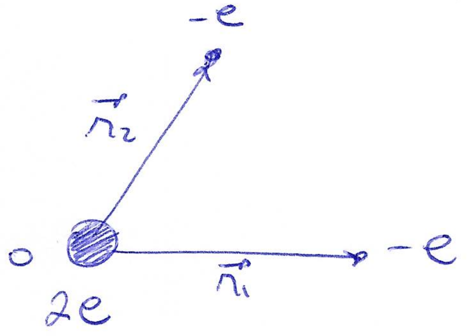
THE HELIUM ATOM



$$H_0 = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2}$$

$$= H_{01} + H_{02}$$

$$W = \frac{+e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

UNPERTURBED H_0:

$$E^{(0)}_{n_1 l_1 m_1, n_2 l_2 m_2} = E^{(0)}_{n_1 l_1 m_1} + E^{(0)}_{n_2 l_2 m_2}$$

WHERE $$E^{(0)}_{nlm} = \frac{-Z^2 e^2}{2(4\pi\epsilon_0) a_0 n^2} = -\frac{Z^2}{2}\alpha^2 \frac{mc^2}{n^2} = -\frac{2\alpha^2 mc^2}{n^2}$$

$$\simeq -\frac{54{,}4\,eV}{n^2}$$

FOR THE HELIUM ATOM, $Z=2$

$\alpha \simeq \frac{1}{137}$ ≡ FINE STRUCTURE CONSTANT $= \frac{e^2}{4\pi\epsilon_0 \hbar c}$

$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = \frac{\hbar}{mc}\frac{1}{\alpha}$ = BOHR RADIUS

THUS,

GROUND STATE : $E_{GS}^{(0)} = E_{100,100}^{(0)} \cong -108.8\,eV$

1^{st} EXCITED STATE : $E_1^{(0)} = E_{200,100}^{(0)} \cong -68\,eV$

PERTURBATION THEORY

- GROUND STATE

$$\Delta E_{GS}^{(1)} = \langle W \rangle_{GS} = \langle 100,100 | \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} | 100,100 \rangle$$

$$\langle \vec{r} | 100 \rangle = R_{10}(r) \underbrace{Y_{00}(\theta,\phi)}_{1/\sqrt{4\pi}}$$

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-\frac{1}{2}\rho} \rho^l L_{n+l}^{2l+1}(\rho)$$

WHERE $\rho = \frac{2Z}{na_0} r$

LAGUERRE POLYNOMIALS : $L_p^q = \frac{d^q}{d\rho^q} L_p(\rho)$

$$L_p(\rho) = e^\rho \frac{d^p}{d\rho^p}(\rho^p e^{-\rho})$$

$$\Rightarrow \begin{cases} R_{10} = \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2 e^{-\frac{Zr}{a_0}} \\ R_{20} = \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \\ R_{21} = \left(Z/2a_0\right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-\frac{Zr}{2a_0}} \end{cases}$$

$$\Rightarrow \Delta E_{G.S}^{(1)} = \int d\vec{r}_1 \int d\vec{r}_2 \; \frac{Z^6}{a_0^6} \frac{2^4}{(4\pi)^2} e^{-2Z\frac{(r_1+r_2)}{a_0}} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

NOW, WE USE THAT

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\gamma}} = \sum_{\ell=0}^{\infty} \frac{r_<^{\ell}}{r_>^{\ell+1}} P_\ell(\cos\gamma)$$

AND $$P_\ell(\cos\gamma) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell m}^*(\theta_1 \phi_1) Y_{\ell m}(\theta_2 \phi_2)$$

