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Hydrogen atom

"harmonic oscillator of atomic physics"

splitting, {perturbation theory, degenerate P.T
non-degenerate P.T ...

{∘ astrophysics – hyperfine structure ...

The Fine STRUCTURE:

$$H^{(0)} = \frac{\bar{p}^2}{2m} - \frac{e^2}{r} \qquad m = \left\{\frac{m_e m_p}{m_e + m_p}\right\}$$ reduced mass of system

Z protons | $e^2 \to Ze^2$. ... $\simeq m_e$.

important length scale: ∘ 'a_0' - Bohr radius ... $= \frac{\hbar^2}{me^2}$ ~ 53 pm

make sure to deduce dimensions from $H^{(0)}$ quickly...

$e \to 0 \{ a_0 \uparrow\uparrow$

$$\circ\ E_n = -\frac{e^2}{2a_0}\left\{\frac{1}{n^2}\right\} \qquad \sim \boxed{E_1\ 2 \atop -13.6\,\mathrm{eV}\ \checkmark}$$

$- \alpha e^4$

n → principal q. no. 1, 2, 3, ...

∘ Looking ahead to Perturbation Theory ...

∘ Electromagnetism is weak ∘ e^- is moving with slow velocities

$$\circ\ \alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \quad \text{fine structure constant...}$$

$$\circ\ \frac{e^2}{a_0} = \frac{me^4}{\hbar^2} = \frac{m\alpha^2\hbar^2c^2}{\hbar^2} = \underline{\underline{\alpha^2 mc^2}} \quad !!$$

$$\boxed{E_{g.s} = \alpha^2 \frac{mc^2}{2}} \; !$$

allows us to think of scales ..

$\left(\frac{1}{19000}\right)$!

so

$$\boxed{E_n = -\frac{1}{2}\alpha^2 mc^2 \left\{\frac{1}{n^2}\right\}}$$

another observation...

momentum $p \sim \frac{\hbar}{a_0} = \frac{me^2}{\hbar} = \frac{m\alpha\hbar c}{\hbar} = \boxed{\alpha(mc)}$!!!

$= \underline{m(\alpha c)}$ atleast for slow velocities...

$v \sim \frac{c}{137}$ ∘ non-relativistic...

$L(l)$: $L(l=0) = S$, $L(l=1) = P$, $L(l=2) = D$, $L(l=3) = F$

Still review... H spectrum...

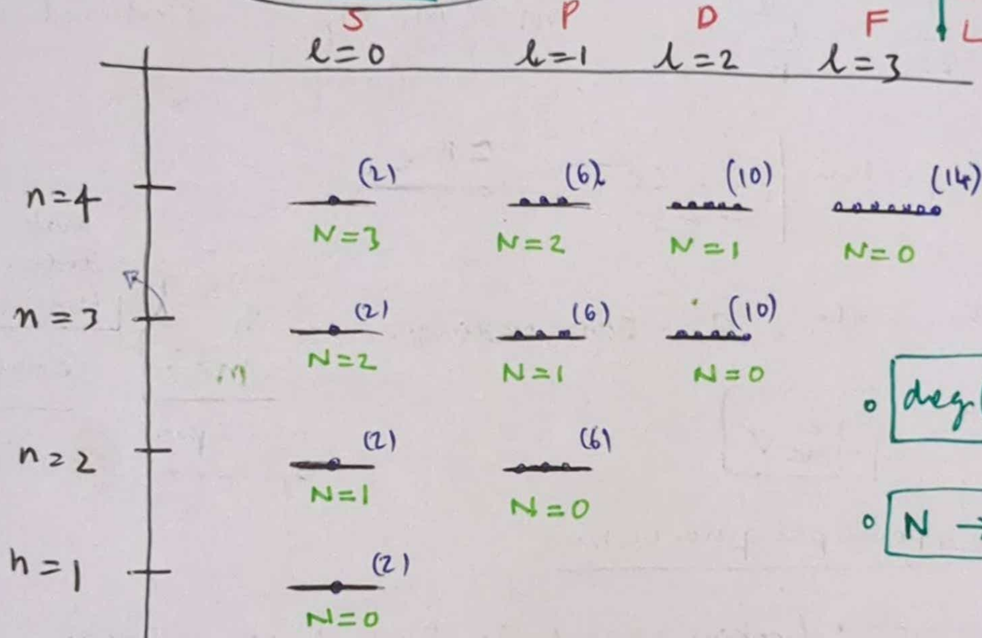


Fig -(*)

