evaluation of $\langle n l m | \underset{\sim}{H}_T | n l m \rangle$

$$\underset{\sim}{H}'_T = -\frac{1}{8}\frac{p^4}{m^3c^2} = -\frac{1}{2}\frac{1}{mc^2}\left(\frac{p^2}{2m}\right)^2$$

but $$\underset{\sim}{H}^0 = \frac{p^2}{2m} - \frac{e^2}{|\underset{\sim}{\vec{x}}|}, \quad \frac{p^2}{2m} = \underset{\sim}{H}^0 + \frac{e^2}{|\underset{\sim}{\vec{x}}|}$$

$$\underset{\sim}{H}'_T = -\frac{1}{2}\frac{1}{mc^2}\left(\underset{\sim}{H}^0 + \frac{e^2}{|\underset{\sim}{\vec{x}}|}\right)^2$$

$$\langle n l m | \underset{\sim}{H}'_T | n l m \rangle = -\frac{1}{2mc^2}\Big[\overbrace{\langle n l m | \underset{\sim}{H}^{0\,2} | n l m \rangle}^{E_n^{0\,2}}$$

$$+ 2\langle n l m | \underset{\sim}{H}^0 \frac{e^2}{|\vec{x}|} | n l m \rangle \quad E_n^0 \leftarrow$$

$$+ \langle n l m | \frac{e^4}{|\vec{x}|^2} | n l m \rangle \Big]$$

$$\rightarrow \langle n l m | \frac{e^2}{|\vec{x}|} | n l m \rangle = -\langle \underset{\sim}{V} \rangle$$

<u>Virial Theorem</u> (relationship between $\langle \underset{\sim}{V} \rangle$ and $\langle \underset{\sim}{T} \rangle = \left\langle \frac{p^2}{2m} \right\rangle$)

(look at p. 35a)

$$\langle \underset{\sim}{T} \rangle = \frac{1}{2}\langle \vec{x} \cdot \vec{\nabla} V(\vec{x}) \rangle$$

Proof is not obvious...

when $|\psi\rangle$ is an eigenstate, $\underset{\sim}{\Omega}$ an operator constant in time:

$$\frac{d}{dt}\langle \psi | \underset{\sim}{\Omega} | \psi \rangle = \frac{d}{dt}\langle \underset{\sim}{\Omega} \rangle = 0$$

but: Ehrenfest's theorem (p. 180)

$$\frac{d\langle \Omega \rangle}{dt} = \frac{i}{\hbar}\langle [H, \Omega] \rangle = 0$$

chose $\Omega = \vec{x}\cdot\vec{p} = \sum_i x_i p_i$

$$H = \frac{\vec{p}^{\,2}}{2m} + V(\vec{x}) = \frac{1}{2m}\sum_j p_j^2 + V(\vec{x})$$

$$[H, \Omega] = \frac{1}{2m}\sum_{ij}[p_j^2, x_i p_i] + \sum_i [V(\vec{x}), x_i p_i]$$

$$[p_j^2, x_i p_i] = x_i \cancelto{0}{[p_j^2, p_i]} + [p_j^2, x_i] p_i$$

$$\underset{A}{} \quad \underset{B\,C}{} \qquad B[A, C] + [A, B]C$$

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$$= -2i\hbar\, p_i p_j \delta_{ij}$$

$$[V(\vec{x}), x_i p_i] = x_i [V(\vec{x}), p_i] + \cancelto{0}{[V(\vec{x}), x_i]} p_i$$

$$= i\hbar\, x_i \frac{\partial V}{\partial x_i}$$

$$[H, \Omega] = \frac{-2i\hbar}{2m}\sum_{ij} p_i p_j \delta_{ij} + i\hbar \sum_i x_i \frac{\partial V}{\partial x_i}$$

$$= -2\frac{\vec{p}^{\,2}}{2m} + \vec{x}\cdot\vec{\nabla} V(\vec{x})$$

$$= -2T + \vec{x}\cdot\vec{\nabla} V(\vec{x})$$

now $\langle [H, \Omega] \rangle = 0 = -2\langle T \rangle + \langle \vec{x}\cdot\vec{\nabla} V(\vec{x}) \rangle$

$$\langle T \rangle = \frac{1}{2}\langle \vec{x}\cdot\vec{\nabla} V(\vec{x}) \rangle$$

suppose $V(\vec{x}) = V_0 |\vec{x}|^s$ (power law potential)

