Lista 1 - Quântica B (2013)

1. Consider a quantum 1D Harmonic Oscillator of mass m and natura frequency ω which is initially prepared $(t = 0)$ in the state

$$|\psi_S(0)\rangle = \exp\left(-\frac{i}{\hbar}P_S x_0\right)|0\rangle \,,$$

where $|0\rangle$ is the ground state, P_S is the momentum operator, and x_0 is a scalar.
(a) In the Heisenberg picture, compute $\langle X_H(t)\rangle$ for $t > 0$ and relate it with the classical trajectory.
(b) How do you interprete this result with the classical initial conditions?

2. Consider a hidrogen atom in its ground state subject to an electric field $\mathbf{E} = \mathbf{E}_0 \cos\omega t$.
(a) What is the minimum frequency of the field in order to have ionization?
(b) What is the transition rate (probability per unit of time) to an ionized state (assuming it can represented by plane waves)?
(c) What is the angular distribution of the ejected electron in this process?
(d) Now consider that the atom is in a certain Eigenstate $|n, l, m\rangle$ and that ω is lower than the corresponding ionization frequency. What can be said about the final Eigenstate $|n', \ell', m'\rangle$?

3. Consider two spin-1/2 particles interacting as

$$V(t) = \frac{E(t)}{\hbar^2}\mathbf{S}_1 \cdot \mathbf{S}_2,$$

where $E(t)$ vanishes when $t \to \pm\infty$ and approaches to a nonzero value of order $\bar{E}$ on the time interval of length τ. (You may think on a gaussian, for instance.)
(a) At $t \to -\infty$, the system is in the state $|+-\rangle$. Compute exactly the state of the system at time t. With this, show that the probability of finding the system in the state $|-+\rangle$ for $t \to +\infty$ depends only on the integral $I = \int_{-\infty}^{\infty} E(t)\mathrm{d}t$.
(b) Compute the same probability in first-order of time-dependent perturbation theory. By comparing your results with those of item (a), discuss the validity of this calculation.
(c) Make some estimations about the value of the contribution to this probability in second-order of perturbation theory in the limits of $\tau \to 0$ and $\tau \to \infty$ and discuss your results with the validity of the approximation conclude in item (b).
(d) Now consider that both spins are subjected to a static magnetic field $\mathbf{B} = B_0\hat{z}$. The corresponding Zeeman Hamiltonian is

$$H_0 = -\frac{\mu_B}{\hbar}B_0\left(g_1 S_1^z + g_2 S_2^z\right),$$

where $g_{1,2}$ are the gyromagnetic ratios (assume them distinct from each other) and μ_B is the Bohr magneton. Consider also that $E(t) = \bar{E}\exp\left(-(t/\tau)^2\right)$. Compute the same probability of the previous itens in first-order of perturbation theory, and discuss its dependence on B_0 and on τ.
(e) (Optional) Like in item (c), compute the second-order contribution $c^{(2)}_{f\leftarrow i}(\infty)$ in the limits $\tau \to 0$ and $\tau \to \infty$.
(*Hint*: Notice that in the limits $\tau \to 0$ and $\tau \to \infty$, for estimation purposes, the exchange can be approximated to $E(t) = \bar{E}\tau\delta(t)$ and $E(t) = \bar{E}\theta(\tau/2 - |t|)$, respectively.)

4. Cohen-Tannoudji - complement E-XIII, problem 9.
Transition probability per unit time under the effect of a random perturbation. Simple relaxation model
A physical system, subjected to a perturbation $W(t)$, is at time $t = 0$ in the Eigenstate $|\varphi_i\rangle$ of its Hamiltonian H_0. Let $P_{f\leftarrow i}(t)$ be the probability of finding the system at time t in another Eigenstate of H_0, $|\varphi_j\rangle$. The transition probability per unit time $w_{f\leftarrow i}(t)$ is defined by $w_{f\leftarrow i}(t) = \frac{\mathrm{d}}{\mathrm{d}t}P_{f\leftarrow i}(t)$.
(a) Show that , to first order in perturbation theory, we have

$$w_{f\leftarrow i}(t) = \frac{1}{\hbar^2}\int_0^t \mathrm{d}\tau W_{fi}(\tau)W^*_{fi}(t-\tau)e^{i\omega_{fi}\tau} + \text{c.c.} \qquad (1)$$

with $\hbar\omega_{fi} = E_f - E_i$.

(b) Consider a very large number $\mathcal{N}$ of systems (k), which are identical and without mutual interactions ($k = 1, 2, \ldots, \mathcal{N}$). Each of them has a different microscopic environment and, consequently, "sees" a different perturbation $W^{(k)}(t)$. It is, of course, impossible to know each of the individual perturbation $W^{(k)}$. We can specify only statistical averages such as:

$$\overline{W_{fi}(t)} = \lim_{\mathcal{N}\to\infty} \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} W_{fi}^{(k)}(t),$$

$$\overline{W_{fi}(t)W_{fi}^{*}(t-\tau)} = \lim_{\mathcal{N}\to\infty} \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} W_{fi}^{(k)}(t)W_{fi}^{(k)*}(t-\tau).$$

This perturbation is said to be "random".

This random perturbation is said to be stationary if the preceding averages are time independent. In this case, we can redifine H_0 in order to make $\overline{W_{fi}} = 0$ and set:

$$g_{fi}(\tau) = \overline{W_{fi}(t)W_{fi}^{*}(t-\tau)},$$

which is called the "correlation function" of the perturbation. Usually, $g_{fi}(\tau)$ goes to zero for $|\tau| \gg \tau_c$, a characteristic time scale, called correlation time of the perturbation, i.e., the perturbation has a "memory" which extend into the past (or future) only to an interval of order of τ_c.

($b.\alpha$) The $\mathcal{N}$ (which can be considered infinity for calculations) systems are in the state $|\varphi_i\rangle$ at time $t = 0$ and are subject to a random stationary perturbation, the correlation function of which is $g_{fi}(\tau)$ with correlation time τ_c. Calculate the proportion $\pi_{fi}(t)$ of systems which go to into the state $|\varphi_j\rangle$ per unit time. Show that after a certain value t_1 of t, to be specified, $\pi_{fi}(t)$ no longer depends on t.

($b.\beta$) For fixed τ_c, how does π_{fi} vary with ω_{fi}? Consider the case in which $g_{fi}(\tau) = |v_{fi}|^2 e^{-|\tau|/\tau_c}$, with v_{fi} constant.

($b.\gamma$) The preceding theory is valid only for $t \ll t_2$ [since Eq. (1) results from perturbation theory]. What is the order of magnitude of t_2? Taking $t_2 \gg t_1$, find the condition for introducing a transition probability per unit time which is independent of t [use the form of $g_{fi}(\tau)$ given in the preceding question]. Would it be possible to extend the preceding theory beyond $t = t_2$?

(c) Application to a system. The $\mathcal{N}$ systems under consideration are spin-1/2 particles, with gyromagnetic ratio γ, placed in a static magnetic field $\mathbf{B}_0$ (set $\omega_0 = \gamma B_0$). These particles are enclosed in a spherical shell of radius R. Each of them bounces constantly back and forth between the walls. The mean time between the collisions of the same particle with the wall is called "time of flight" τ_v. During this time, the particle sees only the magnetic field $\mathbf{B}_0$. In a collision with the wall, each particle remains adsorbed on the surface during a mean time τ_a ($\tau_a \ll \tau_v$), during which it seems, in addition to $\mathbf{B}_0$, a constant microscopic field $\mathbf{b}$ due to paramagnetic impurities contained in the wall. The direction of $\mathbf{b}$ varies randomly from one collision to another; the mean amplitude of $\mathbf{b}$ is b_0.

($c.\alpha$) What is the correlation time of the perturbation seen by the spins? Give the physical justification for the following form, to be chosen for the correlation function of the components of the microscopic magnetic field $\mathbf{b}$:

$$\overline{b_x(t)b_x(t-\tau)} = \frac{1}{3}b_0^2\left(\frac{\tau_a}{\tau_b}\right)e^{-|\tau|/\tau_a},$$

and analogous expressions for the y- and z-components, and all the cross terms $\overline{b_x(t)b_y(t-\tau)} = \overline{b_x(t)b_z(t-\tau)} = \cdots = 0$.

($c.\beta$) Let M_z be the z-component of the total magnetization. (Consider $\mathbf{B} = B_0\hat{z}$.) Show that, under the effect of the collisions with the walls, M_z "relaxes", with a time constant T_1:

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = -\frac{M_z}{T_1}$$

(T_1 is called the longitudinal relaxation time). Calculate T_1 in terms of γ, B_0, τ_v, τ_a, b_0.

($c.\gamma$) Show that studying the variation of T_1 with B_0 permites the experimental determination of the mean adsorption time τ_a.

($c.\delta$) We have at our disposition several cells, of different radii R, constructed of the same material. By measuring T_1, how can we determine experimentally the mean amplitude b_0 of the microscopic field in the wall.

5. Cohen-Tannoudji - complement E-XIII, problem 10.

Absorption of radiation by a many-particle system forming a bound state. The Doppler effect. The recoil energy. The Mössbauer effect

In class, we considered the absorption of radiation by a charged particle attracted by a fixed center (Hydrogen atom with infinitely heavy nucleous). In this exercise, we treat a more realistic situation in which the incident radiation is absorbed by a system of many particles of finite masses interacting with each other and forming a bound state. Thus we are studying the effect on the absorption phenomenon of the degrees of freedom of the center of mass of the system.

I. Absorption of radiation by a free Hydrogen atom. The Doppler effect. The recoil energy

Consider two particles of masses $m_{1,2}$ of opposite charges $q_{1,2}$ and position and momentum operators $\mathbf{R}_{1,2}$ and $\mathbf{P}_{1,2}$ (a Hydrogen atom). Let $\mathbf{R}$ and $\mathbf{P}$, and $\mathbf{R}_G$ and $\mathbf{P}_G$ be the position and momentum observables of the relative particle and center of mass of the system, respectively. $M = m_1 + m_2$ is the total mass and $m = m_1 m_2/M$ is the reduced mass. The Hamiltonian of the system can be written:

$$H_0 = H_e + H_i,$$

where

$$H_e = \frac{1}{2M} P_G^2$$

describes the translational kinetic energy of the free atom (the "external" degrees of freedom), and H_i describes the internal energy of the atom (the "internal" degrees of freedom). We denote by $|\mathbf{K}\rangle$ the eigenstates of H_e, with Eigenvalues $\hbar^2 K^2/(2M)$. We concern ourselves with only two Eigenstates of H_i, $|\chi_a\rangle$ and $|\chi_b\rangle$ of energies E_a and E_b (with $E_b > E_a$), and set $\hbar\omega_0 = E_b - E_a$.

(a) What energy must be furnished to the atom to move it from state $|\mathbf{K}, \chi_a\rangle$ to state $|\mathbf{K}', \chi_b\rangle$?

(b) This atom interacts with a plane electromagnetic wave of wavevector $\mathbf{k}$ and angular frequency $\omega = ck$ polarized along the unit vector $\hat{e}$ perpendicular to $\mathbf{k}$. The corresponding vector potential $\mathbf{A}(\mathbf{r}, t)$ is

$$\mathbf{A}(\mathbf{r}, t) = A_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \hat{e} + \text{c.c.},$$

with A_0 constant. The principal term of the interaction Hamiltonian between this plane wave and the two particle system can be written as

$$W(t) = -\sum_{i=1}^{2} \frac{q_i}{m_i} \mathbf{P}_i \cdot \mathbf{A}(\mathbf{R}_i, t).$$

Express W in terms of $\mathbf{R}$, $\mathbf{P}$, $\mathbf{R}_G$ $\mathbf{P}_G$, m, M, and q (set $q_1 = -q_2 = q$), and show that, in the electric dipole approximation (which consists of neglecting $\mathbf{k}\cdot\mathbf{R}$, but not $\mathbf{k}\cdot\mathbf{R}_G$, in comparison to 1), we have that

$$W = W_0 e^{-i\omega t} + W_0^\dagger e^{i\omega t}, \text{ with } W_0 = -\frac{qA_0}{m} \hat{e} \cdot \mathbf{P} e^{i\mathbf{k}\cdot\mathbf{R}_G}. \tag{2}$$

(c) Show that the matrix element $\langle \mathbf{K}', \chi_b | W_0 | \mathbf{K}, \chi_a \rangle$ is different from zero only if there exist a relation between $\mathbf{k}$, $\mathbf{K}$ and $\mathbf{K}'$ (to be specified). Interpret this relation in terms of momentum conservation of the system atom+photon.

(d) Show that if the atom is in the state $|\mathbf{K}, \chi_a\rangle$ is placed in the radiation field, resonance just occurs when the energy $\hbar\omega$ of the photons differs from the atomic transition energy $\hbar\omega_0$ by an amount δE which is to be expressed in terms of $\hbar$, ω_0, $\mathbf{K}$, $\mathbf{k}$, M, and c (since δE is a corrective term, we can replace ω by ω_0 in the final expression for δE). Show that δE is the sum of two terms, one of which, δE_1, depends on $\mathbf{K}$ and on the angle between $\mathbf{K}$ and $\mathbf{k}$ (the Doppler effect), the other term, δE_2, is independs of $\mathbf{K}$. Give a physical interpretation of δE_1 and δE_2 (showing that δE_2 is the recoil kinetic energy of the atom when, having been initially motionless, it absorbs a resonant photon).

Show that δE_2 is negligible compared to δE_1 when $\hbar\omega_0$ is of order of 10 eV (the domain of atomic physics). Choose, for M, a mass of order of the proton ($Mc^2 \approx 10^9$ eV), and, for K, a value corresponding to the thermal velocity at $T = 300$ K. Would this still be true if $\hbar\omega_0$ were of order of 10^5 eV (the domain of nuclear physics)?

II. Recoilles absorption of radiation by a nucleous vibrating about its equilibrium position in a crystal. The Mössbauer effect

The system under consideration is now a nucleous of mass M vibrating at angular frequency Ω about its equilibrium position in a crystalline lattice (the Einstein model). Again, denote by $\mathbf{R}_G$ and $\mathbf{P}_G$ the position and momentum operators of the center of mass of this nucleous, respectively. Its vibrational energy is given by

$$H_e = \frac{1}{2M} P_G^2 + \frac{1}{2} M\Omega \left(X_G^2 + Y_G^2 + Z_G^2 \right),$$

which is that of the 3D Harmonic Oscillator. Denote by $|n_x, n_y, n_z\rangle$ the Eigenstate of H_e with Eigenenergy $(n_x + n_y + n_z + 3/2)\,\hbar\Omega$. In addition to these "external" degrees of freedom, the nucleous possesses "internal" degrees of freedom which are associated observables that commute with $\mathbf{R}_G$ and $\mathbf{P}_G$ and are described by H_i. As before, let us concern only with the two lowest levels of H_i: $|\chi_a\rangle$ and $|\chi_b\rangle$. Also, set $\hbar\omega_0 = E_b - E_a > 0$. Typically, $\hbar\omega_0$ is in the γ-ray domain, and thus, $\omega_0 \gg \Omega$.

(e) What energy must be given to the nucleous to allow it go from state $|0, 0, 0, \chi_a\rangle$ to state $|n, 0, 0, \chi_b\rangle$?

