Fine structure of ~~hydrogen atom~~

$$H = H^\circ + \lambda H'$$

$$H^0 = \frac{p^2}{2m} - \frac{\alpha \hbar c}{r}$$

$$H' = \underbrace{-\frac{p^4}{8m^3c^2}}_{\text{rel correction to kin en}} + \underbrace{\frac{\alpha \hbar}{2m^2 c r^3} \vec{L}\cdot\vec{S}}_{\text{spin-orbit coupling}}$$

Eigenfunctions are degenerate, but can still use nondeg. pert. th provided one uses the "right basis".
The right basis is ψ_{nljm_j} not $u_{nlm_lm_s}$)

because ψ_{nljm_j} are eigenfunctions of $\vec{L}\cdot\vec{S}$

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

$$\vec{L}\cdot\vec{S}\,\psi_{nljm_j} = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\psi_{nljm_j}$$

$$= \begin{cases} \frac{\hbar^2}{2} l\, \psi_{nljm_j} & \text{for } j = l + \frac{1}{2} \\ \frac{\hbar^2}{2}(-l-1)\,\psi_{nljm_j} & \text{for } j = l - \frac{1}{2} \end{cases}$$

$$\left[\begin{array}{l} (l+\frac{1}{2})(l+\frac{3}{2}) - l(l+1) - \frac{3}{4} = 2l + \frac{3}{4} - l - \frac{3}{4} = l \\ (l-\frac{1}{2})(l+\frac{1}{2}) - l(l+1) - \frac{3}{4} = -\frac{1}{4} - l - \frac{3}{4} = -l-1 \end{array}\right]$$

First order correction to energy

$$E^1_{nlj} = \langle \psi_{nljm_j} | H' | \psi_{nljm_j} \rangle$$

Doesn't depend on m_j due to rotational symmetry

A useful trick:

$$-\frac{p^4}{8m^3c^2} = -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 = -\frac{1}{2mc^2}\left(H^0 + \frac{\alpha\hbar c}{r}\right)^2$$

So

$$\left\langle E_n \left| -\frac{p^4}{8m^3c^2} \right| E_n \right\rangle = -\frac{1}{2mc^2}\left\langle E_n \right| \left(H^0 + \frac{\alpha\hbar c}{r}\right)\left(H^0 + \frac{\alpha\hbar c}{r}\right) \left| E_n \right\rangle$$

$$= -\frac{1}{2mc^2}\left\langle E_n \right| \left(E_n + \frac{\alpha\hbar c}{r}\right)\left(E_n + \frac{\alpha\hbar c}{r}\right) \left| E_n \right\rangle$$

$$= -\frac{1}{2mc^2}\left(E_n^2 + 2\alpha\hbar c E_n \left\langle \frac{1}{r} \right\rangle + (\alpha\hbar c)^2 \left\langle \frac{1}{r^2} \right\rangle \right)$$

Thus the first order correction is

$$E^1_{n,l,l\pm\frac{1}{2}} = \left\langle \psi_{n,l,l\pm\frac{1}{2},m_j} \right| \left(-\frac{p^4}{8m^3c^2} + \frac{\alpha\hbar}{2m^2cr^3}\vec{L}\cdot\vec{S}\right) \left| \psi_{n,l,l\pm\frac{1}{2},m_j} \right\rangle$$

$$= -\frac{1}{2mc^2}\left(E_n^2 + 2\alpha\hbar c E_n \left\langle \frac{1}{r} \right\rangle + (\alpha\hbar c)^2 \left\langle \frac{1}{r^2} \right\rangle \right) + \frac{\alpha\hbar^3}{4m^2cr^3}\begin{Bmatrix} l \\ -l-1 \end{Bmatrix} \left\langle \frac{1}{r^3} \right\rangle$$

where $E_n = -\frac{\frac{1}{2}mc^2\alpha^2}{n^2}$

$$\left\langle \frac{1}{r^k} \right\rangle = \int_0^\infty r^2 dr \; \frac{1}{r^k} \left(R_{nl}(r)\right)^2$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0} = \frac{\alpha m c}{\hbar n^2}$$ (see Griffiths for various tricks)