$$\vec{x}\cdot\vec{\nabla}V(\vec{x}) = \sum_i x_i \frac{\partial V}{\partial x_i} = V_0 \sum_i x_i\, s|\vec{x}|^{s-1}\frac{\partial|\vec{x}|}{\partial x_i}$$

$$\frac{\partial|\vec{x}|}{\partial x_i} = \frac{\partial}{\partial x_i}\left(\sum_i x_i^2\right)^{1/2} = \frac{1}{2}\left(\sum_i x_i^2\right)^{-1/2} 2x_i = \frac{x_i}{|\vec{x}_i|}$$

$$\vec{x}\cdot\vec{\nabla}V(\vec{x}) = V_0\sum_i x_i\, s|\vec{x}|^{s-1}\frac{x_i}{|\vec{x}_i|} = V_0 s|\vec{x}|^{s-1}\frac{|\vec{x}|^2}{|\vec{x}|}$$

$$\vec{x}\cdot\vec{\nabla}V(\vec{x}) = V_0 s|\vec{x}|^s = sV(\vec{x}).$$

$$\boxed{\text{Power Law Potential: } \langle \underset{\sim}{T}\rangle = \frac{s}{2}\langle \underset{\sim}{V}\rangle \quad \text{Power} = s}$$

$s=-1$ ... coulomb potential

$$\langle \underset{\sim}{T}\rangle = -\frac{1}{2}\langle \underset{\sim}{V}\rangle$$

$$\langle n\ell m|\underset{\sim}{H}^0|n\ell m\rangle = E_n^0 = \langle \underset{\sim}{T}\rangle + \langle \underset{\sim}{V}\rangle$$

$$E_n^0 = -\frac{1}{2}\langle \underset{\sim}{V}\rangle + \langle \underset{\sim}{V}\rangle = \frac{1}{2}\langle \underset{\sim}{V}\rangle$$

$$\langle \underset{\sim}{V}\rangle = -\left\langle \frac{e^2}{|\underset{\sim}{\vec{x}}|}\right\rangle = 2E_n^0$$

Finally,

$$\langle n\ell m|\underset{\sim}{H}_T|n\ell m\rangle = \frac{-1}{2mc^2}\left[E_n^{0\,2} + 2E_n^0\left(-2E_n^{0\,2}\right) + e^4\left\langle\frac{1}{|\vec{x}|^2}\right\rangle\right]$$

$$= -\frac{1}{2mc^2}\left[-3E_n^{0\,2} + e^4\left\langle\frac{1}{|\vec{x}|^2}\right\rangle\right].$$

Exercise 17.3.3 :

$$\left\langle\frac{1}{|\vec{x}|^2}\right\rangle = \frac{1}{a_0^2 n^3(\ell+1/2)}$$

$$E_n^0 = -\frac{1}{2}\frac{1}{n^2}\alpha^2 mc^2 = -\frac{1}{2}\frac{1}{n^2}\frac{e^4}{\hbar^2c^2}mc^2 = \frac{-1}{2}\frac{1}{n^2}\frac{e^2}{\left(\frac{\hbar^2}{me^2}\right)} = \frac{-1}{2}\frac{1}{n^2}\frac{e^2}{a_0}$$

$$\langle n\ell m|\underset{\sim}{H}_T|n\ell m\rangle = \frac{-1}{2mc^2}\left[\frac{-3}{4}\frac{1}{n^4}\frac{e^4}{a_0^2} + \frac{e^4}{a_0^2 n^3(\ell+1/2)}\right]$$

$$\langle nlm|\underset{\sim}{H}_T'|nlm\rangle = -\frac{1}{2mc^2}\underbrace{\frac{e^4}{a_0^2}}_{(\alpha^2 mc^2)^2}\left[-\frac{3}{4n^4}+\frac{1}{n^3(l+\frac{1}{2})}\right]$$

$$\boxed{\langle nlm|\underset{\sim}{H}_T'|nlm\rangle = \left(-\frac{1}{2}\frac{\alpha^2 mc^2}{n^2}\right)\cdot\alpha^2\left(-\frac{3}{4n^2}+\frac{1}{n(l+1/2)}\right)}$$

