Revisiting the Hydrogen atom

Review:

$$H = \frac{p^2}{2m} - \frac{e}{r} \qquad m \simeq m_e$$

$$E_n = -\frac{R}{n^2}, \quad R = \frac{e^2}{2a_0}, \quad a_0 = \frac{\hbar^2}{me^2}$$

$$\downarrow$$

$$E_n = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} = \underbrace{\left(\frac{e^4}{\hbar^2 c^2}\right)}_{\alpha^2}(mc^2)\frac{1}{2n^2} = \boxed{-\frac{\alpha^2(mc^2)}{2n^2}}$$

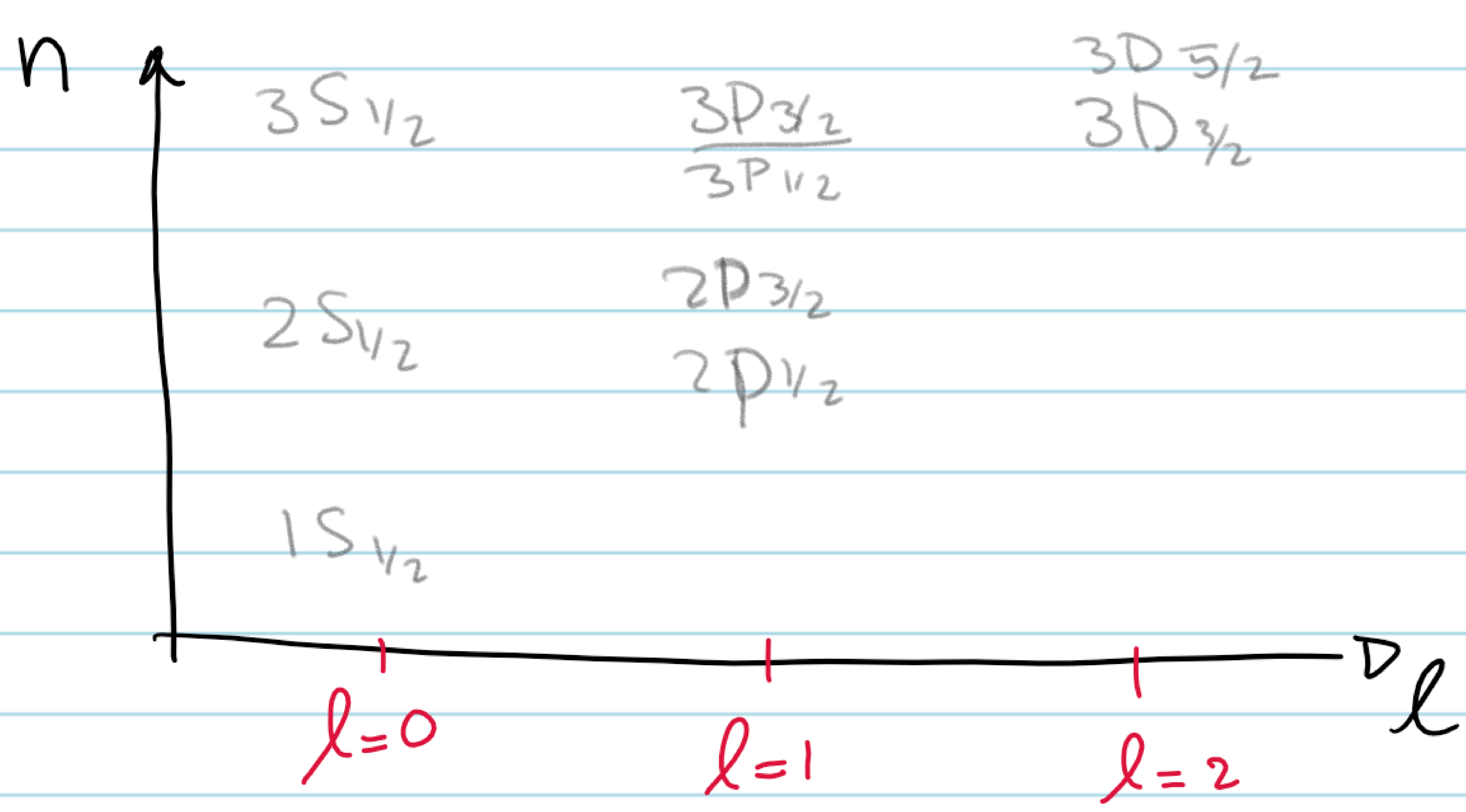
$$\boxed{\alpha = \frac{e^2}{\hbar c}} \sim 1/137$$

This expresses the energy in terms of the rest energy of the electron. → We use this as a scale.

$$P \simeq \frac{\hbar}{a_0} = \frac{me^2}{\hbar} = \left(\frac{e^2}{\hbar c}\right)(mc) = \alpha mc$$

$$\rightsquigarrow \boxed{v \sim \alpha c}$$

Quantum Numbers & energy levels.



Stark Effect

* Selection Rules

$$\langle \psi_{n,\ell m} | Z | \psi_{n'\ell' m'} \rangle$$

Remark 1: $[Z, L_z] = 0 \Rightarrow \overbrace{Z L_z |\psi_{n\ell m}\rangle}^{m\, Z|\psi_{n\ell m}\rangle} = L_z Z |\psi_{n\ell m}\rangle$

$\Rightarrow$ The quantum # m does not change.

$$\langle \psi_{n\ell m} | Z | \psi_{n'\ell' m'} \rangle = \delta_{m,m'} \langle \psi_{n\ell m} | Z | \psi_{n'\ell' m'} \rangle$$

$\hookrightarrow$ m should stay unchanged.

