Fine structure of the hydrogen spectrum

1 electron w/ orbital + spin angular momentum

total ang. mom. $\vec{J} = \vec{L} + \vec{S}$

$$(\text{spin } l) \otimes (\text{spin } \tfrac{1}{2}) = \text{spin } (\underset{j}{\underbrace{l + \tfrac{1}{2}}}) \oplus \text{spin } (l - \tfrac{1}{2})$$

Label states by: l_j

s-state ($l=0$) $\quad (\text{spin } 0) \otimes \text{spin } \tfrac{1}{2} = \text{spin } \tfrac{1}{2} \qquad s_{\frac{1}{2}}$

p-state ($l=1$) $\quad \underbrace{(\text{spin } 1) \otimes (\text{spin } \tfrac{1}{2})}_{6 \text{ states}} = \text{spin } \tfrac{3}{2} \oplus \text{spin } \tfrac{1}{2} \qquad \underbrace{p_{\frac{3}{2}}}_{4 \text{ states}}, \underbrace{p_{\frac{1}{2}}}_{2 \text{ states}}$

d-state ($l=2$) $\quad \underbrace{(\text{spin } 2) \otimes (\text{spin } \tfrac{1}{2})}_{10 \text{ states}} = \text{spin } \tfrac{5}{2} \oplus \text{spin } \tfrac{3}{2} \qquad \underbrace{d_{\frac{5}{2}}}_{6}, \underbrace{d_{\frac{3}{2}}}_{4}$

