Syllabus :-

1st Aug.	Wed.
2n Aug.	Thu.
5th Aug.	Mon.

Extra-class
14th Aug → 2-
8th Aug → 5-8

⇒ Review of single electron system

→ Hydrogen atom: Schrodinger equation, Summary of energy levels, fine structure of hydrogen atom, Lamb shift, Hyperfine structure, Interection of electron with the external field, The stark effect (electric field), the Zeeman effect (magnetic field (weak)), Poschen-Back effect.

⇒ **Many-electron atoms :-**

Central-field approximation & Hatree-Fock method, Thomas-Fermi model, LS, J-J coupling, Alkali spectra, He, complex atom.

Molecules :- election-structure of molecules.
Molecular spectra- Rotational & vibrational spectra.
Diatomic molecule, Infra-red spectra, vibration-rotation spectra.

- Spectroscopic technique :- Interferometer, FTIR, RAMAN, NM, ESR,

→ Some Frontier of Atomic & Molecular spectroscopy
→ Bose-Einstein condensate
→ Atomic clock
→ Quantum computer

RECAP ⇔ QM

→ state

may be complex

$$\phi_K = A \exp[i(K \cdot r - \omega t)]$$

Momentum

$$\hat{P} = -i\hbar \frac{\partial \phi_K}{\partial x} = \boxed{\hbar K} \phi_K$$

$$\omega_K = \frac{\hbar K^2}{2m}$$

$$E_K = \hbar \omega_K = \frac{\hbar^2 K^2}{2m}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} \qquad \hat{p} = -i\hbar \frac{d}{dr}$$

$$(-i\hbar \nabla_r)^2$$

$$\boxed{E_K = \hbar \omega_K = \frac{\hbar^2 K^2}{2m}}$$

$$\int |\phi_K(r)|^2 d^3r = 1$$

Energy spectra -

$$\boxed{\hat{H}\,\phi_K(r) = E_K\,\phi_K(r)}$$

↳ Eigen energy

Hemiltonian operator

good Quantum Number — n, l, m_l

$$\boxed{\psi(r) = \sum c_n \phi_K(r)}$$

$$\int \phi_K^* \phi_{K'}\, d^3r = \delta_{KK'}$$

$$\psi(r) = \sum_K c_K \phi_K$$

↳ Prob. Amplitude to find in state E_K

⇒ The prob. to find the system with energy state E_K will be

$$p_K = \boxed{|c_K|^2 = \left|\int d^3r\, \phi_K^*(r)\, \psi(r)\right|^2}$$

In this case expectation (or mean) of the energy E in the state $\psi(r)$ is given by —

$$\bar{E} = \langle \hat{H} \rangle = \int d^3r\, \psi^*(r)\, \hat{H}\, \psi(r)$$

$$\langle \hat{H} \rangle = \sum_K |c_K|^2 E_K$$

↳ Quantum ket state

$$\hat{H}|\phi_K\rangle = E_K|\phi_K\rangle$$

$$\phi_K(r) = \underbrace{\langle r|\phi_K\rangle}$$

↳ Projection of quantum state on the position ket.

$$\phi_K(p) = \langle p|\phi_K\rangle$$

$$[\hat{r}\,\hat{p}] = i\hbar \neq 0$$

$$\boxed{[\hat{L}_i, \hat{L}_j] = i\hbar\,\varepsilon_{ijk}\,\hat{L}_k}$$

$$[L^2 L_z] = 0$$

$$\hat{L} = \hat{r} \times \hat{p}$$

$$[\hat{L}_i \hat{L}_j]$$

$$[\hat{r}_i \times \hat{p}_i \quad \hat{r}_j \times \hat{p}_j]$$

$$\boxed{\hat{L}^2|l, m\rangle = \hbar^2 l(l+1)|l, m_l\rangle}$$

$$\boxed{L_z|l\, m_l\rangle = \hbar m_l|l, m_l\rangle}$$

$$\boxed{[\hat{S}_i\ \hat{S}_j] = i\hbar\, \epsilon_{ijk}\, \hat{S}_k}$$

Bibhas Ranjan Majhi

$$\hat{S}^2 |s, m_s\rangle = \hbar^2 s(s+1)\, |s, m_s\rangle$$

$$\hat{S}_z |s\ m_s\rangle = \hbar m_s\, |s\ m_s\rangle$$

Tensor product

$$\boxed{\hat{J} = \hat{L}_1 + \hat{L}_2}$$

New angular momentum

$$\hat{J}^2 |j\ l_1\ l_2\ m_j\rangle = \hbar^2 j(j+1)\, |j, l_1, l_2, m_j\rangle$$