∘ $\boxed{\deg(n) = n^2}$ × 2 SPIN

∘ $\boxed{N \to \#\text{nodes.}}$

∘ One formula that says it all -- Degeneracies...

$$n = N + l + 1$$

l → orbital ang. momentum $l = 0, 1, 2, \ldots$

N → degree of polynomial in the wavefunction $N = 0, 1, 2, \ldots$

∘ fixed $\underline{n}$: $l = 0, 1, \ldots, n-1$

∘ for each l, $m = -l, \ldots, l$ $\underline{(2l+1) \text{ values}}$

$$\deg(n) = \sum_{l=0}^{n-1} (2l+1) = n^2.$$

$$\Psi_{nlm} = A\left(\frac{r}{a_0}\right)^l \left(1 + \beta\frac{r}{a_0} + \cdots\cdots + (\sim)\left(\frac{r}{a_0}\right)^N\right) e^{-\frac{r}{na_0}} \cdot Y_{l,m}(\theta, \phi).$$

- more Comments...

$$\psi_{000} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

- Large degeneracy! — corresponds to states with diff values of ang. mom...
  - semi-classically — iso-semi-major axis varying $\boxed{\text{eccentricity}}$ orbits of e^-s —
- most imp. complication ignored here... } → spin...
- Corrections due to spin, RELATIVITY, also see by adding $\vec{E}$, $\vec{B}$

L 4.1

L 4.2

BASIS STATES

- e^- spin, e^- ang. mom → Total ang. momentum = sum "awfully important".
- Angular momentum (general) (j, j_m) $\vec{J}^2$ eigenvs — $\hbar^2 j(j+1)$
  $J_z/\hbar$ " — j_m.
- Electron — spin $(s, m_s) = (\overset{e^-}{\tfrac{1}{2}}, \pm 1/2)$
- Electron — orbital $(l, m_l) =$
- Uncoupled basis (n, l, m, m_s) $s = (s = 1/2)$ ~ electron S_z → knowing ~~each~~ any e^- state in Fig-(*) uniquely...

A.

Coupled basis :

$$\vec{J} = \vec{L} + \vec{S}$$

{we express our basis states in terms of eigenstates of total ang. momentum ...}

{That's it to ang. mom addition ...}

$\vec{L}^2$ eigenstates

$\vec{S}^2$ eigenstates

multiplying / rearranging states

$$\underset{(l,m)}{(l \text{ multiplet})} \otimes \underset{(s,m_s)}{(\text{spin multiplet})} = \sum \underset{(j,j_m)}{j\text{-multiplet}}$$

Can you specify more?

(l, s, j, j_m)

- m, m_s are not good!

review

- Application in H-atom?

"value of l is preserved"

- $\underset{\text{orb}}{l} \otimes \underset{\text{spin-}1/2}{\frac{1}{2}} = \underset{j_{max}}{\left(l+\frac{1}{2}\right)} \oplus \underset{j_{min}}{\left(l-\frac{1}{2}\right)} = L_{l+\frac{1}{2}} \oplus L_{l-\frac{1}{2}}$

$\rightsquigarrow L(l)$

spectroscopic notation

nL_j.

- In Coupled Basis...

	S $l=0$	P $l=1$	D $l=2$
$1 \otimes 1/2 = \frac{3}{2} \oplus 1/2$ $n=3$	$3S_{1/2}$	$3P_{3/2}, 3P_{1/2}$	$3D_{5/2}, 3D_{3/2}$
$n=2$	$2S_{1/2}$	$2P_{3/2}, 2P_{1/2}$	
$0 \otimes \frac{1}{2} = \frac{1}{2}$ $n=1$	$1S_{1/2}$		

(n, l, m, m_s) ~~uncoupled...~~ UNCOUPLED

nL_j

not written

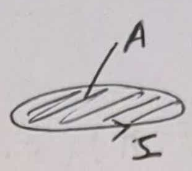
(n, l, j, j_m) ~~uncoupled...~~ COUPLED

PAULI EQUATION:

- First attempt to figure, how the Dirac eqn must be tailored for electron ... Baby version of Dirac eqn...

