnetic field generating an appropriate Zeeman shift. For simplicity, let us assume 5 identical radial solenoids distributed over \( L = 30 \text{ cm} \) as sketched in Fig. 24.12, the only adjustable parameters being the currents in all solenoids, which need to be optimized such as to compensate the Doppler shift along the atom’s trajectory.

e. Simulate the 1D trajectory of an atom cooled by the Zeeman slower.

#### 24.3.3.3 Ex: Dipole trap near an intercombination line

a. Strontium has a strong transition \( (\Gamma_{461} = (2\pi) 30.5 \text{ kHz}) \) at 461 nm and a weak intercombination resonance \( (\Gamma_{689} = (2\pi) 7.6 \text{ kHz}) \) at 689 nm. A Gaussian laser beam with the power \( P = 10 \text{ mW} \) focused to a waist of \( w_0 = 100 \mu\text{m} \) is tuned \( \Delta_{689} = -(2\pi) 10 \text{ GHz} \) below the intercombination transition. Calculate the potential depth and the vibration frequencies for atoms trapped by this laser beam considering both resonances. What is the scattering rate on the two transitions.
b. Supposes that the trapped atomic cloud consists of $N = 10^8$ atoms at the temperature $T = 10 \mu$K. Calculate the atomic density $n_0$ in the center of the cloud.

24.3.3.4 Ex: Dipole trap with a focused beam

a. Calculate the vibration frequencies of $^{87}$Rb atoms confined in an optical trap consisting of a focused laser beam with the power $P = 10$ W and the beam diameter $w_0 = 100 \mu$m. The laser beam is tuned 5 nm to the red side of the rubidium D1 resonance located at $\lambda = 795$ nm.

b. Assume that the trapped atomic cloud consists of $N = 10^8$ atoms at the temperature $T = 100 \mu$K. Calculate the atomic density $n_0$ in the center of the cloud.

c. The cross section for elastic collisions is $\sigma = 10^{-12}$ cm$^2$. How many times do atoms meet on average?

24.3.3.5 Ex: Optical lattice

A laser beam with wavelength $\lambda_{\text{disp}} = 1064$ nm, power $P = 2$ W, and diameter $w_0 = 50 \mu$m is subdivided into three retroreflected beams intersecting at right angles. With this configuration we form a cubic optical lattice for strontium atoms, whose relevant transition lies at $\lambda_{\text{Sr}} = 461$ nm and has a decay width of $\Gamma_{\text{Sr}} = (2\pi) 32$ MHz. Calculate the potential depth and the secular frequencies.

24.3.3.6 Ex: Ring shaped optical potential

An interesting system is the 1D array of annular optical potentials realized in a standing wave formed by red-detuned Gaussian beam and a counterpropagating blue-detuned donut-mode. In general, the tight longitudinal confinement freezes out the axial motion by quantum confinement. It can be readily shown [638] that in the far-off resonance case and if the potential is approximate by a harmonic potential around its minimum the eigenenergy spectrum is given by,

$$E_{pq} = U_0 + \hbar \omega \left( q + \frac{1}{2} \right) + \frac{\hbar^2 p^2}{2mR_0^2}.$$  

It thus reproduces the ro-vibrational spectrum of a 2D artificial molecule and gives rise to two normal motions. In its ground state, we have the atom optical analog of a 2D rigid rotator. Gravity plays formally the same role as static electric fields for molecules. Such systems might be interesting for investigating the selection rules for transitions between ro-vibrational states involving conservation of total angular momentum of light and atoms and yield insight into the concept of orbital angular momentum of light fields.

24.3.3.7 Ex: Time-averaged trap

For sufficiently fast periodic displacements of a far-detuned laser beam it is possible to engineer effective more complicated trapping potential. What are the conditions for modulation speed? Simulate the effective trapping potential generated by a vibrating laser beam.
24.4 Magnetic traps

Purely magnetic traps are widely used in atom optics, where they served, e.g., for the first realizations of Bose-Einstein condensation (BEC). The most important feature that distinguishes magnetic traps is, that they do not need light to confine atoms. Hence, they are free of heating effects caused by photonic absorption, which turned out to be necessary condition for reaching BEC. Magnetic traps rely on the interaction of atomic spins with magnetic fields and gradients designed to contain the atoms. Depending on the sign of $U$ and $F$, atoms in states whose energy increases or decreases with the magnetic field are called 'low-field seekers' or 'high-field seekers', respectively. One might think, that it should be possible to trap atoms in any of these states, generating either a magnetic field minimum or a maximum. Unfortunately, only low-field seekers can be trapped in static magnetic fields, because in free space magnetic fields can not form maxima. Even though low-field seekers are not in the energetically lowest hyperfine levels, they can still be trapped because the rate of spontaneous emission through the magnetic dipole is $\sim 10^{-10} \text{s}^{-1}$, and hence completely negligible. However, spin changing collisions can induce losses and limit the maximum densities. Solve Exc. 24.4.6.1.

The most basic static magnetic trap for neutral atoms is generated by a pair of current-carrying coils in anti-Helmholtz configuration (similar to the geometry used for a MOT), producing an axially symmetric quadrupolar magnetic field. Since this field configuration always has a central point, where the magnetic field disappears, non-adiabatic Majorana transitions can occur when the atom passes through the zero point. The transitions transfers population from a low-field seeking state to a high-field seeker, which consecutively is expelled from the trap. This problem can be overcome by using a different magnetic field geometries. One example is the so-called magnetic bottle also called the Ioffe-Pritchard trap, where the minimum field amplitude has a finite value different from zero. Other methods to eliminate the zero-field point are time-varying potentials, such as the time-orbiting potential (TOP) trap, or the application of an 'optical plug', which consist in an intense dipolar optical laser beam, tuned to the blue of an atomic transition, focused into the center of a quadrupole trap where the magnetic field is zero, and repelling the atoms from this area.

24.4.1 Quadrupolar traps and Majorana spin-flips

The most basic static magnetic trap for neutral atoms is generated by a pair of current-carrying coils in anti-Helmholtz configuration producing an axially symmetric quadrupolar magnetic field, as shown in Fig. 24.13.

Close to the trap center an expansion of the magnetic field generated by anti-Helmholtz coils yields,

$$B = \begin{pmatrix} x \\ y \\ 2z \end{pmatrix} \partial_r B,$$

(24.78)

where the field gradient $\partial_r B$ along radial direction $r^2 = x^2 + y^2$ in the trap center depends on the applied current and the geometry of the coils. However, the 1:2 aspect ratio is generic for all quadrupolar potentials, as we will see in Exc. 24.4.6.2. We easily
verify that,
\[ \nabla \cdot \mathbf{B} = 0 \quad \text{but} \quad \nabla |\mathbf{B}| = \frac{\partial_x B}{\sqrt{r^2 + 4z^2}} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \]  
(24.79)

Thus, the quadrupolar magnetic potential is linear in the spatial coordinates,
\[ U(r) = -|\mu||\mathbf{B}| = \mu_B g_J m_J \partial_r B \sqrt{r^2 + 4z^2}, \]
(24.80)

where \(2\partial_r B = \partial_z B\).

To calculate the \(r_m\)-radius \(r_m\) of a cloud of temperature \(T\) confined to this potential, we set,
\[ k_B T \equiv U(r_m, 0) = \mu_B r_m \partial_r B, \]
(24.81)

and obtain the density distribution \(^6\)
\[ n(r) = n_0 e^{-U(r)/k_B T} = n_0 e^{-\sqrt{r^2 + 4z^2}/r}. \]
(24.82)

Normalization requires,
\begin{align*}
N &= \int_{R^3} n(r) \, d^3r = n_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\sqrt{r^2 + 4z^2}/r} 2\pi r \, dr \, dz \\
&= n_0 2\pi r^2 \int_{-\infty}^{\infty} \int_{-2|z|/r}^{2|z|/r} \xi e^{-\xi} d\xi \, dz = n_0 2\pi r^2 \int_{-\infty}^{\infty} e^{-\frac{2|z|}{r}} \left(1 + \frac{2|z|}{r} \right) \, dz \\
&= n_0 2\pi r^3 \int_{0}^{\infty} e^{-\xi} (1 + \xi) \, d\xi = n_0 4\pi r^3.
\end{align*}

Therefore, the effective volume is, \(V_{eff} = 4\pi r^3\). In application example is discussed in Exc. 24.4.6.3.

\(^6\)See script on Quantum mechanics (2020)24.2.4.
24.4. Magnetic Traps

24.4.1.1 Majorana spin-flips

The quadrupolar trap is the simplest one that can be technically realized. Unfortunately, this trap is not stable because of the phenomenon of Majorana spin-flips, which expel atoms from the trapped cloud. Since this field configuration always has a central point, where the magnetic field disappears, non-adiabatic Majorana transitions can occur when the atom passes through the zero point [see Fig. 24.13(c)]. The disappearance of the field leaves the atoms disoriented, that is, ready to reorient their spins. The transitions transfer population from a low-field seeking state to a high-field seeker, which consecutively is expelled from the trap. This problem is particularly severe for hydrogen, where it can induce a so-called relaxation explosion [281].

From (24.81) we get the rms-radius,

$$\bar{r} = \frac{k_B T}{\mu_B \partial_r B}.$$  (24.84)

The average velocity of an atom is,

$$\bar{v} = \sqrt{\frac{k_B T}{m}}.$$  (24.85)

In order for the atomic motion in the magnetic potential to be adiabatic [so that Eq. (24.80) applies], the local Larmor frequency,

$$\omega_{\text{Larmor}}(r) = \frac{\mu_B}{\hbar} \sqrt{r^2 + 4z^2} \partial_r B$$  (24.86)

must be faster, than any change the atom might experience due to its motion with velocity \(v\). I.e. we need [470],

$$\omega_{\text{Larmor}}(r) > \frac{v \cdot \nabla |B|}{|B|}.$$  (24.87)

This can not be satisfied within a volume located at the trap center. This ellipsoidal volume is delimited by \(r_{sf}\) given by the condition,

$$\omega_{\text{Larmor}}(r_{sf}) \equiv \frac{v \cdot \nabla |B|}{|B|}.$$  (24.88)

For our quadrupole trap,

$$\frac{v \cdot \nabla |B|}{|B|} = v \cdot \frac{\partial_r B}{\partial_r B} \sqrt{\frac{\partial_x B}{r_{sf}^2 + 4z_{sf}^2}} = x_{sf} v_x + y_{sf} v_y + 4z_{sf} v_z.$$  (24.89)

Considering for simplicity only radial motion, \(v = v\hat{e}_r\), then by equating (24.86) and (24.88),

$$\frac{\mu_B}{\hbar} r_{sf} \partial_r B = \omega_{\text{Larmor}}(r_{sf}) = \frac{v}{r_{sf}},$$  (24.90)

that is, the spin-flip volume is on the order of,

$$r_{sf} = \sqrt{\frac{\hbar v}{\mu_B \partial_r B}}.$$  (24.91)
Let us now estimate the spin relaxation rate from the flow of atoms through the volume,

\[ \frac{1}{\tau_{sf}} = N \frac{r_{sf}^3}{V_{eff}} \frac{\bar{v}}{r_{sf}}, \]

(24.92)

where \( r_{sf}^3/V_{eff} \) is simply the fraction of the cloud’s volume overlapping with the spin-flip volume. Then,

\[ \frac{1}{\tau_{sf}} = \frac{N}{4\pi r_{sf}^3} \frac{\bar{v}}{r_{sf}} = \frac{N}{4\pi} \left( \frac{k_B T}{\mu_B \partial_r B} \right)^3 \frac{\hbar \bar{v}}{\mu_B \partial_r B} = \frac{N\hbar}{4\pi (k_B T)^3} (\mu_B \partial_r B)^2 \frac{k_B T}{m} = \frac{N\hbar (\mu_B \partial_r B)^2}{4\pi m (k_B T)^2}. \]

(24.93)

That is, the problem gets worse when the cloud is cooled to low temperatures.

### 24.4.2 Magnetic Ioffe-type traps

The spin-flip problem can be overcome by using a different magnetic field geometries. One example is the so-called magnetic bottle, also called the Ioffe-Pritchard trap illustrated in Fig. 24.14(a), where the minimum field amplitude has a finite value different from zero. Other methods to eliminate the zero-field point are time-varying potentials, such as the time-orbiting potential (TOP) trap illustrated in Fig. 24.14(b) and discussed in Exc. 24.4.6.4 [189, 256], or the application of an ‘optical plug’, which consist in an intense dipolar optical laser beam, tuned to the blue of an atomic transition, focused into the center of a quadrupole trap where the magnetic field is zero, and repelling the atoms from this area (see Fig. 24.22). The advantage of Ioffe-Pritchard-type traps is that they are always harmonic sufficiently close to the trap center, which simplifies the theoretical treatment in many respects, as shown in Exc. 24.4.6.5.

![Figure 24.14](image-url)

**Figure 24.14:** (a) Magnetic trap in Ioffe-Pritchard configuration. (b) Time-Orbiting Potential (TOP) trap. (c) Death-circle in a TOP trap.

Close to the trap center Ioffe-Pritchard-type traps are described by,

\[ U(r) = \mu_B g_F m_F \sqrt{B_0^2 + (r \partial_r B)^2 + (z \partial_z B)^2}, \]

(24.94)

and this magnetic trapping potential can be harmonically approximated by,

\[ U(r) \simeq \mu_B g_F m_F \left( B_0 + \frac{(r \partial_r B)^2}{2B_0} + \frac{(z \partial_z B)^2}{2B_0} \right) \]

\[ \equiv \text{const} + \frac{m}{2} \omega_r^2 r^2 + \frac{m}{2} \omega_z^2 z^2 \equiv k_B T \left( \text{const} + \frac{r^2}{2r^2} + \frac{z^2}{2z^2} \right), \]

(24.95)
where the rms-radius $\bar{r} = \omega_r^{-1} \sqrt{k_B T / m}$ follow from the normalization of the density $n(r) = n_0 e^{-U(r)/k_B T}$ to the number of atoms,

$$N = \int n(r) d^3r = n_0 \int_0^\infty e^{-r^2/2} 2\pi r^2 dr \int_{-\infty}^\infty e^{-z^2/2} dz = n_0 (2\pi)^{3/2} \bar{r}^2 \bar{z} \equiv n_0 V_{\text{ eff}}.$$ (24.96)

The trap frequencies can be calculated as,

$$\omega_{r,z} = \sqrt{\frac{\mu_B (\partial_r B_{r,z})^2}{m B_0}}.$$ (24.97)

The Earth’s gravitational field deforms the trapping potential and, in the case of a harmonic potential, causes a gravitational sag without changing the secular frequencies of the potential. Assuming the potential to be given by,

$$U = \frac{m}{2} \omega_r^2 r^2 + \frac{m}{2} \omega_z^2 z^2 - mgz = \frac{m}{2} \omega_r^2 r^2 + \frac{m}{2} \omega_z^2 (z - g/\omega_z^2)^2 - \frac{m}{2} g^2 / \omega_z^2,$$ (24.98)

the atoms sag to a height of $g/\omega_z^2$. In time-dependent traps, gravity causes a more complex behavior [252]. Important works have been done by [107, 472, 191, 241, 2, 140, 371, 373, 158]. We study the impact of gravitation in Exc. 24.4.6.6.

![Figure 24.15](image)

Figure 24.15: Creation of a repulsive hole by light tuned to the blue of an atomic transition.

### 24.4.2.1 Characterization of Ioffe-type traps

The ‘time-of-flight’ density distribution is,

$$r_{\text{ToF}} = \sqrt{r^2 + \bar{v}^2 t_{\text{ToF}}^2} = \omega_r \omega_z \sqrt{\frac{1}{\bar{r}^2} + \frac{t_{\text{ToF}}^2}{T_{\text{ToF}}} \approx t_{\text{ToF}} \sqrt{\frac{k_B T}{m}}}.$$ (24.99)

The phase space density is,

$$\rho = n_0 \lambda_d^3 = \frac{N}{(2\pi)^{3/2} \bar{r}^2 \bar{z}} \left( \frac{2\pi \hbar^2}{m k_B T} \right)^{3/2} = N \omega_r^3 \omega_z \left( \frac{\hbar}{k_B T} \right)^3 = \zeta(3) \left( \frac{T_c}{T} \right)^3.$$ (24.100)
where $\zeta(3) = 1.202$ is,

$$k_B T_c = \hbar \left( \frac{N \omega_r^2 \omega_z}{\zeta(3)} \right)^{1/3} \quad (24.101)$$

is the critical temperature. The maximum collision rate is,

$$\gamma_{\text{coll}} = n_0 \sigma \bar{v} = n_0 4\pi a_s^2 \sqrt{\frac{k_B T}{m}} \quad (24.102)$$

The average collision rate can be obtained from,

$$\bar{\gamma}_{\text{coll}} N = \frac{1}{N} \int \gamma_{\text{coll}}(r) n(r) d^3 r = \frac{\int \sigma \bar{v} n^2(r) d^3 r}{\int n(r) d^3 r} \quad (24.103)$$

### 24.4.3 Radiative coupling and evaporative cooling

As we saw in the last section, optical cooling becomes ineffective when the density of the gas is high. Hence, we need another dissipation mechanism to cool trapped atoms. A method called **evaporation** has been proposed by Hess [279] for spin-polarized hydrogen (H↑) and was observed by Masuhara et al. [399]. Later, evaporation was used on alkali metals [2, 470, 142]. A detailed review of the subject was published by Ketterle and van Druten [338].

![Image of evaporation](image-url)

Figure 24.16: The basic idea of evaporation consists in removing hot particles from the sample.

Another collision-based cooling mechanism is **sympathetic cooling**. The technique was originally used in ion traps. Later it was applied to neutral atoms confined in magnetic traps. The idea is to get the cloud under study into thermal contact with a cold buffer gas. In some cases, the buffer gas may be optically or evaporatively cooled. Sympathetic cooling has been used in magnetic traps to create double condensates [445] and to cool fermions until the regime of quantum degeneracy [149].
24.4. Evaporative cooling

Evaporation always occurs when energetic particles abandon a system with finite bonding energy, removing more than their share of average energy per particle. Here, we consider the case of a finite-sized trapping potential, that is, the potential has an edge or a beak through which hot atoms, with sufficient kinetic energy to reach that region, may leave the trap. In the ideal case, this will lead to a complete truncation of the hot tail of the equilibrium Maxwell-Boltzmann velocity distribution. If the remaining system finds back to thermal equilibrium, it will do at a lower temperature. The redistribution of kinetic energy between atoms leading to thermalization occurs through elastic collisions.

![Figure 24.17: Principle of (a) rethermalization due to elastic collisions and (b) evaporation.](image)

24.4.4.1 Truncating the Boltzmann distribution

Let us first explain how the truncation leads to colder temperatures.

The objective is to calculate the Boltzmann distribution in a particular trap for a given atom number $N$ and temperature $T$. The first step is to obtain the density-of-states. For an isotropic harmonic trap $\varepsilon = \frac{p^2}{2m} + V(r)$ with $V(r) = \frac{m}{2} \omega^2 r^2$, it is,

$$
\eta(\varepsilon)d\varepsilon = \frac{1}{(2\pi)^3} \int_V d^3r d^3k = \frac{2\pi(2m)^{3/2}}{h^3} \int_V \sqrt{\varepsilon - V(r)}d^3r d\varepsilon = \frac{\varepsilon^2 d\varepsilon}{2(h\omega)^3}.
$$

The atom density is,

$$
n(\varepsilon) = e^{(\mu - \varepsilon)/k_B T} = Ze^{-\varepsilon/k_B T}.
$$

From these expression we obtain the atom number,

$$
N = \int_0^\infty n(\varepsilon)\eta(\varepsilon)d\varepsilon = \int_0^\infty e^{(\mu - \varepsilon)/k_B T} \frac{\varepsilon^2}{2(h\omega)^3}d\varepsilon = Z \frac{(k_B T)^3}{(h\omega)^3},
$$

which we may now use to calibrate the fugacity via

$$
Z = \frac{N (h\omega)^3}{(k_B T)^3},
$$

which finally allows us to calculate the total energy,

$$
E = \int_0^\infty \varepsilon n(\varepsilon)\eta(\varepsilon)d\varepsilon = \int_0^\infty \varepsilon e^{(\mu - \varepsilon)/k_B T} \frac{\varepsilon^2}{2(h\omega)^3}d\varepsilon = 3Z \frac{(k_B T)^4}{(h\omega)^3} = 3Nk_B T.
$$

The evaporation consists in truncating the distribution function \( n(\varepsilon) \) at some energy \( \hbar \omega_{rf} \). We get with \( \beta \equiv \left( \frac{k_B T}{\hbar} \right)^{-1} \),

\[
\tilde{N} = \int_0^{\hbar \omega_{rf}} n(\varepsilon)\eta(\varepsilon)d\varepsilon = N \left( 1 - \frac{2 + 2\beta \hbar \omega_{rf} + (\beta \hbar \omega_{rf})^2}{2e^{\beta \hbar \omega_{rf}}} \right) \tag{24.109}
\]

and

\[
\tilde{E} = \int_0^{\hbar \omega_{rf}} \varepsilon n(\varepsilon)\eta(\varepsilon)d\varepsilon = E \left( 1 - \frac{6 + 6\beta \hbar \omega_{rf} + 3(\beta \hbar \omega_{rf})^2 + (\beta \hbar \omega_{rf})^3}{6e^{\beta \hbar \omega_{rf}}} \right) \tag{24.110}
\]

As the truncation removes the hottest atoms from the cloud, we lose atom number and energy. Assuming the existence of some rethermalization mechanism, we may now use the new values for \( N \) and \( T \) to calculate the new equilibrium Boltzmann distribution starting all over from Eq. (24.105),

\[
N \leftarrow \tilde{N} \quad \text{and} \quad T \leftarrow \frac{\tilde{E}}{3Nk_B} \tag{24.111}
\]

Repeating this over and over the temperature will gradually reduce. The cooling process can be speed up by readjusting the truncation frequency to the actual temperature. This is called forced evaporation (see Fig. 24.18).

![Figure 24.18](#)

(a) Forced evaporation by truncating the Boltzmann distribution over and over again. (b) Evolution of the temperature and (c) of the phase space density with number of remaining atoms.

### 24.4.4.2 Rethermalization

As already mentioned, rethermalization occurs due to elastic collisions. It needs more or less three collisions per atom to rethermalize a cloud [430, 643], so that the collision rate determines the speed of the evaporation process. A large collision rate is desirable to keep the evaporation process faster than trap loss processes. Evaporation ramps between several seconds and a minute are typical.

The maximum rate of elastic collisions between trapped atoms (in the trap center) is,

\[
\gamma_{coll} = n_0 \sigma_{el} \bar{v} \sqrt{2} \propto \rho^3 N^{2/3}, \tag{24.112}
\]
where \( n_0 \) is the peak density,
\[
\sigma_{el} = 8\pi a_s^2 , \tag{24.113}
\]
is the cross-section for elastic collisions and, \( \bar{v} \) being the average thermal velocity of the cloud, \( \sqrt{2}\bar{v} \) is the average relative velocity between two of its atoms [337]. This formula gives the average collision rate at the center of the cloud, where the density is highest. To calculate the total collision rate, we need to integrate over the entire volume of the cloud,
\[
\bar{\gamma}_{coll} = \frac{1}{N} \int \gamma_{coll}(r)n(r)d^3r = \frac{\int \sigma_{el}\bar{v}n^2(r)d^3r}{\int n(r)d^3r} . \tag{24.114}
\]

For harmonic potential we find an average rate reduced by \( 2\sqrt{2} \), for linear potentials by 8. We verify this in Exc. 24.4.6.7. Finally, the rate for collision events is two times smaller, as it involves two atoms at a time.

Obviously, the evaporation process slows down when the cloud cools more, unless the edge of the potential is lowered, such that the hotter atoms of the colder cloud can be evaporated. By continually lowering the edge of the potential, while the atomic cloud keeps on rethermalizing (this procedure is called forced evaporation) very low temperatures in the nano-Kelvin regime can be achieved, and the phase space density can be increased by many orders of magnitude (between a MOT and a BEC there are 6 orders of magnitude) up to the threshold of Bose-Einstein condensation. Of course, this is only possible by sacrificing many hot atoms. Even with a well optimized evaporation ramp (i.e., a controlled lowering of the potential edge), usually only some 0.1% of the atoms reach the condensation phase after about 500 collisions per atom.

Two aspects should be mentioned regarding the optimization of the evaporation ramp. The first aspect is, that elastic collisions with atoms from the residual background vapor of the vacuum chamber limit the lifetime of the trap. Therefore, the evaporation must be sufficiently fast, which requires either a high rate of elastic collisions or a good vacuum. A compromise must be found between a slow but efficient evaporative cooling and a minimization of the losses, which come into play when the evaporation takes too long. The second aspect is, that the dimensionality of the evaporation surface determines the effectiveness of the cooling. In the first demonstration of evaporation, \( H^\uparrow \) atoms of a hot cloud were ejected over a saddle point. The saddle was located a small region away from the trap center, and only atoms with sufficient kinetic energy along a certain direction, \( E_z > U_{edge} \), could leave the trap. In such cases, evaporation is called one-dimensional. Even though ergodic redistribution due to anharmonicities of the potential will drive, sooner or later, all the atoms to this region, this effect becomes less pronounced when the cloud cools down, because the atoms accumulate at the bottom of the approximately harmonic (and therefore separable) potential. This fact has inhibited efficient evaporation of \( H^\uparrow \) below 120 \( \mu \)K [205].

A second evaporative technique has been demonstrated in traps called time-orbiting potential (TOP) [470]. It is a feature of TOP traps to display a spatial region called a 'death-circle', where passing atoms are ejected from the trap. This fatal circle can act as a 2-dimensional evaporation surface, provided the radius of the circle is large enough [256]. However, under the influence of gravity the dimensionality is further reduced to 1D [337].
The most successful evaporation technique implemented so far is based on a radiative coupling of confined and free states. We discuss this technique in the following sections. Publications on evaporative cooling are [384, 418, 470, 487, 50, 414, 430, 190, 193, 269, 449, 279, 399, 142, 338, 642, 257, 394, 174, 281]. See ([124], Sec. 3.1.4) for an overview.

### 24.4.4.3 Adiabatic decompression

The condition for adiabatic decompression of a trapping potential is,

\[
\frac{|\dot{\omega}_{\text{trap}}|}{\omega_{\text{trap}}} \ll \omega_{\text{trap}}.
\]

(24.115)

The population of the quantized levels should not change under adiabatic decompression, \( e^{\hbar \omega_i/\hbar B T_i} = e^{\hbar \omega_f/\hbar B T_f} \), and the phase space density remains unchanged, \( n_i \lambda_{dB,i} = n_f \lambda_{dB,f} \). If this is true, then the temperature and density change as,

\[
\frac{\omega_f}{\omega_i} = \frac{T_f}{T_i} = \left( \frac{n_f}{n_i} \right)^{3/2}.
\]

(24.116)

Solve Exc. 24.4.6.8.

### 24.4.4.4 Radiative coupling of internal state

The most successful evaporation technique implemented so far is based on a radiative coupling of confined and free states. We discuss this technique in the following sections. See ([124], Sec. 3.1.4) for an overview.

The radiative coupling technique originates from an idea proposed by Pritchard et al. [257], who have already had some experience with radiofrequency spectroscopy in magnetically trapped neutral atoms [394, 269]. The spatial dependence of the Zeeman splitting is an intrinsic feature of magnetic traps. Irradiation of a radio wave at a certain frequency couples trapped and untrapped Zeeman substates at a well-defined distance from the trap center. This gives rise to a 3D evaporation surface, where the passing atoms can undergo Landau-Zener transitions and be expelled from the trap. The technical advantages of this technique are substantial: The magnetic trapping potential does not have to be manipulated, for example, by the creation of a nozzle, and the potential edges can be easily controlled by the radiofrequency. If evaporation is forced via a continuous reduction of the radiofrequency and if the evaporation ramp is optimized, the density will increase as well as the collision rate. Rethermalization will accelerate and initiate a self-accelerated evaporation process (run-away evaporation). Rf-evaporation was first demonstrated by Ketterle and colleagues [142]. Solve Exc. 24.4.6.9.

Figure 24.19: Illustration of evaporative truncation.
24.4.4.5 Adiabatic and diabatic limits of rf-induced evaporation

Rf-induced evaporation can be described within the formalism of the dressed atom [114], where the different states \( m_F \) of an atom with spin \( F \) are coupled to an rf-field \(^7\), which we assume to be linearly polarized:

\[
B(t) = B_\epsilon \cos \omega t .
\]

The element of the coupling matrix between the levels, \(|F,m_F\rangle\) and \(|F,m_F \pm 1\rangle\) is,

\[
\Omega = \frac{\mu_B g}{4\hbar} |B_\epsilon \times \hat{e}_B| \sqrt{F(F+1) - m_F(m_F+1)} ,
\]

where \( g \) is the atomic \( g \)-factor and \( \hat{e}_B \) the orientation of the local static magnetic field.

The adiabatic potentials \( U(r) \) are obtained through the eigenvalues of the atomic states dressed by the local magnetic field \( B(r) \). In the dressed atom picture, we consider the total energy of the atom plus the field of \( N \) radiofrequency photons. Without coupling, this simply means that \( N\hbar \omega \) is added to the atomic Zeeman energies, resulting in a Zeeman pattern being vertically shifted by \( N\hbar \omega \) for \( N = 0, \pm 1, \ldots \). At positions where the rf-field is in resonance, curves with \( \Delta N = 1 \) intersect. Here, the coupling develops an avoided crossing, which determines the pattern of adiabatic energy levels [see Fig. 24.20(b)].

![Figure 24.20](code)

(a) (Left) Potentials due to the Zeeman structure of an atom in the ground state with \( F = 1 \). (Right) Adiabatic potentials resulting from the coupling of Zeeman levels via radiofrequency radiation being resonant with the difference of Zeeman levels at the position 0.7.

A slowly moving atom remains on the curve of an adiabatic potential. As an example, let us assume an atom in the hyperfine state \(|F,F\rangle\) moving away from the center of the trap. When it comes close to resonance, the rf-field blends this state with other \( m_F \)-states, from the \(|F,F - 1\rangle\) down to the \(|F,-F\rangle\) state, which changes the slope of the potential curve. Beyond the resonance point, the atomic state is adiabatically transformed into an untrapped high-field seeking state, and the atom is repelled from the trap. Thus, while passing the avoided crossing, the atom has

\(^7\)Alternatively, a microwave frequency may be used to couple different hyperfine levels.
emitted $2F$ rf-photons in a stimulated manner and inverted the orientation of both the electron and the nuclear spin.

In this way the radiofrequency generates an adiabatic potential surface with a depth of approximately $|m_F|\hbar(\omega - \omega_0)$, where $\omega_0$ is the resonant rf-frequency at the center of the trap. The evaporation process corresponds, then, to the removal of the most energetic atoms out of the trap.

For this adiabatic picture to be valid, an adiabaticity condition must be fulfilled. This condition requires that the energy difference at the avoided crossover be larger than the energy uncertainty related to the limited time that an atom with velocity $v$ spends in the resonance region. For a two-level system coupled by a matrix element $V_{12}$ and an atom moving with velocity $v$ along the $z$-axis, the transition probability $P$ between the adiabatic curves is given by the Landau-Zener formula [512],

\[
P = 1 - e^{-\xi} \quad \text{with} \quad \xi = \frac{2\pi|V_{12}|^2}{\hbar g\mu_B\partial_z Bv}.
\]

The Landau-Zener theory is strictly valid only for a two-level system, which we use here only for a qualitative discussion of two following limiting cases.

For a weak rf-field, $\xi \ll 1$, $P$ is much smaller than 1, i.e., the atoms remain predominantly on the diabatic surface shown in Fig. 24.20(a). The probability for a spin flip transition is, $P \approx t$, which describes the diabatic limit of rf-induced evaporative cooling: The atomic energy levels are almost unperturbed, the atoms often spill across the resonance surface, and only after $1/P$ oscillations, they spin-flip from the hyperfine state $|F,F\rangle$ to the $|F,F-1\rangle$.

The adiabatic limit is clearly the ideal situation for evaporative cooling. However, the evaporation process in a trap (with oscillation time $T_{osc}$) saturates at a lower rf-power. The condition for saturation is $P \approx T_{osc}/\tau_{el}$, where $\tau_{el}$ is the average time between two collisions. This means that an energetic atom is evaporated before it collides again.

Only the component of the magnetic field of the rf-radiation which is perpendicular to the magnetic trapping field induces spin-flips. In certain geometries of the confinement potential, for example the quadrupole trap, the magnetic field covers the entire solid angle. Consequently, there are two points where the trapping field and the rf-field are parallel and the elements of the transition matrix consequently zero. Within an area around these points, the coupling is diabatic. In practice however, the rf-transition can be sufficiently saturated that this area is small and does not strongly affect the evaporation efficiency.

Note also that gravitation deforms the equipotential surfaces of the confinement potential, which can reduce the evaporation efficiency [337]. Solve Exc. 24.4.6.10.

Figure 24.21: Effective potential due to a rapid modulation of the trap’s location.
24.4.5 Sympathetic cooling

The efficiency of evaporative cooling depends on the rate of interatomic collisions. However, there are atomic species with unfavorable, that is, small or even negative scattering lengths. Also, while at low temperatures only \( s \)-wave collisions occur (higher partial waves being frozen behind the centrifugal barrier), such collisions are prohibited for fermionic gases. Fermions or species with unfavorable scattering lengths can not be cooled by evaporation. There is, however, another technique called *sympathetic cooling* by thermal contact with another species. The additional species is, in general, actively cooled (e.g., by evaporation), while the species of interest is passively cooled via elastic collisions with atoms of the additional species. Of course, for this scheme to work the *interspecies scattering length* and the mass ratio must be adequate to ensure adequate thermal coupling.

Following [443] the transfer of kinetic energy between two colliding atoms is reduced by a factor depending on the their mass difference, \( \xi \),

\[
\xi = \frac{4m_1m_2}{(m_1 + m_2)^2}.
\] (24.120)

Around \( 3/\xi \) collisions per atom on average are required for complete thermalization of a gas. For example, for the Rb-Li mixture, we have \( 3/\xi = 12.4 \). The collision rate is,

\[
\Gamma_{\text{coll}} = \sigma_{12}\bar{v} \int n_1(\mathbf{r})n_2(\mathbf{r})d^3r,
\] (24.121)

where the average thermal velocity is,

\[
\bar{v} = \sqrt{\frac{8k_B}{\pi} \left( \frac{T_1}{m_1} + \frac{T_2}{m_2} \right)}.
\] (24.122)

The instantaneous temperature is calculated by,

\[
\gamma_{\text{therm}} = -\frac{1}{\Delta T} \frac{dT}{dt},
\] (24.123)
or via simulations: $\Delta T(t + dt) = \Delta T(t) - \Delta T(t)\gamma_{\text{therm}}dt$. Following [148] the rethermalization rate is connected to the collision rate via,

$$\gamma_{\text{therm}} = \frac{\xi}{3} \left( \frac{\Delta E_{1 \rightarrow 2}}{N_1 k_B \Delta T} + \frac{\Delta E_{2 \rightarrow 1}}{N_2 k_B \Delta T} \right) = \frac{\xi}{3} \left( \frac{\Gamma_{\text{coll}}}{N_1} + \frac{\Gamma_{\text{coll}}}{N_2} \right). \tag{24.124}$$

Analytic solutions can be derived for harmonic traps. This will be studied in Excs. 24.4.6.11 and Exc. 24.4.6.12.

### 24.4.6 Exercises

**24.4.6.1 Ex: Lack of trapping potentials for strong field seekers**

Show that it is not possible to create magnetic trapping potentials for atoms in low-field seeking Zeeman states.

**24.4.6.2 Ex: Quadrupolar potential**

Show that for a quadrupolar trap always holds $2 \partial_r B_{\text{qua}} = \partial_z B_{\text{qua}}$.

**24.4.6.3 Ex: Magnetic quadrupole trap**

a. Consider $^{87}\text{Rb}$ atoms confined in a magnetic trap with $\mathbf{B}(x, y, z) = x \ y \ -2z \times 200 \text{ G/cm}$. The atoms are in the state $|F = 1, m_F = -1\rangle$ with the $g$-factor $g_F = 1/2$. Check whether it is reasonable to assume constant vibration frequencies for such traps.

b. Assume that the trapped atomic cloud consists of $N = 10^8$ atoms at temperature $T = 100 \text{ K}$. Calculate the atomic density $n_0$ at the center of the cloud.

c. The cross section for elastic collisions is $\sigma = 10^{-12} \text{ cm}^2$. How many times do atoms meet in the middle of the trap?

**24.4.6.4 Ex: TOP trap**

The TOP trap (time-orbiting potential) was the first design to allow for Bose-Einstein condensation in 1995. It consists of the superposition of a quadrupolar magnetic field, with the radial and axial gradients $2 \partial_r B_{\text{qua}} = \partial_z B_{\text{qua}}$, and a homogeneous magnetic field $B_{\text{top}}$ rotating in the symmetry plane of the quadrupole field. Atoms which oscillate with an amplitude beyond a given radius $r_d$, called the 'circle of death', undergo Majorana transitions and are expelled from the trap.

a. Calculate the radius of the death circle.

b. Plot the time-averaged 'effective' trapping potential.

**24.4.6.5 Ex: Harmonic trap**

Calculate the vibration frequencies of $^{87}\text{Rb}$ atoms trapped in a harmonic trap, when the atoms are in the $|F = 1, m_F = -1\rangle$ hyperfine level of the ground state.
24.4.6.6 **Ex: Gravitational sag in a trap**

Consider (a) a quadrupolar trap and (b) an isotropic harmonic trap. What is the gradient, respectively the curvature of the trapping potential required to suspend a cloud of rubidium subject to gravitation? What is the sag of the cloud in the potential due to gravitation?

24.4.6.7 **Ex: Mean collision rate**

Assuming that the peak collision rate $\gamma_{\text{coll}}$ is known, calculate the average collision rate (a) in a quadrupolar and (b) in a harmonic trap.

24.4.6.8 **Ex: Adiabatic compression**

How does temperature change upon adiabatic compression of (a) a quadrupole trap and (b) a harmonic trap. How do density, phase space density, and elastic collision rate vary. **Help:** Define the compression for quadrupole trap as $\eta \equiv \partial rB_r/final / \partial rB_r/initial$ and for harmonic trap as $\eta \equiv \omega r/final / \omega r/initial$.

24.4.6.9 **Ex: RF-antenna for radiative coupling**

Calculate the Rabi frequency that can be generated by an rf-antenna consisting of a single square loop with side length $L = 2 \text{ cm}$ on a cloud of trapped $^{87}\text{Rb}$ atoms located in the center of the loop on transitions between magnetic sublevels of the $F = 1$ ground state hyperfine structure. Assume the antenna to carry an ac-current with $I = 1 \text{ A}$ amplitude.

24.4.6.10 **Ex: Landau-Zener transitions**

Consider a rubidium-88 cloud in its ground state $^2S_{1/2}, F = 1, m_F = -1$ confined in an isotropic quadrupolar potential with the gradient $200 \text{ G/cm}$. To initiate an efficient radiofrequency evaporation, you want atoms crossing the region where the radiofrequency couples the Zeeman states to make a transition to the untrapped Zeeman state $m_F = 0$ with 95% probability. What is the amplitude of the required magnetic field.

24.4.6.11 **Ex: Damping in mixtures of species**

From Eq. (24.124) derive the interspecies thermalization rate for harmonic potentials.

24.4.6.12 **Ex: Damping in mixtures of species**

Describe the damping in mixtures of species, and show how to use a measurement of the damping time for a determination of the interspecies the scattering length.
24.5 Other traps

24.5.1 Ion traps

The electric charge of ions allow for their efficient manipulation and control by electric and magnetic fields exploiting the Coulomb-Lorentz force. In fact, the control is so good, that it is possible to isolate and store individual ions or even arrays of quantum entangled ions and to perform coherent operations on them, which qualifies them as quantum registers. Two different types of traps have been investigated. In Penning traps [467], electrically charged particles are subjected to a radially attractive quadrupolar electrostatic field superimposed to an axial magnetostatic field forcing the particles into closed circular orbitals. In the so-called radiofrequency trap or Paul trap – Wolfgang Paul received the Nobel Prize in 1989 together with Hans Dehmelt and Norman Ramsey – charged particles subjected to an alternating electric field with quadrupolar symmetry. Hyperboloidal electrode configurations produce saddle-shaped potentials, as shown in Fig. 24.24, which are, at any instant of time, parabolically repulsive in the one direction (axial or radial) and parabolically attractive in the other (radial or axial). The alternating electric field causes a periodic reorientation of the Coulomb force, which leads to a time-averaged parabolic quasi-potential \( \Phi(r,t) \). In this potential the particles perform harmonic oscillations at characteristic frequencies, which are independent of the oscillation amplitude [463]:

\[
\Phi(r,z) = \Phi_0(t)(r^2 - 2z^2), \quad r^2 = x^2 + y^2, \tag{24.125}
\]

where the polarity is alternated at a radiofrequency \( \Omega_a \),

\[
\Phi_0(t) = \Phi_{dc} + \Phi_{ac}\cos(\Omega_a t). \tag{24.126}
\]

\( \Phi_{dc} \) denotes the amplitude of the \( dc \) part of the voltage, \( \Phi_{ac} \) the amplitude of the \( ac \) part. The potential \( \Phi(r,z,t) \) exerts, in the temporal average, a central force on the ion, if the radiofrequency field satisfies specific conditions.

24.5.1.1 Evaluation of the stability diagram

Paul traps do not have to have perfect quadrupolar geometry. To determine the secular frequencies of the pseudo-potential for an arbitrary geometry, we expand the

---

Note that purely electrostatic fields do not lend themselves to trapping, since the necessary condition for the existence of minima in a potential, \( \partial_i \partial_j \phi < 0 \), does not obey the Laplace equation.
potential around the position \( r_0 \) of the potential minimum, which depends on the geometry of the electrodes and the applied voltages,

\[
\Phi(\mathbf{r}) = \Phi_a + (\mathbf{r} - \mathbf{r}_0) \nabla \Phi(\mathbf{r}_0) + \frac{1}{2}[(\mathbf{r} - \mathbf{r}_0) \nabla \Phi(\mathbf{r}_0) + ... \quad (24.127)
\]

\[
\equiv \Phi_a[1 + b_r (r - r_0)^2 + b_z (z - z_0)^2] .
\]

In the last step, we assume that the potential has an almost cylindrical shape. For a given geometry, the curvatures \( b_z, r \) can be extracted from numerical simulations. From the continuity equation, we find \( b_z = -2b_r \). The polarity of the electrodes is modulated with frequency \( \Omega \),

\[
\Phi(\mathbf{r}, t) = \Phi(\mathbf{r})(\zeta - \cos \Omega t) . \quad (24.128)
\]

The equations of motion are derived from \( m \ddot{\mathbf{r}} = -e \nabla \phi(\mathbf{r}, t) \),

\[
m \ddot{r}_j + 2e \Phi_a b_j (\zeta - \cos \Omega t) r_j = 0 . \quad (24.129)
\]

Introducing the parameters \( a \) and \( q \),

\[
a_z = \frac{8e \Phi_a b_z \zeta}{m \Omega^2} = -2a_r \quad \text{and} \quad q_z = \frac{4e \Phi_a b_z}{m \Omega^2} = -2q_r , \quad (24.130)
\]

we arrive at the so-called Mathieu equation \[408, 198\],

\[
\ddot{r}_j + \frac{1}{4} \Omega^2 (a_j - 2q_j \zeta \cos \Omega t) r_j = 0 . \quad (24.131)
\]

These equations predict stable orbits, provided that the parameters \( a \) and \( q \) are within the so-called stability diagram shown in Fig. 24.25.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{phi_rz_u.a.png}
\caption{(code) Two-dimensional illustration of time-dependent potential: at each instant of time the potential has the form of a saddle. The potential rotates around the vertical axis at an appropriate pace.}
\end{figure}

According to these equations, the ion goes through oscillatory motions that are defined by the trap parameters \( a_i \) and \( q_i \). For the motion of the ion to be finite, its oscillation amplitude may not exceed the boundaries defined by the electrodes. This condition imposes an allowed regime for the trap parameters called stability diagram \[408\].

In the limit \( |a_i|, q_i \ll 1 \) the ion travels only a short distance \( s \ll r_0 \) during one modulation period \( \Omega_a \). Then the ion undergoes a slow periodic motion called macro-motion within the trapping potential with the secular frequency \( \zeta_i \). This motion is
modulated by a rapid oscillation called micromotion, which is excited by the modulation field $\Omega_a$. Without dc voltage applied between the ring and the endcaps, $a_i = 0$, the motion of the ion is described by the following simple equation:

$$r_i(t) = r_i^0 \left(1 - \frac{1}{2} q_i \cos \Omega_a t\right) \cos \zeta_i t \quad , \quad \zeta_i = \frac{\sqrt{2}}{q_i \Omega_a} \ , \quad i = r, z . \quad (24.132)$$

The orbit of the ion is confined to the inner region of the trap, if its kinetic energy is less than $m \zeta_i^2 r_i^2 + M \zeta_i^2 z_i^2$. Since the trap is, at any instant of time, focusing in some directions and defocusing others, it is not a conservative potential. The oscillatory motion (disregarding micromotion) of the ion, however suggests a model, where the trap is described by a pseudo-potential [198, ?] whose depth is,

$$D_z = \frac{q_z eV_{ac}}{8} = 2D_r \quad \text{if} \quad a_i = 0 . \quad (24.133)$$

Other geometries, deviating from the perfect quadrupole, are possible for the electrodes. These traps are also well described by equation (24.125), as long as the ion is near the trap center. For example, higher order multipolar traps have been used for trapping ion clouds [618], as well as Paul-Straubl traps [538] and storage rings [612]. Particularly important for the storage of arrays of cooled ions with applications in quantum computing is the linear Paul trap [485, 201, 484], where immobilized ions are aligned on a linear chain. The advantage of the linear trap, as compared to other traps designed for many ions, is the easier optical access to individual ions by focused laser beams and the possibility of canceling the micromotion.
24.5. OTHER TRAPS

24.5.2 Micromotion

The motion of an ion in a Paul trap is a superposition of two vibrations with the respective oscillation frequencies $\Omega_a$ (modulation frequency) and $\zeta_{r,z}$ (secular frequencies for radial and axial direction vibrations). For an ion in thermal equilibrium (i.e., without active cooling), the mean kinetic energies of the micro- and macromotion are equal [60].

The macromotion can be reduced by cooling, in contrast to the micromotion, which is constantly excited by the modulation of the applied electric field [110]. On the other hand, the amplitude of the micromotion decreases with the distance of the ion from the trap center and, in the minimum of the pseudo potential, disappears completely. Therefore, to suppress the micromotion, it is imperative to cool the macromotion and push the ion to the trap center, if necessary, using additional static electric fields. Since the frequency of the micromotion is much higher than that of the macromotion, the dynamic sidebands can be resolved on a sufficiently narrow optical transition. When the modulation frequency $\Omega_a$ is very high, the secular frequencies of the macromotion are also high, so that even large optical transitions are able to resolve the macromotional sidebands. This is called the strong coupling regime.

Because of Coulomb repulsion, only a single atom can be at the center of a Paul trap, such that it is difficult to zero micromovement. One solution is to use a linear trap, where the center is smeared out over a straight line. Solve Exc. 24.5.4.1.

Example 91 (Numerical calculation of the electric field created by a charged surface): To calculate the trapping potential for a charged particle held on top of a planar microtrap structure, we proceed as follows. The energy of a charge in an electric field is $H = -e\Phi$. The electrostatic potential is given by Coulomb’s law,

$$\Phi(r) = \frac{1}{4\pi\varepsilon_0} \sum_n \int_{V_n} \rho(r') \frac{dV'}{\left| r - r' \right|} - \frac{1}{4\pi} \sum_n \int_{S_n} \Phi_n \frac{r - r'}{|r - r'|^3} df' + \frac{1}{4\pi} \sum_n \int_{S_n} E(r') \frac{df'}{|r - r'|},$$

where $\phi_n$ is the voltage applied to the $n$-th boundary. In practice, electric fields are generated by electrodes set to specific voltages. Using the Dirichlet boundary conditions, we only retain the second term. Furthermore, to account for the planar geometry of the chip electrodes, we only consider surface boundaries in the $y' = 0$ plane,

$$\Phi(r) = -\frac{1}{4\pi} \sum_n \Phi_n \int_{S_n} \frac{ydx'dz'}{\sqrt{(x-x')^2 + y^2 + (z-z')^2}},$$

This implies that the field lines cross the chip surface orthogonally, which in reality is only true if the chip electrodes cover the whole area. Therefore, we only consider small gaps between the electrodes. We digitize the integral by dividing every electrode $\Phi_n$ into a number of identical surface elements $\Delta f_m$,

$$\Phi(r) = -\frac{1}{4\pi} \sum_{n,m} \Phi_n \frac{y\Delta f_m}{\sqrt{(x-x_m)^2 + y^2 + (z-z_m)^2}}.$$ 

This formula can easily be evaluated numerically. A concrete example for a microchip ion trap is shown in Fig. 24.27.
Figure 24.27: Possible design for a microchip ion trap. $\Phi_n$ are static potentials except for $\Phi_0$, which is alternates sign with radio frequency.

**Example 92 (Numerical calculation of the magnetic field created by a current wire):** Current-carrying wires may exert Lorentz forces on the ions. The magnetostatic field is given by the Biot-Savart law,

$$B(r) = \frac{\mu_0}{4\pi} \oint_C \frac{(r - r') \times j}{|r - r'|^3} \, dV'. $$

In practice magnetic fields are created by current-carrying wires. Those can be parametrized by one-dimensional currents, $j = I \delta z \, ds$, so that,

$$B(r) = \frac{\mu_0 I}{4\pi} \oint_C ds' \times \frac{(r - r')}{|r - r'|^3} ,$$

$$|B(r)| = \frac{\mu_0 I}{4\pi} \sum_n \sqrt{ds_{y,n}^2 (z - z_n)^2 + ds_{z,n}^2 (x - x_n)^2 + ds_{z,n}^2 (y - y_n)^2} \frac{\sqrt{x - x_n}^2 + (y - y_n)^2 + (z - z_n)^2}.$$ 

can immediately be numerically solved.

### 24.5.2.1 Electronic detection of ions

The presence of ions in the trap can be probed through the damping that they induce a coupled electronic resonance circuit [617, 621].

### 24.5.3 QUEST

Homonuclear atoms and dimers do not have a permanent electrical dipole moment, but they may have a permanent magnetic dipole moment. Therefore, homonuclear dimers must be confined by magnetic field gradients, or else an electric dipole moment must be *induced* by an oscillating electromagnetic field. In the optical regime, this was demonstrated with the quasi-electrostatic trap (QUEST).

In contrast, heteronuclear dimers are polar molecules with a permanent electric dipole moment, which can be quite large if the molecules are deeply bound. According to Earnshaw’s theorem, there is no static magnetic field maximum in free space. Thus, no 'high-field seeking' state can be trapped. In principle, QUEST-type dipolar optical traps can also be used for heteronuclear dimers. The problem is, however, that in contrast to homonuclear molecules, transitions between the vibrational ground state...
levels are possible. Thus, the light generating the QUEST also induces transitions leading to a redistribution of the population over all vibrational states.

Very far from resonance,

\[ U_{\text{dip}}(r) = -\alpha_{\text{stat}} \frac{I(r)}{2\varepsilon_0 c} \cdot \]  

Loosely bound homonuclear molecules are subject to the sum of the restoring forces exerted by magnetic traps on the individual atoms, \( \mu_m = 2\mu_a \) and \( d_m = 2d_a \). This is also true for heteronuclear molecules as long as the trapping potential is much weaker than the binding energy.