$$\hat{J}_z |j\ l_1\ l_2\ m_j\rangle = m_j \hbar\, |\quad\rangle$$

$$|l_1 - l_2| \leq j \leq |l_1 + l_2|$$

$n = 3$ n^2

$l = 0$ m

n^2, $m \to n^2$

$\Rightarrow$
$$\Psi(r, t=0) = \frac{1}{\sqrt{14}}\left[2\Psi_{100}(r) - 3\Psi_{200}(r) + \Psi_{322}(r)\right]$$

$$\langle \hat{H} \rangle,\ \langle \hat{L}^2 \rangle,\ \langle \hat{L}_z \rangle$$

$$\langle H \rangle = \frac{4}{14} \frac{\hbar^2 (100)^2}{2m}$$

$$\langle \hat{H} \rangle = \frac{\hbar^2}{28m}\left[(100)^2 \times 4 + (200)^2 \times 9 + (322)^2 \times 1\right]$$

$$\Psi(r) = \sum c_k \phi_k(r)$$

$$|\Psi\rangle = \frac{1}{\sqrt{14}}\left[2|100\rangle - 3|200\rangle + |322\rangle\right]$$

$$|E_n|^2 = |\langle E_n | \Psi(0)\rangle|^2$$

$$|\Psi(0)\rangle = \sum_n c_n |E_n\rangle$$

$$H|E_n\rangle = E_n|E_n\rangle$$

$$|\Psi(0)\rangle = \sum_n |E_n\rangle\langle E_n|\Psi(0)\rangle$$

$$\langle \Psi(0)| H |\Psi(0)\rangle =$$

$$= \sum_n \langle E_n|\Psi(0)\rangle\, |E_n\rangle$$

$$\langle \Psi(0)| E_n |\Psi(0)\rangle = E_n$$

$E_n \sum$

$$\langle \quad | \sum_n C_n |E_n\rangle E_n\rangle = \sum_n C_n E_n C_n^*$$

$$\sum_n |C_n|^2 E_n$$

$$\frac{2\pi}{\lambda} = k$$

$$\frac{2}{14}$$

$$\Psi(x) = \sum_n c_n \phi_n$$

$k =$

$$\Psi(r) = A\exp[i(k \cdot r - \omega t)]$$

$$\Psi(r) = Ae^{ik \cdot r}$$

$A\exp$

$$p = \hbar k$$

$\hbar$

Hydrogen like atom (one electron atom)

H (atom), He^+ (Helium ion), Li^{2+} (Lithium ion), etc.

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r} \quad (\text{from CM frame})$$

Schrodinger equation :-

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi_{nlm}(r) = E_{nlm}\,\psi(r)$$

principal qn, Azimuthal, magnetic. Quantum number

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

spherical harmonics wave function

Radial.

$$\left\{\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{4\pi\varepsilon_0 r^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}\right\} R_{n,l}(r) = E_{nlm} R_{nl}(r)$$

$$\boxed{u_{rl} = r R_{n,l}(r)}$$

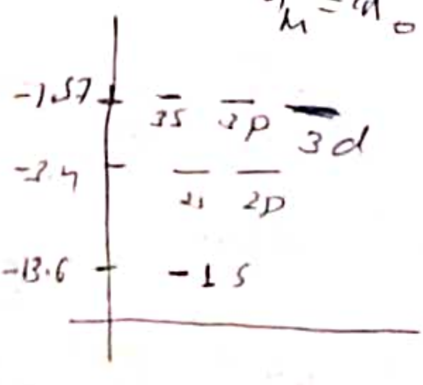
$$\frac{\partial^2 u_{nl}}{\partial r^2} + \frac{2\mu}{\hbar^2}\left[E_{nlm} - V_{eff.}(r)\right] u_{n,l}(r) = 0$$

$$V_{eff} = \underbrace{\frac{-Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)}{2\mu r^2}\hbar^2}$$

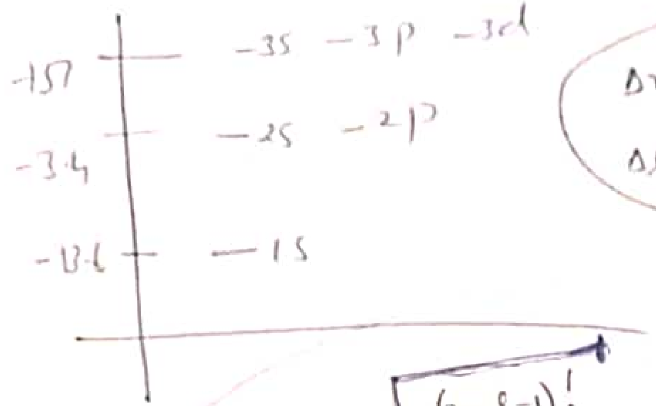
$$E_n = \frac{-Ze^2 z^2}{(4\pi\varepsilon_0)\, a_\mu\, 2h^2}$$

$$a_\mu = \frac{m}{\mu} a_0$$

for H atom $a_\mu = a_0$



Bibhas Ranjan



$\Delta m = 0, \pm 1$

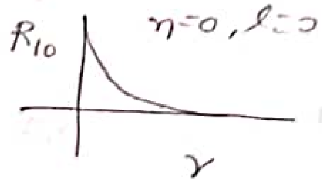
$\Delta l = \pm 1$

$$R_{nl} = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2Z}{na_\mu}\right)^{3/2} e^{-Zr/na_0} \cdot \left(\frac{2Zr}{na_\mu}\right)^{l} \mathcal{L}_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