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{n^3(l+\frac{1}{2})a_0^2} = \frac{(\alpha m c)^2}{\hbar^2 n^3 (l+\frac{1}{2})}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3 l(l+\frac{1}{2})(l+1)a_0^3} = \frac{(\alpha m c)^3}{\hbar^3 n^3 l(l+\frac{1}{2})(l+1)}$$

$$E'_{n,l,l\pm\frac{1}{2}} = \frac{mc^2\alpha^4}{2}\left[-\frac{1}{4n^4} + \frac{1}{n^4} - \frac{1}{n^3(l+\frac{1}{2})} + \frac{\left\{\begin{matrix} l \\ -l-1 \end{matrix}\right\}}{2n^3 l(l+\frac{1}{2})(l+1)}\right]$$

$$= \frac{mc^2\alpha^4}{2}\left[+\frac{3}{4n^4} - \frac{1}{n^3}\left\{\begin{matrix} \frac{1}{l+1} \\ \frac{1}{l} \end{matrix}\right\}\right]$$

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

Due to conspiracy between rel. effects + spin orbit correction depends only on j, not l $\Rightarrow$ degeneracy between $S_{\frac{1}{2}}$ + $P_{\frac{1}{2}}$

$P_{\frac{3}{2}}$ + $d_{\frac{3}{2}}$

etc

$$\left(\begin{matrix} \frac{1}{l+\frac{1}{2}}\left[1 - \frac{1}{2(l+1)}\right] = \frac{1}{l+1} \\ \frac{1}{l+\frac{1}{2}}\left[1 + \frac{1}{2l}\right] = \frac{1}{l} \end{matrix}\right)$$

$(j\uparrow \Rightarrow E\uparrow)$

notes from 1993, I believe

Fine structure

$$H_0 = \frac{p^2}{2\mu} - \frac{Ze^2}{r}$$

① Relativistic mass effects

$$E = \sqrt{(\mu c^2)^2 + (pc)^2} = \mu c^2 \sqrt{1 + \left(\frac{p}{\mu c}\right)^2} = \mu c^2\left[1 + \frac{1}{2}\left(\frac{p}{\mu c}\right)^2 - \frac{1}{8}\left(\frac{p}{\mu c}\right)^4 + \dots\right]$$

$$= \mu c^2 + \frac{1}{2}\frac{p^2}{\mu} - \frac{1}{8}\frac{p^4}{\mu^3 c^2} + \dots$$

$$H_1 = -\frac{1}{8}\frac{p^4}{\mu^3 c^2} = -\frac{1}{2\mu c^2}\left(\frac{p^2}{2\mu}\right)^2 = -\frac{1}{2\mu c^2}\left(H_0 + \frac{Ze^2}{r}\right)^2$$

$$\langle n\ell | H_1 | n\ell\rangle = -\frac{1}{2\mu c^2}\langle n\ell|\left(H_0 + \frac{Ze^2}{r}\right)\left(H_0 + \frac{Ze^2}{r}\right)|n\ell\rangle$$

$$= -\frac{1}{2\mu c^2}\left(E_n^2 + 2E_n Ze^2 \left\langle\frac{1}{r}\right\rangle_{n,\ell} + Z^2 e^4 \left\langle\frac{1}{r^2}\right\rangle_{n,\ell}\right)$$

$$E_n = -\frac{1}{2}\mu c^2\left(\frac{Z\alpha}{n}\right)^2$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{Z}{a_0 n^2} = \frac{Z\alpha\mu c}{\hbar n^2} = \frac{Z\alpha^2 \mu c^2}{e^2 n^2}$$

$$\left\langle\frac{1}{r^2}\right\rangle = \frac{Z^2}{a_0^2 n^3 (\ell + \frac{1}{2})} = \frac{Z^2\alpha^2\mu^2c^2}{\hbar^2 n^3(\ell+\frac{1}{2})} = \frac{Z^2\alpha^4\mu^2c^4}{e^4 n^3(\ell+\frac{1}{2})}$$

$$\langle H_1\rangle = -\frac{1}{2\mu c^2}\left(\frac{\mu^2c^4 Z^4\alpha^4}{4n^4} - \mu c^2\frac{Z^2\alpha^2}{n^2}\frac{Z^2\alpha^2\mu c^2}{n^2} + \frac{Z^4\alpha^4\mu^2c^4}{n^3(\ell+\frac{1}{2})}\right)$$

$$= -\frac{1}{2}\mu c^2 (Z\alpha)^4\left(\frac{1}{4n^4} - \frac{1}{n^4} + \frac{1}{n^3(\ell+\frac{1}{2})}\right)$$

$$= -\frac{1}{2}\mu c^2 (Z\alpha)^4\left[\frac{1}{n^3(\ell+\frac{1}{2})} - \frac{3}{4n^4}\right]$$