Remark 2:

Assignment: Show that

$$[L^2, [L^2, Z]] = 2\hbar^2 (L^2 Z + Z L^2). \quad (*)$$

(Hint: in one of the steps, it may be helpful to show that

$$L_x X + L_y Y + L_z Z = 0 \quad).$$

Using (*), we get

$$L^4 Z - 2L^2 Z L^2 + Z L^4 - 2\hbar^2 (L^2 Z + Z L^2) = 0$$

$\langle \psi_{n\ell m} | \cdot | \psi_{n'\ell' m'} \rangle$

$$\hookrightarrow \hbar^4 \left(\ell^2 (\ell+1)^2 - 2\ell\ell'(\ell+1)(\ell'+1) + \ell'^2 (\ell'+1)^2 - 2\ell(\ell+1) - 2\ell'(\ell'+1) \right)$$

$$\langle \psi_{n\ell m} | Z | \psi_{n'\ell' m} \rangle = 0$$

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$$\to \hbar^4\left(\ell^2(\ell+1)^2 - 2\,\ell\ell'(\ell+1)(\ell'+1) + \ell'^2(\ell'+1)^2 - 2\,\ell(\ell+1) - 2\ell'(\ell'+1)\right)$$
$$\langle \psi_{n\ell m} | z | \psi_{n'\ell' m}\rangle = 0$$

$\ell = \ell' = 0$

$$0 \times \langle \psi_{n\ell m} | z | \psi_{n'\ell' m}\rangle = 0$$

$\to$ So could still be non-zero.

$\ell = \ell' \pm 1$

Similarly $\to$ the factor is zero, and the transition rate could be any thing $\to$ is not restricted.

But if say

$\ell' = \ell = 1$

$$-8\hbar^4 \langle \psi_{n,1,m} | z | \psi_{n',1,m}\rangle = 0$$

$$\to \langle \psi_{n,1,m} | z | \psi_{n',1,m}\rangle = 0 \qquad \forall n, n', m$$

$\to$ These kind of equations indicate that the perturbation is sparse and vanishes for most elements.

The only non-vanishing ones are

$$\forall n \quad \underbrace{\langle \psi_{n,0,0} | z | \psi_{n',0,0}\rangle} \quad \& \quad \langle \psi_{n,\ell,m} | z | \psi_{n',\ell+1,m}\rangle \quad \forall n, m, \ell$$

This is also zero, b/c

z is odd & ψ_{n00} is fully symmetric. So this is zero too.

Using the selection rules above, we conclude that all the diagonal terms of W vanishes which means that

$$\hookrightarrow E^{(1)}_{n,l,m} = 0 \quad \forall n,l,m \longrightarrow \text{No first order correction.}$$

The first correction comes from $E^{(2)}_{n,l,m}$:

$$E^{(2)}_{n,l,m} = \sum_{\substack{m \neq n \\ l' = l \pm 1}} \frac{|\langle \psi_{nlm} | z | \psi_{m,l',m} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$E_{n,l,m} \simeq \frac{-R}{n^2} + (e\mathcal{E})^2 \sum_{\substack{m \neq n \\ l' = l \pm 1}} \frac{|\langle \psi_{nlm} | z | \psi_{m,l',m} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$\hookrightarrow$ Similar to our calculation for the ground state, we can calculate/estimate the Quadratic Polarizability for different levels.

For $n=2$, there's a 4-fold degeneracy (skipping the spin).

$$W = \begin{array}{c} \begin{bmatrix} 0 & 0 & \xi & 0 \\ 0 & 0 & 0 & 0 \\ \xi & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \\ \begin{array}{cccc} l=0 & m=-1 & 0 & 1 \end{array} \\ \underbrace{\qquad\qquad\qquad}_{l=1} \end{array} \qquad \xi = \langle \psi_{210} | z | \psi_{200} \rangle$$

$\hookrightarrow$ Is in fact a bit more challenging.

$n=2$

For $n=2$, there's a 4-fold degeneracy (skipping the spin).

$$W = \begin{array}{c} \\ \begin{bmatrix} 0 & 0 & \xi & 0 \\ 0 & 0 & 0 & 0 \\ \xi & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \\ \begin{array}{cccc} \ell=0 & m=-1 & 0 & 1 \end{array} \\ \qquad \underbrace{\qquad\qquad\qquad}_{\ell=1} \end{array}$$

$\xi = \langle \psi_{210} | z | \psi_{200} \rangle = -3a_0$

All the red ones are zero due to the selection rules.

So, first need to determine $|\psi^{(0)}\rangle$:

$$|\psi_{200}\rangle \rightarrow |\psi^{(0)}_{1,1}\rangle = \frac{|\psi_{200}\rangle + |\psi_{21,0}\rangle}{\sqrt{2}} \rightarrow E^{(1)}_{1,1} = \xi = -3a_0$$

$$|\psi_{2,1,0}\rangle \rightarrow |\psi^{(0)}_{1,2}\rangle = \frac{|\psi_{200}\rangle - |\psi_{2,1,0}\rangle}{\sqrt{2}} \rightarrow E^{(1)}_{1,2} = -\xi = 3a_0$$

$|\psi_{2,1,1}\rangle \rightarrow$?

$|\psi_{2,1,-1}\rangle \rightarrow$?

$\Big\} \rightarrow$ Degeneracy is not lifted by W, so we need to go one layer deeper.

But, for this case, $|\psi_{2,1,1}\rangle$ & $|\psi_{2,1,-1}\rangle$ remain as our zero-order state.

This is b/c W does not mix $m=1$ & $m=-1$.

✓ $|\psi_{2,1,1}\rangle \rightarrow |\psi^{(0)}_{1,3}\rangle \rightarrow E^{(1)}_{1,3} = E^{(1)}_{2,1,1} = 0$

✓ $|\psi_{2,1,-1}\rangle \rightarrow |\psi^{(0)}_{1,4}\rangle \rightarrow E^{(1)}_{1,4} = E^{(1)}_{2,1,-1} = 0$

$$\boxed{E_{1,r} \simeq \frac{-R}{4} + (e\mathcal{E})\, E^{(1)}_{1,r}}$$

Fine - Structure

Review

Original Hamiltonian $H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$

We solved this problem &

$|\psi^{(0)}\rangle \to |\psi^{(0)}_{nlm}\rangle \underbrace{|\chi\rangle}_{\text{Spin}}$ $\qquad E^{(0)} \to E_{nlm} = \frac{-R}{n^2}$

Here we want to consider some interactions that we didn't include so far.

To get to the perturbative problem, we start with the Dirac's Hamiltonian.

Let's try to make the Hamiltonian relativistic.

So far

Free particle: $E = p^2/2m \longrightarrow E = \sqrt{p^2c^2 + m^2c^4}$

QM $\quad \hat{H} = \frac{\hat{p}}{2m} \longrightarrow \boxed{?} \to$ Try to figure this out!