• ANGULAR INTEGRATION: $$\int Y_{\ell m}(\theta_i, \phi_i) d\Omega_i =$$

$$= \sqrt{4\pi} \int Y_{00}^*(\theta_i \phi_i) Y_{\ell m}(\theta_i \phi_i) d\Omega_i$$

$$= \sqrt{4\pi}\, \delta_{\ell 0}\, \delta_{m 0}$$

$$\Rightarrow \Delta E_{G.S}^{(1)} = \frac{Z^6}{\pi^2 a_0^6} \iint dr_1 dr_2 \; r_1^2 r_2^2 \; e^{-\frac{2Z(r_1+r_2)}{a_0}} \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{r_>} \; 4\pi \left(\sqrt{4\pi}\right)^2$$

$$= \frac{(4\pi)^2 Z^6}{\pi^2 a_0^6} \left(\frac{e^2}{4\pi\epsilon_0}\right) \int_0^\infty \left[\int_0^{r_1} e^{-\frac{2Z(r_1+r_2)}{a_0}} \frac{r_2^2 dr_2}{r_1} + \int_{r_1}^\infty e^{-\frac{2Z(r_1+r_2)}{a_0}} \frac{r_2^2 dr_2}{r_2} \right] r_1^2 dr_1$$

$$= \frac{(4\pi)^2 Z^6}{\pi^2 a_0^6} \left(\frac{e^2}{4\pi\epsilon_0}\right) \int_0^\infty a_0^2 \, e^{-\frac{4Zr_1}{a_0}} \frac{r_1 \left[a_0 \left(e^{\frac{2Zr_1}{a_0}} - 1\right) - Z r_1 \right]}{4 Z^3} dr_1$$

$$= \frac{(4\pi)^2 Z^6}{\pi^2 a_0^6} \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{5 a_0^5}{128 Z^5} = \frac{(4\pi)^2}{\pi^2} \frac{5Z}{128} \left(\frac{e^2}{4\pi\epsilon_0 a_0}\right)$$

THUS,

$$\Delta E_{GS}^{(1)} = \frac{5Z}{4}\left(\frac{e^2}{2\times 4\pi\varepsilon_0 a_0}\right)$$

$$= \frac{5Z}{4}\left(\frac{\alpha^2 mc^2}{2}\right) \simeq \frac{5Z}{4}(13.6\,eV)$$

$$= 34\,eV$$

$\Rightarrow \boxed{E_{GS} \simeq -74.8\,eV}$ <u>PHYSICAL STATE</u> : $|100,100\rangle \otimes \underbrace{\left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}\right)}_{\text{SINGLET}}$

EXPERIMENTAL VALUE $\simeq -78.8\,eV$

NOW, <u>PERTURBATION THEORY ON THE EXCITED STATE</u>

CONSIDER THE GENERIC CASE IN WHICH ~~THE~~

THE DEGENERATE STATES ARE

$|n_1\{l_1 m_1\}, n_2\{l_2 m_2\}\rangle$ AND $|n_2\{l_2 m_2\}, n_1\{l_1 m_1\}\rangle$

THE UNPERTURBED ENERGY IS $-\frac{Z^2}{2}\alpha^2 mc^2\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$

THE GENERIC MATRIX ELEMENT IS

$$\langle n_1 l_1 m_1, n_2 l_2 m_2 | W | n_1' l_1' m_1', n_2' l_2' m_2'\rangle$$

SUCH THAT $(n_1, n_2) = (n_1', n_2')$ OR (n_2', n_1')

THE ANGULAR INTEGRATION

$$\int d\Omega_1\, d\Omega_2\; Y^*_{l_1m_1}(\theta_1\phi_1)\, Y^*_{l_2m_2}(\theta_2\phi_2) \sum_{l=0}^{\infty} P_l(\cos\gamma)\, Y_{l_1'm_1'}(\theta_1\phi_1)\, Y_{l_2'm_2'}(\theta_2\phi_2)$$

$$\downarrow$$

$$\frac{4\pi}{(2l+1)} \sum_{m=-l}^{l} Y^*_{lm}(\theta_1\phi_1)\, Y_{lm}(\theta_2\phi_2)$$

$$\Rightarrow \sum_{l}\sum_{m}\left(\frac{4\pi}{2l+1}\right)\left(\int d\Omega_1\, Y^*_{l_1m_1}\, Y^*_{lm}\, Y_{l_1'm_1'}\right)\left(\int d\Omega_2\, Y^*_{l_2m_2}\, Y_{lm}\, Y_{l_2'm_2'}\right)$$