**Example 93 (Permanent electric dipole moment of LiRb):** The interaction energy of two dipoles is,

\[ \hat{H}_{\text{int}} = \frac{1}{4\pi\varepsilon_0} \frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\mathbf{p}_2 \cdot \hat{\mathbf{r}})}{r^3} \cdot \]

Thus, two identical dipoles with 1 Debye = \( 10^{-27}/2.998 \) Cm = \( 10^{-19}/c \) Cm\(^2/s\) = 39.36 \( ea_B \) parallel oriented at a distance \( r = 1 \) \( \mu m \) have the energy,

\[ \hat{H}_{\text{int}} = \frac{1}{4\pi\varepsilon_0} \frac{p^2}{r^3} \approx h \times 1.5 \text{ MHz} \approx k_B \times 73 \mu\text{K} \cdot \]

For example, LiRb has an electrical dipole moment of between -2 and -4.2 Debye depending on the vibrational state of the molecule.
Figure 24.29: Resonance circuit for electronic ion detection. The trap is operated by a radiofrequency, while a DC voltage is scanned across the stability diagram. Simultaneously, an oscillating field is tuned near one of the trap’s secular frequencies. When the stability point is such, that the secular frequency coincides with the frequency of the oscillating field, the motion of the ions is parametrically excited and the resonance circuit is damped. This damping is detected by a narrow-band amplifier.

24.5.4 Exercises

24.5.4.1 Ex: Coulomb repulsion in linear Paul trap

Coulombian repulsion prevents that two ions confined in a linear Paul trap be simultaneously in the ground state. Determine the spatial extent of the ground state and the depth of the potential in the pseudo-potential approximation. What is the equilibrium distance of the ions?

24.5.4.2 Ex: Motion of ions in a surface Paul trap

Programs on the motion of ions in a surface Paul trap.

24.6 Analysing techniques

To analyze the kinetic state of an atomic gas and, for example, to identify the presence of a Bose-Einstein condensate, it is necessary to measure its spatial or momentum distributions. However, the only way to gather information from the atoms is to throw some kind of particles into them and to detect, where these particles are scattered. The most suitable particle to penetrate an ultra-high vacuum chamber surely is the photon. Therefore, apart from few exceptions where electron beams are used, all information on ultra-cold gases has been obtained so far through their reactions to incident laser beams [286, 99, 14, 321, 228].

24.6.1 Time-of-flight imaging

The most common imaging techniques measure the absorption of a laser beam by an atomic cloud after a time-of-flight or the dispersion of a laser beam induced by trapped cloud. The amplitude $E_0$ of a light wave traversing an atomic cloud of diameter $L$
and characterized by the refractive index $\eta$ is modified by a factor $e^{i\omega L\eta/c}$. For an inhomogeneous cloud, we have,

$$E = E_0 e^{i\omega L/c} \exp \left( \frac{i\omega}{c} \int_{-\infty}^{\infty} (\eta(r) - 1) dz \right).$$

(24.135)

We can approximate the refractive index by the atomic susceptibility,

$$\eta = \sqrt{1 + \chi} \simeq 1 + \frac{\chi}{2}, \quad \chi = -\frac{4\pi n(r)}{k^3 (2\Delta/\Gamma + i)}. \quad (24.136)$$

Now, the absorption and dispersion coefficients can be related to the optical cross-section $\sigma(\Delta)$ defined in (1.102) [382], where $\Delta$ is the detuning of light frequency from an atomic resonance, whose linewidth is $\Gamma$. This result is called the optical theorem,

$$\alpha = n \sigma(\Delta) \quad \text{and} \quad \delta = n \sigma(\Delta) \frac{\Delta}{\Gamma}, \quad (24.138)$$

Finally, we obtain the Lambert-Beer law,

$$E = E_0 e^{i\omega L/c} \exp \left[ i\sigma(\Delta) \left( \frac{i}{2} - \frac{\Delta}{\Gamma} \right) \int_{-\infty}^{\infty} n(r) dz \right] \equiv E_0 e^{i\omega L/c} e^{-b/2} e^{i\varphi}. \quad (24.139)$$

For the intensity, $I \propto |E|^2$, we get,

$$\frac{I}{I_0} = \exp \left[ -\sigma(\Delta) \int_{-\infty}^{\infty} n(r) dz \right] \equiv e^{-b}. \quad (24.140)$$

The absorption $b$ describes the loss of intensity for the laser beam due to scattering by the (disordered) atoms. It is strong near resonance, but diminished quadratically with the detuning $\Delta$. The scattering is necessarily accompanied by radiation pressure accelerating and heating the atoms. The dispersion $\varphi$ describes the refraction of the laser beam by the atomic density distribution (which for this purpose can be considered as continuous) [295, 291]. It disappears in resonance and diminishes slowly with increased detuning ($\propto \Delta$). It is connected to the dipole force and, thus, does not heat the atomic cloud. The coefficient $\varphi$ describes the phase shift of the electromagnetic wave transmitted through the atomic cloud.

### 24.6.2 Absorption imaging

Let us now detail the experimental process of absorption imaging (see Fig. 24.31): The trap confining the atomic cloud is suddenly turned off, thus letting the atoms, accelerated by the Earth’s gravitation, fall for a flight time of a few ms. Then a pulse of a resonant laser light, whose diameter is much larger than the size of the cloud, is irradiated. The local attenuation of the beam intensity $I \sim |E|^2$ can be related
Figure 24.30: Sequence of a typical time-of-flight experiment: As soon as the trapping potential is suddenly switched off, the atomic cloud ballistically expands for 18 ms, before it is illuminated by a short resonant laser pulse. The shadow printed by the cloud onto the beam is photographed by a CCD camera.

The shadow printed by the atomic cloud on the transverse profile of the laser beam is recorded by a CCD camera.

We have already noted that the absorption is accompanied by radiative pressure. After some scattering events, due to the photonic recoil, the atoms have accumulated a sufficiently large velocity, and therefore a sufficiently large Doppler shift, to be out of resonance with the laser beam. Subsequent photons are no longer scattered by the atoms and only contribute to increase the illumination of the CCD camera without carrying any information about the presence of atoms. Consequently, it is advantageous to use very short laser pulses. In addition, the intensity of the laser beam should not saturate the transition in order to guarantee an optical cross-section, which is independent of the intensity, and hence to guarantee the validity of the Lambert-Beer law. Finally, the laser frequency must be tuned perfectly to resonance, $\Delta = 0$. Otherwise, the interaction between the laser beam and the atomic cloud becomes partially dispersive, which leads to a focusing or defocusing of the laser beam by refraction and a distortion of the image making it impossible to estimate the size of the cloud.

Fig. 24.31 shows examples of absorption images of an atomic cloud taken at different stages of the evaporation process. Fig. 24.31(a,b) was taken at a temperature of 320 nK; the cloud is large and isotropic and therefore purely thermal. At 250 nK [see Fig. 24.31(c,d)] an elliptically shaped part appears in the center of the thermal cloud.
24.6. ANALYSING TECHNIQUES

Figure 24.31: Absorption images after a time-of-flight allow to identify the presence of a Bose-condensate through its characteristic momentum distribution. Shown are images (a,b) above, (c,d) slightly below, and (e,f) well below the critical temperature for a Bose-Einstein phase transition (figures [256]).

And at 180 nK [see Fig. 24.31(e,f)] the thermal cloud almost completely disappeared for the benefit of the condensate. A quantitative evaluation of the condensed fraction is given in Sec. 25.1.4. Solve the Excs. 24.6.6.2 and 24.6.6.1.

24.6.3 Dispersive imaging

The absorption imaging technique is destructive, because of the involved ballistic expansion and also because of the radiative pressure exerted by the resonant imaging beam, which accelerates and heats the atomic cloud. That is, the measurement process messes up the distributions of the cloud, such that a second image taken after the first one will give different results. However, there is a non-destructive imaging technique called dispersive imaging or phase contrast imaging. In this technique, the laser light is tuned sufficiently far from resonance, $|\Delta| \gg \Gamma$, for spontaneous emission and heating induced by random photonic recoil to be negligible [14]. This permits to take a series of consecutive images and create a movie of the temporal evolution of the cloud. Another advantage of this technique is the low off-resonant optical density, which allows to take pictures of very dense clouds in situ, that is, while they are
confined in a trap.

Figure 24.32: Scheme for dispersive images.

The physical quantity which is measured by this method is the local phase shift of the wavefront of the probe laser. Wavefront distortions are difficult to measure. To transform the phase profile into an intensity profile, a method known from classical optics called \textit{Schlieren method} is used. It is based on the interference of the probe beam with its distorted wavefront and a reference plane wave. In practice, there are several possibilities. For \textit{dark-ground imaging}, the part of the incident beam not having interacted with the atoms is blocked behind the interaction zone (see Fig. 24.32)

\[
\bar{I}_{dg} = \frac{1}{2} |\mathcal{E} - \mathcal{E}_0|^2 = I_0 \left| e^{-b/2+i\varphi} - 1 \right|^2 \to b \rightarrow 0 I_0 \varphi^2 = I_0 b \frac{\Delta^2}{\Gamma^2}. \tag{24.142}
\]

The intensity signal \( \bar{I}_{dg} \) is quadratic in optical density \( b \).

For \textit{phase contrast imaging}, the part of the beam not having interacted with the atoms receives a phase shift of \( \lambda/4 \) with respect to the part of the beam having interacted with the atoms:

\[
\bar{I}_{pc} = \frac{1}{2} |\mathcal{E} - \mathcal{E}_0 + \mathcal{E}_0 e^{\pm\pi/2}|^2 = I_0 \left| e^{-b/2+i\varphi} - 1 + e^{\pm\pi/2} \right|^2 \to b \rightarrow 0 I_0(\pm 1 + \varphi)^2 \simeq I_0 \left( 1 \pm \frac{b \Delta}{\Gamma} \right). \tag{24.143}
\]

The intensity \( \bar{I}_{pc} \) is linear in \( b \) and, consequently, more sensitive to weak signals. Finally, a third technique, called \textit{polarization contrast imaging}, detects the local birefringence of the atomic cloud \[82, 517\].

The imaging techniques shown so far only allow to visualize the instantaneous density distribution of the atomic cloud \( n(r) \). If we are interested in other quantities, we have to conceive the experiment in such a way, that the desired information leaves its signatures in the density distribution. For example, to measure the excitation frequencies of a condensate, which can perturb its shape and observe the subsequent time evolution of \( n(r,t) \) via dispersive imaging \[323, 415, 15, 339\].
24.6.4 Reconstruction of column-integrated absorption images

Assume cylindrical symmetry \( n(r, z) = n(r, z) \), with \( r = \sqrt{x^2 + y^2} \). Absorption images are *column-integrated*, i.e. they are taken by integration along the \( x \)-axis,

\[
\frac{I(y, z)}{I_0(y, z)} = e^{-\sigma \int n(r, z) \, dx} = e^{-\sigma f(y, z)}.
\]  

(24.144)

The radial density can be recovered by tomography [145, 175, 461],

\[
n(r, z) = \frac{1}{(2\pi)^2} \int (\mathcal{F}_y f)(\kappa_y, z) J_0(\kappa_y r) \, d\kappa_y.
\]  

(24.145)

This is called *image reconstruction* or *Fourier reconstruction* or *inverse Abel transform* and will we studied in Exc. 24.6.6.3.

24.6.5 Condensable atomic species

Early work on BEC has been done by [530, 36, 59, 102, 379]. Proposals for atomic gases withe from [264, 585, 581]. An appropriate BEC candidate must fulfill a few conditions: The transition wavelengths must be *accessible by laser light*, the level scheme should exhibit a *closed cycling transition* for laser cooling and have a reasonable pressure in gas phase. Furthermore, it is desirable to have a large HFS, metastable electronic state, no trapping state, large positive scattering length, Feshbach resonances. For sympathetic cooling it may be nice to have several isotopes of the same element.

The most common elements are alkalis, alkali earths and noble gases. The following gases have already been condensed \( ^1\text{H}, ^1\text{He}^*, ^7\text{Li}, ^{23}\text{Na}, ^{85}\text{Rb}, \) and \( ^{87}\text{Rb} [12], [141], [83], [82], [518], [256], [260]. \) Investigations in \( ^1\text{Ne}^*, ^{39}\text{K}, ^{133}\text{Cs}, ^{88}\text{Sr}, ^{95}\text{Cr} \) and \( ^{40}\text{Ca} \) are underway [564], [242], [349], [486], [553], [43], [205].

24.6.6 Exercises

24.6.6.1 Ex: Lensing by cold clouds

The interaction of light with two-level atoms generates a susceptibility which gives rise to a refraction index,

\[
\eta(r) = \sqrt{1 - \frac{4\pi n(r)}{k^3(2\Delta/\Gamma + i)}}.
\]

where \( n(r) \) is the cloud’s density distribution and \( \Gamma/2\pi = 30.5 \text{ MHz} \) for strontium.

a. Calculate the phase-shift suffered by a light beam crossing an ultracold atomic cloud \( (N = 10^5, T = 1 \mu\text{K}) \) confined in an isotropic harmonic trap \( (\omega_{trp} = (2\pi) 100 \text{ Hz}) \) as a function of detuning.

b. Estimate the focal distance of the cloud for \( \Delta = -\Gamma \).
24.6.6.2 Ex: Optical density

A cloud of $N = 10^6 ^{87}$Rb atoms is prepared in a cylindrical harmonic trap characterized by the axial vibration frequencies $\omega_z = (2\pi) 50$ Hz and the radial one $\omega_r = (2\pi) 200$ Hz. The experimenter takes the absorption image after 18 ms time-of-flight, as shown in Fig. 24.31(a). A pixel of the CCD camera corresponds to 5 $\mu$m in real space.

a. At what temperature is the phase transition to Bose-Einstein condensate to be expected?
b. Determine the temperature of the sample.
c. Evaluate its density distribution.
d. Evaluate the resonant optical density for the $D2$-transition at 780 nm along the symmetry axis of the trapped cloud.

24.6.6.3 Ex: Inverse Abel transformation

Calculate the inverse Abel transform using Bessel of an arbitrary function in 2D.
Chapter 25

Thermodynamics of ideal quantum gases

The journey of the quest for Bose-Einstein condensation (BEC) begins with its prediction by Bose and Einstein in 1926. The first hint, that the condensation was more than just a theoretical fantasy came from London [381], who linked the newly discovered phenomenon of superfluidity in $^4$He to BEC. However, the interpretation of the $\lambda$-point in terms of BEC was not obvious, because strong interactions between particles concealed the role of quantum statistics, and the thermodynamic potentials exhibited divergences at the critical temperature instead of discontinuities, as expected for an ideal gas BEC. These uncertainties triggered an intense search for other systems. In 1954, Schafroth pointed out that electron pairs can be seen as composite bosons and may form Bose-Einstein condensates at low temperatures [530]. In 1957, Bardeen, Cooper and Schrieffer developed the microscopic theory of superconductivity [36], after other researchers, including Blutt, Schaffrot, Fröhlich and Bogolubov, had suggested a relationship of this phenomenon to Bose condensation of electron pairs (nowadays called Cooper pairs).

Figure 25.1: Illustration of atomic Broglie waves. From the top to the bottom the temperature of the atoms is decreasing.

Motivated by the need to test the concept of condensation of composite particles
in weakly interacting systems, in 1962 Blatt et al. proposed the investigation of the BEC in gases of excitons [59]. Excitons are bound electron-hole pairs that can form a weakly interacting gas in certain non-metallic crystals. They are interesting because their small mass allows BEC at high temperatures and gas density can be controlled over a wide range, by only modifying the intensity of the optical excitation. Being quasi-particles, excitons can be created and annihilated, that is their number is not conserved. Excitons were discovered in 1968, and the first evidence for Bose-Einstein of biexciton molecules in a CuCl crystal dates back to 1979 [102].

The laser as coherence phenomenon between photons shares many analogies with condensates. However, photons are quasi-particles as well, and again their number is not conserved\(^1\). Hence, there is no phase transition: When an optical cavity containing photonic modes is cooled, the photons prefer to disappear in the walls of the cavity instead of condensing.

Hecht [264] suggested in 1959, followed by Stwalley and Nosanow [585] in 1976, that an atomic hydrogen gas with polarized spins would be an appropriate candidate for BEC. The advantage of this system is that interactions between atoms are weak and only give rise to a negligible quantum depletion below 1%. In 1978 Greytak and Kleppner started at the MIT intensive efforts to generate BECs in dilute hydrogen gases. In the 1990s, important advances in the cooling of atoms using laser light allowed to reach very low temperatures, and the invention of the magneto-optical trap (MOT) for neutral atoms permitted their spatial confinement and the compression of their density. These successes boosted efforts to try to create BEC in alkaline gases, which have electronic level schemes that lend themselves to optical cooling. Later, it was discovered that the phase space density in MOTs is limited by radiation trapping effects. As a solution to this problem, scientists had to learn how to trap atoms without the use of light in conservative traps, e.g. by their magnetic dipole moment, and to replace optical cooling with evaporative cooling. This was the crucial step that finally permitted to reach BEC in alkaline gases in 1995. Later, the hydrogen experiment, which initially stimulated the alkaline experiments, now taking advantage of their success, has been taken to BEC as well [205].

Why did it take so long to reach Bose-Einstein condensation, seven decades after its prediction by Bose and Einstein? How can we see when we have a condensate? What are the characteristics of a BEC accessible to observation and how to measure them? These are the answers that we will answer in the following sections. Solve

---

\(^1\)The chemical potential of photons is \(\mu = 0\).
25.1 Quantum statistics of an ideal Bose gas

The canonical approach to statistical mechanics begins with the probabilistic analysis of Boltzmann’s velocity distribution of an ideal gas. For a gas consisting of particles of mass \( m \) at temperature \( T \), the velocity distribution is given by the well-known Maxwell-Boltzmann law (MB) [298]

\[
g(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T},
\]

where \( k_B \) is the Boltzmann constant. Maxwell-Boltzmann’s law was experimentally proven by Otto Stern in 1920, using a primitive atomic beam and a simple time-of-flight technique based on a rotating drum for selecting atomic velocities. With the advent of laser spectroscopy, the MB law and its limitations can be tested with highly improved accuracy. This law describes well the behavior of weakly interacting hot atoms. Deviations from this law are insignificant until, at low temperatures, quantum effects come into play. For this to happen the temperature must be so low that the atomic Broglie wavelengths become comparable to the average distance between particles. For a gas in thermal equilibrium the characteristic wavelength, called thermal de Broglie wavelength, is,

\[
\lambda_{\text{therm}} = \sqrt{\frac{2\pi}{m k_B T}},
\]

(25.2)

where \( h = h/2\pi \) is Planck’s constant. In a gas of density \( n \), the mean distance between particles is \( n^{-1/3} \). So, quantum effects are expected to emerge when \( n^{-1/3} \sim \lambda_{dB}(T) \), such that the limit for this regime is defined by,

\[
k_B T(n) = \frac{2\pi h^2}{m n^{2/3}}.
\]

(25.3)

For example, an atomic gas with density \( n \sim 10^{16} \text{ cm}^{-3} \) and temperature 900 K is certainly in the classical regime, since \( n^{-1/3} \sim 10^6 \text{ cm} \gg \lambda_{dB} = 10^{-9} \text{ cm} \). To observe quantum effects, we need relatively dense and cold clouds of atoms. In most gases, lowering the temperature or increasing the density promotes the system to liquidity before the quantum regime is reached. Well-known exceptions are spin-polarized hydrogen (H↑), which does not become liquid and helium, which exhibits quantum degeneracy effects in the liquid phase, although these effects are quite complex due to strong interparticle forces.

We have already seen that all particles in the quantum world are either bosons with integer spin or fermions with semi-integer spin. Fermions do not share a quantum state, because they must follow the Pauli’s exclusion principle. They obey a quantum statistical distribution called Fermi-Dirac distribution (FD). In contrast, bosons enjoy to share a quantum state and even encourage other bosons to join them in a process called bosonic stimulation. Bosons obey a quantum statistical distribution called Bose-Einstein distribution (BE). The basic difference between the MB-statistics on one hand and the BE- or FD-quantum statistics on the other is that the former applies to identical particles which, however, are distinguishable from each other, while the
second describes identical indistinguishable particles. For the BE/FD statistics one can derive \([345]\) the occupancy number for a non-degenerate quantum state having the energy \(\epsilon\) when the system is kept at temperature \(T\),

\[
w_{T,\mu} = \frac{1}{(2\pi)^3} \frac{1}{e^{\beta(\epsilon-\mu)} + 1},
\]

(25.4)

where we used the abbreviation \(\beta \equiv 1/k_B T\). The upper sign refers to the BE statistics, the lower sign to the FD statistics. The chemical potential \(\mu\) is an important system parameter, which helps to normalize the distribution (25.4) to the total number of particles,

\[
N = \sum_\epsilon w_{T,\mu}(\epsilon).
\]

(25.5)

Similarly, the total energy of the system is given by,

\[
E = \sum_\epsilon \epsilon w_{T,\mu}(\epsilon).
\]

(25.6)

A very remarkable effect occurs in a bosonic gas at a certain characteristic critical temperature \(T_c\): below this temperature a substantial fraction of the total number of particles occupies the lowest energy state, while all other states are occupied by a negligible number of particles. Above the transition temperature the macroscopic observables of the gas, such as pressure, heat capacity, etc., receive contributions of all states with a certain statistical weight, but without favoring the state of lower energy. Below the transition temperature, the observables are altered by a macroscopic occupation of the ground state, which results in dramatic changes of the thermodynamic properties. The phase transition is named after Shandrasekar Bose [77] and Albert Einstein [184] Bose-Einstein condensation (BEC).

### 25.1.1 Condensation of a free gas confined in a box potential

One of the keys to understanding BEC is the behavior of the chemical potential \(\mu\) at very low temperatures. The chemical potential is responsible for the concentration of a large number of atoms in the ground state \(N_0\). A system with a large number of non-interacting bosons condenses to the ground state when the temperature approaches zero, \(N_0 \to N\). The Bose-Einstein distribution function (25.4) gives the population of the ground state, \(\epsilon = 0\), in the zero temperature limit, \(N = \lim_{T \to 0} (e^{-\beta\mu} - 1)^{-1} = -1/\beta \mu\), or in terms of the fugacity defined by,

\[
Z \equiv e^{\beta \mu},
\]

(25.7)

we may write, \(Z \simeq 1 - 1/N\). It should be noted that the chemical potential in a bosonic system must always be less than the ground state energy in order to guarantee non-negative occupation \(w_{T,\mu}(\epsilon)\) of any state. \(Z \simeq 1\) denotes macroscopic occupation of the ground state. We define the critical temperature for Bose-Einstein condensation via the occupation of the ground state. Above this temperature the occupancy of ground state is not macroscopic, below it is.
For a Bose gas of \( N \) non-interacting particles with mass \( m \) confined inside a box potential of volume \( V = L^3 \) the critical temperature for BEC can be calculated from equation (25.3). The boundary conditions require that the momenta satisfy \( p_j = 2\pi \hbar l_j/L \), where \( j = x, y \) or \( z \) and \( j \) are integers. Each state is labeled by a set of three integers \((l_x, l_y, l_z)\). In the \textit{thermodynamic limit}, the sum over all quantum states can be converted into an integral over a continuum of states,

\[
\sum_{\mathbf{r}, \mathbf{k}} \frac{N \to \infty}{\hbar^3} \int d^3r d^3p = \int d^3r d^3k . \tag{25.8}
\]

For a free gas with energy \( \varepsilon = \frac{p^2}{2m} \) we can derive, simplifying the calculation using the \textit{density of states} \( \eta \) defined by (24.19), which basically depends on the geometry of our system. Using the occupation number \( w_{T,\mu}(\varepsilon) \) for the Bose-Einstein distribution (25.4) in the thermodynamic limit and the density-of-states in a box potential (24.22), let us calculate the total number of particles,

\[
N = N_0 + \int \int w_{T,\mu}(\varepsilon(\mathbf{r}, \mathbf{k}))d^3r d^3k = N_0 + (2\pi)^3 \int_0^\infty w_{T,\mu}(\varepsilon)\eta(\varepsilon)d\varepsilon \tag{25.9}
\]

where the ground state population \( N_0 \) is maintained explicitly. In the process of converting the sum to an integral (25.8) the density of states disappears when we approach the ground state. This error is corrected by adding a contribution of an explicit term \( N_0 \) to the integral.

### 25.1.1.1 Riemann’s zeta function

At this point, to help simplifying the notation, we introduce the \textit{Bose function} and its integral representation,

\[
g_\xi(Z) = \sum_{t=1}^\infty \frac{Z^t}{t^\xi} = \frac{1}{\Gamma(\xi)} \int_0^\infty \frac{x^{\xi-1}dx}{Z^{-1}e^x - 1} . \tag{25.10}
\]

where \( \Gamma(\eta) \) denotes the Gamma function. Analogically, we can define the \textit{Fermi function} via,

\[
f_\xi(Z) = \sum_{t=1}^\infty \frac{(-Z)^t}{t^\xi} = \frac{1}{\Gamma(\xi)} \int_0^\infty \frac{x^{\xi-1}dx}{Z^{-1}e^x + 1} . \tag{25.11}
\]

For classical particles,

\[
c_\xi(Z) = \frac{1}{\Gamma(\xi)} \int_0^\infty \frac{x^{\xi-1}dx}{Z^{-1}e^x + 0} = Z . \tag{25.12}
\]

A particular value is the \textit{Riemann zeta-function},

\[
g_\xi(1) = \zeta(\xi) . \tag{25.13}
\]
With this definition and the definition of the thermal Broglie wavelength (25.2), Eq. (25.9) becomes,

\[ N = N_0 + \frac{V}{\lambda_{\text{th}}^3(T)} g_{3/2}(e^{\beta \mu}) . \]  

(25.14)

We can use Eq. (25.14) to calculate the critical temperature\(^3\) \(T_c(3/2)\) defined for \(N_0 \nearrow 0\) and \(\mu \to 0\). Above the phase transition, \(T > T_c(3/2)\), the population is distributed over all states, each individual state being weakly populated. Below \(T_c(3/2)\) the chemical potential is fixed by \(\mu = 0\) and the number of the particles occupying the excited states is,

\[ N_{\text{th}} = \frac{V}{\lambda_{\text{th}}^3(T)} g_{3/2}(1) = N \left( \frac{T}{T_c(3/2)} \right)^{3/2} , \]  

(25.15)

with \(g_{3/2}(1) = 2.612\). Since \(N_0 + N_{\text{th}} = N\), the number of particles in the ground state is given by,

\[ \frac{N_0}{N} = 1 - \left( \frac{\min(T, T_c(3/2))}{T_c(3/2)} \right)^{3/2} \quad \text{with} \quad k_B T_c(3/2) = \frac{2\pi\hbar^2}{m} \left( \frac{N}{V g_{3/2}(1)} \right)^{2/3} , \]  

(25.16)

\(N_0/N\) is the fraction of the atomic cloud which is condensed in the ground state. The abrupt occurrence of a finite occupation in a single quantum state at temperature below \(T_c(3/2)\) indicates a spontaneous change in the system and a thermodynamic phase transition. Solve Exc. 25.1.5.2.

\(^2\)We must, however, keep in mind that the state density approach is an approximation not valid for experiments with a limited number of atoms.

\(^3\)The superscript \((3/2)\) denotes the box potential shape of the trapping potential. See 25.1.5.3 for an explanation of the notation.
25.1.2 Condensation of a harmonically confined gas

The critical temperature $T_c^0$ can be significantly altered, when the atoms are confined to a spatially inhomogeneous potential. The critical temperature depends on the general shape and the tightness of the potential. Let us consider $N$ particles of an ideal Bose gas distributed over several quantum states of an arbitrary potential. The occupation number $w_{T,\mu}(\varepsilon)$ of particles at an energy level $\varepsilon$ is still given by (25.4), the ground state energy is defined as zero. In the thermodynamic limit, the relation between the chemical potential and the total number of particles is still given by Eq. (25.9), with an adequate density of states $\eta(\varepsilon)$. The state density for an arbitrary confinement potential $U(\mathbf{r})$ can be found by generalizing the calculation to the free gas. The phase space volume between the energy surfaces $\varepsilon$ and $\varepsilon + d\varepsilon$ is proportional to the number of states in this energy range. However, the external potential limits the space available for the gas. For a harmonic potential (24.18) with the mean secular frequency $\bar{\omega}$ the density-of-states $\eta(\varepsilon)$ has already been calculated in Eq. (24.21). With this, we can analogically to (25.9) calculate,

\[
N = N_0 + \int\int w_{T,\mu}(\varepsilon(\mathbf{r}, \mathbf{k}))d^3r d^3k = N_0 + (2\pi)^3 \int_0^\infty w_{T,\mu}(\varepsilon)\eta(\varepsilon)d\varepsilon
= N_0 + \frac{1}{2(h\bar{\omega})^3} \int_0^\infty \frac{\varepsilon^2 d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} = N_0 + \left(\frac{k_B T}{h\bar{\omega}}\right)^3 g_3(Z).
\]

In the same way as for a potential well we find for a harmonic potential,

\[
N_{th} = \left(\frac{k_B T}{h\bar{\omega}}\right)^3 g_3(1) = N \left(\frac{T}{T_c^{(3)}}\right)^3,
\]

with $g_3(1) = 1.202$. Since $N_0 + N_{th} = N$, the number of particles in the ground state is,

\[
\frac{N_0}{N} = 1 - \left(\frac{\min(T, T_c^{(3)})}{T_c^{(3)}}\right)^3 \quad \text{with} \quad k_B T_c^{(3)} = h\bar{\omega} \left(\frac{N}{g_3(1)}\right)^{1/3}.
\]

The superscript (3) indicates the harmonic shape of the trap.

Fig. 25.4(left) traces the condensed fraction $N_c/N$ measured as a function of the reduced temperature $T/T_c^{(3)}$. Experiments [256, 189] confirm Bose’s ideal gas theory in the thermodynamic limit.

We note that smaller trapping volumes (or tighter potentials) increase the critical temperature $T_c$, thus allowing for quantum degeneracy at higher temperatures, which can be advantageous in experimentation. Also, at a given temperature, a strongly confining potential reduces the total minimum number of atoms required to reach condensation.

25.1.3 Energy and heat capacity

When the number of atoms is limited, $N < \infty$, we expect a slightly reduced critical temperature [239]. In addition, the interatomic interaction reduces the critical temperature [29]. The technical resolution of most experiments today is not sufficient to
permit the study of these effects. However, measurements of other thermodynamic quantities such as energy and heat capacity [149, 189] showed significant deviations from the ideal gas behavior due to interaction effects. Therefore, although temperature being the most basic variable of the thermodynamic state, the system needs to be characterized by other quantities.

Heat is not a state variable because the amount of heat needed to raise the temperature of the system depends on how the heat is transferred. The heat capacity quantifies the system’s ability to secure its energy. In conventional systems, the heat capacity is typically given either specified at constant volume or at constant pressure. Together with this specification, heat capacities are extensive state variables. When crossing a phase transition, the temperature-dependent heat capacity measures the degree of change in the system above and below the critical temperature and provides valuable information about the general type of phase transition.

The total energy $E/N \equiv N^{-1} \int \epsilon w(x) d^3 k$ per particle is given by,

$$
\frac{E}{N} = \frac{\int \epsilon w(x, k) d^3 x d^3 k}{\int w(x, k) d^3 x d^3 k} = \frac{\int \epsilon \eta(e) e^{\beta(e-\mu)} - 1 d\epsilon}{\int \eta(e) e^{\beta(e-\mu)} - 1 d\epsilon} = 3k_B T g_4(Z) / g_3(Z) .
$$

(25.20)

For a confined gas, volume and temperature are interdependent, and the concept of pressure is somewhat vague. In this case, we can not refer to the heat capacity at constant volume or pressure. However, one can define the heat capacity for a fixed number of particles,

$$
C(T) = \frac{\partial E(T)}{\partial T} .
$$

(25.21)

Recalling the implicit dependencies of the thermodynamic variables on temperature,
we can evaluate (25.19):

\[ C(T) = \beta \int_0^\infty \varepsilon f(\varepsilon)^2 \rho(\varepsilon) \left[ \mu'(T) + \frac{\varepsilon - \mu}{T} \right] e^{\beta(\varepsilon - \mu)} d\varepsilon , \]  

(25.22)

where the derivative of the chemical potential approaching the phase transition from above, \( T \searrow T_c^0 \), is

\[ \mu'(T_c^+) = -\frac{1}{T} \int_0^\infty \varepsilon f(\varepsilon)^2 \rho(\varepsilon) e^{\beta\varepsilon} d\varepsilon . \]  

(25.23)

Calculating the second moments of the distributions obtained for the same density by time-of-flight of absorption images, we obtain the kinetic energy,

\[ U = \int \frac{p^2}{2m} n(p) d^3p . \]  

(25.24)

For confined ideal gases, the virial theorem ensures \( E_{\text{kin}} + E_{\text{pot}} = 2E_{\text{kin}} \). For real gases, the repulsive energy of the mean field adds to this energy, \( E = E_{\text{kin}} + E_{\text{pot}} + E_{\text{self}} \). The sudden extinction of the trapping potential before time-of-flight takes away the potential energy \( E_{\text{pot}} \) non-adiabatically. The kinetic energy and the self-energy of the condensate are fully converted into kinetic energy during ballistic expansion. It is this energy, \( p^2/2m = E_{\text{kin}} + E_{\text{self}} \), which is sometimes called release energy, which is measured after ballistic expansion \(^4\). Fig. 25.4(right) shows a measurement of the release energy. Solve the Exc. 25.1.5.3.

\(^4\)It is interesting to measure the heat capacity of a partially condensed cloud near the critical point and analyze the discontinuity, because it contains important information about interatomic
25.1.4 Distribution functions for a Bose gas

Bose-Einstein condensates consist of atoms sharing a single quantum state. In inhomogeneous potentials, the condensate and the thermal fraction form spatially separated clouds, concentrated around the center of the potential and therefore very dense. For this reason, interatomic interaction effects generally dominate the density and momentum distribution of the condensed fraction. However, the non-condensed (or normal, or thermal) fraction is also subject to modifications due to the bosonic nature of the atoms. Since the density of the normal fraction is generally much smaller, these modifications are weak. In this section, we will only discuss these effects briefly, but we note that the calculations are analogous to the calculations for fermionic gases presented in Sec. 25.2.4.

For an ideal Bose gas the density and momentum distributions are expressed by Bose functions $g_{3/2}(z)$. For example, as will be derived in Exc. 25.1.5.4(a), the density and momentum distributions are,

$$n(x) = \frac{1}{\lambda_d^3} g_{3/2}(e^{-\beta[U(x)-\mu]})$$

$$n(k) = \frac{a_{\text{trap}}^6}{\lambda_d^3} g_{3/2}(e^{\beta(p^2/2m)})$$

In the classical limit, we can calibrate the chemical potential by Eq. (25.14) for a box potential or by (25.17) for a harmonic potential,

$$g_{3/2}(e^{\beta\mu}) \rightarrow c_{3/2}(e^{\beta\mu}) = e^{\beta\mu} = \begin{cases} \frac{N}{V} \lambda_{th}^3 & \text{for a box potential} \\ c_3(e^{\beta\mu}) = N \left( \frac{\hbar \omega}{k_B T} \right)^3 & \text{for a harmonic potential} \end{cases}$$

Hence, we obtain for the classical density distribution,

$$n(x) = \frac{1}{\lambda_{th}^3} c_{3/2}(e^{-\beta[U(x)-\mu]}) = \frac{e^{\beta\mu}}{\lambda_{th}^3} e^{-\beta U(x)}$$

$$= \begin{cases} \frac{N}{V} e^{-\beta U(x)} & \text{for a box potential} \\ N \sqrt{\frac{m \omega^2}{2\pi k_B T}} e^{-\beta m \omega^2 x^2/2} & \text{for a harmonic potential} \end{cases}$$

Similarly, the momentum density distribution is given by,

$$n(k) = \frac{a_{\text{trap}}^6}{\lambda_{th}^3} c_{3/2}(e^{\beta(p^2/2m)}) = \frac{a_{\text{trap}}^6 e^{\beta\mu}}{\lambda_{th}^3} e^{-\beta p^2/2m}$$

$$= \begin{cases} \frac{N}{V} a_{\text{trap}}^6 e^{-\beta U(x)} & \text{for a box potential} \\ N k_{th}^3 \sqrt{\frac{1}{2\pi m k_B T}} e^{-\beta p^2/2m} & \text{for a harmonic potential} \end{cases}$$

interactions and finite-size effects ([124], Sec. 3.4). In addition, the classification of Bose-Einstein condensation as a phase transition depends very much on the behavior of the thermodynamic potential near the critical point [368, 298].
We see that we recover the Maxwell-Boltzmann velocity distribution, as seen in Fig. 25.6,

\[ n(v) = n(k) \frac{m^3}{\hbar^3} = N \sqrt{\frac{m}{2\pi k_B T}} e^{-\beta m v^2/2}. \]  

(25.29)

Figure 25.6: (a) Density and (b) momentum distribution of a Bose gas (red) and a Boltzmann gas (green) at \( T = 1.1 T_c \) (solid line) and at \( T = 2 T_c \) (dotted line).

### 25.1.4.1 Ballistic expansion

To describe the density distribution of an ultracold Bose-gas after a time-of-flight we replace in the second Eq. (25.25): \( k = m r / \hbar t_{tof} \). We obtain the density distribution,

\[ n_{tof}(r, t_{tof}) = \left( \frac{m}{\hbar t_{tof}} \right)^3 n(k = m r / \hbar t_{tof}) = \left( \frac{m}{\hbar t_{tof}} \right)^3 \frac{a_{trp}^6}{\lambda^3_{th}} g_3/2 \langle e^{(\mu - m r^2 / 2t_{tof}^2)/k_B T} \rangle \]

(25.30)

\[ T \to \infty \left( \frac{m}{\hbar t_{tof}} \right)^3 N \hbar^3 \sqrt{\frac{1}{2\pi m k_B T}} e^{-mr^2/2t_{tof}^2 k_B T} = \frac{N}{(2\pi)^{3/2} r_{rms}^3} e^{-v^2/2r_{rms}^2}, \]

where we defined,

\[ r_{rms} = \frac{k_B T t_{tof}}{m}. \]  

(25.31)

This distribution does not directly depend on the potential \( U(r) \), that is, the expansion is isotropic. However, the chemical potential does depend on the potential. For very long flight times (usually several 10 ms) the density resembles a Gaussian distribution \[124]. In Exc. 25.1.5.4(b) we determine the time-of-flight density distribution of an ultracold Bose gas.

In a time-of-flight experiment, any deviation observed between the results (25.30) and (25.31) points towards an impact of quantum statistics. However, absorption images only record projections of the time-of-flight distribution on a plane.
25.1.4.2 Temperature and excitations

The temperature of a Bose condensate is given by the ratio of the numbers of condensed and thermal atoms. What about collective excitations in pure condensate? Can they be cooled? In fact, an oscillating BEC is not in thermal equilibrium. However, in the presence of some dissipation mechanism the excitations may thermalize evolving towards a steady state. Once the collective excitations have become thermal excitations, they simply increase the thermal fraction.

25.1.5 Exercises

25.1.5.1 Ex: Boson or fermion?

Whether an atom is a fermion or boson solely depends on its total spin. Half-integer spin particles are fermions, integer spin particles are bosons. For example, Rb atoms have in the ground state \( J = 1/2, I = 7/2 \) and \( F \) integer, and therefore are bosons. Ca\(^+\) ions have \( J = 1/2 \) and no hyperfine structure, and thus are fermions. \(^6\)Li has the half-integer \( F \) and is a boson.

Decide on the bosonic or fermionic nature of the following atoms/molecules:

- \(^{85}\)Rb with \( I = 3/2 \) in the state \( ^2S_{1/2} \)
- \(^{88}\)Sr with \( I = 0 \) in the state \( ^1S_0 \)
- \(^{88}\)Sr with \( I = 0 \) in the state \( ^3P_2 \)
- \(^{87}\)Sr with \( I = 9/2 \) in the state \( ^1S_0 \)
- \(^{172}\)Yb\(^+\) with \( I = 0 \) in the state \( ^2S_{1/2} \)
- \(^{171}\)Yb\(^+\) with \( I = 1/2 \) in the state \( ^2S_{1/2} \)

25.1.5.2 Ex: Monoatomic gas

Consider a classical monoatomic gas made up of \( N \) non-interacting atoms of mass \( m \) confined in a container of volume \( V \), at temperature \( T \). The Hamiltonian corresponding to an atom is given by \( \hat{H} = (p_x^2 + p_y^2 + p_z^2)/2m \).

a. Show that the atomic canonical partition function is \( \zeta = V/\lambda^3 \), where \( \lambda = h/\sqrt{2\pi mk_BT} \) is the thermal de Broglie wavelength.

b. Using \( \zeta \) of the previous item, obtain the system’s partition function \( Z \) and the Helmholtz free energy \( F \). Also obtain the free energy per atom \( f = F/N \) in the thermodynamic limit \( N \to \infty, V \to \infty, v = N/V \) fixed.

c. Obtain internal energy \( U \) and the gas pressure \( p \).

d. Calculate the chemical potential and entropy per atom in the thermodynamic limit.

25.1.5.3 Ex: Generalization for arbitrary potentials in reduced dimensions

The calculation of the thermodynamic potentials can be generalized to arbitrary trapping potentials and dimensions [77, 184, 144, 288, 647, 289, 290, 239, 278, 344, 338, 448, 368, 381, 189]. To do so, we consider a generic power law potential confining an ideal Bose gas in \( \alpha \) dimensions,

\[
U(r) = \sum_{i=1}^{\alpha} \left| \frac{x_i}{a_i} \right|^{t_i},
\]
and define a parameter describing the confinement power of the potential,

\[ \xi = \frac{\alpha}{2} + \sum_{i=1}^{\alpha} \frac{1}{t_i}. \]

For example, for a three-dimensional potential, \( \alpha = 3 \). Now, for a 3D harmonic potential, \( \xi = 3 \), and for 3D box potential, \( \xi = 3/2 \).

a. Calculate the density of states \( \eta \) using the equation (24.19) employing Bose functions (25.10).

b. Prove the following expressions:

\[
\begin{align*}
\frac{N_0}{N} &= 1 - \left( \frac{\min(T, T_c)}{T_c} \right)^\xi \\
\frac{E}{N k_B T} &= \xi \frac{g_{\xi+1}(Z) \left( \frac{\min(T, T_c)}{T_c} \right)^\xi}{g_\xi(Z)} \\
\frac{S}{N k_B} &= \frac{4 \xi g_{\xi+1}(Z) - 2 \mu}{k_B T} \\
\frac{C}{N k_B} &= \xi (\xi + 1) \frac{g_{\xi+1}(Z) \left( \frac{\min(T, T_c)}{T_c} \right)^\xi}{g_\xi(Z)} - \xi^2 \frac{g_\xi(Z)}{g_{\xi-1}(Z)} \frac{g_{\eta-1}(Z)}{g_\eta(Z)} \frac{\max(T - T_c, 0)}{T - T_c} \right) \\
\frac{C_{T<T_c}}{N k_B} &= \xi (\xi + 1) \frac{g_{\xi+1}(1)}{g_\xi(1)} \\
\frac{C_{T>T_c}}{N k_B} &= \frac{C_{T<T_c} - C_{T_c^+}}{N k_B} = \xi^2 \frac{g_\xi(1)}{g_{\xi-1}(1)} \\
\end{align*}
\]

25.1.5.4 Ex: Time-of-flight distribution of a Bose-gas

a. Derive the formulae (25.25) describing the density and momentum distribution of an ultracold Bose-gas.

b. Calculate the time-of-flight distribution of a Bose-gas as a function of temperature (i) analytically for a harmonic potential and (ii) numerically for an arbitrary potential.

25.2 Quantum statistics of an ideal Fermi gas

Atoms are fermions or bosons, or depending on their spin is integer or semi-integer. For example, \(^{87}\text{Rb}\) atoms with their total integer spin of \( F \) are bosons, while \(^{40}\text{K}\) atoms having a half-integer spin are fermions. At high phase space densities, atoms have to figure out how they will organize their coexistence. Bosons encourage each other to occupy the same phase space cell, in contrast to the reluctant fermions, which prefer to follow Pauli’s exclusion principle. The different behavior is described by different quantum statistics that determine how the phase space (i.e., the available energy levels) has to be filled by the atoms. The Bose-Einstein distribution is valid for bosons, the distribution of Fermi-Dirac for fermions and both asymptotically approach the Boltzmann distribution at high temperatures. We have seen that bosons undergo a phase transition and condense in the ground state when the temperature is reduced.
below a critical threshold. On the other hand, the fermions organize their phase space, so that their energy levels are arranged like a ladder. The impact of fermionic quantum statistics on a cold cloud of atoms were observed experimentally by DeMarco and Jin [149, 453]. They cooled a two-components Fermi gas of $7 \times 10^5$ potassium atoms down to 300 nK, which corresponded to 60% of the atoms populating energy levels below the Fermi energy. The measured density distribution was found to deviate from the one expected for an ideal Boltzmann gas.

25.2.1 Chemical potential and Fermi radius for a harmonic trap

The phase space density for a degenerate Fermi gas has already been given in (25.4). In the same way as for a Bose gas, the chemical potential must satisfy the normalization condition,

$$N = \int \int w_{T,\mu}(x, k) d^3x d^3k = (2\pi)^3 \int w_{T,\mu}(\varepsilon) \eta(\varepsilon) d\varepsilon$$  \hspace{1cm} (25.32)

$$= \frac{1}{2(\hbar\omega)^3} \int_0^{\infty} \frac{\varepsilon^2 d\varepsilon}{e^{\beta(\varepsilon - \mu)} + 1} = \left(\frac{k_B T}{\hbar\omega}\right)^3 f_3(Z).$$

In the last line, we inserted the density of the states into a harmonic potential (24.21) and used the definition of the Fermi functions (25.11).

For low temperatures, $x \equiv \mu \gg 1$, we can use the Sommerfeld expansion which in first order gives $f_\eta(e^x) \simeq x^n / \Gamma(n+1)$. From this we immediately obtain the energy, the Fermi radius and the momentum of free particles,

$$E_F = \mu(T = 0) = \hbar\omega(6N)^{1/3}$$  \hspace{1cm} (25.33)

$$r_F = \sqrt{\frac{2E_F}{m\omega^2_0}} \quad \text{and} \quad z_F = \sqrt{\frac{2E_F}{m\omega^2_0}}$$

$$K_F = \sqrt{\frac{2mE_F}{\hbar^2}}.$$

Using the second order of the Sommerfeld expansion, $f_\xi(e^x) \simeq \frac{x^4}{\Gamma(\xi+1)} \left(1 + \frac{\pi^2\xi(1 - \xi)}{6x^2} + \ldots\right)$, we obtain for the chemical potential the equation, $0 = \mu^3 + \left(\pi k_B T\right)^2 \mu - E_F^3$. The approximate solution of this equation, neglecting terms such as $4\pi^6 k_B T^6 \ll 27E_F^6$, is

$$\mu = E_F \left[1 - \frac{\pi^2}{3} \left(\frac{k_B T}{E_F}\right)^2\right].$$  \hspace{1cm} (25.34)

\footnote{We note that meanwhile ultracold two-components Fermi gas have been demonstrated to form bosonic Cooper-pairs, similarly to the phenomena known as superconductivity in some metals and as superfluidity of the fermionic $^3$He.}
In the limit of high temperatures, $f_\eta(Z) \xrightarrow{Z \to 1} Z$

$$N = \left( \frac{k_B T}{\hbar \omega} \right)^3 e^{\beta \mu} = \left( \frac{k_B T}{\hbar \omega} \right)^3 (1 + \beta \mu + ...) \quad (25.35)$$

$$\mu \approx k_B T \ln N \left( \frac{\hbar \omega}{k_B T} \right)^3 = k_B T \ln \frac{1}{6} \left( \frac{E_F}{k_B T} \right)^3 (1 + \beta \mu + ...) \quad (25.35)$$

This means that we recover the *Boltzmann gas*, which satisfies an ideal gas equation similar to that of particles in a box potential,

$$N = \left( \frac{k_B T}{\hbar \omega} \right)^3 \quad \text{(Boltzmann)} \quad (25.36)$$

For comparison, for bosons we have,

$$\frac{N_0}{N} = 1 - \left( \frac{T}{T_c} \right)^3 \frac{g_3(Z)}{g_3(1)} \quad \text{(Bose)} \quad (25.37)$$

The chemical potentials are calculated in Fig. 25.7(a).

#### 25.2.2 Energy

The total energy $E_1 \equiv E/N \equiv N^{-1} \iint \epsilon w^d x d^3k$ per particle is given by,

$$E_1 = \frac{\int \epsilon w_{T,\mu}(x,k) d^3x d^3k}{\int w_{T,\mu}(x,k) d^3x d^3k} \approx \frac{3 k_B T f_4(Z)}{f_3(Z)}.$$

Again using the Sommerfeld approximation, we see that for $T \to 0$ the energy is limited by

$$E_1 = \frac{3}{N \beta (\beta \hbar \omega)^3} f_4(e^{\beta \mu}) \quad (25.39)$$

$$= \frac{3 \mu^4}{4 E_F^3} \left( 1 + \frac{2 \pi^2}{(\beta \mu)^2} + ... \right) \xrightarrow{T \to 0} \frac{3}{4} E_F$$

because the atoms are forced to adopt a state of larger dynamics in the outermost regions of the trap. This implies, $E_1/E_F \xrightarrow{T \to 0} 3/4$.

In the limit of high temperatures, $T \to \infty$, a classical gas has the energy per particle,

$$E_1 = \frac{3}{N \beta (\beta \hbar \omega)^3} f_4 \left( f_5^{-1} \left( \frac{(\beta E_F)^3}{6} \right) \right) \approx 3 k_B T \quad \text{(Boltzmann)} \quad (25.40)$$

which is seen by taking the high temperature limit $f_\eta(Z) \xrightarrow{Z \to 1} Z$ and extrapolating to all $Z$. This implies, $E_1/E_F \xrightarrow{T \to \infty} 3 k_B T / E_F$.

Comparing with bosons,

$$E_1 = 3 k_B T g_4(1) \approx 2.7 \quad \text{(Bose)} \quad (25.41)$$
25.2.3 Entropy and heat capacity

The entropy $S = -k_B \int g(\epsilon) \left[ \omega \ln \omega + (1 - \omega) \ln(1 - \omega) \right] d\epsilon$ per particle is,

$$S_1 = 4k_B \frac{f_4(Z)}{f_3(Z)} - \frac{\mu}{T} = \frac{4E_1}{3T} - \frac{\mu}{T}. \quad (25.42)$$

The heat capacity per particle $C_1 = \frac{\partial E}{\partial T}|_N$ is easily calculated using $Z f'_\eta(Z) = f_{\eta-1}(Z)$,

$$C_1 = 3k_B \frac{f_4(Z)}{f_3(Z)} - \frac{3\mu}{T} \left(1 - \frac{f_4(Z)f_2(Z)}{f_3(Z)^2}\right) = \frac{E_1}{T} - \frac{3\mu}{T} \left(1 - \frac{f_4(Z)f_2(Z)}{f_3(Z)^2}\right). \quad (25.43)$$

For fermions well below the Fermi temperature, $T \to 0$, using the Sommerfeld approximation, we calculate,

$$C_1 \xrightarrow{T \to 0} 3\pi^2 k_B T \quad \text{(Fermi)}. \quad (25.44)$$

For high temperature $T$

$$C_1 \approx 3k_B \quad \text{(Boltzmann)}. \quad (25.45)$$

25.2.4 Distributions of a Fermi gas

25.2.4.1 Spatial distribution

The density distribution is,

$$n(x) = \int \omega T, \mu(x, k) d^3k = \frac{1}{(2\pi)^2} \int \frac{2k^2 dk}{e^{\beta [h^2 k^2/2m + U(x) - \mu]} + 1}$$

$$= \frac{1}{(2\pi)^2} \frac{2m}{\hbar^2} \frac{\sqrt{\epsilon} d\epsilon}{e^{\beta \epsilon + U(x) - \mu} + 1} = \frac{1}{(2\pi)^2} \left(\frac{2m}{\beta \hbar^2}\right)^{3/2} \Gamma(3/2) f_{3/2}(e^{-\beta[U(x) - \mu]}),$$

such that,

$$n(x) = \lambda^{-3} d_B f_{3/2}(e^{-\beta[U(x) - \mu]}) \quad \text{(Fermi)}. \quad (25.47)$$

At low temperatures, $T \to 0$, we can apply the Sommerfeld expansion [94], which to first order gives $\mu \to E_F$,

$$n(x) \approx \frac{1}{(2\pi)^2} \frac{\Gamma(3/2)}{\Gamma(5/2)} \left(\frac{2m}{\hbar^2} |\mu - U(x)|\right)^{3/2}$$

$$= \frac{1}{(2\pi)^2} \frac{2}{3} \frac{2m}{\hbar^2} \left(\frac{E_F - m}{2} \omega \rho^2\right)^{3/2} = \frac{8\lambda}{\pi^2 R_F^2} \left(1 - \frac{\rho^2}{R_F^2}\right)^{3/2}. \quad (25.48)$$

At high temperatures, $T \to \infty$, we should recover the Boltzmann gas situation,

$$n(x) = \lambda^{-3} d_B f_{3/2}(e^{-\beta[U(x) - \mu]}) \quad (25.49)$$

$$\approx \lambda^{-3} d_B N (\beta \hbar \omega)^3 e^{-\beta U(x)} = \left(\frac{m \beta \hbar \omega^2}{2\pi}\right)^{3/2} N e^{-\beta m(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)/2}. \quad (25.50)$$
25.2. QUANTUM STATISTICS OF AN IDEAL FERMI GAS

Figure 25.7: (code) Numerical calculation of thermodynamic potentials for Bose (red) and Fermi (green) gases as a function of temperature for a given harmonic trapping potential. (a) Chemical potential, (b) energy, (c) heat capacity per particle, and (d) total heat capacity. The dotted magenta line in (a) shows the chemical potential calculated from the Sommerfeld approximation.