$$\underbrace{E_n^0 \qquad \tfrac{1}{2}10^{-4}}_{\varepsilon}$$

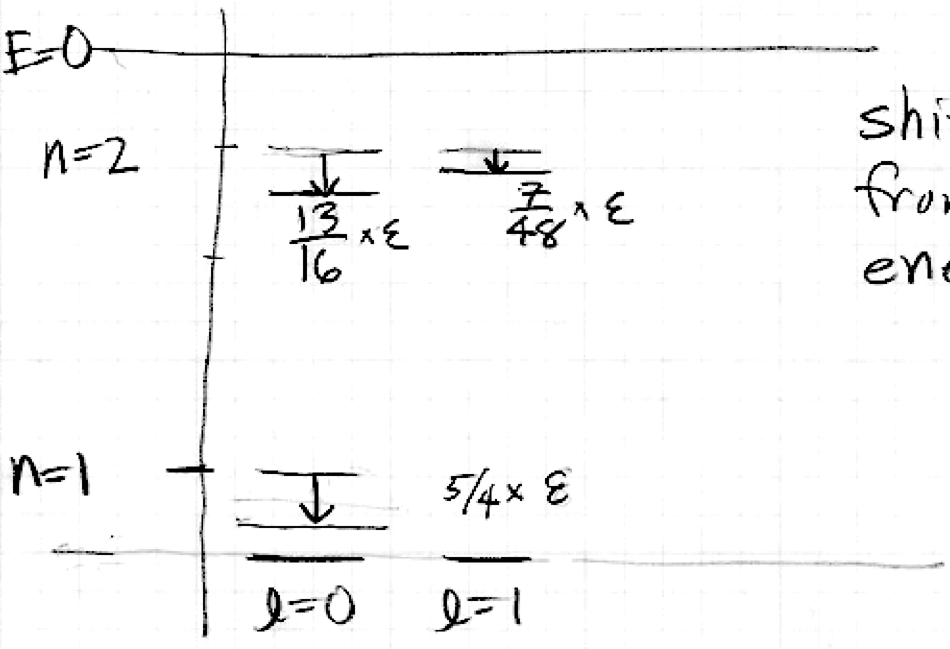
- biggest effect smallest n
- breaks degeneracy of l

This factor

$n=1$, $l=0$: $\quad -\frac{3}{4}+\frac{1}{1/2} = -\frac{3}{4}+2 = 5/4$

$n=2$, $l=1$: $\quad -\frac{3}{16}+\frac{1}{2\cdot 3/2} = -\frac{3}{16}+\frac{1}{3} = \frac{-9+16}{48} = \frac{7}{48}$

$n=2$, $l=0$: $\quad -\frac{3}{16}+\frac{1}{2\cdot\frac{1}{2}} = -\frac{3}{16}+1 = \frac{13}{16} = \frac{39}{48}$

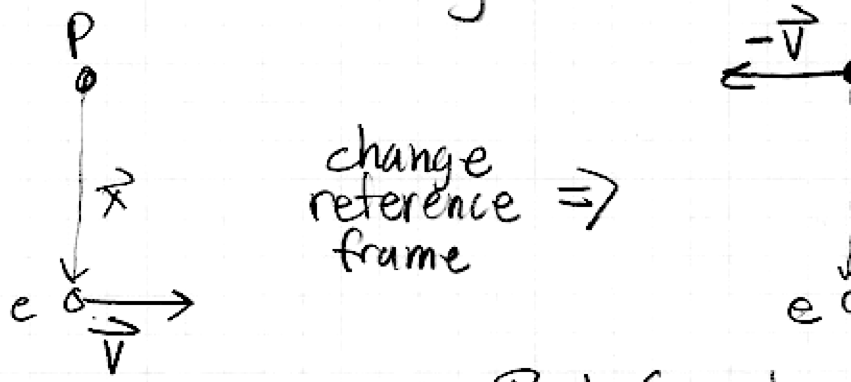


shifts just from relativistic energy effect

But that is not all! There is a second effect, the spin-orbit coupling:

First: magnetic moment of electron >> magnetic moment of proton
(ignore proton... causes "hyperfine")

Second: apparent motion of proton as seen from electron creates a magnetic field on the electron!



$$\vec{B} \propto (-\vec{v}) \times (\vec{x})$$

Biot-Savart $\vec{B} = -\frac{e}{c}\frac{\vec{v}\times\vec{x}}{|\vec{x}|^3}$

(recall, $\vec{B} \propto q, v/c, \frac{1}{|\vec{x}|^2}$)

electron magnetic moment energy: $-\vec{\mu}\cdot\vec{B} = +\frac{e}{cr^3}\,\vec{\mu}\cdot(\vec{v}\times\vec{x})$

$$= \frac{e}{mcr^3}\,\vec{\mu}\cdot\underbrace{(\vec{p}\times\vec{x})}_{-\vec{L}}$$

"Thomas Factor" (Fudge), relativistic acceleration

$$\vec{\mu} = \frac{(g=2)(-e)}{2mc}\vec{S}$$

$$\boxed{H^1_{so} = \frac{1}{2} \times \frac{e^2}{m^2c^2r^3}\,\vec{S}\cdot\vec{L}}$$

energy lowered when $\vec{S}$ and $\vec{L}$ are antiparallel, J small.