well defined values for L_z, S_z $\qquad$ well defined values for J^2, J_z

all have well-defined values for L^2, S^2

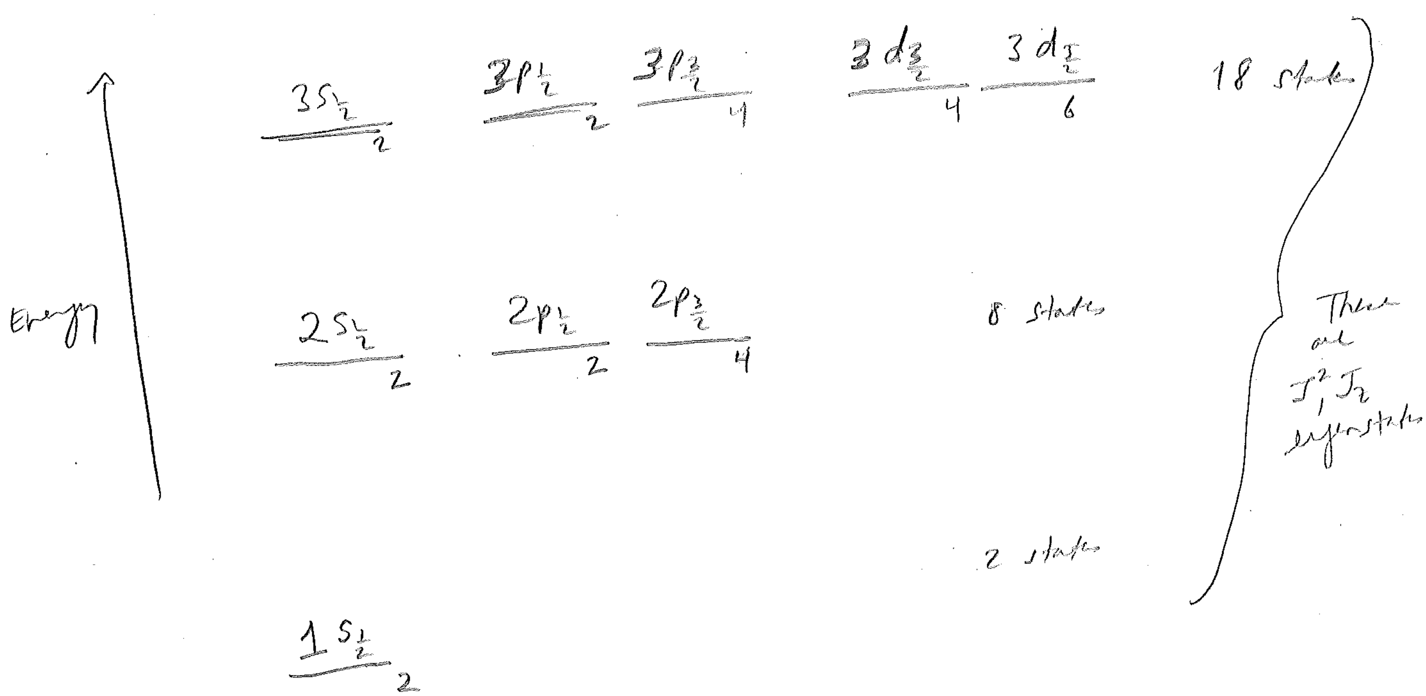
Quantum #s of hydrogen

principal, $n = 1, 2, 3, \ldots$ $\qquad E = -\frac{(\text{Ryd})}{n^2}$

orbital $\;l = 0, 1, \ldots, n-1; \qquad m_l = -l, \ldots, l$

spin $\;s = \frac{1}{2}; \qquad m_s = -\frac{1}{2}, \frac{1}{2}$

$\underbrace{\qquad\qquad\qquad}_{L^2,\, S^2 \text{ eigenvalues}} \quad \underbrace{\qquad\qquad\qquad}_{L_z,\, S_z \text{ eigenvalues}}$



In nonrel approx, all states of same n are degenerate
(in absence of a magnetic field $\Rightarrow$ no Zeeman splitting)

Relativistic corrections break this (accidental) degeneracy
$\Rightarrow$ fine structure

Relativistic corrections to the Bohr model give rise to fine structure and splitting the degeneracy between energy levels

However, total angular momentum $\vec{J}$ is conserved so multiplets of total angular momentum remain degenerate.

1st order Relativistic corrections to the total energy are

$$\delta E = \underbrace{-\frac{p^4}{8m^3c^2}}_{\text{obtained from relativistic kinetic energy}} + \underbrace{\frac{Ke^2}{2m^2c^2r^3}}_{\text{obtained from Dirac eqn (relativistic eqn for electrons)}} \vec{L}\cdot\vec{S}$$

[we'll deal w/ p and r later but let's focus on $\vec{L}\cdot\vec{S}$]

$$\vec{J} = \vec{L}+\vec{S}$$

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

but $[\vec{S},\vec{L}] = 0$ so

$$\vec{L}\cdot\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2) \doteq \frac{1}{2}\left(j(j+1)\hbar^2 - l(l+1)\hbar^2 - \frac{3}{4}\hbar^2\right)$$

$$\delta E = -\frac{p^4}{8m^3c^2} + \frac{Ke^2\hbar^2}{4m^2c^2r^3}\underbrace{\left[j(j+1) - l(l+1) - \frac{3}{4}\right]}_{\text{splits the degeneracy}} \quad \text{on eigenstate}$$

[we'll deal w/ p and r later after solving Schrodinger eqn]

A long calculation ~~[illegible]~~ reveals

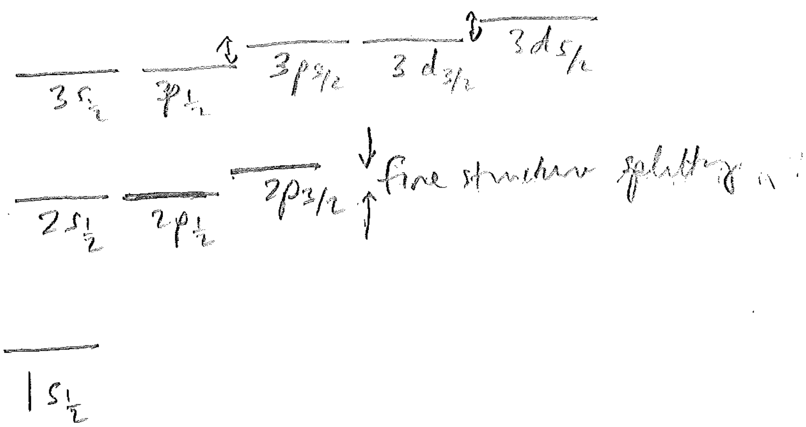
$$\delta E = \frac{1}{2} mc^2 \alpha^4 \left[\frac{3}{4n^4} - \frac{1}{n^3 (j+\frac{1}{2})} \right]$$