(f) This nucleous is placed in the same radiation field as before (and set $\mathbf{k} = k\hat{x}$). It can be shown that, in the electric dipole approximation, the interaction Hamiltonian of the nucleous with the plane wave (responsible for the absorption of γ-rays) can be written as in Eq. (2) with

$$W_0 = A_0 S_i(k) e^{ikX_G},$$

where $S_i(k)$ is an operator which acts on the internal degrees of freedom of the nucleous and, consequently, commutes with $\mathbf{R}_G$ and $\mathbf{P}_G$.

The nucleous is initially in the state $|0, 0, 0, \chi_a\rangle$. Show that under the influence of the incident wave, a resonance appears whenever $\hbar\omega$ coincides with one of the energies calculated in item (e). The intensity of the resonance is $|s(k)|^2 \left|\langle n, 0, 0|\, e^{ikX_G}\, |0, 0, 0\rangle\right|^2$, where the value of k is to be specified and $s(k) = \langle \chi_b\, |S_i(k)|\, \chi_a\rangle$. Show that, because $\omega_0 \gg \Omega$, we can replace k by $k_0 = \omega_0/c$ in the expression for the intensity of the resonance.

(g) Set

$$\pi_n(k_0) = \left|\left\langle \varphi_n \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle\right|^2,$$

where $|\varphi_n\rangle$ are the Eigenstates of the 1D Hamornic Oscillator of position X_G, mass M, and angular frequency Ω.

($g.\alpha$) Calculate $\pi_n(k_0)$ in terms of $\hbar$, M, Ω, k_0, and n. (*Hint*: stablish a recurrence relation between $\left\langle \varphi_n \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle$ and $\left\langle \varphi_{n-1} \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle$, and express all $\pi_n(k_0)$ as a function of $\pi_0(k_0)$, which is to be calculated directly from the wave function of the Harmonic Oscillator. Show that $\pi_n(k_0)$ are given by a Poisson distribution of n with average ξ, where $\xi = \left(\frac{\hbar^2 k_0^2}{2M}\right) / (\hbar\Omega)$.

($g.\beta$) Verify that $\sum_{n=0}^{\infty} \pi_n(k_0) = 1$.

($g.\gamma$) Show that $\sum_{n=0}^{\infty} n\hbar\Omega\pi_n(k_0) = \frac{\hbar^2\omega_0^2}{2Mc^2}$.

(h) Assume that $\hbar\Omega \gg \frac{\hbar^2\omega_0^2}{2Mc^2}$, i.e., the vibrational energy is much greater than the recoil energy (very rigid crystal). Show that the absorption spectrum of the nucleous is essentially composed of a single line at the angular frequency ω_0. This line is called the recoilless absorption line. Justify this name. Why does the Doppler effect disappear?

(i) Now assume that $\hbar\Omega \ll \frac{\hbar^2\omega_0^2}{2Mc^2}$ (very weak crystalline bonds). Show that the absorption spectrum of the nucleous is composed of very large number of equidistant lines whose barycenter (obtained by weighting the abscissa of each line by its relative intensity) coincides with the position of the absorption line of the free and motionless nucleous. What is the order of magnitude of the width of this spectrum (the dispersion of the line with respect to the barycenter)? Show that one recover the results of the first part in the limit $\Omega \to 0$.

6. (Optional) Consider the 1D dynamics of a particle of charge e and mass m under a periodic potential $V(x) = V(x + a)$. Assume that at $t = 0$ a vector potential is turned on $A(t) = -Et$.

(a) Study the quasi-degenerate perturbation theory between the states e^{ikx} and $e^{i(k-\kappa)x}$ (conveniently normalized) when $k \approx \kappa/2$, where $\kappa = 2\pi/a$. Assume that $A(t)$ varies slowly and that $V(x)$ can be treated perturbatively.

(b) Compute the adiabatic Eigenstates of the system around $k = \kappa/2$.

(c) Compute the transition probability from the lowest- to the highest-energy adiabatic Eigenstate assuming that the transition is more likely to happen around $k = \kappa/2$.

Make any approximation you may find convenient in order to compute the integrals involved.

ANSWER:
1.
(a) The equation of motion in the Heisenberg picture is

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}X_H = [X_H, H_H] + i\hbar\frac{\partial}{\partial t}X_H,$$

as X_S does not depend on t, then $\frac{\partial}{\partial t}X_H = U^\dagger\left(\frac{\partial}{\partial t}X_S\right)U = 0$. Taking the average value of the resulting,

$$\left\langle i\hbar\frac{\mathrm{d}}{\mathrm{d}t}X_H\right\rangle = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left\langle X_H\right\rangle = \left\langle [X_H, H_H]\right\rangle,$$

since $|\psi_H\rangle$ does not depend on t. The commutator can be evaluated:

$$\begin{aligned}[X_H, H_H] &= U^\dagger\left[X_S, H_S\right]U = U^\dagger\left[X_S, \frac{1}{2m}P_S^2 + \frac{1}{2}m\omega^2X_S^2\right]U \\ &= U^\dagger\left[X_S, \frac{1}{2m}P_S^2\right]U = U^\dagger\left(\frac{i\hbar}{m}P_S\right)U = \frac{i\hbar}{m}P_H.\end{aligned}$$

Thus,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle X_H\right\rangle = \frac{1}{m}\left\langle P_H\right\rangle.$$

Repeating the same steps for P_H, we arrive at

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle P_H\right\rangle = \frac{1}{i\hbar}\left\langle [P_H, H_H]\right\rangle = -m\omega^2\left\langle X_H\right\rangle.$$

Therefore,

$$\left\langle X_H(t)\right\rangle = A\cos\omega t + B\sin\omega t,$$

where A and B are constants which depends on the initial conditions $\langle X_H(0)\rangle$ and $\langle P_H(0)\rangle$.

$$\left\langle X_H(0)\right\rangle = \left\langle \psi_S(0)\left|X_S\right|\psi_S(0)\right\rangle = \left\langle 0\left|e^{\frac{i}{\hbar}P_Sx_0}X_Se^{-\frac{i}{\hbar}P_Sx_0}\right|0\right\rangle.$$

Using the Baker-Haussdorff identity

$$e^ABe^{-A} = B + [A, B] + \frac{1}{2!}\left[A, [A, B]\right] + \ldots,$$

we find that

$$e^{\frac{i}{\hbar}P_Sx_0}X_Se^{-\frac{i}{\hbar}P_Sx_0} = X_S + \frac{i}{\hbar}\left[P_S, X_S\right]x_0 = X_S + x_0.$$

Thus, $\langle X_H(0)\rangle = \langle 0\left|X_S\right|0\rangle + x_0 = x_0$. As P_S commutes with $e^{-iP_sx_0/\hbar}$, we have that $\langle P_H(0)\rangle = 0$. In this manner,

$$\left\langle X_H(t)\right\rangle = x_0\cos\omega t,$$

as in the classical trajectory.

(b) The operator $e^{-iP_Sx_0/\hbar}$ is the spatial translation operator, i.e., $e^{-iP_Sx_0/\hbar}\left|x\right\rangle = \left|x + x_0\right\rangle$. Thus, we relate the initial condition as the quantum oscillator being in the ground state shifted by an amount x_0, i.e., $\langle x|\,e^{-iP_Sx_0/\hbar}\left|0\right\rangle = \langle x - x_0|0\rangle = \varphi\left(x - x_0\right)$, where $\varphi(x)$ is the ground-state wave function of the Harmonic Oscillator. Thus the initial "position" is x_0. The inital velocity is zero since $\langle\psi_S(0)\left|P_S\right|\psi_S(0)\rangle = \langle 0\left|P_S\right|0\rangle = 0$. These are the same initial conditions yielding to the trajectory $x(t) = \langle X_H(t)\rangle$.

2.
Consider a hidrogen atom in its ground state subject to an electric field $\mathbf{E} = \mathbf{E}_0\cos\omega t$.

(a) The Eigenenergies of the Hydrogen atom are

$$E_n = -\frac{Z^2 m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} = -Z^2\frac{13.6\,\mathrm{eV}}{n^2},$$

with $Z = 1$ for the Hydrogen. Thus, if the ionization is to happen in a single-photon absorption, then $\hbar\omega = hf = -E_1$. Thus, the corresponding frequency is

$$\omega = \frac{m}{2\hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \approx 2\,10^{16}\,\frac{\mathrm{rad}}{\mathrm{s}} \text{ which corresponds to } 3.3\,10^{15}\,\mathrm{Hz}$$

(recall $h = 4.135\,10^{-15}\,\mathrm{eV.s}$).

(b) In 1st order of perturbation theory,

$$P_{f\leftarrow i}(t) = \left|\langle f\,|U_I(t,t_0)|\,i\rangle\right|^2 \approx \frac{1}{\hbar^2}\left|\int_{t_0}^{t}\mathrm{d}t'\,\langle f\,|V(t')|\,i\rangle\, e^{i\omega_{fi}t'}\right|^2.$$

The initial state is the ground-state $|1,0,0\rangle$ and the final one is a plane wave $|\mathbf{k}\rangle$:

$$\langle\mathbf{r}|1,0,0\rangle = \psi_{1,0,0}(\mathbf{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0},$$
$$\langle\mathbf{r}|\mathbf{k}\rangle = \frac{1}{\sqrt{V}}e^{-i\mathbf{k}\cdot\mathbf{r}},$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ is the Bohr radius and V (the volume of the box containing the ejected electron) is a normalization factor. The perturbation is given by

$$V(t) = -e\mathbf{E}_0\cdot\mathbf{r}\cos\omega t.$$

The matrix element

$$\langle f\,|V(t')|\,i\rangle = -e\mathbf{E}_0\cdot\langle f\,|\mathbf{r}|\,i\rangle\cos\omega t = -e\mathcal{E}_0\,\langle f\,|z|\,i\rangle\cos\omega t,$$

in which, for simplicity, we chose $\mathbf{E}_0 = \mathcal{E}_0\hat{z}$.

Let us focus on the time-independent part

$$\langle f\,|z|\,i\rangle = \int \mathrm{d}^3r\frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}z\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0} = \frac{1}{\sqrt{V}}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\int_0^\infty \mathrm{d}r\int \mathrm{d}\Omega r^2 e^{i\mathbf{k}\cdot\mathbf{r}}r\cos\theta e^{-r/a_0}.$$

The angular integral is

$$\int \mathrm{d}\Omega e^{i\mathbf{k}\cdot\mathbf{r}}\times\cos\theta = \int\mathrm{d}\Omega\left(4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} i^\ell Y^*_{\ell,m}(\hat{k})j_\ell\left(kr\right)Y_{\ell,m}(\theta,\varphi)\right)\times\left(\sqrt{\frac{4\pi}{3}}Y_{1,0}(\theta,\varphi)\right),$$

where j_ℓ are the Spherical Bessel functions. From the orthonormality of the Spherical Harmonics, we find that

$$\int\mathrm{d}\Omega e^{i\mathbf{k}\cdot\mathbf{r}}\cos\theta = 4\pi i\sqrt{\frac{4\pi}{3}}Y^*_{1,0}(\hat{k})j_1\left(kr\right) = 4\pi i\sqrt{\frac{4\pi}{3}}Y^*_{1,0}(\hat{k})\left(\frac{\sin\left(kr\right)-\left(kr\right)\cos\left(kr\right)}{\left(kr\right)^2}\right).$$

Notice this implies that the ejected electron has angular momentum $\ell = 1$. Moreover, $m = 0$ because of our choice $\mathbf{E}_0 = \mathcal{E}_0\hat{z}$. If we had chosen other direction, m would take the values ±1.

Integrating over the radial part, we need

$$\int_0^\infty \mathrm{d}r r^3 e^{-r/a_0}\left(\frac{\sin\left(kr\right)-\left(kr\right)\cos\left(kr\right)}{\left(kr\right)^2}\right) = \frac{8a_0^5}{\left(1+\left(a_0k\right)^2\right)^3}k.$$

Putting everything together, we finally arrive at

$$\langle f\,|z|\,i\rangle = \frac{1}{\sqrt{V}}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\times\frac{8a_0^5}{\left(1+(a_0k)^2\right)^3}k\times 4\pi i\sqrt{\frac{4\pi}{3}}Y_{1,0}^*(\hat{k}) = \frac{32\sqrt{\pi}i\,(a_0k)}{\left(1+(a_0k)^2\right)^3}\sqrt{\frac{a_0^3}{V}}\times a_0\cos\theta_k,$$

where θ_k is the angle between the direction of the electric field $\mathbf{E}_0$ and the wavevector $\mathbf{k}$ of the ejected electron. (Notice with this result we can already answer question (c).)

We now focus on the time-dependent part of the integral

$$\left|\int_{t_0=0}^{t}\mathrm{d}t'\cos\omega t' e^{i\omega_{fi}t'}\right|^2 = \frac{\sin^2\left((\omega-\omega_{if})\frac{t}{2}\right)}{(\omega-\omega_{if})^2}+\frac{\sin^2\left((\omega+\omega_{if})\frac{t}{2}\right)}{(\omega+\omega_{if})^2} - \frac{\sin^2\left((\omega+\omega_{if})\frac{t}{2}\right)+\sin^2\left((\omega-\omega_{if})\frac{t}{2}\right)-\sin^2\left(\omega\frac{t}{2}\right)}{(\omega+\omega_{if})(\omega-\omega_{if})}.$$

Using that

$$\lim_{t\to\infty}\frac{\sin^2(xt/2)}{x^2} = \frac{\pi}{2}\delta(x),$$

we simplify the above integral to

$$\lim_{t\to\infty}\left|\int_0^t\mathrm{d}t'\cos\omega t' e^{i\omega_{fi}t'}\right|^2 \to \frac{\pi}{2}\left(\delta(\omega-\omega_{fi})+\delta(\omega+\omega_{fi})\right)t,$$

if $\omega\neq 0$. For $\omega=0$, it becomes $2\pi\delta(\omega_{fi})\,t$. This is because the last term is only nonzero when $\omega=0$.