What is the magnetic moment $\vec{\mu}$ of an electron?

Classically : (Gaussian units)



$$\boxed{\vec{\mu} = \frac{I\vec{A}}{c}}.$$

$$\boxed{\bar{\mu} = \frac{q}{2mc}\bar{L}} \rightsquigarrow \xrightarrow{\text{Expect}} \bar{\mu} = \text{"}g\text{"}\frac{q}{2mc}\vec{s}$$

g: fudge factor, no reason for it to work...

For electrons $g=2$, $\vec{\mu} = 2\left(\frac{-e}{2mc}\right)\frac{\hbar}{2}\vec{\sigma}$

$$\boxed{\vec{\mu}_e = -\frac{e\hbar}{2mc}\vec{\sigma}}$$

Why $g=2$?

{ We'll see the beginning of this...

Bext:

$$H = -\vec{\mu}\cdot\vec{B}$$
$$= \frac{e\hbar}{2mc}\bar{\sigma}\cdot\bar{B}.$$

- $\frac{\bar{p}^2}{2m}\psi = E\psi \rightsquigarrow \frac{\bar{p}^2}{2m}\underline{\chi} = E\underline{\chi}$ $\quad \mathbb{1}_{2\times2}$. $\quad \chi = \begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}$.

Pauli spinor!

Pauli noticed something funny... $(\bar{\sigma}\cdot\bar{a})(\bar{\sigma}\cdot\bar{b}) = (\bar{a}\cdot\bar{b})\mathbb{1} + i\bar{\sigma}\cdot(\bar{a}\times\bar{b})$.

$(\bar{\sigma}\cdot\bar{p})(\bar{\sigma}\cdot\bar{p}) = p^2\mathbb{1} + 0.$

$$H = \frac{\bar{p}^2}{2m} \mathbb{1} = \frac{(\bar{\sigma}\cdot\bar{p})(\bar{\sigma}\cdot\bar{p})}{2m}$$

↳ rewriting in some provocative way.. xD

↓

Couple to E.M by $\bar{p} \to \bar{\pi} = \bar{p} - \frac{q}{c}\bar{A}$. $\begin{cases} A(\hat{x}) \\ V(\hat{x}) \end{cases}$

$$H_{Pauli} = \frac{(\bar{\sigma}\cdot\bar{\pi})(\bar{\sigma}\cdot\bar{\pi})}{2m} = \frac{1}{2m}\left((\bar{\pi}\cdot\bar{\pi})\mathbb{1} + i\bar{\sigma}\cdot(\bar{\pi}\times\bar{\pi})\right)$$

$L \times L = i\hbar L$

$$(\bar{\pi}\times\bar{\pi})_k = \epsilon_{ijk}\pi_i\pi_j = \frac{1}{2}\epsilon_{ijk}[\pi_i,\pi_j] = \frac{i\hbar q}{c}(\partial_i A_j - \partial_j A_i)$$

$$= \frac{i\hbar q}{c}\vec{B}.$$

$$H_{Pauli} = \frac{1}{2}\frac{\bar{\sigma}}{m}\frac{i\hbar q}{c}\bar{B} + \dots$$

$$= \frac{e\hbar}{2mc}\bar{\sigma}\cdot\bar{B} \quad \dots$$

suggests $g = 2$ ...

+ L4.4:

Dirac Eqn: 24.4.

$$p^2c^2 + m^2c^4 = (\; ? \;)^2$$

$$= \left(c\vec{\alpha}\cdot\vec{p} + \beta mc^2\right)^2$$

$$\cancel{= (c\alpha_1 p_1 + c\alpha_2 p_2 +}$$

$H_{DIRAC} = c\vec{\alpha}\cdot\left(\vec{p} + \frac{e\vec{A}}{c}\right) + \beta mc^2 + V(r)$

derivation in R. Shankar.