{Final result depends only on n and j, not l
$\Rightarrow$ $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ states remain degenerate!

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

[as we saw in problem set]

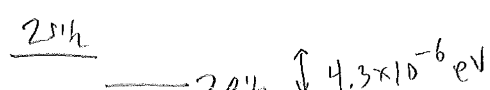
$n=2 \quad j=\frac{1}{2} \Rightarrow$ ---
$n=2 \quad j=3/2$
$n=3 \quad j=1/2$



[picture in Griffiths p 275]

$$E(2p_{3/2}) - E(2p_{1/2}) = +\frac{mc^2\alpha^4}{2}\left[-\frac{1}{8\cdot 2} + \frac{1}{8\cdot 1}\right] = \underbrace{\underbrace{\frac{mc^2\alpha^2}{2}}_{13.6\,eV} \underbrace{\left(\frac{\alpha^2}{16}\right)}_{3.3\times10^{-6}}}_{4.5\times10^{-5}\,eV}$$

QFT corrections split degeneracy between $2s_{\frac{1}{2}}$ + $2p_{\frac{1}{2}}$
(Lamb shift) 1st measured using WWII microwave technol.



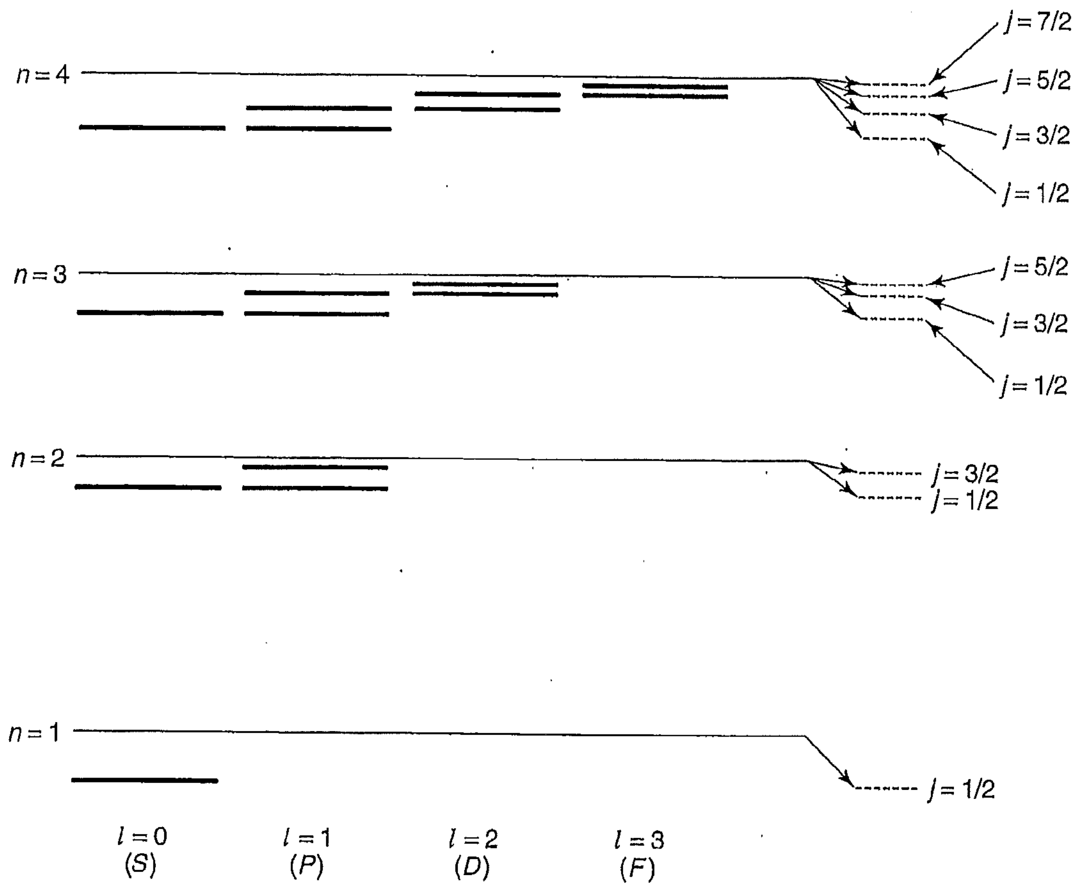
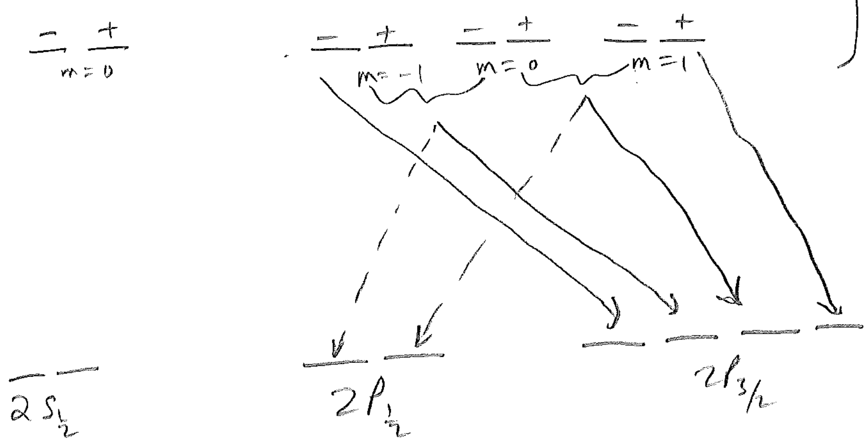