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

$$2\,\underset{\sim}{\vec{S}}\cdot\underset{\sim}{\vec{L}} = \frac{1}{2}\left(\underset{\sim}{\vec{J}}^2 - \underset{\sim}{\vec{S}}^2 - \underset{\sim}{\vec{L}}^2\right)$$

e.v. $j(j+1)$ $\quad s(s+1)$ $\quad l(l+1)$ $\quad \times \hbar^2$

since electron is spin-$\frac{1}{2}$ $\quad s=\frac{1}{2}$ $\quad l=j-1/2$ $\;(j=l+\frac{1}{2})$
$\quad l=j+1/2$ $\;(j=l-\frac{1}{2})$

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

$l=j-\frac{1}{2}$
$$=\frac{1}{2}\left(j^2+j-\frac{3}{4}-(j-1/2)(j+\tfrac{1}{2})\right)$$
$$=\frac{1}{2}\left(j^2+j-\frac{3}{4}-j^2+\frac{1}{4}\right)=\frac{1}{2}(j-\tfrac{1}{2})=\frac{1}{2}l$$

$j=l-\frac{1}{2}$
$l=j+\frac{1}{2}$
$$=\frac{1}{2}\left(j^2+j-\frac{3}{4}-(j+\tfrac{1}{2})(j+\tfrac{3}{2})\right)$$
$$=\frac{1}{2}\left(\cancel{j^2}+j-\frac{3}{4}-\cancel{j^2}-2j-\frac{3}{4}\right)=\frac{1}{2}\left(-j-\frac{3}{2}\right)=-\frac{1}{2}(l+1)$$

The degeneracy between the two spin $\frac{1}{2}$ states is SPLIT

$$\langle nlm|\underset{\sim}{H}'_{so}|nlm\rangle = \frac{\hbar^2 e^2}{4m^2c^2}\langle nlm|\frac{1}{r^3}|nlm\rangle \begin{cases} l & j=l+\frac{1}{2} \\ -(l+1) & j=l-\frac{1}{2}\end{cases}$$

$\langle nlm|\frac{1}{r^3}|nlm\rangle$: near origin $\propto \int d^3x\,\frac{r^{2l+2}}{r^3}$

→ diverges for $l=0$

→ but then $j=1/2$ ONLY, so angular term vanishes too, and together they give correct answer (SURPRISE)

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

Exercise 17.3.3 p.470

$j = l + \frac{1}{2}$ $$\langle nlm | \underset{\sim}{H}'_{so} | nlm \rangle = \frac{\hbar^2 e^2}{4m^2c^2 n^3} \frac{\cancel{l}}{\cancel{l}(l+\frac{1}{2})(l+1)} \frac{1}{a_0^3}$$

$$\frac{\hbar^2 e^2}{m^2c^2} \frac{1}{a_0^3} = \frac{\hbar^2 e^2}{m^2 c^2} \frac{1}{\frac{\hbar^6}{m^3 e^6}} = mc^2 \frac{e^8}{\hbar^4 c^4} = \alpha^4 mc^2$$

$$\langle nlm | \underset{\sim}{H}'_{so} | nlm \rangle = \left(-\frac{1}{2} \frac{\alpha^2 mc^2}{n^2}\right) \frac{1}{2}\alpha^2 \left(\frac{-1}{n(l+\frac{1}{2})(l+1)}\right)$$

Same order as $\langle nlm | \underset{\sim}{H}'_T | nlm \rangle$ (α^4)

always pushes up

	H'_{so}	H'_T	total
$n=1$, $l=0$, $j=\frac{1}{2}$	$\frac{1}{2} \times \frac{-1}{1(\frac{1}{2})(1)} = -1$	$+\frac{5}{4}$	$= \frac{1}{4}$
$n=2$, $l=1$, $j=\frac{3}{2}$	$\frac{1}{2} \times \frac{-1}{2 \cdot \frac{3}{2} \cdot \cancel{2}} = -\frac{1}{12}$	$+\frac{7}{48}$	$= +\frac{3}{48} = \frac{1}{16}$
$n=2$, $l=0$, $j=\frac{1}{2}$	$\frac{1}{2} \times \frac{-1}{2 \cdot \frac{1}{2} \cdot 1} = -\frac{1}{2} = \frac{-24}{48}$	$+\frac{39}{48}$	$= \frac{15}{48} = \frac{5}{16}$