Associated Laggu-r's polynomial

$$\boxed{\mathcal{L}_n^{K}(x) = (-1)^K \frac{d^K}{dx^K} \mathcal{L}_{n+1}(x)}$$

$$\Rightarrow R_{10} = 2\left(\frac{Z}{a_\mu}\right)^{3/2} e^{-Zr/a_\mu},$$



$$R_{20} = 2\left(\frac{Z}{a_\mu}\right)^{3/2}\left(1 - \frac{Zr}{2a_\mu}\right) e^{-Zr/2a_\mu}.$$

Prob. of finding the e^- b/w r & $r+dr$.

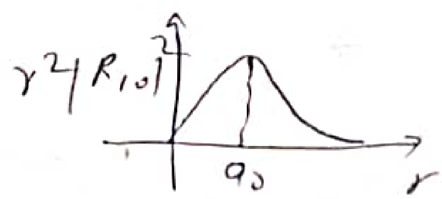
n=2, l=0

Prob. density

$$|\psi_{nlm}|^2 = |R_{nl}|^2 |Y_l^m(\theta,\phi)|^2$$

$$\text{Prob} = \int_0^{r \to r+dr} \int_0^{\pi} \int_0^{2\pi} |R_{nl}|^2 |Y_l^m(\theta,\phi)|^2 r^2 d\phi \sin\theta\, dr$$

$$= r^2 |R_{nl}|^2 dr$$



$$\Rightarrow \langle r^{r} \rangle_{nlm} = \int_0^\infty r^{2+r} |R_{nl}(r)|^2 dr$$

$$\langle r \rangle_{nl} = \frac{a_0}{2Z}\left[3n^2 - l(l+1)\right]$$

$$\langle r^{-1} \rangle_{nl} = \frac{Z}{a_0 n^2}$$

$$\langle r^{-2}\rangle_{nl} = \frac{Z^2}{a_0^2 n^3 (l+1/2)}$$

$Y_l^m(\pi-\theta, \pi+\phi) = (-1)^l Y_{lm}(\theta,\phi)$

Check the parity of the orbital.

Z

r, θ, ϕ

$r \to r$

$\theta \to \pi - \theta$

$\phi \to 2\pi + \phi$

$l = 0, 1, 2, 3, 4, 5$

$\downarrow$ e, o, e, o, e, o. parity

(spin) o $\Rightarrow$ $H_0 = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}$ (Non-relativistic e^-)

$H' = H_1' + H_2' + H_3'$, $H_1' = \frac{-p^4}{8m^3c^2}$ → Relativistic correction to the K.E.

$$\boxed{H_2' = \frac{1}{r}\frac{\partial V(r)}{\partial r}\vec{L}\cdot\vec{S}}$$ {spin-orbit coupling}

$$H_3' = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(r)$$

↑ Darwin term.

$v^2 = \langle \frac{p_e^2}{m^2} \rangle$

$p_e = mv$, $\langle p_e^2\rangle = m^2\langle v\rangle^2$

$\frac{1}{2}m\langle v\rangle^2 = \frac{1}{2m}\langle p_e^2\rangle$

$$\langle T\rangle_{100} = \langle n=1, l=0, m=0 \left| \frac{p^2}{2m} \right| 100\rangle$$

$$= E_{100} - \langle V\rangle_{100}$$

$$\Rightarrow \frac{-Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\right\rangle_{100} \to Z/a_0$$

$$\langle T\rangle_{100} = \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2}$$

$$= \frac{1}{2}Z^2\alpha^2 m_e c^2$$

α ← fine structure Const.