It’s easy to check, $\int n(x) d^3x = N$. Introducing the peak density $n_0$, we obtain,

$$n(x) = n_0 e^{-\mu r^2/2k_B T} \quad \text{(Boltzmann)}.$$  \hspace{1cm} (25.50)

The rms-radius of the distribution is $\sigma_j = \sqrt{k_BT/m\omega_j^2}$, which seems contrary to the above results, $m\omega_j^2 \langle x_j^2 \rangle = k_BT$. In comparison,

$$n(x) = \lambda_{dB}^{-3} g_3/2 \left[ e^{\beta(\mu-U(x))} \right] \quad \text{(Bose gas above } T_c \text{)}.$$  \hspace{1cm} (25.51)

where $\lambda_{dB} = \sqrt{2\pi \hbar^2/mk_BT} \ e \ a_{tr} = \sqrt{\hbar/m\bar{\omega}}$. 
25.2.4.2 Momentum distribution

The momentum distribution is,
\[
\tilde{n}(k) = \frac{1}{(2\pi)^3} \int w_{T,\mu}(x, k) d^3x = \frac{1}{(2\pi)^2} \int e^{\beta[\epsilon(k) + m\omega_r^2p^2/2 - \mu]} + 1 \, rdrdz \tag{25.52}
\]

such that,
\[
\tilde{n}(k) = \lambda_{dB}^{-3} a^6_{tr} f_{3/2}(e^{\beta(\mu - \epsilon)}) \quad \text{(Fermi)} \tag{25.53}
\]

At low temperatures, \(T \to 0\),
\[
\tilde{n}(k) \approx \frac{1}{(2\pi)^2} \left( \frac{2}{\beta m\omega_r^2} \right)^{3/2} \Gamma(3/2) \Gamma(5/2) (\beta |\mu - \epsilon|)^{3/2} \tag{25.54}
\]

This can easily be integrated by dimensions,
\[
\tilde{n}_{T \to 0}(k_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \tilde{n}_{cl}(k) dk_x dk_y = \frac{8}{\pi^2} N K_F^3 \int_{|k| \leq K_F} \left( 1 - \frac{k_x^2}{K_F^2} \right)^{3/2} dk_x dk_y \tag{25.55}
\]

It is easy to check \(\int_{-\infty}^{\infty} \tilde{n}_{T \to 0} dk_z = N\), with Maple.

At high temperatures, \(T \to \infty\), we should recover the Boltzmann gas situation,
\[
\tilde{n}(k) \approx \left( \frac{\hbar^2\omega_r^2}{2\pi m\omega_r^2} \right)^{3/2} Ne^{-\beta\epsilon} \quad \text{(Boltzmann)} \tag{25.56}
\]

Since \(\epsilon\) is the kinetic energy, the \(rm\)-radius \(\sqrt{k^2}\) of this distribution is \(\beta\hbar^2\langle k^2 \rangle = m\).

Example 94 (Integrated momentum distribution of a Fermi gas): To integrate the momentum distribution of finite temperature Fermi gas by dimen-
We rewrite the exponent,

\[ \tilde{n}(k_z) = \frac{1}{(2\pi)^3} \left( \frac{2}{\beta m \omega_{tr}^2} \right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{4\pi \tilde{r}^2 d\tilde{r}}{e^{\beta \epsilon - \beta \mu + \tilde{r}^2} + 1} dk_x dk_x = \frac{1}{(2\pi)^3} \left( \frac{2}{\beta m \omega_{tr}^2} \right)^{3/2} \int_0^{2\pi} \int_0^{\infty} \frac{4\pi \tilde{r}^2 d\tilde{r}}{e^{\beta \omega_{tr}^2/k_\epsilon^2/2m + \beta \omega_{tr}^2/k_\epsilon^2/2m - \beta \mu + \tilde{r}^2} + 1} k_\rho dk_\rho \]

\[ = \frac{1}{\pi} \left( \frac{2}{\beta m \omega_{tr}^2} \right)^{3/2} \int_0^{2\pi} \int_0^{\infty} \frac{1}{e^{\beta \omega_{tr}^2/k_\epsilon^2/2m - \beta \mu + \tilde{r}^2} + 1} \tilde{r}^2 d\tilde{r} \]

\[ = \frac{1}{\pi} \left( \frac{2}{\beta m \omega_{tr}^2} \right)^{3/2} \left( \frac{2m}{\beta \omega_{tr}^2} \right) \int_0^{\infty} \tilde{r}^2 \ln \left( 1 + e^{\beta \omega_{tr}^2/k_\epsilon^2/2m - \tilde{r}^2} \right) d\tilde{r} . \]

### 25.2.4.3 Time-of-flight distribution

To describe time-of-flight images we substitute \( k = m\tilde{r}/\hbar t \). We obtain the density distribution from a convolution,

\[ n_{ToF}(x, t) = \frac{1}{(2\pi)^3} \int d^3x_0 d^3k \frac{\delta^3(x - x_0 - pt/m)}{e^{\beta(H(x_0, p) - \mu)} + 1} \]

\[ = \frac{1}{(2\pi)^3} \int \frac{d^3k}{e^{\beta(H(x + pt/m, p) - \mu)} + 1} \]

\[ = \frac{1}{(2\pi)^3} \int \frac{dk_x dk_y dk_z}{e^{\beta \sum_j [h^2 k_j^2/2m + \frac{1}{2} m \omega_j^2 (x_j + \hbar k_j t/m)^2]} / Z + 1} . \]

We rewrite the exponent,

\[ h^2 k_j^2/2m + \frac{1}{2} m \omega_j^2 (x_j + \hbar k_j t/m)^2 = h^2 k_j^2/2m(1 + \omega_j^2 t^2) + \omega_j^2 t x_j \hbar k_j + \frac{1}{2} m \omega_j^2 x_j^2 \]

\[ = \left( \sqrt{\frac{h^2 k_j^2}{2m}(1 + \omega_j^2 t^2) + \frac{\omega_j^2 t x_j \sqrt{2m}}{2\sqrt{1 + \omega_j^2 t^2}}} \right)^2 + \frac{m \omega_j^2 x_j^2}{2(1 + \omega_j^2 t^2)} \]

\[ = \xi_j + \frac{m}{2} \omega_j^2 x_j^2 . \]

where we define \( \tilde{\omega}_i \equiv \omega_i (1 + \omega_i^2 t^2)^{-1/2} \). With the substitution \( d\xi_j = dk_j \sqrt{2h^2 \xi_j / m} (1 + \omega_j^2 t^2) \)

we obtain

\[ n_{ToF}(x, t) = \frac{1}{(2\pi)^3} \left( \frac{mk_B T}{2\hbar^2} \right)^{3/2} \frac{1}{\prod_i (1 + \omega_i^2 t^2)} \int \frac{\beta^{3/2} (\xi_j \xi_y \xi_z)^{-1/2} d\xi_x d\xi_y d\xi_z}{e^{\beta \sum_j [\xi_j + \frac{m}{2} \omega_j^2 x_j^2]} / Z + 1} \]

\[ = \frac{1}{2^3 \pi^{3/2}} \lambda_{dB}^3 \omega^3 \int \frac{\beta^{3/2} \xi^{-3/2} 4\pi \xi^2 d\xi}{e^{\beta \sum_j [\xi_j + \frac{m}{2} \omega_j^2 x_j^2]} / Z + 1} . \]
where \( \bar{\omega} \equiv (\omega_x \omega_y \omega_z)^{1/3} \) and \( \bar{\omega} \equiv (\bar{\omega}_x \bar{\omega}_y \bar{\omega}_z)^{1/3} \).

\[
n_{ToF}(x, t) = \frac{1}{\lambda_{dB}^3 \bar{\omega}^3} f_{3/2} \left( e^{\beta(\mu - \frac{1}{2} \beta m \Sigma \omega^2 \xi^2)} \right).
\] (25.62)

For long times-of-flight \( t \gg \omega^{-1} \),
\[
n_{ToF}(x, t) = \frac{1}{\lambda_{dB}^3 \bar{\omega}^2 t^2} f_{3/2} \left( e^{\beta(\mu - \frac{1}{2} \beta m \xi^2)} \right) = \left( \frac{m}{\hbar t} \right)^3 \tilde{n}(m \xi / t).
\] (25.63)

![Figure 25.8](image)

Figure 25.8: (code) Time-of-flight velocity distribution of (red) a Li Fermi gas at \( T = 0 \) with vanishing initial spatial distribution [94] and (green) a thermal gas at \( T = T_F \).

At low temperatures,
\[
n_{ToF}(x, t) = \left( \frac{m}{\hbar t} \right)^3 \frac{N}{k_F^3 \pi^2} \left( 1 - \frac{(m \xi / \hbar t)^2}{k_F^2} \right)^{3/2}
\] (25.64)

At high temperatures,
\[
n_{ToF}(x, t) \approx \left( \frac{mk_B T}{2 \pi \hbar^2} \right)^{3/2} \frac{1}{\bar{\omega}^2 t^2} N \left( \frac{\hbar \bar{\omega}}{k_B T} \right)^3 e^{-\beta m \xi^2 / 2t^2} \approx N \frac{\bar{\omega}}{t^2} \left( \frac{m}{2 \pi k_B T} \right)^{3/2} e^{-\beta m \xi^2 / 2t^2}.
\] (25.65)
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A rms-width is,

\[
\langle r^2_{ToF} \rangle = \int r^2 n_{ToF}(x, t) d^3 x \tag{25.66}
\]

\[
= \frac{1}{\lambda_{DB}^3 \omega_3} \int r^2 f_{3/2} \left( e^{\beta \mu - \frac{1}{2} \beta m \Sigma_j \omega_j^2 x_j^2} \right) d^3 x
\]

\[
= \frac{2}{m \omega_3^2 N} \int \frac{\epsilon g(\epsilon) d\epsilon}{e^{\beta (\epsilon - \mu)} + 1} = \frac{k_B T g_4(Z)}{m \omega_3^2 g_3(Z)}.
\]

This shows that the width of the flight-of-time distribution can simply be obtained from the spatial distribution by substituting \(\omega \rightarrow \omega / \sqrt{1 + \omega^2 t^2}\). Of course this does not hold for condensed gases Bose.

25.2.5 Equipartition theorem

We find for harmonic traps,

\[
E_{pot,1} = \frac{\int U(x) w_{T,\mu}(x, k) d^3 x d^3 k}{\int w_{T,\mu}(x, k) d^3 x d^3 k} = \frac{1}{(2\pi)^3 N^2} \int \frac{m \omega_3^2 r^2 d^3 x d^3 k}{e^{\beta [h^2 k^2 / 2m + m \omega_3^2 r^2 / 2 - \mu]} + 1} \tag{25.67}
\]

\[
= \frac{1}{(2\pi)^3 N^2} \int \frac{h^2 k^2 d^3 x d^3 k}{e^{\beta [h^2 k^2 / 2m + m \omega_3^2 r^2 / 2 - \mu]} + 1} = \frac{h^2 k^2 w_{T,\mu}(x, k) d^3 x d^3 k}{2m \int w_{T,\mu}(x, k) d^3 x d^3 k} = E_{kin,1}.
\]

This confirms the **equipartition theorem** for confined particles, which postulates,

\[
E = E_{kin} + E_{pot} = 2E_{kin} \tag{25.68}
\]

In flight time, however, \(E_{pot}\) suddenly vanishes.

25.2.5.1 Calibrating the number of atoms

Experimentally, to calibrate \(N\), we can use either the measured value of \(\langle k^2 \rangle\) at \(T = 0\), which gives \(\mu = E_F = 4E/3\) and consequently,

\[
N = 32 \left( \frac{h^2 \langle k^2 \rangle}{6m \hbar \omega} \right)^3. \tag{25.69}
\]

Or we determine the temperature \(T_g\) where the Boltzmann gas turns into a Fermi gas \(3\mu/4 = 3k_B T_g\),

\[
N = 32 \left( \frac{k_B T_g}{\hbar \omega} \right)^3. \tag{25.70}
\]

25.2.6 Density and momentum distribution for anharmonic potentials

25.2.6.1 Width of momentum distribution for anharmonic potentials

If the potential is non-harmonic, the widths of Fermi distributions must in general be calculated numerically. I.e. first \(g(\epsilon)\) is determined by integrating for every value
of $\epsilon$ the root $\sqrt{\epsilon - U(x)}$ over the entire volume, where $U(x) < \epsilon$, i.e. in the case of cylindrical symmetry,
\[
g(\epsilon) = \frac{(2m)^{3/2}}{2\pi\hbar^3} \int \sqrt{\epsilon - U(r,z)} r \, dr \, dz .
\] (25.71)

Second the chemical potential must also be calculated numerically from
\[
N = \int g(\epsilon) \left( e^{\beta(\epsilon - \mu)} + 1 \right)^{-1} \, d\epsilon
\] by minimizing the function,
\[
o(Z) = \left| \beta N - \int \frac{g(\epsilon/\beta) \, d\epsilon}{e^{\epsilon/Z} + 1} \right| .
\] (25.72)

Finally, the \textit{rms}-momentum width of a degenerate Fermi-gas is calculated from,
\[
\left\langle k^2 \right\rangle = \frac{E_1}{E_F} = \frac{1}{NE_F} \int \frac{\epsilon g(\epsilon) \, d\epsilon}{e^{\beta(\epsilon - \mu)} + 1} .
\] (25.73)

It is important to note that the temperature cannot be obtained from $\hbar^2 \left\langle k^2 \right\rangle / 2m = 3Nk_BT$ any more. Rather for a given $\left\langle k^2 \right\rangle$ the parameter $\beta$ in the integral (25.71) must be fitted to satisfy the equation.

Alternatively, we may assume a polynomial potential for which the density of states can be described by $g(\epsilon) \propto \epsilon^n$. Then,
\[
\frac{\left\langle k^2 \right\rangle}{k_F^2} = \frac{3T}{T_F} \frac{f_4(Z)}{f_3(Z)} ,
\] (25.75)

and for hot clouds the classical limit holds,
\[
\frac{\left\langle k^2 \right\rangle}{k_F^2} = \frac{n + 1}{\beta E_F} .
\] (25.76)

Must for a single dimension the value be divided by three? $\hbar^2 \left\langle k^2 \right\rangle / 2m = 2mk_BT f_4(Z) / f_3(Z)$ setting $\epsilon = \hbar^2 k^2 / m$.

For a harmonic potential $g(\epsilon) \propto \epsilon^2$ and for a linear potential $g(\epsilon) \propto \epsilon^{7/2}$. Intermediate values are possible for non isotropic traps, which are linear in some directions and harmonic in others, e.g. for a radially quadrupolar and axially harmonic trap, we expect $g(\epsilon) \propto \epsilon^3$ and thus $E = 4Nk_BT$. In general, we may have more complicated situations, where the trap becomes non-harmonic beyond a certain distance from the origin. In those cases, the density of states may be approximated by series,
\[
g(\epsilon) \propto \epsilon^2 + \eta \epsilon^3 ,
\] (25.77)

where $\eta$ is a small parameter, so that,
\[
\frac{\left\langle k^2 \right\rangle}{k_F^2} = \frac{1}{E_F} \int \frac{(3 + \eta^2)(e^{\beta(\epsilon - \mu)} + 1)^{-1} \, d\epsilon}{(\epsilon^2 + \eta \epsilon^3)(e^{\beta(\epsilon - \mu)} + 1)^{-1} \, d\epsilon} = \frac{T}{T_F} \frac{3f_4(Z) + 12\eta f_5(Z)}{f_3(Z) + 3\eta f_4(Z)} ,
\] (25.78)
which in the classical limit gives rise to energies $E = 3.4Nk_BT$ depending on the value of $\eta$.

Such effects must be considered when the time-of-flight method is used for temperatures measurements. For example, if we underestimate $g(\epsilon)$ by assuming a harmonic potential at all $\epsilon$, although the potential is quadrupolar at large $\epsilon \gg k_BT$, we get a wrong estimate for the temperature $T_{\text{wrrng}} = E/3Nk_B$ instead of $T_{\text{corr}} = E/4Nk_B$.

### 25.2.6.2 Width of the density distribution for anharmonic potentials

The result also permits to calculate the $\text{rms}$ spatial width,

$$\sum_{j=1}^{3} \frac{m_\omega_j^2 \langle x_j^2 \rangle}{2} = 3k_BT \frac{f_4(Z)}{f_3(Z)}.$$  

Let us for simplicity assume $\omega_i = \omega_j$. So in the classical limit,

$$\frac{\langle x_j^2 \rangle}{R^2_F} = \frac{\langle x^2 \rangle}{3R^2_F} = \frac{E_1}{3E_F} = \frac{1}{1.13T}.$$  

If the potential is non-harmonic, the widths of Fermi distributions must in general be calculated numerically. We may use the same results for the density of states and the chemical potential as for the momentum width calculations. Then,

$$\frac{\langle x_j^2 \rangle}{R^2_F} = \frac{E_1}{3E_F} = \frac{1}{3E_F} \int \frac{\epsilon g(\epsilon) \left( e^{\beta(\epsilon-\mu)} + 1 \right)^{-1} d\epsilon}{Z_0 - 0}.$$  

### 25.2.7 Classical gas

For a harmonic potential [142] the fraction of particles with energy smaller than $\eta k_BT$ is,

$$N(\eta) = \frac{1}{2N(h\omega)^3} \int_0^{\eta k_BT} \frac{d\epsilon}{e^{\beta\epsilon}/Z - 0} \approx 1 - \frac{2 + 2\eta + \eta^2}{2e^\eta},$$  

$$E(\eta) = \frac{1}{2N(h\omega)^3} \int_0^{\eta k_BT} \frac{\epsilon^2 d\epsilon}{e^{\beta\epsilon}/Z - 0} \approx 3 - \frac{6 + 6\eta + 3\eta^2 + \eta^3}{6e^\eta},$$

while for a quadrupole potential,

$$N(\eta) \approx -2\sqrt{\pi} \frac{105 + 70\eta + 28\eta^2 + 8\eta^3}{\sqrt{105}e^\eta} + \text{erf}(\sqrt{\eta})$$

$$E(\eta) \approx -\frac{2}{9} \sqrt{\pi} \frac{945 + 630\eta + 252\eta^2 + 72\eta^3 + 16\eta^4}{\sqrt{105}e^\eta} + \frac{9}{2} \text{erf}(\sqrt{\eta}).$$
25.2.7.1 Momentum distribution for a classical gas

For high temperatures, \( T \to \infty \), we should recover the ideal Boltzmann gas situation, 
\[ f_{3/2} \to id, \]

\[ \tilde{n}_{T \to \infty}(k) = \frac{1}{(2\pi)^3} \int \frac{4\pi \rho^2 d\rho}{e^{\beta[\varepsilon + \rho^2/2 - \mu]}} \]
\[ = \left( \frac{1}{2\pi \beta \omega_{tr}^2} \right)^{3/2} e^{-\beta(\varepsilon - \mu)} = \lambda^{-3/2} dB^6 e^{\beta(\mu - \varepsilon)}. \]

Since the chemical potential satisfies the normalization, \( \int \tilde{n}_{T \to \infty}(k) d^3k = 1 \),

\[ \tilde{n}_{T \to \infty}(k) = \left( \frac{1}{2\pi \beta \omega_{tr}^2} \right)^{3/2} N \left( \frac{\hbar \omega_{tr}}{k_B T} \right)^3 e^{-\beta \varepsilon} = N \sqrt{\frac{\hbar^2}{2\pi mk_B T}} e^{-\hbar^2 k^2/2mk_B T}. \]

(25.84)

This is easy to integrate by dimensions, so that,

\[ \tilde{n}_{T \to \infty}(k_z) = \int_\infty^{-\infty} \int_\infty^{-\infty} \tilde{n}_{T \to \infty}(k) dk_x dk_y = N \sqrt{\frac{\hbar^2}{2\pi mk_B T}} e^{-\hbar^2 k^2/2mk_B T}. \]

(25.85)

The rms-width of this distribution is,

\[ \Delta k_z = \frac{\sqrt{mk_B T}}{\hbar}. \]

(25.86)

25.2.7.2 Correlating fluctuations in the number of atoms

Experimentally the atom number will fluctuate. To minimize this problem we can renormalize it to a norm number \( N_{\text{norm}} \) by multiplying the measured time-of-flight variance \( \langle \tilde{x}_{tof}^2 \rangle \) with,

\[ C_T(N) = \frac{\langle \tilde{x}_{tof}^2 \rangle}{\langle \tilde{x}_{tof}^2 \rangle_{\text{norm}}} = \frac{N f_4(\tilde{Z})}{N_{\text{norm}} f_4(\tilde{Z})} \]
\[ = \frac{N}{N_{\text{norm}}} \frac{f_4 \left[ f_3^{-1}(N_{\text{norm}}(\beta h\omega)^3) \right]}{f_4 \left[ f_3^{-1}(N(\beta h\omega)^3) \right]}. \]

(25.87)

25.2.8 Intensive and extensive parameters

The distinction between an intensive parameter and an extensive parameter is based on the concept that the system under investigation can be subdivided into smaller, identical and non-interconnected entities within which the parameter in question has the same properties, such that this parameter does not change, when the system is divided or subentities are combined. An intensive property is a global property, meaning that it is a physical property of a system that does not depend on the system

---

6How to derive the thermodynamic potentials from the macrocanonical partition function? How to calculate pressure and volume? [check thermodynamic derivations from Romero-Rochin [see Freddy’s thesis].]
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size or the amount of material in the system. Examples of intensive properties are the temperature and the hardness of an object. No matter how small a diamond is cut, it maintains its intrinsic hardness.

By contrast, an extensive property is one that is additive for independent, non-interacting subsystems. The property is proportional to the amount of material in the system. For example, both the mass and the volume of a diamond are directly proportional to the amount that is left after cutting it from the raw mineral. Mass and volume are extensive properties, but hardness is intensive.

The ratio of two extensive properties, such as mass and volume, is scale-invariant, and this ratio, the density, is hence an intensive property.

Intensive parameter are: chemical potential, concentration, density (or specific gravity), ductility, elasticity, electrical resistivity, hardness, magnetic field, magnetization, malleability, melting point and boiling point, molar absorptivity, pressure, specific energy.

Extensive parameter are: energy, entropy, Gibbs energy, length, mass, particle number, momentum, number of moles, volume, magnetic moment, electrical charge, weight.

25.2.9 Signatures for quantum degeneracy of a Fermi gas

Whether an atom is a fermion or a boson uniquely depends on its total spin. Halfinteger spin particles are fermions, integer spin particles are bosons. E.g. Rb atoms have in the ground state \( J = 1/2, I = 7/2 \), integer \( F \), and are therefore bosons. Ca\(^+\) ions have \( J = 1/2 \) and no hyperfine structure so that \( F \) is halfinteger, and are therefore fermions. \(^{6}\)Li has half-integer \( F \) and is a boson.

For a composite particle the quantum statistical nature may depend on the interaction strength of the partners. For weak interaction, e.g. Feshbach the total spins of the partners will couple to a total total spin, which determines the nature of the composite particle. A fermion pairing with a fermion or a boson pairing with a boson will be bosons. A fermion pairing with a boson will be a fermion. Composite trimers may be either bosonic or fermionic depending on the coupling scheme. Can the quantum nature change with the tightness of the binding? What is the total spin of a deeply bound molecule? [497, 78, 221], [?, 283, 471, ?]

25.2.9.1 Optical density of a Fermi gas

With the local density of a Fermi gas,

\[
n_{loc} = \frac{k_F^3}{3\pi^2} \tag{25.89}\]

the optical density is at \( T = 0 \),

\[
\int \sigma dy = \frac{8\sigma}{\pi^2} \frac{N}{R_F^3} \int_{-R_F}^{R_F} \left( 1 - \frac{x^2 + y^2}{R_F^2} - \frac{z^2}{Z_F^2} \right)^{3/2} dy \tag{25.90}
\]

\[
= \frac{8\sigma}{\pi^2} \frac{N}{R_F^3} \left( 1 - \frac{x^2}{R_F^2} - \frac{z^2}{Z_F^2} \right)^{3/2} \int_{-R_F}^{R_F} \left( 1 - \frac{y^2}{R_F^2 - x^2 - R_F^2 z^2/Z_F^2} \right)^{3/2} dy .
\]
Writing \( a = R_F/\sqrt{R_F^2 - x^2 - R_F^2 z^2/Z_F^2} \),

\[
\int \sigma ndy = \frac{8\sigma N}{\pi^2 R_F^2 a^4} \int_{-a}^{a} (1 - \tilde{y}^2)^{3/2} d\tilde{y} = \frac{2\sigma N}{\pi^2 R_F^2 a^4} \left( 9a\sqrt{1 - a^2} - 2a^3\sqrt{1 - a^2} + 3 \arcsin a \right).
\]

In the center, \( a = 1 \),

\[
\int \sigma ndy = \frac{3N\sigma}{\pi R_F^2} = \frac{9m\omega_r^2 N}{k_L E_F},
\]

such that for \( E_F \approx 1 \mu K \) we expect \( n_{\text{loc}} \approx 4 \times 10^{12} \text{ cm}^{-3} \).

### 25.2.9.2 Superfluid suppression of sympathetic cooling

The fermions inside the bosonic cloud can be regarded as impurities. If they travel too slow, \( v < c \), and if the condensed fraction is too large, the motion will be frictionless and thermalization stops. If they travel fast, quasiparticles are excited, which can be removed by evaporation. With the typical velocity of sound in the BEC \( c = \hbar \sqrt{16\pi n a/2m_B} \approx 2 \text{ mm/s} \), or \( \frac{m}{2}c^2 \approx k_B \times 20 \text{ nK} \), we see that this is no real danger.

### 25.2.9.3 Component separation

If the interspecies interaction \( h \) is stronger than the inter-bosonic interaction, the components may separate \([452]\). Otherwise a small fermionic cloud stays inside the BEC.

### 25.2.9.4 Excess energy modifies 2\textsuperscript{nd} moment

Independent on any model, just look deviation from Gaussian (interaction energy plays no role for the fermions). Also calculate the 2\textsuperscript{nd} moment \( U = \int E_{\text{kin}}(k)n(k)dk \), where \( n(k) \) is measured in time-of-flight and \( E_{\text{kin}} = \hbar^2 k^2/2m \).

### 25.2.9.5 Modification of light scattering

The unavailability of final momentum states inhibits scattering in a similar way as the Lamb-Dicke effect. Forward scattering is suppressed, because all small momentum states are occupied. Furthermore, spontaneous emission is suppressed like in photonic band gaps. However, here it is rather an atomic momentum band gap. Could it be that because scattering is suppressed, in-situ images of fermions are hampered?

A condition for this effect to play a role is \( k_{\text{rec}} \ll k_F \). For Li the temperature must be \( k_B T_F = \hbar^2 k_F^2/2m = \hbar \omega(6N)^{1/3} \gg \hbar^2 k_L^2/2m \approx k_B \times 3 \mu K \). I.e. we need quite large Fermi gases.

### 25.2.9.6 Hole heating

Loss processes that remove particles from an atom trap leave holes behind in the single particle distribution if the trapped gas is a degenerate fermion system. The appearance of holes increases the temperature, because of an increase in the energy
share per particle if cold particles are removed. Heating is significant if the initial temperature is well below the Fermi temperature. Heating increases the temperature to \( T > T_F / 4 \) after half of the system’s lifetime, regardless of the initial temperature. The \textit{hole heating} has important consequences for the prospect of observing Cooper pairing in atom traps.

### 25.2.10 Fermi gas in reduced dimensions

In \( n \) dimensions with the energy \( \varepsilon = ap^s + br^t \) \([377]\) we have to generalize the results of the last chapter, 

\[
N = g \frac{\Gamma \left( \frac{n}{2} + 1 \right) \Gamma \left( \frac{n}{4} + 1 \right)}{(2\hbar)^{n}a^{n/2}b^{n/4}} (k_BT)^{n/4} f_{n/4}(z). \tag{25.93}
\]

This gives for a harmonic trap where \( \varepsilon = \frac{1}{2m}p^2 + \frac{m}{2}\omega^2 r^2 \) and with the spin degeneracy factor \( g = 1, \)

\[
N = \left( \frac{k_BT}{\hbar\omega} \right)^{n} f_{n}(z). \tag{25.94}
\]

The Fermi energy again follows from Sommerfeld’s expansion, 

\[
E_F = (n!N)^{1/n} \hbar\omega. \tag{25.95}
\]

We now assume a 1D potential \( V = \frac{m}{2}\omega^2 r^2 \) embedded in a 3D trap. A true 1D situation arises when the atoms occupy all low-lying axial levels with the lowest radial vibrational quantum number, i.e. \( E_F \ll \hbar\omega \) which gives,

\[
N \ll \frac{\omega_r}{\omega_z}. \tag{25.96}
\]

Such quantum degenerate 1D fermion gases realize the so-called \textit{Luttinger liquid}. One of the hallmarks of Luttinger liquids is \textit{spin-charge separation}.

**Example 95 (Estimations for 1D):** Let us consider a Fermi gas in a very elongated microtrap: \( \omega_r = \sqrt{87/2}\pi \times 1.4 \text{ kHz} \) and \( \omega_z = \sqrt{87/2}\pi \times 15 \text{ Hz} \) for Rb. With \( N_{L4} = 10^5 \) the Fermi temperature is as high as \( T_F \approx 5 \mu\text{K} \). However we need \( N \ll 100 \) to see 1D features.

Assume \( \varepsilon = \frac{1}{2m}p^2 + \frac{m}{4}b^4r^4, \)

\[
N = \frac{1}{(\hbar b)^n} \frac{\Gamma \left( \frac{n}{2} + 1 \right) \Gamma \left( \frac{3n}{4} + 1 \right)}{\Gamma \left( \frac{n}{4} + 1 \right)} (k_BT)^{3n/4} f_{3n/4}(z).
\]

\[
E_F \approx (\hbar b)^{4/3} \left( \frac{N \Gamma \left( \frac{n}{2} + 1 \right) \Gamma \left( \frac{3n}{4} + 1 \right)}{\Gamma \left( \frac{n}{4} + 1 \right)} \right)^{4/3n}.
\]

In 1D,

\[
N = \frac{1.02}{\hbar b} (k_BT)^{3/4} f_{3/4}(z)
\]

\[
E_F \approx 0.87(N\hbar)^{4/3}.
\]
25.2.11 Exercises

25.2.11.1 Ex: Li Fermi gas

Programs on Li Fermi gases.
Chapter 26

Bose-Einstein condensation

26.1 Bose-Einstein condensation of dilute gases

The challenge of the experimental realization of Bose-Einstein condensation is the preparation of a very dense sample of very cold atoms. In practice, the first step consists in providing an atomic gas, for example, of an alkali metal. This is done by heating the metal in an oven (or sometimes in a dispenser). The atoms being ejected from the metal and forming a hot gas are then forced through a nozzle out of the oven, where they form a hot atomic beam. Some experiments employ a Zeeman slower, which is a device that decelerates the fast atoms of the beam by means of a counterpropagating laser exerting a radiative pressure force. A position-dependent magnetic field applied along the trajectory of the atoms is calculated in order to compensate for the Doppler decreasing shift of the decelerated atoms and to ensure that the laser always stays in resonance with an atomic transition (see Exc. 14.4.6.3). Velocities around 30 m/s are realistic and low enough to allow the capture of the atoms by a magneto-optical (MOT) trap. Usually, some $10^9$ atoms are captured in a few seconds.

MOTs do not only trap atoms, but simultaneously cool them down to the Doppler limit of typically some 10 µK. Quasi-resonant optical traps, such as MOT, are afflicted by the problem of radiation trapping (see Sec. 24.3.1), which limits the densities of atomic clouds to typically $10^{11}$ cm$^3$. This corresponds (at temperatures close to the Doppler limit) to phase space densities several orders of magnitude away from the threshold to Bose-Einstein condensation. For this reason, the atoms are transferred from the MOT to a potential exempt of radiative pressure force, for example, an optical dipole potential or a magnetic trap.

Once the atoms are confined in such a conservative potential, all the light beams are turned off, and the technique of evaporative cooling is activated (see Sec. 24.4.3). That is, the effective potential is deformed (for example, by an irradiated radiofrequency) in a way to skim out hot atoms and leave behind a cooler sample. This however supposes that the atomic cloud finds back to thermal equilibrium afterwards. As the rethermalization happens by elastic collisions, a high atomic density is necessary, which is often achieved via a compression of the trapping potential. In general, 99.9% of the atoms must be sacrificed to condense the rest. Finally, the momentum distribution is imaged after a time of free expansion. This is done by irradiation of a probe laser pulse (see Fig. 24.31). The entire process of producing a condensed cloud usually takes between 10 s and 60 s.
26.1.1 Condensate of alkaline gases

The first experimental observation of Bose-Einstein condensation was done with a dilute rubidium gas by Cornell and Wieman at the Joint Institute for Laboratory Astrophysics (JILA) [12]. A group from the University of Texas [256, 126] used rubidium as well. A group led by Ketterle from the Massachusetts Institute of Technology (MIT) created the first sodium condensate. And a group led by Hulet from Rice University opted for lithium [83, 81], which has a slightly negative scattering length, $a = -27.3a_B$. In this situation, only small condensates are expected to be stable [515, 582], which explains the observation of a limited number of about 1400 condensed lithium atoms. Meanwhile, Bose-Einstein condensation has been achieved with many other species, such as $^1$H [205], $^{85}$Rb [122], $^4$He$^*$ [508], $^{133}$Cs [564], $^{39}$K [486], $^4$Ne [43], $^{88}$Sr [574], or even molecules [645].

26.1.2 Condensation of hydrogen

Hydrogen is a very interesting element to study condensation, because its short scattering length, $a \approx 1.23a_B$, makes it an almost ideal gas. Consequently, the three-body collision rate causing losses is weak, even at very high densities. Since the mass of hydrogen is small, the critical temperature is high. The simplicity of its electronic structure allows precise calculations of the interaction potentials based on fundamental principles, which can thus be tested experimentally.

Twenty years after having started the project of condensing dilute hydrogen gases, Greytak and Kleppner [205] crossed the phase transition at a temperature of 50 $\mu$K with an atomic density of $5 \times 10^{15}$ cm$^{-3}$. The number of condensed atoms was $10^9$, which corresponds to a condensed fraction below 10% $^1$. The condensed cloud had a needle-like shape of 15 $\mu$m diameter and 5 mm length. It was detected by an in situ measurement technique of the atomic velocity distribution.

![Spectrum of condensed hydrogen.](image)

$^1$When the condensed fraction and the density are too high, losses induced by dipolar spin-flip processes predominate over the gain due to evaporative cooling of the thermal cloud [281].
26.1.3 Recognizing Bose-Einstein condensates

‘How to recognize the presence of a condensate, what are its signatures?’ We have already seen in Sec. 25.1.4 that, trapped inside a confinement potential, an ultracold ideal Bose-gas has a modified density distribution when Bose-Einstein statistics come into play. Below the critical temperature the density distribution is well described by a superposition of a condensed cloud concentrated in the trap’s ground state and a thermal cloud distributed over several vibrationally excited states. We thus expect distinct distribution functions for both clouds, and the same is true for the momentum distribution. The splitting of the distribution functions in two fractions occurs abruptly during the phase transition to quantum degeneracy. In a real gas, however, the interatomic collisions have a drastic influence on the distribution functions and the behavior of the gas at the phase transition, and we are obliged to develop a more general theory in order to quantitatively understand the thermodynamic properties (temperature, critical point, heat capacity, ...) through the measured static quantities (density, number of atoms, condensed fraction, ...).

‘What observables can be measured in the laboratory?’ In fact, with few exceptions, the only accessible quantity is the spatial density distribution of the atomic cloud \( n(r) \) measured after a time of ballistic expansion. Information on non-trivial properties of the condensate, for example, its dynamic behavior (excitations, superfluidity, turbulence, ...) or its coherent features (phase, correlations, ...), can only be gathered through an observation of the condensate’s response to applied perturbations. Solve the Excs. 26.1.5.1 and 26.1.5.2.

26.1.4 Photon condensation

An interesting question is that of the possibility of photon condensation and its relationship to the laser. The relationship is not that obvious because, on one hand atomic condensates are produced by evaporating a ensemble in constant thermal equilibrium, while on the other hand the photonic laser requires inversion, which is a highly non-equilibrium situation. And under the constraint of having to reduce its energy, a photon gas trapped in an optical cavity has the simpler alternative to let photons escape into the void by annihilating them on the cavity walls, as it happens for black-body radiation. Since the number of photons in a cavity is not conserved, the chemical potential disappears, \( \mu = 0 \). The density of states can be written,

\[
u(\nu) = \frac{8\pi V}{e^3} \frac{E^2 dE}{\hbar^2}.
\]

(26.1)

It is the same as in the Debye model. Planck’s formula now follows from,

\[
\nu(\epsilon) d\epsilon = \frac{1}{V} \epsilon f_{BE}(\epsilon) \rho(\epsilon) d\epsilon,
\]

(26.2)

where \( f_{BE} \) is the Bose-Einstein distribution. Hence, the treatment of the photons as indistinguishable particles following the Bose-Einstein distribution is equivalent to assuming a Boltzmann distribution for waves with quantized energies.

Nevertheless, one can imagine a photonic gas in thermal equilibrium with an atomic gas through Compton scattering [339]. In fact, photon condensation was
observed experimentally [346]. Also, there are theories about superfluid photon gases [105].

26.1.5 Exercises

26.1.5.1 Ex: Condensation of ions
Discuss the possibility of creating Bose-Einstein condensates from ionic clouds.

26.1.5.2 Ex: Isobaric impurities
Discuss the possibility of creating Bose-Einstein condensates with isobaric species.

26.2 Quantum theory

As detailed above, interatomic interactions strongly influence the properties of Bose-Einstein condensates, even their density and momentum distributions. For a correct interpretation of the experimental measurements a theoretical many-body treatment taking care of these interactions is compulsory. This is done through a description of the atomic distribution as a scalar field of matter called second quantization, where the atoms are treated as delocalized Broglie waves. However, we will leave a thorough introduction of this formalism to [616].

26.2.1 Description of the atom as a scalar field

In position space a state with \( n \) particles can be described in a canonically quantized way by a field operator,

\[
\hat{\Psi}(\mathbf{r}_1, ..., \mathbf{r}_n, t) = \hat{\psi}^\dagger(\mathbf{r}_1, t) \cdot \cdot \cdot \hat{\psi}^\dagger(\mathbf{r}_n, t) \hat{\Psi}_0, \quad \hat{\psi}(\mathbf{r})\hat{\Psi}_0 = 0,
\]

where \( \hat{\Psi}_0 \) is the vacuum state. The field operators \( \hat{\psi}(\mathbf{r}, t) \) and \( \hat{\psi}^\dagger(\mathbf{r}, t) \) annihilate, respectively create, an atom at position \( \mathbf{r} \) and time \( t \). This state represents a bosonic

Bose-Einstein condensation occurs in thermal equilibrium when entropy is maximized by putting a macroscopic population of atoms into the ground state of the system. It might appear counterintuitive that an apparently highly ordered state as the Bose condensate maximizes entropy. However, only the particles in excited states contribute to the entropy. Their contribution is maximized at a given total energy by forming a Bose condensate in the ground state and distributing the remaining atoms among higher energy states. A macroscopic population of atoms in the ground state of the system is achieved simply by lowering the temperature of the sample. This is in contrast to the optical laser where a non-equilibrium process is necessary to place a macroscopic population of photons in a single mode of the electromagnetic field. This is due to the fact that, unlike photons, the number of atoms is conserved. For bosonic atoms, the lowest entropy state below a certain temperature includes a macroscopic population of the ground state. In contrast, when one cools down a blackbody cavity, the cavity empties. Photons do not Bose condense into the ground state of the cavity, but are absorbed by the walls. The absorbed energy leads to a larger entropy than forming a Bose condensate. The laser phenomenon requires inversion of the active medium characterized by a 'negative' temperature. In that sense, 'lasing' of atoms is a simpler phenomenon than lasing of light—all you need to do is cool a gas! However, if a photon gas would thermalize while the number of photons is conserved, it would be described by a Bose-Einstein distribution with non-zero chemical potential and could form a Bose condensate. Thermalization with number conservation is possible, for example, by Compton scattering with a thermal electron gas [339].
26.2. QUANTUM THEORY

Fock state and can be generated from the empty state by a sequence of individual particle creation operators. Applying the notions and rules developed for the harmonic oscillator in Sec. 4.5.1, we can define a coherent state of bosonic matter as,

$$|\Phi(t)\rangle = \sum_{n=0}^{\infty} \frac{N^n}{\sqrt{n!}} |\Psi(r_1, ..., r_n, t)\rangle .$$  (26.4)

The field operators for particle creation and annihilation are normalized to the number of atoms and satisfy the following commutation rules,

(i) $[\hat{\psi}(r), \hat{\psi}^\dagger(r')] = \delta^3(r - r')$

(ii) $[\hat{\psi}(r), \hat{\psi}^\dagger(r')] = \delta^3(r - r')$

(iii) $[\hat{\psi}(r), \hat{N}] = \hat{\psi}(r)$

(iv) $[\hat{\psi}(r), \hat{p}] = \frac{\hbar}{i} \nabla \hat{\psi}(r)$

(v) $[\hat{\psi}(r), \hat{H}] = i\hbar \frac{\partial}{\partial t} \hat{\psi}(r)$

The last equation is the Heisenberg equation of motion and describes the dynamics of a system whose many-body Hamiltonian $H \equiv H_{cm} + H_{self}$ for $N$ bosons interacting within an external potential $V_{trap}$ in second quantization is defined by 3,

$$H_{cm} \equiv \int d^3r \hat{\psi}^\dagger(r) \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{trap}(r, t) \right) \hat{\psi}(r)$$

$$H_{self} \equiv \int d^3r \int d^3r' \hat{\psi}^\dagger(r) \hat{\psi}^\dagger(r') V_{coll}(r - r') \hat{\psi}(r') \hat{\psi}(r)$$  (26.6)

The equations (26.5) and (26.6) represent the foundation of the theory of ultracold bosonic gases. However, to solve the equations, we will need to apply some simplifications, which will be discussed in the following sections. For example, we will generally assume that the temperature of the sample is $T = 0$, and that all atoms are condensed. Also, in a first time, we will neglect quantum fluctuations, replacing field operators with complex numbers. And finally, we will need to handle the nonlinear term appearing in $H_{self}$ and which signs responsible for collisions between atoms.

26.2.2 Quantum scattering at low temperatures

To simplify the term $H_{self}$, we have to go back to Secs. 12.2.5 (and following) and study the phenomenon of the elastic collisions in the ultracold regime. For simplicity, we consider two particles without internal degrees of freedom with masses $m_1$ and $m_2$ approaching each other along the z-axis [113, 622]. Neglecting spin-spin and spin-orbit interactions, the Schrödinger equation in the inertial center-of-mass system is

$$\mathcal{K} = H_{cm} + H_{self} - \int d^3r \hat{\psi}^\dagger(r) \mu \hat{\psi}(r) ,$$

where $\mu$ is the chemical potential.

---

3Sometimes the Kamiltonian is used for canonical and macrocanonic ensembles. It defined by, $K = H_{cm} + H_{self} - \int d^3r \hat{\psi}^\dagger(r) \mu \hat{\psi}(r)$, where $\mu$ is the chemical potential.
given by \((12.115)\),
\[
\left(-\frac{\hbar^2}{2m^*}\nabla^2 + V_{\text{coll}}(r)\right)\hat{\psi}(r) = E\hat{\psi}(r),
\]
(26.7)
where \(r = r_1 - r_2\) is the momentary interatomic separation, \(r = |r|\), and \(m^* \equiv m_1 m_2/(m_1 + m_2)\) is the reduced mass of atomic collision partners. We assume that the interatomic potential, \(V_{\text{coll}}(r)\), is spherically symmetrical. In the asymptotic limit of large separations \(^4\), and in the Born-approximation (12.135), the solution of Eq. (26.7) can be seen as the sum of an incident plane wave and a scattered spherical wave modulated with a certain amplitude \(f(\theta)\),
\[
\psi(r) = e^{ikz} + f(\theta)\frac{e^{ikr}}{r},
\]
(26.8)
where \(k = \sqrt{2m^*E/\hbar^2}\) is the amplitude of the wavevector of the incident and scattered waves and \(\theta\) the angle between \(r\) and \(z\). The function \(f(\theta)\) is called scattering amplitude and determines the scattering cross-section for \(s\)-wave collision through the expression [see (12.123)],
\[
\frac{d\sigma}{d\Omega} = |f(\theta)|^2.
\]
(26.9)
where \(d\Omega = \sin \theta d\theta d\phi\) is an element of the solid angle. To calculate the scattering amplitude, we expand the wavefunction (26.8) into spherical partial waves of orders \(\ell\) of the angular momentum, as done in (12.136),
\[
f_k(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell + 1) P_\ell(\cos \theta) e^{i\delta_\ell} \sin \delta_\ell.
\]
(26.10)
The collision cross section has been shown in (12.148) to be given by,
\[
\sigma = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin^2 \delta_\ell.
\]
(26.11)
For a potential with finite range, that is, a potential falling faster than \(r^{-3}\) with the distance (interatomic potentials usually fall as \(r^{-6}\) or \(r^{-7}\)), the phase shift satisfies,
\[
\delta_\ell \propto k^{2\ell+1}
\]
(26.12)
for small \(k\). In ultra-cold gases, the collision energy is very low and \(k \to 0\). Thus the scattering will be dominated by terms with \(\ell = 0\). This is the so-called limit of \(s\)-wave scattering. In this limit the Eqs. (26.10) can be approximated as,
\[
f_k(\theta) = \frac{1}{k} e^{ik\delta_0} \sin \delta_0.
\]
(26.13)

### 26.2.3 Scattering length

For \(\ell = 0\), taking the limit \(k \to 0\), we define the scattering length \(a_s\) via,
\[
\frac{\text{Im} f_k(\theta)}{\text{Re} f_k(\theta)} = \tan \delta_0 \equiv -\tan ka_s.
\]
(26.14)
\(^4\)This means, \(r \gg r_0\), where \(r_0\) is the range of potential \(V(r)\).
Therefore, the scattering length and cross section are given at very low temperatures at the asymptotic boundary by,

\[ a_s = -\frac{\delta_0}{k} \quad \text{and} \quad \sigma = 4\pi a_s^2. \] (26.15)

The scattering process can be interpreted as follows: During a collision, the system’s wavefunction undergoes a phase shift, \( \delta_0 \), which may be positive or negative, depending on the sign of \( a_s \). If \( a_s < 0 \), the phase is ‘delayed’ by the collision. This corresponds to an attractive interaction. In contrast, if \( a_s > 0 \), the phase is ‘advanced’ and the interaction is repulsive. Of course, the intensity of the interaction is proportional to the value of \( |a_s| \). The expression for \( \sigma \) in Eq. (26.15) indicates, that the atoms behave like hard spheres with radius \( |a_s| \). The specific value of \( a_s \) will depend on the interaction potential, however, the details of the potential are unimportant, as all information about the collision is already contained in \( a_s \). Consequently, in the low-energy limit, we can assume that the collision is mediated by an effective potential \( V_{\text{coll}}(r) \), which has the particularity,

\[ \int V_{\text{coll}}(r)d^3r = \frac{4\pi\hbar^2}{m}a_s \equiv g. \] (26.16)

This has been shown in Sec. 12.1.2. Consequently, the effective interaction between two particles at positions \( r \) and \( r' \) can be considered as contact interaction given by \(^5\),

\[ V_{\text{coll}}(r, r') = \frac{g}{2}\delta(r - r'). \] (26.17)

\[ \begin{array}{c}
\ \end{array} \]

Figure 26.2: (code) Interpretation of the scattering length in terms of a phase shift of the relative Broglie wave of two colliding atoms.

The interatomic interaction potential decides on the value of the scattering length \( a_s \): A repulsive potential corresponds to a positive \( a_s \). For a purely attractive potential

\(^5\)The Hartree-Fock-Bogolubov method (HFB) for the mean-field theory disregards corrections of higher orders, for example, due to the renormalization of the scattering length. It also neglects quantum depletion due to the correlation effects of the order of \( N_{\text{out}}/N = \frac{2}{\pi}\sqrt{\pi|a_s|n_0} \). The theory mean-field supposes the validity of the Born approximation, that is, two-body correlations are neglected, \( \hat{\psi}(r') \approx \hat{\psi}(r) \) and \( \int d^3RV_{\text{coll}}(R) = \frac{g}{2} \).
that does not support bound states $a_s$ is negative, and for an attractive potential that supports bound states $a_s$ may be positive or negative depending on the proximity of the last bound vibrational state of the interaction potential below the dissociation limit.

26.2.4 The mean field approximation

The mean-field theory (MFT) or local density approximation (LDA) is based on the assumption of hard sphere collisions between atoms (as described by the potential (26.17)) propagating through a locally homogeneous mean-field potential, $\frac{g}{2}|\hat{\psi}(\mathbf{r})|^2$. The procedure is also called regularization of the interaction.

Thus, the mean-field energy of a condensate is proportional to the density of the gas $n$ and to a single atomic constant, which is the scattering length $a_s$. Its presence in the Gross-Pitaevskii equation emphasizes its impact on shape, dynamic stability and many other properties of the condensate. For example, the mean-field interaction contributes to the broadening of a condensed wavepacket, and consequently contracts its momentum distribution in comparison with an ideal gas. Homogeneous condensates with a negative scattering length are unstable, because the attempt of such a condensate to lower its self-energy by increasing its density also increases the rate of inelastic three-body collisions until the condensate collapses.

26.2.5 Gross-Pitaevskii equation

The Heisenberg equation [last line of (26.5)] is equivalent to the variational principle, as stated by the Ehrenfest theorem,

$$i\hbar \frac{d\hat{\psi}}{dt} = \frac{\delta H}{\delta \hat{\psi}^\dagger} .$$  \hspace{1cm} (26.18)

This facilitates the derivation of the equation of motion for the atomic field. With the Hamiltonian (26.6) in the mean-field approximation,

$$\mathcal{H}_{atom} \equiv \mathcal{H}_{cm} + \mathcal{H}_{mf} \quad \text{with} \quad \mathcal{H}_{mf} \equiv \int d^3 r \hat{\psi}^\dagger(\mathbf{r},t) \left( \frac{g}{2} |\hat{\psi}(\mathbf{r},t)|^2 + \right) \hat{\psi}^\dagger(\mathbf{r},t) ,$$  \hspace{1cm} (26.19)

we find the non-linear Schrödinger equation,

$$\left[ - \frac{\hbar^2}{2m} \nabla^2 + V_{trap}(\mathbf{r},t) + g|\hat{\psi}(\mathbf{r},t)|^2 \right] \hat{\psi}(\mathbf{r},t) = i\hbar \frac{\partial}{\partial t} \hat{\psi}(\mathbf{r},t) .$$  \hspace{1cm} (26.20)

Remember that, despite their symbol $\hat{\psi}$, which usually is associated to wavefunctions, and the fact that they satisfy a non-linear Schrödinger equation the field operators are represented by matrices acting of many-body states. That is, Eq. (26.20) also represents a Heisenberg equation for the field operators.