The total probability of excitation is given by

$$P_{\{f\}\leftarrow i}(t) = \sum_f P_{f\leftarrow i}(t).$$

As the final state is in a continuum (where $\mathbf{k}$ is a good quantum number), then the sum can be replaced by an integral

$$P_{\{f\}\leftarrow i}(t) = \sum_f P_{f\leftarrow i}(t) \to \frac{1}{\delta k^3}\int\mathrm{d}^3kP_{f\leftarrow i}(t) = \frac{V}{(2\pi)^3}\int\mathrm{d}^3kP_{f\leftarrow i}(t).$$

It is then convenient to exchange the integral in k by an integral in energy:

$$\mathrm{d}^3k = \mathrm{d}\Omega k^2\mathrm{d}k = \mathrm{d}\Omega\frac{2mE}{\hbar^2}\left(\frac{\sqrt{m}\mathrm{d}E}{\hbar\sqrt{2E}}\right) = \mathrm{d}\Omega\frac{m\sqrt{2mE}}{\hbar^3}\mathrm{d}E = \frac{(2\pi)^3}{V}\rho(E)\,\mathrm{d}\Omega\mathrm{d}E,$$

which defines the density of states $\rho(E) = Vm\sqrt{2mE}/(2\pi\hbar)^3$. Notice also we used the free-electron dispersion relation $2mE = (\hbar k)^2$ and that we are disregarding the spin degeneracy since the transition conserves the electron spin. Then,

$$\begin{aligned}
P_{\{f\}\leftarrow i}(t) = &\int\mathrm{d}\Omega_k\rho(E_f)\,\mathrm{d}E_f\times\frac{1}{\hbar^2}\left|-e\mathcal{E}_0\frac{32\sqrt{\pi}i\,(a_0k)}{\left(1+(a_0k)^2\right)^3}\sqrt{\frac{a_0^3}{V}}\times a_0\cos\theta_k\right|^2\frac{\pi}{2}\left(\delta(\omega+\omega_{fi})+\delta(\omega-\omega_{fi})\right)t \\
=&2\pi\int_0^{\pi}\mathrm{d}\theta_k\sin\theta_k\cos\theta_k^2\,(e\mathcal{E}_0a_0)^2\left(\frac{32\sqrt{\pi}\,(a_0k)}{\left(1+(a_0k)^2\right)^3}\right)^2\times\frac{\pi}{2\hbar}\rho(E_i+\hbar\omega)\,\frac{a_0^3}{V}t \\
=&2\pi\frac{2}{3}(e\mathcal{E}_0a_0)^2\left(\frac{32\sqrt{\pi}\,(a_0k)}{\left(1+(a_0k)^2\right)^3}\right)^2\times\frac{\pi}{2\hbar}\frac{m\sqrt{2m(E_i+\hbar\omega)}}{(2\pi\hbar)^3}a_0^3t \\
=&(e\mathcal{E}_0a_0)^2\left(\frac{16\,(a_0k)}{\left(1+(a_0k)^2\right)^3}\right)^2\frac{m\sqrt{2m(E_i+\hbar\omega)}}{3\hbar^4}a_0^3t = (e\mathcal{E}_0a_0)^2\left(\frac{16\,(a_0k)}{\left(1+(a_0k)^2\right)^3}\right)^2(ka_0)\,\frac{ma_0^2}{3\hbar^3}t,
\end{aligned}$$

where we have kept only the possible transition (absorption) in which $\omega_f = \omega_i + \omega$, $E_i = E_0 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = -13.6\,\text{eV}$. Notice also that the ejected electron has wavevector $k = \sqrt{2m\left(E_0 + \hbar\omega\right)}/\hbar$. Finally, the transition rate is

$$w = \frac{\mathrm{d}}{\mathrm{d}t}P_{\{f\}\leftarrow i}(t) = \frac{256}{3}\left(e\mathcal{E}_0 a_0\right)^2 \frac{\left(a_0 k\right)^3}{\left(1 + \left(a_0 k\right)^2\right)^6}\frac{m a_0^2}{\hbar^3}.$$

If we consider a field such that $\hbar\omega = 2\left|E_0\right|$, then the corresponding wavevector is $k = \sqrt{2m\left|E_0\right|}/\hbar = 1/a_0 \approx 1.9\,10^{-10}\,\text{m}^{-1}$. The decay rate is roughly $w = 4\left(e\mathcal{E}_0 a_0\right)^2 \frac{m a_0^2}{3\hbar^3}$. Let us assume a low field of order $\mathcal{E}_0 = 100\,\text{V/m}$ (the classical field inside the atom is of order $10^{11}\,\text{V/m}$), we find that $w \approx 2\,10^{-5}\,\text{Hz}$.

(c) This is given by the dependence on θ_k and φ_k of $P_{f\leftarrow i}(t)$. As we have shown that $\langle f\left|z\right|i\rangle \propto \cos\theta_k$, then we conclude that the angular distribution of the ejected electrons is

$$P_{f\leftarrow i}(t) = \text{const}_k \times \cos^2\theta_k,$$

where θ_k is the angle between the direction of the ejected electron and the direction of the external electric field. The multiplicative prefactor const_k depends only on the magnitude of $\mathbf{k}$.

(d) The selection rules are given by

$$\langle n', \ell', m'\left|V\right|n, \ell, m\rangle \propto \mathbf{E}_0 \cdot \langle n', \ell', m'\left|\mathbf{r}\right|n, \ell, m\rangle = \mathbf{E}_0 \cdot \langle n', \ell', m'\left|(x, y, z)\right|n, \ell, m\rangle .$$

Recall the Eigenfunctions are

$$\langle \mathbf{r}|n, \ell, m\rangle = R_{n,\ell}(r) Y_{\ell,m}(\theta, \varphi),$$

where

$$R_{n,\ell} = \sqrt{\left(\frac{2Z}{n a_0}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}} e^{-\rho/2}\rho^\ell L_{n+\ell}^{2\ell+1}(\rho),$$

$$Y_{\ell,m} = (-1)^m \sqrt{\frac{2\ell}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos\theta) e^{im\varphi} \text{ for } m \geq 0,$$

and $Y_{\ell,m} = (-1)^m Y_{\ell,|m|}^*$ for $m < 0$. Here, the $\rho = 2Zr/(n a_0)$ ($Z = 1$ for Hydrogen), L_p^q is the associated Laguerre polynomial defined as

$$L_p^q(\rho) = \frac{\mathrm{d}^q}{\mathrm{d}\rho^q} L_p\left(\rho\right), \text{ and } L_p\left(\rho\right) = e^\rho \frac{\mathrm{d}^p}{\mathrm{d}\rho^p}\left(\rho^p e^{-\rho}\right).$$

The associated Legendre polynomials are (for $m \geq 0$)

$$P_\ell^m(x) = \left(1 - x^2\right)^{\frac{m}{2}} \frac{\mathrm{d}^m}{\mathrm{d}x^m} P_\ell\left(x\right), \text{ and } P_\ell\left(x\right) = \frac{(-1)^\ell}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}\rho^\ell}\left(1 - x^2\right)^\ell .$$

The first selection rule can be obtained from the azimutal angle φ. There will be integrals of the form

$$\langle m'\left|(x, y, z)\right|m\rangle \sim \int \mathrm{d}\varphi e^{-im'\varphi}\left(e^{\pm i\varphi}, e^{\pm i\varphi}, 1\right) e^{im\varphi} \propto \left(\delta_{m',m\pm1}, \delta_{m',m\pm1}, \delta_{m',m}\right).$$

Thus, $m' = m$ or $m' = m \pm 1$.

With respect to the polar angle θ, we will have integrals of type

$$\int_{-1}^{1} \mathrm{d}\cos\theta Y_{\ell',m'}^*\left(\theta, \varphi\right)\left(\sin\theta, \sin\theta, \cos\theta\right) Y_{\ell,m}\left(\theta, \varphi\right) \propto \int \mathrm{d}\Omega Y_{\ell',m'}^*\left(Y_{1,\pm1}, Y_{1,\pm1}, Y_{1,0}\right) Y_{\ell,m}$$
$$= \int \mathrm{d}\Omega\left(P_{\ell'}^{m+1} P_1^1 P_\ell^m, P_{\ell'}^m P_1^0 P_\ell^m\right).$$

It can be shown that the integral is nonzero only when $\ell' = \ell \pm 1$. This comes from the fact that $P_1 P_\ell = c_+ P_{\ell+1} + c_- P_{\ell-1}$.

There is another way of showing this selection rule.
Let $r_\pm = x \pm iy$. Then

$$[L_z, r_\pm] = [xp_y - yp_x, r_\pm] = x\,[p_y, \pm iy] - y\,[p_x, x] = \pm\hbar x + i\hbar y = \pm\hbar r_\pm.$$

Now we compute

$$\langle n', \ell', m' |([L_z, r_\pm] \mp \hbar r_\pm)| n, \ell, m\rangle = 0 = \hbar\,(m' - m \mp 1)\,\langle n', \ell', m' |r_\pm| n, \ell, m\rangle\,.$$

Thus, $\langle n', \ell', m' |(x, y)| n, \ell, m\rangle$ is nonzero only when $m' = m \pm 1$. For z, since $[L_z, z] = 0$, then $\langle n', \ell', m' |[L_z, z]| n, \ell, m\rangle = 0 = \hbar\,(m' - m)\,\langle n', \ell', m' |z| n, \ell, m\rangle$. Thus, the selection rule $m = m'$.

Now we apply the same idea with the other quantum number

$$L^2 = L_X^2 + L_y^2 + L_z^2.$$

Computing the commutator

$$\begin{aligned}\left[L^2, z\right] &= \left[L_x^2, z\right] + \left[L_y^2, z\right] = L_x\,[yp_z - zp_y, z] + [L_x, z]\,L_x + L_y\,[zp_x - xp_z, z] + [L_y, z]\,L_y\\ &= - i\hbar L_x y - i\hbar y L_x + i\hbar L_y x + i\hbar x L_y = -i\hbar L_x y - i\hbar\,(L_x y - i\hbar z) + i\hbar\,(-i\hbar z + xL_y) + i\hbar x L_y\\ &= 2i\hbar\,(xL_y - L_x y) = 2i\hbar\,(L_y x - L_x y + i\hbar z)\,.\end{aligned}$$

where we have used that $[L_x, y] = [yp_z - zp_y, y] = i\hbar z$ and $[L_y, x] = [zp_x - xp_z, x] = -i\hbar z$. Notice the symmetry between the ciclic interchange $x \to y \to z$:

$$\begin{aligned}\left[L^2, x\right] &= \left[L_y^2, x\right] + \left[L_z^2, x\right] = L_y\,[zp_x - xp_z, x] + [L_y, x]\,L_y + L_z\,[xp_y - yp_x, x] + [L_z, x]\,L_z\\ &= - i\hbar\,(L_y z + zL_y) + i\hbar\,(L_z y + yL_z) = -i\hbar\,(i\hbar x + 2zL_y) + i\hbar\,(i\hbar x + 2L_z y)\\ &= 2i\hbar\,(L_z y - zL_y) = 2i\hbar\,(yL_z - L_y z)\,,\\ \left[L^2, y\right] &= \left[L_x^2, y\right] + \left[L_z^2, y\right] = L_x\,[yp_z - zp_y, y] + [L_x, y]\,L_x + L_z\,[xp_y - yp_x, y] + [L_z, y]\,L_z\\ &= i\hbar\,(L_x z + zL_x) - i\hbar\,(L_z x + xL_z) = i\hbar\,(-i\hbar y + 2zL_x) - i\hbar\,(2L_z x - i\hbar y)\\ &= 2i\hbar\,(zL_x - L_z x) = 2i\hbar\,(L_x z - xL_z)\,.\end{aligned}$$

As the commutator $\left[L^2, z\right]$ does not have L^2 or z. We then commute the entire thing with L^2 once again

$$\begin{aligned}\left[L^2, \left[L^2, z\right]\right] &= 2i\hbar\left(L_y\left[L^2, x\right] - L_x\left[L^2, y\right] + i\hbar\left[L^2, z\right]\right) = -4\hbar^2\left[L_y\,(yL_z - L_y z) - L_x\,(L_x z - xL_z) + \frac{1}{2}\left[L^2, z\right]\right]\\ &= - 4\hbar^2\left[yL_yL_z - L_y^2 z - L_x^2 z + xL_xL_z + \frac{1}{2}\left[L^2, z\right]\right] = 4\hbar^2\left[\left(L_x^2 + L_y^2\right)z - (xL_x + yL_y)\,L_z - \frac{1}{2}\left[L^2, z\right]\right]\\ &= 4\hbar^2\left[L^2 z - (\mathbf{r}\cdot\mathbf{L})\,L_z - \frac{1}{2}\left[L^2, z\right]\right] = 4\hbar^2\left[L^2 z - \frac{1}{2}\left[L^2, z\right]\right]\\ &= 2\hbar^2\left(L^2 z + zL^2\right).\end{aligned}$$

By simple expection, it can be shown that $\mathbf{r}\cdot\mathbf{L} = \mathbf{L}\cdot\mathbf{r} = 0$. The last equation is our desirable result $\left(L^2\right)^2 z - 2L^2 zL^2 + z\left(L^2\right)^2 - 2\hbar^2\left(L^2 z + zL^2\right) = 0$. Thus,

$$\begin{aligned}0 &= \hbar^4\Big(\left[\ell'\,(\ell'+1)\right]^2 - 2\ell\ell'\,(\ell+1)\,(\ell'+1) + \left[\ell\,(\ell+1)\right]^2 - 2\ell'\,(\ell'+1) - 2\ell\,(\ell+1)\Big)\,\langle n', \ell', m' |z| n, \ell, m\rangle\\ 0 &= \hbar^4\left(\mathcal{L}'^2 - 2\mathcal{L}'\,(\mathcal{L}+1) + \mathcal{L}\,(\mathcal{L}-2)\right)\langle n', \ell', m' |z| n, \ell, m\rangle\,.\end{aligned}$$

with $\mathcal{L} = \ell\,(\ell+1)$. Therefore, we conclude that $\langle n', \ell', m' |z| n, \ell, m\rangle \neq 0$ only when $0 = \mathcal{L}'^2 - 2\mathcal{L}'\,(\mathcal{L}+1) + \mathcal{L}\,(\mathcal{L}-2)$, which implies $\ell' = \ell \pm 1$. (The other two solutions are unphysical $\ell' = -\ell$ and $\ell' = -\ell - 2$.)

Finally, there is no selection rule with respect to the principal quantum number n. The radial integral is of type

$$I = \int_0^\infty r^2 \mathrm{d}r \times R^*_{n', \ell'}\, r R_{n, \ell}.$$

Let us pick as an example, the case in which $n' = n$. The simplest case in which there is still a transition, is when $n = 2$, $m' = m = 0$, and $\ell = 0 = \ell' - 1$. In this case,

$$I \propto \int_0^\infty \rho^2 \mathrm{d}\rho \left[\rho e^{-\rho/2}\right] \rho \left[(2-\rho)\, e^{-\rho/2}\right] = 72 \neq 0.$$

Notice this case would violate energy conservation because $E_f - E_i \neq \hbar\omega$. However, the energy conservation is taken care by the time integral yielding to the delta function.

In Sum, the selection rules are

$$\ell' = \ell \pm 1 \text{ and } m' = m,\, m \pm 1.$$

3.

(a) The system can be diagonalized easily by noticing that the spin operators are time independent. Thus the usual singlet-triplet states are the actual Eigenstates. We label them as

$$|s\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right),\; |t_0\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right),\; |t_1\rangle = |++\rangle,\; |t_{-1}\rangle = |--\rangle.$$

Inserting these in the Schrödinger equation

$$H\,|\psi\rangle = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi\rangle\,, \quad \Rightarrow \quad \frac{E\,(t)}{2\hbar^2}\left(S^2 - S_1^2 - S_2^2\right)\sum_k a_k\,(t)\,|k\rangle = i\hbar\sum_k \dot{a}_k\,(t)\,|k\rangle\,,$$

where $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ is the total spin angular momentum, and the vectors $|k\rangle$ labels the singlet and triplet states, we find that

$$-\frac{3}{4}E(t)a_s = i\hbar\dot{a}_s, \text{ and } \frac{1}{4}E(t)a_k = i\hbar\dot{a}_k \text{ for } k = t_{-1,0,1}.$$

The solutions of which are

$$a_s\,(t) = a_s\,(-\infty)\exp\left(\frac{3i}{4\hbar}\int_{-\infty}^t E(t')\mathrm{d}t'\right) \text{ and } a_k\,(t) = a_k\,(-\infty)\exp\left(-\frac{i}{4\hbar}\int_{-\infty}^t E(t')\mathrm{d}t'\right), \text{ for } k = t_{-1,0,1}.$$

As the initial state $(t = -\infty)$ is $|+-\rangle = \frac{1}{\sqrt{2}}\left(|s\rangle + |t_0\rangle\right)$, then, we have that $a_s\,(-\infty) = a_{t_0}\,(-\infty) = \frac{1}{\sqrt{2}}$, and $a_{t_{\pm 1}}\,(-\infty) = 0$. Therefore

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}e^{\frac{3i}{4\hbar}I_t}\,|s\rangle + \frac{1}{\sqrt{2}}e^{-\frac{i}{4\hbar}I_t}\,|t_0\rangle\,,$$

with $I_t = \int_{-\infty}^t E(t')\mathrm{d}t'$. Notice $I = I_\infty$.