$v_{100}^{rms} = \sqrt{\langle v^2 \rangle_{100}}$

$\boxed{v_{100}^{rms} = Z\alpha c}$

$T = \sqrt{p^2c^2 + m_e^2c^4} - m_e c^2$

$= m_e c^2 \left[\sqrt{1 + \frac{p^2}{m_e^2 c^2}} - \cancel{m_e c^2} \right]$

$= \frac{p^2}{2m_e} - \frac{p^4}{8 m_e^3 c^4} + \cdots$

$\Rightarrow$ Time independent perturbation theory

$H' = H_0 + \lambda H_1$

$\Delta E^{(1)} = \langle \psi_{lmn}^{(0)} | H_1 | \psi_{lmn}^{(0)} \rangle$

Correction in the ~~energy due to~~ K.E due to the relativistic effect,

$S_R = \frac{-p^4}{8 m_e^3 c^2}$

$\boxed{H_0 = \frac{p^2}{2m} + V}$

$(H_0 - V)^2 = \left(\frac{p^2}{2m}\right)^2$

$\Delta E_R = \langle nlm | S_R | nlm \rangle$

$\langle nlm | H_0^2 - 2H_0V + V^2 | nlm \rangle$

$= \frac{1}{2m_e c^2} \langle nlm | H_0$

$\frac{1}{2m_e c^2} \quad H_0^2 + V^2 - 2H_0V$

$= \frac{p^4}{8m^3 c^2}$

$H_0 | nlm \rangle = E_n | nlm \rangle$

$H_0^2 | nlm \rangle = E_n^2 | nlm \rangle$

$\Rightarrow \langle H_0 V \rangle_{nlm}$

$= \langle nlm | H_0 V | nlm \rangle$

$= -E_n$

$= -E_n \frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle_{nlm}$

Z/a_0

$= \frac{-E_n}{} \times \frac{Z^2 e^2}{4\pi\varepsilon_0}$

$\langle V^2 \rangle_{nlm} = \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \left\langle \frac{1}{r^2} \right\rangle_{nlm}$

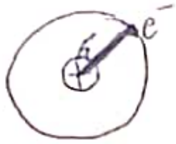
$$= \left(\frac{Z^2 e^2}{4\pi\varepsilon_0}\right)^2 \times \frac{1}{n^3 a_0^{Z}(l+\frac{1}{2})}$$

$$\frac{L}{m}$$

$$\Delta E_R = \frac{-1}{2m_e c^2}\left[E_n^2 - 4E_n^2 + E_n^2 \frac{4n}{l+\frac{1}{2}}\right]$$

$$\Delta E_R = -\frac{E_n^2}{2m_e c^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right]$$

$\Rightarrow$



Lab frame

from electron frame: $E'B'$

$\vec{v}$ from electron frame

$$\rightarrow B' = \frac{1}{2}\frac{\vec{E}\times\vec{v}}{c^2}$$

$$\Rightarrow H'_{SOI} = -\vec{\mu}_e \cdot \vec{B}' = +g_0 \mu_B \frac{\vec{S}}{\hbar}\cdot\vec{B}$$

$$\mu_B = \frac{e\hbar}{2m_e}$$

$$H'_{SO} = \frac{e}{m_e}\vec{S}\cdot\vec{B}$$

$$g_0 \frac{e\hbar}{2m_e \hbar}\vec{S}\cdot\vec{B}$$

$$= \frac{e}{m_e}\vec{S}\cdot\left(\frac{\vec{E}\times\vec{v}}{c^2}\right)$$

$$\vec{E} = -\vec{\nabla}V$$

$$\hat{r}\times\vec{v} = \frac{1}{m_e}\hat{r}\times\vec{p}$$

$$E = -\hat{r}\frac{\partial V}{\partial r}$$

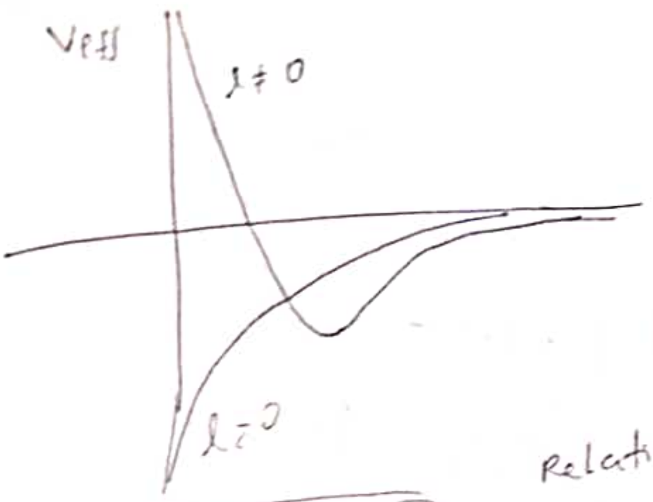
$$= \frac{1}{r m_e}\vec{L}$$

$$\boxed{H'_{SO} = -\frac{e}{2m_e^2 c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{L}\cdot\vec{S}}$$