$+$ means energy more negative

$$j = l - \tfrac{1}{2} \quad \langle nlm | H'_{so} | nlm \rangle = \frac{\hbar^2 e^2}{4m^2c^2} \frac{-(l+1)}{n^3 l(l+\frac{1}{2})(l+1)} \frac{1}{a_0^3}$$

$$= \left(-\frac{1}{2}\alpha^2 \frac{mc^2}{n^2}\right) \frac{1}{2}\alpha^2 \frac{1}{n\, l(l+\frac{1}{2})}$$

$\underline{H'_{so}}$ $\underline{H'_T}$

$n=2$
$l=1$
$j=\frac{1}{2}$

$$\frac{1}{2}\frac{1}{2\cdot 1\cdot \frac{3}{2}} = \frac{1}{6} = \frac{8}{48} + \frac{7}{48} = \frac{15}{48} = \frac{5}{16}$$

→ same as $n=2,\ l=0,\ j=\frac{1}{2}$

Could it be that all that matters is j?

$j = l + \frac{1}{2}$

$$\langle nlm | (H'_{so} + H'_T) | nlm \rangle = -\frac{1}{2}\frac{\alpha^2 mc^2}{n^2}\left(-\frac{3}{4n^2} + \underbrace{\frac{1}{n(l+\frac{1}{2})} - \frac{1}{2n(l+\frac{1}{2})(l+1)}}\right)$$

$$\frac{1}{n(l+\frac{1}{2})}\left(1 - \frac{1}{2(l+1)}\right) = \frac{2l+2-1}{2(l+1)}$$

$$\frac{1}{n\cancel{(l+\frac{1}{2})}} \frac{\cancel{2}(l+\frac{1}{2})}{\cancel{2}(l+1)} = \frac{1}{n(l+1)} \qquad l+1 = j+\tfrac{1}{2}$$

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

$j = l - \frac{1}{2}$

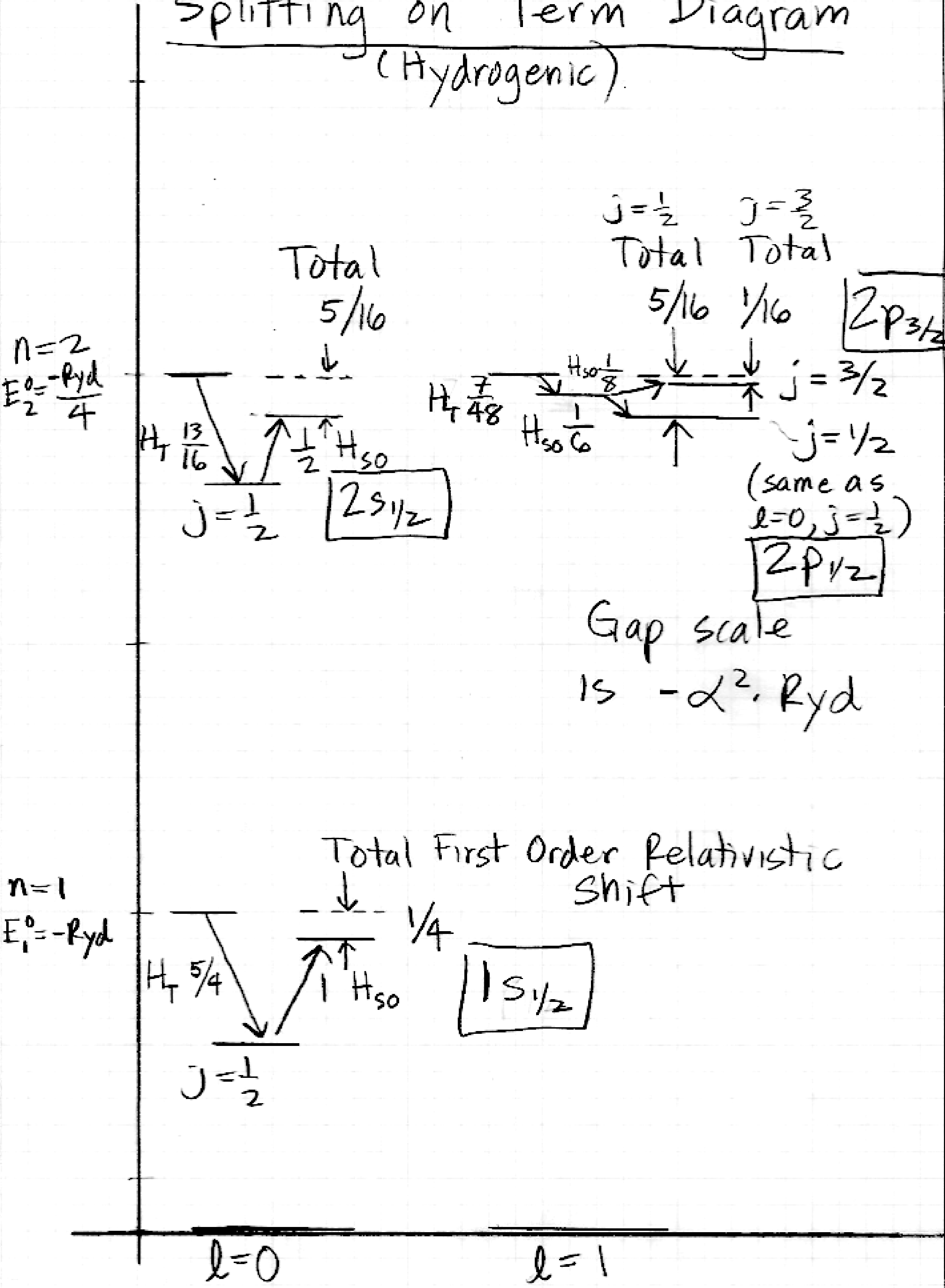
$$\langle nlm | (H'_{so} + H'_T) | nlm \rangle = -\frac{1}{2}\frac{\alpha^2 mc^2}{n^2}\left(-\frac{3}{4n^2} + \underbrace{\frac{1}{n(l+\frac{1}{2})} + \frac{1}{2n(l+\frac{1}{2})l}}\right)$$