Finally, the probability of finding the system in the $|-+\rangle$ state at $t \to \infty$ is

$$P_{\text{exact}} = |\langle -+|\psi\,(\infty)\rangle|^2 = \frac{1}{4}\left|-e^{\frac{3i}{4\hbar}I_\infty} + e^{-\frac{i}{4\hbar}I_\infty}\right|^2 = \frac{1}{4}\left|e^{\frac{i}{4\hbar}I}\left(-e^{\frac{2i}{4\hbar}I} + e^{-\frac{2i}{4\hbar}I}\right)\right|^2 = \sin^2(I/\left(2\hbar\right)).$$

(b)

In first-order of perturbation theory, the probability amplitude of transition is given by

$$c^{(1)}_{f\leftarrow i}(t) = \frac{1}{i\hbar}\int_{-\infty}^t \left\langle -+\left|e^{i\omega_{fi}t}V(t')\right|+-\right\rangle \mathrm{d}t'.$$

Here, because $H_0 = 0$, we have that $\omega_f = \omega_i = 0$. Moreover,

$$\langle -+|V(t')|+-\rangle = \frac{E}{\hbar^2}\left(\left\langle -+\left|\frac{1}{2}S_1^+S_2^- + \text{h.c.}\right|+-\right\rangle + \langle -+|S_1^zS_2^z|+-\rangle\right) = \frac{E}{\hbar^2}\left(\frac{1}{2}\hbar^2 + 0\right).$$

Thus,

$$P_{\text{1st}} = \left|c^{(1)}_{f\leftarrow i}(\infty)\right|^2 = \frac{1}{4\hbar^2}\left|\int_{-\infty}^\infty E(t)\mathrm{d}t\right|^2 = \left(\frac{I}{2\hbar}\right)^2.$$

Comparing with the exact result $P_{\text{exact}} = \sin^2(I/(2\hbar))$, it is straightforward to conclude that first-order of perturbation theory gives a precise answer as long as $I \ll 2\hbar$.

(c) The sencond-order contribution to the probability amplitude is

$$\begin{aligned}
c^{(2)}_{f\leftarrow i}(\infty) &= \left(\frac{1}{i\hbar}\right)^2 \sum_k \int_{-\infty}^{\infty} \mathrm{d}t e^{i\omega_{fk}t} \int_{-\infty}^{t} \mathrm{d}t' e^{i\omega_{ki}t'} \langle -+| V(t) |k\rangle \langle k| V(t') |+-\rangle \\
&= \left(\frac{1}{i\hbar}\right)^2 \sum_k \int_{-\infty}^{\infty} \mathrm{d}t \int_{-\infty}^{t} \mathrm{d}t' \langle -+| V(t) |k\rangle \langle k| V(t') |+-\rangle \\
&= \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{\infty} \mathrm{d}t \int_{-\infty}^{t} \mathrm{d}t' \left(\langle -+| V(t) |+-\rangle \langle +-| V(t') |+-\rangle + \langle -+| V(t) |-+\rangle \langle -+| V(t') |+-\rangle\right) \\
&= \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{\infty} \mathrm{d}t \int_{-\infty}^{t} \mathrm{d}t' \left(\frac{E(t)}{4} \times \frac{E(t')}{2} + \frac{E(t)}{2} \times \frac{E(t')}{4}\right) = \frac{1}{4}\left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{\infty} \mathrm{d}t E(t) \int_{-\infty}^{t} \mathrm{d}t' E(t').
\end{aligned}$$

First, let us discuss the $\tau \to 0$ limit in which we consider $E(t) = \bar{E}\tau\delta(t - t_0)$ where t_0 is the instant around which $E(t) \neq 0$. In this case,

$$\int_{-\infty}^{t} \mathrm{d}t' E(t') \sim \bar{E}\tau\theta\left(t - t_0\right),$$

where $\theta(x)$ is the Heaviside step function. Thus,

$$c^{(2)}_{f\leftarrow i}(\infty) \sim \frac{1}{4\hbar^2} \times \frac{1}{2}\left(\bar{E}\tau\right)^2 \sim \frac{1}{2} \times \left(\frac{I}{2\hbar}\right)^2$$

which is smaller than $c^{(1)}_{f\leftarrow i}(\infty) \sim I/(2\hbar)$.

Now, let us discuss on the $\tau \to \infty$ limit. In this limit, let us say that $E(t) = \bar{E} = \text{const}$. Now we have that

$$\int_{-\infty}^{t} \mathrm{d}t' E(t') \sim \bar{E} \times \left(\min\left\{t, \tau/2\right\} + \frac{1}{2}\tau\right).$$

The probability amplitude can now be estimated as

$$c^{(2)}_{f\leftarrow i}(\infty) \sim \frac{1}{4\hbar^2} \times \left(\bar{E}\tau\right)^2 \sim \left(\frac{I}{2\hbar}\right)^2,$$

which is much greater than $c^{(1)}_{f\leftarrow i}(\infty)$. Notice that in both cases $c^{(2)}_{f\leftarrow i}(\infty) \sim \left(\bar{E}\tau\right)^2$. The

(d) Now consider that both spins are subjected to a static magnetic field $\mathbf{B} = B_0\hat{z}$. The corresponding Zeeman Hamiltonian is

$$H_0 = -\frac{\mu_B}{\hbar} B_0 \left(g_1 S_1^z + g_2 S_2^z\right),$$

where $g_{1,2}$ are the gyromagnetic ratios (assume them distinct from each other). Consider also that $E(t) = \bar{E}\exp\left(-\left(t/\tau\right)^2\right)$. Compute the same probability of the previous itens in first-order of perturbation theory and discuss its dependence on the magnitude B_0.

The only difference from item (b) is due to the fact that $H_0 \neq 0$. As the initial and final states are Eigenvectors of H_0, we have that

$$c_{f\leftarrow i}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} \left\langle -+ \left| e^{i\omega_{fi}t} V(t') \right| +- \right\rangle \mathrm{d}t',$$

with $\hbar\omega_{fi} = E_{-+}^{(0)} - E_{+-}^{(0)} = \mu_B B_0\left((-g_1+g_2)-(g_1-g_2)\right)/2 = \mu_B B_0\left(g_2-g_1\right)$. Therefore,

$$
\begin{aligned}
P_{\rm 1st} &= \frac{1}{4\hbar^2}\left|\int_{-\infty}^{\infty}{\rm d}t e^{i\omega_{fi}t}E(t)\right|^2 = \frac{\bar{E}^2}{4\hbar^2}\left|\int_{-\infty}^{\infty}{\rm d}t e^{-\left(t^2/\tau^2 - i\omega_{fi}t\right)}\right|^2 = \frac{\bar{E}^2}{4\hbar^2}\left|\int_{-\infty}^{\infty}{\rm d}t e^{-\tau^{-2}\left(\left(t-\frac{i}{2}\omega_{fi}\tau^2\right)^2 - \left(\frac{i\omega_{fi}\tau^2}{2}\right)^2\right)}\right|^2 \\
&= \frac{\bar{E}^2}{4\hbar^2}\left|\int_{-\infty}^{\infty}{\rm d}t e^{-\tau^{-2}\left(t-\frac{i}{2}\omega_{fi}\tau^2\right)^2} e^{\tau^{-2}\left(\frac{i\omega_{fi}\tau^2}{2}\right)^2}\right|^2 = \frac{\bar{E}^2}{4\hbar^2}e^{-(\omega_{fi}\tau)^2/2}\left|\int_{-\infty}^{\infty}{\rm d}t e^{-\tau^{-2}\left(t-\frac{i}{2}\omega_{fi}\tau^2\right)^2}\right|^2 \\
&= \frac{\bar{E}^2}{4\hbar^2}e^{-(\omega_{fi}\tau)^2/2}\left|\sqrt{\pi}\tau\right|^2 = \pi\frac{\bar{E}^2}{4\hbar^2}\tau^2 e^{-(\omega_{fi}\tau)^2/2} \sim \left(\frac{I}{2\hbar}\right)^2 e^{-(\omega_{fi}\tau)^2/2}.
\end{aligned}
$$

Notice $P_{\rm 1st}$ is depends strongly on B_0, namely, $P_{\rm 1st} \sim \tau^2\exp\left(-\left(B_0\tau/\alpha\right)^2\right)$ [with $\alpha = \hbar/(\mu_B(g_2-g_1))$]. Bigger B_0, smaller the transition probability. This is because B_0 sets the energy difference between the inital and final states. For small B, we recover the result of item (b) since

In the samme manner, bigger τ also implies smaller $P_{\rm 1st}$. This is because the variation of the perturbation is inversely proportional to τ. In the limit $\tau \to \infty$, it is like the system is extremely slowly perturbed. As a result, no transition takes place. (This is the essence of the Adiabatic theorem.) On the other hand for small τ, we have that $P_{\rm 1st} \sim \tau^2$ which agrees with the fact that $U_I \approx \int V {\rm d}t \sim t$ for small times.

(e) Again, we will have to compute

$$
\begin{aligned}
c_{f\leftarrow i}^{(2)}(\infty) &= \left(\frac{1}{i\hbar}\right)^2\sum_k\int_{-\infty}^{\infty}{\rm d}t e^{i\omega_{fk}t}\int_{-\infty}^{t}{\rm d}t' e^{i\omega_{ki}t'}\left\langle -+\right|V(t)\left|k\right\rangle\left\langle k\right|V(t')\left|+-\right\rangle \\
&= \left(\frac{1}{i\hbar}\right)^2\int_{-\infty}^{\infty}{\rm d}t\int_{-\infty}^{t}{\rm d}t'\left(\left\langle -+\right|V(t)\left|-+\right\rangle\left\langle -+\right|V(t')\left|+-\right\rangle e^{i\omega_{fi}t'} + e^{i\omega_{fi}t}\left\langle -+\right|V(t)\left|+-\right\rangle\left\langle +-\right|V(t')\left|+-\right\rangle\right) \\
&= \frac{1}{8}\left(\frac{1}{i\hbar}\right)^2\left(\int_{-\infty}^{\infty}{\rm d}tE(t)\int_{-\infty}^{t}{\rm d}t' e^{i\omega_{fi}t'}E(t') + \int_{-\infty}^{\infty}{\rm d}tE(t)e^{i\omega_{fi}t}\int_{-\infty}^{t}{\rm d}t'E(t')\right).
\end{aligned}
$$

Again, let us discuss the limits $\tau \to 0$ [$E(t) = \bar{E}\tau\delta(t-t_0)$] and $\tau \to \infty$ [$E(t) = \bar{E}$)]. In the former case,

$$
c_{f\leftarrow i}^{(2)}(\infty) = \frac{1}{8}\left(\frac{1}{i\hbar}\right)^2\left(\bar{E}\tau\right)^2 e^{i\omega_{fi}t_0} \sim \left(\frac{I}{2\hbar}\right)^2,
$$

which is much smaller than the first-order contribution.

In the latter case ($\tau \to \infty$), we have that

$$
\begin{aligned}
c_{f\leftarrow i}^{(2)}(\infty) &= \frac{1}{8}\left(\frac{1}{i\hbar}\right)^2\bar{E}^2\left(\int_{-\tau/2}^{\tau/2}{\rm d}t\int_{-\tau/2}^{t}{\rm d}t'\theta\left(\tau/2-t\right)e^{i\omega_{fi}t'} + \int_{-\tau/2}^{\tau/2}{\rm d}te^{i\omega_{fi}t}\int_{-\tau/2}^{t}\theta\left(\tau/2-t\right){\rm d}t'\right) \\
&= \frac{1}{8}\left(\frac{1}{i\hbar}\right)^2\bar{E}^2\left[\frac{i}{\omega_{fi}^2}\left(\omega_{fi}\tau e^{-i\omega_{fi}\frac{\tau}{2}} - 2\sin\left(\omega_{fi}\frac{\tau}{2}\right)\right) - \frac{i}{\omega_{fi}^2}\left(\omega_{fi}\tau e^{i\omega_{fi}\frac{\tau}{2}} - 2\sin\left(\omega_{fi}\frac{\tau}{2}\right)\right)\right] \\
&= \frac{1}{4}\left(\frac{1}{i\hbar}\right)^2\bar{E}^2\frac{\tau}{\omega_{fi}}\sin\left(\omega_{fi}\frac{\tau}{2}\right),
\end{aligned}
$$

which recovers the result of item (c) when $\omega_{fi} = 0$, i.e., $c_{f\leftarrow i}^{(2)} \sim \left(\bar{E}\tau\right)^2$. However, for $\omega_{fi} \neq 0$, $c_{f\leftarrow i}^{(2)}$ is a rapid oscillatory function which averages out to zero. But how do we compare this result with $c_{f\leftarrow i}^{(1)}$ since we cannot expand the result in item (d) in the limit $\tau \to \infty$? In order to make comparison, let us compute $c_{f\leftarrow i}^{(1)}$ in the same limit $\tau \to \infty$ [$E(t) = \bar{E}$)]:

$$
c_{f\leftarrow i}^{(1)}(\infty) = \frac{1}{i\hbar}\int_{-\infty}^{\infty}{\rm d}te^{i\omega_{fi}t}\left\langle -+\right|V(t')\left|+-\right\rangle = \frac{1}{i\hbar}\frac{\bar{E}}{2}\int_{-\tau/2}^{\tau/2}{\rm d}te^{i\omega_{fi}t} = \frac{1}{i\hbar}\frac{\bar{E}}{\omega_{if}}\sin\left(\omega_{if}\frac{\tau}{2}\right).
$$

Then, we conclude that $c_{f\leftarrow i}^{(1)}(\infty) \ll c_{f\leftarrow i}^{(2)}(\infty)$ as was the case analyzed in item (c).

4.