$u_{nl} = rR_{nl}(r)$

$$\frac{\partial^2 u_{nl}}{\partial r^2} + \frac{2\mu}{\hbar^2}\left[E_{nlm} - V_{eff}(r)\right] u_{nl}(r) = 0$$

$$V_{eff} = \frac{-Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$



At $r = 0$, for $l \neq 0$

$u_{nl}(r=0) = 0$

Relativistic Correction

$$\boxed{\Delta E_R = \frac{-E_n^2}{2m_e c^2}\left[\frac{4n}{l+1/2} - 3\right]}$$

Correction due to spin-orbit coupling —

$$H'_{SO} = -\vec{\mu}_e \cdot \vec{B} \quad \left(\frac{\vec{E} \times \vec{v}}{2c^2}\right)$$

$$E' = -\vec{\nabla} U = -\hat{r}\frac{\partial}{\partial r} U$$

$$\mu_e = g\mu_B \hat{S}/\hbar$$

$H'_{SO} = \cancel{\mu_e \cdot B}$

$E = \cancel{-\vec{\nabla} U =}$

$$H'_{SO} = \frac{-g\mu_B}{\hbar}\hat{S} \cdot \underbrace{\left(\frac{\partial U}{\partial r}\right)}_{\frac{-Ze^2}{4\pi\varepsilon_0 r^2}}\left[\frac{\vec{r} \times \vec{v}}{|r|}\right]\frac{1}{2c^2}$$

$$H'_{SO} = \frac{Ze^3}{8\pi\varepsilon_0 m_e^2 c^2}\left\{\frac{1}{r^3}\right\} \vec{L} \cdot \vec{S}$$

$$\Delta E_{SO} = \langle \Psi_{nlm} | H'_{SO} | \Psi_{nlm} \rangle$$

$$\Delta E_{SO} = \frac{Ze^3}{8\pi\varepsilon_0 m_e^2 c^2}\left\langle \frac{1}{r^3} \right\rangle \langle \vec{L} \cdot \vec{S} \rangle$$

$\vec{J} = \vec{L} + \vec{S} \Rightarrow J^2 = L^2 + S^2 + 2L \cdot S$ — lasering optics (PH305)

$|S_1 S_2|$ $|S_1 + S_2|$

$\hat{L} \cdot \hat{S} = \frac{1}{2}[J^2 - L^2 - S^2]$

$S = \frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 0 1

$\langle \hat{L} \cdot \hat{S} \rangle$

$\|$

$\langle n l m_l j m_j | \hat{L} \cdot \hat{S} | n l m_l j m_j \rangle$

$S|j m_j\rangle = m_j \hbar |j m_j\rangle$

$S = \frac{1}{2}$

$\frac{1}{2}\left[J^2 - L^2 - S^2 | n l m_l j m_j \rangle\right.$

$\Rightarrow \cancel{\frac{\hbar^2}{2}\{ j(j+1) - s(s+1)\}} - \hbar^2 l(l+1)$

$\frac{1}{2}\{ s^2 j(j+1) \; | n l m_l j m_j$

$= \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - s(s+1)\right]$

$\Delta E_{SO}^{(1)} = \langle \frac{1}{r^3} \rangle \frac{\hbar^2}{2} \times \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2} \left[j(j+1) - l(l+1) - s(s+1)\right]$

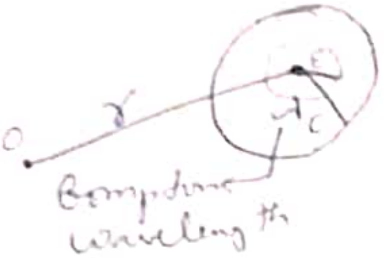
$\Rightarrow \langle \frac{1}{r^3} \rangle = \frac{Z^3}{n^3 a_0^3 l(l+\frac{1}{2})(l+1)}$

$$\boxed{\Delta E_{SO}^{(1)} = \frac{E_n^2}{m_e c^2} \, n \, \frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1)\cdot(l+\frac{1}{2})}}$$

⇒ Darwin Term ⇐

$$H'_{Darwin} = \frac{1}{8}\left(\frac{\hbar}{m_e c}\right)^2 \nabla^2 V$$

electron is not of fixed state, it is fluctuating



$\lambda_c = \frac{\hbar}{m_e c}$

$$V(r+\epsilon) \simeq V(r) + \epsilon_i \cdot \nabla V(r) + \frac{1}{2}\sum_{i,j} \epsilon_i \epsilon_j \partial_i \partial_j V(r)$$