From Dirac eqn — hydrogen atom Hamiltonian..

$$H = \underbrace{\frac{\vec{p}^2}{2m} + V(r)}_{H^{(0)}} - \underbrace{\frac{\vec{p}^4}{8m^3c^2}}_{\delta H_{rel}} + \underbrace{\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot\vec{L}}_{\delta H_{SO}}$$

$$+ \underbrace{\frac{\hbar^2}{8m^2c^2}\nabla^2 V}_{\boxed{\delta H_{Darwin}}}$$

$H^{(0)} \sim \alpha^2(mc^2)$

$\delta H \sim \alpha^4(mc^2)$

surprising term...

Charles Galtin Darwin...

$$\nabla^2 V = 4\pi\,\delta(r)$$

Fine Structure...

L-4.5:

Darwin term

$H^0 \sim \alpha^2(mc^2)$

$\delta H \sim \alpha^4(mc^2)$

1. Darwin

rel.

S.O.

put it all together...

Darwen term

$$V = -\frac{e^2}{r}, \quad \nabla^2 V = -e^2 \nabla^2\left(\frac{1}{r}\right) = $$
$$= \underline{4\pi e^2 \delta(\vec{r})},$$

$$\delta H_{Darwen} = \frac{\pi}{2} \frac{e^2\hbar^2}{m^2c^2} \delta(\vec{r}) \;\; \cancel{= \frac{\pi}{2m^2} \frac{\hbar^2 c^2 \alpha^2}{c^2} \delta(\vec{r})}$$

$$\cancel{= \frac{\pi \hbar^2}{2m^2} (\alpha^2) \delta(\vec{r})}$$

usual..

$\langle \psi^{(0)} | \delta H | \psi^{(0)} \rangle$ → 1st order correction...

$\delta(\vec{r})$ → * ~~...~~ ψ vanishes at 0 *

→ the correction vanishes...

• $\langle \ldots | \delta H_{Darwen} | \ldots \rangle$
$l=0$ $\quad$ $l=0$

all wavefunctions vanish at $r=0$ unless $\boxed{l=0}$.

δH_{Darwen} only effects $\boxed{l=0}$!

$l = 0$

$$E^{(1)\,Darwen} = \langle \psi_{n00} | \delta H_{Darwen} | \psi_{n00} \rangle$$

$$= \frac{\pi e^2 \hbar^2}{2m^2c^2} \underbrace{|\psi_{n00}(\vec{0})|^2}_{}$$

normalized wavefunction? a clever way...

HW: $|\psi(0)| \sim \left\langle \frac{dV}{dr} \right\rangle$

$l=0$ probs

$$\boxed{|\psi_{n00}(\vec{0})|^2 = \frac{1}{\pi n^3 a_0^3}}$$

$$\boxed{E^{\text{Darwin}}_{\text{nov}} = \alpha^4 mc^2\left(\frac{1}{2n^3}\right), \quad l=0 \text{ states}} \quad (*')$$

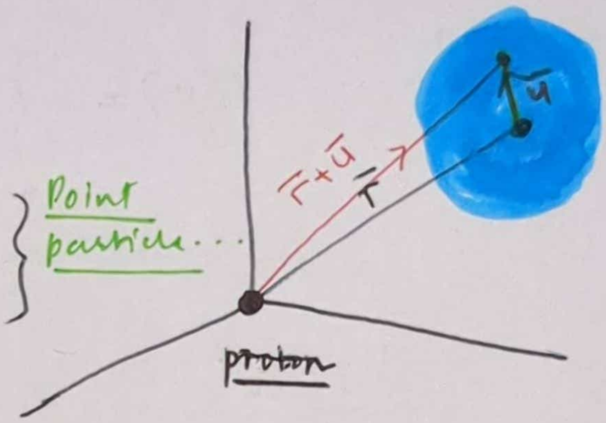
What's the story? Where does it come from? The physics of it... Darwin!

• The e^- is distributed fuzzy ball of charge... not just a ~~ball~~ -point particle.

due to proton.

∘ $V(\bar{r}) = -e\,\Phi(r)$

$= -e\left(\frac{e}{r}\right) = -\frac{e^2}{r}$ } Point particle...



↓

∘ $\tilde{V}(\bar{r}) = \int_{e^-} dq\,\Phi$ {charge density of e^-} $\rho(\bar{u}) = -e\,\rho_0(\bar{u})$

$\int_e d^3u\,\rho_0(\bar{u}) = 1$ ✓

$= \int_e d^3u\,\rho(\bar{u})\,\Phi(\bar{r}+\bar{u})$ } e centre at $\bar{r}$.