(a) In first order of perturbation theory, the amplitude probability of transition is

$$c_{f\leftarrow i} = \frac{1}{i\hbar}\int_0^t \mathrm{d}t' \left\langle\varphi_f\right| W(t') \left|\varphi_i\right\rangle e^{i\omega_{fi}t'}.$$

Thus,

$$P_{f\leftarrow i} = \left|c_{f\leftarrow i}\right|^2 = \frac{1}{\hbar^2}\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \left\langle\varphi_f\right| W(t') \left|\varphi_i\right\rangle \left(\left\langle\varphi_f\right| W(t') \left|\varphi_i\right\rangle\right)^* e^{i\omega_{fi}\left(t'-t''\right)}.$$

The transition rate is then

$$w_{f\leftarrow i} = \frac{1}{\hbar^2}\left[\left(W_{fi}(t)e^{i\omega_{fi}t}\right)\int_0^t \mathrm{d}t'' W^*_{fi}(t'')e^{-i\omega_{fi}t''} + \int_0^t \mathrm{d}t' W_{fi}(t')e^{i\omega_{fi}t'}\left(W^*_{fi}(t)e^{-i\omega_{fi}t}\right)\right].$$

Calling $\tau = t - t''$, we find that

$$w_{f\leftarrow i} = \frac{1}{\hbar^2}\left[\int_0^t \mathrm{d}\tau \left(W_{fi}(t)W^*_{fi}(t-\tau)e^{i\omega_{fi}\tau}\right) + \text{c.c.}\right].$$

($b.\alpha$)
We start with the previous result

$$w^{(k)}_{f\leftarrow i}(t) = \frac{1}{\hbar^2}\left[\int_0^t \mathrm{d}\tau \left(W^{(k)}_{fi}(t)W^{(k)*}_{fi}(t-\tau)e^{i\omega_{fi}\tau}\right) + \text{c.c.}\right].$$

Averaging over the many systems, we arrive at

$$\begin{aligned}\pi_{fi}(t) &= \lim_{\mathcal{N}\to\infty}\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}} w^{(k)}_{f\leftarrow i}(t) = \frac{1}{\hbar^2}\left[\int_0^t \mathrm{d}\tau \left(g_{fi}\left(\tau\right)e^{i\omega_{fi}\tau}\right) + \text{c.c.}\right] \\ &= \frac{1}{\hbar^2}\left[\int_0^{\tau_c} \mathrm{d}\tau \left(g_{fi}\left(\tau\right)e^{i\omega_{fi}\tau}\right) + \int_{\tau_c}^t \mathrm{d}\tau \left(g_{fi}\left(\tau\right)e^{i\omega_{fi}\tau}\right) + \text{c.c.}\right].\end{aligned}$$

If $t > \tau_c$, the second integral vanishes and π_{fi} becomes time independent. Thus, we conclude that $t_1 = \tau_c$.
($b.\beta$)
From the previous result,

$$\begin{aligned}\pi_{fi}(t) &= 2\frac{\left|v_{fi}\right|^2}{\hbar^2}\int_0^t \mathrm{d}\tau e^{-\tau/\tau_c}\cos(\omega_{fi}\tau) \\ &= 2\frac{\left|v_{fi}\right|^2}{\hbar^2\left(1+\omega_{fi}^2\tau_c^2\right)}\left[1 + e^{-t/\tau_c}\left[\omega_{fi}\tau_c\sin(\omega_{fi}t) - \cos(\omega_{fi}t)\right]\right]\tau_c.\end{aligned}$$

Thus, for long times $t \gg \tau_c$, π_{fi} becomes time independent, as expected. Moreover, in the limit $\omega_{fi}\tau_c \gg 1$ (but recall $\tau_c \ll t$),

$$\pi_{fi}(t) \approx 2\frac{\left|v_{fi}\right|^2}{\hbar^2\left(1+\omega_{fi}^2\tau_c^2\right)}\tau_c \to \frac{2\pi}{\hbar^2}\left|v_{fi}\right|^2\delta\left(\omega_{fi}\right),$$

which recovers Fermi's golden rule for transition between states in a discrete spectrum.
($b.\gamma$)
We need to go further in perturbation theory:

$$c_{f\leftarrow i} = \frac{1}{i\hbar}\int_0^t \mathrm{d}t' W_{fi}(t')e^{i\omega_{fi}t'} + \frac{1}{2}\left(\frac{1}{i\hbar}\right)^2\sum_j\int_0^t \mathrm{d}t'\int_0^t \mathrm{d}t'' \mathcal{T}\left[W_{fj}(t')W_{ji}(t'')\right]e^{i\left(\omega_{fj}t'+\omega_{ji}t''\right)} + \cdots = I_1 + I_2 + \ldots,$$

where $\mathcal{T}$ is the time ordering operator. Thus,

$$P_{f\leftarrow i} = \left|c_{f\leftarrow i}\right|^2 = \left|I_1\right|^2 + I_1 I_2^* + I_1^* I_2 + \left|I_2\right|^2 = \left|I_1\right|^2\left(1 + \frac{\left|I_2\right|^2}{\left|I_1\right|^2}\right).$$

Notice that we disregarded the cross terms because they average to zero:

$$\overline{I_1 I_2^*} \propto \sum_k \overline{W_{fi}(t) W_{fj}(t') W_{ji}(t'')} = 0,$$

since $\overline{W_{fi}^n(t)} = 0$, for n odd.

For short times, $|I_1|^2 \sim |W_{fi}(0)|^2 \left(\frac{t}{\hbar}\right)^2$ and $|I_2|^2 \sim |W_{fi}(0)|^4 \left(\frac{t}{\hbar}\right)^4$. Thus, for $|I_2|^2 / |I_1|^2 \ll 1$, we have that

$$t \ll t_2 = \frac{\hbar}{|W_{fi}(0)|} \sim \frac{\hbar}{|v_{fi}|}.$$

This is the general result of perturbation theory. Let us now be more specific and use the previous results:

$$\pi_{fi}^{(1)} = 2 \frac{|v_{fi}|^2}{\hbar^2 \left(1 + \omega_{fi}^2 \tau_c^2\right)} \left[1 + e^{-t/\tau_c} f(t)\right] \tau_c,$$

with $f(t) = \omega_{fi}\tau_c \sin(\omega_{fi} t) - \cos(\omega_{fi} t)$. Notice that for $t \ll \tau_c$, then

$$\pi_{fi}^{(1)}(t \ll \tau_c) \sim \frac{|v_{fi}|^2}{\hbar^2} \left(\omega_{fi}\tau_c\right)^2 t.$$

On the other hand, for $t \gg \tau_c$,

$$\pi_{fi}^{(1)}(t \gg \tau_c) \sim \frac{|v_{fi}|^2}{\hbar^2} \tau_c.$$

As we show below, the second-order correction is

$$\pi_{fi}^{(2)}(t \ll \tau_c) \sim \sum_j \frac{|v_{fj}|^2 |v_{ji}|^2}{\hbar^4} t^3 \sim \frac{|v_{fi}|^4}{\hbar^4} t^3, \text{ and } \pi_{fi}^{(2)}(t \gg \tau_c) \sim \sum_j \frac{|v_{fj}|^2 |v_{ji}|^2}{\hbar^4} \tau_c^3 \sim \frac{|v_{fi}|^4}{\hbar^4} \tau_c^3.$$

Therefore, for $t_2 \ll t \ll \tau_c$, there is no guarantee that $\pi_{fi}^{(2)} \ll \pi_{fi}^{(1)}$. However, if $t_2 \gg \tau_c$, then we know that $\pi_{fi}^{(2)}(\tau_c) \ll \pi_{fi}^{(1)}(\tau_c)$. Since both of them becomes constant for $t \gg \tau_c$, i.e., $\pi_{fi}^{(1,2)}(t \gg \tau_c) \approx \pi_{fi}^{(1,2)}(\tau_c)$, then the approximation remains valid for $t \gg t_2$. This will happen in all orders of perturbation theory since

$$\pi_{fi}^{(n)}(t \gg \tau_c) \sim \frac{|v_{fi}|^{2n}}{\hbar^{2n}} \left(\min\{t, \tau_c\}\right)^{2n-1} = t_2^{-2n} \left(\min\{t, \tau_c\}\right)^{2n-1}.$$

Then, for $\tau_c \gg t_2$, the perturbation theory is valid as long as $\pi_{fi}^{(n+1)} \ll \pi_{fi}^{(n)}$, thus $t \ll t_2$. On the other hand for $\tau_c \ll t_2$, then perturbation theory is valid whenever $\tau_c^{2n+1} t_2^{-2n-2} \ll \tau_c^{2n-1} t_2^{-2n}$, which implies that $\tau_c^2 \ll t_2^2$, but this follows from our assumption that $\tau_c \ll t_2$. Therefore, when $\tau_c \ll t_2 \sim \hbar |v_{fi}|^{-1}$, then perturbation theory works for any t. This is illustrated in Fig. 1

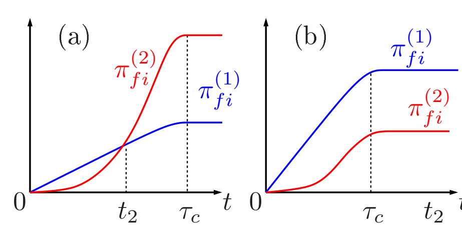

Figure 1: The contributions to the transition rates in first and second order in perturbation theory as a function of time. Case (a) $\tau_c > t_2$, the first order perturbation theory breaks down for $t > t_2$. On the other hand for (b) $\tau_c < t_2$, first order remains valid for any t.

Let us now show that $\pi_{fi}^{(2)}$ has indeed the forementioned behavior. For simplicity, let us consider that W_{if} is real. Thus, $\overline{W_{fi}^{(k)}(t) W_{fi}^{(k)*}(t-\tau)} = g(\tau) = \overline{W_{fi}^{(k)}(t) W_{fi}^{(k)}(t-\tau)}$.

It is useful to write the second-order correction separating real and imaginary parts:

$$
\begin{aligned}
c^{(2)}_{f\leftarrow i} &= \left(\frac{1}{i\hbar}\right)^2 \sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 W_{fj}(t_1) W_{ji}(t_2) e^{i(\omega_{fj}t_1+\omega_{ji}t_2)} \\
&= \left(\frac{1}{i\hbar}\right)^2 \sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \left[\frac{W_{fj}(t_1) W_{ji}(t_2) e^{i(\omega_{fj}t_1+\omega_{ji}t_2)} + W^*_{fj}(t_1) W^*_{ji}(t_2) e^{-i(\omega_{fj}t_1+\omega_{ji}t_2)}}{2}\right] \\
&\quad + \left(\frac{1}{i\hbar}\right)^2 \sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \left[\frac{W_{fj}(t_1) W_{ji}(t_2) e^{i(\omega_{fj}t_1+\omega_{ji}t_2)} - W^*_{fj}(t_1) W^*_{ji}(t_2) e^{-i(\omega_{fj}t_1+\omega_{ji}t_2)}}{2}\right] \\
&= \left(\frac{1}{i\hbar}\right)^2 \left[F_R(t) - F_R(0) + i\left(F_I(t) - F_I(0)\right)\right].
\end{aligned}
$$

Then, the derivative with respect to time becomes simple:

$$
\begin{aligned}
\hbar^4 w^{(2)}_{f\leftarrow i} =& \hbar^4 \frac{\mathrm{d}}{\mathrm{d}t} P^{(2)}_{f\leftarrow i} = 2\left(F_R(t) - F_R(0)\right)\partial_t F_R(t) + 2\left(F_I(t) - F_I(0)\right)\partial_t F_I(t) \\
=& \frac{1}{2}\left(\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 W_{fj}(t_1) W_{ji}(t_2) e^{i(\omega_{fj}t_1+\omega_{ji}t_2)} + W^*_{fj}(t_1) W^*_{ji}(t_2) e^{-i(\omega_{fj}t_1+\omega_{ji}t_2)}\right) \times \\
& \sum_l \int_0^t \mathrm{d}t_3 W_{fl}(t) W_{li}(t_3) e^{i(\omega_{fl}t+\omega_{li}t_3)} + W^*_{fl}(t) W^*_{li}(t_3) e^{-i(\omega_{fl}t+\omega_{li}t_3)} \\
& + \frac{1}{2}\left(\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 W_{fj}(t_1) W_{ji}(t_2) e^{i(\omega_{fj}t_1+\omega_{ji}t_2)} - W^*_{fj}(t_1) W^*_{ji}(t_2) e^{-i(\omega_{fj}t_1+\omega_{ji}t_2)}\right) \times \\
& \sum_l \int_0^t \mathrm{d}t_3 W_{fl}(t) W_{li}(t_3) e^{i(\omega_{fl}t+\omega_{li}t_3)} - W^*_{fl}(t) W^*_{li}(t_3) e^{-i(\omega_{fl}t+\omega_{li}t_3)}.
\end{aligned}
$$

When averaging, the only surviving terms are of two types: direct terms, such as $\overline{W^{(k)}_{fj}(t_1) W^{(k)}_{fl}(t)} = g_{fj}(t_1 - t)\delta_{j,l}$ and $\overline{W^{(k)*}_{ji}(t_2) W^{(k)*}_{li}(t_3)} = g_{ji}(t_2 - t_3)\delta_{j,l}$, and cross terms, such as $\overline{W^{(k)}_{fj}(t_1) W^{(k)*}_{fl}(t)} = g_{fj}(t_1 - t)\delta_{j,l}$, $\overline{W^{(k)}_{ji}(t_2) W^{(k)*}_{li}(t_3)} = g(t_3 - t_2)\delta_{j,l}$. Thus, the cross terms vanish

$$
\begin{aligned}
\hbar^4 \pi^{(2)}_{fi} =& \frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t - t_1) e^{-i\omega_{fj}(t-t_1)} g_{ji}(t_3 - t_2) e^{-i\omega_{ji}(t_3-t_2)} \\
& + \frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t_1 - t) e^{i\omega_{fj}(t-t_1)} g_{ji}(t_3 - t_2) e^{i\omega_{ji}(t_3-t_2)} \\
& - \frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t_1 - t) e^{i\omega_{fj}(t_1-t)} g_{ji}(t_2 - t_3) e^{i\omega_{ji}(t_2-t_3)} \\
& - \frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t - t_1) e^{i\omega_{fj}(t-t_1)} g_{ji}(t_3 - t_2) e^{i\omega_{ji}(t_3-t_2)} \\
=& 0,
\end{aligned}
$$

because $g(\tau) = g(-\tau)$. The direct terms yields to

$$\begin{aligned}
\hbar^4\pi_{fi}^{(2)} =&\frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t-t_1)e^{i\omega_{fj}(t+t_1)}g_{ji}(t_3-t_2)e^{i\omega_{ji}(t_3+t_2)}\\
&+\frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t_1-t)e^{-i\omega_{fj}(t+t_1)}g_{ji}(t_3-t_2)e^{-i\omega_{ji}(t_3+t_2)}\\
&+\frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t_1-t)e^{i\omega_{fj}(t_1+t)}g_{ji}(t_2-t_3)e^{i\omega_{ji}(t_2+t_3)}\\
&+\frac{1}{2}\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t-t_1)e^{-i\omega_{fj}(t+t_1)}g_{ji}(t_3-t_2)e^{-i\omega_{ji}(t_3+t_2)}.\\
=&\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t-t_1)e^{i\omega_{fj}(t+t_1)}g_{ji}(t_3-t_2)e^{i\omega_{ji}(t_3+t_2)}\\
&+\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t-t_1)e^{-i\omega_{fj}(t+t_1)}g_{ji}(t_3-t_2)e^{-i\omega_{ji}(t_3+t_2)}\\
=&2\sum_j \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{fj}(t-t_1)g_{ji}(t_3-t_2)\cos\left(\omega_{fj}\left(t+t_1\right)+\omega_{ji}\left(t_3+t_2\right)\right).
\end{aligned}$$

For $t \ll \tau_c$, we can approximate $g(t) = |v|^2$. In this case, we find that

$$\hbar^4\pi_{fi}^{(2)}(t \ll \tau_c) = \sum_j |v_{fj}|^2 |v_{ji}|^2 \left(t^3 + \mathcal{O}(t^5)\right).$$

On the other hand for $t \gg \tau_c$, we have the following approximation

$$\begin{aligned}
\hbar^4\pi_{fi}^{(2)} =&2\sum_j \int_0^t \mathrm{d}t_1 g_{fj}(t-t_1) \int_0^{t_1} \mathrm{d}t_2 \int_0^t \mathrm{d}t_3 g_{ji}(t_3-t_2)\cos\left(\omega_{fj}\left(t+t_1\right)+\omega_{ji}\left(t_3+t_2\right)\right)\\
\propto&\sum_j \int_0^t \mathrm{d}t_1 g_{fj}(t-t_1) \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 g_{ji}(t_3-t_2)\cos\left(\omega_{fj}\left(t+t_1\right)+\omega_{ji}\left(t_3+t_2\right)\right)\\
=&\sum_j |v_{fj}|^2 |v_{ji}|^2 \tau_c^3 \int_0^x \mathrm{d}x_1 e^{-(x-x_1)} \int_0^{x_1} \mathrm{d}x_2 \int_0^{x_2} \mathrm{d}x_3 e^{-(x_2-x_3)} \cos\left(\tau_c\omega_{fj}\left(x+x_1\right)+\tau_c\omega_{ji}\left(x_3+x_2\right)\right).
\end{aligned}$$

This can be integrated exactly. In the limit $x \to \infty$, it simplifies to

$$\hbar^4\pi_{fi}^{(2)} \propto \sum_j |v_{fj}|^2 |v_{ji}|^2 \tau_c^3 \times f(t, \omega_{ji}, \omega_{fj}),$$

with $f(t, \omega_{ji}, \omega_{fj})$ being a function of $\sin(\omega t)$ and $\cos(\omega t)$, i.e., a function that does not diverges with t in the limit $t \to \infty$.