A common approximation is the Bogolubov prescription, where the field operators describing the condensate and its fluctuations are decomposed into a complex function, $\psi_0(\mathbf{r}) \equiv \langle \hat{\psi}(\mathbf{r}) \rangle$ called condensed wavefunction, which can be chosen as the order parameter of the system, and a small perturbation, $\delta \hat{\psi}(\mathbf{r}) \equiv \hat{\psi}(\mathbf{r}) - \psi_0(\mathbf{r})$ describing thermal excitations. At zero temperature, we can neglect the excitations [40], and our
system is completely described by a single wavefunction, $\psi_0(r,t)$, obeying the famous Gross-Pitaevskii equation (GPE),

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(r,t) + g|\psi_0(r,t)|^2 \right] \psi_0(r,t) = i\hbar \frac{\partial}{\partial t} \psi_0(r,t).$$  \hspace{1cm} (26.21)

### 26.2.5.1 Spontaneous breaking of gauge symmetry

The description of a condensate by a single macroscopic wavefunction means that we attribute a well-defined phase to it. However, the GPE does not allow us to predict, which phase between 0 and $2\pi$ this will be, and we have to assume, that the BEC chooses its phase spontaneously when it undergoes the phase transition to quantum degeneracy. This principle is called spontaneous breaking of gauge symmetry \footnote{An alternative way of modeling the development of a BEC phase is based on measurement theory. See also (15.71) for an analogy to the correct state of a laser.}. In Exc. 26.2.6.2 we study the relation between the fact of having exactly $N$ atoms in a condensate and a well-defined phase $\varphi$, knowing that these two quantities are conjugate variables having to satisfy a Heisenberg uncertainty relation.

### 26.2.6 Exercises

#### 26.2.6.1 Ex: Derivation of the non-linear Schrödinger equation

Derive the non-linear Schrödinger equation using (a) the commutator relation (26.5)(v) and (b) the variational expression (26.18).

#### 26.2.6.2 Ex: Spontaneous breaking of gauge symmetry

One of the primary characteristics of a condensate is its phase coherence. Now, consider a condensate with exactly $N$ atoms. The exact knowledge of the atom number implies a totally uncertain phase of the condensate, according to Heisenberg’s uncertainty relation. Explain this contradiction!

### 26.3 Approximate solutions of the Gross-Pitaevskii equation

#### 26.3.1 Stationary GPE

In cases where the external potential is stationary, $V_{\text{trap}}(r,t) = V_{\text{trap}}(r)$, the temporal dependency of the GPE can be removed by the ansatz,

$$\psi_0(r,t) = \psi_0(r)e^{-i\mu t/\hbar}. \hspace{1cm} (26.22)$$

This gives the stationary Gross-Pitaevskii equation,

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(r) + g|\psi_0(r)|^2 \right] \psi_0(r) = \mu \psi_0(r), \hspace{1cm} (26.23)$$

where $\mu$ is called the chemical potential. Solve Exc. 26.3.4.1.
26.3.2 Trapped condensates and the Thomas-Fermi limit

26.3.2.1 Free particles

The wavefunction of free particles, \( V(r) = 0 \), can be described by a plane wave,

\[ \psi(r) = \sqrt{n} e^{i k \cdot r}, \quad (26.24) \]

also called the Hartree solution. Inserted it into the equation of Gross-Pitaevskii equation,

\[ E(k) = \frac{\hbar^2 k^2}{2m} + gn, \quad (26.25) \]

we observe a gap in the energy spectrum due to the interaction.

26.3.2.2 Ideal gas in a harmonic potential

Most experiments apply non-isotropic (often cylindrical) potentials, which are additionally distorted by the mean-field. Hence, the non-linear term of the GPE is important, and the spatial coordinates can not be separated. However, assuming an ideal gas and a harmonic potential, the dimensions could be separated, as demonstrated in Sec. 4.4.5, even when the potential is not isotropic. It is then sufficient to consider one-dimensional problems with \( g = 0 \),

\[ \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m}{2} \omega_x^2 \hat{x}^2 \right] \psi_n = \mu_n \psi_n. \quad (26.26) \]

In this limit, the GPE is nothing more than the usual Schrödinger equation, which has the well-known spectrum (4.91) and the solutions (4.90).

26.3.2.3 Ideal gas in an isotropic potential

In the case of an ideal gas trapped in a spherically symmetric potential, as shown in (3.33), the Schrödinger equation can be reduced to its radial component,

\[ \left[ \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{l(l+1)}{r^2} + V_{trap}(r) \right] f_{nlm}(r) = \mu_n f_{nlm}(r), \quad (26.27) \]

with the solution (3.17),

\[ \psi_n(r, \vartheta, \varphi) = \sum_{l,m} f_{nlm}(r) Y_{lm}(\vartheta, \varphi) \quad (26.28) \]

The differential equation (26.27) can be solved numerically by Runge-Kutta type methods,

\[ \left( f'' \right) = \left( \begin{array}{c} \frac{2}{1} \mu + \frac{l(l+1)}{r^2} - V_{trap}(r) \\ 0 \end{array} \right) \left( \begin{array}{c} f' \end{array} \right). \quad (26.29) \]
### 26.3. APPROXIMATE SOLUTIONS OF THE GROSS-PITAEVSKII EQUATION

#### 26.3.2.4 Thomas-Fermi limit for strong interactions

In the case of strong interactions, the kinetic energy term can be neglected, at least in the center of the cloud, where the mean-field energy is stronger. For this case, called *Thomas-Fermi limit*, the GPE solution is easy,

\[ |\psi_0(r)|^2 = \frac{\mu - V_{\text{trap}}}{g}. \]  

(26.30)

The chemical potential follows from the normalization condition,

\[ N = \int_{n(r) > 0} n(r) d^3r. \]  

(26.31)

In the case of an cylindrical harmonic oscillator potential, \( V_{\text{trap}}(r, z) = \frac{m}{2} (\omega_r^2 r^2 + \omega_z^2 z^2) \), the chemical potential is,

\[ \mu = \left( \frac{15Ng}{8\pi} \right)^{2/5} \left( \frac{m}{2} (\omega_r^2 \omega_z)^{2/3} \right)^{3/5}. \]  

(26.32)

The radial size \( \sigma \) of the condensate follows from \( n(r_{hw}, 0) = \frac{n(0,0)}{2} \),

\[ r_{hw} = \sqrt{\frac{\mu}{m\omega_r^2}}. \]  

(26.33)

Solve the Excs. 26.3.4.2 and 26.3.4.3.

#### 26.3.3 Variational treatment of the GPE

The many-body Hamiltonian (26.19) can be used as an energy functional,

\[ E[\psi_0] \equiv \langle \mathcal{H}[\psi_0] \rangle = \int d^3r \left[ \frac{\hbar^2}{2m} |\nabla \psi_0|^2 + V_{\text{trap}}(r)|\psi_0|^2 + \frac{g}{2} |\psi_0|^4 \right], \]  

(26.34)

from which, using the variational condition (26.18), we have derived the Gross-Pitaevskii equation (26.21). Hence, the wavefunction \( \psi_0 \) minimizes the functional [169]. By inserting an ansatz for the wavefunction with adjustable parameters, the functional provides conditions to optimize these parameters.

The variational method is useful e.g. for finding the ground state wavefunction of a condensate in an arbitrarily shaped trap or to perform a stability analysis of a condensate with attractive interatomic forces.

#### 26.3.3.1 Finding the fundamental state of the GPE

This problem of finding the ground state wavefunction of a condensate consists in finding the \( \psi \) for which the energy \( \mathcal{H}[\psi] \) goes to a minimum. In general, the functional has the form \( \mathcal{H}[\psi] = \int \mathcal{H}[\psi, \nabla \psi] d^3r \). The fastest way to the minimum is to reduce the energy by varying \( \psi \) in that direction, where the gradient \( \delta \mathcal{H}/\delta \psi^* \) is largest, that is,

\[ \mathcal{H} \rightarrow \mathcal{H}[\psi + \tau \frac{\delta \mathcal{H}}{\delta \psi^*}], \]  

\[ \psi \rightarrow \psi + \tau \frac{\delta \mathcal{H}}{\delta \psi^*}, \]  

(26.35)
with the boundary condition, that the normalization must be preserved. Formally, this problem is similar to a time-dependent Gross-Pitaevskii equation, but with \textit{imaginary time}. Physically, the procedure, called the \textit{steepest descent method}, can be interpreted as applying a heavily ‘overdamped’ friction force,

\begin{equation}
\frac{\partial \psi}{\partial \tau} = \frac{\delta \mathcal{H}}{\delta \psi^*} .
\end{equation}

(26.36)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure26.3}
\caption{(code) Calculation of the BEC wavefunction by the steepest descent method (red dots). Also shown are the ideal gas approximation (yellow line) and the Thomas-Fermi approximation (magenta line), as well as the ground state energy (black line) and the chemical potential (green line).}
\end{figure}

In practice, the procedure is as follows: we start with a trial wavefunction, for example, the exact solution of the interaction-free case. This function is now propagated in imaginary time, using the complete Hamiltonian including the non-linear term, and then renormalized:

\begin{equation}
\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \mathcal{H}(\mathbf{r}) \psi(\mathbf{r}, t) .
\end{equation}

(26.37)

Substituting the imaginary unit $i$ in the time-dependent Gross-Pitaevskii equation (26.21) by $-1$, we obtain,

\begin{equation}
\psi(\mathbf{r}, t + dt) = [1 - \hbar^{-1} \mathcal{H}(\mathbf{r}) dt] \psi(\mathbf{r}, t)
\end{equation}

(26.38)

\begin{equation}
\psi'(\mathbf{r}, t) \equiv \frac{\psi(\mathbf{r}, t + dt)}{|\psi(\mathbf{r}, t + dt)|} \to \psi(\mathbf{r}, t).
\end{equation}

This procedure is repeated until the function converges. Since this method is derived from a variational principle, it only serves to find the ground state of the trapping potential. It can not be used for excited states (with the exception of vortex states, where in cylindrical coordinates the Hamiltonian differs by an additional centrifugal term).

\subsection{26.3.3.2 Collapse and stabilization of condensates with attractive interactions}

Attractive interactions destabilize a Bose-Einstein condensate. Since the interaction energy, $4\pi \hbar^2 a_s n/m$, of a condensate with negative scattering length decreased with
increasing density $n$, the condensate attempts to lower its interaction energy by increasing its density until it succumbs to inelastic two-body spin-changing collisions of to three-body collisions leading to the formation of molecules [582]. Strictly speaking, this only holds true for homogeneous condensates. In the presence of a trapping potential, however, the zero-point energy exerts a kinetic pressure, which counteracts the condensate collapse to a certain extent, such that small condensates are stabilized. This can be verified by inserting a Gaussian wavefunction $\psi_0 \propto e^{-r^2/2\bar{r}^2}$ into the energy functional (26.34). Varying the radius $\bar{r}$ of the condensate, we find a local minimum where the condensate is stable. Calculations for spherical traps predict [515, 134],

$$N_{\text{min}} \simeq 0.575 \frac{a_{\text{trp}}}{|a_s|},$$

(26.39)

where $a_{\text{trp}} = \sqrt{\hbar/m\omega_{\text{trp}}}$.

The atomic species $^7\text{Li}$ has a slightly negative scattering length $a_s = -27.3 a_B$. As can be seen in Fig. 26.4, small condensates can survive in a confining trap, since the energy functional has a local minimum [83, 81, 516]. Solve Exc. 26.3.4.4.

Figure 26.4: (code) Energy of a $^7\text{Li}$ condensate in a harmonic isotropic potential with $\omega_{\text{trp}} = (2\pi) 50$ Hz with $N = 500$ atoms (linha inferior) up to $N = 3000$ (linha superior) when the radius $\bar{r}$ of the condensate is varied.

### 26.3.4 Exercises

**26.3.4.1 Ex: GPE in dimensionless units**

Use the following abbreviations to rewrite the Gross-Pitaevskii equation and its solution for a harmonic isotropic potential in dimensionless units,

- $V_1 \equiv V_{\text{trap}}/\hbar\omega_{\text{trp}}$
- $r_1 \equiv r/a_{\text{trp}}$
- $\mu_1 \equiv \mu/\hbar\omega_{\text{trp}}$
- $\psi_1 \equiv \psi/a_{\text{trp}}^{3/2}$
- $g \equiv 4\pi\hbar^2a/m$
- $V_{\text{trap}} = \frac{m\omega_{\text{trp}}^2r^2}{2}$
- $a_{\text{trp}} = \sqrt{\hbar/m\omega_{\text{trp}}}$
- $T_1 \equiv k_B T/\hbar\omega_{\text{trp}}$
- $p_1 \equiv a_{\text{trp}} p/\hbar$
- $g_1 \equiv 8\pi N_0 a/a_{\text{trp}}$
26.3.4.2 Ex: Interacting gas in an isotropic potential

Consider the potential \( V(r) = V(r) \), such that the wavefunction will have radial symmetry, \( \psi(r) = \frac{\phi(r)}{r} \). Rewrite the Gross-Pitaevskii equation for the function \( \phi \) [286].

26.3.4.3 Ex: Interacting gas in a cylindrical potential

Consider the potential \( V(r) = V(\rho, z) \), such that the wavefunction will have rotational symmetry, \( \psi(\rho, z, \varphi) = \frac{\phi(\rho, z)}{\rho} \). Rewrite the Gross-Pitaevskii equation for the function \( \phi \) [286].

26.3.4.4 Ex: Collapse of condensate with attractive interactions

A Bose-Einstein condensate of \(^7\)Li may become unstable due to attractive interatomic forces, the scattering length being \( a_s = -27.3a_B \). Consider the radial Gross-Pitaevskii Hamiltonian with an external harmonic potential with the oscillation frequency \( \omega_{\text{trap}}/(2\pi) = 50 \text{ Hz} \). Using the variational method, determine the maximum number of atoms allowing for a stable condensate. (Note that the derived minimization condition must be evaluated numerically.)

26.4 Elementary excitations

The dynamics of Bose-Einstein condensates is usually studied by observing the change of their shape in response to temporal variations in the trapping potential. The simplest variation surely consists in suddenly removing the trapping potential altogether. Consequently, the first experiment performed with a BEC was the study of its ballistic expansion [12, 190, 99] (see Sec. 26.7.1).

On the other hand, the temporal variation of the potential can also be a small oscillatory or pulsed perturbation, for example, a small modification of the amplitude of the trapping field, a displacement or a local anisotropy induced by the dipole force of a laser beam tuned far away from resonance. It is even conceivable to manipulate the self-energy of the condensate or to irradiate electromagnetic waves, which couples internal atomic excitation levels or states of the atomic motion [40, 13, 572, 323, 415, 556, 181, 583, 324, 455, 571, 217]. The response of the condensate to such small perturbations can be understood by a linearized model of the Gross-Pitaevskii equation, which we will present in the following sections.

26.4.1 Bogolubov spectrum of excitations

To analyze the spectrum of a condensate’s response to small perturbations, let us follow Bogolubov’s treatment of the time-dependent Gross-Pitaevskii equation [569]. We start by substituting Eq. (26.20) [180],

\[
\hat{\psi}(\mathbf{r}, t) \rightarrow \hat{\psi}(\mathbf{r}, t)e^{-i\mu t/\hbar},
\] (26.40)
which gives us,
\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(r) + g|\psi(r,t)|^2\right] \dot{\psi}(r,t) = \left[\mu + i\hbar \frac{\partial}{\partial t}\right] \dot{\psi}(r,t) .
\] (26.41)

The Bogolubov prescription now consists in approximating the field operators of the condensate by a sum of the equilibrium wavefunction, which is interpreted as a complex number, and a small perturbation, which conserves its operator character,
\[
\hat{\psi}(r,t) \simeq \psi_0(r) + \delta \hat{\psi}(r,t) .
\] (26.42)

This treatment assumes that most atoms are condensed, \( N - N_0 \ll N_0 \), and only a few thermal atoms are left out.

Applying the Bogolubov transform,
\[
\delta \hat{\psi}(r,t) \equiv \sum_k u_k(r) \hat{a}_k(t) + v_k^*(r) \hat{a}_k(t)^\dagger ,
\] (26.43)

the perturbation is expressed as a superposition of amplitudes for annihilation and creation of non-interacting quasi-particles. By inserting this ansatz into the Gross-Pitaevskii equation, we obtain a linear system of equations called Bogolubov-de Gennes equations.

### 26.4.1.1 Semi-classical approximation

To simplify the equations, let us neglect the operator character of the quasi-particle by doing the substitutions,
\[
\hat{a}_k \rightarrow e^{-i\omega_k t} \quad \text{and} \quad \hat{a}_k^\dagger \rightarrow e^{i\omega_k t} .
\] (26.44)

That is, we insert the ansatz (26.42) with,
\[
\delta \hat{\psi}(r,t) \equiv u_k(r)e^{-i\omega_k t} + v_k^*(r)e^{i\omega_k t} ,
\] (26.45)

into the Gross-Pitaevskii equation (26.41), we look for the lowest order,
\[
\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}} + g|\psi_0|^2\right) \psi_0 = \mu \psi_0 ,
\] (26.46)

and we collect the terms of first order in \( e^{\pm i\omega_k t} \), neglecting terms of order \( u_k^2, v_k^2 \) or higher,
\[
\begin{align*}
-\frac{\hbar^2}{2m} \nabla^2 u_k + V_{\text{trap}} u_k + 2g\psi_0^2 u_k - g\psi_0^2 v_k^* &= \mu u_k + \hbar \omega_k u_k \quad (26.47) \\
\frac{\hbar^2}{2m} \nabla^2 v_k - V_{\text{trap}} v_k - 2g\psi_0^2 v_k + g\psi_0^2 u_k^* &= -\mu v_k + \hbar \omega_k v_k .
\end{align*}
\]

Introducing the abbreviations \( n = \psi_0^2 \) and,
\[
\mathcal{L} \equiv -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{trap}} + 2gn - \mu ,
\] (26.48)

\[
\begin{align*}
-\frac{\hbar^2}{2m} \nabla^2 u_k + V_{\text{trap}} u_k + 2gn u_k - gn v_k^* &= \mu u_k + \hbar \omega_k u_k , \\
\frac{\hbar^2}{2m} \nabla^2 v_k - V_{\text{trap}} v_k - 2gn v_k + gn u_k^* &= -\mu v_k + \hbar \omega_k v_k .
\end{align*}
\]
we can write
\[
\left( \begin{array}{cc}
\mathcal{L} - \hbar \omega_k & gn \\
 gn & \mathcal{L} + \hbar \omega_k
\end{array} \right) \left( \begin{array}{c}
u_k \\
v_k
\end{array} \right) = \left[ \left( \begin{array}{cc}
\mathcal{L} & gn \\
 gn & \mathcal{L}
\end{array} \right) - \hbar \omega_k \hat{\sigma}_z \right] \phi_k = 0,
\] (26.49)

with \( \hat{\sigma}_z \) being the third Pauli matrix. The solution of Eq. (26.49) is given by the requirement, that the determinant of the matrix be 0,
\[
\hbar \omega_k = \sqrt{\mathcal{L}^2 - (gn)^2}.
\] (26.50)
The object
\[
\phi_k \equiv \left( \begin{array}{c}
u_k(r) \\
v_k(r)
\end{array} \right)
\] (26.51)
is called a normal mode of the condensate. The normal modes (26.50) are orthonormal,
\[
\langle \phi_k|\phi_{k'} \rangle = \int d\mathbf{r} \phi_k^*(\mathbf{r}) \hat{\sigma}_z \phi_{k'}(\mathbf{r}) = \delta_{k,k'},
\] (26.52)
which means that the modes do not interact, that is, the quasi-particles do not collide.

For homogeneous systems or at the interior of a large condensate with strong interactions, we can assume that the potential is approximately constant, \( V_{\text{trap}} \rightarrow 0 \), and kinetic energy negligible compared to the self-energy, and Eq. (26.41) shows us, \( \mu \rightarrow gn \). Assuming plane waves,
\[
u_k(r) \equiv u e^{i \mathbf{k} \cdot \mathbf{r}} \quad \text{and} \quad v_k(r) \equiv v e^{i \mathbf{k} \cdot \mathbf{r}},
\] (26.53)
we obtain the Bogolubov spectrum of elementary excitations,
\[
\hbar \omega_k = \sqrt{\frac{\hbar^2 k^2}{2m} \left( \frac{\hbar^2 k^2}{2m} + 2 \mu \right)}.
\] (26.54)
which corresponds to a dispersion relation for Bose-Einstein condensates. For an interacting gas, the collective modes are distortions of the condensate, caused by restoring forces originating in the finite compressibility of the gas.

### 26.4.1.2 Phonon- and particle-like excitations

The coefficients \( u \) and \( v \) describe the annihilation and \( u^* \) and \( v^* \) the creation of quasi-particles called phonons or elementary excitations. Two limits are interesting. In the low energy limit, \( \frac{\hbar^2 k^2}{2m} \ll gn(\mathbf{r}) \), we create phonon-like excitations. The Bogolubov spectrum becomes,
\[
\hbar \omega_k^{ph} \simeq c_s \hbar k \quad \text{with} \quad c_s \equiv \sqrt{\frac{gn}{m}}.
\] (26.55)
Here is \( c_s \) the sound velocity inside the condensate. The fact that, comparing (26.54) and (26.55), we find,
\[
\hbar \omega_k > \hbar \omega_k^{ph}
\] (26.56)
for all \( \mathbf{k} \) is the Landau criterion for the superfluidity of the condensate. It means that, for an object being dragged through the condensate with a velocity less than \( c_s \), it does
26.4. ELEMENTARY EXCITATIONS

not become energetically favorable to produce excitations, see Fig. 26.5. Therefore, the object will move without dissipation, which is an important characteristic of superfluids. Experiments demonstrated this manifestation of superfluidity by slowly stirring a strongly focused blue-detuned laser through a condensate. We will come back to this in Sec. 27.1.1.

In the high energy limit, $\frac{\hbar^2 k^2}{2m} \gg gn(r)$, we create particle-like excitations. The Bogolubov spectrum becomes,

$$\hbar \omega_{k}^{pa} = \frac{\hbar^2 k^2}{2m}.$$  

In this limit, we recover the quadratic dispersion relation of free particles, as seen in Fig. 26.5.

![Figure 26.5](image-url)

Figure 26.5: (code) Bogolubov spectrum (red), phonon limit (blue line) and particle limit (green line).

Experimentally, the complete Bogolubov spectrum (26.54) can be measured by Bragg spectroscopy [576, 570] (see Sec. 28.2). Solve Exc. 26.4.4.1.

26.4.2 Excitation of normal modes

In the simplest case, we generate a perturbation as a weak additional potential in the Gross-Pitaevskii equation (26.41),

$$\left[ \mathcal{L} - gn + f_+(r)e^{-i\omega pt} + f_-(r)e^{i\omega pt} \right] \hat{\psi} = i\hbar \frac{\partial}{\partial t} \hat{\psi}(r,t).$$  

After the Bogolubov transform (26.45) we now have,

$$\begin{pmatrix} \mathcal{L} & gn \\ gn & \mathcal{L} \end{pmatrix} - \hbar \omega_k \sigma_3 \begin{pmatrix} u(r) \\ v(r) \end{pmatrix} = - \begin{pmatrix} f_+(r)\psi_0(r) \\ f_-(r)\psi_0^*(r) \end{pmatrix}.$$  

The solution of this equation is found by expanding the amplitudes $u(r)$ and $v(r)$ into normal modes,

$$\begin{pmatrix} u(r) \\ v(r) \end{pmatrix} = \sum_k c_k \phi_k(r) \quad \text{and} \quad \begin{pmatrix} f_+(r)\psi_0(r) \\ f_-(r)\psi_0^*(r) \end{pmatrix} = \sum_k g_k \phi_k(r),$$  

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where $g_k$ is given by the overlap integral,

$$g_k = \int d\mathbf{r} \phi_k^{\dagger}(\mathbf{r}) \sigma_3 \left( f_+(\mathbf{r})\psi_0(\mathbf{r}) \right).$$  \hspace{1cm} (26.61)

To calculate the response of the condensate to a given perturbation $f_{\pm}(\mathbf{r})$, we must first calculate the normal mode spectrum $\phi_k(\mathbf{r})$ from the Bogolubov equation (26.49). After that, we can calculate the coefficients (26.61). Inserting the expansions into the Eq. (26.59), we obtain the response of the condensate,

$$\begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix} = -\sum_k \frac{g_k}{\hbar \omega_k - \omega} \phi_k.$$

(26.62)

The deviation, which is observed for resonant excitation, is due to the neglected losses and non-linear effects.

### 26.4.3 Classification of normal modes

BECs often have cylindrical symmetry, $\psi(\mathbf{r}) = \psi_0(r, z)$. In this case, similar calculations to those shown above, result in analytical expressions for the frequencies of the elementary excitations. These frequencies were derived by [133] \footnote{It is worth mentioning that the linearized theory applies to small perturbations. Strong disturbances render the dynamics chaotic, since the energy is coupled to many modes of excitation.}. The modes can be classified by their main quantum numbers $n_r$ and by their multipolar moment $\ell$. Examples are the surface excitation or shape oscillation ($n_r = 0$) and the compression oscillation ($n_r \neq 0$). Special cases are called shaking mode, breathing mode ($n_r = 1, \ell = 0$), and swirling mode. In the case of cylindrical symmetry, the projection of the angular momentum onto the symmetry axis $m$ is the relevant quantum number. The dispersion relations are,

$$\omega(\ell, m = \ell) = |m| \omega_r^2$$

$$\omega(\ell, m = \ell - 1) = |m| \omega_r^2 + \omega_z^2$$

$$\omega(\ell, m = \ell - 2) = \omega_r^2 \left[ 2|m| + 2 + \frac{3}{2} \lambda^2 \mp \sqrt{(|m| + 2 - \frac{3}{2} \lambda^2)^2 + 2 \lambda^2(|m| + 1)} \right]$$

$$\omega(\ell, m = \ell - 3) = \omega_r^2 \left[ 2|m| + 2 + \frac{7}{2} \lambda^2 \mp \sqrt{(|m| + 2 - \frac{5}{2} \lambda^2)^2 + 6 \lambda^2(|m| + 1)} \right],$$

where $\lambda$ is the aspect ratio $\lambda = \omega_z/\omega_r$. Obviously, higher excitation orders depend on the trap geometry. Moreover, we can easily see, that occasional degeneracies must arise for specific aspect ratios. For example, when $\omega_+(2, 0) = 2\omega(2, 2)$, we derive from (26.63) the condition $\lambda = \sqrt{16/7}$, and when $\omega_+(2, 0) = 2\omega_{-}(2, 0)$, we derive $\lambda = \frac{1}{6} \sqrt{77 + 5 \sqrt{145}}$.

### 26.4.3.1 Quantum depletion

Following Bogolubov’s theory the quantum depletion is given by,

$$\frac{\delta N}{N} = \frac{1}{N} \sum_k \int d^3r |v_k(\mathbf{r})|^2.$$

(26.64)
Resonantly excite the shape oscillations. The subsequent free oscillations were clearly visible as periodic.

By a non-selective “step” excitation, we used a five-cycle sinusoidal modulation of the trapping coils to locate the modes.

The higher frequency mode was primarily a radial breathing mode (fig. 14b). After locating the modes, quadrupolar modes observed at JILA, with out-of-phase oscillations along the axial and radial directions.

Figure 14. – Shape of low-lying collective excitations: a) slow=0 radial oscillation (MIT), c) fast=0 quadrupolar condensate oscillations viewed in time-of-flight absorption imaging. Oscillations in = 0 quadrupolar oscillation (JILA, MIT), b) fast=0 quadrupolar oscillation (JILA). (d) Non-destructive measurements of quadrupolar vibrations of a BEC [571].

### 26.4.3.2 Fluctuations in BECs

Fluctuations in condensates are reduced as compared to thermal ensembles. Non-linearities are always very sensitive to fluctuations (see the laser). Therefore, we have to look at closer at collisions. For 3-body decay in a thermal source, \( \langle \rho(r)^3 \rangle \sim 6 \langle \rho(r) \rangle^3 \), and in a coherent source: \( \langle \rho(r)^3 \rangle \sim \langle \rho(r) \rangle^3 \) [92, 564].

### 26.4.4 Exercises

#### 26.4.4.1 Ex: Sound velocity in the Thomas-Fermi regime

Consider a condensate of \( N = 10^5 \) \(^{87}\)Rb atoms confined to an isotropic harmonic potential with secular frequency \( \omega_{trp} = (2\pi) 50 \) Hz. Remember \( a_s = 110 a_B \) and use the Thomas-Fermi approximation.

a. Evaluate the chemical potential.
b. Calculate the sound velocity at the center of the condensate.

### 26.5 Hydrodynamics and the propagation of sound

#### 26.5.1 Hydrodynamic regime

The question arises how the elementary excitations relate to the phenomenon of sound, well known from the hydrodynamic theory of superfluid \(^4\)He proposed by Landau [368]. The hydrodynamic regime is characterized by the dominance of collisions. On the other hand, Bogolubov’s theory describes elementary excitations in the collisionless regime, where quasi-particles do not interact. There is, therefore, a great

---

8Collisions prevent condensation, because they localize the particles. This is the reason for the large quantum depletion, which in \(^4\)He is of the order of 10% and hides effects of quantum statistics. Quantum depletion prevents any form of long-range order, as this requires delocalization.

9Bogolubov’s theory assumes that the only impact of collisions is to deform the dispersion relationship, keeping the collective modes orthogonal.
motivation to study excitations with condensates in a very dense regime, where one can expect to recover predictions of hydrodynamic theory.

The hydrodynamic regime is reached, when the free path of the particles is smaller than the wavelength of the sound, that is \(^{10}\),

\[
l_{mfp} < \frac{\lambda}{2\pi} .
\]  

(26.65)

26.5.2 Zero, first and second sound

The occurrence of several types of sound was related by Tisza and London to the existence of superfluid and normal components in \(^4\)He \([451]\). The second sound is a quantum phenomenon, where the heat transfer occurs as an wave-like motion instead of being diffusive. Heat takes the place of pressure in normal sound waves called first sound. This induces a very high thermal conductivity. At temperatures below the \(\lambda\)-point, \(^4\)He has the highest known conductivity of all materials (a few hundred times higher than copper).

The zero sound was introduced by Landau to name quantum vibrations in Fermi quantum liquids. This sound can not be seen as a simple wave of compression and rarefaction. In gaseous condensates, the zero sound corresponds to the elementary excitation called phonon-like.

![Figure 26.7: (code) Consecutive measurements of the BEC density profile showing the propagation of zero sound. The sound was excited by a blue-detuned laser tuned focused into the middle of the BEC (lower curve). The other curves show how the perturbation propagates towards the edges of the BEC.](image)

Finally, the excitation called particle-like or ballistic, observed in gaseous condensates has no correspondence in dense superfluids, since the mean free path there is too short. The various regimes accessible in condensed gasses are listed in the following

\(^{10}\)Note the similarity to the Ioffe-Regel criterion.
### 26.6 Momentum representation

We showed in Sec. 2.3.7, that the wavefunctions can be represented in the spatial or the momentum domain. These notions can be extended to the second quantization.

#### Table 1:

<table>
<thead>
<tr>
<th>Regime</th>
<th>Range Scale</th>
<th>Energy Range</th>
<th>Condensate</th>
<th>Thermal Cloud</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collision-less</td>
<td>$k^{-1} &lt; \xi &lt; l_{mfp}$</td>
<td>$\frac{\hbar^2}{2m_{mfp}} &lt; gn_0 &lt; \frac{\hbar^2 k^2}{2m}$</td>
<td>Ballistic</td>
<td>Ballistic</td>
</tr>
<tr>
<td>Collision-less</td>
<td>$\xi &lt; k^{-1} &lt; l_{mfp}$</td>
<td>$\frac{\hbar^2}{2m_{mfp}} &lt; \frac{\hbar^2 k^2}{2m} &lt; gn_0$</td>
<td>Zero Sound</td>
<td>Ballistic</td>
</tr>
<tr>
<td>Hydrodynamic</td>
<td>$\xi &lt; l_{mfp} &lt; k^{-1}$</td>
<td>$\frac{\hbar^2 k^2}{2m} &lt; \frac{\hbar^2}{2m_{mfp}} &lt; gn_0$</td>
<td>Second Sound</td>
<td>First Sound</td>
</tr>
</tbody>
</table>

(26.66)

<table>
<thead>
<tr>
<th>Normal modes</th>
<th></th>
<th>$q R \ll 1$</th>
<th>$qa \ll 1$</th>
<th>$qa &gt; 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscopic</td>
<td></td>
<td>$E_{self} \gg E_{kin}$</td>
<td>$8 \pi Na \gg a_{ho}$</td>
<td>$a_{ho} \gg \xi$</td>
</tr>
<tr>
<td>Beyond Bogolubov</td>
<td></td>
<td>$E_{self} \ll E_{kin}$</td>
<td>$8 \pi Na \ll a_{ho}$</td>
<td>$a_{ho} \ll \xi$</td>
</tr>
<tr>
<td>Superfluid (TF limit, LDA)</td>
<td>$??$</td>
<td>$\gamma_{col} \ll \frac{\hbar q^2}{2m}$</td>
<td>$q l_{mfp} \ll 1$</td>
<td>$q l_{mfp} &gt; 1$</td>
</tr>
<tr>
<td>Collision-less</td>
<td></td>
<td>$\gamma_{col} \gg \frac{\hbar q^2}{2m}$</td>
<td>$q l_{mfp} \ll 1$</td>
<td>$q l_{mfp} &gt; 1$</td>
</tr>
<tr>
<td>Hydrodynamic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(26.67)

With $l_{mfp} \simeq 1/n_{th} \sigma$. Typical values are,

\[
\begin{align*}
    a &= 0.1000a_B = 0.50 \text{ nm} \\
    n^{-1/3} &= 20.200 \mu m \\
    2\pi / q &= 0.2..\infty \mu m \\
    \xi &= \sqrt{8\pi na^{-1}} = 0.03..30 \mu m \\
    a_{ho} &= \sqrt{\hbar / m \omega_{tr}} = 0.1..3 \mu m \\
    2\pi / k_F &= 2\pi a_{ho}(48N)^{-1/6} = 30..70 \mu m
\end{align*}
\]

(26.68)

The various regimes of sound are distinguished by frequency shifts and damping rates of the collective modes, which depend on the density (determining the mean-field energy and the mean free path) and the temperature (controlling the ratio between condensed and normal fraction). The quantity

\[
\xi = \frac{1}{\sqrt{8\pi a_s n}},
\]

(26.69)

is called **healing length**.

#### 26.6. Momentum representation

We showed in Sec. 2.3.7, that the wavefunctions can be represented in the spatial or the momentum domain. These notions can be extended to the second quantization.
procedure by generalizing the equations (2.100),

\[ \hat{a}_k \equiv \frac{1}{\sqrt{(2\pi)^3 V}} \int \hat{\psi}(r) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3 r, \quad \hat{\psi}(r) \equiv \sqrt{\frac{V}{(2\pi)^3}} \int \hat{a}_k e^{i\mathbf{k} \cdot \mathbf{r}} d^3 k. \]  

Differently from (2.100) we chose here a normalization, which leaves the field operators \( a_k \) without unit.

### 26.6.1 Confined particles

In the case of confined atoms, \( \mathcal{H} = \mathcal{H}_{cm} + V_{\text{trap}}(r) + \mathcal{H}_{\text{self}} \), we get sharp eigenvalues,

\[ \hat{a}_k = \frac{1}{V} \sum_{k'} \hat{a}_{k'} \delta^{(3)}(\mathbf{k} - \mathbf{k}'). \]

We insert this in equation (26.70),

\[ \hat{\psi}(r) = \sqrt{\frac{1}{(2\pi)^3 V}} \sum_{k'} \hat{a}_{k'} \int \delta^{(3)}(\mathbf{k} - \mathbf{k}') e^{i\mathbf{k} \cdot \mathbf{r}} d^3 k \]

\[ = \sqrt{\frac{1}{(2\pi)^3 V}} \sum_{k'} \hat{a}_{k'} e^{i\mathbf{k} \cdot \mathbf{r}} = \sum_{k} u_k(r) \hat{a}_k, \]

thus making an expansion of the condensate into plane waves,

\[ u_k(r) = \frac{1}{\sqrt{(2\pi)^3 V}} e^{i\mathbf{k} \cdot \mathbf{r}}, \]

which is particularly adapted to the 3D box potential, \( V_{\text{trap}}(r) \equiv \infty \) se \( r > R \). Also, we calculate,

\[ \hat{a}_k = \sqrt{\frac{1}{(2\pi)^3 V}} \int \hat{\psi}(r) e^{-i\mathbf{k} \cdot \mathbf{r}} d^3 r = \int \hat{\psi}(r) u^*_k(r) d^3 r. \]
26.6. MOMENTUM REPRESENTATION

We obtain the observable commutation rules from (26.5),

$$ [\hat{a}_k, \hat{a}_{k'}^\dagger] = \delta_{kk'} \quad , \quad [\hat{a}_k, \hat{a}_{k'}] = 0 \quad , \quad \hat{N} = \sum_k \hat{a}_k^\dagger \hat{a}_k \ . \quad (26.75) $$

Using the following mathematical relationships,

$$ \frac{1}{(2\pi)^3} \sum_k e^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} = \delta^3(\mathbf{r} - \mathbf{r}') \quad \text{ and } \quad \frac{1}{(2\pi)^3} \int d^3r e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} = \delta_{kk'} \ , \quad (26.76) $$

and easy to show for plane waves,

$$ \sum_k u_k^*(\mathbf{r}) u_k(\mathbf{r}') = \delta^3(\mathbf{r} - \mathbf{r}') \quad \text{ and } \quad \int u_k^*(\mathbf{r}) u_k(\mathbf{r}) d^3r = \delta_{kk'} \ . \quad (26.77) $$

In Exc. 26.6.4.1 we will check the validity of the commutation rules (26.75), and in Exc. 26.6.4.2 we derive the following representation of the Hamiltonian:

$$ \mathcal{H} = \int d^3r \hat{\psi}^\dagger(\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(\mathbf{r}) \right) \hat{\psi}(\mathbf{r}) + \frac{g}{2} \int d^3r \int d^3r' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}') \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}') \right) , \quad (26.78) $$

with the abbreviation,

$$ V_{k,k'} = \int u_k^*(\mathbf{r}) V_{\text{trap}}(\mathbf{r}) u_{k'}(\mathbf{r}) d^3r = \frac{1}{(2\pi)^3} \int V_{\text{trap}}(\mathbf{r}) e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d^3r \ . \quad (26.79) $$

The equation of motion for the momentum wavefunction now becomes,

$$ i\hbar \frac{\partial}{\partial t} \hat{a}_k = [\hat{a}_k, \mathcal{H}] = \hbar^2 \frac{k^2}{2m} \hat{a}_k + \sum_{k,k'} V_{k,k'} \hat{a}_{k'} + g \sum_{k,k',k''} \hat{a}_k^\dagger \hat{a}_{k'}^\dagger \hat{a}_{k''} \hat{a}_{k+k'-k''} \ . \quad (26.80) $$

26.6.1.1 Harmonically confined particles

In harmonic traps, $V_{\text{trap}}(r) = \frac{m}{2} \omega_{\text{trap}}^2 r^2$, the motion can be canonically quantized,

$$ \hat{a} = \frac{1}{\sqrt{2}} \left( \hat{r} \mp i \frac{\mathbf{p}}{a_{\text{trap}}} \right) \quad , \quad \mathcal{H}_{\text{cm}} = \sum_k \hbar \omega_{\text{trap}} \hat{a}_k^\dagger \hat{a}_k \ , \quad (26.81) $$

with the size of the ground state,

$$ a_{\text{trap}} = \sqrt{\frac{\hbar}{m \omega_{\text{trap}}} } . \quad (26.82) $$

As an alternative notation we could introduce,

$$ |r\rangle \equiv \hat{\psi}^\dagger(\mathbf{r}) \quad \text{ and } \quad |k\rangle \equiv \hat{a}_k^\dagger . \quad (26.83) $$

Hence, just considering the ground state of the trap, that is, assuming that the atomic motion be frozen, our Hamiltonian becomes:

$$ \mathcal{H}_{\text{cm}} + \mathcal{H}_{\text{self}} = \hbar \omega_{\text{trap}} \hat{a}^\dagger \hat{a} + \frac{g}{2} \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a} . \quad (26.84) $$
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26.6.2 Thomas-Fermi limit

In the limit of negligible kinetic energy (that is, in the middle of a large condensate) with the analytical form of the condensate wavefunction,

\[ \hat{\psi}(\mathbf{r}) \propto \sqrt{n_0 \left( 1 - \frac{r^2}{r_0^2} \right)} , \quad (26.85) \]

the transformation (26.70) allows us to derive an expression for the momentum distribution,

\[ |a(k)| \propto \frac{J_1(k \cdot r_0)}{(k \cdot r_0)^2} . \quad (26.86) \]

26.6.2.1 Width of the momentum distribution

It is interesting to compare the size of an ideal gas condensate with the size of an interacting condensate. We can express the Thomas-Fermi radius as,

\[ \Delta r_{TF} = a_{trp} \sqrt{\frac{\mu}{\hbar \omega_{trp}}} . \quad (26.87) \]

The Heisenberg limit requires,

\[ \Delta p_{TF} = \frac{\hbar}{\Delta r_{TF}} . \quad (26.88) \]

Since \( \sqrt{\frac{\mu}{\hbar \omega_{trp}}} > 1 \), the interaction increases the volume of the condensate, but restricts the distribution of its velocities. For a hypothetical thermal Boltzmann gas having the same temperature,

\[ \Delta r_{th} = a_{trp} \sqrt{k_B T / \hbar \omega_{trp}} \quad \text{and} \quad \Delta p_{th} = \frac{\hbar}{a_{trp} \sqrt{k_B T / \hbar \omega_{trp}}} . \quad (26.89) \]

The thermal cloud is not at the Heisenberg limit, because \( \sqrt{k_B T / \hbar \omega_{trp}} > 1 \).

These relationships were experimentally confirmed [576] by measurements of the velocity distributions of condensates using a Bragg spectroscopy technique (see Sec. 28.2). It is interesting to note that the measured widths of velocity distributions were lower than the photonic recoil limit, \( \hbar k / m \simeq 30 \text{ mm/s} \) for \( ^{87}\text{Rb} \).

26.6.3 Master equation approach

The Hamiltonian that describes a BEC in second quantization in an orthonormal set of energy eigenfunctions reads:

\[ \mathcal{H} = \sum_{i,j} \mathcal{H}_{\text{atom}}^{(ij)} \hat{a}_i^\dagger \hat{a}_j + \sum_{i,j,k,l} \frac{1}{2} W^{(ijkl)} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l \quad (26.90) \]

\[ \mathcal{H}_{\text{atom}}^{(ij)} = \langle \phi_i | \frac{1}{2m} \mathbf{p}^2 + V_{\text{trap}}(\mathbf{r}) | \phi_j \rangle \]

\[ W^{(ijkl)} = g \int \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_k(\mathbf{r}) \phi_l(\mathbf{r}) d^3 r . \]
The inclusion of spontaneous processes (one-body-loss, dephasing) requires a master equation including a Lindblad term within a density matrix formalism. The von Neumann equation for the density operator reads:

$$\frac{d}{dt} \hat{\rho} = -i[V, \hat{\rho}] + L\hat{\rho}$$

(26.91)

- **$L_{one\text{-body loss}}$**
  \[ \kappa(2\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} - \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}) \]

- **$L_{one\text{-body feeding}}$**
  \[ \kappa(2 + 2\hat{a}^\dagger\hat{\rho} - \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} - \hat{\rho}\hat{a}^\dagger\hat{a}) \]

- **$L_{two\text{-body loss}}$**
  \[ \kappa(2\hat{a}^2\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}^2\hat{\rho} - \hat{\rho}\hat{a}^\dagger\hat{a}^2) \]

### 26.6.4 Exercises

#### 26.6.4.1 Ex: Commutators in momentum space

Demonstrate the validity of the commutation rules (26.75).

#### 26.6.4.2 Ex: Commutators in momentum space

Derive the representation (26.78) of the Hamiltonian.

### 26.7 Condensates at finite temperature

#### 26.7.1 Ballistic expansion of a bosonic gas

As discussed in Sec. 24.6, the atomic density distributions are revealed through their interaction with a laser beam. The problem with imaging a confined condensate is, on the one hand, its very high optical density, which inhibits the penetration of resonant light and, on the other hand, its very small size, which is often below the diffraction limit and prevents its optical resolution. As discussed in Sec. 24.6, both problems can be avoided by the time-of-flight imaging technique, which consists in quickly switching off the trap and dropping the atomic cloud (see Fig. 24.30). If the switching-off process is fast enough, the potential energy is lost, but in the course of ballistic expansion, the self-energy is transformed into kinetic energy. Both the self-energy transformed to kinetic energy and the inherent initial kinetic energy contribute to blow up the size of the atomic cloud, so that the density rapidly decreases. After a few 10 ms, when the optical density is sufficiently low (on the order of 1), the cloud can be imaged via its absorption of a resonant laser beam. The condensate, which is about 10 times denser than the thermal cloud, has a much larger repulsive self-energy. When the condensate is suddenly released from its trap, its explosion is accelerated by this self-energy, and the acceleration is faster in those directions, where the confining potential was stronger [286, 99]. Therefore, the aspect ratio of the condensate’s shape is inverted during the flight time [339, 99]. In contrast, the self-energy of the thermal cloud is relatively insignificant. Therefore, its spatial density after a time of free expansion reflects the pure velocity distribution of the atomic cloud while it was trapped. This allows the interpretation of the spatial distribution of the expanded cloud in terms of a temperature of the trapped cloud.
26.7.1.1 Popov approximation

The Popov decomposition separates the condensed part, described by a c-number $\phi \equiv \langle \hat{\psi} \rangle$ and normalized to the number of condensed atoms $N_0$ from the thermal part $\tilde{\psi} \equiv \hat{\psi} - \phi$, which keeps track of the quantum nature of the Bose-gas [171],

$$K = K_0 + K_1 + K_1^\dagger + K_2$$

$$K_0 = \int d^3 r \phi^* (r) \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(r) + \frac{g}{2} |\phi|^2 - \mu \right) \phi(r)$$

$$K_1 = 0 \quad \text{if} \quad [\mathcal{L} - gn_0(r)]\phi(r) = 0$$

$$K_2 = \int d^3 r \left[ \tilde{\psi}^+ (r) \mathcal{L} \tilde{\psi} (r) + \frac{g}{2} \left( \phi(r)^2 \tilde{\psi}^+ (r) \tilde{\psi} (r) + \phi^*(r)^2 \tilde{\psi} (r) \tilde{\psi}^+ (r) \right) \right]$$

$$\mathcal{L} \equiv -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{trap}}(r) - \mu + 2gn(r)$$

$$n(r) = n_0(r) + n_T(r) = |\phi(r)|^2 + \langle \tilde{\psi}^+ (r) \tilde{\psi} (r) \rangle.$$

We perform the Bogolubov transform to the diagonalized Hamiltonian,

$$K_{\text{Popov}} = K_0 + \sum_j \varepsilon_j \hat{b}_j^\dagger \hat{b}_j$$

$$\tilde{\psi} (r) = \sum_j u_j (r) \hat{b}_j - v_j^* (r) \hat{b}_j^\dagger$$

$$\delta_{jk} = \int d^3 r \left( u_j u_k^* - v_j v_k^* \right)$$

$$\delta_{jk} = [\hat{b}_j, \hat{b}_k^\dagger].$$

This yields a set of equations for elementary excitations (quasi-particle excitations in a diagonalized energy space),

$$N_j = \left[ \exp(\varepsilon_j / k_B T) - 1 \right]^{-1}$$

$$n_T(r) = \sum_j \left[ (|u_j|^2 + |v_j|^2) N_j + |v_j|^2 \right]$$

$$\mathcal{L} u_j (r) - gn_0(r)v_j (r) = \varepsilon_j u_j (r),$$

$$\mathcal{L} v_j (r) - gn_0(r)u_j (r) = -\varepsilon v_j (r).$$

Figure 26.9: Inversion of aspect ratio during time-of-flight. The frequencies of the harmonic trap were $\omega_r = (2\pi) \cdot 248$ Hz and $\omega_r = (2\pi) \cdot 16$ Hz [339].
The quantum depletion at $T = 0$ [last term in the density $n(r)$] may be neglected. In this zero-temperature limit, the equations simplify to yield the Gross-Pitaevskii equation. We may separate these equations using auxiliary functions 

$$\psi_j^{(\pm)}(r) = u_j(r) \pm v_j(r)$$ (26.95)

$$\hat{h}_0 \equiv L - g n_0(r)$$

$$\hat{h}_0 \psi_j^{(+)}(r) = E_j \psi_j^{(-)}(r).$$

The eigenvalue equations that one gets after substituting (III.2.5) into (III.2.4) may be solved by expanding in a set of eigenfunctions of $\hat{h}_0$:

$$\psi_j^{(\pm)}(r) \equiv \sum_\alpha c_\alpha^{(j)} \phi_\alpha(r)$$ (26.96)

$$\sum_\beta (M_{\alpha\beta} + \varepsilon_\alpha \delta_{\alpha\beta}) \varepsilon_\beta c_\alpha^{(j)} = E_j^2 c_\alpha^{(j)}$$

$$M_{\alpha\beta} = 2g \int \phi_\alpha^*(r)n_0(r)\phi_\beta(r) d^3r.$$

### 26.7.2 Hartree-Fock approach

#### 26.7.2.1 Two-gas model for $T > 0$

The two phases of a condensate above $T = 0$ have a specific interdependence, which makes it possible to treat the problem with an approximation, where only the condensed part influences the non-condensed and not vice versa [170] DOI. The HFB equation (III.2.11) is solved for the condensed part alone, assuming $n_{th} = 0$. The condensate wavefunction and the chemical potential are derived from that, e.g. using numerical methods like the method of steepest descent. The effective potential for the thermal cloud in the presence of a condensate is:

$$V_{1,\text{eff}}(r_1) = V_{1,\text{trap}}(r_1) + g_1 |\psi_1(r_1)|^2.$$ (26.97)

Next, we diagonalize the Schrödinger equation:

$$[-\nabla_1^2 + V_{1,\text{eff}}(r_1)]\psi_{1,j}(r_1) = 2E_{1,j}\psi_{1,j}(r_1),$$ (26.98)

maintaining the normalization,

$$1 = \int |\psi_{1,j}(r_1)|^2 d^3r_1.$$ (26.99)

This provides us with the energy eigenvalues of the excited trap states and their eigenfunctions. One can e.g. guess an eigenvalue and numerically solve the Schrödinger equation using Runge-Kutta integration routines. The eigenfunction will probably diverge. In this case, we vary the eigenvalue until the solution converges.

Finally, we can calculate the thermal density distribution:

$$N_j = \frac{\exp((E_{1,j} - \mu_j)/k_B T_1) - 1}{-1}$$ (26.100)

$$n_{th}(r_1) = \sum_j N_j |\psi_{1,j}(r_1)|^2,$$
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and all thermodynamic potentials, as shown in Sec. 25.1.2.

A more sophisticated method uses self-consistent recursion [301]. Here, the thermal density is plugged back into the HFB equation, and the whole procedure is repeated until it converges.

26.7.2.2 Hartree-Fock approximation

We have already seen that, inside a trap the condensate occupies the lowest vibrational level, whereas the atoms of the thermal gas are distributed among all levels. The trapping potential is often harmonic,

\[ U_{\text{trp}}(r) = \frac{m}{2} \omega_r^2 r^2, \]

with secular frequencies \( \omega_r \) typically on the order of several tens or hundreds of Hz. The spatial (radial) extent of the vibration levels varies a lot with their quantum number,

\[ r_j = \sqrt{2j + 1} \frac{\hbar}{m \omega_r}. \]

This naturally produces a separation of the thermal (or normal) and condensate fractions at \( T > 0 \), which does not exist for a homogeneous gas and which allows (up to a certain degree) an individual treatment of the two fractions. The details of the interaction between the two fractions are very complicated and are still under intense theoretical investigation. However, to understand the shape of a trapped atomic cloud and other characteristics, we can use a simple approximate model [?, 301], assuming that the condensate is only weakly disturbed by the thermal cloud. In contrast, the presence of the condensate dramatically modifies the potential for the thermal atoms. Therefore, we must first calculate the density of the condensate \( n_0(r) \), before calculating that of the thermal cloud. If this procedure is applied iteratively, it is called Hartree-Fock method:

i. We start with \( n_{th}(r) = 0 \);

ii. we solve the GPE

\[ \left( -\frac{\hbar^2}{2m} \Delta + V_{\text{trap}}(r) - \mu + g |\psi(r)|^2 + n_{th}(r) \right) \psi(r) \]

numerically with the steepest descent method, we derive \( \mu \) and \( \psi \), and also \( n(r) = |\psi(r)|^2 + n_{th}(r) \);

iii. assuming that collisions between atoms of the thermal cloud, the density of which is weak, can be neglected, we can view the cloud as an ideal gas in a potential modified by the strongly anharmonic mean field of the condensate, \( V_{\text{trap}}(r) + 2gn(r) \), we calculate the thermal density \( n'_{th}(r) = \lambda_{dB}^{-3/2} \left( \exp \frac{V_{\text{trap}}(r) - \mu + 2gn(r)}{k_B T} \right) \);

iv. we start over at (ii) using the new thermal density.