∘ $$\boxed{\tilde{V}(\bar{r}) = \int_{\text{electron}} d^3u\,\rho_0(\bar{u})\,V(\bar{r}+\bar{u})}$$

→ afterall the ball is small...

$$V(\bar{r}+\bar{u}) \simeq V(\bar{r}) + \sum_i \frac{\partial V}{\partial x^i}\bigg|_{\bar{r}} u^i + \frac{1}{2}\sum_{i,j}\frac{\partial^2 V}{\partial x^i \partial x^j}\bigg|_{\bar{r}} u^i u^j$$

$$\tilde{V}(\bar{r}) = V(\bar{r})\int d^3u\,\rho_0(\bar{u}) + \sum_i \frac{\partial V}{\partial x_i}\bigg|_{\bar{r}} \underbrace{\int d^3u\,\rho_0(\bar{u})\,u^i}_{\to 0}$$ sph symmetry...

$$+\frac{1}{2}\sum_{i,j}\frac{\partial^2 V}{\partial x_i \partial x_j}\bigg|_{\bar{r}} \int d^3u\,\rho_0(\bar{u})\,u^i u^j$$

$$\tilde{V}(\bar{r}) = V(\bar{r}) + \frac{1}{2} \sum_{i,j} \frac{\partial^2 V}{\partial x_i \partial x_j}\bigg|_r \int d^3u \, \frac{1}{3} \delta_{ij} \, \rho(u) u^2$$

assume $\boxed{\rho_0(\bar{u}) = \rho_0(u)}$

$$\boxed{\tilde{V}(r) = V(\bar{r}) \cancel{a} + \frac{1}{6} \nabla^2 V(r) \int d^3u \, \rho_0(u) u^2}$$

assume electron - ball of radius $\lambda = \frac{\hbar}{mc}$.

$$\rho_0(u) = \begin{cases} \frac{3}{4\pi\lambda^3} & u < \lambda \\ 0 & u > \lambda \end{cases}$$

$$\frac{3}{5} \lambda^2$$

$$\boxed{\tilde{V}(r) = V(r) + \frac{1}{10} \frac{\hbar^2}{m^2 c^2} \nabla^2 V.}$$

$\frac{1}{8} - \frac{1}{16}$ ✓

rough assump...

- Compton wavelength of e^- fundamental in QFT

$\lambda \longrightarrow$ size of a photon where $E =$ rest mass of e^-.

{ enough ~~energy~~ photon to push e^-, positron pair.. }

- $$E^{(1)\,rel}_{nlm} = -\frac{1}{8m^3c^2}\langle \psi_{nlm_l} | \bar{p}^4 | \psi_{nlm_l}\rangle$$

$$\boxed{\bar{p}^4 = \bar{p}^2 \cdot \bar{p}^2}$$

for non-degenerate !!! system

↑ degeneracy ...

- so, we better think through...

- $[\bar{p}^4, \bar{L}^2] = 0$, $[\bar{p}^4, L_z] = 0$. !

$[p^2, L_i] = 0$ rotat^nal invariance

if $\hat{O}$ hermitian commutes with your perturbation for which ur eigenstates are of $\hat{O}$ with diff. e.vs. ...

Good basis!

!

- diff l - version
  diff m_l - version : In the subspace of

δH is actually diagonal !!

$$E^{(1)}_{nlm_l} = \frac{-1}{8m^3c^2}\langle p^2\psi_{nlm} | p^2\psi_{nlm}\rangle$$

$$\left(\text{use } \left(\frac{\bar{p}^2}{2m} + V(r)\right)\psi_{nlm} = E_n\psi_{nlm}\right).$$

$$= \frac{-1}{2mc^2}\langle (E_n - V(r))\psi_{nlm} | (E_n - V(r))\psi_{nlm}\rangle$$

- $\langle \frac{1}{r} \rangle = \frac{1}{n^2 a_0}$.

$$\boxed{E^{(1)\,rel}_{n l m_l} = -\frac{1}{8}\alpha^4 (mc^2)\left\{ \frac{4n}{(l+\frac{1}{2})} - 3 \right\}} \quad (*^2)$$

{ Fine structure is something one should must do in their life ... so do them ... }

$\langle n\, l\, m_l\, m_s | \delta H_{rel} | n\, l\, m_l\, m_s \rangle$ — uncoupled basis elements .. (diagonal ...