SINCE $Y_{lm} \propto e^{im\phi} \Rightarrow$ SELECTION RULE : $\begin{cases} m_1 + m = m_1' \\ m_2 = m + m_2' \end{cases}$

THUS, $m = m_1' - m_1 = m_2 - m_2'$

$$\Rightarrow \boxed{m_1' + m_2' = m_1 + m_2}$$

ACTUALLY, IT IS KNOWN THAT

$$\int Y_{l_1m_1}\, Y_{l_2m_2}\, Y_{l_3m_3}\, d\Omega = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

WIGNER 3J SYMBOLS

WHICH IS FINITE

WHEN $m_1+m_2+m_3=0$

- CLEARLY, THE GENERAL MATRIX ELEMENT BECOMES INVOLVING TO DEAL WITH.

- FOR SIMPLICITY, THEN LET US CONSIDER THE SPECIAL CASE ~~IN~~ WHICH ONE OF THE STATES IS THE 100

THE DEGENERATE MULTIPLET IS THUS ⑥

$\{ |100, n\ell m\rangle , |n\ell m, 100\rangle \}$

• $\langle 100\, n\ell_2 m_2 | W | 100\, n\ell_2' m_2' \rangle$

THE ANGULAR INTEGRATION INVOLVES

* $\int d\Omega_1\, Y_{100}^* Y_{\ell m}^* Y_{100} = \frac{1}{\sqrt{4\pi}} \delta_{\ell,0} \delta_{m,0}$

* $\int d\Omega_2\, Y_{\ell_2 m_2}^* Y_{\ell m} Y_{\ell_2' m_2'} \to \int d\Omega_2 \frac{Y_{\ell_2 m_2} Y_{\ell_2' m_2'}}{\sqrt{4\pi}} = \frac{\delta_{\ell_2\ell_2'} \delta_{m_2 m_2'}}{\sqrt{4\pi}}$

$\Rightarrow \langle W \rangle = 4\pi \times \frac{1}{\sqrt{4\pi}} \times \frac{1}{\sqrt{4\pi}} \times$ RADIAL INTEGRATION $\times \delta_{\ell_2\ell_2'} \delta_{m_2 m_2'}$

$= \int dr_1\, r_1^2 \int dr_2\, r_2^2\, R_{10}^*(r_1) R_{10}(r_1) \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{1}{r_>} R_{n\ell_2}^*(r_2) R_{n\ell_2'}(r_2)\, \delta_{\ell_2\ell_2'} \delta_{m_2 m_2'}$

$= I_{n\ell_2} \delta_{\ell_2\ell_2'} \delta_{m_2 m_2'}$

• $\langle n\ell_1 m_1, 100 | W | n\ell_1' m_1', 100 \rangle = I_{n\ell_1} \delta_{\ell_1\ell_1'} \delta_{m_1 m_1'}$

(JUST LIKE ABOVE)

• $\langle 100, n\ell_2 m_2 | W | n\ell_1 m_1, 100 \rangle$

THE ANGULAR INTEGRATION INVOLVES

* $\int d\Omega_1\, Y_{00}^* Y_{\ell m}^* Y_{\ell_1 m_1} = \frac{1}{\sqrt{4\pi}} \delta_{\ell,\ell_1} \delta_{m,m_1}$

* $\int d\Omega_2\, Y_{\ell_2 m_2}^* Y_{\ell m} Y_{00} = \frac{1}{\sqrt{4\pi}} \delta_{\ell,\ell_2} \delta_{m,m_2}$

$$\Rightarrow \langle W \rangle = \frac{4\pi}{2l_1+1} \times \frac{1}{\sqrt{4\pi}} \times \frac{1}{\sqrt{4\pi}} \times \text{RADIAL INTEGRATION} \times \delta_{l_1 l_2}\, \delta_{m_1 m_2}$$

$$= \frac{\delta_{l_1 l_2}\,\delta_{m_1 m_2}}{2l_1+1} \int dr_1 dr_2\, r_1^2 r_2^2\, R_{10}^*(r_1)\, R_{nl_1}^*(r_2) \left(\frac{e^2}{4\pi\epsilon_0}\right) \frac{r_>^{l_1}}{r_<^{l_1+1}}\, R_{nl_1}(r_1)\, R_{10}(r_2)$$

$$= J_{nl_1}\, \delta_{l_1 l_2}\, \delta_{m_1 m_2}$$

NOW, WE CAN WRITE DOWN THE PERTURBATION W ONTO THE DEGENERATE MULTIPLET.