$$\frac{1}{n\cancel{(l+\frac{1}{2})}}\left(1 + \frac{1}{2l}\right) = \frac{\cancel{2}(l+\frac{1}{2})}{\cancel{2}l}$$

$$= \frac{1}{nl} \qquad l = j + \tfrac{1}{2}$$

$$-\frac{1}{2}\frac{\alpha^2 mc^2}{n^2}\left(-\frac{3}{4n^2} + \frac{1}{n(j+\frac{1}{2})}\right) \leftarrow \text{SAME}$$

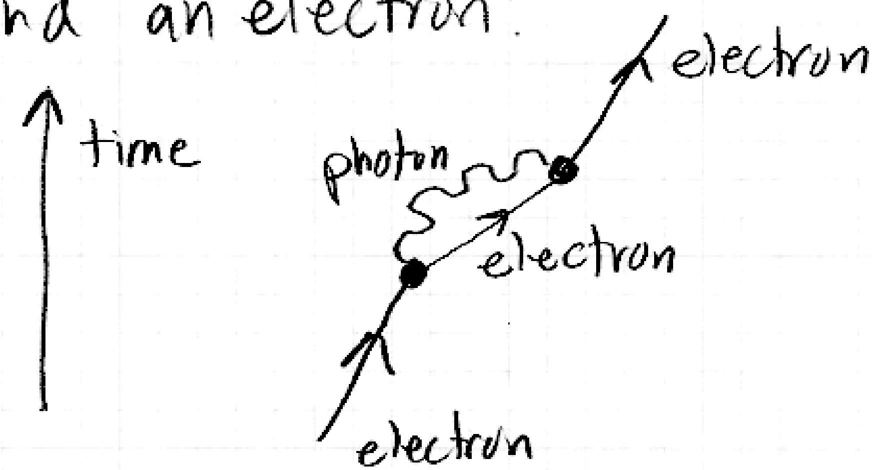
Splitting on Term Diagram
(Hydrogenic)



Note, the $2s_{1/2}$ and $2p_{1/2}$ levels appear to be degenerate.

Turns out, there is an order α^3 splitting between them!

Measured first in 1947 by Lamb & Retherford, called the "Lamb Shift". The physics behind it is Quantum Field Theory; in particular, sometimes an electron "spontaneously" splits into a photon and an electron:



"Feynman" diagram.

Causes the splitting between the $2s_{1/2}$ & $2p_{1/2}$ levels.