$\to 0$

$\to$ mean $\to$ $i=j$ only survives at whole

$$\overline{V(r+\epsilon)} = V(r) + \frac{1}{2}\sum_i \overline{\epsilon_i^{\,2}}\, \partial_i^2 V(r)$$

$$= V(r) + \frac{1}{3}\,\overline{\epsilon}^2 \times \frac{1}{2}\nabla^2 V(r)$$

$$\boxed{\Delta U = \frac{1}{6}\lambda_c^2 \nabla^2 U(r)}$$

$\downarrow$

$\nabla^2 U = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$

$$H'_{Darwin} = 1/8 \left(\frac{\hbar^2}{m_e c}\right)^2 \nabla^2 \left(\frac{Ze^2}{4\pi\epsilon_0 r}\right)$$

$$H'_{Darwin} = \frac{\pi\hbar^2}{2m_e^2c^2} \times \frac{Ze^2}{4\pi\epsilon_0}\,\delta^3(r)$$

$l=0$ contributes only because $\int \delta(0) = 1$ only at $r=0$ and $\int \delta(x) = 0$, $x \neq 0$

$$\Delta E^{(1)}_{Darwin} = \frac{\pi\hbar^2}{2m^2c^2}\,\frac{Ze^2}{4\pi\epsilon_0}\langle \psi_{n00} | \delta^3(r) | \psi_{n00}\rangle$$

$$\psi(0) = \frac{1}{(4\pi)^{1/2}}\, 2\left(\frac{Z}{n a_0}\right)^{3/2} \cdot \text{ for }, l = 0$$

$$\boxed{\Delta E^{(1)}_{Darwin} = \frac{2n}{m_e c^2} E_n^2}$$

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(r)\right]\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$ Engineering optics (PH305) $\boxed{V \Rightarrow 0}$

$$\Psi(r,\theta,\phi) = R(r)\,Y_l^m(\theta,\phi)$$

$$Y_l^m(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$$

$$\Theta_l^m(\theta) = \sqrt{\frac{(2l+1)}{2}\frac{(l-|m|)!}{(l+|m|)!}}\,P_l^m(\cos\theta)$$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$Y_l^m = |lm\rangle$

$$\boxed{Y_l^m = (-1)^{(m+|m|)/2}\,\Theta_l^m(\theta)\,\Phi_m(\phi)}$$

$$L^2|lm\rangle = l(l+1)\hbar^2|lm\rangle$$
$$L_z|lm\rangle = m\hbar|lm\rangle$$
$$L^2$$

$$\langle r\rangle = \langle nlm|r|nlm\rangle$$

$dv = dr.\ r\sin\theta\, d\phi\ r d\theta$

$$= \oint_r \boxed{\langle nlm|r\rangle\langle r|nlm\rangle}$$

$$= \int \Psi^*_{nlm}(r)\,\Psi_{nlm}\,dv$$

$$= \int_0^{2\pi}\int_0^{\pi}\int_0^{r} r|\Psi_{nlm}(r)|^2\,.\,r^2\sin\theta\,d\theta\,dr\,d\phi$$

$\hat{x}|E\rangle = E|x\rangle$

$\langle E|\hat{x} = E^*\langle n|$

$$\langle r\rangle = \int_0^r |R_{nl}(r)|^2\,dr \Rightarrow \langle nlm|r|nlm\rangle$$

$$\langle nlm|r\rangle\ \langle r|nlm\rangle$$

Ψ^* Ψ

$$= \int r|\Psi(x,t)|^2\,dv$$

(I) - Rel correction

$$\Delta E_R^{(1)} = \frac{E_n^{(0)2}}{2m_e c^2}\left[\frac{4n}{l+1/2} - 3\right]$$

(II) - Spin-orbit coupling
(Coupling b/w the electron spin & its orbital motion)

$$\Delta E_{SO}^{\prime(1)} = \frac{E_n^{(0)2}}{m_e c^2}\, n\, \frac{j(j+1) - l(l+1) - 3/4}{l(l+1/2)(l+1)}$$

$$|l - 1/2| \leq j \leq (l + 1/2)$$

$$\boxed{|l - s| \leq j \leq (l+s)}$$

$H' =$ Darwin

Due to finite size correction of an electron which have radius of the order of Compton wavelength

$$H'_{Darwin} = \frac{\pi \hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} \delta^3(r)$$

$\Delta E^{(1)}_{Darwin}$ will have contribution only for $l=0$, because $l \neq 0$ radial orbital vanishes at $r=0$.

$$\Delta E^{(1)}_{Darwin} = \frac{\pi \hbar^2}{2m_e^2 c^2} \frac{Ze^2}{4\pi\varepsilon_0} |\psi_{n00}(0)|^2$$

-13.6

$$\Delta_n^{(1)} = \langle n l j m_j | \underbrace{H^{(1)}_{rel} + H^{(1)}_{SO}} | n l j m_j \rangle$$

$$= \frac{E_n^{(0)2}}{2m_e c^2}\left[3 - \frac{4n}{l+1/2} + 2n\, \frac{j(j+1) - l(l+1) - 3/4}{l(l+1/2)(l+1)}\right.$$

$$= \frac{E_n^{(0)^2}}{2m_e c^2}\left\{ 3 + 2n\left[\frac{j(j+1) - 3l(l+1) - 3/4}{l(l+1/2)(l+1)}\right]\right.$$

