Fine structure of ~~hydrogen atom~~

$$H = H^0 + \lambda H^1$$

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

$$H^1 = \underbrace{-\frac{p^4}{8m^3c^2}}_{\text{rel. correction to Kin en}} + \underbrace{\frac{\alpha \hbar}{2m^2cr^3}}_{\text{spin-orbit coupling}} \vec{L}\cdot\vec{S}$$

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 $\vec{L}\cdot\vec{S} = \frac{1}{2}[J^2 - L^2 - S^2]$ $\Rightarrow$ H' commutes w/ J^2, L^2, S^2, J_3 but not w/ L_3, S_3

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

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

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

First order correction to energy

$$E^1_{nl_z} = \langle \psi_{nl_z m_z} | H' | \psi_{nl_z m_z} \rangle$$

Doesn't depend on m_z 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

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

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

$$= -\frac{1}{2mc^2}\left(E_n^{0\,2} + 2\alpha\hbar c E_n^0 \left\langle \frac{1}{r} \right\rangle + (\alpha\hbar c)^2 \left\langle \frac{1}{r^2} \right\rangle\right)$$

Thus the first order correction is

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

$$= -\frac{1}{2mc^2}\left(E_n^{0\,2} + 2\alpha\hbar c E_n^0 \left\langle \frac{1}{r} \right\rangle + (\alpha\hbar c)^2 \left\langle \frac{1}{r^2} \right\rangle\right) + \frac{\alpha\hbar^3}{4m^2c}\left\{ \begin{matrix} l \\ -l-1 \end{matrix} \right\} \left\langle \frac{1}{r^3} \right\rangle$$

where $E_n^0 = -\frac{\frac{1}{2}mc^2\alpha^2}{n^2}$

$$\left\langle \frac{1}{r^k} \right\rangle = \int_0^\infty r^2\,dr\ \frac{1}{r^k}\left(R_{n\ell}(r)\right)^2 \underbrace{\int d\Omega\,|Y_{\ell m}|^2}_{1}$$

$E = -T = \frac{1}{2}V$

$\frac{1}{2}\frac{\alpha^2(mc^2)}{n^2} = \frac{1}{2}\frac{\alpha\hbar c}{r}$

$\Downarrow$

$\left\langle \frac{1}{r}\right\rangle = \frac{\alpha mc}{\hbar n^2}$

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

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{n^3(\ell+\frac{1}{2})\,a_0^2} = \frac{(\alpha mc)^2}{\hbar^2 n^3(\ell+\frac{1}{2})}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{n^3\ell(\ell+\frac{1}{2})(\ell+1)\,a_0^3} = \frac{(\alpha mc)^3}{\hbar^3 n^3\ell(\ell+\frac{1}{2})(\ell+1)}$$

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

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

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

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

$$\left(\begin{matrix}\frac{1}{\ell+\frac{1}{2}}\left[1 - \frac{1}{2(\ell+1)}\right] = \frac{1}{\ell+1}\\[8pt] \frac{1}{\ell+\frac{1}{2}}\left[1 + \frac{1}{2\ell}\right] = \frac{1}{\ell}\end{matrix}\right)$$

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