Ⓐ Expand $mc^2\sqrt{\frac{p^2}{m^2c^2}+1} \simeq$

$$E = mc^2\left[1 + \frac{p^2}{2m^2c^2} \underbrace{- \frac{p^4}{8m^4c^4}} + \cdots\right]$$

We can this as a first order correction & treat it as a perturbation.

Optional ↓

Ⓑ Klein _ Gordon eq. :

Let's say $\hat{H}^2 = \hat{P}^2c^2 + m^2c^4$.

$$\frac{\partial^2}{\partial t^2}|\psi\rangle = \left(\frac{-i}{\hbar}\right)^2\left(c^2\underset{i\hbar\nabla}{\hat{P}^2} + m^2c^4\right)|\psi\rangle$$

$$\hookrightarrow \left(\underbrace{\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2} + \frac{m^2c^2}{\hbar^2}\right)\psi = 0$$

$$\left(\Box^2 + \mu^2\right)\psi = 0 \quad \rightarrow \text{KG\_ eq.}$$

Dirac Equation

Let's assume that $\left(p^2c^2 + m^2c^4\right)$ can be written as a square of a quantity that is linear in P.

That is:

$$p^2c^2 + m^2c^4 = (c\alpha p + \beta mc^2)^2 .$$

Then we would need to solve for α & β such that

$\to \alpha_i^2 c^2 P_i^2 = c^2 P_i^2 \Rightarrow \alpha_i^2 = 1 \quad \forall i$

$\beta^2 m^2 c^4 = m^2 c^4 \Rightarrow \beta^2 = 1$

but also
$$\left\{\begin{array}{l} \alpha_x \alpha_y = \alpha_y \alpha_x = 0 \\ \{\alpha_i, \alpha_j\} = 0 \\ \{\alpha_i, \beta\} = 0 \end{array}\right\}^{i \neq j} \to \text{They cannot be numbers.}$$

$\hookrightarrow$ The smallest d this works for is $d = 4$.

Question: Check that $\alpha_i = \left[\begin{array}{c|c} 0 & \sigma_i \\ \hline \sigma_i & 0 \end{array}\right]$ works.

$\sigma_i \to$ Paulis

$i = 1, 2, 3$

$\alpha_x \quad \alpha_y \quad \alpha_z$

$$\beta = \left[\begin{array}{c|c} \mathbb{1} & 0 \\ \hline 0 & -\mathbb{1} \end{array}\right]$$

$\hookrightarrow$ If we find such matrices, then

$$\bar{H} = \alpha c \hat{P} + mc^2 \beta$$

This leads to Dirac's eq. :

$$i\hbar \frac{\partial|\psi\rangle}{\partial t} = \left(c\ \alpha . P + (mc^2)\beta\right)|\psi\rangle$$

$$\hookrightarrow i\hbar \frac{\partial \psi}{\partial t} = \left(c\,\alpha . \bar{P} + (mc^2)\beta\right)\psi$$

$\hookrightarrow$ Should be 4-D.

$\hookrightarrow$ Lorentz - spinor

$\hookrightarrow$ This does describe the electron. $\longrightarrow$ See chpt 20 of Shankar's book.

$\hookrightarrow$ Now, let's include the interaction with an E&M field.

Classically: $p \longrightarrow (p - qA/c)$

$$\hookrightarrow i\hbar \frac{\partial \psi}{\partial t} = \left(c\vec{\alpha}.\left(\hat{P} - \frac{q\vec{A}}{c}\right) + \beta mc^2 + q\phi\right)\psi$$

Potential

Let's consider $\phi = 0$: with $\psi(t) = \psi e^{-iEt/\hbar}$, $\psi = \begin{bmatrix} \chi \\ \Phi \end{bmatrix}$

Not to be confused with E.

$\boxed{\bar{E} = E + mc^2}$

$$\bar{E}\begin{bmatrix} \chi \\ \Phi \end{bmatrix} = \begin{bmatrix} mc^2 & c\vec{\sigma}.(\vec{P} - q\vec{A}/c) \\ c\vec{\sigma}(\vec{P} - q\vec{A}/c) & -mc^2 \end{bmatrix}\begin{bmatrix} \chi \\ \Phi \end{bmatrix}$$

$$\Rightarrow (mc^2 - \bar{E})\chi + c\vec{\sigma}.\left(\vec{P} - \frac{q\vec{A}}{c}\right)\phi = 0$$

$$(mc^2 + \bar{E})\Phi - c\vec{\sigma}.\left(\vec{P} - q\vec{A}/c\right)\chi = 0 \Rightarrow \Phi = \left(\frac{c\vec{\sigma}.(\vec{P} - \frac{q\vec{A}}{c})}{E + mc^2}\right)\chi$$

Show that for the non-relativistic case, $(v \ll c)$ $\frac{\Phi}{\chi} \simeq \frac{1}{2}\left(\frac{v}{c}\right) \ll 1$

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$$(mc^2 - E)\chi + c\vec{\sigma}\cdot\left(\vec{P} - \frac{q\vec{A}}{c}\right)\phi = 0 \qquad (*)$$

$$(mc^2 + E)\Phi - c\vec{\sigma}\cdot\left(\vec{P} - q\vec{A}/c\right)\chi = 0 \qquad (**)$$

For $v \ll c \rightarrow$

$$(*) \quad (E - mc^2)\chi = c\,\vec{\sigma}\cdot\left(\vec{P} - \frac{q\vec{A}}{c}\right)\Phi$$

$$(**) \quad \Phi = \frac{c\,\vec{\sigma}\cdot\left(\vec{P} - \frac{q\vec{A}}{c}\right)}{E + mc^2}\chi$$

$$\underbrace{(E - mc^2)}_{E}\chi = \frac{c^2\left(\vec{\sigma}\cdot\left(\vec{P} - \frac{q\vec{A}}{c}\right)\right)\left(\vec{\sigma}\cdot\left(\vec{P} - \frac{q\vec{A}}{c}\right)\right)}{(E + mc^2)}\chi$$

$$\left(\frac{v}{c}\right) \ll 1 \Rightarrow E + mc^2 \simeq 2mc^2$$

$$\hookrightarrow E\chi = \frac{1}{2m}(\vec{\sigma}\cdot\vec{\pi})(\vec{\sigma}\cdot\vec{\pi})\chi \quad \rightarrow \text{This is the Pauli eq.}$$

* Show that $(\vec{\sigma}\cdot\vec{A})(\vec{\sigma}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\vec{\sigma}\cdot(\vec{A}\times\vec{B})$.

$$E\chi = \frac{1}{2m}\left(\pi^2 + i\vec{\sigma}\cdot\vec{\pi}\times\vec{\pi}\right)$$

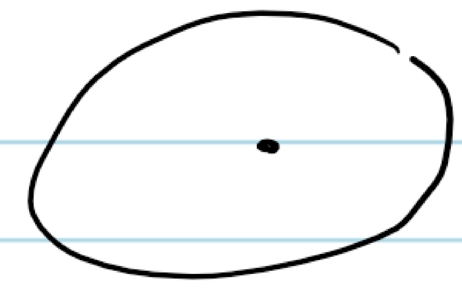
* $\vec{\pi}\times\vec{\pi} = \frac{i\hbar q\vec{B}}{c} \rightarrow$ (hint, $\vec{P} \rightarrow \nabla \rightarrow$ gives $\nabla\times A \propto \vec{B}$)

$$\Rightarrow E\vec{\chi} = \left(\underbrace{\frac{\left(\vec{P} - \frac{q\vec{A}}{c}\right)^2}{2m}}_{\text{We already}} - \frac{\hbar q}{2mc}\vec{\sigma}\cdot\vec{B}\right)\chi \rightarrow \text{spinor} = \begin{pmatrix}\psi_\uparrow \\ \psi_\downarrow\end{pmatrix}$$

$$\boxed{\text{Optional} \uparrow}$$

Spin-Orbit Coupling

Imagine that the p is rotating around the e.



From classical E & M:

$$B = \frac{1}{m_e c} \vec{E} \times \vec{P} \quad , \quad E = -\nabla\phi = \frac{1}{e}\frac{\vec{r}}{r}\frac{dV(r)}{dr}$$

$$\to B = \frac{1}{m_e c}\frac{1}{r}\frac{dV}{dr} \underbrace{\vec{r} \times \vec{P}}_{\vec{L}}$$

The magnetic moment of the electron interacts with this $\vec{B}$

$$H_{S.O} = \vec{\mu}_B \cdot \vec{B} = \frac{e}{mc}\vec{S} \cdot B = \frac{1}{m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S} \cdot \vec{L}$$

$\to$ This is off by a factor of two:

$$H_{SO} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S} \cdot \vec{L}$$

This is b/c the electron rest frame is not inertial.
We need to transform into the proton rest frame $\to$ Thomas Precession
But we will take a different approach later that gives the factor two correction.

Since $V = \frac{-e^2}{r} \to \frac{dV}{dr} = \frac{e^2}{r^2}$

$$H_{S.O} = \frac{e^2\hbar^2}{2m^2c^2}\frac{1}{r^3}\frac{\vec{S} \cdot \vec{L}}{\hbar^2}$$

First Order

$$H = \frac{\lambda}{r^3} \vec{S}.\vec{L}$$

① What's a good basis ?

$|\psi_{n\ell m, m_s}\rangle$: Not an eigen state of $\vec{S}.\vec{L}$.

$\hookrightarrow \{\vec{L}^2, L_z, \vec{S}^2, S_z\}$ & $[L_z, \vec{S}.\vec{L}] \neq 0$

But what if we used

$$\{ J^2 = (\vec{L}+\vec{S})^2, \vec{L}^2, \vec{S}^2, \vec{J}_z \}$$

instead. The new basis would still be eigen states of H_0, and also eigenstates of $\vec{S}.\vec{L}$.

$$|j, j_m, l, s\rangle = |j, j_m, l\rangle \quad , \boxed{s = 1/2} \to \text{is fixed.}$$

Assignment: Prove eq. 9.76 of your book.

$$\Psi_{n,l,j=l\pm\frac{1}{2},m} = R_{nl}(r)\left[\sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}} Y_{l,m+\frac{1}{2}} \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \pm \sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}} Y_{l,m-\frac{1}{2}} \left|\frac{1}{2}, \frac{1}{2}\right\rangle\right], \quad (9.76)$$

$$\langle n\, j\, \ell\, m_j | \frac{\vec{S}\cdot\vec{L}}{r^3} | n\, j\, \ell\, m_j \rangle :$$

$$\vec{S}\cdot\vec{L} = \frac{\vec{J}^2 - L^2 - S^2}{2} \Rightarrow$$

$$\frac{\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - 3/4 \right) \langle n\, \underbrace{j}\, \underbrace{j_m}\, \ell | \frac{1}{r^3} | n\, \underbrace{j}\, \underbrace{j_m}\, \ell \rangle$$

$|n\ell\rangle \to R_{n\ell}(r)$

$$= \frac{\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - 3/4 \right) \frac{2}{n^3 a_0^3\, \ell(\ell+1)(2\ell+1)}$$

$$E^{(1)}_{SO} = \underbrace{\frac{e^2 \hbar^2}{2m^2 C^2} \frac{1}{n^3 a_0^3}} \left[\frac{j(j+1) - \ell(\ell+1) - 3/4}{\ell(\ell+1)(2\ell+1)} \right]$$

$$\underbrace{\left(\frac{e^2}{2a_0} \frac{1}{n^2} \right)}_{E_n^{(0)}} \underbrace{\left(\frac{\hbar^2}{m^2 c^2 a_0^2} \right)}_{\alpha^2} \frac{1}{n}$$

$$\leq \frac{e^2 \hbar^2}{2m^2 c^2} \frac{1}{a_0^3}$$

How big is this?

$$H_{S.O} = \boxed{\frac{e^2\hbar^2}{2m^2c^2}} \frac{1}{r^3} \frac{\vec{S}\cdot\vec{L}}{\hbar^2}$$

$$E_n^{(0)} = \frac{-R}{n^2}, \quad R = \frac{e^2}{2a_0}, \quad a_0 = \frac{\hbar^2}{me^2} \Rightarrow \frac{e^2\hbar^2}{2m^2c^2} = \left(\frac{e^2}{2a_0}\right)\left(\frac{\hbar^2 a_0}{m^2c^2}\right)$$

$\hbar^2 / me^2$

$\hbar^4$

$$E_n = -\frac{R}{n^2}, \quad R = \frac{e^2}{2a_0}, \quad a_0 = \frac{\hbar^2}{me^2}$$

$$E_n = -\frac{me^4}{2\hbar^2}\frac{1}{n^2} = \underbrace{\boxed{\left(\frac{e^4}{\hbar^2c^2}\right)}}_{\alpha^2}(mc^2)\frac{1}{2n^2} = \boxed{-\frac{\alpha^2(mc^2)}{2n^2}}$$

$$\boxed{\alpha = \frac{e^2}{\hbar c}} \sim 1/137$$

$$\frac{E_n^{(1)}}{E_n^{(0)}} \simeq \frac{\alpha^2}{n} \longrightarrow \alpha = \frac{1}{137} \longrightarrow \text{This is a small perturbation.}$$

Relativistic Correction

$$E = mc^2 \sqrt{\frac{p^2}{m^2c^2}+1} \simeq$$

$$E = mc^2 \left[1 + p^2/2m^2c^2 - \underbrace{\frac{p^4}{8m^4c^4}}_{\text{We can take this as a first order correction}} + \cdots \right]$$

& treat it as a perturbation.

$$H = H_0 + mc^2 \underbrace{- \frac{1}{8m^3c^2} \hat{p}^4}_{\text{Perturbation}}$$

$$E_r^{(1)} = \frac{-1}{8m^3c^2} \langle \psi_{njJ_ml} | \hat{p}^4 | \psi_{njJ_ml} \rangle$$

$$= \;\text{"}\; \langle \psi_{nl} | \hat{p}^4 | \hat{p}^4 \rangle = -\frac{m^{\cancel{4}} e^8}{\hbar^4 n^4} \frac{1}{8\cancel{m^3}c^2} \left(\frac{8n}{2l+1} - 3 \right)$$

$$= -\frac{\alpha^2 E_n^{(0)}}{4n^2} \left(\frac{8n}{2l+1} - 3 \right)$$

$$\boxed{j = l \pm 1/2}$$

$$E_{FS} = E_{SO}^{(1)} + E_r^{(1)} = \frac{E_n^{(0)} \alpha^2}{4n^2} \left[\frac{4n\left(j(j+1) - l(l+1) - 3/4\right)}{l(l+1)(2l+1)} - \frac{8n}{2l+1} - 3 \right]$$

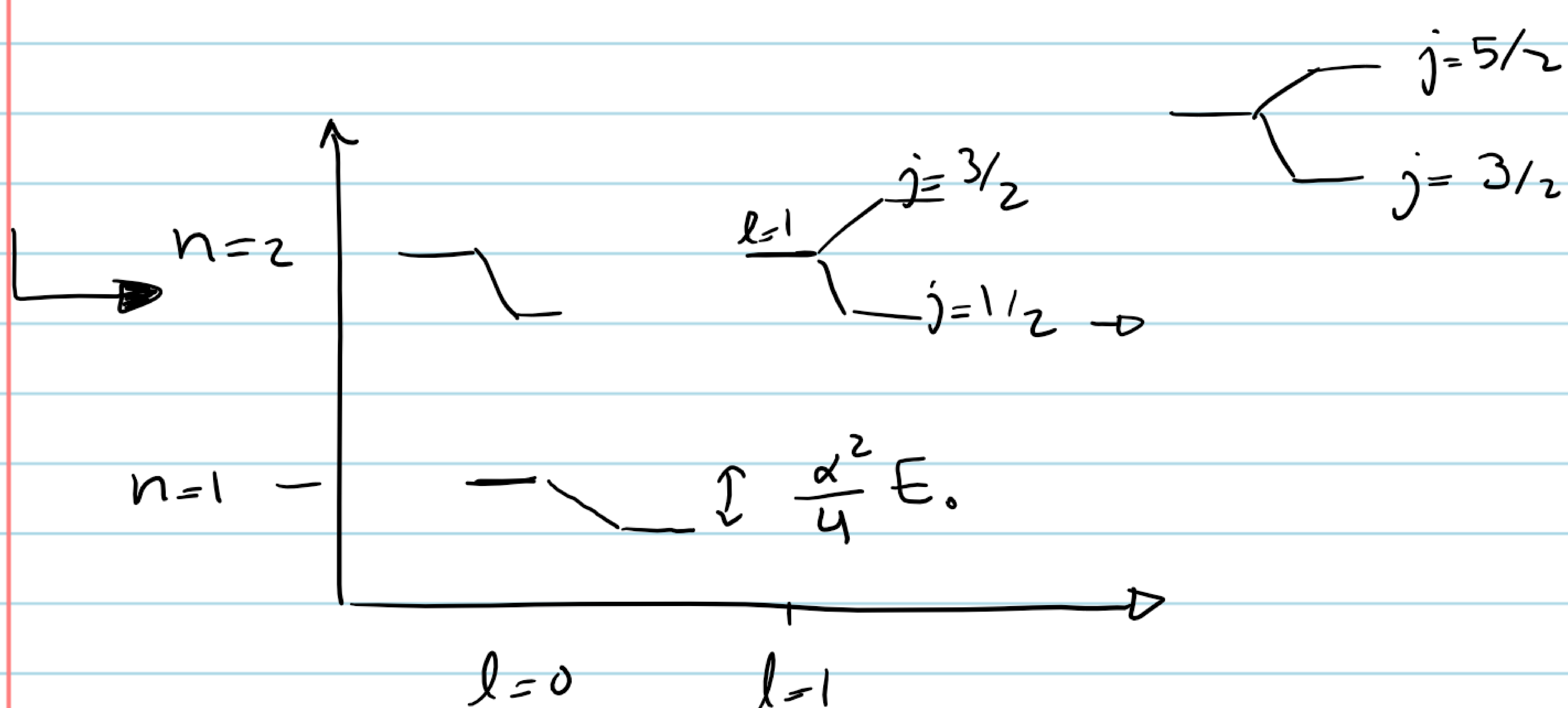
$\boxed{j = l \pm 1/2}$

$$E_{FS} = E^{(1)}_{SO} + E^{(1)}_{r} = \frac{E_n^{(0)}\alpha^2}{4n^2}\left[\frac{4n\left(j(j+1) - l(l+1) - 3/4\right)}{l(l+1)(2l+1)} - \frac{8n}{2l+1} - 3\right]$$

$\boxed{j = l + 1/2} \rightarrow \boxed{l = j - 1/2}$

$$\Rightarrow E_{FS} = \frac{-E_n^{(0)}\alpha^2}{4n^2}\left(\frac{(4n)\left(j(j+1) - (j-1/2)(j+1/2) - 3/4\right) - 8n(j-1/2)(j+1/2) - 3(2j)(j+1/2)(j+1/2)}{(j-1/2)(j+1/2)(2j)}\right)$$

$$= \boxed{\frac{|E_n^{(0)}|\alpha^2}{4n^2}\left(3 - \frac{4n}{j+1/2}\right)} \rightarrow \text{The same for } j = l - 1/2.$$



$\underline{n=2,\ l=1}$: $j = 1/2 \rightarrow E_F^{(1)} = \frac{|E_2^{(0)}|}{16}\alpha^2 \left(\overset{-5}{3 - 8}\right) = -\frac{5}{16}\alpha^2 |E_2^{(0)}|$

$j = 3/2 \rightarrow E_F^{(1)} = \ \dots\ \left(\overset{-1}{3 - 4}\right) = -\frac{5}{16}\alpha^2 |E_n^{(0)}|$

They both would go down.

$\underline{n=3,\ l=2}$: $j = 3/2 \rightarrow |E_3^{(0)}|\frac{\alpha^2}{36}\left(\overset{-3}{3 - \frac{12}{2}}\right) = -\frac{\alpha^2}{12}|E_3^{(0)}|$

$j = 5/2 \rightarrow$ ″ ″ $(3 - 4) =$

Some Remarks:

Degenerate PT vs Non-degenerate PT ?

Which one should we use for H_{FS} ?

H_0 is highly degenerate. So naturally we need to use DPT.

Take $n=2$. $\underline{l=0}$ (2) $\underline{l=1}$ (6)

For H_R : $\vec{P}^4 = (\vec{P}^2)(\vec{P}^2)$ and $[P^4, L^2] = [P^4, L_z] = 0$

Also P^4 has nothing to do with S so $[P^4, S_i] = 0$.

$$\Rightarrow \quad [P^4, \vec{J}^2] = 0 \quad , \quad [P^4, J_z] = 0$$

$$\Rightarrow \langle n j l m_j | P^4 | n j' l' m_j' \rangle \propto \delta_{jj'} \delta_{ll'} \delta_{m_j m_j'}$$

This indicates that the perturbation is already diagonal in $|n j l m_j\rangle$ basis which make the good basis for $|\psi^{(0)}\rangle$ for DPT.

Similarly, for the H_{SO}, we get $H_{SO} \propto \frac{\vec{S}.\vec{L}}{r^3}$

$[\vec{S}.\vec{L}, L^2] = [\vec{S}.\vec{L}, \vec{J}^2] = [\vec{S}.\vec{L}, \vec{J}_z] = 0$ → Double check for yourselves!

$[\frac{1}{r^3}, L^2] = [\frac{1}{r^3}, L_z] = 0$ and has nothing to do with the spin.

$$\Rightarrow \langle n j l m_j | \frac{\vec{S}.\vec{L}}{r^3} | n j' l' m_j' \rangle \propto \delta_{jj'} \delta_{ll'} \delta_{m_j m_j'}$$

↳ This is diagonal too.

Zeeman Effect

$$H_z = -\vec{\mu}_B \cdot \vec{B} - \mu_s \cdot \vec{B} = \frac{e}{2mc} \vec{L} \cdot \vec{B} + \frac{e}{mc} \vec{S} \cdot \vec{B}$$

$B = B_z \rightarrow$ Breaks the symmetry:

$$H_z = \frac{e B_z}{2mc} \left(L_z + 2 S_z \right)$$

Two situations

* $H_z \gg H_{FS}$: Strong Magnetic Field

* $H_z \ll H_{FS}$: Weak field

$$\frac{H_z}{H_{FS}} : \frac{\mu_B B}{W} \underbrace{\left(\frac{L_z + 2S_z}{S \cdot L} \right)}_{\sim 1} : B \quad \text{vs} \quad W/\mu_B \rightarrow B_{int}$$

Assignment: Estimate an upper-bound for $\frac{W}{\mu_B}$ to use that for a scale for B.

Weak_field

Since H_{FS} is stronger, we need to use the basis set by H_{SO}, i.e. $|\psi_{n,j,l,m_j}\rangle$.

$$E_z^{(1)} = \mu_B B \langle n,j,l,m_j | L_z + 2S_z | n,j,l,m_j \rangle$$

$$L_z + 2S_z = J_z + S_z$$

This is easy. It commutes with H_0

?

Assignment: Show that (Projection Lemma)

$$\langle j, m_j | S_z | j, m_j \rangle = \frac{\langle j, m_j | \vec{J}\cdot\vec{S} | j, m_j \rangle}{\hbar^2 j(j+1)} \langle j m_j | J_z | j m_j \rangle$$

Using the eq. above, we get

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

$$E_z^{(1)} = \mu_B B \underbrace{\left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2\hbar^2 j(j+1)} \right]}_{g_j} j_m = \mu_B B j_M g_j$$

$$g_j = \left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2\hbar^2 j(j+1)} \right] \rightarrow \text{Gyro-magnetic ratio}$$

☐ Zeeman effect

☐ Hyperfine structure

Zeeman: Weak field

$$H = \underbrace{H_0 + H_{SO}}_{\tilde{H}_0} + H_z \longrightarrow \left\{ |n, j, l, m_j\rangle ,\ E = E^{(0)} + E^{(1)} \right\}$$

↳ Note that these are not the exact eigen-system of $\tilde{H}_0$.

$$H_z = \frac{\mu_B B}{\hbar}\left(L_z + S_z + S_z \right) = \frac{\mu_B B}{\hbar}\left(J_z + S_z \right)$$

This is diagonal. ✓

$$H_z = \frac{\mu_B B}{\hbar} J_z + \frac{\mu_B B}{\hbar} S_z$$

$$E_z^{(1)} = \mu_B B\, m_j + \frac{\mu_B B}{\hbar} \underbrace{\langle n, j, l, m_j | S_z | n, j, l, m_j \rangle}$$

How do we calculate this?

$$\hbar^2\, j^2 (j+1)^2 \langle A\rangle - 2 j j' (j+1)(j'+1) + j'^2 (j'+1)^2 \langle A \rangle$$

$j^2 + j^4 + 2j^3$ $\quad j^2 + j + j'^2 + j'$ $\quad = -\frac{1}{2}\left(j(j+1) + j'(j'+1) \right)$

Use $\frac{1}{4\hbar^2}\left[\vec{J}^2, \left[\vec{J}^2, \vec{A} \right]\right] = \left(\vec{J}\cdot\vec{A} \right)\vec{J} - \frac{1}{2}\left(\vec{J}^2 \vec{A} + \vec{A}\vec{J}^2 \right)$ (eq *)

(This is true for any vector operator $\vec{A}$).

* Prove the eq. above.

$\vec{A} \to \vec{S}$, take z component.

$\langle n j_1 l_1 m_j | (eq.*) | n j l m_j \rangle \Rightarrow L.H.S = 0$

$$\Rightarrow \langle (\vec{S}.\vec{J})\,\vec{J} \rangle = \hbar^2 j(j+1) \langle \vec{S} \rangle$$

$$\langle \vec{S} \rangle = \frac{\langle (\vec{S}.\vec{J})\,\vec{J} \rangle}{\langle \vec{J}^2 \rangle} \longrightarrow \underline{\text{Projection of } \vec{S}}$$

$$\langle S_z \rangle = \frac{\langle (\vec{S}.\vec{J})\, J_z \rangle}{\hbar^2 j(j+1)} = \frac{\hbar m_j}{\hbar^2 j(j+1)} \langle S.J \rangle$$

$$\langle \vec{S}.\vec{J} \rangle : \quad \vec{L} = \vec{J} - \vec{S} \Rightarrow \vec{L}^2 = \vec{J}^2 + \vec{S}^2 - 2\vec{S}.\vec{J}$$

$$\Rightarrow \boxed{\langle S_z \rangle} = \frac{\hbar m_j}{\hbar^2 j(j+1)} \left\langle \frac{\vec{J}^2 + \vec{S}^2 - \vec{L}^2}{2} \right\rangle$$

$$\boxed{= \left(\frac{j(j+1) + 3/4 - l(l+1)}{j(j+1)} \right) \hbar m_j}$$

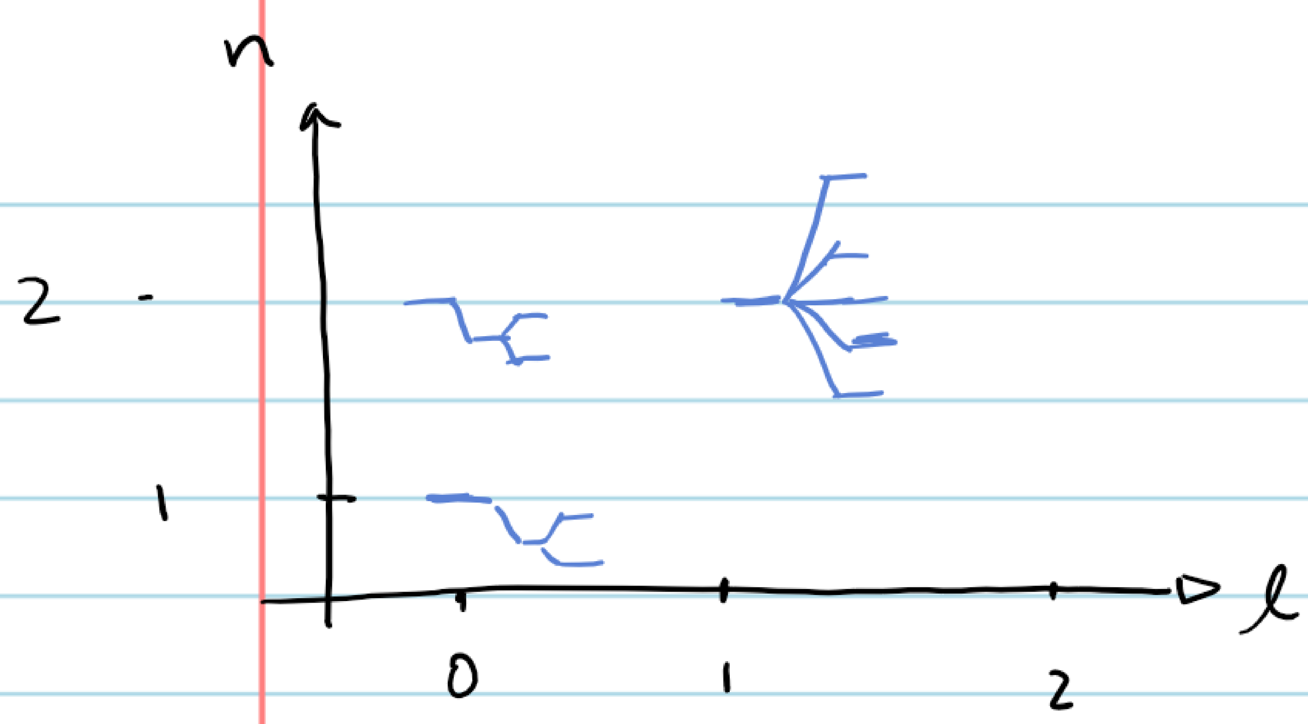
$$\Rightarrow E_z^{(1)} = \mu_B B \underbrace{g_{jl}}_{g_j(l)} m_j$$

$$g_{jl} \text{ or } g_j(l) = \left[1 + \frac{j(j+1) + 3/4 - l(l+1)}{j(j+1)} \right]$$

Landé g-factor or the gyro-magnetic ratio.

↳ The electron has a different responce to the magnetic field based on it's state. But it would always be splitted for different m_j values.

This is one of the reasons why the notation ${}^{2S+1}L_j$ is useful.



$\underline{n=1}$, $l=0 \to j=1/2 \Rightarrow m_j = \pm 1/2$

$\hookrightarrow E^{(1)} = \pm \mu_B B$

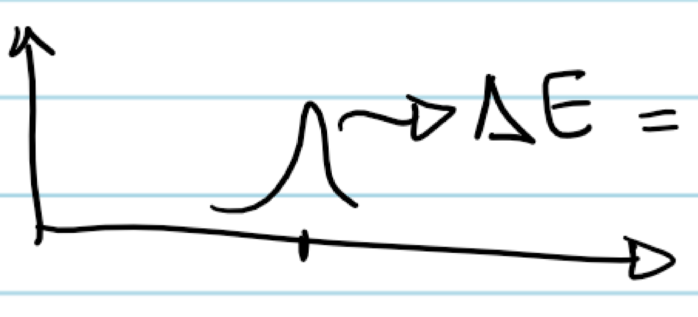
$(g=2,\ m_j = 1/2)$

$n=2,\ l=0 \to j=1/2 \Rightarrow g=2 \to E^{(1)} = \pm \mu_B B$

$n=2,\ l=1 \to j=3/2 \rightsquigarrow g = 4/3 \rightsquigarrow E^{(1)} = 4/3\, \mu_B B \, \{-3/2,\ -1/2,\ 1/2,\ 3/2\}$ (m_j)

$\hookrightarrow j = 1/2 \rightsquigarrow g = 2/3 \to E^{(1)} = \pm 1/3\, \mu_B B$

$\underline{\text{Spectroscopy}}$: we get the spacing between levels

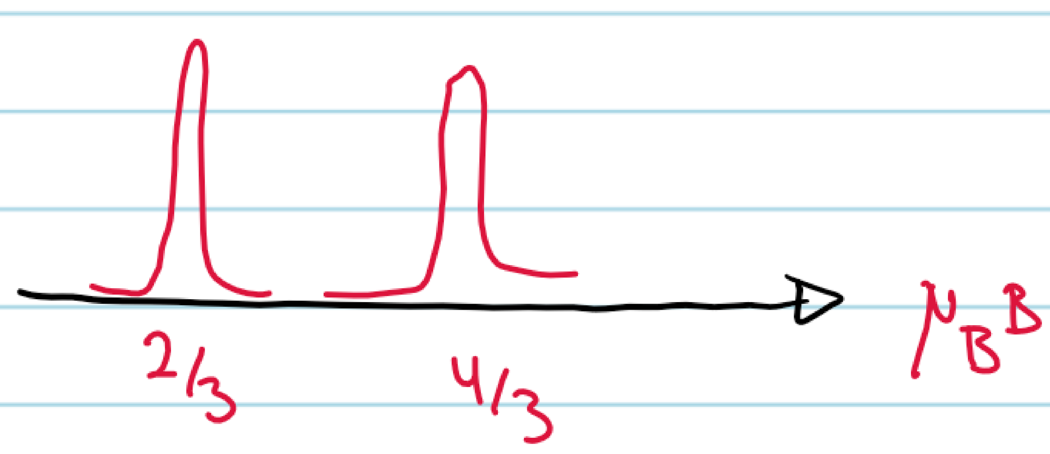


$\rightsquigarrow \Delta E = E_m - E_n$

$n=1 \rightsquigarrow \Delta E = \Delta E^{(1)} = 2\mu_B B$

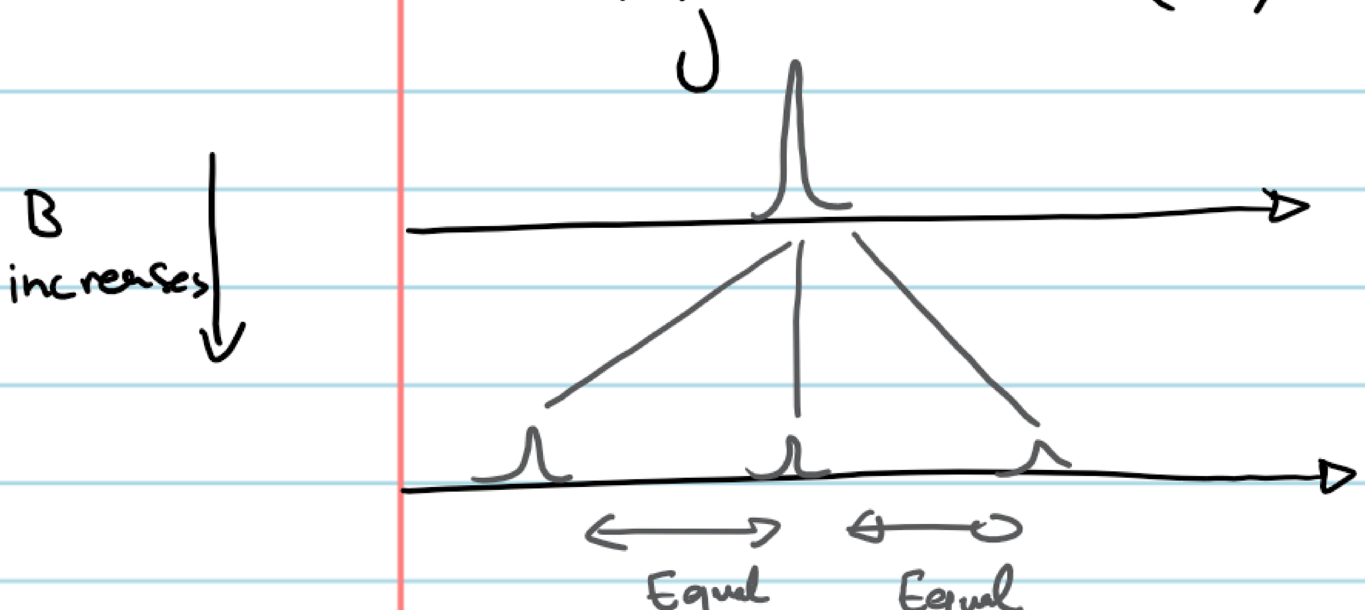
within $\begin{pmatrix} n=2 \\ l=0 \end{pmatrix} \rightsquigarrow \Delta E = \Delta E^{(1)} = 2\mu_B B$

$\begin{pmatrix} n=1 \\ l=1 \end{pmatrix} \rightsquigarrow \Delta E = \Delta E^{(1)} = \begin{cases} j=3/2 \rightsquigarrow 4/3\, \mu_B B \\ j=1/2 \rightsquigarrow 2/3\, \mu_B B \end{cases}$ $\to$ Spacing is not equal for all the levels with $l=1$.



$\underline{\text{Normal Zeeman}}$

$\Delta E \propto m_j \rightsquigarrow \text{Const}(l)$



Anomalous Zeeman

$g_{j,l} \rightsquigarrow$ depends on l