$= \underbrace{f(n,l)}$ indep of $\boxed{m_l, m_s}$

is anticomb

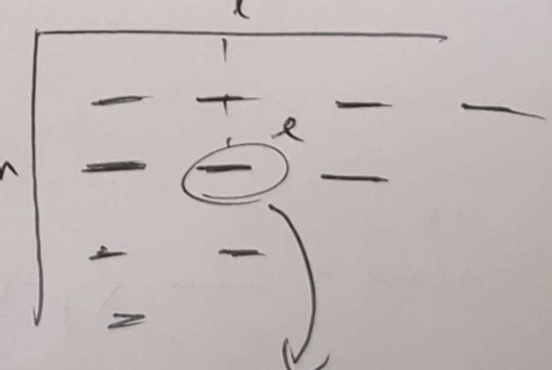
$\langle n\, l\, j\, m_j | \delta H_{rel} | n\, l\, j\, m_j \rangle$ — redo!?

- I don't have to!

- reors. w.r.t. j, m_j.

but only in j, m_j ...

- another arg() : abstractly



In this subspace → The basis makes perturbation diagonal ...

infact $\propto \mathbb{1} \cdot f(n,l)$

this same .. : (⌒

$\propto \mathbb{1}$ in any Ortho basis

- $\delta H_{SO} = \dfrac{e^2}{2m^2c^2}\dfrac{1}{r^3}\vec{S}\cdot\vec{L}$, $\vec{S}\cdot\vec{L} = \frac{1}{2}(J^2 - S^2 - L^2)$

Coupled basis :

- $$E^{(1)\,S.O}_{nljm_j} = \frac{e^2}{2m^2c^2}\langle \underline{n} l j m_j | \frac{\vec{S}\cdot\vec{L}}{r^3} | \underline{n} l j m_j\rangle$$

  - what about degeneracies?

    do we have the right to use NDPT again?

Yes, $\dfrac{\vec{S}\cdot\vec{L}}{r^3}$ commutes w. $\underline{L^2, J^2, J_z}$. !!! Good basis...

Check! do it...

$$E^{(1)\,S.O}_{nl,jm_j} = \frac{e^2\hbar^2}{4m^2c^2}\Big(j(j+1) - l(l+1) - \underbrace{\tfrac{3}{4}}_{s(s+1),\ s=\frac{1}{2}}\Big)\langle nljm_j|\frac{1}{r^3}|nljm_j\rangle$$

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

- doesn't depend on m_l! so cool.

So, $$\boxed{E^{(1)\,S.O}_{nljm_j} = \frac{(E_n^{(0)})^2}{mc^2}\,\frac{n\,[j(j+1)-l(l+1)-\frac{3}{4}]}{l(l+\frac{1}{2})(l+1)}}$$

$E_n^{(0)} = -\frac{1}{2}\alpha^2mc^2\left(\frac{1}{n^2}\right)$

- much of difficulty in DPT, NDPT, Good Basis } that's it.

$l=0$, s.o coupling (gets messy)...

they say s.o vanishes.

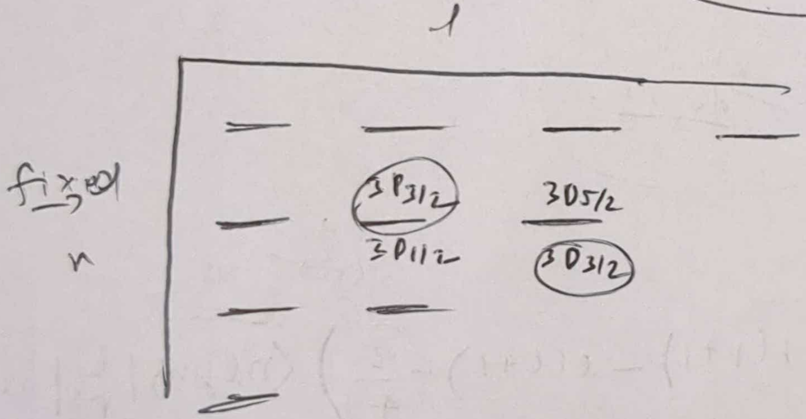
$l=0$ — s.o $\xrightarrow[\text{limits to}]{}$ δ Darwin !!