$j = l + 1/2$

$j = l + 1/2 \rightarrow$

$j = l - 1/2$

$-2/l$

$$f(j,l) = \frac{(l-1/2)(l+1/2) - 3l(l+1) - 3/4}{l(l+1)(l+1/2)}$$

$l = j - 1/2$

$l = j - 1/2$

$$\frac{l^2 - \cancel{1/4} - 3l^2 - 3l - \cancel{3/4} - 1}{}$$

$$\frac{l^2 - 3l^2 - 3l - 1}{l(l+1)(l+1/2)}$$

$$\frac{j(j+1) - 3(j-1/2)(j+1/2) - 3/4}{(j-1/2)\,j\,(j+1/2)}$$

$j^2 - 1/4$

$$\frac{j^2 + j - 3j^2 + \cancel{3/4} - \cancel{3/4}}{(j-1/2)\,j\,(j+1/2)}$$

$-2j^2 + j$

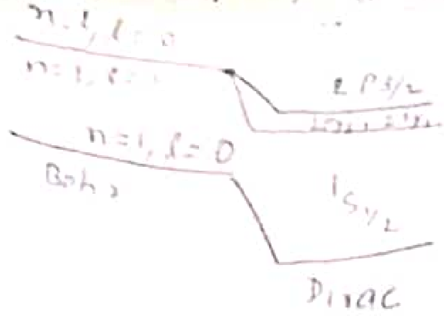
$$\frac{-2\cancel{j}\left[\cancel{j - 1/2}\right]}{\cancel{j}\,\cancel{(j-1/2)}(j+1/2)} = \frac{-2}{j+1/2}$$

$$f(j,l)\Big|_{l = j+1/2} = \frac{-2}{j+1/2}$$

$$\boxed{E^{(1)} = \frac{2n E_n^{(0)^2}}{m_e c^2}\left[\begin{array}{l}\text{Darwin,}\\ \text{only for } l=0\end{array}\right]} + \frac{E_n^{(0)^2}}{m_e c^2}\times\left[-2n + 3/2\right]$$

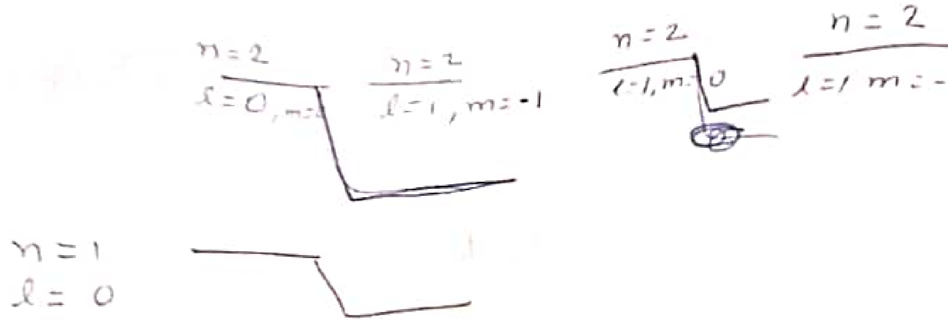
$$E^{(1)} = E_{rel}^{(1)} + E_{so}^{(1)} \quad , \; l \neq 0$$

$$= \frac{E_n^2}{m_e c^2}\left\{3 + (2n)\cdot\frac{-2}{j+1/2}\right\} = \frac{E_n^2}{2m_e c^2}\left\{3 - \frac{4n}{j+1/2}\right\}$$



$n\ell_j$

$\ell = 1 + \frac{1}{2}$



Single electron Atom

$$H = H_{Schrodinger} + H'_{Dirac}$$

Correction due to finite size of an relativistic electron

$$H'_{Dirac} \rightarrow H'_{Rel} + H'_{SO} + H'_{Darwin} + H'_{Lamb}$$

$H'_{Rel} \equiv -\frac{\hat{p}^4}{8 m_e^3 c^2}$ (Relativistic correction)

H'_{SO}: Coupling b/w orbital motion & spin of an electron.