We can now calculate the total energy,

\[
U = \int d^3r \left( \psi(r) - \frac{\hbar^2 \nabla^2}{2m} \psi(r) + V_{\text{trap}}(r)n(r) + \frac{g}{2} [2n(r)^2 - n_0(r)] + \hbar^3 \int d^3k \frac{-\hbar^2 k^2}{2m} n(r,k) \right)
\]

\[
= \int d^3r \left( \psi(r) - \frac{\hbar^2 \nabla^2}{2m} \psi(r) + V_{\text{trap}}(r)n(r) + \frac{g}{2} [2n(r)^2 - n_0(r)] + \frac{3k_B T}{2\lambda_{dB} g_{3/2}} \left[ \exp \frac{V_{\text{trap}}(r) - \mu + 2gn(r)}{k_B T} \right] \right)
\]

and other thermodynamic quantities.
26.7.3 Ideal gas limit

Consider the ideal gas in an isotropic harmonic potential. The excitation spectrum then takes the form:

\[ f(k, r) = n(k, r) \]
\[ \varepsilon_{HF}(k, r) = \mathcal{L}(k, r) = \frac{\hbar^2 k^2}{2m} + V(r) - \mu. \]

We can immediately calculate:

\[ g \rightarrow 0 \]
\[ \mu \rightarrow \frac{3}{2} \hbar \omega \]
\[ \phi(r) \rightarrow \frac{\sqrt{N_0}}{\pi^{3/4} a_{\text{trap}}^{3/2}} \exp\left(-\frac{r^2}{2a_{\text{trap}}^2}\right) \]
\[ E_{\text{kin}} = \int \phi(r) - \frac{\hbar^2 \Delta}{2m} \phi(r) d^3r = -\frac{9}{4} N_0 \hbar \omega \]
\[ n_{th}(r) \rightarrow \int f(r \cdot k) d^3k = \frac{1}{\lambda_{dB}^3} g_{3/2} \left[ \exp\left(\frac{V_{\text{trap}}(r) - \mu}{k_B T}\right)\right] \]
\[ N_{th} \rightarrow \int n_{th}(r) d^3r = \left(\frac{k_B T}{\hbar \omega}\right)^3 g_{3} \left[ \exp\left(\frac{-\mu}{k_B T}\right)\right] \]
\[ U \rightarrow \int \varepsilon_{HF} f(r \cdot k) d^3r \cdot d^3k = 3k_B T \left(\frac{k_B T}{\hbar \omega}\right)^3 g_{4} \left[ \exp\left(\frac{-\mu}{k_B T}\right)\right]. \]

26.7.4 Exercises

26.7.4.1 Ex: Ballistic expansion of a condensate

Calculate the ballistic expansion of a $^{87}\text{Rb}$ BEC initially confined in a cylindrically symmetric trap with secular frequencies $\omega_z = 20 \text{ Hz}$ and $\omega_r = 100 \text{ Hz}$.

26.8 Numerical simulations of the Gross-Pitaevskii equation

To simulate the one-dimensional evolution of a wavepacket following the Gross-Pitaevskii equation,

\[ i\hbar \frac{\partial}{\partial t} \psi(z, t) = \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V_{\text{trap}}(z) + |\psi(z, t)|^2 \right] \psi(z, t). \]

we solve iteratively [479],

\[ \psi(z, t + dt) = \psi(z, t) + dt \dot{\psi}(z, t). \]

As initial state we choose, $\psi(z, 0) = e^{-z^2/2\bar{z}^2} e^{ikz}$, where $k \equiv \sqrt{2mE}/\hbar$ is the wavevector.

The numerical propagation is conveniently performed using the time-splitting spectral algorithm [34, 33, 32, 213], which can be easily extended to two dimensions.
26.8.1 Crank-Nicholson-Crout algorithm

26.8.1.1 Crank-Nicholson-Crout algorithm for the time-dependent Schrödinger equation

The Crank-Nicholson algorithm goes as follows. The time-dependent Schrödinger equation in one dimension,
\[
\frac{\partial}{\partial t} \psi(x, t) = \frac{i\hbar}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) - \frac{i\hbar}{\hbar} V(x) \psi(x, t)
\]  
(26.106)

is a parabolic partial differential equation. We usually seek a solution on an interval \( x \in [a, b] \) and \( t > 0 \). The solution is uniquely determined from boundary conditions: \( \psi(a, t) = \psi(b, t) = 0 \) and \( \psi(x, 0) = g(x) \). One method for numerical solution solves for the values of the wavefunction on a regular grid of dimension \( h = (b - a)/N_x \) in \( x \) and \( \tau \) in \( t \):
\[
\psi_j^k = \psi(a + jh, k\tau) .
\]  
(26.107)

The derivatives are replaced by simple finite differences. The r.h.s. of the equation at the grid point \((i, j)\) is then,
\[
\frac{i\hbar}{2m\hbar^2} \left( \psi_{j+1}^k - 2\psi_j^k + \psi_{j-1}^k \right) - \frac{i\hbar}{\hbar} V(a + jh) \psi_j^k = \sum_{m=0}^{N} iH_{jm} \psi_j^k ,
\]  
(26.108)

where \( H \) is a real symmetric tridiagonal matrix (provided \( V(x) \) is real). The l.h.s. of the equation can be replaced either by a forward or backward difference,
\[
\frac{\psi_{j+1}^k - \psi_j^k}{\tau} \quad \text{or} \quad \frac{\psi_j^k - \psi_{j-1}^k}{\tau} ,
\]  
(26.109)

which, when combined with the r.h.s. gives the explicit algorithm,
\[
\psi^{k+1} = (1 + iH\tau)\psi^k \quad \text{or} \quad \psi^k = (1 - iH\tau)\psi^{k+1} .
\]  
(26.110)

The Crank-Nicholson Algorithm averages both,
\[
(1 - iH\tau/2)\psi^{k+1} = (1 + iH\tau/2)\psi^k .
\]  
(26.111)

This method is a second order algorithm in \( t \), i.e. the discretization error decreases as \( \tau^2 \). The finite difference representation of the second derivative \( d^2/dx^2 \) is also good to second order in \( h^2 \). The Crank-Nicholson Algorithm also gives a unitary evolution in time. That is especially useful for quantum mechanics where unitarity assures that the normalization of the wavefunction is unchanged over time. The algorithm steps the solution forward in time by one time unit, starting from the initial wavefunction at \( t = 0 \). According to the Crank-Nicholson scheme, the time stepping process is half explicit and half implicit. The implicit part involves solving a tridiagonal system. That solution is accomplished by Crout reduction, a direct method related to Gaussian elimination and LU decomposition.

To simplify the algorithm we have chosen units in which the Planck constant \( \hbar = 1 \), time step \( \tau = 1 \) and the spatial separation \( h = 1 \). This can always be arranged by an appropriate redefinition of mass and potential: \( m = m_{SI} h^2/\tau\hbar \) and \( V = V_{SI} \tau/h \).
26.8. NUMERICAL SIMULATIONS OF THE GP EQUATION

26.8.1.2 Crank-Nicholson algorithm for the time-dependent Gross-Pitaevskii equation

The Crank-Nicholson algorithm [4],

\[
\frac{i(\varphi_j^{n+1} - \varphi_j^n)}{\Delta} = -\frac{\varphi_{j+1}^{n+1} - 2\varphi_j^{n+1} + \varphi_{j-1}^{n+1} + \varphi_{j+1}^n - 2\varphi_j^n + \varphi_{j-1}^n}{2\hbar^2} + \frac{1}{2} \left( \frac{c(x_j)^2}{4} + n \frac{|\varphi_j^n|^2}{(x_j)^2} \right) (\varphi_j^{n+1} + \varphi_j^n).
\]  

(26.112)

Introducing abbreviations,

\[
B(\varphi_j^{n+1} - \varphi_j^n) = -A \left( \varphi_{j+1}^{n+1} - 2\varphi_j^{n+1} + \varphi_{j-1}^{n+1} + \varphi_{j+1}^n - 2\varphi_j^n + \varphi_{j-1}^n \right) + C_j^n \left( \varphi_j^{n+1} + \varphi_j^n \right).
\]

(26.113)

Can be rewritten as,

\[
A\varphi_{j+1}^{n+1} + (-2A + B - C_j^n) \varphi_j^{n+1} + A\varphi_{j-1}^{n+1} = -A\varphi_{j+1}^n + (2A + B + C_j^n) \varphi_j^n - A\varphi_{j-1}^n = X_j^n.
\]

(26.114)

The set of equations,

\[
\begin{pmatrix}
-2A - B - C_1^n & A & 0 & \cdots & 0 \\
A & -2A - B - C_2^n & A & \cdots & 0 \\
0 & A & -2A - B - C_3^n & \ddots & 0 \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & \cdots & A & -2A - B - C_J^n
\end{pmatrix}
\begin{pmatrix}
\varphi_1^{n+1} \\
\varphi_2^{n+1} \\
\varphi_3^{n+1} \\
\vdots \\
\varphi_J^{n+1}
\end{pmatrix}
= \begin{pmatrix}
X_1^n \\
X_2^n \\
X_3^n \\
\vdots \\
X_J^n
\end{pmatrix}
\]

(26.115)

can be solved by inverting tridiagonal matrix. Set \(\varphi_0^{n+1} = \varphi_0^{n+1} = 0\). Run a loop \(j = 1, \ldots, J\). Assume given \(\varphi_1^n = \varphi_J^n\),

\[
\varphi_{j+1}^{n+1} = \frac{X_j^n}{A} + \frac{2A - B + C_j^n}{A} \varphi_j^{n+1} - \varphi_{j-1}^{n+1}.
\]

(26.116)

26.8.2 Time-splitting spectral algorithm: Coherent propagation

We write the one-dimensional GPE in the form,

\[
ith \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(x,t) + V(x)\psi(x,t) + \frac{4\pi \hbar^2 a_s}{m(2r_h)^2} |\psi(x,t)|^2 \psi(x,t)
\]

(26.117)

for \(a < x < b\). Choose periodic boundary conditions, \(\psi(a,t) = \psi(b,t)\) and \(\psi_x(a,t) = \psi_x(b,t)\). Various methods are known to solve the GPE numerically, such as the Crank-Nicholson algorithm. The time-splitting spectral algorithm (TSSA) consists in solving the first and the second of the following equations in two distinct steps [34, 33, 32, 213],

\[
\frac{\partial \psi(x,t)}{\partial t} = -\frac{iV(x)}{\hbar} \psi(x,t) - \frac{g_{1D}}{\hbar} |\psi(x,t)|^2 \psi(x,t)
\]

(26.118)

\[
\frac{\partial \psi(x,t)}{\partial t} = \frac{i}{2m} \psi_{xx}(x,t),
\]
i.e. we discretize in space using \( x = a + j(b - a)/M \) and \( k = 2\pi l/(b - a) \) such that \( k(x - a) = 2\pi lj/M \). We propagate half the way, \( \Delta t/2 \), in time,

\[
\varphi_x \equiv e^{-\frac{i}{\hbar}(V(x) + g_1D|\psi(x,t)|^2)\Delta t}\psi(x,t) \tag{26.119}
\]

for \( j = 0, \ldots, M-1 \). Now we propagate the spectral components, \((\mathcal{F}\varphi)_k \equiv \sum_{j=0}^{M-1} \varphi_x e^{-2\pi ij/M} \), in momentum space and transform back, \((\mathcal{F}^{-1}\varphi)_x \equiv M^{-1} \sum_{l=-M/2}^{M/2-1} \varphi_k e^{2\pi ilj/M} \),

\[
\phi_x \equiv \mathcal{F}^{-1} \left[ e^{\frac{i\hbar}{2m}k^2\Delta t}(\mathcal{F}\varphi)_k \right]. \tag{26.120}
\]

for \( l = -M/2, \ldots, M/2 - 1 \). Finally, we propagate the remaining time, \( \Delta t/2 \),

\[
\psi(x, t + dt) = e^{-\frac{i}{\hbar}(V(x) + g_1D|\phi_x|^2)\Delta t}\phi_x. \tag{26.121}
\]

Compared to the Crank-Nicholson algorithm time-splitting spectral algorithm has several advantages:

- TSSA is much much faster, especially, for large arrays;
- No divergence, perfect reversibility;
- Imaginary version yields same density shape as steepest descent.

But there are problems:

- The coherent version changes shape, maybe it’s due to ifft(fft(x))!=x;
- The imaginary version mixes up real and imag parts;
- Don’t know how to generalize to coupled GPEs.

### 26.8.2.1 Time-splitting spectral algorithm for coupled GPEs

Write the one-dimensional GPE in the form,

\[
\begin{align*}
\hbar \frac{\partial \psi_1(x, t)}{\partial t} &= -\frac{\hbar^2}{2m} \nabla^2 \psi_1(x, t) + V(x)\psi_1(x, t) + \frac{4\pi\hbar^2a_s}{m(2r_h)^2} |\psi_1(x, t)|^2 \psi_1(x, t) \quad (26.122) \\
&\quad + \frac{\hbar}{2} \Omega_{mw}\psi_2(x, t) + \hbar \Delta_{mw}\psi_1(x, t) \\
\hbar \frac{\partial \psi_2(x, t)}{\partial t} &= -\frac{\hbar^2}{2m} \nabla^2 \psi_2(x, t) + V(x)\psi_2(x, t) + \frac{4\pi\hbar^2a_s}{m(2r_h)^2} |\psi_2(x, t)|^2 \psi_2(x, t) \\
&\quad + \frac{\hbar}{2} \Omega_{mw}\psi_1(x, t)
\end{align*}
\]
for \( a < x < b \). Choose periodic boundary conditions, \( \psi(a, t) = \psi(b, t) \) and \( \psi_x(a, t) = \psi_x(b, t) \). We generalize the time-splitting spectral algorithm,

\[
\frac{\partial \psi_1(x, t)}{\partial t} = -\frac{i}{\hbar} V(x) \psi_1(x, t) - \frac{i}{\hbar} g_{1D} |\psi_1(x, t)|^2 \psi_1(x, t) - i \Delta_m \psi_1(x, t) - \frac{i}{2} \Omega_{mW} \psi_2(x, t) \\
\frac{\partial \psi_2(x, t)}{\partial t} = -\frac{i}{\hbar} V(x) \psi_2(x, t) - \frac{i}{\hbar} g_{1D} |\psi_2(x, t)|^2 \psi_2(x, t) - \frac{i}{2} \Omega_{mW} \psi_1(x, t) \\
\frac{\partial \psi_1(x, t)}{\partial t} = i \frac{\hbar}{2m} \psi_{xx1}(x, t) \\
\frac{\partial \psi_2(x, t)}{\partial t} = i \frac{\hbar}{2m} \psi_{xx2}(x, t) ,
\]

(26.123)

i.e. we discretize in space and propagate half the way, \( \Delta t/2 \), in time,

\[
\varphi_{x1} \equiv \psi_1(x, t) - \left[ \left( \frac{\hbar}{i} V(x) + \frac{i}{\hbar} g_{1D} |\psi_1(x, t)|^2 + i \Delta_{mW} \right) \psi_1(x, t) - \frac{i}{2} \Omega_{mW} \psi_2(x, t) \right] \frac{\Delta t}{2} \\
\varphi_{x2} \equiv \psi_2(x, t) - \left[ \left( \frac{\hbar}{i} V(x) + \frac{i}{\hbar} g_{1D} |\psi_2(x, t)|^2 \right) \psi_2(x, t) - \frac{i}{2} \Omega_{mW} \psi_1(x, t) \right] \frac{\Delta t}{2} .
\]

(26.124)

Since we here use the first order Taylor expansion of the exponential function, we introduce an error that we have to keep low by renormalizing the wavefunction after each step. Now we propagate the spectral components in momentum space and transform back,

\[
\phi_{x1} \equiv \mathcal{F}^{-1} \left[ e^{\frac{\hbar}{2m} k^2 \Delta t \mathcal{F}(\varphi_{x1})} \right] \\
\phi_{x2} \equiv \mathcal{F}^{-1} \left[ e^{\frac{\hbar}{2m} k^2 \Delta t \mathcal{F}(\varphi_{x2})} \right] ,
\]

for \( l = -M/2, \ldots, M/2 - 1 \). Finally, we propagate the remaining time, \( \Delta t/2 \),

\[
\psi_1(x, t + dt) = \phi_{x1} - \left[ \left( \frac{\hbar}{i} V(x) + \frac{i}{\hbar} g_{1D} |\phi_{x1}|^2 + \frac{i}{2} \Delta_{mW} \right) \phi_{x1} - \frac{i}{2} \Omega_{mW} \phi_{x2} \right] \frac{\Delta t}{2} \\
\psi_2(x, t + dt) = \phi_{x1} - \left[ \left( \frac{\hbar}{i} V(x) + \frac{i}{\hbar} g_{1D} |\phi_{x2}|^2 \right) \phi_{x2} - \frac{i}{2} \Omega_{mW} \phi_{x1} \right] \frac{\Delta t}{2} .
\]

(26.126)

### 26.8.2.2 Spinor notation

It may be possible to simplify the notation by writing the wavefunction as a spinor, \( \vec{\psi} = \left( \begin{array}{c} \psi_1 \\ \psi_2 \end{array} \right) \). Now the non-kinetic part of the coupled GPE can be written,

\[
\frac{\partial \vec{\psi}(x, t)}{\partial t} = M \vec{\psi}(x, t) ,
\]

(26.127)

with the matrix,

\[
M = \left( \begin{array}{cc} -\frac{i}{\hbar} V(x) - \frac{i}{\hbar} g_{1D} |\psi_1(x, t)|^2 - i \Delta_{mW} & -\frac{i}{2} \Omega_{mW} \\ -\frac{i}{2} \Omega_{mW} & -\frac{i}{\hbar} V(x) - \frac{i}{\hbar} g_{1D} |\psi_2(x, t)|^2 \end{array} \right) ,
\]

(26.128)

and the solution,

\[
\vec{\psi}(x, t) = e^{Mt} \vec{\psi}(x, 0) .
\]

(26.129)
Let us now abbreviate the matrix by,

\[ M = \begin{pmatrix} A & B \\ B & D \end{pmatrix} \]  

(26.130)

The matrix is diagonalized with the unitary transforms,

\[ U = \frac{1}{\sqrt{2\Delta}} \begin{pmatrix} A-D & \Delta \\ 1 & -1 \end{pmatrix} \quad \text{and} \quad U^{-1} = \frac{1}{\sqrt{2\Delta}} \begin{pmatrix} 1 & -A-D \\ 1 & A-D \end{pmatrix} + \Delta \]  

(26.131)

The eigenvalue matrix is,

\[ U^{-1}MU = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \]  

(26.132)

with \( E_1,2 = \frac{1}{2} A \pm \frac{1}{2} D \pm B\Delta \). Here we used the abbreviation \( \Delta = \sqrt{(D-A)^2} + 1 \). The formal solution now reads,

\[ \vec{\psi}(x,t) = \exp \left[ U \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} U^{-1}t \right] \vec{\psi} = U \begin{pmatrix} e^{E_1t} & 0 \\ 0 & e^{E_2t} \end{pmatrix} U^{-1} \vec{\psi}(x,0) . \]  

(26.133)

This formula can easily be computed, because the block matrices of transform \( U \) are diagonal in \( x \).

### 26.8.3 Wavepacket propagation

#### 26.8.3.1 1D simulations

We want to describe the one-dimensional evolution of an atomic wavepacket according to the Schrödinger equation. The problem is fully described by [479],

\[ i\hbar \frac{\partial}{\partial t} \psi(z,t) = -\hbar^2 \frac{d^2}{2m \, d z^2} \psi(z,t) + V(z)\psi(z,t) . \]  

(26.134)

Numerically the Schrödinger equation is integrated via,

\[ \psi(z,t+dt) = \psi(z,t) + dt\dot{\psi}(z,t) . \]  

(26.135)

The initial state of the wavepacket is set to \( \psi(z,0) = e^{-z^2/2\sigma^2} e^{ikz} \), where \( k \equiv \sqrt{2mE}/\hbar \) is its wavevector.

The numerical propagation is conveniently done with the time-splitting spectral algorithm [34, 33, 32, 213].

The flux is,

\[ \psi \nabla \psi = 0 . \]  

(26.136)

#### 26.8.3.2 2D simulations

We want to describe the two-dimensional evolution of an atomic wavepacket according to the Schrödinger equation. The problem is fully described by,

\[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dz^2} \right) \Psi(x,z,t) + V(x,z)\Psi(x,z,t) = i\hbar \frac{\partial}{\partial t} \Psi(x,z,t) . \]  

(26.137)
Since the potential is conservative, we separate the time-evolution,
\[ \Psi(x, z, t) = \psi(x, z)e^{-iEt/\hbar} \] (26.138)

The initial shape of the wavefunction moving along the \( y \) coordinate could be a Gaussian,
\[ \psi(x, z) = \psi_x(x, 0)\psi_z(0, z) = (2\pi\sigma_x\sigma_z)^{-1/2} e^{-x^2/4\sigma_x^2 - z^2/4\sigma_z^2} . \] (26.139)

We can assume \( \sigma_z \gg \sigma_x \) and obtain an effectively one-dimensional model, \( E = E_{k_z} \).

Set,
\[ \psi(x, z, 0) = \phi(x, z)e^{-i\kappa_z z} \] (26.140)

and,
\[ -\frac{d^2}{dz^2} \phi(x, z) + 2i\kappa_z \frac{d}{dz} \phi(x, z) = \frac{d^2}{dx^2} \phi(x, z) + \left[ \frac{2m}{\hbar^2} E_{k_z} - \frac{2m}{\hbar^2} V(x, z) - k_z^2 \right] \phi(x, z) \] (26.141)

and,
\[ \frac{d}{dz} \phi(x, z) = \frac{1}{2i\kappa_z} \frac{1}{dx^2} \left[ \phi(x - dx, z) - 2\phi(x, z) + \phi(x + dx, z) \right] - \frac{m}{i\kappa_z^2 \hbar^2} V(x, z) \phi(x, z) . \]

Discretize in steps \( dz \).

### 26.8.3.3 Reflection from a potential barrier

Now we allow for a change of direction. We assume that a matter wave with wavevector \( k_0 = k_{0x} \hat{e}_x + k_{0y} \hat{e}_y = k_0 \hat{e}_x \sin \alpha + k_0 \hat{e}_y \cos \alpha \), runs towards a potential step. If the step is sharp, \( V(x) = V_1 \theta(-x) + V_2 \theta(x) \), the following ansatz is reasonable,
\[ \psi_0(x, y) = e^{ixk_x + iyk_y} \] (26.143)
\[ \psi_1(x, y) = re^{-ixk_x + iyk_y} \]
\[ \psi_2(x, y) = te^{ixk'_x + iyk_y} \]

and we have to solve the equations,
\[ \frac{-\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) (\psi_0 + \psi_1) = (E - V_1) (\psi_0 + \psi_1) \] (26.144)
\[ \frac{-\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) \psi_2 = (E - V_2) \psi_2 . \]

In the step is smooth, \( V(x \to -\infty) = V_1 < V_2 = V(x \to \infty) \), the situation is more complicated. Let us set \( V(x) = (V_1 - V_2) \frac{1}{\pi} \arctan x + \frac{1}{2}(V_1 + V_2) \).

### 26.8.4 Exercises

#### 26.8.4.1 Ex: Propagation of wavefunctions

Programs on the propagation of wavefunctions.
Figure 26.10: (code) Reflection of a wavepacket at a potential barrier. Do evanescent matter waves propagate along the barrier? Is there an atomic analogue to the Goos-Hänchen shift?

26.8.4.2 Ex: Programs on wavepackets reflected from potential barriers

Programs on wavepackets reflected from potential barriers.
Superfluid and coherent properties of Bose-Einstein condensates

Superfluid liquids or gases are distinguished by their ability to sustain flow without dissipation, i.e. flow which is free of viscous damping. The phenomenon of superfluidity is a well-known property of liquid $^4$He, but the relationship between superfluidity and Bose-Einstein condensation in this strongly interacting system is not trivial. The situation is much simpler in weakly interacting Bose gases, where the superfluid fraction is almost identical with the condensed fraction and the normal phase of the fluid with the thermal fraction. The availability of dilute gas Bose-Einstein condensates now offers the unique opportunity to study the complicated interdependence between superfluidity and condensation.

27.1 Superfluidity in quantum gases

The superfluidity of a gaseous condensate, which is one of its most apparent properties, is intrinsically linked to interatomic collisions. To characterize this phenomenon, it is useful to define some parameters. In the local-density approximation, the homogeneity of a gas of $N$ atoms with the thermal de Broglie wavelength (24.9) confined inside a harmonic trap with the ground state size defined by (4.66), is characterized by,

$$\frac{k_B T}{\hbar \omega_{trp}} = \frac{2\pi a_{trp}^2}{\lambda_{therm}^2}. \quad (27.1)$$

For a typical experimental situation, $k_B T / \hbar \omega_{trp} \approx N^{1/3} \approx 100$. This shows that the assumption of a locally homogeneous gas is generally a good approximation. With the definition of the healing length (26.69), the degree of superfluidity of a condensate with density $n$ can be cast into the form,

$$\frac{gn}{\hbar \omega_{trp}} = \frac{a_{trp}^2}{\xi^2}. \quad (27.2)$$
For a typical experimental situation, $a_{trp}^2/\xi^2 \approx 100$. A parameter that well characterizes the importance of interatomic forces within a condensate is the gas dilution,

$$na_s^3 = \frac{a_s^2}{8\pi\xi^2}. \quad (27.3)$$

The typical numerical value $na_s^3 \approx 10^{-5}$ shows that atomic gases are usually very dilute, although interatomic forces play an important role in the dynamics of condensates. In contrast, three-body collisions can be totally neglected, because the probability to have three atoms close to each other is even lower than the probability for two atoms.

There are several manifestations of phenomena linked to superfluidity, such as the behavior of collective elementary excitations, superfluid flow of non-circulating topological modes, quantized flux in vortices and matter wave solitons, which will be discussed in the following sections.

### 27.1.1 Landau’s criterion for superfluidity

According to Landau, the phenomenon of superfluidity is rooted in the particular character of the Bogolubov spectrum of elementary excitations (26.54). Let us consider a bosonic fluid at a given temperature moving with velocity $v$. A macroscopic obstacle in the path of the superfluid can generate elementary excitations. That is, a fraction of the kinetic energy of the fluid is transferred to these excitations, thereby decelerating the fluid and causing viscosity. With the excitation energy $E(p)$ and the momentum $p$, the total energy of the fluid interacting with the obstacle is,

$$E = E(p) + \frac{(p + Mv)^2}{2M} = E(p) + p \cdot v + \frac{1}{2} Mv^2 + \frac{p^2}{2M} \simeq E(p) + p \cdot v + \frac{1}{2} Mv^2, \quad (27.4)$$

where $M$ is the total mass of the superfluid. Since the term $Mv^2/2$ is the initial kinetic energy of the fluid, $E(p) + p \cdot v$ represents the excitation energy. And since the kinetic energy of the superfluid can only be diminished by the excitation, we need $E(p) + p \cdot v < 0$. Finally, as $E(p)$ must be positive, the condition for generating elementary excitations is,

$$E(p) \leq pv,$$

where $p$ and $v$ are antiparallel.

Therefore, there is a relative minimum velocity between the fluid and the obstacle, called critical Landau velocity, for creating excitations,

$$v_c = \min \left( \frac{E(p)}{p} \right). \quad (27.5)$$

For velocities below $v_c$, it is impossible to generate excitations, and there is no mechanism to decrease the kinetic energy of the fluid. As a result, the system becomes superfluid [368].

The spectrum of elementary excitations for a weakly interacting condensate, is the Bogolubov spectrum (26.54). The graph Fig. 27.1 shows, that for velocities below the sound velocity given by (26.56), $v < c_s$, the curve representing the propagation of
27.1. SUPERFLUIDITY IN QUANTUM GASES

the perturbation does not cross the Bogolubov spectrum. That is, the perturbation
can not be converted into excitations, which is only possible when \( v > c_s \).

In an ideal condensate without interactions, \( a_s = 0 \), the Bogolubov spectrum
reduces to the quadratic dispersion relation of free particles, which means that there
is no critical velocity, \( v_c = c_s \). Consequently, it is always possible to excite the
condensate, that is, an ideal condensate can not be superfluid, and, as first pointed out
by Landau: superfluidity and Bose-Einstein condensation are different phenomena.

![Figure 27.1](image.png)

Figure 27.1: (code) Landau’s criterion for superfluidity. Slow perturbations (blue line)
do not cross the Bogolubov spectrum (red line) and do not generate excitations. Rapid
perturbations (green line) cross the spectrum and can be dissipated.

27.1.2 Impurity scattering

A first hint for the superfluid nature of Bose-Einstein condensates is the fact that
the hydrodynamic theory of superfluidity describes well the collective excitations (see
Sec. 26.5). Moreover, several experiments provided direct evidence for the superfluid
nature of condensates. For example, via a calorimetric measurement \([494]\): A con-
densate, stirred around by a rotating far blue-detuned laser beam, dissipated atoms
to the thermal fraction of the atomic cloud, provided the stirring velocity exceed a
certain critical velocity \( v_c \): At lower velocities, the perturbation did not lead to dis-
sipation. At higher velocities, phonons were excited and the cloud was heated. In
a subsequent experiment, perturbation-induced density fluctuations were observed \textit{in vivo} and \textit{in situ} \([456]\). When the stirring speed was below the critical velocity, the
density was almost homogeneous, thus indicating superfluid flow. When, however,
the stirring speed exceeded \( v_c \), atoms piled up in front of the stirring beam, and the
resulting pressure gradients led to a turbulent flow around the perturbation and to
dissipation.

The critical velocity \( v_c \) found in the stirring experiments was about ten times
smaller than the local sound velocity \( c_s \),

\[
c_s \equiv \sqrt{\frac{gn}{m}} = \frac{\hbar}{\sqrt{2m\xi}}. \tag{27.7}
\]

In fact, while the onset of dissipation is accelerated by turbulence around the \textit{macro-
scocpic object} traversing the superfluid, the local sound velocity (27.8) is derived for
a microscopic object. Puzzled by this discrepancy, Chikkatur et al. [106] studied the motion of microscopic atomic impurities through a condensate. The impurity was created by transferring a few atoms out of the original BEC from the trapped state \( |F = 1, m_F = -1 \rangle \) to the free state \( |F = 1, m_F = 0 \rangle \) via induced Raman transitions. The initial velocity was adjusted by the laser beams exciting the Raman transition (polarization, incident angle and relative detuning) to satisfy the Bragg condition (see Sec. 28.2). After the free impurity passed through the BEC, the trap was switched off, a Stern-Gerlach magnetic field gradient was pulsed to separate atoms in different Zeeman states, and finally the atoms were detected via time-of-flight imaging (see Sec. 24.6.1). When the initial velocity of the impurity was well above a critical value given by the local velocity of sound, ultracold s-wave collisions between impurity atoms and the stationary condensate distributed the momenta of the collision partners uniformly. In TOF images this appeared as a circular halo centered around the center-of-mass momentum of the collision partners (see Fig. 27.2). When, however, the initial velocity of the impurity was reduced, its collision rate with the stationary condensate was suppressed and the trajectory became superfluid.

![Unscattered Impurities, Condensate, Collision Halo](image)

Figure 27.2: (a) Scattering of impurities at velocities above the critical velocity. The presence of a halo indicates the occurrence of collisions between the impurity and the condensate dissipating the relative kinetic energy. (b) For velocities below the critical velocity the halo disappears.

### 27.1.3 Hydrodynamic theory of superfluidity

For the description of superfluidity a hydrodynamic theory is adequate. Therefore, we will rewrite the time-dependent Gross-Pitaevskii equation (26.21). We consider the general case, in which the external potential \( V_{\text{trp}}(r, t) \) depends on time. The wavefunction can be written by defining the density and the velocity fields,

\[
\phi(r, t) = \sqrt{n_0(r, t)}e^{i\theta(r, t)}
\]

\[
v_s(r, t) = \frac{j(r, t)}{n_0(r, t)} = \frac{1}{2im} \frac{1}{n(r, t)} [\phi^*(r, t)\nabla\phi(r, t) - \nabla\phi^*(r, t)\phi(r, t)] .
\]

This gives,

\[
v_s(r, t) = \frac{\hbar}{m} \nabla \theta(r, t) .
\]

From the GPE we derive the continuity and the Navier-Stokes equations:

\[
\frac{\partial n}{\partial t} + \nabla (v_s n) = 0
\]

\[
m \frac{\partial v_s}{\partial t} + \nabla \left( V_{\text{trp}} + gn - \frac{\hbar^2 a}{2m \sqrt{n}} \nabla^2 \sqrt{n} - \mu + \frac{m}{2} v_s^2 \right) = 0 .
\]
27.2. **TOPOLOGICAL MODES**

We can see that the hydrodynamic behavior of a BEC depends greatly on the quantum phase \( \theta \). When the kinetic pressure is small compared to the mean-field energy,

\[
m \frac{\partial v_s}{\partial t} + \nabla \left( V_{trp} + gn + \frac{m}{2} v_s^2 \right) = 0.
\]  

(27.11)

This is the *Euler equation* for a fluid with a potential flow. This equation and the *continuity equation* have the typical structure of equations describing superfluids at \( T = 0 \). This is due 1. to the presence of a Bose-Einstein condensate allowing us to formulate an equation for a complex *order parameter*, and 2. to the presence of interactions, included via the pressure term in the Euler equation, which are necessary condition for superfluidity.

At zero temperature, the entire fluid is superfluid. Moreover, in the Gross-Pitaevskii approximation, the whole fluid is condensed. Therefore, \( v_s(r,t) \) is the velocity flow of the superfluid ¹.

### 27.2 Topological modes

Significant manifestations of superfluidity are associated with rotational phenomena. An example is the occurrence of *scissor modes* [243], which are excited, when an angular momentum is suddenly applied to a condensate confined in an anisotropic trap. This can be done via a sudden reorientation of the symmetry axis of the trap [392, 391]. The condensate responds to this perturbation by an oscillation of its inclination implemented by an *irrotational superfluid flow*. The excitation spectrum reflects the strong reduction of the inertial momentum for superfluids.

The most rigorous manifestation of superfluidity, however, is the occurrence of a quantized and persistent current, called *quantized vortex*. In contrast to the elementary excitations, which must be created by perturbations, the vortex is a *stationary* (or *topological mode*) solution of the Gross-Pitaevskii equation Eq. (26.21).

Work on vortices has been done by [401, 388, 494, 456, 106, 243, 392, 389, 104, 10, 511, 168, 312, 95, 654].

#### 27.2.1 Vortices

From Eq. (27.9) it is easy to see, that the superfluid is non-rotational, that is,

\[
\nabla \times v_s(r,t) = 0.
\]  

(27.12)

This raises the question, how vortices are possible. The solution to this apparent contradiction is, that Eq. (27.12) does not apply, when the phase exhibits a singularity. Consider, for example, a closed loop \( C \) around the singularity. In a vortex, the superfluid current is pulled by the phase gradient, \( \mathbf{v} = \frac{\hbar}{m} \nabla \theta \). For the condensate wavefunction to be well defined, the phase variation \( \Delta \theta \) around the loop must be a multiple of \( 2\pi \), that is,

\[
\Delta \theta = \oint_C \nabla \theta \cdot d\mathbf{l} = 2\pi \ell.
\]  

(27.13)

¹This is not the case for strongly interacting superfluids, such as superfluid helium, where the normal fluid fraction is considerable.
where $\ell$ is an integer. Therefore, we can calculate the circulation $\Gamma$ around the closed loop, that is,

$$
\Gamma = \oint_C \mathbf{v}_s(r,t) \cdot dl = \frac{h}{m} \ell. 
$$

(27.14)

Apparently, the superfluid circulation is quantized in units of $\hbar/m$. The parameter $\ell$ is called charge of the vortex and measures, in unit of $\hbar$, the quantized angular momentum of the vortex.

In addition, the flow must be persistent, because its circulation can only be changed in a discontinuous way, by overcoming a discrete energy barrier, which requires energy coming e.g. from thermal excitations. Clearly, the normal (thermal) fraction of a gas can also have a circular flow. However, the disordered microscopic motion of each individual particle causes a viscous drag that prevents the persistence of the flow in the absence of a torque. This is in contrast to superfluid flow, which persists even without external torque. The issues of vortex stability, formation, and topology were addressed in recent experiments [400, 388, 389, 104, 10]. Solve the Excs. 27.2.6.1 and 27.2.6.2.

The kinetic energy per unit vortex length can be estimated from a semi-classical approach. First, we define as the mass density $\rho_m$ of the superfluid. If $n$ is the particle density, $\rho_m = nm$. The kinetic energy of a flux line at the radius $r$ is,

$$
E_{\text{kin}} = \frac{1}{2} \rho_m v_s^2 = \frac{\hbar^2 \ell^2}{2m} \frac{n}{r^2}. 
$$

(27.15)

To obtain the kinetic energy per unit length, we integrate the expression (27.21) over a plane perpendicular to the vortex axis. Note, however, that the velocity field is $v_s \propto r^{-1}$ and, therefore, can not be integrated from zero. Instead, we begin the integration at a radius given by the healing length $\xi$, which represents a measure of the vortex core size. Now, the kinetic energy per unit length is,

$$
E_{\text{semi}} = \int_0^{2\pi} \int_0^R \varepsilon_{\text{kin}}(r) r dr d\theta = \frac{\pi n}{m} \frac{\hbar^2 \ell^2}{\ln \left( \frac{R}{\xi} \right)}. 
$$

(27.16)

Note, that a multiply charged vortex carrying the entire angular momentum $\ell = \ell_0$ of the superfluid is energetically less favorable than an ensemble of $\ell_0$ vortices with unit charge $\ell = 1$. Therefore, a multiply charged vortex is unstable and may decay to several single charge vortices.

To calculate exactly the energy of a vortex, we do the following ansatz,

$$
\Phi_0(r) = \phi(r,z) e^{i\ell \vartheta},
$$

(27.17)

we then solve the Gross-Pitaevskii equation (26.21) numerically, and calculate the expectation value of the energy of the vortex through the expression,

$$
\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \int d^3r \left[ \frac{\hbar^2}{2m} |\nabla \Phi_0(r,z)|^2 + V_{\text{trp}}|\phi(r,z)|^2 + g|\phi(r,z)|^4 \right], 
$$

(27.18)

where $\hat{H}$ is the Gross-Pitaevskii Hamiltonian.

The calculation yields for energy per unit length of a single charge vortex in a uniform cylindrical condensate [469],

$$
E_{\text{unif}} = \pi n \frac{\hbar^2}{m} \ln \left( \frac{1.464 R}{\xi} \right), 
$$

(27.19)
which is very close to our semi-classical prediction. Although the wavefunction $|\phi(r, z)|$ has no analytic form, it can be shown by a variational approach, that the trial wavefunction,

$$|\phi(r, z)| = \frac{nr}{\sqrt{2\ell^2 \xi^2 + r^2}} \quad (27.20)$$

is a good approximation [469]. Note that the healing length $\xi$ characterizes the size of the vortex. For a superfluid, we can calculate the total energy of the vortex exactly, because the fluid is confined in all directions,

$$E_{\text{tot}} = \frac{4\pi n_0^3}{3} \frac{\hbar}{m} \ln \left( \frac{0.671 R_z}{\xi_0} \right), \quad (27.21)$$

where $n_0$ and $\xi_0$ are, respectively, the density and healing length at the center of the fluid. $R_z$ and $R_r$ are, respectively, the extensions of the cloud along the axial and radial directions within the Thomas-Fermi approximation.

### 27.2.1.1 Creation and detection of vortices

The first superfluid vortex was observed 1979 in $^4$He [650]. For gaseous condensates, two approaches have been employed to produce vortices. Either one stirs the atomic cloud in order to impart an angular momentum to it. This can be done by rotating the (anisotropic) trap during the process of forced evaporation with time-orbiting magnetic fields or with an optical spoon. The vortex state is formed when the critical temperature for condensation is crossed. An alternative method is to imprint a $2\pi$ circular phase gradient into a previously created condensate. Indeed, the local phase of a matter wave can be manipulated via a local modification of the potential depth, which can be achieved by a Stark shift induced by a far-detuned laser beam [168]. Focused into a tiny spot which is moved across the condensate, the laser beam will create a phase gradient, which in turn will cause a velocity flow. It is important to force the local density at the center of the vortex to zero, which can be achieved via a proper design of the trapping potential (e.g., a Mexican hat-shaped potential), and let the BEC then relax to the vortex state.

A variation of this method [631] avoids the need for relaxation processes. In this configuration the phase gradient is created through a local Raman coupling between two internal atomic states (for example, in $^{87}$Rb the two trappable Zeeman states $|F, m_F\rangle = |1, -1\rangle$ to $|2, 1\rangle$). At the spots, where the focused Raman beams hit the condensate, atoms were dynamically converted from the ground state to the excited state. The circular trajectory of the spots and the rotation speed were calculated such as to generate a toroidal topology for the adiabatic population transfer. The process was coherent and allowed to directly construct and shape the vortex wave function. We study this experiment in more detail in the Exc. 27.2.6.3.

In confined single-species condensates the diameter of the vortex core is on the order of the healing length, $2\xi$. With typical values of $2\xi \approx 0.4 \mu m$ it is thus way too small to be imaged in situ, and ballistic expansion times of several 10 ms are necessary. On the other hand, in double condensates formed by two repelling species (e.g. the two states $|2, 1\rangle$ and $|1, -1\rangle$ in $^{87}$Rb), one of the species can form a vortex around the second. In this case, the diameter of the vortex core, is determined by the diameter of the condensate of the second species and, hence, much larger. When
the second species is selectively removed (e.g. by the radiative pressure exerted by a resonant laser), and the vortex in the first species can be studied by in situ imaging of the confined density distribution [401].

A particularly smart detection method for vortices is based on matter wave interferometry (see Sec. 27.3.3). Here, two matter waves, that is, the vortex state in $|2,1\rangle$ and a (reference) ground state BEC in $|1,-1\rangle$ are coherent mixed via a resonant two-photon radiofrequency $\pi/2$-pulse. The resulting matter wave interference patterns reveals the phase profile of the vortex (see Fig. 27.3).

### 27.2.1.2 Stability

In a topologically 'singly-connected' trap, for example a potential harmonic, vortices do not represent the lowest energy eigenstate, and they must decay to the ground state. If the mean-field energy of the condensate is weak compared to the kinetic energy, $g n_0 / h \omega \ll 1$, the healing length will exceed the size of the BEC, $\xi \gg a_{trp}$, and the vortex rapidly decays by dissipating its excess energy to thermal excitation. Such BECs can not be considered superfluid. If the mean-field interaction is strong, the vortex spontaneously breaks azimuthal symmetry, moves away from the center and exits the condensate on a spiral-shaped trajectory [511]. Nevertheless, the decay time may be quite long.

On the other hand, a vortex can be the ground state of a 'multiply-connected' trap (for example, a toroidal potential). Such a potential can be realized as the temporal average of a harmonic potential with a small rotating anisotropy [388]. In such geometries vortices are extremely stable.

### 27.2.1.3 Vortex precession

A radial force acting on a vortex results in a radial displacement and a precession about the symmetry axis. The effect, known as \textit{Magnus effect} [312], is due to pressure...
imbalances on the vortex surface. A radial force naturally arises, when the core is displaced from the center, because local pressure gradients will force the vortex out of the center toward regions with lower densities. Experimentally, a slow precession (\(\sim 1\) Hz) spiraling the vortex toward the rim of the condensate has been observed [10] by taking a succession of nondestructive images.

### 27.2.2 Vortex lattices

Superfluid \(^4\)He in a rotating bucket spontaneously develops symmetrically organized vortex patterns. Similar phenomena can be observed, when a dilute gas Bose-Einstein condensate is forced to rotate [95] at a given frequency \(\Omega\). The energy in the rotating system receives an additional contribution from the centrifugal term, \(U_{rot}(r) = U_{trp}(r) - \Omega L_z\), where \(L_z = \hbar N l_z\), and \(l_z = i(y \partial_x - x \partial_y)\) is the angular momentum of the individual atoms. If the rotation is slow, the energy \(\Omega L_z\) is too small to force the condensed wavefunction to rotate. If the rotation frequency is beyond a critical value \(\Omega_c\), the *time-averaged* potential, \(U_{rot}(r)\) eventually develops a local minimum in the center, thus adopting the toroidal shape. For non-interacting gases, the critical frequency coincides with the radial secular frequency, \(\Omega_c = \omega_r\). Then the radial restoring force of the trap does not balance the centrifugal force, such that atoms can escape from the trap. However, for superfluid gases the critical frequency is reduced, \(\Omega_c < \omega_r\). Between the rotation frequencies \(\Omega = \Omega_c\) and \(\Omega = \omega_r\), the state with the lowest energy in the toroidal potential is the vortex, whose filament is pinned to the symmetry axis. For even higher rotation frequencies, we could expect a single vortex with a larger winding number (more than the phase winding of \(2\pi\) for a single turn). However, individual multiple-order vortices in harmonic traps are unstable. Instead, vortex lattices [95] called *Abricosov lattices* will form. For a given trapping potential and mean-field energy, the symmetry of the lattice and the number of vortices depend on the rotation frequency \(\Omega\). Counter-intuitively, the angular momentum of individual particles \(l_z\) is *not quantized*. When we vary \(\Omega\), regimes of forbidden \(l_z\) (i.e. when no vortex pattern is formed) alternate with allowed regimes. The discontinuous transition from one vortex pattern to another is a first-order phase transition, which spontaneously breaks one symmetry to form another. An upper limit for the rotation speed is given by the equilibrium between the centrifugal force and the radial restoring force of the trapping potential at \(\Omega = \omega_r\).

![Figure 27.4: Abricosov vortex lattice.](image)

These patterns of vortex lattices were observed in experiments using the *stirring method*, which consists in brushing a far-detuned focused laser (‘optical spoon’) around the rim of a condensate [388] at a certain frequency \(\Omega\). In this experiment, the ratio of the mean-field energy to the kinetic energy was \(gn_0/\hbar \omega_z = a_{trp}^2/2\xi^2 > 100\). Beyond a certain critical rotation frequency, \(\Omega_c \approx 2\pi \times 150\) Hz, a single central vortex
was formed. At even higher frequency, a symmetrical vortex lattice appeared in a transverse plane (see Fig. 27.4). Finally, at rotation frequencies near the radial trap frequency \( \omega_r \), the condensate wavefunction became turbulent and finally disappeared. As soon as the optical spoon was removed, the vortex lattice gradually decayed losing the vortices one by one.

### 27.2.3 Solitons

Work on solitons has been done by [653, 630, 400, 631, 435, 502, 311, 444, 93, 27, 178, 89, 157].

#### 27.2.3.1 Dark solitons

Solitons are non-singular solutions of any equation satisfying,

\[
|\psi(r, t)| = |\psi(r - vt)|. \tag{27.22}
\]

Solitons are well known to occur in non-linear optical media, for example in optical fibers, when dispersion is counterbalanced by self-phase modulation, such that optical signals propagate without spreading. The Gross-Pitaevskii equation is another example for a nonlinear wave equation supporting soliton-like solutions. States called dark soliton or twisted state with a dynamically stable density dip are expected in condensates with repulsive interactions [435, 502, 311, 444]. In contrast to topologically stable states, for example, vortices, dark solitons are pseudo-defects, the decay of which, even though it may be slow, is topologically trivial. Due of the greater freedom of movement of their wavefunctions, solitons can be distorted by complex deformations [93]. Soliton-like matter wave states were initially observed in superfluid \(^3\)He-B [27]. In dilute gases, the size of the solitons is of the order of healing length.

The first dark solitons in dilute gases were created by applying an inhomogeneous phase shift to a condensate [89, 157]. One half of the condensate was irradiated by a far-detuned laser pulse (detuning \( \Delta \), Rabi frequency \( \Omega \), duration \( \tau \ll \hbar/gn_0 \)) in order to advance the phase of this part of the condensate by \( \varphi = \Omega^2 \tau / 4\Delta \). When the phase shift was set to \( \pi \), an abrupt phase gradient developed at the boundary delimiting the two halves. The condensate reacted to the phase gradient by developing a deep density minimum all along the boundary corresponding to a soliton (see Fig. 27.5). The phase distribution can also be imaged by interferometric techniques based on Bragg diffraction (see Sec. 28.2). In one dimension, the density dip of the soliton corresponds to a node of the dipolar topological mode [631, 435, 444].

The abrupt phase gradient at the boundary plane exerts a force trying to increase the gap, while repulsive interactions work to heal it. At zero temperature, this balance ensures the dynamic stability of the soliton. While a perfect dark soliton should be stationary, experiments [89, 157] revealed that solitons with finite contrast propagate along the direction of the plane’s normal vector with a velocity, which must always be less than the local sound velocity,

\[
v_{\text{sol}} = c_s \sqrt{\frac{n_{\text{sol}}}{n}}, \tag{27.23}
\]

where \( n \) is the peak density of the condensate and \( n_{\text{sol}} \) the density at the bottom of the dark soliton [502, 311]. Fig. 27.5 shows that the soliton develops a curvature
when it propagates. One reason for this is a slower sound velocity, $c_s = \sqrt{gn_0/m}$, on the edges of the condensate, where the density is lower. The second reason is, that the density in the dip, $n_{sol}$, goes to zero at the edges. In the presence of a thermal cloud, dissipation reduces the contrast of the density dip and accelerates the soliton, until it reaches the sound velocity $c_s$ and finally disappears.

![Image of solitons](image)

**Figure 27.5:** Solitons.

### 27.2.3.2 Bright solitons

In condensates with attractive interactions *bright solitons* have been observed, as well [342, 330].

### 27.2.4 Description of general topological modes

A coherent *topological mode* is a stationary solution of the *Gross-Pitaevskii equation*,

$$
\left[ -\frac{\hbar^2}{2m} \nabla^2 + U_{tr}(r) + \frac{4\pi \hbar^2 a_s}{m} N|\phi_n|^2 \right] \phi_n(r) = E_n \Phi(r).
$$

(27.24)

These modes can be calculated using an *optimized perturbation theory* [124]. We separate the Hamiltonian into an unperturbed part and a perturbed part, $\hat{H} = \hat{H}_0 + \Delta \hat{H}$, where the unperturbed part now depends on variational parameters,

$$
\hat{H} = \hat{H}_0(u,v,..) + \Delta \hat{H}.
$$

(27.25)

As usual, the first-order energy correction is,

$$
E_n^{(1)}(u,v,..) = E_n^{(0)}(u,v,..) + \langle \Phi_n^{(0)} | \Delta \hat{H} | \Phi_n^{(0)} \rangle,
$$

(27.26)

where the $\Phi_n^{(0)} = \Phi_n^{(0)}(u,v,..)$ are the solutions of the unperturbed Hamiltonian $\hat{H}_0$. Once the energies are found, we must minimize them in terms of the variational parameters,

$$
\frac{\partial E_n}{\partial u} = 0 \quad , \quad \frac{\partial E_n}{\partial v} = 0... .
$$

(27.27)

With these parameters, we obtain the energies and the wavefunctions.

---

2Excited modes can be understood stationary matter waves with the trap serving as a cavity.
27.2.4.1 Creation of topological modes

One possibility of creating topological modes is to apply a temporal modulation to the trapping potential [653]. The modulation frequency must be resonant with the energy difference between the excited mode and the ground state. Another possibility is to vary the interaction energy via a modulation of the scattering length in the vicinity of a Feshbach resonance [126].