$$\langle n\, l\, j\, m_j \,|\, \delta H_{rel} + \delta H_{so} \,|\, n\, l\, j\, m_j \rangle$$

$$= \cancel{\alpha^4 mc^2}\ \cancel{-2\frac{(E_n^{(0)})^2}{mc^2}}\ \frac{(E_n^{(0)})^2}{mc^2} \times \left\{ 3 + 2n \left\{ \frac{j(j+1) - 3l(l+1) - \frac{3}{4}}{l(l+\frac{1}{2})(l+1)} \right\} \right\}$$

!!!

$\downarrow$ $\underline{f(j,l)}$.



j - fixed.

$$\begin{cases} l = j - 1/2 \\ l = j + 1/2 \end{cases}$$

$$\left.\begin{aligned} f(j,l)\big|_{l=j-1/2} &= \\ f(j,l)\big|_{l=j+1/2} &= \end{aligned}\right\} \boxed{-\frac{2}{j+1/2}}$$

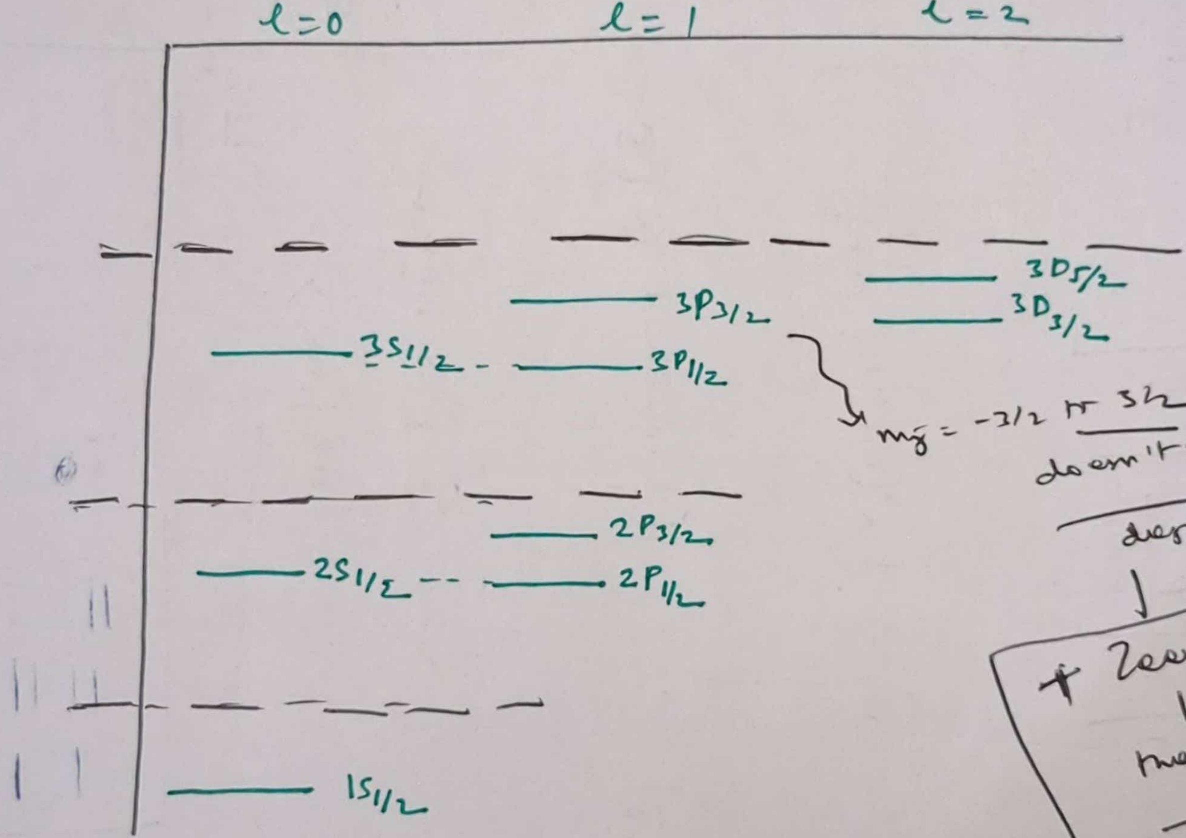
The whole structure just depends on "j" !!!