$(c.\alpha)$

We sketch in Fig. 2 the perturbing magnetic field seen by the particles as a function of time for a given direction. Clearly, the correlation time is set by the adsorption time τ_a. Thus, $\overline{b_x(t)b_x(t-\tau)} \sim e^{-t/\tau_a}$ for $\tau \gg \tau_a$.

Analysing Fig. 2, we can also obtain $\overline{b_x(t)b_x(t)}$. It is simply the mean value of the of all those peaks squared:

$$\frac{\overline{b_x^2} \times \tau_a + 0 \times \tau_v}{\tau_a + \tau_v} \approx \frac{\tau_a}{\tau_v}\overline{b_x^2} = \frac{1}{3}b_0^2\left(\frac{\tau_a}{\tau_v}\right),$$

since $\tau_v \gg \tau_a$, and that $\overline{b_x^2} = \overline{b_y^2} = \overline{b_z^2} = \frac{1}{3}b_0^2$ and $\overline{b_x(t)b_y(t')} = 0$. Therefore, the correlation function of the components of

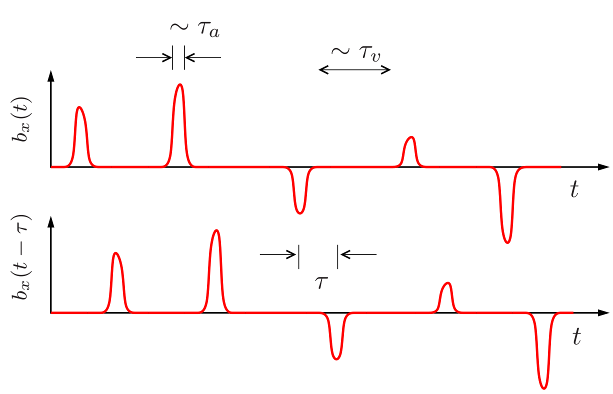

Figure 2: The x-component of the impurity magnetic field as a function of time. Analogous behavior is found for the other directions.

the microscopic magnetic field $\mathbf{b}$ becomes

$$\overline{b_n(t)b_{n'}(t-\tau)} = \frac{1}{3}b_0^2\left(\frac{\tau_a}{\tau_b}\right)e^{-|\tau|/\tau_a}\delta_{n,n'},$$

with $n, n' = x,\, y,\, z$ or any other direction.

$(c.\beta)$

The dimensionless magnetization is given by $M_z = N_\uparrow - N_\downarrow = 2N_\uparrow - \mathcal{N}$, where $\mathcal{N} = N_\uparrow + N_\downarrow$. Then $\dot{M}_z = 2\dot{N}_\uparrow$. The number of up-spins are given by

$$N_\uparrow(t+\mathrm{d}t) = N_\uparrow(t) - N_\uparrow(t)\pi_{\downarrow\uparrow}\mathrm{d}t + N_\downarrow(t)\pi_{\uparrow\downarrow}\mathrm{d}t,$$

where $\pi_{\downarrow\uparrow}$ is the transition rate from the initial state $|\uparrow\rangle$ to the final one $|\downarrow\rangle$. Thus,

$$\dot{N}_\uparrow = -N_\uparrow(t)\pi_{\downarrow\uparrow} + N_\downarrow(t)\pi_{\uparrow\downarrow}.$$

The transition rates can be obtained using the previous results:

$$\pi_{\uparrow\downarrow} = 2\frac{|v_{\uparrow\downarrow}|^2}{\hbar^2\left(1+\omega_{\uparrow\downarrow}^2\tau_c^2\right)}\left[1+e^{-t/\tau_a}\left[\omega_{\uparrow\downarrow}\tau_a\sin(\omega_{\uparrow\downarrow}t) - \cos(\omega_{\uparrow\downarrow}t)\right]\right]\tau_a \to 2\frac{|v_{\uparrow\downarrow}|^2}{\hbar^2\left(1+\omega_{\uparrow\downarrow}^2\tau_a^2\right)}\tau_a,$$

where we used the the interesting regime $t \gg \tau_a$. Notice also that $\pi_{\uparrow\downarrow} = \pi_{\downarrow\uparrow}$, since $\omega_{\uparrow\downarrow} = -\omega_{\downarrow\uparrow} = \gamma B_0 = \omega_0$ and that $|v_{\uparrow\downarrow}|^2 = |v_{\downarrow\uparrow}|^2$. We now need to compute $|v_{\downarrow\uparrow}|^2$. In order to do so, let us give a step back and compute

$$\begin{aligned} w_{\downarrow\leftarrow\uparrow} &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{\hbar^2}\left|\int_0^t \mathrm{d}t' e^{i\omega_{\downarrow\uparrow}t'}\langle\downarrow| - \gamma\mathbf{b}(t)\cdot\mathbf{S}\,|\uparrow\rangle\right|^2 = \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{\hbar^2}\left|\int_0^t \mathrm{d}t' e^{-i\omega_0 t'}\langle\downarrow| - \gamma\left(b_xS_x + b_yS_y\right)|\uparrow\rangle\right|^2 \\ &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{\hbar^2}\left|\int_0^t \mathrm{d}t' e^{-i\omega_0 t'}\left(\frac{-\gamma\hbar}{2}\right)(b_x+ib_y)\right|^2 = \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{\hbar^2}\left|\int_0^t \mathrm{d}t' e^{-i\omega_0 t'}W_{\downarrow\uparrow}(t')\right|^2, \end{aligned}$$

with $W_{\downarrow\uparrow} = -\frac{1}{2}\gamma\hbar\left(b_x(t) + ib_y(t)\right)$. Thus

$$\begin{aligned} \pi_{\downarrow\uparrow} &= \hbar^{-2}\int_0^t \mathrm{d}\tau e^{-i\omega_0\tau}\overline{W_{\downarrow\uparrow}(t)W_{\downarrow\uparrow}^*(t-\tau)} + \text{c.c.} = \frac{\gamma^2}{4}\int_0^t \mathrm{d}\tau e^{-i\omega_0\tau}\overline{\left(b_x(t)+ib_y(t)\right)\left(b_x(t-\tau) - ib_y(t-\tau)\right)} + \text{c.c.} \\ &= \frac{\gamma^2}{4}\int_0^t \mathrm{d}\tau e^{-i\omega_0\tau}\left[\overline{b_x(t)b_x(t-\tau)} + \overline{b_y(t)b_y(t-\tau)}\right] + \text{c.c.} = \hbar^{-2}\int_0^t \mathrm{d}\tau e^{-i\omega_0\tau}g(\tau) + \text{c.c.}, \end{aligned}$$

with $g(\tau) = |v_{\downarrow\uparrow}|^2 e^{-\tau/\tau_a}$, with $|v_{\downarrow\uparrow}|^2 = \frac{\tau_a}{6\tau_v}\left(\hbar\gamma b_0\right)^2$. Finally,

$$\pi_{\uparrow\downarrow} = \pi_{\downarrow\uparrow} = \frac{1}{2T_1} = \frac{|v_{\uparrow\downarrow}|^2}{\hbar^2\left(1+\omega_{\uparrow\downarrow}^2\tau_a^2\right)}\tau_a = \frac{1}{6}\frac{\left(\gamma b_0\tau_a\right)^2}{1+\left(\omega_0\tau_a\right)^2}\left(\frac{1}{\tau_v}\right).$$

Returning the the rate equation

$$\dot{N}_\uparrow = -N_\uparrow(t)\pi_{\downarrow\uparrow} + N_\downarrow(t)\pi_{\uparrow\downarrow} = -\frac{1}{2T_1}\left(N_\uparrow - N_\downarrow\right) = -\frac{M_z}{2T_1}.$$

Therefore,

$$\frac{\mathrm{d}M_z}{\mathrm{d}t} = 2\dot{N}_\uparrow = -\frac{M_z}{T_1},\ \text{with } T_1 = 3\left(\frac{1+\left(\gamma B_0\tau_a\right)^2}{\left(\gamma b_0\tau_a\right)^2}\right)\tau_v.$$

$(c.\gamma)$

Measuring T_1 as a function of B_0, we should find a parabolic behavior such as $T_1 = a_0 + a_1B_0 + a_2B_0^2$, with $a_1 = 0$. Fitting the experimental data, we can determine the coefficients a_0 and a_2. The ratio between them gives us the adsorption time:

$$\frac{a_0}{a_2} = \frac{1}{\left(\gamma\tau_a\right)^2}, \quad \Rightarrow \quad \tau_a = \frac{1}{\gamma}\sqrt{\frac{a_2}{a_0}}.$$

$(c.\delta)$

Cells of different radii R have different time of flights τ_v, which are related via $R = \overline{v}\tau_v$, with $\overline{v} = \sqrt{\frac{8k_BT}{\pi m}}$ being the mean velocity of the particles (which can be obtained from a Maxwell-Boltzmann distribution). Repeat the same experiment done in the previous item, we can measure the coefficients a_0 and a_2 as a function of R:

$$a_0 = \frac{3\overline{v}}{(\gamma b_0 \tau_a)^2} R = \alpha R \text{ and } a_2 = 3\overline{v}\frac{(\gamma\tau_a)^2}{(\gamma b_0\tau_a)^2} R = \beta R.$$

Then, after fitting α and β from the experiments, the microscopic field can be obtained either as

$$b_0 = \frac{1}{\gamma\tau_a}\sqrt{\frac{3\overline{v}}{\alpha}} \text{ or } b_0 = \sqrt{\frac{3\overline{v}}{\beta}}.$$

(Notice the mass of the particles are needed. We can perform the same experiments but changing the temperature in order to obtain precise values for b_0 in the above expressions.)

Notice the exponential decay law here derived is rigorously valid as long as $\tau_c \ll t_2$ [c.f. item (b.γ)]. In this particular case, $\tau_c \approx \tau_a$ and $t_2 \approx 1/(\gamma b_0)$. The results of the experiments in (c.γ) and (c.δ) will permit us to compare these time scales. Specially, from item (c.δ), we notice that $\tau_c/t_2 \approx \tau_a \gamma b_0 = \sqrt{3\overline{v}/\alpha} \sim \sqrt{k_BT/(m\alpha)}$.

5.

(a) Let $E_{\mathbf{K},\alpha}$ be the Eigenenergy for state $|\mathbf{K},\chi_\alpha\rangle$, with $\alpha = a, b$. Then,

$$\Delta E = E_{\mathbf{K}',b} - E_{\mathbf{K},a} = \left(\frac{\hbar^2 K'^2}{2M} + E_b\right) - \left(\frac{\hbar^2 K^2}{2M} + E_a\right) = \frac{\hbar^2}{2M}\left(K'^2 - K^2\right) + \hbar\omega_0.$$

(b)

$$W(t) = -qA_0\left(\frac{1}{m_1}\mathbf{P}_1\cdot\hat{e}e^{i\mathbf{k}\cdot\mathbf{R}_1} - \frac{1}{m_2}\mathbf{P}_2\cdot\hat{e}e^{i\mathbf{k}\cdot\mathbf{R}_2}\right)e^{-i\omega t} + \text{c.c.}$$

We now need the definitions

$$\mathbf{R}_1 = \mathbf{R}_G + \frac{m_2}{M}\mathbf{R},\quad \mathbf{R}_2 = \mathbf{R}_G - \frac{m_1}{M}\mathbf{R},$$
$$\mathbf{P}_1 = \frac{m_1}{M}\mathbf{P}_G + \mathbf{P},\quad \mathbf{P}_2 = \frac{m_2}{M}\mathbf{R}_G - \mathbf{P}.$$

Then, in the electric dipole approximation, we will have that $\exp i\mathbf{k}\cdot\mathbf{R}_1 \approx \exp i\mathbf{k}\cdot\mathbf{R}_2 \approx \exp i\mathbf{k}\cdot\mathbf{R}_G$, yielding

$$\frac{\mathbf{P}_1}{m_1}\cdot\hat{e}e^{i\mathbf{k}\cdot\mathbf{R}_1} - \frac{\mathbf{P}_2}{m_2}\cdot\hat{e}e^{i\mathbf{k}\cdot\mathbf{R}_2} \approx \left[\left(\frac{\mathbf{P}_G}{M} + \frac{\mathbf{P}}{m_1}\right) - \left(\frac{\mathbf{P}_G}{M} - \frac{\mathbf{P}}{m_2}\right)\right]\cdot\hat{e}e^{i\mathbf{k}\cdot\mathbf{R}_G} = \frac{1}{m}\mathbf{P}\cdot\hat{e}e^{i\mathbf{k}\cdot\mathbf{R}_G}.$$

Therefore,

$$W = W_0 e^{-i\omega t} + W_0^\dagger e^{i\omega t},\text{ with } W_0 = -\frac{qA_0}{m}\hat{e}\cdot\mathbf{P}e^{i\mathbf{k}\cdot\mathbf{R}_G}.$$

Notice the negative sign is irrelevant. By interchanging the particle labels, we can make it positive.

(c)

$$\langle\mathbf{K}',\chi_b|W_0|\mathbf{K},\chi_a\rangle = -\frac{qA_0}{m}\hat{e}\cdot\langle\chi_b|\mathbf{P}|\chi_a\rangle\left\langle\mathbf{K}'\left|e^{i\mathbf{k}\cdot\mathbf{R}_G}\right|\mathbf{K}\right\rangle.$$

Notice $\mathbf{P}$ is the momentum of the relative particle and thus, do not acts on the “external” degrees of freedom. We now need to study the “selection rules” arising from $\left\langle\mathbf{K}'\left|e^{i\mathbf{k}\cdot\mathbf{R}_G}\right|\mathbf{K}\right\rangle$:

$$\left\langle\mathbf{K}'\left|e^{i\mathbf{k}\cdot\mathbf{R}_G}\right|\mathbf{K}\right\rangle = \frac{1}{N}\int \mathrm{d}^3 R_G e^{-i\mathbf{K}'\cdot\mathbf{R}_G}e^{i\mathbf{k}\cdot\mathbf{R}_G}e^{i\mathbf{K}\cdot\mathbf{R}_G} \propto \delta^{(3)}\left(\mathbf{K}' - \mathbf{k} - \mathbf{K}\right),$$

where N is a normalization constant. Thus, the transition happens only when momentum is conserved: $\hbar\mathbf{K}' = \hbar\mathbf{k} + \hbar\mathbf{K}$, i.e., the momentum of the final state equals the sum of the momenta of the initial state and that of the absorbed photon.