notes from 1993, I believe

Fine structure

② Spin-orbit effect

$$H_2 = -\vec{M}\cdot\vec{B}$$

$$\vec{B} = \underset{\substack{\uparrow \\ \text{Thomas}}}{\left(\tfrac{1}{2}\right)}\left(-\frac{\vec{v}\times\vec{E}}{c}\right) = \left(\tfrac{1}{2}\right)\left(+\frac{\vec{v}\times\vec{\nabla}\phi}{c}\right)$$

$$\phi = +\frac{Ze}{r}, \quad \vec{\nabla}\phi = \hat{r}\frac{d\phi}{dr} = \vec{r}\,\frac{1}{r}\frac{d\phi}{dr} = -\vec{r}\,\frac{Ze}{r^3}$$

$$\vec{B} = \frac{-1}{2\mu c}(\vec{p}\times\vec{r})\frac{Ze}{r^3} = +\frac{1}{2\mu c}\vec{L}\,\frac{Ze}{r^3}$$

$$\vec{M} = -\frac{ge}{2\mu c}\vec{S}$$

$$H_2 = +\frac{gZe^2}{4\mu^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L}$$

$$\vec{S}\cdot\vec{L} = \tfrac{1}{2}\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

$j = l + \frac{1}{2}$, $\quad \langle \vec{S}\cdot\vec{L}\rangle = \frac{\hbar^2}{2}\left(\left(l+\tfrac{1}{2}\right)\left(l+\tfrac{3}{2}\right) - l(l+1) - \tfrac{3}{4}\right) = \frac{\hbar^2 l}{2}$

$j = l - \frac{1}{2}$, $\quad \langle \vec{S}\cdot\vec{L}\rangle = \frac{\hbar^2}{2}\left(\left(l+\tfrac{1}{2}\right)\left(l-\tfrac{1}{2}\right) - l(l+1) - \tfrac{3}{4}\right) = \frac{\hbar^2}{2}(-l-1)$

$$\left\langle \frac{1}{r^3}\right\rangle_{nl} = \frac{Z^3}{a_0^3 n^3 l\left(l+\tfrac{1}{2}\right)(l+1)} = \frac{Z^3\alpha^4\mu^3c^4}{e^2\hbar^2 n^3 (l)\left(l+\tfrac{1}{2}\right)(l+1)}$$

$$\langle H_2\rangle = +\frac{gZ^4\mu c^2\alpha^4}{8}\,\frac{1}{n^3 l\left(l+\tfrac{1}{2}\right)(l+1)}\begin{cases} l & \text{if } j = l+\tfrac{1}{2} \\ -l-1 & \text{if } j = l-\tfrac{1}{2}\end{cases}$$

$$= \frac{\mu c^2 (Z\alpha)^4}{2}\left[\frac{1}{2n^3 l\left(l+\tfrac{1}{2}\right)(l+1)}\begin{Bmatrix} l & \text{if } j = l+\tfrac{1}{2} \\ -l-1 & \text{if } j = l-\tfrac{1}{2}\end{Bmatrix}\right]$$

Fine structure

$$\langle H_1\rangle + \langle H_2\rangle = \frac{\mu c^2 (Z\alpha)^4}{2}\left[\frac{3}{4n^4} + \frac{1}{n^3} f(l,j)\right]$$

$$f(l, j = l+\tfrac{1}{2}) = -\frac{1}{(l+\frac{1}{2})} + \frac{l}{2l(l+\frac{1}{2})(l+1)} = \underbrace{\frac{1}{l+\frac{1}{2}}\left[\frac{1}{2l+2} - 1\right]} = -\frac{1}{l+1}$$

$$f(l, j = l-\tfrac{1}{2}) = -\frac{1}{(l+\frac{1}{2})} + \frac{(-l-1)}{2l(l+\frac{1}{2})(l+1)} = \frac{-1}{l+\frac{1}{2}}\left[1 + \frac{1}{2l}\right] = -\frac{1}{l}$$

ie $\quad f(l,j) = -\frac{1}{j+\frac{1}{2}}$

$$\langle H_{\text{fine structure}}\rangle = \frac{1}{2}\mu c^2 (Z\alpha)^4 \left[\frac{3}{4n^4} - \frac{1}{n^3(j+\frac{1}{2})}\right]$$

so $j\uparrow \Rightarrow E\uparrow$