The steady-state situation of a cloud in a stationary trap is thermal equilibrium, that is, inversion is not possible. At a time-dependent (e.g. shaking) potential however, for example, transitions to excited vibrational levels can be driven. These can generate inversion, provided collision-induced relaxation is not too fast.\footnote{The dynamics of atoms trapped in a harmonic potential is similar to the Jaynes-Cummings dynamics of an optical mode. However, the non-linear condensate self-interaction changes the situation and makes the collisions being collective.}

27.2.5 Turbulence

The issue of turbulence is one of the most important problems of classical physics yet to be solved [197]. In superfluids, restrictions imposed by quantum mechanics constrain the emergence of turbulence, which is then called quantum turbulence. On the other hand, the study of quantum turbulence can improve our understanding of classical turbulence [173]. Recently, the study of the dynamics of a ensemble of vortices in a Bose-Einstein condensate allowed the identification of signatures of quantum turbulence [275, 259].

![Figure 27.6: Turbulence.](image)

27.2.6 Exercises

27.2.6.1 Ex: Comparison between the quantum and the classical vortex

Consider a vortex around a straight line along the z-axis at \( r = 0 \). Compare the radial velocity variation of a quantum vortex with that of a classical one.

27.2.6.2 Ex: Singularity in vortices

Show for the above simple example,

\[
\nabla \times \mathbf{v}_s(r, t) = \frac{\ell \hbar}{m} \delta(x) \delta(y) .
\]
27.2.6.3 **Ex: Phase-engineering of a vortex state**

The first vortex in a dilute gas was created at the JILA [401]. Study the paper and explain in detail, how the vortex was created.

27.3 **Atom optics**

Unlike the photons [367], there is no doubt about the fact that atoms are particles. On the other hand, the deep analogy between light and matter, resulting from the particle-wave duality, prompted de Broglie in 1924 to ascribe a *wave* to each massive particle, whose wavelength would be a function of the particle’s momentum. Whether an atom behaves more like a particle or a wave depends on the specific experimental situation. For example, interferometers emphasize its wave nature: Atoms are able to interfere with *themselves*, when their Broglie wavelength is coherently split and then recombined. (Bosonic) atoms are able to interfere with other atoms, if their de Broglie wavelengths are greater than their distances. For this to happen, it requires high densities and very low temperatures, that is, high phase space densities. When the phase space densities are so high that the Broglie waves come into contact, effects of quantum statistics begin to influence the dynamics of the atoms, and fermions will behave differently from bosons.

Analogously to the distinction between classical and laser optics, we can separate the area of conventional atomic optics working with individual, mutually incoherent atoms, from the area of coherent atomic optics working with Bose-Einstein condensates. Unlike for the study of phenomena related to superfluidity, gases with weak interatomic interactions are generally more useful for the study of the coherent properties of condensates and for application in atomic optics. Nevertheless, interatomic collisions increase the complexity of the dynamics of matter waves interacting with atom optical devices, by introducing non-linearities analogous to those known from nonlinear optics and thus raising the field of *nonlinear atom optics*.

27.3.1 **Atomic optical tools**

The basic equipment of an atomic optics laboratory [425, 3, 473, 203, 489] comprises atomic beams, atom traps, lenses and waveguides, various types of mirrors and resonators, Stern-Gerlach type matter wave polarizers, de Broglie wave phase shifters based on Bragg diffraction, and a multitude of atomic beam gratings. Obviously, gratings allow the construction of atom interferometers, which are used in experiments and high precision devices, for example, atomic gyroscopes and gravimeters. Other applications for atomic beams controlled by atom optical elements are in atomic holography for the projection of complex pattern into integrated semiconductor circuits [436], in lithography [599], and in microscopy [167].

An important feature of atoms (as compared to light) is the existence of a rich internal structure providing a wealth of additional degrees of freedom, whose dynamics (of the Bloch vector) is frequently entangled with the motional dynamics (of the de Broglie wave). This allows to monitor (e.g. in matter wave interferometers) the evolution of the motional state of the matter wave via an observation of the internal
excitation. Moreover, in some interferometers, the de Broglie wave is not even split, and one does interferometry with completely immobile atoms or ions [299].

The epitome of a coherent light source is the laser, and we may ask whether there is a material analogue, which would be a source of coherent matter [636, 76, 567, 285, 442, 347] serving for coherent atom optics. In fact, we may already consider a trapped condensate as a stationary atom laser pulse with the trapping potential playing the role of the laser resonator. While most atom optical devices (including conventional atomic interferometers) do not require mutual coherence of atoms, certain applications take advantage of an intense, highly directional, monochromatic, and coherent atom source. In this respect, atom lasers are much superior to thermal atomic beams. While a thermal beam contains about $10^{-12}$ atoms per mode and a magneto-optical trap about $10^{-6}$, a condensed mode may contain more than $10^6$ atoms. Condensates offer the advantage of large de Broglie wave amplitudes and de Broglie wavelengths as long as their actual size (which can be much longer than optical wavelengths). And for an atom laser, the coherence length can even be longer than that of the condensate from which it emerged. This obviously has a major impact on the sensitivity and resolution of atom optical elements, in particular those, where atomic coherence is important, for example, atom interferometers. Without doubt atom lasers will replace conventional atomic beams in precision measurement of fundamental constants and tests of fundamental symmetries ([Phys. World (mar,97) p.43]). Finally, atom lasers are crucial for nonlinear optics.

Also of interest are the references [566, 436, 495, 369, 514, 30, 274, 176, 488, 156, 282, 503, 310, 533, 54, 167, 624].

27.3.2 The atom laser

A large number of techniques for making an atom laser has already been developed [413, 16, 417, 11, 63, 250, 395] and theories on atom lasers have been formulated [248, 440, 635, 614, 300]. The following sections are devoted to explaining, why the term atom laser is justified. For the reasoning we will let as guide by the optical laser.

We already mentioned the trapping potential (replacing the resonator in lasers) as a major ingredients of an atom laser. Another necessary feature would be the availability of an output coupling mechanism, which we still need to discuss in the following. Apart from these more practical aspects, we need to prove, that atom lasers are indeed phase-coherent, and we have to clarify the role of bosonic stimulation and of irreversibility in the production process of a BEC.

27.3.2.1 Bosonic stimulation and irreversibility

The gain mechanism for optical lasers is photonic stimulation of atoms inciting them to emit other photons into the stimulating mode. The atomic laser operates in a similar way. Atoms trapped in a potential constitute a thermal reservoir. Binary collisions redistribute the atoms among the vibrational energy levels of the potential. If a vibrational level already contains an atomic population, Bose-Einstein quantum

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4 Coherent reflection of atom laser beams has been demonstrated [69, 18, 7], and an atom laser cavity with efficient transverse focusing has been built [65]
27.3. ATOM OPTICS

statistics will encourage atoms involved in a collision process to join this level. Ultimately, this comes down to an irreversible pumping of a single level, where the atoms accumulate to build a single degenerate quantum state. Bose condensation is always the result of bosonic stimulation. However, the dynamics and time scale for the formation of a condensate have been controversially discussed, until some experiments [417] could directly visualize in vivo the process of nucleation and the exponential amplification at the center of a thermal cloud (see Fig. 27.7).

![Figure 27.7](image)

Figure 27.7: (a) Illustration of the idea of bosonic stimulation. (b) The curves show the growth of a condensate toward thermal equilibrium for different initial numbers of condensed atoms.

The very high concentration of population in a single phase space cell during the creation of a condensate represents a dramatic reduction of entropy. Since the total entropy can not decrease, the condensate must be coupled to a thermal reservoir receiving the excess entropy. This coupling is necessarily irreversible. In practice, the reservoir is the cloud of thermal atoms, whose energy is spread over many vibrational states. Irreversibility is introduced by collisions and the subsequent removal of the hottest atoms.

27.3.2.2 Phase of a condensate and first and higher-order coherences

First-order coherence and long-range order are necessary conditions for assigning a single global phase to the condensate. The existence of a single phase, and the possibility of measuring it, were questioned in the past. Certainly, the phase of a BEC is not observable by itself, but only the relative phase of two condensates.

The intrinsic phase-coherence of condensates has demonstrated in many experiments. An early example [254] employed internal state interferometry by splitting and remixing $^{87}\text{Rb}$ condensates trapped in the different Zeeman states $|F, m_F\rangle = |1, -1\rangle$ and $|2, 1\rangle$. They found that the phase was remembered for times longer than 150 ms. In another experiment [13, 339, 614], illustrated in Fig. 27.8, a condensate was spatially split in two halves and then recombined. The interpenetration of the two halves at a well-defined relative velocity gave rise to a clear matter wave interference pattern. This ability of ballistically expanding condensates to interfere demonstrated the absence of a random phase lag during the expansion process and that the preservation of the condensates' long range order. However, under the repulsive influence of the mean-field energy, the phase profile of a released condensate evolves in a non-uniform...
but well-defined manner [555].

The homogeneity of the phase of a confined condensate was also confirmed experimentally [575, 249, 64] through interferometric techniques based on Bragg diffraction (see Sec. 28.2.2). The spatial coherence of an output coupled atom laser has been verified with a double-slit experiment [64]. And the temporal coherence of an atom laser beam was shown to be Fourier-limited by the finite output coupling time [?].

Similar to Young’s double-slit experiment in optics, the observation of matter wave interference only indicates first-order coherence, i.e. amplitude fluctuations in the matter field. Signatures for the presence of higher-order coherences in condensates were discovered in other experiments: The second-order correlation function, which represents a measure for intensity fluctuations (number of particles) in the matter field, was derived from measurements of the condensate’s release energy [341]. And the third-order coherence can be deduced from a comparison of the three-body recombination rates for condensed and thermal clouds [92].

![Image of interference](image_url)

Figure 27.8: (a) Scheme for observation of matter wave interference. (b) Interference fringes.

A reliable characterization of atom number fluctuations and matter wave phase fluctuations in condensates is important for the simple reason, that these fluctuations will limit ultimately the resolution of atom interferometers, analogous to the Schawlow-Townes limit in lasers.

### 27.3.2.3 Output coupling

The output coupler for a trapped condensate plays a role similar to that of the partially reflecting mirror of a laser resonator. It transfers a fraction of condensed atoms out of the trapping potential through a coherent coupling to untrapped states. The coupling can be conveniently implemented via adiabatic potentials (see 16.1.3 and 24.4.3) generated by radiation (e.g. radiofrequency pulses [413] or continuous radiofrequency [63]). Also, pairs of laser beams in Raman configuration can create a coherent quasi-
continuous and well-collimated atomic beam [250] and tunneling can give rise to a pulsed mode-locked atom laser (mode-locked laser) [11].

A trapped condensate represents a finite reservoir from which an atom laser can be fed. For a really cw atom laser, an incoherent pumping mechanism, continuously feeding the BEC, while it delivers atoms to the atom laser, is still lacking [390].

Figure 27.9: Several types of atomic lasers realized, from left to right at the MIT in 1997, in Munich in 1999, at Yale in 1998, and at NIST in 1999. The vertical sizes of the images are, from left to right: 5, 2, 0.5, and 1 mm.

27.3.3 Atomic interferometry with Bose-Einstein condensates

The most obvious use of an atom laser is within an atomic interferometer [576, 568, 70, 249, 64, 555, 341, 92, 460, 154, 423, 438]. Many types of interferometers have been developed over the years. First of all, we note that the interferometric idea can be realized in the spatial domain (e.g. an atomic beam passing through a light wave) or in the time domain (e.g. a trapped atomic cloud or an immobile trapped ion irradiated by a pulsed light) [75, 299, 655, 219].

Furthermore, depending on the involved degree of freedom (kinetic or internal excitation), we may distinguish two types of interferometers. Matter wave interferometers operating with the kinetic degree of freedom often use beam splitters based on Bragg diffraction [355, 460, 249, 555]. Matter wave interferometers involving internal degrees of freedom generally couple two species of condensates, that is, two condensates in different states of internal excitation, for example, in different Zeeman [577], hyperfine [445, 254, 423], or dressed states [372]. The phases of two BECs in different internal states, which we will call $|\pm\rangle$, evolve according to their respective chemical
potentials, $\varphi_{\pm}(t) = \mu_{\pm} t$. The accumulated phases are not directly observable, but their difference, $\Delta \varphi(t)$, can be measured by Ramsey interferometry.

### 27.3.4 Non-linear atomic optics

In classical nonlinear optics, the interaction between matter (e.g. dilute gases) and light is described by Maxwell’s equations. The electromagnetic field $E$ creates a macroscopic polarization,

$$P(r, t) = \chi(E)E(r, t) = \chi^{(1)} \cdot E + \chi^{(3)} : E E E + \ldots \quad (27.28)$$

which in turn acts back onto the field. Higher-order processes, such as self-focusing, second-harmonic generation, four-wave mixing, etc. are described by the non-linear susceptibility $\chi^{(3)}$. These processes require the presence of a non-linear medium (the vacuum polarization itself being too small [331, 240]).

The role of binary collisions in coherent matter wave optics, as described by the nonlinear term in the Gross-Pitaevskii equation (26.21), is very similar to the role of the third-order nonlinear susceptibility in quantum optics [374, 355, 155, 224, 600, 332, 261, 333, 376, 133, 263]. For example, if the atomic interaction is repulsive, the nonlinear term tries to increase the size of the condensate as much as possible within the limits imposed by the trapping potential. This behavior is analogous to the phenomenon of self-defocusing known in non-linear optics.

Small-amplitude elementary oscillations are well described by the Bogolubov-de Gennes equations, which are a linearized version of the Gross-Pitaevskii equation [124]. On the other hand, large-amplitude oscillations, which are sensitive to the nonlinear mean-field interaction [563], showed a splitting of the frequency for quasi-particle excitation, in analogy with the generation of the second-harmonic (SHG) in quantum optics [263].

Other phenomena, such as matter wave phase conjugation and four waves mixing (4WM) [224] have been observed in experiments [155]. The three matter wave modes for the nonlinear mixing were produced out of a single condensate by applying two short consecutive sequences of Bragg diffraction pulses. The condensates are created in the same spatial region, but at different times. The nonlinear mixing during the process of spatial separation was observed by time-of-flight images.

The geometry of the laser beams is shown in Fig. 27.10(a) in the laboratory system. A first standing wave light pulse is generated by lasers $k_1$ and $k_2$ detuned from each other by an amount, such that the Bragg condition is satisfied and the momentum $p_2 = \hbar k_1 - \hbar k_2$ is transmitted to the diffracted atoms. Then, a second standing wave light pulse formed by lasers $k_1$ and $k_3 = -k_1$ transmits to the diffracted atoms the momentum $p_3 = 2\hbar k_1$. The duration and intensity of the standing waves are adjusted such as to create an approximately equal distribution of $N_0$ atoms in all three condensate momentum modes, each mode having a different momentum, $p_1 = 0$, $p_2$, and $p_3$. Initially, the three wavepackets $\psi_j \equiv \hat{\psi}_0(r)e^{ip_jr/\hbar}$ overlap. The nonlinear term in the Gross-Pitaevskii equation mixes the wavepackets while they separate to
form other wavepackets, \( \hat{\psi}_4 \sim g \hat{\psi}_j^\dagger \hat{\psi}_m \hat{\psi}_n e^{i \mathbf{p}_4 \cdot \mathbf{r} / \hbar} \), where,

\[
N_4 = -N_j + N_0 = N_m - N_0 = N_n - N_0 = \sum_{\kappa=1}^{3} (N_0^\kappa - N_\kappa) \tag{27.29}
\]

\[
\mathbf{p}_4 = -\mathbf{p}_j + \mathbf{p}_m + \mathbf{p}_n,
\]

\[
p_4^2 = -p_j^2 + p_m^2 + p_n^2.
\]

To produce the new momenta, \( \mathbf{p}_4 \neq \mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3 \), the corresponding wavepackets must gather atoms from all three initial packets \( \mathbf{p}_1 \neq \mathbf{p}_2 \neq \mathbf{p}_3 \).

The experimental observation of a newly emerging wavepacket \( \hat{\psi}_4 \) has two complementary interpretations: In the inertial system defined by \( \mathbf{p}_1 = -\mathbf{p}_3 \) [see Fig. 27.10(b)], the wavepackets \( \hat{\psi}_1 \) and \( \hat{\psi}_3 \) suffer elastic collisions. The direction in which the condensates are scattered is, a priori, isotropic. The injection of a third condensate \( \hat{\psi}_2 \) bosonically stimulates the formation of a forth one, \( \hat{\psi}_4 \), in a predefined direction \( \mathbf{p}_4 = -\mathbf{p}_2 \). The laws of conservation for the particle numbers, momenta, and energies (27.29) only allow processes, which can be interpreted as degenerate 4WM in this inertial system. Each of the wavepackets \( \hat{\psi}_1 \) and \( \hat{\psi}_3 \) sacrifice \( N_4 \) atoms to create a new wavepacket \( \hat{\psi}_4 \) and to amplify the wavepacket \( \hat{\psi}_2 \). The redistribution of atoms is a coherent process.

Figure 27.10: Matter wave 4WM can be illustrated (a) in the laboratory system, or (b) in the inertial system defined by \( \mathbf{p}_1 = -\mathbf{p}_3 \), or (c) in the system defined by \( \mathbf{p}_1 = -\mathbf{p}_2 \). In each system the process has a different physical interpretation (see text). The right image shows the experimental result.

The second interpretation becomes clear in the inertial system, in which \( \mathbf{p}_1 = -\mathbf{p}_2 \) [see Fig. 27.10(c)]. The conservation of energy only allows scattering products satisfying \( \mathbf{p}_4 = \mathbf{p}_3 \), that is, \( \hat{\psi}_1^\dagger \hat{\psi}_2 \hat{\psi}_3^\dagger \) and \( \hat{\psi}_2^\dagger \hat{\psi}_1 \hat{\psi}_3^\dagger \). In this system, the process can be interpreted as Bragg diffraction of the wavepacket \( \hat{\psi}_3 \) by the matter wave lattice formed by \( \hat{\psi}_1 \) and \( \hat{\psi}_2 \). The wavepacket \( \hat{\psi}_4 \) is nothing more than the first diffraction order. Unlike the Bragg diffraction in an optical lattice (see Sec. 28.2), the Bragg diffraction by a matter wave lattice requires nonlinear mixing through binary atomic collisions. Thus, the number of redistributed atoms depends on parameters such as the interatomic interaction strength, the size of the condensate, and the collision time between the wavepackets, i.e. the time that the wavepackets spend together before separating.

Despite the similarity with the optical counterpart, matter wave 4WM is fundamentally different: The number of particles must be conserved and the energy-momentum dispersion relation is not linear. Furthermore, while photons require the
presence of a nonlinear medium in order to participate in higher-order processes, atomic matter waves mix through binary collisions.

27.4 Quantum atom optics

When describing a condensate by the Gross-Pitaevskii equation, we specify a phase and an atom number. However, both are conjugate quantities, which cannot be specified without uncertainty. So, what does the BEC really look like: a Glauber state or rather a Fock state? We need to be careful. Certainly, it makes no sense talking about the absolute phase of a single BEC. Only the relative phase between two BECs matters. The condition for interference is, that we do not know, from which condensate the interfering atom came: \[ \Delta N \Delta \varphi \geq 1. \] So, the relative atom number must be uncertain.

27.4.1 Quantum transport

Now, let us imagine two BECs in a double-well potential. Atoms may be move between the wells via Josephson tunneling, even if the height of the barrier is higher than the atomic energy. Hence, the motion is a type of quantum transport. Be \[ \psi(\mathbf{r}, t) = \psi_1(\mathbf{r}) e^{i \mu_1 t/\hbar} + \psi_2(\mathbf{r}) e^{i \mu_2 t/\hbar}. \] In elongated traps the Josephson current is obtained as the expectation value of the flux operator,

\[
I(z, t) = \frac{i \hbar}{2m} \int \left( \psi(\mathbf{r}, t) \frac{d}{dz} \psi^*(\mathbf{r}, t) - c.c. \right) dxdy. \tag{27.30}
\]

One obtains,

\[
I(z, t) = \frac{i \hbar}{2m} \int \left( \psi_1 \frac{d \psi_2^*}{dz} + \psi_1 \frac{d \psi_1^*}{dz} e^{i(\mu_1 - \mu_2) t/\hbar} + \psi_1 \frac{d \psi_1^*}{dz} e^{i(\mu_1 - \mu_2) t/\hbar} - c.c. \right) dxdy. \tag{27.31}
\]

Choosing the original phase of the two condensates equal to zero, the time-independent terms are real and cancel each other, leaving,

\[
I(z, t) = \frac{i \hbar}{2m} \int \left( \frac{d \psi_2}{dz} - \frac{d \psi_1}{dz} \right) 2i \sin \left( \frac{\mu_1 - \mu_2}{\hbar} t \right) dxdy \tag{27.32}
\]

\[
\equiv I_0 \sin \left( \frac{\mu_1 - \mu_2}{\hbar} t \right). \]

This shows that the current oscillates in time. This feature is well-known for Josephson junction in superconductors.

The question is now, what will be the steady-state of the two BECs [457]. Experiments have shown, that the BECs will gradually evolve into a superposition of number states, until they are coherent. The time scale is set by Josephson tunneling. The same interference pattern would result from BECs initially having well-defined phases.

5 Also, a spin-squeezed state i.e. a state with sub-Poissonian number statistics approaching pure number states have been compared to coherent states. Superposition of the first ones exhibited no interference while superposition of the second ones lead to observable interference.

6 If two Josephson-coupled BECs are initially in Fock-states, the current must initially be a quan-
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27.4.2 Optical lattices and the Mott insulator

We have already pointed out in Sec. 24.3.2, that laser beams tuned far away from resonances serve to construct trapping potentials for atoms. Laser beams incident on the atomic cloud under various angles allow the engineering of a large diversity of geometries for attractive potentials (with red tuned lasers) or repulsive potentials (with blue tuned lasers). Various cooling methods can be combined with dipolar traps, for example, Doppler cooling [302], Raman cooling [255], evaporative cooling [2], or gravitational Sisyphus cooling [449]. A particularly interesting geometry is that of an optical lattice, which we will discuss in the following sections.

27.4.2.1 Bragg scattering from optical lattices

In solid state physics the structure of crystal is studied by Bragg or von Laue scattering with X-ray radiation. Similar techniques can be used in optical lattices [57, 534, 619, 620, 559]. Under certain conditions, we can even expect to open a photonic band gap [17, 159, 535], which draws an analogy between optical lattices and photonic crystal.

A great advantage of optical lattices is the possibility of directly visualizing the momentum distribution of the confined atoms, that is, the distribution of atoms over the Brillouin zone.

27.4.2.2 Bloch bands and Bloch oscillations

The Bloch model plays a very important role in solid state theory and can be applied to describe the dynamics of atoms in optical lattices (see Chp. 6.1.6). To learn about Landau-Zener tunneling and Wannier ladders consult [244, 640].

Atoms in optical lattices subject to an accelerating force (e.g. gravitation \(mg\)), can execute Bloch oscillations. This phenomenon was originally expected to occur with electrons in solid state crystals accelerated by an electric force \(-eE\), but there it is very difficult to observe, due to electron scattering at lattice defects. It has, finally, been observed in semiconductor superlattices, in ultra-thin Josephson junctions, and with cold atoms in optical lattices [258, 396].

27.4.2.3 Bloch bands with mean field interaction

The Gross-Pitaevski equation is,

\[
H\psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + v \cos Kx + c|\psi|^2 = \mu \psi .
\] (27.33)

We have a periodic potential, \(U(x) = U(x+X)\). In the following, we restrict ourselves to 1D. Assume e.g. a sine wave potential,

\[
U(x) = U_0 \cos(2Kx) .
\] (27.34)

The Gross-Pitaevskii equation is rescaled via \(k/K \to k, 2Kx \to x, 4\varepsilon t \to t, \psi/\sqrt{n} \to \psi\) and \(C = \pi na_s/K^2\). All frequencies are scaled like \(U/4\varepsilon \to U\). Then,

\[
-\frac{1}{2} \frac{\partial^2 \psi}{\partial x^2} + (U \cos x - U) \psi + C|\psi|^2 \psi = \mu \psi .
\] (27.35)
The Bloch-theorem says that the Schrödinger equation be solved by any Bloch state. Those are superpositions of plane-wave momentum states \[\psi(x) = e^{ikx}u_k(x),\] (27.36)
with \(u_k(x) = u_k(x+X)\). We obtain,
\[-\frac{1}{2} \left( \frac{\partial}{\partial x} + ik \right)^2 u_k + U \cos x u_k + C |u_k|^2 u_k = [\mu(k) + U]u_k.\] (27.37)
Inserting the plane-wave expansions \(u_k(x) = \sum_{q=-N}^{N} a_q(k)e^{iqx}\) into the Schrödinger equation, we get,
\[\sum_{q=-N}^{N} \left[ \frac{1}{2} (q+k)^2 a_q e^{iqx} + \frac{1}{2} U a_q(e^{i(q+1)x} + e^{i(q-1)x}) \right] + C \sum_{m,n=-N}^{N} a_m a_n^* e^{i(m-n+q)x} - [\mu(k) + U]a_q e^{iqx} = 0\] (27.38)
\[\frac{1}{2} (q+k)^2 a_q + \frac{1}{2} U(a_q - a_{q-1} + a_{q+1}) + C a_q \sum_{n=-N}^{N} |a_n|^2 - [\mu(k) + U]a_q = 0.\]
We choose a cut-off \(q_0\) so that \(a_{q>q_0} = 0\). For a given \(k\) the coefficients \(a_q\) and the chemical potential \(\mu\), and thus the Bloch wave \(u_k(x)\) can easily be calculated by minimizing the left hand side of the above equation. Note that for \(C = 0\) we have we linear set of differential equation that can be solved as an eigenvalue problem (see Sec. 6.1.3).

Figure 27.11: (code) Nonlinear interaction matrix finds just one minimum, dependence on \(k\), [639, 641].

If we only consider the two lowest Bloch bands
\[u_k(x) = e^{ikx}a(x) + e^{i(k-K)x}b(x)\] (27.39)
with $|a|^2 + |b|^2 = 1$, so that

$$|u_k|^2 = (e^{ikx}a + e^{i(k-K)x}b)(ae^{ikx} + be^{i(k-K)x}) = 1 + 2ab \cos Kx,$$

and insert this into the Gross-Pitaevski equation Eq. (??), we find that the system of differential equations Eq. (??) simplifies to

$$\left( \frac{\hbar^2 k^2}{2m} + c \right) \left( \begin{array}{c} \frac{v}{2} + abc \\ \frac{v}{2} + abc \frac{\hbar^2(k-K)^2}{2m} + c \end{array} \right) \left( \begin{array}{c} a \\ b \end{array} \right) = \mu \left( \begin{array}{c} a \\ b \end{array} \right).$$

(27.41)

For $-2ab = \frac{v}{c}$ the off-diagonal elements vanish, and because the interacting BEC shields the potential. Since $|2ab| \leq 1$, this is only possible for $c \geq v$.

If we substitute $\mu = \tilde{\mu} + \frac{1}{2} \frac{\hbar^2 k^2}{2m} + \frac{1}{2} \frac{\hbar^2(k-K)^2}{2m} + \frac{3}{2} c$, multiply the first row with $b$, the second with $a$ and add both rows, we obtain,

$$2\tilde{\mu} = \frac{v}{2ab}.$$  

(27.42)

**Example 96 (Estimations):** Estimated radial BEC size $r_i \simeq 10 \mu m$, estimated number of atoms per antinode $n_{1D} \simeq 1000 \mu m^{-1}$,

$$\omega_r = \frac{\hbar k^2}{2m} = 2\pi \cdot 3.8 \text{ kHz}$$  

(27.43)

$$g_{1D} = \frac{4\pi \hbar^2 a_s}{m r_i^2}$$  

(27.44)

$$g_{1D} n_{1D} = \hbar \cdot 77 \text{ Hz}$$  

(27.45)

Since we need at least two Bloch bands to see interesting effects, we must arrange for much stronger mean fields.

### 27.4.2.4 The Mott insulator

In the Mott insulating state, the atoms are localized at individual sites of an optical lattice. On one hand, the localization impedes any phase relation between atoms at different sites, that is, at a given site the phase uncertainty $\Delta \phi$ is complete. But at the same time, there is a perfect correlation of the atom number at each site known as spin squeezing$^7$, because (in a homogeneous lattice) every site contains exactly the same number of atoms, that is, the atom number uncertainty $\Delta N$ tends to zero. At a given lattice site, the number of atoms and the phase of the wavefunction can not be simultaneously fixed: $\Delta N \Delta \phi > 1$.

The absence of relative coherence between different sites and of the ability to interfere prohibits the description of the system by a single global wavefunction and the use of the Gross-Pitaevskii equation. Nevertheless, the Mott insulating state is not equivalent to a completely randomized sample. On the contrary, the coherence only changes its character$^8$.

---

$^7$The spin squeezing feature makes the Mott insulator interesting for spectroscopy at the Heisenberg limit and for quantum computation.

$^8$Remember, that the Fock state is a complicated superposition of Glauber states. The disappearance and reappearance of coherence is reminiscent to the phenomenon of collapse and revival in the Jaynes-Cummings model.
The Mott transition of a condensate from a superfluid state and to state of a Mott insulator occurs as a quantum phase transition, because it is driven by quantum fluctuations rather than of thermal noise. Therefore, it is a direct result of Heisenberg’s uncertainty relation.

Figure 1 Schematic three-dimensional interference pattern with measured absorption images taken along two orthogonal directions. The absorption images were obtained after ballistic expansion from a lattice with a potential depth of $V_0 = 10E_r$ and a time of flight of 15 ms.

Figure 2 Absorption images of multiple matter wave interference patterns. These were obtained after suddenly releasing the atoms from an optical lattice potential with different potential depths $V_0$ after a time of flight of 15 ms. Values of $V_0$ were: a, $0 E_r$; b, $3 E_r$; c, $7 E_r$; d, $10 E_r$; e, $13 E_r$; f, $14 E_r$; g, $16 E_r$; and h, $20 E_r$.

Figure 27.12: Signature of the Mott phase.

27.4.2.5 The Bose-Hubbard model

The Bose-Hubbard model gives an approximate description of the physics of interacting bosons in a lattice. The model is closely related to the fermionic Hubbard model, used in solid state physics for the description of superconducting systems and the hopping of electrons between the atoms of a solid crystalline lattice.
The Bose-Hubbard model starts from the following Hamiltonian \[457, 230\],

\[
\hat{H} = -J \sum_{(i,j)} \hat{a}_i \hat{a}_j + \sum_i \varepsilon_i \hat{n}_i + \frac{1}{2} U \sum_i \hat{n}_i (\hat{n}_i - 1),
\]  

(27.46)

where

\[
J \equiv \int d^3x \ w^*(x - x_i) \left[ -\frac{\hbar^2}{2m} \Delta + V_0(x) \right] w(x - x_i),
\]  

(27.47)

and

\[
U \equiv \frac{4\pi a_s \hbar^2}{m} \int d^3x |w(x)|^4,
\]  

(27.48)

with \( \varepsilon_i \equiv \frac{4\pi a_s \hbar^2}{m} \int d^3x V_{\text{trap}}(x)|w(x - x_i)|^2 \approx V_{\text{trap}}(x) \) and \( w(x) = w(x)w(y)w(z) \) are the Wannier functions for an individual particle. We assume for the moment a homogeneous condensate.

The Hilbert space dimension of the Bose-Hubbard model grows exponentially with the number of atoms \( N \) and the number of sites \( L \),

\[
D_b = \frac{(N_b + L + 1)!}{N_b!(L - 1)!}.
\]  

(27.49)

For the Fermi-Hubbard model, the Pauli exclusion principle leads to the Hilbert space dimension,

\[
D_f = \binom{L}{N_f}.
\]  

(27.50)

In three dimensional lattices the Hilbert space grows even faster. Therefore, it is a difficult computational task to model or simulate such systems, and generally not possible for more than 20 atoms and 20 lattice sites.

At zero temperature, the Bose-Hubbard model (in the absence of disorder) predicts the atomic ensemble to be an a Mott insulating state (MI) when \( J \ll U \), a superfluid state (SF) when \( J \gg U \), or a supersolid phase (SS), where both solid and superfluid phases (diagonal and off-diagonal) coexist. Mott insulation phases are characterized by integer site occupation numbers, by the existence of an energy gap for particle-hole excitations, and zero compressibility. In the presence of disorder, a third phase, the Bose glass exists. This phase is insulation because of the Anderson localization effects. Bose glass is characterized by a finite compressibility, the absence of a gap, and an infinite superfluid susceptibility \[200\]. See also (watch talk).

In the limit of strong tunneling and weak interactions, \( J \gg U \), the matter wave function looks like a Bloch state,

\[
|\psi_{SF}\rangle \sim \left( \sum_{i=1}^M \hat{a}_i \right)^N |0\rangle.
\]  

(27.51)

The variance of the number of particles per site is Poissonian, \( \sigma_{SF} \sim \sqrt{N_i} \), that is, the wavefunction per lattice site is (quasi)-coherent. However, the total wavefunction is delocalized over all lattice sites, the local wavefunctions have a rigid phase relationship.
and no long-range coherence. Otherwise, the matter wave function is an independent product of Fock states,
\[ |\psi_{MI}\rangle \sim \prod_{i=1}^{M} (\hat{a}_i^\dagger)_n |0\rangle. \tag{27.52} \]

The momentum distribution in terms of Wannier functions is,
\[ n(k) = |w(k)|^2 \sum_{i,j} e^{ik(r_i - r_j)} \langle \hat{a}_i^\dagger \hat{a}_j \rangle. \tag{27.53} \]

### 27.4.3 Schrödinger cats

Ruostekoski et al. [513] proposed a double BEC system consisting of two momentum sidemodes and a far-off resonance laser beam that constantly spontaneously redistributes the atoms between the sidemodes. Homodyne detection of the scattered photons established relative phase information in such a way, that the relative number information is blurred in such a way that both sidemodes evolve into a simultaneous superposition of phase and number states. They disregard thermal excitations and two-body collisions. The cats are very sensitive to decoherence.

Cirac et al. [109] and Gordon et al. [?] consider Josephson double species condensates. The relative atom numbers Rabi flop. Mediated by the mean-field the systems may evolve into cats. The proposals have been reexamined by Dalvit et al. [138]. Other contributions come from [223], [280], [519], [496], [314]. First experiments on spin-squeezed states have been made by [457].

### 27.4.4 Exercises

#### 27.4.4.1 Ex: Superfluid to Mott insulator transition
Chapter 28

Interaction of Bose-Einstein condensates with light

Light can essentially be used in two ways for the manipulation of matter waves: 1. Tuned far from resonance, light serves to create conservative optical dipole potentials (see Secs. 24.3.2 and 27.4.2). In such circumstances the states of internal atomic excitation can be adiabatically eliminated from the description of the center-of-mass dynamics. 2. Close to resonance the situation is quite different, but even then, the coherent excitation of internal states may allow for a controlled manipulation of the atomic motion. Among the examples discussed in the following sections are the adiabatic sweeps, the Raman output coupler, Bragg pulses, photoassociation, and matter wave superradiance (see Fig. 28.1).

![Figure 28.1](image)

Figure 28.1: Different types of coherent coupling: (a) coherent coupling of hyperfine levels, (b) coupling from a confined state to the continuum of free states, (c) mutual coupling of different velocity states of an atom, and (d) coupling between a (collisional) state of two free atoms with a bound molecular state.

28.1 Scattering of light by degenerate gases

28.1.1 The structure factor for degenerate quantum gases

We introduced in Sec. 20.1.1 the notion of the structure factor, where it was used to characterize the scattering of light by thermal distributions of atoms. To characterize the scattering of matter waves, we must generalize the notion of the structure factor. We wrote in (20.3) the Fourier transform of the density distribution, which now becomes, after inserting $\hat{n}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})$ and the plane wave expansion (26.70),

$$\hat{\rho}^\dagger(\mathbf{q}) = \int \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}d^3r = \frac{V}{(2\pi)^3} \int \int \hat{a}_{\mathbf{k}}^\dagger\hat{a}_{\mathbf{k}'}e^{i(\mathbf{k}' - \mathbf{k} + \mathbf{q})\cdot\mathbf{r}}d^3k'd^3kd^3r. \quad (28.1)$$

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With (26.76) and assuming sharp momenta (26.71),
\[
\hat{\rho}^\dagger(q) = V^2 \int \int \hat{a}_{k'}^\dagger \hat{a}_k \delta(k' + q) d^3k' d^3k = \sum_{k', k} \hat{a}_{k'}^\dagger \hat{a}_k \delta(k' + q) .
\] (28.2)

Finally,
\[
\hat{\rho}^\dagger(q) = \sum_k \hat{a}_k^\dagger + q \hat{a}_k = \sum_k \langle k + q | k \rangle .
\] (28.3)

Hence, \(\hat{\rho}^\dagger(q)\) describes the scattering of an atom with the momentum \(k\) to \(k + q\). We also find,
\[
\hat{\rho}^\dagger(-q) = \hat{\rho}(q) .
\] (28.4)

Understanding the fundamental state \(|g\rangle\) as the state without excitations, we define the static structure factor (20.5) now normalized to the number of particles [568],
\[
S(q) \equiv \frac{1}{N} \langle g | \hat{\rho}(q) \hat{\rho}^\dagger(q) | g \rangle ,
\] (28.5)
as a generalization of the classical structure factor. The static structure factor describes the probability to excite a condensate by creating a quasi-particle with momentum \(k\). We will need these notions in the Sec. 28.2.4.

The dynamic structure factor is obtained from
\[
S(q, \omega) = \int S(q, \omega) d\omega
\]
and measures the density of correlations in the ground state with 0 momentum. The formula describes, how an atom probes its environment by scattering quasi-particles back and forth,
\[
S(q, \omega) = \frac{1}{N} \sum_f \langle g | \hat{\rho}(q) | f \rangle \langle f | \hat{\rho}(q) | g \rangle \hbar \delta(\hbar \omega - E_f + E_g) .
\] (28.6)

For the norm, the kinetic energy, and the compressibility [412], we have the following sum rules,
\[
S(q) = \int S(q, \omega) d\omega
\] (28.7)
\[
\frac{\hbar^2 q^2}{2m} = \left. \int \hbar \omega S(q, \omega) d\omega \right|_{q \to 0}
\]
\[
\frac{\kappa^2}{2} = \left. \int \frac{S(q, \omega)}{\hbar \omega} d\omega \right|_{q \to 0} .
\]

### 28.1.1.1 Spatial coherence and the correlation function

The spatial coherence can be defined by [CCT & Aspect],
\[
F(x) \equiv \int \langle r | \hat{\rho} | r + x \rangle d^3r = \int e^{ik \cdot x} \langle k | \hat{\rho} | k \rangle d^3k .
\] (28.8)

We will demonstrate this relationship in Exc. 28.1.6.1. The coherence length \(\xi\) is given by \(F(\xi) = \frac{1}{e} F(0) = \frac{1}{e} .\) A second order correlation function is defined by,
\[
g^{(2)}(r_1, r_2) = \frac{\langle \hat{\psi}^\dagger(r_1) \hat{\psi}^\dagger(r_2) \hat{\psi}(r_2) \hat{\psi}(r_1) \rangle}{\langle \hat{n}(r_1) \rangle \langle \hat{n}(r_2) \rangle} .
\]
\[
g^{(2)}(r) \equiv g^{(2)}(r, r + r)
\] (28.9)
Solve the Excs. 28.1.6.2, 28.1.6.3, 28.1.6.4, and 28.1.6.5.

28.1.2 The structure factor in Bragg spectroscopy

28.1.2.1 The Hamiltonian of the Rayleigh scattering process

In Sec. 2.5.2 we saw the Galilei-boost (2.187),

$$|k+q⟩ = e^{i q · r} |k⟩.$$  \hfill(28.10)

In the second quantization we generalize to,

$$|k+q⟩ = \int \hat{\psi}^{\dagger} (r) e^{i q · r} \hat{\psi} (r) d^{3} r |k⟩ = \hat{\rho}^{\dagger} (q) |k⟩.$$  \hfill(28.11)

Thus, we can do the second quantization by simply replacing $e^{i q · r}$ by $\hat{\rho}^{\dagger} (q)$. Now, the Hamiltonian for the process of a photon absorption from the mode $\hat{c}_{k_{i}}$, taking into account the photonic recoil, was introduced in (16.6),

$$\hat{H}_{int} = \hbar \Omega (\hat{r}) e^{-i k_{i} · \hat{r}} \hat{c}_{k_{i}} \hat{\sigma}^{+} + c.c.$$ \hfill(28.12)

If the process is followed by the reemission of a photon to the mode $\hat{c}_{k_{f}}$,

$$\hat{H}_{int} = \hbar \Omega (\hat{r}) e^{i (k_{f} - k_{i}) · \hat{r}} \hat{c}_{k_{f}} \hat{c}_{k_{i}}.$$ \hfill(28.13)

Going to second quantization, as done in (28.11), and doing the Fourier transform \hfill(1),

$$\tilde{\hat{H}}_{int} = C \sum_{p_{f},p_{i}} \hat{c}_{k_{f}}^{\dagger} \hat{c}_{k_{i}} \hat{a}_{p_{f}}^{\dagger} \hat{a}_{p_{i}} \hat{\delta}_{k_{f} - k_{i} + p_{f}, - p_{i}}.$$ \hfill(28.14)

We assume here, that the light modes $k_{i}$ and $k_{f}$ are predefined, but the velocities $p_{i}$ are distributed. Otherwise, in the expression (28.14), we must also sum over light modes \hfill(2),

$$\tilde{\hat{H}}_{int} = C \sum_{k_{i},k_{f},p_{f},p_{i}} \hat{c}_{k_{f}}^{\dagger} \hat{c}_{k_{i}} \hat{a}_{p_{f}}^{\dagger} \hat{a}_{p_{i}} \hat{\delta}_{k_{f} - k_{i} + p_{f}, - p_{i}}.$$ \hfill(28.15)

where $C$ is a normalization constant. This Hamiltonian describes the elementary scattering process as a process of four wave mixing (4WM) \hfill[339, 569]. The light and the atoms are treated on equal footings as modes which can receive (quasi-)particle populations, and the scattering corresponds to a redistribution of populations between the modes \hfill(3).

The Hamiltonian (28.15) can be applied to various situations, such as spontaneous or stimulated Rayleigh scattering or Bragg scattering, depending on which ones of the modes $k_{f}, k_{i}, p_{f}$, and $p_{i}$ are populated or filtered by imposed boundary conditions.

---

1. $\hat{a}_{p}$ and $\hat{a}_{p}^{\dagger}$ are the operators of the quantized atomic field, while $\hat{c}_{k}$ and $\hat{c}_{k}^{\dagger}$ are the operators of the light fields.

2. Note the different form of this Hamiltonian as compared to (20.10).

3. This is analogous to the way, in which a ‘collision’ redistributes atomic populations between momentum modes. We will discuss this general concept of 4WM in Secs. 28.3.4 and 27.3.4.
Using momentum conservation \( q \equiv k_f - p_i = -p_f + p_i \), we obtain the cross section,

\[
\left( \frac{d\sigma}{d\Omega} \right)_{k_i \to k_f} = C^2 \sum_f |\langle f | \hat{H}_{\text{int}} | i \rangle|^2 = C^2 \sum_f |\langle f | \sum_{p_i} \hat{c}_{k_i+q} \hat{a}^\dagger_{k_i-q} \hat{a}_{p_i} | i \rangle|^2 , \tag{28.16}
\]

**Example 97 (Description of Bragg scattering via the structure factor):** In this example we irradiate two plane waves in directions \( k_1 \) and \( k_2 \) into a Bose-Einstein condensate. The total intensity will be,

\[
I_{\text{mod}}(r, t) = I \cos(q \cdot r - \omega t) \quad \text{with} \quad q = k_1 - k_2 . \tag{28.17}
\]

and the optical potential,

\[
V_{\text{mod}} = \frac{\hbar \Gamma^2}{8\Delta} I \cos(q \cdot r - \omega t) = \frac{\hbar \Gamma^2}{8\Delta} \frac{I}{2I_{\text{sat}}} (e^{i\mathbf{q} \cdot \mathbf{r} - i\omega t} + e^{-i\mathbf{q} \cdot \mathbf{r} + i\omega t}) \tag{28.18}
\]

\[
\rightarrow V_{\text{mod}} = \frac{V}{2} [\hat{\rho}^i(q)e^{-i\omega t} + \hat{\rho}^j(-q)e^{i\omega t}] .
\]

Now, the transition rate is [569],

\[
\frac{W}{N} = 2\pi \Omega_R^2 \Omega(q, \omega) = \frac{2\pi}{N\hbar} \left( \frac{V}{2} \right)^2 \sum_f |\langle f | \hat{\rho}^i(q) | g \rangle|^2 \delta(h\omega - (E_f - E_g)) , \tag{28.19}
\]

with \( \frac{V}{2} = \hbar \Omega_R \).

**28.1.3 Bosonic stimulation**

We assume in the following weak light intensities (and hence a negligible contribution of the Mollow fluorescence spectrum). That is, without cooperative effects the light would be elastically scattered by Rayleigh scattering. Now, we adopt a notation labeling the multimodal state by the numbers of photons and atoms distributed over the available light and momentum modes. That is, the initial state consists of \( n_p \) atoms distributed over momentum atomic states \( p \) and \( N_k \) photons distributed over wave vector modes \( k \) denoted by \( \ldots |N_{k_f}\ldots \rangle_{\text{rad}} \otimes |n_{p_f}\ldots \rangle_{\text{at}} :\)

\[
|i\rangle \equiv |n_{p_f}\ldots \rangle_{\text{at}} \otimes |N_{k_f}\ldots \rangle_{\text{rad}} . \tag{28.20}
\]

A particular scattering process can be treated like a ‘collision’ by redistributing the initial populations to final populations:

\[
|f\rangle = |n_{p_f}\ldots - 1 \ldots n_{q_f} + 1 \ldots \rangle_{\text{at}} \otimes |N_{k_f}\ldots - 1 \ldots N_{k_f} + 1 \ldots \rangle_{\text{rad}} . \tag{28.21}
\]

We write the matrix element,

\[
\langle f | \hat{H}_{\text{int}} | i \rangle \propto \langle \ldots N_{k_f} \ldots N_{k_f} \ldots \rangle_{\text{at}} \otimes \langle \ldots n_{p_f} \ldots n_{p_f} \ldots \rangle_{\text{rad}} \tag{28.22}
\]

\[
C \sum_{k_i, k_j, p_i, p_j} \hat{c}_{k_i}^\dagger \hat{c}_{k_j} \hat{a}^\dagger_{p_i} \hat{a}_{p_j} \delta_{k_i - k_j + p_f - p_i} | \ldots n_{p_f} \ldots n_{p_i} \ldots \rangle_{\text{at}} \otimes | \ldots N_{k_f} \ldots N_{k_i} \ldots \rangle_{\text{rad}} .
\]
Assuming that all modes are not degenerate, such that \( [\hat{a}_{p_f}, \hat{a}^\dagger_{p_i}] = \delta_{p_f, p_i} \), that is, \( \hat{a}^\dagger_{p_f} \) and \( \hat{a}_{p_f} \) only act on the mode \( |n_{p_f}\rangle_{at} \), etc.,

\[
\sum_{p'_f} \hat{a}_{p'_f}|...n_{p_i}...\rangle_{at} = \sum_{p_i} \sqrt{n_{p_i}}|...n_{p_i} - 1...\rangle_{at} \tag{28.23}
\]

and

\[
\sum_{p'_f} \hat{a}^\dagger_{p'_f}|...n_{p_f}...\rangle_{at} = \sum_{p_f} \sqrt{n_{p_f} + 1}|...n_{p_f} + 1...\rangle_{at},
\]

as well as,

\[
\sum_{k'_f} \hat{c}_{k'_f}|...N_{k_f}...\rangle_{rad} = \sum_{k_f} \sqrt{N_{k_f}|...N_{k_f} - 1...\rangle_{rad}} \tag{28.24}
\]

and

\[
\sum_{k'_f} \hat{c}^\dagger_{k'_f}|...N_{k_f}...\rangle_{rad} = \sum_{k_f} \sqrt{N_{k_f} + 1|...N_{k_f} + 1...\rangle_{rad}} \tag{28.25}
\]

Let us now assume for a moment, that the photon is scattered to the vacuum, that is, the final mode of light is initially empty, \( N_{k_f} = 0 \).

\[
\langle f|\hat{R}_{in\text{el}}(1)|_{in\text{el}} \propto \sqrt{N_{k_i}|...N_{k_i} - 1...\rangle_{rad}} \tag{28.26}
\]

\[
= \sum_{p_f, p_i, k_f, k_i} \sqrt{N_{k_i} \sqrt{n_{p_f}} + 1|...n_{p_i}...n_{p_i} - 1...n_{p_f} + 1...\rangle_{at} \otimes |...N_{k_i} - 1...k_f...\rangle_{rad}}
\]

\[
= \sum_{p_f, p_i, k_f, k_i} \sqrt{N_{k_i} \sqrt{n_{p_f} + 1|...n_{p_i}...n_{p_i} - 1...n_{p_f} + 1...\rangle_{at}}}
\]

Obviously, the differential scattering cross-section,

\[
\left( \frac{d\sigma}{d\Omega} \right)_{in\text{el}} \propto N_{k_i} (n_{p_f} + 1)n_{p_i}, \tag{28.27}
\]

depends, in addition to the numbers of provided photons \( N_{k_i} \) and atoms \( n_{p_i} \) in the initial mode, also on the number of atoms in the final mode \( n_{p_f} \). This amplification of the probability of the scattering process is called bosonic stimulation.

Now, we consider the degenerate case, where the initial atomic momentum mode coincides with the final mode, \( n_{p_f} = n_{p_i} \). In this case,

\[
\sum_{p_f = p'_i} \hat{a}^\dagger_{p_f} \hat{a}_{p'_i}|...n_{p_i}...n_{p_f}...\rangle_{at} = \sum_{p'_i} \hat{a}_{p'_i} \hat{a}^\dagger_{p'_i}|...n_{p_i}...n_{p_i}...\rangle_{at} = \sum_{p_i} n_{p_i}|...n_{p_i}...n_{p_i}...\rangle_{at}, \tag{28.28}
\]

\[\text{We will discuss later the case, where the scattering is (bosonically) stimulated by the number of photons already present in the final mode prior to the scattering process.}\]
and a calculus analogous to (28.26) yields,

$$\langle f|\hat{H}_{\text{int}}|i\rangle_{\text{el}} \propto \text{rad} \langle ...N_k',...N_k'...| \otimes...n_{p'}...n_{p'}...| \sum_{p_i,k_f,k_i} \sqrt{N_k_i} n_{p_i}|...n_{p_i}...n_{p_i}...\rangle_{\text{at}} \otimes |...N_k_i - 1...1_k_f...\rangle_{\text{rad}}$$

$$= \sum_{p_i,k_f,k_i} \sqrt{N_k_i} n_{p_i} \text{rad} \langle ...N_k',...N_k'...|\text{at}|...n_{p'}...n_{p'}...|...n_{p_i}...n_{p_i}...\rangle_{\text{at}}$$

$$= \sum_{p_i,k_f,k_i} \sqrt{N_k_i} n_{p_i} \delta_{N_k',N_k_i} - \delta_{N_k',N_k_i} \delta_{n_{p'},n_{p_i}} \delta_{n_{p'},n_{p_i}} = \sqrt{N_k_i} n_{p_i}. \tag{28.29}$$

Now, the differential scattering cross-section,

$$\left( \frac{d\sigma}{d\Omega} \right)_{\text{el}} \propto N_k_i n_{p_i}^2 , \tag{28.30}$$

only depends on the number of provided photons $N_k_i$ and the number of atoms $n_{p_i}$ in the initial mode.