(1) fine structure

$$\boxed{E_{nljm_j} = -\alpha^4 (mc^2)\frac{1}{2n^4}\left[\underbrace{\frac{n}{j+1/2} - \frac{3}{4}}_{\text{always positive.}}\right].} \quad — (**)$$

• Consequence of "j" symmetry in Dirac eqn...

• how the spectrum looks...



$m_j = -3/2$ or $3/2$

doesn't change...

degeneracy still...

+ Zeeman

may break...

final $E^{(1)}_{n,l}\Big|_{\text{fine structure}, \, nljm_j} = -\alpha^4(mc^2)\frac{1}{2n^4}\left\{\frac{n}{j+1/2} - \frac{3}{4}\right\}.$

• $E^{(1)}_{n,l}\Big|_{rel, \, nljm_j} = \frac{-1}{8}\alpha^4(mc^2)\left(\frac{4n}{(l+1/2)} - 3\right)$

• $E^{(1)}_{n}\Big|_{SO, \, njlm_j} = \frac{(E^{(0)}_n)^2}{mc^2}\left\{n\left(\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l\,(l+\frac{1}{2})(l+1)}\right)\right\}$ $\quad E^{(0)}_n = -\frac{1}{2}\alpha^2 mc^2\left(\frac{1}{n^2}\right)$

• $E^{(1)}_{n}\Big|_{Darwin, \, n,l,j,m_j} = \alpha^4 mc^2\left(\frac{1}{2n^3}\right).$

FINE STRUCTURE . . .

- $\lim_{\ell \to 0} \delta H^{SO} = \delta H^{Darwin}$. $\delta H^{Darwin} = \begin{cases} \delta H^{SO} & \ell = 0 \\ = 0 & \ell \neq 0 \end{cases}$

- $$H_{\text{Fine structure}} = \overbrace{\left[\frac{\bar{p}^2}{2m} + V(r)\right]}^{H^{(0)}} - \overbrace{\left[\frac{\bar{p}^4}{8m^2c^2}\right]}^{\delta H^{rel}} + \overbrace{\left[\frac{1}{2m^2c^2} \frac{1}{r}\frac{dV}{dr} \vec{S}\cdot\vec{L}\right]}^{\delta H^{spin\text{-}orbit}} + \overbrace{\left[\frac{\hbar^2}{8m^2c^2} \nabla^2 V\right]}^{\delta H^{Darwin}}$$

$$\vec{S}\cdot\vec{L} = \frac{1}{2}(J^2 - L^2 - S^2) \qquad \frac{e^2}{r^3} \qquad \nabla^2 V = 4\pi\delta(r)$$

- $E_n^{(0)} = -\frac{1}{2}\alpha^2 mc^2\left(\frac{1}{n^2}\right)$ ◦ $E^{(1)\,rel}_{n,\ell,j,m_j} = -\frac{1}{8}\alpha^4(mc^2)\left\{\frac{4n}{(\ell+\frac{1}{2})} - 3\right\}$ ◦ $E^{(1)\,SO}_{n\ell j m_j} = \frac{(E_n^{(0)})^2}{mc^2} n \cdot \left\{\frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{\ell(\ell+\frac{1}{2})(\ell+1)}\right\}$

◦ $E_n^{(1)\,Darwin} = \alpha^4(mc^2)\left(\frac{1}{2n^3}\right)$ ◦ $(\ell\text{-multi}) \otimes (s\text{-multiplets}) = \sum j\text{-multi}$

$j = \ell - 1/2$ to $\ell + 1/2$

Un Coupled Basis ~~~ **Coupled Basis**

$|n\,\ell\,m_\ell\,m_s\rangle$ $\qquad$ $|n\,\ell\,j\,m_j\rangle \hookrightarrow n\,L(\ell)_j$

notation

$$\boxed{E_n^{(1)\,F.S} = \frac{-\alpha^4(mc^2)}{2n^4}\left\{\frac{n}{j+1/2} - \frac{3}{4}\right\}}$$

Final Spectrum: