Fine Structure and The Anomalous Zeeman Effect:

One of the most useful applications of perturbation theory is to calculate the energy corrections for the H atom. Here we are interested to calculate the corrections due to the fine structure and the Zeeman effect.

① Fine structure: The fine structure is due to two effects, the relativistic correction and the spin-orbit coupling.

ⓐ Relativistic correction:

The kinetic energy of the electron in the H atom is

$$K = \sqrt{p^2c^2 + m^2c^4} - \underbrace{mc^2}_{\text{rest energy} \approx 0.51 \text{ MeV}} = mc^2\left(1 + \frac{p^2}{m^2c^2}\right)^{1/2} - mc^2$$

$$= mc^2\left[\left(1 + \frac{p^2}{m^2c^2}\right)^{1/2} - 1\right] \; ; \text{ Now } \frac{p^2}{m^2c^2} \ll 1$$

$$\frac{v}{c} = \frac{mv}{mc} = \frac{p}{mc} \; ; \quad p \sim \frac{\hbar}{a_0}$$

$$\approx \frac{\hbar}{a_0 mc} \; ; \quad a_0 = \frac{\hbar^2}{me^2}$$

$$\approx \frac{\hbar}{\frac{\hbar^2}{me^2} mc} \approx \frac{e^2}{\hbar c} = \alpha = \frac{1}{137} \quad \text{fine structure constant}$$

$$\Rightarrow \frac{p^2}{m^2c^2} = \left(\frac{p}{mc}\right)^2 = \left(\frac{1}{\alpha}\right)^2 = \frac{1}{\alpha^2} \ll 1$$

$$\Rightarrow K = mc^2\left[\cancel{1} + \frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\frac{p^4}{m^4c^4} - \cancel{1}\right] \approx \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{relativistic correction to } K} + \cdots$$

$$\Rightarrow H = \frac{\hat{p}^2}{2m} - \frac{e^2}{r} - \frac{\hat{p}^4}{8m^3c^2} = H_o + H' \quad ; \quad H_o = \frac{p^2}{2m} - \frac{e^2}{r}$$

$$H' = -\frac{\hat{p}^4}{8m^3c^2}$$

Now $E_n^{(1)} = \langle nlm | H' | nlm \rangle = \frac{-1}{8m^3c^2} \langle nlm | \hat{p}^4 | nlm \rangle$

using $\hat{H}_o = \frac{\hat{p}^2}{2m} - \frac{e^2}{r} \Rightarrow \hat{p}^2 = 2m\left(\hat{H}_o + \frac{e^2}{r}\right)$; $H_o|nlm\rangle = E_n|nlm\rangle$

$$\Rightarrow \langle nlm | \hat{p}^4 | nlm \rangle = (2m)^2 \langle nlm | \left(\hat{H}_o + \frac{e^2}{r}\right)^2 | nlm \rangle$$

$$= (2m)^2 \langle nlm | \hat{H}_o^2 + \hat{H}_o \frac{e^2}{r} + \frac{e^2}{r}\hat{H}_o + \frac{e^4}{r^2} | nlm \rangle$$

$$= (2m)^2 \Big[E_n^2 + E_n \langle nlm | \frac{e^2}{r} | nlm \rangle + \langle nlm | \frac{e^2}{r} | nlm \rangle E_n + \langle nlm | \frac{e^4}{r^2} | nlm \rangle$$

now using $E_n = \frac{-e^2}{2a_0 n^2}$

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

$$\Rightarrow E_n^{(1)} = -\frac{(2m)^2}{8m^3c^2} \left[\frac{e^4}{4a_o^2 n^4} - \frac{2e^2}{2a_o n^2}\frac{e^2}{n^2 a_o} + \frac{2e^4}{n^3 a_o^2 (2l+1)} \right]$$

$$= -\frac{1}{2mc^2} \left[-\frac{3}{4}\frac{e^4}{a_o^2 n^4} + \frac{2e^4}{n^3 a_o^2 (2l+1)} \right] ;$$

using $a_o = \frac{\hbar^2}{me^2}$

$$a_o^2 = \frac{\hbar^4}{m^2 e^4} = \frac{\hbar^2}{m^2 \frac{e^4}{\hbar^2}} = \frac{\hbar^2}{m^2c^2 \frac{e^4}{\hbar^2 c^2}} \alpha^2 = \frac{\hbar^2}{m^2c^2\alpha^2}$$

$$= -\frac{1}{2mc^2} \left[-\frac{3}{4}\frac{e^4 m^2 c^2 \alpha^2}{\hbar^2 n^4} + \frac{2e^4 m^2 c^2 \alpha^2}{\hbar^2 n^3 (2l+1)} \right]$$

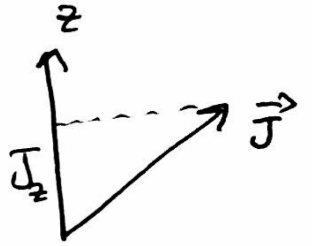
$$= -\frac{1}{2} mc^2 \frac{e^4}{\hbar^2 c^2} \left[\frac{2\alpha^2}{n^3(2l+1)} - \frac{3\alpha^2}{4n^4} \right]$$

$$E_n^{(1)} = -\frac{1}{2} mc^2 \alpha^2 \left[\frac{2\alpha^2}{n^3(2l+1)} - \frac{3\alpha^2}{4n^4} \right] \quad \text{----- (8)}$$

Quick Review of the vector model in QM:

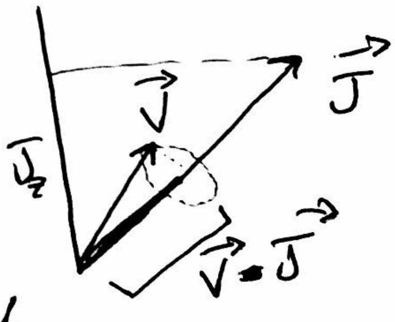
Before we discuss the topic of spin orbit coupling (next section), I think it is important to talk about the vector model in Quantum mechanics.

- consider the total angular momentum vector $\vec{J}$. since there are no external torques acting on the system, the total angular momentum is conserved. in the absence of any external perturbation on the system, we are free to choose the z direction the way we wish. if, however, a magnetic field is applied, there is a preferred direction in space and the z direction is conventionally taken along the direction of the external magnetic field.



the length of $\vec{J}$ is fixed $|\vec{J}| = \hbar\sqrt{j(j+1)}$ and the length of its projection along z takes quantized values $J_z = m_j\hbar$; $-j \leq m_j \leq j$

- Now consider an arbitrary vector $\vec{V}$ that points along an arbitrary direction and precess around $\vec{J}$. the magnitude of the vector $\vec{V}$ is fixed but it may points in any direction, so the component of $\vec{V}$ along the z direction (V_z) has no definite value. so how do we calculate the expectation value of V_z. the ~~answer~~ answer is using the vector model. now the vector $\vec{V}$ precess around the vector $\vec{J}$ continuously, therefor, $\vec{V}$ has an equal probabilities of being in any particular direction along the precessional path and consequently, its projection on the z axis (V_z) would give



different values depending on the position along this precessional path. for this reason, V_z is not a good quantum number.

∴ let us summarize, the vector $\vec{V}$ has a fixed value $|\vec{V}|$; the projection of $\vec{V}$ on $\vec{J}$ has a definite value. the vector model tells us that if we want to find the expectation value of V_z, we project $\vec{V}$ on $\vec{J}$ and then project the resulting vector on the z axis.

from last diagram, we see that $\vec{V} = a\vec{J}$; a is a constant to be determined. now the projection of $\vec{V}$ on $\vec{J}$ is $(\vec{V}\cdot\vec{J})$

$$\vec{V}\cdot\vec{J} = ((a\vec{J})\cdot\vec{J}) = aJ^2 \Rightarrow a = \frac{\vec{V}\cdot\vec{J}}{J^2} \Rightarrow \vec{V} = \frac{\vec{V}\cdot\vec{J}}{J^2}\vec{J}$$

$$\text{so } \langle\psi|V_z|\psi\rangle = \langle\psi|\frac{\vec{V}\cdot\vec{J}}{J^2}J_z|\psi\rangle ; \quad J^2 = j(j+1)\hbar^2$$

$$= \langle\psi|\frac{\vec{V}\cdot\vec{J}}{J^2}|\psi\rangle \langle\psi|J_z|\psi\rangle$$

$$= \langle\psi|\vec{V}\cdot\vec{J}|\psi\rangle \underbrace{\langle\psi|\frac{1}{J^2}|\psi\rangle}_{\frac{1}{\hbar^2 j(j+1)}} \underbrace{\langle\psi|J_z|\psi\rangle}_{\hbar m_j}$$

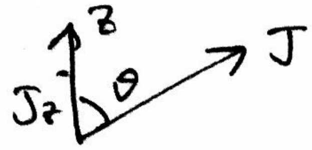
so one need to find $\langle\vec{V}\cdot\vec{J}\rangle$ to be able to calculate $\langle V_z\rangle$.

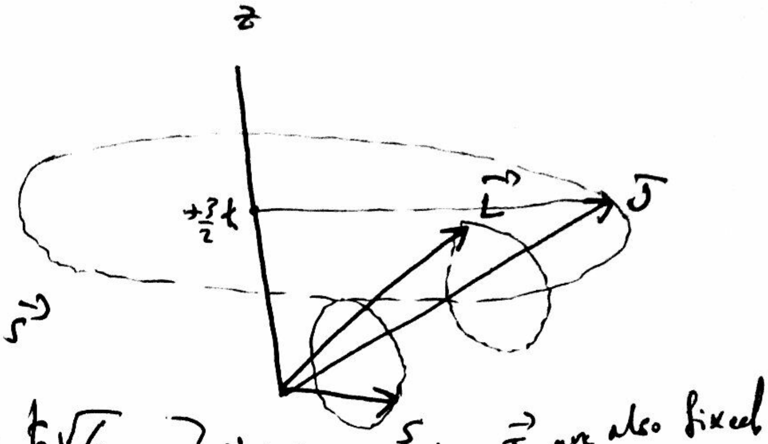
in principle, the vector $\vec{V}$ could be $\vec{L}$ (orbital angular momentum) or $\vec{S}$ (spin angular momentum)

- Example: consider the following diagram that is constructed for a particle with $l=2$, $s=1/2$, $j=5/2$, $m_j=3/2$. $\vec{J}$ precesses around z-axis and both $\vec{S}$ and $\vec{L}$ precess around J. $\vec{J}$ and J_z have a fixed values

$$|\vec{J}| = \hbar\sqrt{j(j+1)} = \frac{1}{2}\sqrt{35}\hbar = \sqrt{\frac{35}{4}}\hbar$$

$$J_z = \hbar(3/2) = \frac{3}{2}\hbar$$





$$\cos\theta = \frac{J_z}{|J|} = \frac{3/_2\, \hbar}{\frac{\sqrt{35}}{2}\hbar} = \frac{3}{\sqrt{35}}$$

now the magnitude of $\vec{L}$ and $\vec{s}$ are fixed at $|\vec{L}| = \hbar\sqrt{l(l+1)} = \hbar\sqrt{6}$

$|\vec{s}| = \hbar\sqrt{s(s+1)} = \frac{\hbar}{2}\sqrt{3}$ } their projections along $\vec{J}$ are also fixed

however, the direction of $\vec{L}$ and $\vec{s}$ is not fixed in space. we note that both $\vec{L}$ and $\vec{s}$ have equal probabilities of being in any particular direction $\Rightarrow$ their projects on z-axis gives different values depending on their directions. thus L_z and S_z are not fixed and they are not good quantum numbers. so using the vector model, we can calculate $\langle l_z \rangle$ and $\langle S_z \rangle$

$$\langle l,s,j,m_j | L_z | l,s,j,m_j \rangle = \langle l,s,j,m_j | \frac{\vec{L}\cdot\vec{J}}{J^2} J_z | l,s,j,m_j \rangle$$

now to find $\vec{L}\cdot\vec{J}$, we use the fact $\vec{J} = \vec{L} + \vec{S} \Rightarrow \vec{S} = \vec{J} - \vec{L}$

$$\Rightarrow S^2 = J^2 + L^2 - 2\vec{L}\cdot\vec{J} \Rightarrow \vec{L}\cdot\vec{J} = \frac{1}{2}(J^2 + L^2 - S^2)$$

$$\Rightarrow \langle l,s,j,m_j | \vec{L}\cdot\vec{J} | l,s,j,m_j \rangle = \frac{\hbar}{2}\left(j(j+1) + l(l+1) - s(s+1) \right) = 7\hbar$$

$$\Rightarrow \langle L_z \rangle = \frac{7\hbar \;\; 3/_2\,\hbar}{\hbar\, \frac{5}{2}\times\frac{7}{2}} = \frac{6}{5}\hbar$$

similarly $\langle S_z \rangle = \langle \frac{\vec{S}\cdot\vec{J}}{J^2} J_z \rangle$; using $\vec{L} = \vec{J} - \vec{S}$

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

$$\vec{S}\cdot\vec{J} = \frac{1}{2}(J^2 + S^2 - L^2)$$

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

$$= \frac{14}{8}\hbar$$

$$= \frac{\frac{14}{8}\hbar \cdot \frac{3}{2}\hbar}{\hbar\,\frac{5}{2}\times\frac{7}{2}} = \frac{3}{10}\hbar$$

(b) spin-orbit coupling:

the spin-orbit coupling in the H atom arises from the interaction between the electron's spin magnetic moment $\vec{\mu}_s$ and the proton's orbital magnetic field $\vec{B}$. The origin of the magnetic field experienced by the electron moving at a velocity $\vec{v}$ in a circular orbit around the proton can be explained classically as follows: the electron within its rest frame, sees the proton moving at $-\vec{v}$ in circular orbit around it. from the classical electrodynamics, the magnetic field experinsed by the electron is

$$\vec{B} = -\frac{1}{c}\vec{v}\times\vec{E} = -\frac{1}{m_e c}\vec{P}\times\vec{E} = \frac{1}{mc}\vec{E}\times\vec{P} \quad ; \text{ when } \vec{E} = -\nabla\phi \; ; \; \phi = \frac{e}{r}$$

internal field

$$\vec{E} = -\frac{d\phi}{dr}\hat{r} \; ; \; \hat{r} = \frac{\vec{r}}{r} = -\frac{\vec{r}}{r}\frac{d\phi(r)}{dr}$$

$$= \frac{1}{mc}\left(-\frac{\vec{r}}{r}\frac{d\phi}{dr}\times\vec{P}\right)$$

$$= -\frac{1}{mcr}\frac{d\phi}{dr}\vec{r}\times\vec{P}$$

$$= -\frac{1}{mcr}\frac{d\phi}{dr}\vec{L} \quad ; \text{ when } \vec{L} = \vec{r}\times\vec{P}$$

now using $\vec{\mu}_s = \frac{-e}{mc}\vec{S} \Rightarrow H' = -\vec{\mu}_s\cdot\vec{B} = \frac{-e}{m^2c^2}\frac{1}{r}\frac{d\phi}{dr}\vec{S}\cdot\vec{L}$

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

it was found that H' is twice the observed spin-orbit interaction. So we have to divide this H' by 2 (called Thomas factor)

$$\Rightarrow H' = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S}$$

$$\text{so } H = H_0 + H' = \frac{P^2}{2m} - \frac{e^2}{r} + \underbrace{\frac{e^2}{2m^2c^2r^3}\vec{L}\cdot\vec{S}}_{\text{Perturbation}}$$

Now what are the unperturbed states to be used to calculate energy corrections ??

answer: since the spin is taken into account, then the total wave-function is a product of spatial part $\psi_{nlm}(r,\theta,\phi)$ and a spin part $|\chi_\pm\rangle$. so we have two choices: first the joint eigenstates $|nlm_lm_s\rangle$ of L^2, L_z, S^2, S_z, and the second is the joint eigen-states $|nljm\rangle$ of J^2, J_z, L^2, L_z. Now H_0 is diagonal in both representations, but H' is diagonal in the second representation but not in the first. So the second choice is good for this problem.

i.e in the first repres

$|nlm_lm_s\rangle$ $\quad [\vec{L}, \vec{L}\cdot\vec{S}] \neq 0$ $\quad [\vec{S}, \vec{L}\cdot\vec{S}] \neq 0$ $\Rightarrow$ $\vec{L}$ and $\vec{S}$ are not conserved

where
$[\vec{L}, \vec{L}\cdot\vec{S}] = i\hbar\, \vec{S}\times\vec{L}$
$[\vec{S}, \vec{L}\cdot\vec{S}] = i\hbar\, \vec{L}\times\vec{S}$

in the second repres

$|nljm\rangle$ $\quad [\vec{J}, \vec{L}\cdot\vec{S}] = 0 \Rightarrow \vec{J}$ is conserved

as a result, the eigenstates $|nljm\rangle$ are simultaneously eigenstates of J^2, J_z, L^2, S^2, and $\vec{L}\cdot\vec{S}$

now $\vec{L}\cdot\vec{S}\,|nljm\rangle = \frac{1}{2}(J^2 - L^2 - S^2)|nljm\rangle$; where $\vec{J} = \vec{L}+\vec{S}$, $J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$

$$= \frac{\hbar^2}{2}\{j(j+1) - l(l+1) - s(s+1)\}|nljm\rangle$$

when j takes only two values $j = l \pm 1/2$; $s = 1/2$

$$\Rightarrow \langle nljm|\vec{L}\cdot\vec{S}|nljm\rangle = \frac{\hbar^2}{2}\{j(j+1) - l(l+1) - 3/4\}$$

$$= \begin{cases} \frac{1}{2} l\hbar^2 ; & j = l + 1/2 \\ -\frac{1}{2}(l+1)\hbar^2 ; & j = l - 1/2 \end{cases}$$

where

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

$$\langle n l j m | H' | n l j m \rangle = \frac{e^2\hbar^2}{4m^2c^2}\left[j(j+1) - l(l+1) - 3/4\right] \langle n l | \frac{1}{r^3} | n l \rangle$$

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

$$\Rightarrow E_n^{(1)} = \langle n l j m | H' | n l j m \rangle = \frac{e^2\hbar^2}{2m^2c^2}\left[\frac{j(j+1) - l(l+1) - 3/4}{n^3 l(l+1)(2l+1)a_0^3}\right]$$

$$= \frac{e^2\hbar^2}{2m^2c^2n^3a_0^3}\left[\frac{j(j+1) - l(l+1) - 3/4}{l(l+1)(2l+1)}\right] \quad ; \quad a_0 = \frac{\hbar^2}{me^2}$$

multiply by $\frac{c^2}{c^2}$

$$= \frac{e^2\hbar^2 m^3 e^6}{2n^3m^2c^2\hbar^6}\cdot\frac{c^2}{c^2}\left[\frac{j(j+1) - l(l+1) - 3/4}{l(l+1)(2l+1)}\right] \quad ; \quad \alpha = \frac{e^2}{\hbar c}$$

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

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

$$= \frac{1}{4}mc^2\alpha^4 \left\{\begin{array}{ll} \frac{l}{n^3 l(l+1)(l+1/2)} & ; \ j = l+1/2 \\ \frac{-l-1}{n^3 l(l+1)(l+1/2)} & ; \ j = l-1/2 \end{array}\right\} \text{ valid for } l \neq 0$$

for $n=2$, $l = 0, 1$, $s = 1/2$ $\Rightarrow$ $j = l+1/2$, $l-1/2$

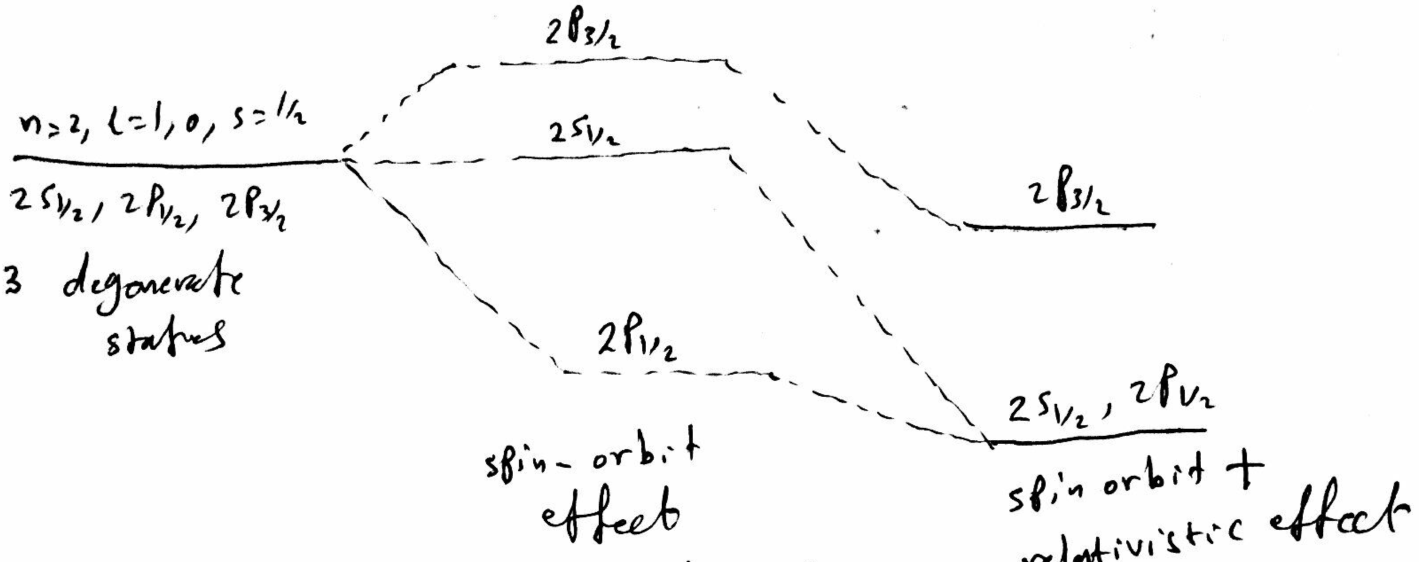
if $l=0$ $\Rightarrow$ No spin orbit coupling i.e the $2S_{1/2}$ is not affected

if $l=1$ $\Rightarrow$ $j = l+1/2 = 1+1/2 = 3/2$ or $j = l-1/2 = 1-1/2 = 1/2$

$$\Rightarrow E_n^{(1)} = \left\{\begin{array}{ll} \frac{1}{96}mc^2\alpha^4 & ; \ l=1 \ ; \ j = 3/2 \Rightarrow 2P_{3/2} \\ \frac{-1}{48}mc^2\alpha^4 & ; \ l=1, \ j = 1/2 \Rightarrow 2P_{1/2} \end{array}\right.$$

$\Delta E = \frac{1}{32}mc^2\alpha^4$

See back



Now adding the corrections of both Relativistic and spin orbit, we get what is called the fine structure correction

$$E_{FS}^{(1)} = E_{SO}^{(1)} + E_R^{(1)} = \frac{1}{4} m c^2 \alpha^4 \left[\frac{j(j+1) - l(l+1) - 3/4}{n^3 l(l+1)(l+1/2)} \right] - \frac{1}{4} m c^2 \alpha^4 \left[\frac{4}{n^3(2l+1)} - \frac{3}{2n^4} \right]$$

if $j = l + 1/2 \Rightarrow l = j - 1/2$

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

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

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

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

$$= \frac{1}{4} mc^2 \frac{\alpha^4}{2n^4} \left[\frac{-4n}{j+1/2} + 3 \right] = \frac{1}{8} mc^2 \frac{\alpha^4}{n^4} \left[3 - \frac{4n}{j+1/2} \right]$$

valid for $l = j \pm 1/2$ and also for $l = 0$

→ see back

Now for $j = l - 1/2 \Rightarrow l = j + 1/2$, we will have the same result

so for $n = 2$, $l = 1, 0$

- $l = 0 \Rightarrow j = 0 + 1/2 = 1/2 \Rightarrow 2S_{1/2} \Rightarrow E_{FS}^{(1)} = \frac{-5}{128} mc^2\alpha^4 \longrightarrow 128$

- $l = 1 \Rightarrow j = 1 - 1/2 = 1/2 \Rightarrow 2P_{1/2} \Rightarrow E_{FS}^{(1)} = -\frac{5}{128} mc^2\alpha^4 \longrightarrow 128$

  $j = 1 + 1/2 = 3/2 \Rightarrow 2P_{3/2} \Rightarrow E_{FS}^{(1)} = \frac{-1}{128} mc^2\alpha^4$

Notice that after adding up the two corrections, the $2S_{1/2}$ and $2P_{1/2}$ states become degenerate as shown in the previous figure.

the energy to first order can be written as

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

$$= E_n^{(0)} - \frac{\alpha^2}{4n^2} E_n^{(0)}\left[3 - \frac{4n}{j + 1/2}\right] \quad \text{using } E_n^{(0)} = -\frac{\alpha^2 mc^2}{2n^2}$$

$$= E_n^{(0)} + \frac{\alpha^2}{4n^2} E_n^{(0)}\left[\frac{4n}{j + 1/2} - 3\right] \quad \text{---- (9)}$$

Remark! <u>spectroscopic notations!</u>

$^{2S+1}L_j$ designate an atomic state whose spin is S, its total angular momentum is j, and whose orbital angular momentum is L, where $L = 0, 1, 2, 3, \ldots$

$\downarrow$

$s, p, d, f \ldots$

so state	$^2S_{1/2}$	$^2P_{1/2}$	$^2P_{3/2}$	$^2D_{3/2}$	...
g_j	2	$\frac{2}{3}$	$\frac{4}{3}$	$\frac{4}{5}$	