FIGURE 6.9: Energy levels of hydrogen, including fine structure (not to scale).

$\boxed{n=2}$

2



] eigenstates of S^2, L^2, S_z, L_z

] eigenstates of S^2, L^2, J^2, J_z

Recall from prob

$$\overset{j\ m_j}{\left|\tfrac{3}{2},\tfrac{3}{2}\right\rangle} = \overset{m_\ell\ m_s}{\left|1; \tfrac{1}{2}\right\rangle} = Y_{11}\,\chi_{\frac{1}{2}}$$

$$\left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|0; \tfrac{1}{2}\right\rangle + \tfrac{1}{\sqrt{3}}\left|1; -\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\,Y_{10}\,\chi_{\frac{1}{2}} + \sqrt{\tfrac{1}{3}}\,Y_{11}\,\chi_{-\frac{1}{2}}$$

$$\left|\tfrac{3}{2},-\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|0; -\tfrac{1}{2}\right\rangle + \tfrac{1}{\sqrt{3}}\left|-1; \tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{3}{2},-\tfrac{3}{2}\right\rangle = \left|-1; -\tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\left|0; \tfrac{1}{2}\right\rangle - \sqrt{\tfrac{2}{3}}\left|1; -\tfrac{1}{2}\right\rangle$$

$$\left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle = -\sqrt{\tfrac{1}{3}}\left|0; -\tfrac{1}{2}\right\rangle + \sqrt{\tfrac{2}{3}}\left|-1; -\tfrac{1}{2}\right\rangle$$

Fine structure

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

① Relativistic mass effects

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

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

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

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

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

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

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

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

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

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

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

Fine structure

② Spin-orbit effect

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

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

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

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

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

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

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

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

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

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

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

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

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 $j\uparrow \Rightarrow E\uparrow$