BECAUSE OF THE KRONECKER DELTAS, THE STATES ARE CONNECTED IN A SIMPLER FORM, i.e., THE MATRIX W IS BLOCK DIAGONAL WITH 2×2 BLOCKS

$$\begin{array}{c|c|c} & |100\, nlm\rangle & |nlm\, 100\rangle \\ W_{nlm} = & \begin{pmatrix} I_{nl} & J_{nl} \\ J_{nl} & I_{nl} \end{pmatrix} & \begin{array}{l} \langle 100\, nlm| \\ \langle nlm\, 100| \end{array} \end{array}$$

FOR THE CASE $n=2$, THE SET OF STATES IS

$\{ |100\,200\rangle, |200\,100\rangle; |100,210\rangle, |210\,100\rangle, |100\,211\rangle, |211\,100\rangle, |100\,21{-1}\rangle, |21{-1}\,100\rangle \}$

(8 STATES IN TOTAL)

$$\Rightarrow W = \begin{array}{cccc} 1S\,2S & 1S\,2p\,(m=0) & 1S\,2p\,(m=1) & 1S\,2p\,(m=-1) \end{array}$$
$$\begin{pmatrix} \begin{matrix} I_{20} & J_{20} \\ J_{20} & I_{20} \end{matrix} & 0 & 0 & \\ 0 & \begin{matrix} I_{21} & J_{21} \\ J_{21} & I_{21} \end{matrix} & 0 & 0 \\ & 0 & \begin{matrix} I_{21} & J_{21} \\ J_{21} & I_{21} \end{matrix} & \\ & & & \ddots \end{pmatrix}$$

WE GET IDENTICAL BLOCKS WHEN ℓ IS THE SAME,

i.e., THE BLOCK $\begin{pmatrix} I_{n\ell} & J_{n\ell} \\ J_{n\ell} & I_{n\ell} \end{pmatrix}$

APPEARS $2\ell+1$ TIMES (FOR EACH m)

FOR THE $|1s\ 2s\rangle$ STATES ($|1s\ 2s\rangle$ AND $|2s\ 1s\rangle$)

THE DEGENERACY IS SPLITTED AS

$$\begin{array}{c|cc} & |1s\ 2s\rangle & |2s\ 1s\rangle \\ \langle 1s\ 2s| & I_{20} & J_{20} \\ \langle 2s\ 1s| & J_{20} & I_{20} \end{array} \Rightarrow \frac{1}{\sqrt{2}}\left(|1s\ 2s\rangle \pm |2s\ 1s\rangle\right)$$

WITH ENERGIES $I_{20} \pm J_{20}$

THESE ARE SYMMETRIC AND ANTI-SYMMETRIC STATES.

NOW, WE HAVE TO CONSIDER ONLY <u>PHYSICAL</u> STATES.

THESE 2 e's ARE IDENTICAL SPIN-1/2 FERMIONS,

THUS, $\frac{1}{\sqrt{2}}\left(|1s\ 2s\rangle + |2s\ 1s\rangle\right) \otimes \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}\right)$ (SINGLET)