### 28.1.3.1 Elastic and inelastic scattering

The interpretation of the result is the following: Light can be scattered in two ways: (i) with or (ii) without change of atomic moment distribution. The event of a photon scattering (28.21) then it consists of two terms (28.27) and (28.30) [478],

$$\frac{d\sigma}{d\Omega} = \left( \frac{d\sigma}{d\Omega} \right)_{\text{el}} + \left( \frac{d\sigma}{d\Omega} \right)_{\text{inel}}. \tag{28.31}$$

The first term of (28.31) occurs when the momentum of the scattering atom does not change, $p = q$, that is, when the populations of the momentum states $n_p$ and $n_q$ do not change. The corresponding term (28.30) describes elastic Rayleigh scattering. This process is coherent, that is, the phase relationship between the incident wave and the outgoing wave is fixed, because the photon emission is self-stimulated. I.e. it decays to the original mode via forward scattering within the angle defined by the phase matching condition $\vartheta < \lambda/d$, where $d$ is the size of the atomic sample [339]. This contribution is dispersive, reversible, and conservative, and it is at the origin of the dipole force.

The second term of (28.31) is the inelastic part of Rayleigh scattering, where an atom with the initial momentum $p_p$ is scattered to the momentum state $n_q$. This term is absorptive, dissipative, and spontaneous. The frequency of the photons is shifted, a momentum is imparted to the atom, such that the process is incoherent. Hence, a suggestive way of expressing the differential scattering cross-section (28.21) is,

$$\frac{d\sigma}{d\Omega} \propto \left| \sum_i n_i \langle i|\hat{H}_{\text{int}}|i\rangle \right|^2 + \sum_{i \neq f} n_i (1 + n_f) |\langle i|\hat{H}_{\text{int}}|f\rangle|^2 , \tag{28.32}$$

where $|i\rangle$ and $|f\rangle$ denote momentum states of the atomic sample.

The bosonic stimulation of inelastic Rayleigh scattering represents a way to overcome, on one hand the restrictive phase matching condition, and on the other the
incoherence of the scattering into large angles. For non-interacting systems of localized bosons $S(q, \omega)$ can be expressed using single particle states $|i\rangle$ with energy $E_i$ and population $N_i$ [see (20.3) and (20.6)],

$$S(q, \omega) = N \left| \sum_i n_i \langle i| \hat{H}_{\text{int}}|i\rangle \right|^2 \delta(\omega) + N \sum_{i \neq f} |\langle f| \hat{H}_{\text{int}}|i\rangle|^2 n_i (n_f + 1) \delta[\omega - (E_f - E_i)/\hbar],$$

\(28.33\)

with $S_0(q) = |\langle \hat{\rho}^\dagger(q) \rangle|^2 = \left| \sum_i n_i \langle i| \hat{H}_{\text{int}}|i\rangle \right|^2$.

### 28.1.3.2 Dielectric properties of condensates

In a way, the Bose-Einstein condensate represents a new form of matter with indistinguishable and totally delocalized atoms. It is thus sensible to raise the question, whether this object scatters light differently than a non-degenerate gas. That is, how are the dielectric properties of condensates? What is the role of interatomic collisions?

Experiments have shown high dielectric activity of condensed gases [261]. In a scheme of electromagnetically induced transparency, (EIT), a reduction of the speed of light down to 17 m/s was observed. However, this effect is not related to quantum degeneracy of the gas, but can also be observed in classical gas cells [333].

### 28.1.4 Playing with bosonic and fermionic states

Here, we want to address the question, whether scattering processes are influenced by bosonic stimulation or cooperative enhancement. Let us consider the case of $N$ atoms (bosons or fermions) generated from vacuum by operators $\hat{a}_m^\dagger(q)|0\rangle$, where $m$ indicates some additional quantum number (for example, the vibrational state of a loose trapping potential) helping us to enumerate fermionic states, and $q$ indicates the momentum (considered independent from the trapping potential for short enough times). The operators respect the rules $[\hat{a}_m(q), \hat{a}_{m'}^\dagger(q)]_\pm = \delta_{m,m'} \delta_{0,q}$ and $\hat{a}_m(q)|0\rangle = 0$. Initially the $N$ atoms are in the bosonic, respectively, fermionic many-body state [433],

$$\begin{align*}
|\Psi_b^{(N)}(0)\rangle &= \frac{1}{\sqrt{N!}} \hat{a}_0^\dagger(0)^N |0\rangle \quad \text{resp.} \quad |\Psi_f^{(N)}(0)\rangle = \prod_{n=0}^{N-1} \hat{a}_n^\dagger(0) |0\rangle.
\end{align*}$$

\(28.34\)

Note that $|\Psi_b^{(N)}(0)\rangle = |N\rangle$ is a Fock state satisfying $\langle \Psi_b^{(N)}(0)|\Psi_b^{(N)}(0)\rangle = 1$, while $|\Psi_f^{(N)}(0)\rangle$ is a product state being normalized as well, $\langle \Psi_f^{(N)}(0)|\Psi_f^{(N)}(0)\rangle = 1$.

\(5\) Normally, the refractive index of a gas can only be increased to the detriment of transmission. However, in a gas of multilevel atoms, it is possible to electromagnetically induce quantum interference effects eliminate absorption and increasing the transparency of the gas. In certain cases, the dispersion $dn/d\omega$ may be high enough to strongly influence the propagation velocity of light [332]. The group velocity for a light pulse in a dielectric medium with refractive index $n(\omega)$ at the laser frequency $\omega$ is,

$$v_g = c \left( n(\omega) + \omega \frac{dn}{d\omega} \right)^{-1}.$$
Probing the number of atoms in a many-body state is done by,

\[ N = \langle \Psi | \hat{N} | \Psi \rangle \quad \text{where} \quad \hat{N} = \int \hat{\psi}^\dagger (r) \hat{\psi}(r) d^3 r = \sum_{m,k} \hat{a}_m^\dagger (k) \hat{a}_m (k), \quad (28.35) \]

or if we are only interested in a particular momentum state \( k \) and vibrational state \( m \),

\[ \langle \Psi | \hat{N}_m (k) | \Psi \rangle = \langle \Psi | \hat{a}_m^\dagger (k) \hat{a}_m (k) | \Psi \rangle = | \hat{a}_m (k) | \Psi \rangle |^2. \quad (28.36) \]

For the subsequent arguments the following side calculation will be useful,

\[ \hat{a}_m (k) \hat{a}_n^\dagger (q) N = \delta_{m,n} \delta_k,q \hat{a}_m^\dagger (q) N - 1 + \hat{a}_n^\dagger (q) \hat{a}_m (k) \hat{a}_n (q) N - 1 \quad (28.37) \]

which can be generalized to,

\[ \hat{a}_m (k) \hat{a}_n^\dagger (q_1) + \hat{a}_n^\dagger (q_2) \] \( N \)

\[ = N \delta_{m,n} (\delta_k,q_1 + \delta_k,q_2) \hat{a}_m^\dagger (q_1) + \hat{a}_n^\dagger (q_2) \] \( N \) \( -1 \) \( + \) \( \hat{a}_n^\dagger (q_1) + \hat{a}_n^\dagger (q_2) \] \( N \) \( \hat{a}_m (k) \).

Other possible states are bosonic or fermionic product states,

\[ \begin{vmatrix} | \Psi^{(N_1)} (0) \rangle | \Psi^{(N_2)} (q) \rangle \end{vmatrix}. \quad (28.39) \]

We will see in 28.1.6.7 that product states are normalized if the partial states are normalized. Explicitly,

\[ | \Psi^{(N_1)}_b (0) \rangle | \Psi^{(N_2)}_b (q) \rangle = \frac{1}{\sqrt{N_1! N_2!}} \hat{a}_0^\dagger (0)^{N_1} \hat{a}_0^\dagger (q)^{N_2} | 0 \rangle \quad (28.40) \]

\[ | \Psi^{(N_1)}_f (0) \rangle | \Psi^{(N_2)}_f (q) \rangle = \prod_{n=0}^{N_1-1} \hat{a}_n^\dagger (0) \prod_{n=0}^{N_2-1} \hat{a}_n^\dagger (q) | 0 \rangle. \]

Note, that product states in the same mode need renormalization when merged,

\[ | \Psi^{(N_1)}_b (0) \Psi^{(N_2)}_b (0) \rangle = \frac{1}{\sqrt{N_1! N_2!}} \hat{a}_0^\dagger (0)^{N_1+N_2} | 0 \rangle = \sqrt{\binom{N_1+N_2}{N_1}} | \Psi^{(N_1+N_2)}_b (0) \rangle \quad (28.41) \]
for example, \( |\Psi_b^{(N)}(0)\Psi_{b}^{(1)}(0)\rangle = \sqrt{N + 1}|\Psi_b^{(N+1)}(0)\rangle \).

A \( \pi/2 \)-Bragg pulse has the faculty to transfer 50% of the atoms into a momentum mode \( q \), thus creating a new state where every single atom lives in a coherent superposition of two momenta,

\[
|\Psi_b^{(bragg,N)}(0, q)\rangle = \left[ \hat{a}^{\dagger}_0(0) + \hat{a}^{\dagger}_0(q) \right]^N|0\rangle = \sum_{n=0}^{N} \binom{N}{n} \frac{\hat{a}^{\dagger}_0(0)^N \hat{a}^{\dagger}_n(q)^{N-n}}{\sqrt{2^N N!}}|0\rangle.
\]

\[
|\Psi_f^{(bragg,N)}(0, q)\rangle = \prod_{n=0}^{N-1} \frac{[\hat{a}^{\dagger}_n(0) + \hat{a}^{\dagger}_n(q)]}{\sqrt{2^N}}|0\rangle
\]

(28.42)

### 28.1.4.1 Bosonic stimulation versus cooperative enhancement by a Bragg grating

Now, we scatter a photon, whose fate is not of interest here, but which triggers possible transitions of an atom sitting together with \( N_1 \) atoms in the momentum state \( 0|0\rangle \) towards another momentum state \( 0|0\rangle \) initially populated with \( N_2 \) atoms via the operator,

\[
\hat{H} = \sum_{m} \hat{a}^{\dagger}_m(k)\hat{a}_m(0).
\]

Applying this process to bosonic or fermionic clouds, as defined in (28.34), we find bosonic stimulation only in the case of bosons,

\[
\langle \Psi^{(N_1-1)}(0)\Psi^{(N_2)}(q)|\hat{H}|\Psi^{(N_1)}(0)\Psi^{(N_2-1)}(q)\rangle = \delta_{k,q} \left\{ \begin{array}{ll} \sqrt{N_1N_2} & \text{for bosons} \\ \frac{1}{4} & \text{for fermions} \end{array} \right.
\]

as will be shown in Exc. 28.1.6.8(a). The transition probabilities are is then,

\[
\frac{d\sigma}{d\Omega} = |\langle f|\hat{H}|i\rangle|^2 = \delta_{k,q} \left\{ \begin{array}{ll} \frac{N_1N_2}{4} & \text{for bosons} \\ 1 & \text{for fermions} \end{array} \right.
\]

(28.45)

Note, that these results does not change in the presence of a Bragg grating not participating in the dynamics: \( |\Psi^{(N_1-1)}(0)\Psi^{(N_2)}(q)|\hat{a}^{\dagger}_{bragg,N}(0, q)|\Psi^{(N_1-1)}(0)\Psi^{(N_2)}(q)|\psi^{(bragg,N)}_{b,f}(0, q)\rangle \). However, applying the same scattering process to the Bragg state defined in (28.44) we find the same expression for bosons and for fermions,

\[
\langle \Psi^{(N_1-1)}_{b,f}(0, q)|\hat{H}|\Psi^{(N_2)}_{b,f}(0, q)\rangle = \sqrt{\frac{N}{2}} \left[ \delta_{k,0} \pm \frac{N - 1}{2}(\delta_{k,0} + \delta_{k,q}) \right]
\]

(28.46)

as will be shown in Exc. 28.1.6.8(b). The transition probabilities are is then,

\[
\frac{d\sigma}{d\Omega} = |\langle f|\hat{H}|i\rangle|^2 = \delta_{k,q} \left\{ \begin{array}{ll} \frac{N}{2} \frac{(N-1)^2}{4} & \text{for bosons} \\ 1 & \text{for fermions} \end{array} \right.
\]

(28.47)

This means that, if \( k = 0 \) or \( k = q \), the scattering is subject to cooperative enhancement by a factor of \( N/2 \) (which is the number of atoms in each of the momentum state.
0 and \( q \) independently on the quantum nature of the atom (boson or fermion). That is, the probability that the scattered atoms joins one of the two momentum goes, for large \( N \), like \( N^2 \), but for \( N = 1 \) there is no enhancement possible. Do Exc. 28.1.6.9.

### 28.1.5 Collective scattering for condensates with interactions

Correlations are introduced in a BEC by interactions between the atoms. Therefore, collective scattering effects are influenced by interactions, while on the other hand an ideal gas \((g_n \to 0)\) scatters like an ultra-cool non-degenerate thermal cloud. In this sense, particle-like excitations \( (p^2/2m \gg gn) \) in an interacting BEC behave like thermal atoms. The mean-field energy can be seen as resulting from excitations of phonon pairs. These pairwise excitations populate the momentum modes, which modify the scattering of light via bosonic stimulation. That is, an interacting condensate \((g_n > 0)\) gives a collective response to an incident light beam. Note that \( \mu > 0 \) is possible when \( V(r) \neq 0 \) and \( g_n \neq 0 \) even if \( T \to 0 \), which is the case here considered.

What is the nature of the collective behavior? 1. The Bogolubov spectrum is modified. In the phononic regime, the absence of dispersion allows the definition of a speed of sound. 2. The scattering of light can be suppressed by excitation of phonon pairs. This effect is anisotropic and more pronounced in forward direction. That is, the resonance at which the light is scattered is shifted and broadened. The latter effect is understood via destructive interference of two processes: Scattering from a BEC to the momentum mode \( k \) and from the momentum mode \(-k\) to a BEC.

It is important to be aware that the notion of bosonic stimulation \( \sim n_i(1+n_f) \) and fermionic inhibition \( \sim n_i(1-n_f) \) also has its limitations, when interatomic interactions are not negligible, that is, when the quantum depletion is remarkable \([226, 404]\).

The effect of interatomic collisions can be taken into account as contributions of pair correlations to the ground state of the BEC,

\[
|\psi_0, n_0 \rangle = |n_0, 0, 0 \rangle - \sum_k (v_k^2/u_k^2) |n_0-2, 1, 1 \rangle + \sum_k (v_k^2/u_k^2)^2 |n_0-4, 2, 2 \rangle - ... , \tag{28.48}
\]

where \( |n_0, n_k, n_{-k} \rangle \) denotes the state with \( n_0 \) atoms in the trap’s ground state and \( n_{\pm k} \) atoms in the momentum mode \( k \), where \( v_k^2 \) is the average population of momentum mode \( k \). The populated recoil modes result in a increase of spontaneous emission by a factor of \( v_k^2 = 1 + u_k^2 \). We can also understand the modification of the scattering rate as resulting from small scale inhomogeneities generated by pair correlations. The effect is strongest at small scattering angles, that is in forward direction.

### 28.1.6 Exercises

#### 28.1.6.1 Ex: Spatial coherence of a condensate

Derive the relationship (28.8).

#### 28.1.6.2 Ex: Interaction energy of a condensate via spatial coherence

Show that the total energy of a condensate is given by \( \langle U \rangle = \frac{1}{2} \int n(r_1) U(r_1 - r_2) g^{(2)}(r_1, r_2) n(r_2) d^3 r_1 d^3 r_2 \).
28.1. SCATTERING OF LIGHT BY DEGENERATE GASES

28.1.6.3 **Ex: Structural factor of a condensate in the local density approximation**

Calculate the structure factor of a condensate in the local density approximation (LDA) [88, 568].

28.1.6.4 **Ex: Structure structure of a Fermi gas**

Calculate the structure factor for Bragg scattering on a Fermi gas.

28.1.6.5 **Ex: Structure factor of a heteronuclear mixture**

In this exercise we discuss the structure factor of a heteronuclear mixture (specifically contemplating $^6$Li mixed with $^{87}$Rb) generalizing the available theory for Li spin mixtures to heteronuclear mixtures [121, 209, 210, 605]. The total dynamic structure factor is,

$$ S(q, \omega) = S_{87,87}(q, \omega) + S_{6,6}(q, \omega) + S_{6,87}(q, \omega) + S_{87,6}(q, \omega) . $$

Exciting the Bragg resonance for Li, the Rb cloud would stay unaffected, the such that around $\omega/2\pi = 295$ kHz, $S_{87,87}(q, \omega) = 0$, as well as, $S_{6,87}(q, \omega) = S_{87,6}(q, \omega) = 0$. For Fermi gas $S_{6,6}(q, \delta) \to 1$, except if Bose gas induces Li-Li correlations, as in the case of BCS-pairing of phonon-mediated Efimov states. How does Rb influence the Bragg scattering of Li? Via a variation of the apparent mass as a displacement of the Bragg resonance or as a second peak appearing at a specific detuning of the Bragg beams at $\omega_{6,6}/(6 + 87)$?

28.1.6.6 **Ex: Structure factor for Bragg scattering**

Demonstrate the following relationships,

$$ \frac{dp_{cm}(q, \omega)}{dt} = -m\omega^2 z_{cm} + \hbar q \frac{\Omega_{br}^2}{2} \int d\delta'[S(q, \omega') - S(-q, -\omega')] \sin(\omega - \omega') t_{br} $$

$$ \ddot{p}_{cm}(q, \omega) + \omega^2 p_{cm} = \hbar q \frac{\Omega_{br}^2}{2} \int d\omega'[S(q, \omega') - S(-q, -\omega')] \cos(\omega - \omega') t_{br} \to 0 . $$

28.1.6.7 **Ex: Extracting the atom number from many-body states**

Verify the normalization of (a) the bosonic Fock state (28.34), (b) the fermionic product state (28.34), (c) the bosonic product state (28.39), (d) the bosonic Bragg grating state (28.41), and (e) the fermionic Bragg grating state (28.41).

28.1.6.8 **Ex: Bosonic stimulation and cooperative enhancement by lattices of bosons and fermions**

Compare bosons and fermions with respect to (a) bosonic stimulation and (b) cooperative enhancement.
28.1.6.9 Ex: Cooperative enhancement versus bosonic stimulation

CARL amplification comes from cooperativity not from bosonic stimulation [433, 340, 537], that is, it should work for fermions and boltzons. To demonstrate this proceed as follows:

a. Set up the single-atom Hamiltonian for a 3D harmonic potential in which the atoms (bosons or fermions) are initially placed allowing for the possibility of momentum recoil by photon scattering. This disregards the trap’s inhomogeneity, but is a good assumption for short times. What are the eigenfunction of this Hamiltonian? Calculate the expectation value for the density distribution. Express the field operators in momentum space. Express the lowest energy states for a bosonic/fermionic cloud in momentum representation.

b. Now apply a \( \pi/2 \)-Bragg-pulse imparting the recoil \( \mathbf{K} \) to the cloud. What is the resulting state? Recalculate the expectation value for the density distribution.

c. Now, assume the presence of another free (test) atom (or photon). Write down the Hamiltonian and the wavefunction for this atom. It is supposed to interact with the atomic cloud via the (perturbatively treated) interaction potential,

\[
\hat{V} = \lambda \int d^3r \hat{\psi}_1^\dagger(r) \hat{\psi}_2^\dagger(r) \hat{\psi}_2(r) \hat{\psi}_1(r) .
\]

Calculate the probability that the atom is scattered at a particular wavevector, i.e. determine the cooperative enhancement factor.

d. Is cooperative enhancement possible with just one atom?

e. How about cooperative enhancement in a cavity, when cooperativity is ensured by a single atom plus all its mirror images?

28.2 Bragg diffraction

An important technique for manipulating the atomic motion is by Bragg diffraction\(^6\). It allows the coherent transfer of atoms to other states of motion or to superpositions of motional states, and is extremely useful for applications, such as the realization of matter wave beamsplitters [355] and atomic lasers, or for the targeted excitation of quasi-particles [355, 575, 568].

To implement Bragg diffraction, we consider two laser pulses with different frequencies and propagation directions \( \omega, \mathbf{k}_\omega \) and \( \omega - \Delta \omega, \mathbf{k}_{\omega - \Delta \omega} \), detuned from an atomic resonance and intersecting at the position of atoms under an angle \( \vartheta \), as shown in Fig. 28.3(a). The superposition of the electric fields of the light beams,

\[
E = E_0 e^{i(k_\omega \cdot r - \omega t)} + E_0 e^{i(k_{\omega - \Delta \omega} \cdot r - (\omega - \Delta \omega) t)} = E_0 e^{i(k_\omega \cdot r - \omega t)} \left( 1 + e^{-i(q \cdot r - \Delta \omega t)} \right)
\]

\[
= 2E_0 e^{i(k_\omega \cdot r - \omega t)} e^{-\frac{i}{2}(q \cdot r - \Delta \omega t)} \cos \frac{q \cdot r - \Delta \omega t}{2} ,
\]

(28.49)

where \( q = k_\omega - k_{\omega - \Delta \omega} \), produces a standing light wave with an intensity proportional to,

\[
|E|^2 = 4E_0^2 \cos^2 \frac{q \cdot r - \Delta \omega t}{2} = 2E_0^2 \left[ 1 + \cos(q \cdot r - \Delta \omega t) \right] ,
\]

(28.50)

\(^6\)The idea is analogous to the manipulation of the \( \mathbf{k} \)-vector of light waves by acousto-optic modulators.
with which the atoms interact.

The Bragg diffraction technique has proven extremely efficient: up to 100% of the atoms can be transferred to well-defined momentum sidemodes. In general, the components of a cloud with different momentum modes overlap during the time scale of the Bragg pulses. They only separate spatially after a ballistic flight time, which then allows their identification via absorption imaging.

![Figure 28.3: Bragg scattering of atoms at a standing light wave. (a) Geometric layout: Short pulses of two laser beams in Raman configuration enclosing an angle of $\vartheta$ and detuned from each other by $\Delta \omega$ are simultaneously irradiated into the cloud. (b) Bogolubov dispersion relation for interacting condensates (blue line). The quadratic dispersion relation (cyan) holds for free particles, and the linear dispersion relation (magenta) for phonon excitations.](image)

### 28.2.1 Interpretations of the Bragg diffraction process

Bragg’s diffraction can be treated within the formalism developed in Sec. 28.1.2, as will be shown later, in Sec. 28.2.4. But before that, let us present a simplified approach and several simple pictures illustrating the dynamics of Bragg diffraction.

#### 28.2.1.1 Bragg diffraction picture

The first interpretation of this phenomenon is as matter wave Bragg diffraction at a standing light wave (i.e. an one-dimensional optical lattice) formed by two crossing pulsed laser beams. We consider atoms initially at rest exposed to the standing wave \(28.49\) with \(\Delta \omega = 0\) and \(q \equiv q \hat{e}_z\), such that the dipolar potential \(U \propto |E|^2\) is, with \(28.50\),

\[
U(z) = U_0 \cos^2 \frac{qz}{2} . \tag{28.51}
\]

---

\(^7\)Note, that the initial population of the recoil mode should be small. Otherwise, since Bragg diffraction is a coherent and thus reversible process, atoms initially in the recoil mode are transferred back to the original matter wave mode.
Assuming a given finite interaction time $\tau$, the modulation of the local phase of the atoms becomes
\[\psi_\tau(z) = \psi_0(z)e^{iU(z)\tau/\hbar} = \psi_0(z)e^{\frac{1}{2i\hbar}U_0\tau(cosqz+1)} = \psi_0(z)e^{iU_0\tau/2\hbar} \sum_n i^n J_n(U_0\tau/2\hbar)e^{inz},\]
(28.52)

where $J_n$ are the Bessel functions of the first kind.

The condensed wavefunction evolves into a superposition of motional modes, which correspond to the diffraction orders of Bragg scattering and their amplitudes through the Bessel functions $J_n$. The diffraction efficiency increases with laser intensity and with time.

Now, we need to generalize this result to the propagating standing wave of the expression (28.50). The intensity generates a dipole potential,
\[U(z,t) \approx U_0 \cos^2 \frac{qz - \Delta \omega t}{\Delta \omega},\]
(28.53)

so that the condensate now evolves according to,
\[\psi(z,t) = \psi_0(z)e^{i/\hbar \int_0^t U(z,t)dt} = \psi_0(z)e^{i/\hbar \int_0^t U_0 \cos^2 \frac{qz - \Delta \omega t}{\Delta \omega} dt} .\]
(28.54)

For short interaction times, $\tau \ll 2\pi/\Delta \omega$, ...

28.2.1.2 Compton scattering picture

The second interpretation is that of Compton scattering. Spontaneous Rayleigh scattering of a photon from a mode $k_\omega$ into a solid angle around $k_\omega - \Delta \omega$ leaves an atom with the recoil momentum $\hbar q \equiv p_f \cdot p_i$. Of course, one can stimulate the Rayleigh scattering process by providing the laser mode $k_\omega - \Delta \omega$ at the entrance. By replacing the spontaneous output mode with a stimulated input mode, we increase the probability for an atomic recoil in the momentum mode $\hbar q$, which is thus pre-selected by the choice of $k_\omega - \Delta \omega$. Since the elementary scattering process must conserve energy and total momentum,
\[\hbar \omega + \frac{p_i^2}{2m} = \hbar (\omega - \Delta \omega) + \frac{p_f^2}{2m}\]
(28.55)
\[\hbar k_i + p_i = \hbar k_f + p_f ,\]
we obtain the Bragg condition,
\[E = \Delta \omega = \frac{p_f^2}{2m} - \frac{p_i^2}{2m} = \frac{(p_f - p_i)^2}{2m} + \frac{(p_f - p_i) \cdot p_i}{m} = \frac{q^2}{2m} + \frac{q \cdot p_i}{m} .\]
(28.56)

Expressed by the Bragg angle, the condition reads,
\[q = \sqrt{(p_f - p_i)^2} = \sqrt{\hbar^2 k_i^2 + \hbar^2 k_f^2 - 2\hbar^2 k_i k_f} \approx \hbar k_i \sqrt{2 - 2 \cos \theta} = 2\hbar k_i \sin \theta / 2 .\]
(28.57)

The efficiency for transferring atoms to the recoil mode depends on the fulfillment of this condition. The Bragg condition can be employed to select higher diffraction orders.

---

8Using the Jacobi-Anger expansion, $e^{i\beta \cos x} = \sum_n i^n J_n(\beta)e^{inx}$.

9Andreas got $\psi_0(z) \sum_n J_n^2(U_0\tau/2\hbar)e^{inz}/2$. 
28.2.1.3 Stimulated Raman scattering picture

A third interpretation is as stimulated Raman scattering between two different kinetic states of the atom [see 28.3(b)]. In fact, the momentum modes $p_i$ and $p_f$ have different energies, which, for a condensate, are determined by the Bogolubov spectrum [220]. By varying the angle $\vartheta$ in the Bragg condition (28.56), we can choose the amount of energy to be transferred and thus probe the spectrum, i.e. measure the excitation energy $E(q, \mu)$ as a function of the momentum $q$ and the chemical potential $\mu$ in the particle regime $q^2/2m \gg \mu$, as well as in the phonon regime $q^2/2m \ll \mu$. On the other hand, varying the detuning $\Delta \omega$ in the Bragg condition (28.56), we selectively address different velocity classes of a gas or condensate, which allows us to probe its velocity distribution. This procedure is called spectroscopy of recoil-induced resonances (RIR) [127, 575]. RIR spectroscopy also provides detailed information on the mean-field energy and the (inhomogeneous) density distribution of a condensate. Note, finally, that Bragg scattering is closely related to Kapitza-Dirac scattering of atomic beams, well-known in conventional atom optics [329, 227].

![Figure 28.4: Bragg scattering of atomic clouds. (a) Geometric layout as in 28.3. Here, we assume $p_i = 0$. (b) Experiment showing coherent splitting by a Bragg pulse.](image)

28.2.1.4 Coherent splitting

There is a general interest in the possibility of dividing phase space by coherent coupling of otherwise independent modes. We are talking, of course, about double slits or beamsplitters, which represent an essential tool of quantum mechanics. Bragg diffraction realizes a beamsplitter for atomic clouds analogous to the optical beamsplitter. In fact, Bragg diffraction has been used for the realization of output couplers for atom lasers and for atom interferometers. A suggestion that is sometimes made is the following: 'A condensate is a macroscopically populated momentum mode. The Bragg beamsplitter divides the phase space into two entangled output modes. Shouldn‘t it be possible to generate a macroscopic superposition of two condensates, i.e. a really macroscopic Schrödinger cat?’. Their is an obvious fundamental interest to study such states and the mechanisms leading to their decoherence (see Sec. 17.1.1).

To clarify the situation, we first have to say, what we mean by Schrödinger cat. A Schrödinger cat is a quantum superposition of many-body states. A perfect cat made of $N$ two-level atoms can be expressed as $|++...\rangle \pm |--...\rangle$. The Einstein-Podolsky-Rosen (EPR) and the Greenberger-Horne-Zeilinger states (GHz) belong to this category. The degree of entanglement of the cat is measured by the information entropy defined as $S = -\langle \log_2 \hat{\rho} \rangle$, where $\hat{\rho}$ is the density operator. The information
entropy measures the amount of classical information that can be encoded in the quantum state. For example, the entropy of a perfect cat state is $S = 1$ bit, because if we find one of the atoms in the state $|+\rangle$, we know that all others are in the same state.

Second, we have to explain, what we mean by a beamsplitter. Subject to a beam splitting process, every individual atom has the choice between one of two output ports. However, if the process is coherent, every atom will evolve into a coherent superposition, but it does so independently from the other atoms. That is, we can write the state of the atomic cloud as a product state of Schrödinger kittens ($|+\rangle \pm |-\rangle$)$^N$, but no real cat. The information entropy is $S = N$ bit, as for independent atoms. Nevertheless, the beamsplitter creates a certain correlation between the two modes (see Sec.15.5).

![Figure 28.5: Bragg interferometer.](image)

How can it be, that a condensate composed of totally delocalized atoms, subject to the homogeneous light fields of the Bragg pulse (the photons being totally delocalized over the field mode), which interact with the condensate in a coherent way, increase its entropy from 1 to $N$ bits? At this point, it is useful to remember that, even in condensates, the photons are scattered by individual atoms. The interaction with the light localizes one atom in the condensate before removing it from there by recoil.\(^{10}\)

\(^{10}\)However, cooperative interaction of several atoms with a light mode is possible, e.g. in superradiance or when the photons are recycled by means of an optical cavity, as in the Jaynes-Cummings model.
28.2. BRAGG DIFFRACTION

28.2.2 Bragg interferometry of a thermal gas

Even above the critical temperature the momentum distribution of a dilute thermal gas is (slightly) modified by quantum statistics, i.e. by the classical, bosonic or fermionic nature of the gas. The momentum distributions have been calculated in Chp. 25.2.11. We have already emphasized that Bragg interferometry can be used to measure the momentum distribution of a gas via RIR spectroscopy, whether the gas is condensed or thermal. Now, let us discuss Bragg interferometry on a thermal gas, based on the articles [398] and [147].

\[ \Delta \omega \]

\[ \Delta L \]

\[ 2q \]

\[ k_z \]

\[ \Delta \omega \]

\[ \Delta L \]

\[ 2q \]

\[ k_z \]

Figure 28.6: Illustration of a Raman transition between two points of the free-particle dispersion curve, when the atoms are initially thermally distributed.

As illustrated in Fig. 28.6, for \( T \gg T_{\text{rec}} \) the atomic cloud occupies many momentum states, such that the Bragg scattering produces a RIR-like signal, that is, the scattering probability is proportional to the population difference of the initial and final momentum states, as discussed in Sec. 22.4.1. The number of scattered atoms/photons is, therefore,

\[ \dot{N}_{\text{brg}} \propto \Omega_{\text{ram}} \frac{\partial \tilde{n}(k_z)}{\partial k_z} \bigg|_{k_z=\hbar m \Delta \nu / q} . \]  

(28.58)

with \( \Omega_{\text{ram}} = \Omega_1 \Omega_2 / 2 \Delta L \). For \( T \ll T_r \), when the atomic cloud occupies only a single momentum state,

\[ \dot{N}_{\text{brg}} \propto \Omega_{\text{ram}} \tilde{n}(k_z) . \]  

(28.59)

The transition rate per atom is given by [569],

\[ \frac{W}{N} = \frac{2\pi \hbar}{\Omega_{\text{ram}}^2} \sum_f |\langle f | \hat{\rho}^\dagger(k) | g \rangle|^2 \delta(\hbar \nu - E_f + E_g) \equiv 2\pi \Omega_{\text{ram}}^2 S(k, \nu) . \]  

(28.60)

To scatter an atom with the initial wavevector \( k_z \) to the next higher momentum state \( k_z + 2q \), the Bragg condition requires,

\[ \nu_R = \nu_{R2} - \nu_{R1} = \frac{\hbar(k_z + 2q)^2}{2m} - \frac{\hbar k_z^2}{2m} = \frac{2\hbar q}{m} (k_z + q) . \]  

(28.61)

If we tune \( \omega(\pm \Delta k_z) \) until the Bragg signal \( \dot{N}_{\text{brg}} \) drops to \( e^{-1/2} \),

\[ \nu_R(\Delta k_z) - \nu_R(-\Delta k_z) = \frac{4\hbar \Delta k_z q}{m} = \frac{4\hbar q \sqrt{mk_B T}}{m} = 4q \sqrt{k_B T / m} . \]  

(28.62)

The initial distribution is \( \phi_0(k_z) = (\hbar^2 / 2\pi m k_B T)^{1/2} e^{-\hbar^2 k_z^2 / 2mk_B T} \).
### 28.2.2.1 Bragg scattering by free particles

Based on the interpretation of Bragg scattering as a Raman transition between two momentum states, we can use the same model as in Secs. 28.4 to describe the process quantitatively [58, 398, 147]. We assume that during the Bragg pulse only two discrete atomic momentum states $j = 0, 1$ are coupled, and that the impact of the trapping potential can be neglected. This is justified for Bragg pulse sequences much shorter than an oscillation period of the trap. The probability amplitudes for the two momentum states are denoted by $a_{j,k_z}$. They correspond to atoms with initial momenta $\hbar k_z$ that are coupled to states with momentum $\hbar k_z' = \hbar(k_z + 2q)$. The temporal evolution of the amplitudes under the action of the Bragg light is given by the solutions of the Schrödinger equation [398]$_{\text{DOI}}$, [147]$_{\text{DOI}}$,

\[
\begin{pmatrix}
a_{0,k_z}(t) \\
a_{1,k_z}(t)
\end{pmatrix} = e^{-i\hat{H}_\tau t/\hbar} \begin{pmatrix} a_{0,k_z}(0) \\ a_{1,k_z}(0) \end{pmatrix},
\]

with the Hamiltonian,

\[
\hat{H}_\tau = \left( \begin{array}{cc} \hbar^2 k_z^2 \frac{m}{2} & \frac{1}{2} \Omega_R \\ \frac{1}{2} \Omega_R & \hbar^2 k_z^2 - \delta \end{array} \right).
\]

When the Bragg light is switched off, the Hamiltonian simplifies to,

\[
\hat{H}_{\Delta t} = \left( \begin{array}{cc} \hbar^2 k_z^2 \frac{m}{2} & 0 \\ 0 & \hbar^2 k_z^2 - \delta \end{array} \right).
\]

Concatenating temporal evolutions described by $e^{-i\hat{H}_\tau t/\hbar}$ and $e^{-i\hat{H}_{\Delta t} t/\hbar}$, the phase evolution of individual atoms in momentum state superpositions can be calculated for arbitrary sequences of pulses separated by intervals of free evolution, for example, Ramsey-type sequences.

If the atoms initially form a thermal cloud, they will be distributed according to the Maxwell-Boltzmann distribution, such that,

\[
\phi(k_z) = \frac{1}{\sqrt{(2\pi m k_B T)}} e^{-\frac{\hbar^2 k_z^2}{2m k_B T}}.
\]
To obtain the atomic momentum distribution after the application of a pulse sequence, we calculate the evolution of the amplitudes $a_{j,k_z}$ for a variety of initial momenta and weigh the final populations of the momentum states with the distribution function $\phi(k_z)$. The number of atoms expected in the zeroth and first Bragg diffraction order is, therefore,

$$N_j(t) = \int \phi(k_z) |a_{j,k_z}(t)|^2 dk_z . \quad (28.67)$$

The procedure neglects interatomic interactions, which is always a good presumption for an ultracold Fermi gas [149].

### 28.2.2 Bragg scattering by trapped particles

When trapped atoms are considered, the problem arises that the Hilbert space of momentum states is simultaneously coupled by two interactions: a moving optical lattice (generated by the Bragg lasers) and the (harmonic) trap. However, the situation gets simpler if a separation of the scales is possible. In general, the duration of a pulse is very short, $\tau \ll 2\pi/\omega_z$. In contrast, the duration of a free evolution period $\Delta t$ (e.g. in a Ramsey cycle) may be such, that it is no more negligible compared to a trap oscillation period, so that we need to account for the action of the trapping potential explicitly.

As the trap couples the atomic momenta with the atomic positions ($E_{\text{kin}} + E_{\text{pot}} = \text{const}$), the initial spatial distribution of the atoms must now be considered. For simplicity, we describe it as a thermal Gaussian, similarly to what has been done in Eq. (28.66) for the momentum distribution,

$$\psi(z) = \left(\frac{m\omega_z^2}{2\pi k_B T}\right)^{1/2} e^{-m\omega_z^2 z^2 / 2k_B T} . \quad (28.68)$$

Beginning with the positions $z$ and initial momenta $k_z$, after a diffraction pulse transferring the recoil $2q$ to part of the atoms and being short enough not to change their positions, the atoms follow classical trajectories. The atomic momenta (now depending on time) are,

$$\tilde{k}_z(t) = k_z \cos \omega_z t - \frac{\hbar \omega_z}{m} z \sin \omega_z t , \quad (28.69)$$

$$\tilde{k}_z(t) = (k_z + 2q) \cos \omega_z t - \frac{\hbar \omega_z}{m} z \sin \omega_z t ,$$

where the first expression holds for non-diffracted atoms and the second for diffracted atoms. These momenta are substituted for $k_z$ and $k_z'$, respectively, in the Hamiltonians (28.64) and (28.65). As the Bragg pulses are short compared to the oscillation period, $\tau \ll 2\pi/\omega_z$, the effect of the trapping potential may be neglected during Bragg scattering. This means that the Hamiltonian $\tilde{H}_\tau$ depends on $\tilde{k}_z(t)$, but can be treated as time-independent for the short intervals $\tau$. In contrast, the Hamiltonian for free propagation $\tilde{H}_{\Delta t}$ depends on the time, if $\Delta t$ is long. In this case, the phase evolution of the atoms in both coupled states can be described by the time evolution operator as,

$$e^{-i\tilde{H}_{\Delta t} t/\hbar} = \begin{pmatrix} \exp \left(-i \int_0^t dt \frac{\hbar}{2m} \tilde{k}_z(t) \right) & 0 \\ 0 & \exp \left(-i \int_0^t dt \frac{\hbar}{2m} \tilde{k}_z(t) - \delta \right) \end{pmatrix} . \quad (28.70)$$
Since the amplitudes $a_{j,z,k_z}$ now also depend on the initial atomic positions, the final populations of the momentum states must be additionally weighted with the initial spatial distribution. Therefore, the Eq. (28.67) for the expected numbers of diffracted and non-diffracted atoms must be replaced by,

$$N_j(t) = \int \int \phi(k_z)\psi(z) |a_{j,z,k_z}(t)|^2 dk_z dz .$$

(28.71)

### 28.2.2.3 Bloch equations approach

Experimentally, we observe decoherence of the dynamics described above on a very slow time scale. This phenomenon can be included in a description based on Bloch equations,

$$\frac{d}{dt} \tilde{\rho}_{k_z}(\tau) = M_j \tilde{\rho}_{k_z}(\tau) ,$$

(28.72)

with

$$\tilde{\rho}_{k_z}(\tau) = \begin{pmatrix} \rho_{00,k_z}(\tau) \\ \rho_{01,k_z}(\tau) \\ \rho_{10,k_z}(\tau) \\ \rho_{11,k_z}(\tau) \end{pmatrix}$$

and

$$M_j = \begin{pmatrix} 0 & \Gamma & \frac{i}{2} \Omega_{ram} & -\frac{i}{2} \Omega_{ram} \\ 0 & -\Gamma & -\frac{i}{2} \Omega_{ram} & \frac{i}{2} \Omega_{ram} \\ \frac{i}{2} \Omega_{ram} & -\frac{i}{2} \Omega_{ram} & -\gamma - i \Delta_j & 0 \\ -\frac{i}{2} \Omega_{ram} & \frac{i}{2} \Omega_{ram} & 0 & -\gamma + i \Delta_j \end{pmatrix}$$

(28.73)

with the solution,

$$\tilde{\rho}_{k_z}(\tau) = e^{M_{3t}} e^{M_{2t}} e^{M_{1t}} \tilde{\rho}_{k_z}(0) .$$

(28.74)

with,

$$\Delta_1 = \frac{\hbar}{2m} (k_z + 2q)^2 - \Delta \nu - \frac{\hbar}{2m} k_z^2$$

(28.75)

$$\Delta_3 = \frac{\hbar}{2m} [((k_z + 2q) \cos \omega_{tr} \tau]^2 - \frac{\hbar}{2m} [(k_z + 2q) \cos \omega_{tr} \tau - 2q]^2 - \Delta \nu .$$

We weigh populations with the initial momentum distribution,

$$N_i(\tau) \equiv \int \phi_i(k_z) \rho_{ii,k_z}(\tau) dk_z .$$

(28.76)

### 28.2.3 Kapitza-Dirac scattering

An atomic beam with longitudinal de Broglie wavelength $\lambda_{dB} = \hbar/p$ diffracted by a solid periodic grating with a slit distance of $d$ receives a transverse amplitude modulation. In the far field, this generates focuses at angles defined by $n \lambda_{dB}/d = \sin \vartheta$. Alternatively, the grating may consist of a standing light wave detuned from resonances. The standing wave will create a periodic optical potential, which imprints a transverse phase modulation on the atomic beam. In the far field, the result will be the same as for the solid grating. Each atom will evolve into a superposition of momentum sidemodes $\pm n 2\hbar k$, without any momentum having been transferred to the atoms. The diffraction angle is again $\sin \vartheta = \pm n 2\hbar k / p = \pm n \lambda_{dB} / (\lambda/2)$, where $\lambda/2 = d$ is the periodicity of the standing light wave. However, this is only true if the phase shift is much smaller than $\pi$. This scheme is called the Raman-Nath regime.
or the regime of Kapitza-Dirac scattering. An equivalent condition for this regime is, that the interaction time is less than a period of oscillation in the optical potential, $\tau \ll \sqrt{\hbar/\omega_{\text{rec}}/U}$, or $v_{\text{trans}} \tau \ll \lambda$.

The Raman-Nath regime is realized by a very focused optical standing wave. A wave that is not plane can be considered a superposition of many spatial modes. Since (off-resonant) scattering (absorption followed by induced emission) corresponds to a photon redistribution between spatial modes, in a tight waist the phase matching condition is somewhat relaxed and minor corrections to the energy balance are possible. In a certain sense, Kapitza-Dirac scattering is the inverse process of 'forward scattering' of a laser beam passing through an atomic cloud: the roles of light and atoms are exchanged. The requirement that the interaction time be short implies, that the light grating is 'optically dilute' for the atomic beam.

### 28.2.4 Bragg spectroscopy of a condensate

To measure the Bogolubov spectrum, we need to excite perturbations in a condensate and study its reaction [569].

Let us now imagine that the potential has the form of a standing wave. Technically this can be done by two laser beams having the same frequency crossing at the position of the atoms,

$$V_{\text{trap}}(r,t) \equiv V e^{i q_1 \cdot r - i \omega t} + \frac{\sqrt{V}}{2} e^{i q_2 \cdot r - i \omega t} .$$

(28.77)

Choosing the coordinate system such that, $q_1 \equiv (k_x, 0, k_z)$ and $q_1 \equiv (k_x, 0, -k_z)$,

$$V_{\text{trap}}(r,t) \equiv \frac{V}{2} e^{i k_x z - i \omega t} + \frac{\sqrt{V}}{2} e^{-i k_x z + i \omega t} ,$$

(28.78)

with $V_x \equiv V e^{i k_x x}$. With this weak perturbation applied to the atoms, we make the ansatz,

$$\psi(r,t) = e^{-i \mu t/\hbar} \left( \psi_0(r,t) + u(t)e^{i k_x z - i \omega t} - v(t)e^{-i k_x z + i \omega t} \right) ,$$

(28.79)

where the amplitudes of the perturbation, $u(t)$ and $v(t)$, only vary slowly in time. Assuming that $\psi_0$ is fairly homogeneous, i.e. $\langle \psi_0 | \nabla_z | \psi_0 \rangle \simeq 0$, the momentum transferred to the BEC is,

$$\langle \psi(r,t) | -i \hbar \nabla_z | \psi(r,t) \rangle = \hbar k_x (|u|^2 - |v|^2) .$$

(28.80)

We can now solve the Gross-Pitaevskii equation (26.20) in the same way as in Sec. 26.4.1 inserting the ansatz (28.79). The terms proportional to $e^{i k_x z - i \omega t}$ are,

$$\frac{\hbar^2 k_x^2}{2m} u + \frac{V}{2} \psi_0 + g (|\psi_0|^2 + |u|^2 + |v|^2) u + g\psi_0^2 v + g|\psi_0|^2 u = \left( i \hbar \frac{\partial}{\partial t} + \hbar \omega + \mu \right) u ,$$

(28.81)

and the analogously for $e^{-i k_x z + i \omega t}$. Using $\mu = gn = g|\psi_0|^2$ and assuming that the perturbation is weak, $|u|, |v| \ll |\psi_0|$, we obtain,

$$\left( \frac{\hbar^2 k_x^2}{2m} + gn \right) u + \frac{V}{2} \psi_0 - gnu = \left( i \hbar \frac{\partial}{\partial t} + \hbar \omega \right) u$$

(28.82)

and

$$\left( \frac{\hbar^2 k_x^2}{2m} + gn \right) v - \frac{V}{2} \psi_0 + gn v = \left( -i \hbar \frac{\partial}{\partial t} + \hbar \omega \right) v .$$

---

11Note, that we usually employ the term of optical diluteness the other way round, i.e. an atomic cloud can be optically dilute (or dense) for a laser beam.
This effect is called \textit{Bragg diffraction} of atoms by a standing light wave.

\[ \Delta \varepsilon / \hbar \ (\text{kHz}) \]

\[ gn_0 / \hbar \ (\text{kHz}) \]

\[ 6402 \]

\[ n_0 \ (\text{cm}^{-3}) \]

\[ 6 \]

\[ S(q) \]

\[ 0 \]

\[ 0.5 \]

\[ 1 \]

\[ 6 \]

\[ 8 \]

\[ \Delta \varepsilon / \hbar (\text{kHz}) \]

\[ gn_0 / \hbar (\text{kHz}) \]

\[ 6402 \]

\[ 4 \]

\[ 0 \]

\[ 2 \]

\[ 4 \]

\[ n_0 (\text{cm}^{-3}) \]

\[ 6 \]

\[ 8 \]

\[ \Delta \varepsilon / \hbar (\text{kHz}) \]

\[ gn_0 / \hbar (\text{kHz}) \]

\[ 6402 \]

\[ 4 \]

\[ 0 \]

\[ 2 \]

\[ 4 \]

\[ n_0 (\text{cm}^{-3}) \]

\[ 6 \]

\[ 8 \]

\[ \Delta \varepsilon / \hbar (\text{kHz}) \]

\[ gn_0 / \hbar (\text{kHz}) \]

\[ 6402 \]

\[ 4 \]

\[ 0 \]

\[ 2 \]

\[ 4 \]

\[ n_0 (\text{cm}^{-3}) \]

\[ 6 \]

\[ 8 \]

Figure 28.8: Spectrum of elementary excitations.

Figure 28.9: Spectrum of elementary excitations.

Using \( \mathcal{L} = \frac{\hbar^2 k^2}{2m} + V_{\text{trap}} + 2gn - \mu - i\hbar \frac{\partial}{\partial t} \), we can write,

\[
\begin{pmatrix}
\mathcal{L} - \hbar \omega_k & -gn \\
-gn & \mathcal{L} + \hbar \omega_k
\end{pmatrix}
\begin{pmatrix}
u \\
u^*
\end{pmatrix} = 0 .
\] (28.83)

These equations can be decoupled using the Bogolubov transform.

We calculate the momentum transferred to the BEC, assuming \( \psi_0 \) to be fairly homogeneous,

\[
\langle \psi(\mathbf{r}, t) | - i\hbar \nabla | \psi(\mathbf{r}, t) \rangle = \hbar \mathbf{q} (|u|^2 - |v|^2) .
\] (28.84)

28.2.5 Exercises

28.2.5.1 Ex: Bragg diffraction of fermionic clouds

List of programs on Bragg diffraction of fermionic clouds.
28.3 Matter wave superradiance

28.3.1 Classical superradiance

The Bragg beam splitter introduced in the last section does not give rise to collective scattering, even when the atoms are as strongly correlated as in a condensate. On the other hand, collective scattering is known to occur in a classical gas: When two atoms excited to an internal energy level, \( \sim \frac{hc}{\lambda} \), are separated by a distance \( R \) too large to form a molecule, but smaller than the wavelength of the excited transition, \( a_B \ll R \ll \lambda \), the atoms are coupled to the electromagnetic continuum by the same radiation that they emit (see Fig. 28.10). The dipole moments of the atoms stimulate each other to emit, and we observe a synchronized and accelerated relaxation, resulting in a coherent and directional burst of radiation [162, 498]. The directionality of the radiation is due to a destructive interference of the dipolar radiation patterns emitted by the atoms in all directions except the direction chosen by the first emitted photon. This direction is random (except when bosonically stimulated). The atomic sample evolves, during this time, to a state of coherent superposition, until all the atoms are deexcited. This phenomenon is called \textit{Dicke superradiance}. A similar effect exists for matter waves, and will be discussed in the following sections [304].

![Figure 28.10: Superradiance assumes small interatomic distances compared to the wavelength of the excited dipole. Toroidal interference patterns interfering constructively in only one direction.](image)

28.3.2 Matter wave superradiance & CARL

We consider the process of Rayleigh scattering from a condensate. The scattering rate obviously depends on the number of atoms and the laser intensity. The crucial point now is, that this rate can be stimulated by populations in the output modes, that is, the modes of scattered light and the atomic recoil modes. Matter and light participate in the scattering process as equal partners. In Sec. 28.2.1 we showed that Bragg scattering can be interpreted as \textit{optical stimulation of matter wave scattering}. By analogy, it is possible to imagine a process of \textit{wave matter stimulation of light scattering}. We will now discuss such a process, called \textit{superradiant Rayleigh scattering} or \textit{matter wave superradiance} (MWSR) [304], with the help of the small cartoon shown in Fig. 28.11. See also (watch talk).

Let us imagine an elongated condensate, subject to a magnetic field directed along its long axis and illuminated perpendicularly to the long axis by a linearly polarized laser beam. The scattered light is emitted into a (toroidal) dipolar radiation pattern. The fraction of the light scattered into the solid angle \( \Omega_j \), which is inclined by angle \( \vartheta_j \) with respect to the polarization of the incident laser is \( \Omega_j \sin^2 \vartheta_j/(8\pi/3) \). Of course,
the number of scattered photons also depends on the optical cross section $\sigma$ and the number of scattering atoms $N_0$. When an atom, recoiling due to the transfer of one unit of photonic momentum, moves with a speed of a few centimeters per second through the condensate, it interferes with other atoms of the condensate, thus forming a wave matter grating. The grating, the lifetime of which is long in comparison to the scattering rate, now stimulates subsequent photons to follow the same path $\Omega_j$ and receives, in turn, the scattering atoms. In other words, the bosonic stimulation of the scattering process by the $N_j$ atoms already populating the recoil mode amplifies the photon scattering rate by a factor of $N_j + 1$. The differential optical cross section (power $P_j$ scattered into the direction $\Omega_j$ divided by the laser intensity $I$) is \[ \frac{d\sigma}{d\Omega_j} = \frac{P_j}{I} = \frac{\Omega_j \sin^2 \vartheta_j}{8\pi/3} \frac{\sigma N_0(N_j + 1)}{N_0}. \] (28.85)

Each scattering event of a photon into the mode $\Omega_j$ transfers an atom to the recoil mode $N_j$:

\[ \dot{N}_j = \frac{P_j}{\hbar \omega} \equiv G_j N_j \quad \text{where} \quad G_j = \frac{I}{\hbar \omega} \frac{\Omega_j \sin^2 \vartheta_j}{8\pi/3} N_0. \] (28.86)

The phase matching condition is satisfied for a solid angle of approximately $\Omega_j = \lambda^2/A_j$, where $A_j$ is the cross-sectional area of the condensate. If $l_j$ is the length of condensate, we can write,

\[ G_j = \frac{I}{\hbar \omega} \frac{\sin^2 \vartheta_j}{8\pi/3} n_0 \lambda^2 l_j. \] (28.87)

With the atomic density $n_0 = N_0/(A_j l_j)$, the factor $n_0 \lambda^2 l_j$ describes the optical density of the BEC in the direction of the scattering. Therefore, we obtain exponential gain for the atom number $N_j$, that is, the process is self-amplifying.