(d) The resonance occurs when

$$\hbar\omega = E_{\mathbf{K}',b} - E_{\mathbf{K},a} = \frac{\hbar^2}{2M}\left(K'^2 - K^2\right) + \hbar\omega_0, \quad \Rightarrow \quad \delta E = \hbar\left(\omega - \omega_0\right) = \frac{\hbar^2}{2M}\left(K'^2 - K^2\right).$$

Now using the momentum conservation

$$\delta E = \frac{\hbar^2}{2M}\left(2\mathbf{K}\cdot\mathbf{k} + k^2\right) = \frac{\hbar^2}{2M}\left(2\mathbf{K}\cdot\mathbf{k} + \left(\frac{\omega}{c}\right)^2\right) = \delta E_1 + \delta E_2,$$

with $\delta E_1 = \hbar^2 K k \cos\theta / M \approx \hbar^2 \omega_0 K \cos\theta / \left(Mc\right)$, and $\delta E_2 = \left(\hbar\omega\right)^2 / \left(2Mc^2\right) \approx \left(\hbar\omega_0\right)^2 / \left(2Mc^2\right)$.

Physical interpretation:

If the atom were motionless, δ_2 would be the energy acquired by the center of mass of the atom due to momentum conservation: Final momentum equals that of the photon, thus $\mathbf{K}' = \mathbf{k}$. Thus, the energy is $\delta E_2 = \hbar^2 k^2/(2M)$. But the momentum of the photon is related to its frequency by $\omega = ck$. Finaly, $\delta E_2 = \left(\hbar\omega\right)^2 / \left(2Mc^2\right)$, as computed before.

Due to the motion of the atom, the frequency of the photon seen by the atom is different from ω. Due to the Doppler effect, it is equal to $\omega' = \omega\left(c - v_{\text{observer}}\right) / \left(c - v_{\text{source}}\right) = \omega\left(c - \hbar K\cos\theta/M\right)/c$, where $\hbar K \cos\theta / M$ is the velocity of the atom in the direction of the photon, and $v_{\text{source}} = 0$. Thus, $\hbar\omega' = \hbar\omega - \hbar^2\omega K\cos\theta/\left(Mc\right)$. Therefore, the incident energy seen by the atom is less by an amount equal to $\delta E_1 = \hbar\omega - \hbar\omega' = \hbar^2\omega K\cos\theta/(Mc) = \hbar^2 k K \cos\theta / M$. Therefore, there is an offset in the resonance equal to δE_1, as computed before.

For $\hbar\omega_0 = 10\,\text{eV}$ and $M = 10^9\,\text{eV}/c^2$, we have that $\delta E_2 = 5\,10^{-8}\,\text{eV}$. At $T = 300\,\text{K}$, the thermal energy is of order $\frac{1}{2}mv^2 = \frac{\hbar^2 K^2}{2M} = k_B T = 8.6\,10^{-5}\,\text{eV/K} \times 300\,\text{K} = 2.6\,10^{-2}\,\text{eV}$. Then, for $\cos\theta = 1$, we have that $\delta E_1 = \left(\hbar\omega_0\right)\left(\hbar K\right)/\left(Mc\right) = \left(\hbar\omega_0\right)\sqrt{\frac{(\hbar K)^2}{2M}} \times \sqrt{\frac{2}{Mc^2}} = 10\,\text{eV}\sqrt{2.6\,10^{-2}} \times \sqrt{\frac{2}{10^9}} = 7.2\,10^{-5}\,\text{eV}$. Finally, $\delta E_1 \approx 10^3 \delta E_2$.

Repeating the same calculations for $\hbar\omega_0 = 10^5\,\text{eV}$, we have that $\delta E_2 = 5\,\text{eV}$ and $\delta E_1 = 0.72\,\text{eV}$, i.e., $\delta E_1 \approx 10^{-1}\delta E_2$.

In the realm of atomic physics, the Dopple effect is much more relevant than the kinetic effects (recoil energy). On the other hand, in the realm of nuclear physics, the recoil energy cannot be disregarded.

(e) As in item (a),

$$\Delta E = E_{n,0,0,b} - E_{0,0,0,a} = \hbar\left(n\Omega + \omega_0\right) = \hbar\omega_{fi}.$$

(f) We have that $W(t) = W_0 e^{-i\omega t} + \text{h.c.}$, with $W_0 = A_0 S_i(k) e^{ikX_G}$, and $[S_i(k), \mathbf{R}_G] = [S_i(k), \mathbf{P}_G] = 0$. Up to first order in perturbation theory

$$\begin{aligned} P_{f\leftarrow i}(t) =& \frac{1}{\hbar^2}\left|\int_0^t \mathrm{d}t' e^{i\omega_{fi}t'}\left(\langle n,0,0,\chi_b|\, W_0\, |0,0,0,\chi_a\rangle\, e^{-i\omega t'} + \text{c.c}\right)\right|^2 \\ =& \frac{1}{\hbar^2}\left|\langle n,0,0,\chi_b|\, A_0 S_i(k) e^{ikX_G}\, |0,0,0,\chi_a\rangle\right|^2 \left|\int_0^t \mathrm{d}t' e^{i(\omega_{fi}-\omega)t'}\right|^2 \\ &+ \frac{1}{\hbar^2}\left|\langle n,0,0,\chi_b|\, A_0 S_i^\dagger(k) e^{-ikX_G}\, |0,0,0,\chi_a\rangle\right|^2 \left|\int_0^t \mathrm{d}t' e^{i(\omega_{fi}+\omega)t'}\right|^2. \end{aligned}$$

Notice the cross term was neglected because it vanishes in the $t \to \infty$ limit. As we know from the Fermi's golde rule, the time-integrals yields to delta functions at the resonance frequencies: $\omega = \pm\left(n\Omega + \omega_0\right)$. [$\left|\int_0^t \mathrm{d}t' e^{i(\omega_{fi}+\omega)t'}\right|^2 = \frac{\sin^2(\omega_{fi}\mp\omega)t/2}{(\omega_{fi}\mp\omega)^2} \propto \delta\left(\omega_{fi} \mp \omega\right)$.] The negative sign is related to the second term which corresponds to the transition $|0,0,0,\chi_a\rangle \to |n,0,0,\chi_b\rangle$, i.e., the stimulated emission, and therefore, will be neglected. Finally, the relative intensity of the resonances are proportional to

$$\left|\langle n,0,0,\chi_b|\,\frac{A_0}{\hbar^2} S_i(k) e^{ikX_G}\,|0,0,0,\chi_a\rangle\right|^2 \propto \left|\langle\chi_b|\, S_i(k)\,|\chi_a\rangle\right|^2 \left|\langle n,0,0|\, e^{ikX_G}\,|0,0,0\rangle\right|^2 = |s(k)|^2 \left|\langle n,0,0|\, e^{ikX_G}\,|0,0,0\rangle\right|^2.$$

Notice that the resonances occur when $\omega = \omega_{fi} = \left(n\Omega + \omega_0\right)$. For $\omega_0 \gg \Omega$ and for n small (such that $\omega_0 \gg n\Omega$), then the resonance occurs approximately when $\omega = \omega_0$. As the radiation field wavevector is $k = \omega/c$, then it can be replaced by $k_0 = \omega_0/c$.

$(g.\alpha)$

Let us rewrite X_G in terms of the criation and anihillation operators:

$$X_G = \sqrt{\frac{\hbar}{2M\Omega}}\left(a + a^\dagger\right) = \frac{1}{k_0}\sqrt{\frac{\hbar^2 k_0^2}{2M} \times \frac{1}{\hbar\Omega}}\left(a + a^\dagger\right) = \frac{1}{k_0}\sqrt{\xi}\left(a + a^\dagger\right).$$

Moreover, let us make use of the Glauber's formula: $e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}$, whenever $[A,[A,B]] = [B,[A,B]] = 0$. As $\left[a, a^\dagger\right] = 1$, then $\left[i\sqrt{\xi}a, i\sqrt{\xi}a^\dagger\right] = -\xi$. Finally, we are able to compute

$$\begin{aligned}\left\langle \varphi_n \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle &= \left\langle \varphi_n \left| e^{i\sqrt{\xi}\left(a+a^\dagger\right)} \right| \varphi_0 \right\rangle = e^{\frac{\xi}{2}} \left\langle \varphi_n \left| e^{i\sqrt{\xi}a} e^{i\sqrt{\xi}a^\dagger} \right| \varphi_0 \right\rangle \\ &= e^{\frac{\xi}{2}} \sum_{j,l=0}^{\infty} \left\langle \varphi_n \left| \frac{\left(i\sqrt{\xi}a\right)^j}{j!} \times \frac{\left(i\sqrt{\xi}a^\dagger\right)^l}{l!} \right| \varphi_0 \right\rangle.\end{aligned}$$

From this, it is clear that the surviving terms are those in which $l - j = n$. In order to get the correct prefactors, we need

$$\begin{aligned} a^\dagger \left|\varphi_k\right\rangle &= \sqrt{k+1}\left|\varphi_{k+1}\right\rangle, \quad \Rightarrow \quad \left(a^\dagger\right)^l \left|\varphi_0\right\rangle = \sqrt{l!}\left|\varphi_l\right\rangle, \\ a\left|\varphi_k\right\rangle &= \sqrt{k}\left|\varphi_{k-1}\right\rangle, \quad \Rightarrow \quad a^j\left|\varphi_l\right\rangle = \sqrt{\frac{l!}{(l-j)!}}\left|\varphi_j\right\rangle, \text{ provided that } j \le l. \end{aligned}$$

Thus,

$$\begin{aligned}\left\langle \varphi_n \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle &= e^{\frac{\xi}{2}} \sum_{j,l=0}^{\infty} \frac{\left(i\sqrt{\xi}\right)^{l+j}}{j!l!} \sqrt{\frac{l!}{(j-l)!}} \sqrt{l!} \left\langle \varphi_n | \varphi_{l-j} \right\rangle = e^{\frac{\xi}{2}} \sum_{j,l=0}^{\infty} \left(i\sqrt{\xi}\right)^{l+j} \sqrt{\frac{l!}{(j-l)!}} \sqrt{l!}\delta_{n,l-j} \\ &= e^{\frac{\xi}{2}} \sum_{j=0}^{\infty} \frac{\left(i\sqrt{\xi}\right)^{n+2j}}{j!} \sqrt{\frac{1}{n!}} = e^{\frac{\xi}{2}} \frac{\left(i\sqrt{\xi}\right)^n}{\sqrt{n!}} \sum_{j=0}^{\infty} \frac{(-\xi)^j}{j!} = \frac{\left(i\sqrt{\xi}\right)^n}{\sqrt{n!}} e^{-\frac{\xi}{2}}.\end{aligned}$$

Therefore,

$$\pi_n(k_0) = \left|\left\langle \varphi_n \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle\right|^2 = \frac{\xi^n}{n!} e^{-\xi},$$

which is a Poisson distribution.

($g.\beta$) The normalization of the Poisson distribution is verified

$$\sum_{n=0}^{\infty} \pi_n(k_0) = \sum_{n=0}^{\infty} \frac{\xi^n}{n!} e^{-\xi} = e^{+\xi} e^{-\xi} = 1.$$

Notice this result comes from the completeness of the wavefunctions $\langle X_G | \varphi_n \rangle$ and that $e^{ik_0 X_G}$ has modulus 1: $\sum_{n=0}^{\infty} \pi_n(k_0) = \sum_{n=0}^{\infty} \left\langle \varphi_0 \left| e^{-ik_0 X_G} \right| \varphi_n \right\rangle \left\langle \varphi_n \left| e^{ik_0 X_G} \right| \varphi_0 \right\rangle = \langle \varphi_0 | \varphi_0 \rangle = 1$.

($g.\gamma$) The mean energy of the function $e^{ik_0 X_G}$ (shifted by the zero-point energy $\hbar\Omega/2$) is

$$\begin{aligned}\sum_{n=0}^{\infty} n\hbar\Omega\pi_n(k_0) &= \hbar\Omega e^{-\xi} \sum_{n=0}^{\infty} n\frac{\xi^n}{n!} = \hbar\Omega e^{-\xi} \sum_{n=1}^{\infty} \frac{\xi^n}{(n-1)!} = \hbar\Omega e^{-\xi}\xi \sum_{n=1}^{\infty} \frac{\xi^{n-1}}{(n-1)!} \\ &= \hbar\Omega e^{-\xi}\xi \sum_{m=0}^{\infty} \frac{\xi^m}{m!} = \hbar\Omega\xi = \hbar\Omega\left(\frac{\hbar^2 k_0^2}{2M\hbar\Omega}\right) = \frac{\hbar^2\omega_0^2}{2Mc^2},\end{aligned}$$

which is the energy of a free particle of momentum $\hbar k_0$. This should be the case since $e^{ik_0 X_G}\left|\varphi_0\right\rangle$ is the ground state of the 1D Harmonic Oscillator with additional moment k_0. The kinetic part of the Hamiltonian will give this kinetic energy (which should be related to the recoil energy if a photon is absorbed by this oscillator) while the potential part of the Hamiltonian will give $\hbar\Omega/2$ (which was originally shifted out).

(h) The condition $\hbar\Omega \gg \frac{\hbar^2\omega_0^2}{2Mc^2}$ means that the energy of the "internal" degrees of freedom are much less than the energy scale of the center of mass ("external" degrees of freedom). This corresponds to the case $\xi \ll 1$. As we have seen in item (f), the absorption amplitude is proportional to $P_{n\leftarrow 0} \propto |s(k)|^2 \left|\langle n,0,0|\, e^{ikX_G}\, |0,0,0\rangle\right|^2$. Thus, it is proportional to $\pi_n(k_0)$ in 1D. As $\xi \ll 1$, the only relevant transition is to state $n=0$:

$$\pi_n = \frac{\xi^n}{n!}e^{-\xi} \approx \frac{\xi^n}{n!}\left(1-\xi\right),$$

thus, $P_{0\leftarrow 0} \propto 1-\xi \gg P_{1\leftarrow 0} \propto (1-\xi)\,\xi$. Thus, the center of mass remains still, and the energy is totally absorbed by the internal degrees of freedom. This justify the name of the line: recoilless absorption line. This line will be peaked at the absorbed energy. The incident energy is $\hbar\omega$. The internal transition is resonant at $\hbar\omega_0$. The difference between these energies were discussed in item (d): the Doppler effect energy shift, δE_1, and the recoil energy δE_2. As we have just argued, the recoil energy does not appear in the $0 \leftarrow 0$ transition. The Doppler energy shift is also absent because the nucleous is bounded about its equilibrium position. Naively, one could say that the initial momentum of the nucleous is zero, $\mathbf{K}=0$. This directly yields $\delta E_1 = 0$. However, $\mathbf{K}$ is not a good quantum number for the Harmonic Oscillator. The argument is that its mean value is zero. Thefore, the mean value of the shift is approximately zero. The fact that $\left\langle K^2\right\rangle \neq 0$ will provide a width to the resonance line. If the nuleous were in a higher excited state, the width of the line would be broader. Thus, since $\delta E_1 = \delta E_2 = 0$, we conclude the resonance will appear exactly when $\hbar\omega = \hbar\omega_0$.