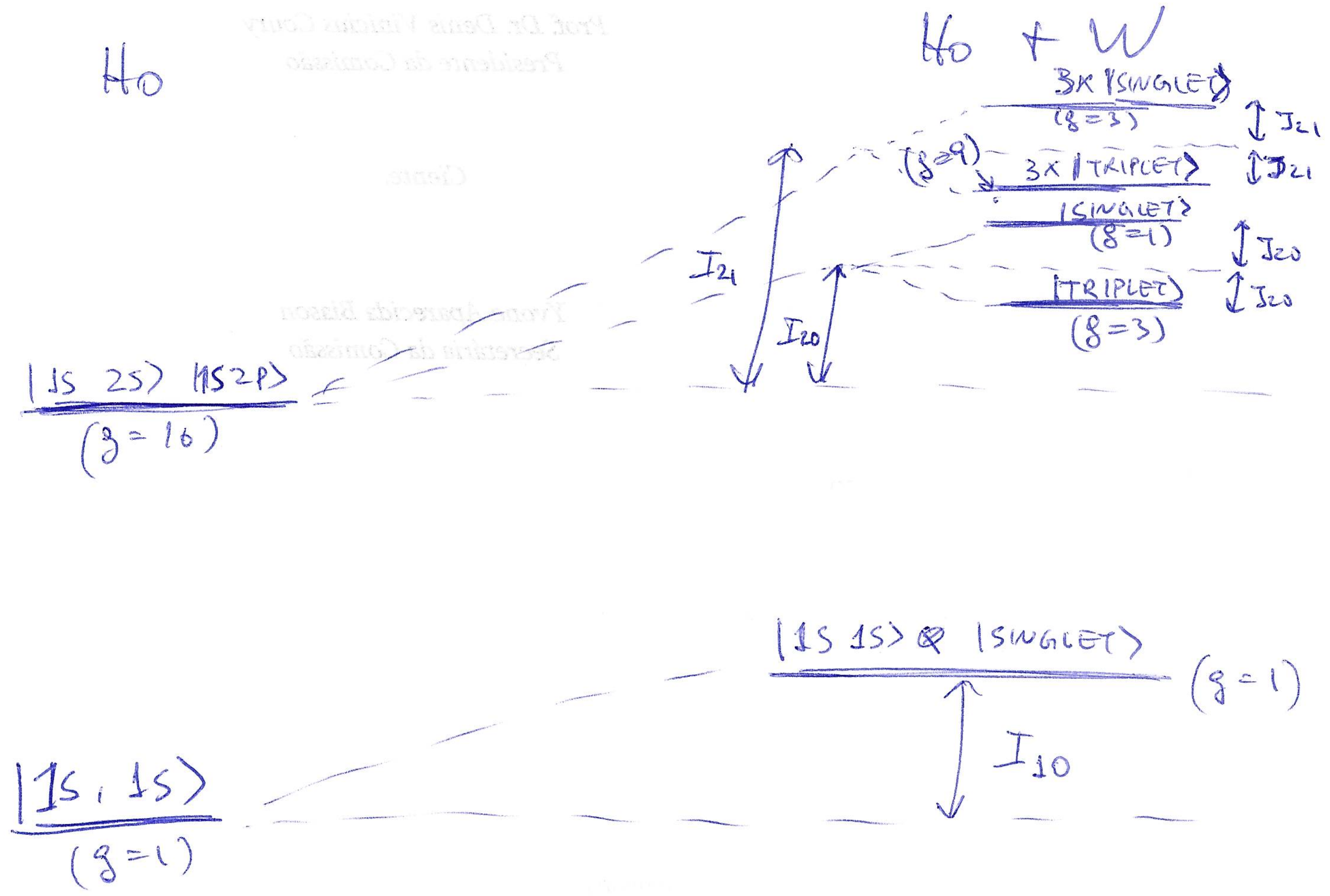
$$\frac{1}{\sqrt{2}}\left(|1s\ 2s\rangle - |2s\ 1s\rangle\right) \otimes \begin{cases} |++\rangle \\ \frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \\ |--\rangle \end{cases}$$ (TRIPLET)

THE SINGLET IS HIGHER IN ENERGY THAN THE TRIPLET SINCE

$$J_{20} = \int d\vec{r}_1 \int d\vec{r}_2 \, \psi^*_{100}(\vec{r}_1)\, \psi^*_{200}(\vec{r}_2) \left(\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \right) \psi_{200}(\vec{r}_1)\, \psi_{100}(\vec{r}_2) > 0$$

PLAYING THE SAME GAME FOR $|1s\,2p\rangle$ THE DEGENERACY IS LIFTED TO $I_{21} \pm J_{21}$

ENERGY DIAGRAM (OR GROTRIAN DIAGRAM)



PHYSICAL INTERPRETATION

- WHY THE SINGLET IS ENERGETICALLY HIGHER THAN THE TRIPLET?

  - THE SPIN SINGLET IS ANTI-SYMMETRIC
    ⇒ THE ORBITAL STATE IS SYMMETRIC

    THE SPIN TRIPLET IS SYMM. WHILE THE CORRESPONDING ORBITAL STATE IS ANTI-SYMM.

  AN ORBITAL ANTISYMMETRIC WAVE FUNCTION MEANS THAT THE TWO ELECTRONS ARE LESS LIKELY TO BE NEAR EACH OTHER THAN THE CASE OF SYMMETRIC ORBITAL WAVE FUNCTIONS. AS THEY REPEL EACH OTHER, THE ANTI-SYMMETRIC ORBITAL WAVEFUNCTION IS LESS ENERGETIC.

  ⇒ SPIN SINGLET IS HIGH IN ENERGY THAN THE SPIN TRIPLET.

- WHAT IS THE PHYSICAL IMPLICATION?

  - SPIN SINGLETS AND SPIN TRIPLETS ARE <u>DIFFERENT</u> IN ENERGY.

BUT SPIN SINGLETS AND TRIPLETS ARE MAGNETIC STATES.

FOR INSTANCE THEY ARE THE EIGENSTATES OF

$$H = J\left(\frac{\vec{S}_1 \cdot \vec{S}_2}{\hbar^2}\right)$$

THE SINGLET $\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}$ HAS ENERGY $-\frac{3}{4}J$

THE TRIPLET $|++\rangle, |--\rangle, \frac{|+-\rangle + |-+\rangle}{\sqrt{2}}$ HAS ENERGY $+\frac{1}{4}J$

FAVORS FERROMAGNETISM

THUS, IN OUR CALCULATION, THE EFFECTIVE COUPLING ENERGY $\boxed{J = -2J_{m\ell}} < 0$

WHERE $J_{m\ell} = \int d\vec{r}_1 d\vec{r}_2\, \psi^*_{100}(\vec{r}_1)\, \psi^*_{m\ell m}(\vec{r}_2)\, U(|\vec{r}_1 - \vec{r}_2|)\, \psi_{m\ell m}(\vec{r}_1)\, \psi_{100}(\vec{r}_2)$

$\equiv$ EXCHANGE INTEGRAL

WHILE $I_{m\ell} = \int d\vec{r}_1 d\vec{r}_2 \left|\psi_{100}(\vec{r}_1)\right|^2 U(|\vec{r}_1 - \vec{r}_2|) \left|\psi_{m\ell m}(\vec{r}_2)\right|^2$

$\equiv$ DIRECT INTEGRAL

NOTICE, THEREFORE, THAT MAGNETISM ARISES FROM PURELY ELECTRIC INTERACTIONS IN QUANTUM MECHANICS. THE INVOLVED PRINCIPLES ARE COULOMB REPULSION AND THAT ELECTRONS ARE INDISTINGUISHABLE PARTICLES

THE DIRECT AND EXCHANGE INTEGRALS (12)

$$I_{nl} = \int d\vec{r}_1 \, d\vec{r}_2 \, \left|\psi_{100}(\vec{r}_1)\right|^2 \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \left|\psi_{nlm}(\vec{r}_2)\right|^2$$

$$J_{nl} = \int d\vec{r}_1 \, d\vec{r}_2 \, \psi^*_{100}(\vec{r}_1)\, \psi^*_{nlm}(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \psi_{nlm}(\vec{r}_1)\, \psi_{100}(\vec{r}_2)$$

$$* \quad \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} = \frac{\hbar^2}{m a_0^2} \frac{a_0}{|\vec{r}_1 - \vec{r}_2|} \quad , \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = \frac{\hbar}{m c \alpha}$$

$$= \alpha^2 m c^2 \left(\frac{a_0}{|\vec{r}_1 - \vec{r}_2|} \right)$$

$$* \quad \psi_{100} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}} \times \frac{1}{\sqrt{4\pi}} \qquad Y_{00}$$

$$* \quad \psi_{200} = \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} \times \frac{1}{\sqrt{4\pi}} \qquad Y_{00}$$

$$* \quad \psi_{210} = \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \frac{Zr}{\sqrt{3}\, a_0} e^{-\frac{Zr}{2a_0}} \times \sqrt{\frac{3}{4\pi}} \cos\theta \qquad Y_{10}$$

$$* \quad \psi_{21\pm1} = \quad -''- \quad \times \left(\mp\sqrt{\frac{3}{8\pi}}\right) \sin\theta \, e^{\pm i\phi} \qquad Y_{1\pm1}$$

VARIABLE CHANGING : $\frac{Z\vec{r}}{a_0} = \vec{\rho}$

$$I_{20} = Z\alpha^2 mc^2 \cancel{\left(\frac{a_0}{Z}\right)^6} \int d\vec{\rho}_1 d\vec{\rho}_2 \; 4\cancel{\left(\frac{Z}{a_0}\right)^3} e^{-2\rho_1} \frac{1}{|\vec{\rho}_1 - \vec{\rho}_2|} \cancel{\left(\frac{Z}{2a_0}\right)^3} (2-\rho_2)^2 e^{-\rho_2} \underbrace{|Y_{00}^{(1)}|^2 |Y_{00}^{(2)}|^2}_{\left(\frac{1}{4\pi}\right)^2}$$

$$= \frac{Z\alpha^2 mc^2}{2(4\pi)^2} \int d\vec{\rho}_1 d\vec{\rho}_2 \; e^{-2\rho_1 - \rho_2} (2-\rho_2)^2 \underbrace{\frac{1}{|\vec{\rho}_1 - \vec{\rho}_2|}}_{\sum_{\ell=0}^{\infty} \frac{\rho_<^\ell}{\rho_>^{\ell+1}} \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_{\ell m}^*(1) Y_{\ell m}(2)}$$

THE ANGULAR INTEGRATION YIELDS

$$\int d\Omega_1 Y_{\ell m}^*(\theta_1,\phi_1) = \sqrt{4\pi}\, \delta_{\ell,0}\, \delta_{m,0} = \int d\Omega_2 Y_{\ell m}(\theta_2,\phi_2)$$

$$\Rightarrow I_{20} = \frac{Z\alpha^2 mc^2}{2(4\pi)^2} (4\pi)^2 \underbrace{\int_0^\infty d\rho_1 \int_0^\infty d\rho_2 \; \rho_1^2 \rho_2^2 (2-\rho_2)^2 \frac{1}{\rho_>} e^{-2\rho_1 - \rho_2}}_{\frac{34}{81}}$$

$$\Rightarrow \boxed{I_{20} = \frac{17}{81} Z\alpha^2 mc^2}$$

$$J_{20} = \frac{Z\alpha mc^2}{2}\int d\vec{\rho}_1 d\vec{\rho}_2\, e^{-\frac{3}{2}(\rho_1+\rho_2)}(2-\rho_1)(2-\rho_2)\, *$$

$$* \, Y_{00}^*(1)\, Y_{00}(1)\, |Y_{00}(2)|^2 \frac{1}{|\rho_1-\rho_2|}$$

NOTICE IT IS THE SAME ANGULAR INTEGRAL AS I_{20}.

$$\Rightarrow J_{20} = \frac{Z\alpha^2 mc^2}{2}\underbrace{\int_0^\infty d\rho_1\int_0^\infty d\rho_2\, \rho_1^2\rho_2^2(2-\rho_1)(2-\rho_2)\frac{1}{\rho_>}\, e^{-\frac{3}{2}(\rho_1+\rho_2)}}_{\frac{32}{729}}$$

$$\Rightarrow \boxed{J_{20} = \frac{16}{729} Z\alpha^2 mc^2}$$

NOW, WE TAKE CARE OF THE CASE $|1s\,2p\rangle$, i.e., $\underline{\ell = 1}$

THE SAME VARIABLE CHANGING IS CONVENIENT.

$$I_{21} = Z\alpha^2 mc^2 \times \frac{4}{3}\times\frac{1}{2^3}\int d\vec{\rho}_1 d\vec{\rho}_2\, e^{-2\rho_1-\rho_2}\rho_2^2\, \frac{|Y_{00}(1)|^2\, |Y_{1M}(2)|^2}{|\vec{\rho}_1-\vec{\rho}_2|}$$

$$= \frac{Z\alpha^2 mc^2}{6}\int d\vec{\rho}_1 d\vec{\rho}_2\, \rho_2^2 e^{-\rho_2-2\rho_1}\sum_{\ell, m}\frac{\rho_<^\ell}{\rho_>^{\ell+1}}\frac{4\pi}{2\ell+1}|Y_{00}(1)|^2 Y_{\ell m}^*(1)\, |Y_{1M}(2)|^2 Y_{\ell m}(2)$$

THE INTEGRATION OVER $d\Omega_1$ YIELDS TO

$$\int d\Omega_1 \, |Y_{00}(1)|^2 \, Y^*_{\ell m}(1) = \frac{\delta_{\ell,0}\,\delta_{m,0}}{\sqrt{4\pi}}$$

THE INTEGRATION OVER $d\Omega_2$ THEN BECOMES

$$\int d\Omega_2 \, |Y_{1M}(2)|^2 \, Y_{\ell m}(2) \to \int d\Omega_2 \, |Y_{1M}(2)|^2 \, Y_{00}(2) = \frac{1}{\sqrt{4\pi}}$$

WHICH INDEPENDENT ON M
AS WE HAVE ALREADY SHOWN

THUS, $$I_{21} = \frac{Z\alpha^2 mc^2}{6} \underbrace{\int_0^\infty d\rho_1 \, d\rho_2 \, \rho_1^2 \rho_2^4 \, e^{-2\rho_1-\rho_2} \, \frac{1}{\rho_>}}_{\frac{118}{81}}$$

$$\Rightarrow \boxed{I_{21} = \frac{59}{243} Z\alpha^2 mc^2}$$

FINALLY,

$$J_{21} = \frac{Z\alpha^2 mc^2}{6} \int d\rho_1 \, d\rho_2 \, \rho_1 \rho_2 \, e^{-\frac{3}{2}(\rho_1+\rho_2)} \sum_{\ell,m} \frac{\rho_<^\ell}{\rho_>^{\ell+1}} \frac{4\pi}{2\ell+1} Y^*_{00}(1) Y_{1M}(1) Y^*_{\ell m}(1) Y^*_{1M}(2) Y_{00}(2) Y_{\ell m}(2)$$

THE ANGULAR INTEGRALS ARE

$$\int d\Omega_1 \, \underset{\downarrow \atop \frac{1}{\sqrt{4\pi}}}{Y^*_{00}(1)} \, Y_{1M}(1) \, Y^*_{\ell m}(1) = \frac{1}{\sqrt{4\pi}} \delta_{\ell,1} \, \delta_{M,m} = \int d\Omega_2 \, Y^*_{1M}(2) \, Y_{\ell m}(2) \, \underset{\downarrow \atop \frac{1}{\sqrt{4\pi}}}{Y_{00}(2)}$$

THEN,

$$J_{21} = \frac{Z\alpha^2 mc^2}{6} \underbrace{\int_0^{\infty} d\rho_1 d\rho_2\, \rho_1^3 \rho_2^3\, e^{-\frac{3}{2}(\rho_1+\rho_2)} \frac{\rho_<}{\rho_>^2}}_{\frac{224}{729}} \times \frac{1}{3}$$

$$\Rightarrow \boxed{J_{21} = \frac{112}{6561} Z\alpha^2 mc^2}$$

FOR He-ATOM $(Z=2)$, $mc^2 \simeq 511$ KeV, $\alpha \simeq \frac{1}{137}$

THEN, $I_{20} \simeq 11.4$ eV

$J_{20} \simeq 1.2$ eV

$I_{21} \simeq 13.2$ eV

$J_{21} \simeq 0.9$ eV