H'_{Lamb}: [Quantised nature of electromagnetic field] Quantum electrodynamics

① $$\Delta E_{Rel}^{(1)} = -\frac{E_n Z^2 \alpha^2}{n} \left[\frac{3}{4n} - \frac{1}{\ell + \frac{1}{2}} \right]$$

α = fine structure const.
$= \frac{1}{137}$

② $$\Delta E_{SO}^{(1)} = -\frac{E_n Z^2 \alpha^2}{n \ell (\ell + \frac{1}{2})(\ell + 1)}, \ \ell \neq 0 \quad = -\frac{E_n (Z\alpha)^2}{n \ell (\ell + \frac{1}{2})(\ell + 1)} (-\ell - 1) \ \ j = \ell$$

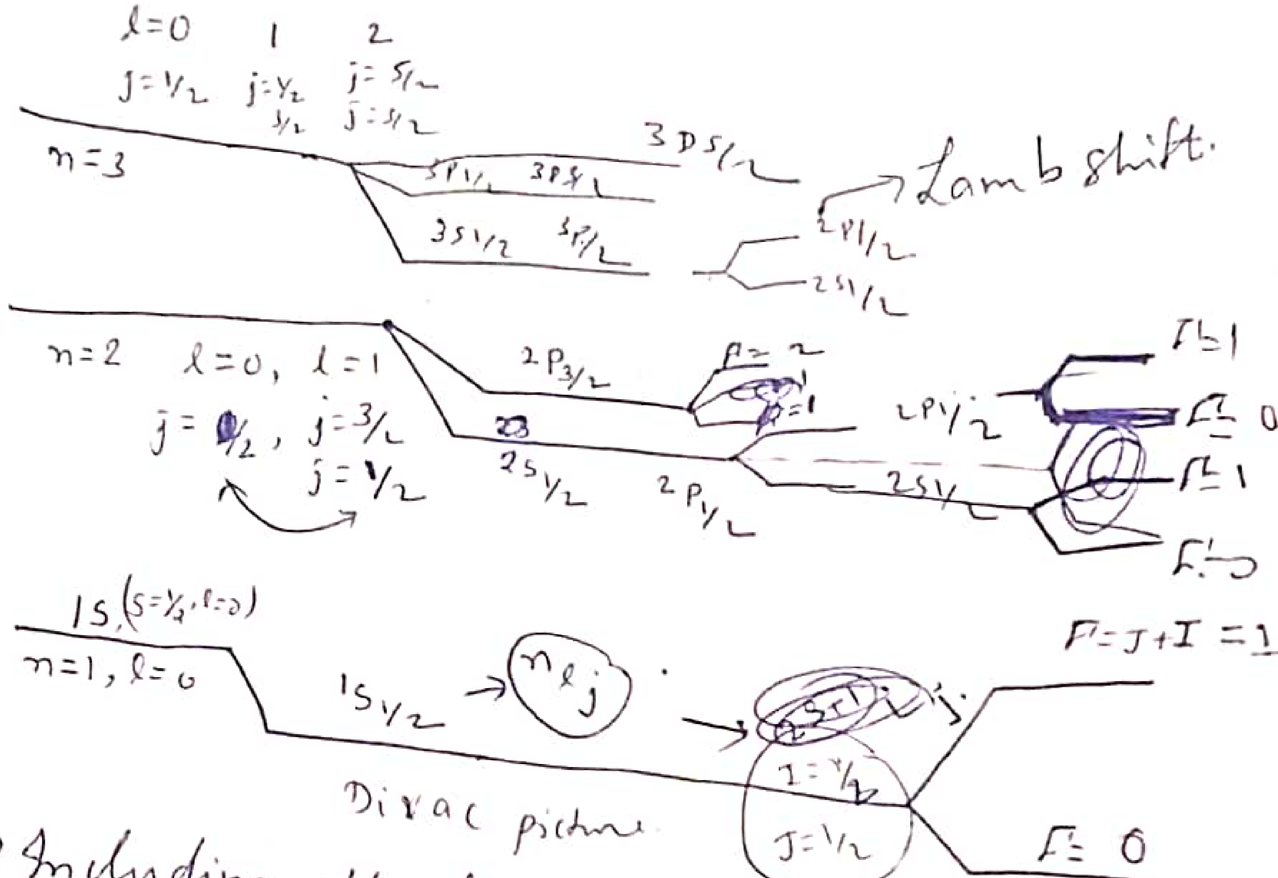
$$\Delta E_{SO}^{\prime(1)} = 0 \qquad \ell = 0$$

$$\Delta E^{(1)}_{Darwin} = -E_n \frac{(Z\alpha)^2}{n}, \quad l=0$$

$$\Delta E^{(1)}_{Rel} + \Delta E^{(1)}_{SO}$$

$$= -E_n \left[1 + \frac{(Z\alpha)^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n} \right) \right]$$

only depends on j, not on l.



F=j

Selection Rule
$\Delta j = 0, \pm 1$
$\Delta l = \pm 1$

$\Rightarrow$ Including the spin of nucleus, we will have new angular momentum like operator

$$\boxed{\hat{F} = \hat{J} + \hat{I}}$$

$\hat{I} \rightarrow$ spin of the nucleus.

$$\boxed{H'_{HF} = -\vec{\mu}_N \cdot \vec{B}_{Total}}$$