(i) The limit $\hbar\Omega \ll \frac{\hbar^2\omega_0^2}{2Mc^2}$ (or $\xi \gg 1$) corresponds to the limit in which it is much easier to excite the motion of the center mass of the nucleous than to excite its internal degrees of freedom. Thus, we are simply exciting an 1D Harmonic Oscillator. The spectrum of such is discrete and the distance between consecutive levels are constant equal to $\hbar\Omega$ [as shown in item (e)]. The intensity of this lines are given by π_n. From the properties of the Poisson distribution, we conclude that the highest peak will happen for $\bar{n} \approx \xi$ (the most probable target state $\bar{n}$) and the width of this transition is $\Delta n \approx \sqrt{\xi}$. As $\xi \gg 1$, there will be many equidistant transition lines.

Let us compute the barycenter of the spectrum (shifted by the zero-point energy $\frac{1}{2}\hbar\Omega$):

$$\hbar\overline{\omega} = \sum_{n=0}^{\infty} \hbar\omega_n \pi_n = \sum_{n=0}^{\infty} \hbar n\Omega \times \frac{\xi^n}{n!}e^{-\xi} = \frac{\hbar^2\omega_0^2}{2Mc^2},$$

as we have seen in item (g.γ). This coincides with the absorption line of a free nucleous initially at rest: the recoil energy δE_2 as seen in item (d) and argued in item (g.γ). Notice that we are not considering the frequency ω_0 found in item (e) because we are neglecting a transition between the internal states $|\chi_a\rangle \to |\chi_b\rangle$.

Let us compute the width of these lines:

$$\Delta\omega = \sqrt{\overline{\omega^2} - \overline{\omega}^2}.$$

We need to compute

$$\sum_{n=0}^{\infty} n^2 \frac{\xi^n}{n!}e^{-\xi} = \sum_{n=1}^{\infty} n\frac{\xi^n}{(n-1)!}e^{-\xi} = e^{-\xi}\sum_{j=0}^{\infty}(j+1)\,\frac{\xi^{j+1}}{j!} = e^{-\xi}\xi\left(\sum_{j=1}^{\infty}\frac{\xi^j}{(j-1)!} + \sum_{j=1}^{\infty}\frac{\xi^j}{j!}\right) = \xi\left(\xi+1\right).$$

Therefore,

$$\Delta\omega = \hbar\Omega\sqrt{\xi^2+\xi-(\xi)^2} = \hbar\Omega\sqrt{\xi} = \sqrt{\frac{\hbar^2\omega_0^2}{2Mc^2}\times\hbar\Omega}.$$

Notice the line width $\Delta\omega \to 0$ in the limit $\Omega \to 0$. This limit corresponds to a free nucleous (no potential energy). Thus, we expect a single resonance at the free energy particle $\hbar\overline{\omega}$.

6.

Firstly, let us focus on the static problem. The Hamiltonian reads

$$H = \frac{1}{2m}P^2 + V(x),$$

where $V(x)$ is perturbative. The Eigenfunctions of H_0 are plane waves: $\langle x|k\rangle = \varphi_k(x) = e^{ikx}/\sqrt{L}$, where L (which will be set to infinity later) is the size of the 1D box containing the particle. Using periodic boundary conditions, we have that $e^{ikL}=1$, and thus, $k_n = 2\pi n/L$, with $n \in \mathbb{Z}$. Since V is periodic, we can write its Fourier series:

$$V(x) = \sum_n V_n e^{in\kappa x},\ \text{with}\ \kappa = \frac{2\pi}{a},\ \text{and}\ V_n = \langle k+n\kappa\,|V(x)|\,k\rangle = \frac{1}{L}\int \mathrm{d}x V(x)e^{-in\kappa x}. \tag{3}$$

The dispersion relation is simple: $H_0 |k\rangle = \epsilon_k |k\rangle$, with $\epsilon_k = \hbar^2 (k - n\kappa)^2 / (2m)$. Thus, there is degeneracy around the points $k = n\kappa/2$ (the boarders of the Brillouin zones) (see Fig. 3).

Lets apply quasi-degenerate perturbation theory. The main idea is to solve exactly the quasi-degenerate states while applying conventional perturbation theory for the remaining states. Denoting by $|i\rangle$ the Eigenvectors of H_0, we rewritte the perturbation as

$$V = \sum_{i,j} |i\rangle \langle i| V |j\rangle \langle j| = V_1 + V_2,$$

where

$$\begin{aligned} V_1 &= |n\rangle \langle n| V |n\rangle \langle n| + |n\rangle \langle n| V |m\rangle \langle m| \\ &\quad + |m\rangle \langle m| V |n\rangle \langle n| + |m\rangle \langle m| V |m\rangle \langle m| , \\ V_2 &= \sum_{i,j\neq m,n} |i\rangle \langle i| V |j\rangle \langle j| , \end{aligned}$$

where $|m\rangle$ and $|n\rangle$ are the quasi-degenerate states, i.e., $\epsilon_n \approx \epsilon_m$. We now treat the subspace spanned by $|m\rangle$ and $|n\rangle$ in the best way possible (exactly, for instance) while treating the remaining Hilbert space approximately. This means we treat $H' = H_0 + V_1$ exactly because V_2 does not acts on this subspace: $\langle n |V_2| n\rangle = \langle n |V_2| m\rangle = \langle m |V_2| n\rangle = \langle m |V_2| m\rangle = 0$. Thus, the corresponding matrix of H' in this subspace reads

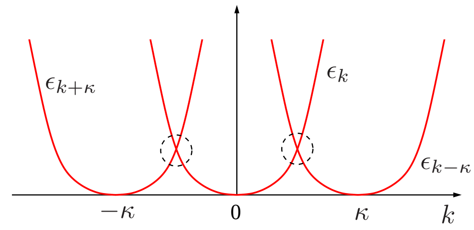

Figure 3: The dispersion relation of a free particle in a periodic potential. Degeneracies happen whenever the parabolas meet.

$$H' = \begin{pmatrix} \epsilon_n + \langle n |V| n\rangle & \langle n |V| m\rangle \\ \langle m |V| n\rangle & \epsilon_m + \langle m |V| m\rangle \end{pmatrix} = \begin{pmatrix} \epsilon_n + V_{nn} & V_{nm} \\ V_{mn} & \epsilon_m + V_{mm} \end{pmatrix},$$

which can be easily diogonalized. The new Eigenenergies are

$$\epsilon_\pm = \frac{\epsilon_m + \epsilon_n}{2} + \frac{V_{nn} + V_{mm}}{2} \pm \sqrt{\left(\frac{\epsilon_n + V_{nn} - \epsilon_m - V_{mm}}{2}\right)^2 + |V_{mn}|^2}.$$

Notice that when $\epsilon_m = \epsilon_n$, this recovers the the usual first order of degenerate perturbation theory.

(a) Let us now consider the vector potential:

$$H_0 = \frac{1}{2m} (p - eA)^2 , \text{ with } A(t) = -Et.$$

Assuming that $A(t)$ varies slowly in time, then we can apply the addiabatic approximation. The instanteneous basis $|k\rangle$ remains the same:

$$\langle x|k\rangle \varphi(x) = \frac{1}{\sqrt{L}} e^{ikx}.$$

However, its spectrum becomes time-dependent $\epsilon_{k-\kappa} = \frac{\hbar^2}{2m} (k - \kappa - eA/\hbar)^2$, as we show below:

$$\begin{aligned} H_0 |k\rangle &= \frac{1}{2m} \left(p^2 - 2eAp + (eA)^2\right) |k\rangle = \frac{1}{2m} \left(\hbar^2 k^2 - 2\hbar eAk + (eA)^2\right) |k\rangle \\ &= \frac{\hbar^2}{2m} \left(k - \frac{eA(t)}{\hbar}\right)^2 |k\rangle . \end{aligned}$$

We are now able to study the quasi-degenerate pertubation theory of state $|k\rangle$ and $|k - \kappa\rangle$ around $k = \frac{1}{2}\kappa$. We will have to diagonalize the matrix

$$H' = \begin{pmatrix} \epsilon_k + V_0 & V_1^* \\ V_1 & \epsilon_{k-\kappa} + V_0 \end{pmatrix},$$

where $V_n = \langle k + j\kappa |V| k + (j + n) \kappa\rangle = \frac{1}{L} \int \mathrm{d}x e^{in\kappa} V(x)$ [see Eq. (3)]. The Eigenenergies are

$$E_\pm = \frac{\epsilon_k + \epsilon_{k-\kappa}}{2} + V_0 \pm \sqrt{\left(\frac{\epsilon_k - \epsilon_{k-\kappa}}{2}\right)^2 + |V_1|^2}.$$

As we are interested near the degenerate point, set $q = k - \frac{1}{2}\kappa$, the momentum measured from the Brillouin zone. Thus,

$$E_{\pm} = \frac{\epsilon_k + \epsilon_{k-\kappa}}{2} + V_0 \pm \sqrt{\left(\frac{\hbar^2}{2m}\left(q - \frac{eA}{\hbar}\right)\kappa\right)^2 + |V_1|^2}.$$

Therefore, there is a level splitting around the $n\frac{\kappa}{2}$ points as shown in Fig. 4. The arising gap Δ equals $E_+ - E_-$ when $q = 0$, i.e., $\Delta = \sqrt{|V_1|^2 + \left(\frac{\hbar^2}{2m}\frac{eA}{\hbar}\kappa\right)^2}$.

The Eigenstates are the Eigenvectors of H':

$$|+\rangle = \alpha\,|k\rangle + \beta\,|k-\kappa\rangle\,, \text{ and } |-\rangle = \beta\,|k\rangle - \alpha\,|k-\kappa\rangle\,,$$

which have cumbersome expressions. However, at $k = \frac{1}{2}\kappa$, notice $\epsilon_k = \epsilon_{k-\kappa}$, The expressions simplify yielding to

$$|\pm\rangle = \frac{1}{\sqrt{2}}\left(|k\rangle \pm |k-\kappa\rangle\right).$$

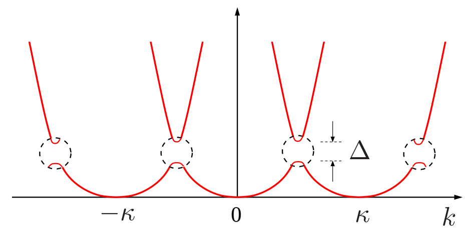

Figure 4: The dispersion relation of a free particle in a periodic potential. Degeneracies are lifted around the Brillouin zones.

(b)

The adiabatic Eigenstates are the instantaneous Eigenstates multiplied by the dynamical phase (there is no Berry phase since $\partial_t\,|k\rangle = 0$):

$$\left|\tilde{\pm}\right\rangle = e^{\frac{1}{i\hbar}\phi_{\pm}(t)}\,|\pm\rangle\,.$$

The dynamical phases at $k = \frac{1}{2}\kappa$ ($q = 0$) are

$$\begin{aligned}\phi_{\pm}(t) &= \int_0^t \mathrm{d}t' E_{\pm}(t') = \int_0^t \mathrm{d}t' \frac{\hbar^2}{2m}\left(\frac{1}{4}\kappa^2 + \left(\frac{eEt'}{\hbar}\right)^2\right) + V_0 \pm \sqrt{\left(\frac{\hbar^2}{2m}\left(\frac{eEt'}{\hbar}\right)\kappa\right)^2 + |V_1|^2}.\\ &= \frac{\hbar^2}{2m}\left(\frac{1}{4}\kappa^2 t + \frac{1}{3}\left(\frac{eE}{\hbar}\right)^2 t^3\right) + V_0 t \pm \int_0^t \mathrm{d}t' \sqrt{\left(\frac{\hbar^2}{2m}\left(\frac{eEt'}{\hbar}\right)\kappa\right)^2 + |V_1|^2}.\end{aligned}$$

The last integral is cumbersome but we will not need it in what follows.

(c)

The transition should happen where the distance between the lower and uper bands is smallest. Thus, at $k = \frac{1}{2}\kappa$. In first order of adiabatic perturbation theory, we have that

$$P_{+\leftarrow -}(t) = \left|\int_0^t \mathrm{d}t' \frac{\left\langle \tilde{+}\left|\dot{H}(t')\right|\tilde{-}\right\rangle}{E_+(t') - E_-(t')}\right|^2.$$

The matrix element

$$\left\langle \tilde{+}\left|\dot{H}(t')\right|\tilde{-}\right\rangle = e^{\frac{i}{\hbar}(E_+ - E_-)}\left\langle + \left|\frac{1}{m}\left(p - eA\right)\left(-e\dot{A}\right)\right| - \right\rangle = e^{\frac{i}{\hbar}(\phi_+ - \phi_-)}\frac{eE}{m}\left\langle + |p| - \right\rangle.$$

We now have to compute

$$\begin{aligned}\langle + |p| - \rangle &= \frac{1}{2}\left(\left\langle \frac{1}{2}\kappa\,|p|\,\frac{1}{2}\kappa\right\rangle + \left\langle -\frac{1}{2}\kappa\,|p|\,\frac{1}{2}\kappa\right\rangle - \left\langle \frac{1}{2}\kappa\,|p| - \frac{1}{2}\kappa\right\rangle - \left\langle -\frac{1}{2}\kappa\,|p| - \frac{1}{2}\kappa\right\rangle\right)\\ &= \frac{1}{2}\left(\frac{1}{2}\hbar\kappa + 0 - 0 - \left(-\frac{1}{2}\hbar\kappa\right)\right) = \frac{1}{2}\hbar\kappa.\end{aligned}$$

Thus,

$$P_{+\leftarrow -}(t) = \left(\frac{eE}{2m}\hbar\kappa\right)^2 \left|\int_0^t \mathrm{d}t' \frac{\exp\left[\frac{i}{\hbar}\left(2V_0 t' + m\left(\frac{1}{4}\kappa^2 t' + \frac{1}{3}\left(\frac{eE}{\hbar}\right)^2 t'^3\right)\right)\right]}{\frac{\hbar^2}{m}\left(\frac{1}{4}\kappa^2 + \left(\frac{eEt'}{\hbar}\right)^2\right) + 2V_0}\right|^2.$$

For small time and electric field, i.e., $eEt \ll \hbar\kappa, \sqrt{mV_0}$, then we can approximate the integral to

$$P_{+\leftarrow-}(t) \approx \left(\frac{eE}{2m}\hbar\kappa\right)^2 \left|\int_0^t \mathrm{d}t' \frac{\exp\left[\frac{i}{\hbar}(\Delta t)\right]}{\Delta}\right|^2 = \left(\frac{eE}{2m}\hbar\kappa\right)^2 \left|2\frac{\hbar}{\Delta^2}\sin(\omega t)\right|^2,$$

where $\Delta = 2\left(\frac{\hbar^2\mathcal{K}^2}{2m} + V_0\right)$, where $\mathcal{K} = \frac{1}{2}\kappa$, and $\hbar\omega = \Delta$. Finally,

$$P_{+\leftarrow-}(t) \approx \frac{4\hbar^2}{\Delta^4}\left(\frac{eE}{2m}\hbar\kappa\right)^2 \sin^2\omega t.$$