Using the terms of the dressed atom picture, we would say that the excited state of our system is formed by the BEC and the laser mode. This state relaxes to a state formed by the recoiled atoms and the scattered photons. The exponential gain occurs, when this system exhibits inversion. The inversion is maintained, until the BEC is completely transferred to the momentum recoil modes \(^{12}\).

\(^{12}\)Superradiant scattering is due to a nonlinear coupling between two matter waves and two optical waves in a four-wave mixing process (4WM) interpreted as scattering of light from a wave matter stimulated by a wave matter mode. The process does not require nonlinearity due to collisions, but it works with an ideal gas, $g \rightarrow 0$. This distinguishes it from the 4WM of four matter waves, studied in Sec. 27.3.4 and interpreted as a scattering of atoms by a matter wave stimulated by matter wave mode, and 4WM in quantum optics involving four photons. But in all cases bosonic stimulation is crucial.
It is instructive to compare Dicke superradiance and matter wave superradiance. Dicke superradiance is induced by an electronic coherence between adjacent atoms. It requires a sufficiently long coherence time for the atomic dipoles. On the other hand, MWSR is a coherence effect between two states of the atomic center-of-mass motion, i.e. the condensed state and a momentum sidemode. A long lifetime of this coherence is necessary to allow for correlations between successive scattering events. The coherence lifetime corresponds to a coherence length, which for a condensate is equal to its physical size, whereas for a thermal cloud, it only corresponds to its thermal Broglie wavelength. This explains why it is difficult to observe MWSR with non-condensed atomic clouds.

Since the scattered photons quickly leave the BEC, there is no feedback or bosonic stimulation by the optical output mode. This can be interpreted as a fast decaying cavity mode, and the regime is called the bad cavity limit. Let us now imagine, that the photons were recycled, for example, via an optical cavity constructed around the BEC and reflecting back the photons emitted in the solid angle $\Omega_j$. The mirrors of the cavity create reflection images of the radiating atoms, which increase the density of states, the scattering rate, and the gain $G_j$ increase by a factor of $8F/\pi$. An interesting question now is, what happens in the limit $F \to \infty$. If the decay of the cavity mode, and therefore the removal of photons from the coherent interaction zone (which is precisely the volume occupied by the BEC) is slow, the MWSR process seems to be doubly stimulated, optically and atomically. However, in this case we also expect the inverse process, where photons are scattered back to the original mode, to occur and to be stimulated by the number of atoms $N_0$ in the condensate. We see that the simple picture of bosonic stimulation does not work in this case, and a more complete model including the possibility of Rabi oscillations amplified by stimulated emission is necessary.

---

13 Alternatively, we may imagine a scheme decelerating of the group velocity of the light pulse.

14 The phenomenon of the matter wave superradiance can be understood without quantization of the atomic motion \[?] and, in particular, without quantum degeneracy. A cold and dense thermal cloud can show the phenomenon of MWSR \[651\]. The scattered light forms together with the pump light, a propagating standing light wave, from which the atoms are scattered by Bragg diffraction. Atoms are accelerated by the CARL effect \[127, 72, 370, 432, 431, 358, 306, 305\] through a coherent redistribution of photons between the pump and scattered modes. However, as was shown later-on, the different recoil modes of the condensate exhibit phase-coherence, which is not explained by a theories treating the atomic motion semi-classically.
28.3.3 Amplification of matter and light waves

The feedback-induced exponential gain giving rise to the phenomenon of MWSR can be used to construct a phase-coherent amplifier of matter and light waves. After all, the momentum side modes observed in the MWSR process [304] already represent amplified vacuum fluctuations. To experimentally realize a coherent matter wave amplifier [358, 306], it is sufficient to replace the vacuum fluctuations of the original MWSR experiment with a small seed condensate: \( \sim 0.1\% \) of the ‘mother condensate’ proved sufficient to stimulate the matter wave amplifier. The seed condensate was created by Bragg diffraction transferring atoms from the mother BEC to another momentum state (see Sec. 28.2). The matter wave grating formed by interference of the seed condensate and the mother BEC was subsequently amplified by a MWSR pulse. The gain for the atom number in the seed condensate was 10 to 100 depending on the intensity and duration of the MWSR pulse. Finally, the coherence of the amplification process was demonstrated by active atom interferometry using the Ramsey scheme: One of the interferometer arms consisted of the amplified seed condensate and the other of a reference condensate (local oscillator) especially created by Bragg diffraction from the mother condensate. The observation of interference between these two matter waves proved the coherence of the amplification process and the existence of a well-defined phase relationship between the input and the output of the matter wave amplifier.

![Figure 28.13: Matter wave amplification of a ‘seed condensate’ at the expense of a ‘mother condensate’. Time-of-flight imaging visualizes the condensate’s momentum distribution.](image)

In analogy to electronics, we may consider the coherent matter wave amplifier as an active device complementing the atom optical toolbox of passive devices (see Sec. 27.3.1).

28.3.4 Four-wave mixing of optical and matter waves

We will now make an attempt to categorize the various scattering processes involving condensates. Let us first return to the radiation pressure [Fig. 28.14(a)], where an incident photon is spontaneously scattered into a random direction. The isotropy of the scattering process can, however, be broken when certain directions (i.e. spatial modes) are favored by bosonic stimulation. The symmetry of the roles of matter wave modes and light modes allows us to treat both on the same footing, for example, we can stimulate scattered modes either by matter of light waves.

Let us first have a look at stimulation by optical modes [Fig. 28.14(b) and (c)]. Fig. (b) describes optical four-wave mixing (4WM) in nonlinear optical media, i.e. optically stimulated scattering of photons from a standing light wave, which is a 4WM
process of 4 photons. Fig. (c) describes Bragg scattering, i.e. an optically stimulated scattering of atoms by a standing light wave, which is a 4WM process of 2 photons and 2 atoms.

Similarly, a scattering process can also be stimulated by a macroscopic number of atoms in a recoil mode [Fig. 28.14(d) and (f)]. Fig. (d) describes superradiant Rayleigh scattering and matter wave amplification, i.e. scattering of photons stimulated by a de Broglie wave, which again corresponds to 4WM of 2 photons and two atoms. Fig. (e) describes amplification of a laser pulse by superradiant Rayleigh scattering, i.e. scattering of photons in a matter wave with double stimulation by light waves and de Broglie waves, which once again is a 4WM process of 2 photons and 2 atoms. Finally, Fig. (f) describes the basic process of nonlinear atom optics, i.e. the scattering of atoms by a matter wave stimulated by de Broglie waves, which is a 4WM process of 4 atoms.

![Figure 28.14](image-url)

**Figure 28.14**: Schematic comparison of 4WM processes between light and matter wave modes. (a) Spontaneous emission, (b) classical 4WM of light modes, (c) Bragg scattering, (d) superradiant Rayleigh scattering, respectively, matter wave amplification, (e) optical amplification, and (f) 4WM of matter waves.

### 28.4 Condensates in electronically excited states

The interaction between condensates and light has, so far, been treated in the limit where the population of excited states can be neglected or adiabatically eliminated. An example was the coherent coupling of different kinetic states of an atom by a method called Bragg diffraction discussed in Sec. 28.2.

On the other hand, atoms can have metastable excited states, which can introduce new degrees of freedom, and a whole world of new problems emerges that need to be addressed: How do condensed atoms move, when they are in different states of internal excitation (or superposition of states), and how do atoms in different states interact with each other? We will now turn our attention to coherent coupling of internal states \(^15\).

---

\(^15\)We will disregard, for the moment, possible effects due to inhomogeneous broadening caused by the finite volume of the cloud inside the potential (Zeeman shift in magnetic traps or dynamic Stark
In Sec. 28.4.1 we will show how to generalize the second-quantized formalism introduced in 26.2.1 in order to deal with coupled condensates in different states of internal excitation.

In Sec. 28.4.2 we will discuss examples of how coherent coupling of two states can be accomplished either by radiofrequency/microwave radiation or by two laser beams in Raman configuration. In order to avoid spontaneous relaxation, we often choose state with low excitation energy, for example, within the hyperfine structure $\hat{H} \sim \mathbf{I} \cdot \mathbf{J}$ or the Zeeman structure $\hat{H} \sim \mu \cdot \mathbf{B}$ of the electronic ground state. But one can also consider the coupling between different kinetic states of free atoms $\hat{H} \sim \mathbf{p}^2/2m$, or the output coupling of atoms confined to a trapping potential $\hat{H} \sim m^2 \omega^2 \mathbf{r}^2$, or even a chemical coupling between a vibrational state of two atoms bound together to form a molecular and a state, where the same two atoms are free and involved in an elastic collision.

Finally, in Sec. 28.4.3 we will show how to harness the forces induced by atom-light coupling in order to design new geometries of trapping potentials.

28.4.1 Theory of the interaction of condensates with light

Let us consider two Bose-Einstein condensates in the mean-field approximation consistent of atoms in two different internal excitation states, $\psi_1$ and $\psi_2$, separated by the energy $\hbar \omega_0$. We illuminate the BEC by a plane wave of monochromatic light with the frequency $\omega$. The formal procedure consists of constructing the Hamiltonian of individual atoms, as done in Eq. (16.2), and then quantizing the field of matter [475],

$$\hat{H}_{atom} = |1\rangle \langle 1| (\hat{H}_{cm}^{(1)} + \hbar \omega_0) + |2\rangle \langle 2| (\hat{H}_{cm}^{(2)} + \hbar \omega_0),$$

where we allow for the fact that the trapping potentials can be different for the two excitation states. We assume that atoms in different states of excitation are distinguishable, such that their respective wavefunctions commute:

$$[\hat{\psi}_j, \hat{\psi}_j'] = \delta_{jj'} \delta(\mathbf{r} - \mathbf{r}').$$

However, we need to consider interatomic collisions which, in the mean-field approximation (26.19) are described by,

$$\hat{H}_{mf}^{(j)} = \int \hat{\psi}_j^\dagger (\mathbf{r}) \frac{2\pi \hbar^2 a_s}{m} \hat{\psi}_j (\mathbf{r}) d^3 r.$$

The total atomic Hamiltonian is then a generalization of the many-body Hamiltonian (26.6),

$$\hat{H}_{atom} = \int \hat{\psi}_1^\dagger (\mathbf{r}) \left( \hat{H}_{cm}^{(1)} + \hat{H}_{mf}^{(1)} \right) \hat{\psi}_1 (\mathbf{r}) d^3 r + \int \hat{\psi}_2^\dagger (\mathbf{r}) \left( \hat{H}_{cm}^{(2)} + \hat{H}_{mf}^{(2)} + \hbar \omega_0 \right) \hat{\psi}_2 (\mathbf{r}) d^3 r.$$

shift optical traps) or effects due to interatomic interactions. But we have to keep in mind, that interatomic interaction can have a big impact on the dynamics, because the chemical potential of each condensate depends on its number of atoms. Thus, in view of the inhomogeneity of the trapping potential, the transfer of atoms can excite oscillations and sound waves in the condensates.
28.4. CONDENSATES IN ELECTRONICALLY EXCITED STATES

28.4.1.1 Interaction with a single light mode

The normalized annihilation operator for a photon in mode $k$ is,

$$\tilde{E}^+(\mathbf{r}) = \sqrt{\frac{\hbar \omega}{2 \varepsilon_0 V}} \epsilon_0 \mathbf{e}_a \mathbf{e}_k \cdot \mathbf{r}.$$  \hfill (28.92)

The semi-classical Hamiltonian (the light not being quantized) of individual particles is, in the rotating wave approximation,

$$\hat{H}_{field} = \hbar \omega \hat{a}^+ \hat{a} \quad \text{and} \quad \hat{H}_{int} = -\mathbf{d} \cdot \tilde{E} = -|2\rangle \hat{a}^+ \langle 1| - |1\rangle \hat{a}^- \langle 2|.$$  \hfill (28.93)

For a condensate we still need to second-quantize the interaction part of the Hamiltonian which, disregarding collisions gives $^{16}$,

$$\mathcal{H} = \hat{H}_{field} + \mathcal{H}_{atom} - \int \left( \hat{a}^+ \cdot \tilde{E}^+ \hat{\psi}_2^+(\mathbf{r}) \hat{\psi}_1(\mathbf{r}) + \hat{a}^- \cdot \tilde{E}^- \hat{\psi}_1^+(\mathbf{r}) \hat{\psi}_2(\mathbf{r}) \right) d^3r.$$  \hfill (28.94)

With the Hamiltonian (28.94) we derive the Heisenberg equations for the condensate respecting the commutation rules (28.89) $^{17}$,

\begin{align*}
\dot{\hat{\psi}}_2 &= -\frac{i}{\hbar} (\hat{H}_{cm} + \hbar \omega_0) \hat{\psi}_2 + \frac{i}{\hbar} \hat{a}^+ \cdot \tilde{E}^+ \hat{\psi}_1 \\
\dot{\hat{\psi}}_1 &= -\frac{i}{\hbar} \hat{H}_{cm} \hat{\psi}_1 + \frac{i}{\hbar} \hat{a}^- \cdot \tilde{E}^- \hat{\psi}_2.
\end{align*}

We transform to the non-rotating coordinate system by $\tilde{\psi}_2 \equiv \psi_2 e^{i\omega t}$ and $\tilde{\mathcal{E}}^+ \equiv \mathcal{E}^+ e^{i\omega t}$ introducing the detuning $\Delta \equiv \omega - \omega_0$:

$$\partial_t \tilde{\psi}_2 = i(\Delta - \frac{1}{\hbar} \hat{H}_{cm}) \tilde{\psi}_2 + \frac{i}{\hbar} \hat{a}^+ \cdot \tilde{E}^+ \tilde{\psi}_1.$$  \hfill (28.95)

Making the adiabatic approximation $\partial_t \tilde{\psi}_2 = 0$ and disregarding the external degree of freedom, $\hat{H}_{cm} = 0$, we obtain,

$$\tilde{\psi}_2 = \frac{\hat{a}^+ \cdot \tilde{E}^+}{\hbar \Delta} \tilde{\psi}_1.$$ \hfill (28.97)

28.4.1.2 Heisenberg equation for the light field

Similarly, we can write the Heisenberg equation for the light mode,

$$\frac{d\hat{a}}{dt} = \frac{i}{\hbar} [\mathcal{H}, \hat{a}] = -\omega \hat{a} + i \sqrt{\frac{\omega}{2 \varepsilon_0 V}} \int \hat{E} e^{-i\mathbf{k} \cdot \mathbf{r}} \left( \hat{a}^+ \hat{\psi}_2^+(\mathbf{r}) + \hat{a}^+ \hat{\psi}_1^+(\mathbf{r}) \hat{\psi}_2(\mathbf{r}) \right) d^3r.$$ \hfill (28.98)

The integration of this gives the distribution of the fields (incident and scattered), such that,

$$\tilde{E}^+(\mathbf{r}) = \tilde{E}^+_{inc}(\mathbf{r}) + \int K(\mathbf{d}, \mathbf{r} - \mathbf{r}') \hat{\psi}_1^+(\mathbf{r}') \hat{\psi}_1(\mathbf{r}) d^3r',$$ \hfill (28.99)

$^{16}$Or, by defining the Rabi frequency $g_1$ generated by a single photon, $\mathcal{H}_{int} = -\hbar g_1 \hat{a} \int d^3r \hat{\psi}_2^+(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} \hat{\psi}_1(\mathbf{r}) + h.c.$

$^{17}$In the first quantization, these equations would simply be the equations of motion for the amplitudes of the fundamental and excited states.
with the kernel:

\[
K(d, r) = \frac{1}{4\pi \varepsilon_0} \left[ k^2 (\mathbf{R} \times d) \times \frac{R e^{ikR}}{R} + [3\mathbf{R} (\mathbf{R} \cdot d - d)] \left( \frac{1}{R^3} - \frac{ik}{R^2} \right) e^{ikR} \right].
\]  

(28.100)

We focus on the first term dominating in the far-field, and neglect the second term by letting \( \mathbf{R} \approx r - \mathbf{\hat{e}}_R \cdot \mathbf{r}' \) and \( \mathbf{\hat{R}} \approx r \). We also define \( k_s \equiv k\mathbf{\hat{e}}_R \), and we only retain the term of order \( 1/R \). In this Born approximation for optically thin media, we obtain,

\[
K(d, r) \approx \frac{1}{4\pi \varepsilon_0} \frac{e^{ikR}}{r} k^2 (r \times r) \times d e^{-ik_s r'}.
\]  

(28.101)

![Figure 28.15: Scheme for the light scattering off a condensate.](image)

### 28.4.1.3 Incident plane waves

When we now excite the condensate by a plane wave,

\[
\tilde{\mathbf{\tilde{E}}}^+(r) = \frac{1}{2} \mathbf{\hat{e}} e^{ik_s r},
\]  

(28.102)

we derive in the Born approximation of the equation (28.99):

\[
\tilde{\mathbf{\tilde{E}}}^+(r) = \frac{1}{4\pi \varepsilon_0} \frac{e^{ikR}}{r} k^2 (r \times \mathbf{\hat{d}}) \int e^{-ik_s r'} \psi_1^+(r') \psi_2(r') d^3 r',
\]  

and from this the fluorescence spectrum.

### 28.4.2 STIRAP & adiabatic sweep

A frequent problem for experimenters is the need to transfer a magnetically trapped atomic cloud from one Zeeman or hyperfine state to another. We will present here two techniques called STImulated Raman Adiabatic Passage and adiabatic sweep.

#### 28.4.2.1 Adiabatic sweep

To discuss the adiabatic sweep, we consider the example of a \(^{87}\)Rb cloud trapped in the state \(|F, m_F\rangle = |2, -2\rangle\). The application of resonant radiofrequency radiation to the transition \(|2, -2\rangle - |2, -1\rangle\) also couples all other \(m_F\) states and causes a diffusion of the atomic populations toward an uncontrollable mixture of states. An alternative is the application of a ramp sweeping the radiofrequency from red to blue (or vice versa).
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Such a ramp is able to transfer the entire population toward the opposite Zeeman state $|2, +2\rangle$. To see this, we solve the Schrödinger equation, $|\psi(t + dt)\rangle = e^{iH dt}|\psi(t)\rangle$, iteratively,

$$H = \begin{pmatrix}
0 & \frac{1}{2}\Omega & 0 & 0 & 0 \\
\frac{1}{2}\Omega & -\Delta & \frac{1}{2}\Omega & 0 & 0 \\
0 & \frac{1}{2}\Omega & -2\Delta & \frac{1}{2}\Omega & 0 \\
0 & 0 & \frac{1}{2}\Omega & -3\Delta & \frac{1}{2}\Omega \\
0 & 0 & 0 & \frac{1}{2}\Omega & -4\Delta
\end{pmatrix}. \quad (28.104)$$

The initial population distribution is $|\psi(t)\rangle = (1 \ 0 \ 0 \ 0 \ 0)^t$. $\Omega$ is the Rabi frequency generated by the radiofrequency, $\Delta(t)$ is the instantaneous detuning. The curves of Fig. 28.16 show the temporal evolution of populations $|\langle k|\psi(t)\rangle|^2$.

Figure 28.16: (code) Adiabatic sweep through the ground state $^{87}$Rb $F = 2$. The Rabi frequency is $\Omega = (2\pi)8$ kHz. The frequency ramp is $\Delta(t) = \frac{t}{t_m} (2\pi)50$ kHz with $t_m = 10$ ms. The red line shows the evolution of the population in the state $|2, -2\rangle$, the green line of state $|2, +2\rangle$, and the blue line is the sum of the populations of all other states.

The disadvantage of this method is that only the external (fully stretched) states $|m_F| = F$ can be interconverted.

28.4.2.2 Sweep through a dark resonance

To discuss STIRAP, let us think of how to transfer atoms from the state $|1\rangle \equiv |2, 2\rangle$ to $|2\rangle \equiv |2, 1\rangle$. The general idea consists in applying two radiation fields with Rabi frequencies $\Omega_{13}$ and $\Omega_{23}$, tuned a bit out of resonance with an intermediate state $|3\rangle$, $\Delta_{13} = \Delta_{23} \neq 0$, in a counterintuitive pulse sequence. That is, the field $\Omega_{23}$ is applied first and then adiabatically turned down, while the field $\Omega_{13}$ is ramped up. This method is capable of transferring all atoms.

Considering the example of the preceding section, we will discuss here another option (see Fig. 28.17). We consider continuous microwave fields with fixed tunings $\Delta_{13}$ to the red of the state $|3\rangle \equiv |1, 1\rangle$ state. Now, we apply a ramp to the second microwave field $\Delta_{23}$, such that the two radiation fields, at some point, cross the Raman resonance, for example,

$$\nu_{mw1} = \nu_{hf} + 3\nu_{zm} + \Delta_{13} \quad \text{and} \quad \nu_{mw2}(t) = \nu_{hf} + 2\nu_{zm} + \Delta_{23}(t). \quad (28.105)$$

The evolution of the populations can be simulated by iterative solution of the Schrödinger
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Figure 28.17: STIRAP.

The initial population distribution is $|\psi(t)\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$. The curves of Fig. 28.18 show the temporal evolution of the populations $|\langle k|\psi(t)\rangle|^2$.

Figure 28.18: (code) STIRAP ramp through a dark resonance. Here, the Rabi frequencies are $\Omega_{13} = \Omega_{23} = 2\pi 10 \text{ kHz}$. The frequency of the first microwave is $\Delta_{13} = (2\pi)10 \text{ kHz}$ and the frequency ramp of the second microwave is given by $\Delta_{23}(t) = \frac{2t-t_m}{t_m} (2\pi)100 \text{ kHz}$, where $t_m = 10 \text{ ms}$.

28.4.3 Condensate in adiabatic potentials

Adiabatic potentials have already been introduced in Secs. 16.1.3 and 24.4.3. Here, we will focus on the dynamics of condensed atoms in different states of electronic excitation, when these states are subject to different potentials and radiation fields that can induce transitions between the states. In particular, we consider paramagnetic atoms in different Zeeman states placed in inhomogeneous static magnetic fields and subject to single-mode or multi-mode radiofrequency radiation fields [125]DOI. To simplify the problem, let us concentrate on two-level systems, e.g. a system with the total spin $F = \frac{1}{2}$ [656]DOI, and only consider the one-dimensional case.
28.4.3.1 Coupled Gross-Pitaevskii equations

For a single atom the Hamiltonian is the one given in (16.12),
\[ \hat{H}(\mathbf{r}) = |1\rangle \left( \frac{1}{2} \mu_B g_F B(\mathbf{r}) - \frac{i}{2} \hbar \omega \right) \langle 1 | + |2 \rangle \left( -\frac{1}{2} \mu_B g_F B(\mathbf{r}) + \frac{i}{2} \hbar \omega \right) \langle 2 | + |1\rangle \frac{1}{2} \hbar \Omega (2 | + |2) \frac{1}{2} \hbar \Omega \langle 1 | . \]  
(28.107)

With the definition,
\[ \hat{\psi}_k(\mathbf{r}) \equiv \langle k | \hat{\psi}(\mathbf{r}) \rangle , \]  
(28.108)
and the abbreviation \( \hbar \Delta(\mathbf{r}) \equiv \mu_B g_F B(\mathbf{r}) - \hbar \omega(\mathbf{r}) \) we proceed to the second quantization via,
\[
\mathcal{H} = \sum_{k \neq m} \int d^3 r \ \hat{\psi}_k^\dagger \left[ -\frac{\hbar^2 \nabla^2}{2m} + \frac{1}{2} u_{kk} \hat{\psi}_k \hat{\psi}_k + \frac{1}{2} u_{km} \hat{\psi}_m \hat{\psi}_m \right] \hat{\psi}_k \\
+ \left[ (-1)^k \frac{\hbar}{2} \Delta(\mathbf{r}) \hat{\psi}_k \hat{\psi}_k + \frac{\hbar}{2} \Omega(\mathbf{r}) (\hat{\psi}_k \hat{\psi}_m + \hat{\psi}_m \hat{\psi}_k) \right] . \]  
(28.109)

The total energy of the system is the sum of the energies of the individual condensates (kinetic, potential, and collisional interaction) plus the interspecies collisional interaction energy. The coefficients \( u_{kl} = 4 \pi \hbar^2 a_{kl}/m \) with the scattering lengths \( a_{kl} \) govern the impact of the collisions.

The interaction with the radiofrequency field leads to Rabi oscillations with frequency \( \Omega \). \(^{18}\) The tuning of the radiofrequency depends on the position, due to the non-homogeneous Zeeman shift \( \Delta \). Also, to simplify the model, we assume \( u_{kl} = 0 \) for \( k \neq l \),
\[
\hat{H} = \sum_{k \neq m} \int d^3 r \ \hat{\psi}_k^\dagger \left[ -\frac{\hbar^2 \nabla^2}{2m} + \frac{1}{2} u_{kk} \hat{\psi}_k \hat{\psi}_k \right] \hat{\psi}_k + \left[ (-1)^k \frac{\hbar}{2} \Delta(\mathbf{r}) \hat{\psi}_k \hat{\psi}_k + \frac{\hbar}{2} \Omega(\mathbf{r}) (\hat{\psi}_k \hat{\psi}_m + \hat{\psi}_m \hat{\psi}_k) \right] . \]  
(28.110)

From the Heisenberg equations of motion for the field operators of the matter wave and the light, we obtain \([656]_{\text{DOI}},\)
\[
\dot{\hat{\psi}}_1 = -\frac{i}{\hbar} [\hat{H}, \hat{\psi}_1] = \frac{\delta \hat{H}}{\hbar \delta \psi_1^\dagger} = \left( -\frac{\hbar^2 \nabla^2}{2m} + u_{11} \hat{\psi}_1 \hat{\psi}_1 - \frac{\hbar}{2} \Delta(\mathbf{r}) \right) \hat{\psi}_1 + \frac{\hbar}{2} \Omega \hat{\psi}_2 \]  
(28.111)
\[
\dot{\hat{\psi}}_2 = -\frac{i}{\hbar} [\hat{H}, \hat{\psi}_2] = \frac{\delta \hat{H}}{\hbar \delta \psi_2^\dagger} = \left( -\frac{\hbar^2 \nabla^2}{2m} + u_{22} \hat{\psi}_2 \hat{\psi}_2 + \frac{\hbar}{2} \Delta(\mathbf{r}) \right) \hat{\psi}_2 + \frac{\hbar}{2} \Omega \hat{\psi}_1 . \]

The adiabatic potentials follow from a point-wise diagonalization of the Hamiltonian, assuming that the atomic movement evolves in sufficiently small steps.

28.4.3.2 One-dimensional case

The reduction of the dimensionality of the Gross-Pitaevskii equation is shown in Sec. ???. Applying this to our case, we consider a one-dimensional potential \( V(r) = V(z) \) and assume condensates being radially homogeneous within the radial diameter

\(^{18}\)We are neglecting the possibility, that the coupling force may, in principle, be inhomogeneous, if the orientation of the magnetic field is not uniform.
In this case, we can neglect the radial kinetic energy. As normalization then requires,
\[
\int_{-r_h}^{r_h} \int_{-r_h}^{r_h} \int_{-\infty}^{\infty} |\hat{\psi}(r)|^2 d^3r = (2r_h)^2 \int_{-\infty}^{\infty} |\hat{\psi}(z)|^2 dz = 1 ,
\]
replacing \(\hat{\psi}(r) = \frac{\hat{\phi}(z)}{2r_h}\) and \(g_{kk} = \frac{u_{kk}}{(2r_h)^2}\), the Gross-Pitaevskii equation and the normalization condition adopt a particularly simple form,
\[
\hbar \frac{\partial}{\partial t} \hat{\phi}(z) = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + V_{\text{trap}}(z) + Ng_1D|\hat{\phi}(z)|^2\right) \hat{\phi}(z) .
\]

The coupled equations are now,
\[
i \hat{\phi}_1 = \left( -\frac{\partial^2}{2m} + g_{11} \hat{\phi}_1^\dagger \hat{\phi}_1 - \frac{m}{4} \omega_z^2 z^2 - \frac{1}{2} \Delta_0 \right) \hat{\phi}_1 + \frac{1}{2} \Omega \hat{\phi}_2 \\
i \hat{\phi}_2 = \left( -\frac{\partial^2}{2m} + g_{22} \hat{\phi}_2^\dagger \hat{\phi}_2 + \frac{m}{4} \omega_z^2 z^2 + \frac{1}{2} \Delta_0 \right) \hat{\phi}_2 + \frac{1}{2} \Omega \hat{\phi}_1 .
\]

with,
\[
\int_{-\infty}^{\infty} |\hat{\phi}_1(z)|^2 + |\hat{\phi}_2(z)|^2 dz = 1 .
\]

This set of equations can be solved numerically by first identifying the ground state using the 'steepest descent' method and then propagating it in real time while slowly varying \(\Delta(r, t)\) or \(\Omega(t)\).

![Figure 28.19: (code) Two coupled condensates.](image)

### 28.4.3.3 Damping

A heuristic way of introducing damping could be as follows: We write down the condensate velocity field as,
\[
mv(r, t) = \hbar \frac{\hat{\phi}^*(r, t) \nabla \hat{\phi}(r, t) - \nabla \hat{\phi}^*(r, t) \hat{\phi}(r, t)}{2m(r, t)} ,
\]

\[\text{(28.116)}\]
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and subject it to a friction force,

\[ E_{fr} = -\gamma rv . \tag{28.117} \]

The problem with the coupled GPE approach is that in the absence of damping any even small modification of the coupling triggers collective oscillations, so that the ground state is not found. A numerical method to minimize the total energy cannot be used, because the minimum is the untrapped state, so that all atoms are lost. It seems that a master equation approach is necessary to introduce damping. An alternative (but cheap) way is the following. The coupled GPEs were written in the dressed states basis. Thus, if the Rabi frequency is strong enough to completely decouple the dressed states, the dressed states represent good quantum numbers, and the GPEs are appropriately written in a diagonal basis, i.e. the GPEs decouple on adiabatic potentials \(^{19}\),

\[ V_{ad,k}(z) = -(-1)^k \frac{1}{2} \sqrt{\hbar^2 \Omega^2 + [\mu_B g_F B(z) - \hbar \omega]^2} , \tag{28.118} \]

and we obtain,

\[ \dot{\phi}_k = \left( -\frac{\partial^2}{2m} + V_{ad,k}(z) + g_{kk} \phi_k^\dagger \phi_k \right) \phi_k . \tag{28.119} \]

28.4.3.4 Ex: Multiple BECs coupled by radiation via GPEs

Programs on multiple BECs coupled by radiation via GPEs.

28.5 Interaction between condensates and optical cavities

In 28.4.1 we have set up the many-body Hamiltonian (28.94) describing the interaction of a matter wave (treated in mean-field approximation) with an incident light field. We emphasized the role of photonic recoil in (28.119). In the following sections we aim at applying this theory to the particular case of atoms interacting with two counterpropagating modes of an optical ring cavity. The system has already been studied in Chp. 22.6.7 in the context of CARL, where the atomic motion, as well as the light fields, have mostly been treated classically.

CARL is based on a coherent redistribution of photons between the two counterpropagating modes of a moving standing light wave mediated by atoms which are located in the mode volume. Cooperative Compton scattering induces a collective atomic recoil and a self-bunching of the atoms, which results in an exponential gain for the optical mode receiving the scattered photons. The recent observation of the MWSR [304] in a BEC raises the question about an ultra-cold version of CARL [432, 280]. In MWSR the long coherence time of a BEC establishes a strong correlation between subsequent elastic Rayleigh scattering events mediated by very stable quasi-particle excitations. The feedback of these excitations on the laser creates an exponential gain for the optical mode receiving the scattered photons [305, 127, 72, 370, 432, 431, 358, 306, 305].

\(^{19}\)Gravitation can be included by \( V_{ad,k}(z) \rightarrow V_{ad,k}(z) + mgz. \)
We have discussed the classical CARL earlier in the superradiant as well as the good-cavity regime. We have also generalized the problem to the case of quantized atomic field (see Sec. 22.5) and to quantized radiation fields (see Sec. 22.6). The internal states were always adiabatically eliminated. In the following, we will fully quantize the bosonic atomic particle field.

The advantages of this second quantization is that interatomic interactions, quantum fluctuations, and decoherence of the matter wave can be taken into account. Various proposals have been made focusing on either one of the above three aspects.

The system under consideration is a BEC of two-level atoms with transition resonant frequency $\omega_0$ trapped in an external magnetic trap, located inside the mode volume of a ring cavity and interacting with its light modes. The atomic field operators obey the commutation relations,

\[
[\hat{\psi}_k(r), \hat{\psi}_m^\dagger(r')] = \delta_{km}\delta^{(3)}(r,r') \quad (28.120)
\]

\[
[\hat{\psi}_k(r), \hat{\psi}_m(r')] = 0 = [\hat{\psi}_k^\dagger(r), \hat{\psi}_m(r')] ,
\]

where $k, m = 1, 2$ label the internal state of the atoms. In general, the light field consists of only two counterpropagating monochromatic modes with Rabi frequencies $2g\hat{a}_\pm^\dagger\hat{a}_\pm$. Choosing the coordinate system properly, we can set the wavevectors of the modes as $k_+ \cdot \hat{e}_r = k_+ = -k_- \cdot \hat{e}_r$. The second-quantized Hamiltonian is a generalization of (22.4),

\[
\mathcal{H} = \mathcal{H}_{\text{atom}} + \mathcal{H}_{\text{atom-atom}} + \mathcal{H}_{\text{atom-cav}} + \hat{H}_{\text{cav}} + \hat{H}_{\text{laser-cav}} ,
\]

where,

\[
\mathcal{H}_{\text{atom}} = \int d^3r \hat{\psi}_1^\dagger(r) \left( \frac{\hat{p}^2}{2m} + V_1(r) \right) \hat{\psi}_1(r) + \int d^3r \hat{\psi}_2^\dagger(r) \left( \frac{\hat{p}^2}{2m} + V_2(r) - \Delta_a \right) \hat{\psi}_2(r) ,
\]

\[
\mathcal{H}_{\text{atom-atom}} = \sum_{i=1,2} \int d^3r \hat{\psi}_i^\dagger(r) \hat{\psi}_i^\dagger(r) \frac{u_{ii}}{2} \hat{\psi}_i(r) \hat{\psi}_i(r) + \int d^3r \hat{\psi}_i^\dagger(r) \hat{\psi}_i^\dagger(r) \frac{u_{ii}}{2} \hat{\psi}_i(r) \hat{\psi}_i(r) ,
\]

\[
\mathcal{H}_{\text{atom-cav}} = \sum_{i=\pm} g\hat{a}_\pm \int d^3r \hat{\psi}_1^\dagger(r) e^{\pm ikz} \hat{\psi}_1(r) + h.c. ,
\]

\[
\hat{H}_{\text{cav}} = -\Delta_c \hat{\psi}_1^\dagger \hat{a}_\pm ,
\]

\[
\hat{H}_{\text{laser-cav}} = -\sum_{i=\pm} m\hat{\psi}_1^\dagger (\hat{a}_\pm - \hat{a}_\pm^\dagger)
\]

with $u_{ij} = 4\pi\hbar^2 a_{s,ij}/m$.

Various approximations can be made depending on the subject of interest. For example, if only one cavity mode, $\hat{a}_\pm$, is strongly pumped, such that the field becomes intense, we may remove the term $\hat{H}_{\text{laser-cav}}$ and describe the field mode classically by a Rabi frequency $\Omega$. The interaction between the pump mode and the cavity is then, $\hat{H}_{\text{atom-pump}} = \frac{\hbar\Omega}{2} e^{-i\omega_2 t} \int d^3r \hat{\psi}_2^\dagger(r) e^{ikz} \hat{\psi}_1(r) + h.c.$.

A talk on this subject is available at (watch talk).
28.5. Interaction between condensates and optical cavities

28.5.1 Ideal gas Hamiltonian after adiabatic elimination

Assuming the light fields to be tuned far from resonance we disregard spontaneous emission, as explained in Sec. 22.1.2, and adiabatically eliminate the internal states, as shown in Sec. 22.1.3 [483, 115]. On the other hand, we treat the light field and the atomic motion in second quantization. The canonical way to describe a BEC interacting with two optical modes \( \hat{a}_\pm \) is to second-quantize the single-particle Hamiltonian (22.27),

\[
H \approx \int d^3r \hat{\psi}^\dagger(r) \left( \frac{\hat{p}^2}{2m} + V_{\text{trap}}(r) + \frac{u}{2} \hat{N}(r) \right) \hat{\psi}(r) + (\hat{N}U_0 - \Delta_c) \sum_{\pm} \hat{a}_\pm^\dagger \hat{a}_\pm \\
+ U_0 \hat{a}_+^\dagger \hat{a}_- \int d^3r \hat{\psi}^\dagger(r) e^{-2ikz} \hat{\psi}(r) + \text{h.c.} - i \sum_{\pm} \eta_{\pm} (\hat{a}_\pm - \hat{a}_\pm^\dagger) ,
\]

(28.123)

where \( \hat{\psi}(r) \) is now the ground-state wave function of the matter wave, \( u = 4\pi\hbar^2a_s/m \) in the mean field approximation and,

\[
U_0 = \frac{g^2}{\Delta_a} ,
\]

(28.124)

when the mode to mode coupling strength. This adiabatically approximated Hamiltonian looks very similar to (22.27).

28.5.2 Expansion into momentum states

It is useful to convert the Hamiltonian to momentum space via a plane wave expansion of the BEC according to (26.70),

\[
\hat{\psi}(r) = \sqrt{\frac{V}{(2\pi)^3}} \int \hat{c}_q e^{iq \cdot r} d^3q \quad \text{with} \quad [\hat{a}_q, \hat{a}_{q'}] = \delta_{q,q'} .
\]

(28.125)

The conversion of that Hamiltonian part \( H_{\text{bec}} \) to momentum space has been demonstrated in (26.78),

\[
H_{\text{bec}} = \sum_q \frac{q}{2m} \hat{c}_q^\dagger \hat{c}_q + \sum_{q,q'} \hat{c}_q^\dagger V_{q',q} \hat{c}_q + \frac{u}{2} \sum_{q,q',q''} \hat{c}_q^\dagger \hat{c}_{q'}^\dagger \hat{c}_{q''} \hat{c}_q + \hat{q}' - \hat{q}'' .
\]

(28.126)

The light field part \( H_{\text{cav}} \) remains unchanged and the atom-light interaction becomes using (28.3),

\[
H_{\text{bec-cav}} = U_0 \int \hat{\psi}^\dagger(r) \hat{a}_+^\dagger \hat{a}_- e^{-i(k_+ - k_-) \cdot r} \hat{\psi}(r) d^3r + \text{h.c.}
\]

\[
= i\hbar U_0 \hat{a}_+^\dagger \hat{a}_- V \int \int \hat{c}_q^\dagger(\hat{q}') \hat{c}(\hat{q}) \delta^3(\hat{q} - \hat{q}' - 2k_\hat{e}_z) d^3q d^3q' = U_0 \hat{a}_+^\dagger \hat{a}_- \sum_q \hat{c}_q^\dagger - 2k \hat{c}_q .
\]

(28.127)
All in all,

\[
H = \sum_q \frac{q^2}{2m} \hat{c}_q^\dagger \hat{c}_q + \sum_{q,q'} \hat{c}_q^\dagger \hat{c}_q V_{q,q'} \hat{c}_{q'} + \frac{u}{2} \sum_{q,q',q''} \hat{c}_q^\dagger \hat{c}_{q'} \hat{c}_{q''} \hat{c}_{q+q'-q''} + (\hat{N} U_0 - \Delta_c) \sum_n \hat{a}_n^\dagger \hat{a}_n + U_0 \hat{a}_+^\dagger \hat{a}_- \hat{c}_n + \sum_q \hat{c}_q^\dagger \hat{c}_{q-2k} \hat{c}_q - i \sum_n \sum_{\pm} \eta_{\pm} (\hat{a}_\pm - \hat{a}_\pm^\dagger) .
\]

The BEC-CARL equations of motion are readily obtained from the Heisenberg equations,

\[
i \frac{d\hat{c}_{\pm}}{dt} = [\hat{c}_{\pm}, H] = \frac{q^2}{2m} \hat{c}_{\pm} + \sum_q V_{p,q} \hat{c}_q + u \sum_{q,q'} \hat{c}_q^\dagger \hat{c}_p \hat{c}_{q'q} + U_0 \hat{a}_+^\dagger \hat{a}_- \hat{c}_{p+2k} + h.c.
\]

\[
i \frac{d\hat{a}_\pm}{dt} = [\hat{a}_\pm, H] = (\hat{N} U_0 - \Delta_c) \hat{a}_\pm + U_0 \hat{a}_+^\dagger \hat{a}_- \hat{c}_n + \eta_{\pm} .
\]

### 28.5.2.1 Discretization of the momentum space

Assuming the BEC to be initially at rest with 0 temperature, its momentum state can be written as \( \hat{c}_0 \). And if the dynamics only involves the \( z \)-axis, then all momentum states are separated by multiples of \( 2\hbar k \), such that we may replace the labeling by integer numbers: \( \hat{c}_q \rightarrow \hat{c}_n \). We get,

\[
H = \sum_n \frac{n^2 q^2}{2m} \hat{c}_n^\dagger \hat{c}_n + \sum_{n,n'} \hat{c}_n^\dagger V_{n',n} \hat{c}_n + \frac{u}{2} \sum_{n,n',n''} \hat{c}_n^\dagger \hat{c}_n^\dagger \hat{c}_{n'} \hat{c}_{n''} \hat{c}_{n+n'-n''} + (\hat{N} U_0 - \Delta_c) \sum_n \hat{a}_n^\dagger \hat{a}_n + U_0 \hat{a}_+^\dagger \hat{a}_- \hat{c}_n + h.c. - \eta_{\pm} (\hat{a}_\pm - \hat{a}_\pm^\dagger) .
\]

Neglecting the external trapping potential and collisions the Heisenberg equations for the field and the atomic motion now read,

\[
\frac{d\hat{c}_n}{dt} = -i[\hat{c}_n, H] = -\frac{n^2 k^2}{2m} \hat{c}_n + U_0 \hat{a}_+^\dagger \hat{a}_- \hat{c}_{n+1} + h.c.
\]

\[
\frac{d\hat{a}_\pm}{dt} = -i[\hat{a}_\pm, H] = (\hat{N} U_0 - \Delta_c) \hat{a}_\pm + U_0 \hat{a}_+^\dagger \hat{a}_- \hat{c}_n + \eta_{\pm} .
\]

These equations look identical to those found in (??).

### 28.5.3 BECs in two internal states coupled by a cavity

A lossy cavity can act as an effective zero temperature reservoir. One possible implementation [316] realizes a three-level cycling scheme, with two BECs in two ground states \( |g_1\rangle \) and \( |g_2\rangle \) coherently coupled by a two-photon transition (Raman-lasers or microwave-radiofrequency combination). The ground states are additionally coupled by an irreversible Raman transition via an intermediate spontaneously decaying level \( |e\rangle \). One transition is not driven but stimulated by a ring cavity mode \( \hat{a} \).
28.5. INTERACTION BETWEEN CONDENSATES AND OPTICAL CAVITIES

The Hamiltonian consists of three parts, the BEC energy $H_{\text{bec}}$, the interaction energy with the coherent coupling assumed to be classical $H_{\text{cpl}}$ and the interaction with the mode of a ring cavity $H_{\text{cav}}$ treated quantum mechanically ($\hbar = 1$),

$$ H = H_{\text{bec}} + H_{\text{cpl}} + H_{\text{cav}} $$

$$ = \int d^3r \left( \frac{-\nabla^2}{2m} + V + \frac{u_{11}}{2} \hat{\psi}_1^\dagger \hat{\psi}_1 + \frac{u_{12}}{2} \hat{\psi}_1^\dagger \hat{\psi}_2 + h.c. \right) \hat{\psi}_1 + \\
+ \int d^3r \left( \frac{-\nabla^2}{2m} + V + \frac{u_{12}}{2} \hat{\psi}_1^\dagger \hat{\psi}_2 + \frac{u_{22}}{2} \hat{\psi}_2^\dagger \hat{\psi}_2 \right) \hat{\psi}_2 + \\
+ \int d^3r \left( -\Delta_{mw} \hat{\psi}_1^\dagger \hat{\psi}_1 + \frac{\Omega_{mw}}{2} \hat{\psi}_1^\dagger \hat{\psi}_2 + h.c. \right) + \int d^3r \left( g_{cv} \hat{a} \hat{\psi}_1^\dagger \hat{\psi}_2 + h.c. \right) - \Delta_{cv} \hat{a}^\dagger \hat{a} .$$

The BEC energy consists of the two energies (kinetic, potential, self) of the individual BECs and the cross-species interaction proportional to $u_{kl} = 4\pi \hbar^2 a_{kl}/m$. The interaction energy with the classical microwave frequency (mostly we will assume $\Delta_{mw} = 0$) leads to Rabi flopping with frequency $\Omega_{mw}$. Finally, the incident light field is treated classically with a Rabi frequency $\Omega_{lf}$ and a detuning $\Delta_{lf}$, while the cavity field is treated quantum mechanically with a coupling constant $\Omega_{cv}$ and a detuning $\Delta_{cv}$. The irreversible coupling leads to an energy contribution where $g_{cv} \equiv \Omega_{lf} \Omega_{cv}/2\Delta_{lf}$ is the two-photon Rabi-frequency if the auxiliary state is adiabatically eliminated. From the Heisenberg equations of motion for the matter wave and the optical field operators

---

Figure 28.20: (code) (a) Level scheme with a microwave-driven hyperfine structure, a laser-driven optical transition, and a cavity-enhanced Raman deexcitation. (b) Ring cavity used for the experiment. (c) Scheme for coupling the Zeeman states $|2,1\rangle$ and $|1,-1\rangle$ with a two-photon transition in a magnetic trap.
we obtain,

\begin{equation}
\dot{\hat{\psi}}_1 = i[H, \hat{\psi}_1] = -i \frac{\delta H}{\delta \hat{\psi}_1^\dagger} \tag{28.133}
\end{equation}

\begin{equation}
= -i \left( \frac{-\nabla^2}{2m} + V + u_{11}|\hat{\psi}_1|^2 + u_{12}|\hat{\psi}_2|^2 \right) \hat{\psi}_1 - i \left( \frac{\Omega_{mw}}{2} + g_{cv} \hat{a} \right) \hat{\psi}_2 - i \Delta_{mw} \hat{\psi}_1 ,
\end{equation}

\begin{equation}
\dot{\hat{\psi}}_2 = i[H, \hat{\psi}_2] = -i \frac{\delta H}{\delta \hat{\psi}_2^\dagger} \tag{28.134}
\end{equation}

\begin{equation}
= -i \left( \frac{-\nabla^2}{2m} + V + u_{12}|\hat{\psi}_1|^2 + u_{22}|\hat{\psi}_2|^2 \right) \hat{\psi}_2 - i \left( \frac{\Omega_{mw}}{2} + g_{cv} \hat{a}^\dagger \right) \hat{\psi}_1 ,
\end{equation}

\begin{equation}
\dot{\hat{a}} = i[H, \hat{a}] - \frac{\kappa}{2} \hat{a} = -i \frac{\delta H}{\delta \hat{a}^\dagger} - \frac{\kappa}{2} \hat{a} \tag{28.135}
\end{equation}

\begin{equation}
= -i \int d^3r \ g_{cv} \hat{\psi}_1 \hat{\psi}_2^\dagger - (i\Delta_{cv} + \frac{\kappa}{2}) \hat{a} .
\end{equation}

**Example 98 (Single atoms in two states interacting with a cavity):**

As a first example, we start from the matter wave Hamiltonian (28.132) for two coupled BECs and neglect the center-of-mass motion (and consequence the condensate part, i.e. self-interaction, kinetic energy and the external potential). Furthermore, we assume \( \hat{\psi}_i(r) = \hat{c}_i \delta^3(r) \),

\begin{equation}
\mathcal{H} = \mathcal{H}_{bec} + \mathcal{H}_{clp} + \mathcal{H}_{cav} \tag{28.136}
\end{equation}

\begin{equation}
= -\Delta_{mw} \hat{c}_1^\dagger \hat{c}_1 + \frac{\Omega_{mw}}{2} \hat{c}_1^\dagger \hat{c}_2 + g_{cv} \hat{a} \hat{c}_1^\dagger \hat{c}_2 + h.c. - \Delta_{cv} \hat{a}^\dagger \hat{a} .
\end{equation}

Consequently, the Heisenberg equations of motion are simply,

\begin{equation}
\dot{\hat{c}}_1 = -i \left( \frac{\Omega_{mw}}{2} + g_{cv} \hat{a} \right) \hat{c}_2 - i \Delta_{mw} \hat{c}_1 \tag{28.137}
\end{equation}

\begin{equation}
\dot{\hat{c}}_2 = -i \left( \frac{\Omega_{mw}}{2} + g_{cv} \hat{a}^\dagger \right) \hat{c}_1 \tag{28.138}
\end{equation}

\begin{equation}
\dot{\hat{a}} = -ig_{cv} \hat{c}_1 \hat{c}_2^\dagger - (i\Delta_{cv} + \frac{\kappa}{2}) \hat{a} .
\end{equation}

Obviously, since the matter wave degree of freedom is ignored, the dynamics only concerns the Bloch vector. Simulations of these equations are exhibited in Fig. 28.21 and in movies that can be watched under (watch movie) and (watch movie).

Figure 28.21: (code) Bloch vector phase stabilization in the cavity. (a) Populations and (b) coherences.
Example 99 (Interpretation of the ultracold fusion via analogy with two-level system): The chemical potential of the BECs in both states shifts the energy levels up depending on the inversion, \( \mu_2 - \mu_1 \propto N_2 - N_1 \). If the inversion oscillates the spontaneous Raman cycle periodically meets resonance, and takes place. Note that, since atomic motion is not considered, the energy gap due to the finite cavity detuning can only be bridged in resonance, \( \mu_2 - \mu_1 = \kappa \). Oscillation simulates Doppler shift of thermal motion in Doppler cooling. Raman scattering takes the role of spontaneous emission in the cooling process. The only role of the cavity is to introduce irreversibility. Raman scattering is only supported in one direction: However, it is not relevant to have a ring cavity.

28.5.4 Exercises

28.5.4.1 Ex: BEC damping in cavities
Programs on BEC damping in cavities.

28.5.4.2 Ex: Second-quantized CARL equations
Calculate the commutators \([\hat{\psi}_j(r), \mathcal{H}]\) and \([\hat{a}_\pm, \mathcal{H}]\), where \( \mathcal{H} \) is the Hamiltonian (28.122) and \( \hat{\psi}_1 \) and \( \hat{\psi}_2 \) the ground and excited state wave functions, respectively.

28.5.4.3 Ex: Second-quantized adiabatically approximated CARL Hamiltonian
a. Derive the adiabatically approximated CARL Hamiltonian in second quantization.
b. Derive the CARL equations of motion from the adiabatically approximated Hamiltonian in second quantization.
c. Show that the derived Hamiltonian simplifies to (22.27) in the single atom limit.

28.5.4.4 Ex: BEC-CARL equations from the adiabatically approximated CARL Hamiltonian
Derive the BEC-CARL equations from the adiabatically approximated CARL Hamiltonian (28.125).

28.5.4.5 Ex: Origin of quantum correlations
The BEC-CARL Hamiltonian has been shown to generate quantum correlations between optical and matter wave modes [432, 475]. Discuss whether they are a many-body effect (bosonic stimulation) or just due to coherences between motional states of single atoms.

28.5.4.6 Ex: Ultracold fusion
Derive from Eqs. (28.135) using the definitions (??) and (??) the Eqs. (??).
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