

## Hydrogen Fine Structure II

Now we will look at the effect of the spin-orbit coupling. We found before that the perturbation Hamiltonian is

$$h = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 m_e^2 c^2} \frac{\mathbf{S} \cdot \mathbf{L}}{r^3}$$

● We expect that the size of the effect coming from  $h$  is similar to that from the relativistic KE. So to be consistent we should consider both together. However, as we shall see, it turns out that the correct basis of states to use for dealing with the spin-orbit interaction is automatically OK for the relativistic KE as well. So for the time being we'll just deal with the spin-orbit part and temporarily forget about the relativistic KE.

### A. Spin and Degeneracy

The most important difference from the problems we have considered previously is the appearance of

$\underline{S}$  in the Hamiltonian. So we have to use basis states which describe the spin as well as the spatial degrees of freedom. The original Hamiltonian

$$H = \frac{p^2}{2m} + V(r)$$

is spin independent so the simplest basis is

$$|n, l, m, m_s\rangle = |n, l, m\rangle |m_s\rangle$$

remember  $m_s = \pm \frac{1}{2}$ . If you write it out as a wavefn it's

$$\Psi_{n, l, m, m_s} = \psi_{n, l, m}(r, \theta, \phi) \times \begin{cases} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ for } m_s = +\frac{1}{2} \\ \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ for } m_s = -\frac{1}{2} \end{cases}$$

and of course  $H \Psi_{n, l, m, m_s} = E_n \Psi_{n, l, m, m_s}$

because  $H$  doesn't care about the spin. But

$$\frac{\hbar}{r^3} \underline{L} \cdot \underline{L}$$

does care. We also have lots of degeneracy;

eg the states  $|n, l, m, +\frac{1}{2}\rangle$  and  $|n, l, m', -\frac{1}{2}\rangle$

are degenerate. ~~So it matters to find the states~~

It's easy to check that the matrix element

$$M = \langle n, l, m, +\frac{1}{2} | h | n, l, m+1, -\frac{1}{2} \rangle \neq 0$$

so we really do need to take account of the degeneracy

(~~we'll do this calculation later~~). However, there is

a short-cut which tells us what to do. Let's

introduce the total angular momentum operator

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

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

John March Russell already showed you that

$J_x, y, z$  satisfy the standard commutation rules for angular momentum ~~so the~~ and <sup>so</sup> have eigenstates

$$\underline{J}^2 |j, m_j\rangle = \hbar^2 j(j+1) |j, m_j\rangle$$

$$J_z |j, m_j\rangle = \hbar m_j |j, m_j\rangle$$

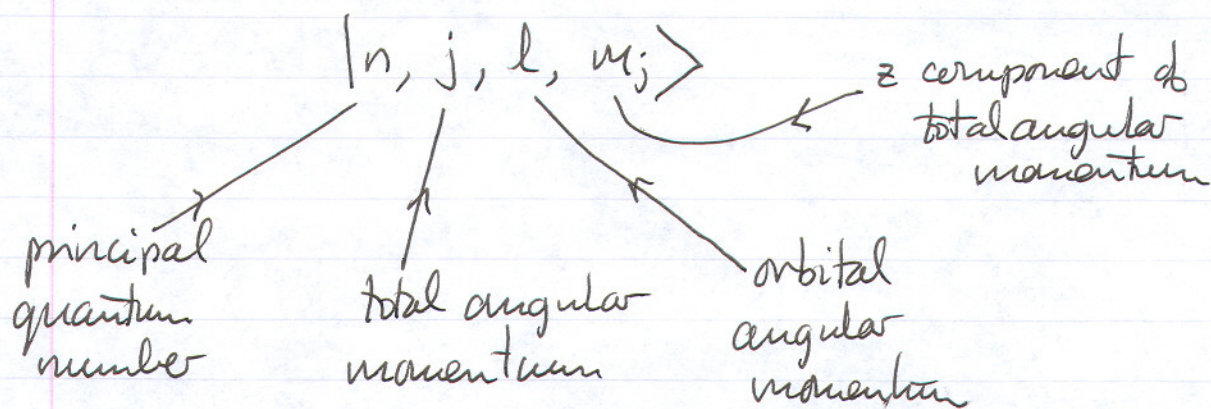
with, in this case,  $j = l + \frac{1}{2}$  or  $j = l - \frac{1}{2}$

by using the quantum mechanical rules for adding

~~angular~~ angular momentum  $l$  (orbital) to angular

momentum  $\frac{1}{2}$  (spin).

Now we know that  $\underline{L}^2$  and  $\underline{S}^2$  commute because they act on the spatial and spin parts of the wavefunction which are separate.  $\S$   $\underline{S}^2$  just tells us that the electron has spin  $\frac{1}{2}$ , and surely this fact is independent of the total angular momentum so we guess that  $[\underline{S}^2, \underline{J}^2] = 0$ . Having got this far let's guess that the same argument works for  $\underline{L}^2$  so that  $[\underline{L}^2, \underline{J}^2] = 0$ . In fact these statements are all true, we'll check them later, so the states for an electron in the Hydrogen atom can be written



We don't bother to put  $s$  in because it's always  $\frac{1}{2}$ .

If we use these states as a basis ~~there are no~~ matrix elements of  $H$  between degenerate states are 0 and we

can use {non-degenerate} perturbation theory

## B. The Energy Shift

Using first order perturbation theory we have

$$E' = E_n + \langle n, j, l, m_j | \frac{e^2}{8\pi\epsilon_0} \frac{1}{m_e^2 c^2 r^3} (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) | n, j, l, m_j \rangle$$

$$= E_n + \frac{e^2 \hbar^2}{16\pi\epsilon_0 m_e^2 c^2} (j(j+1) - l(l+1) - \frac{1}{2}(\frac{1}{2}+1))$$

↓ because  $s = \frac{1}{2}$

$$\times \int_0^\infty \frac{(R_{n,l}(r))^2}{r^3} r^2 dr$$

$$= \frac{1}{a^3 n^3 l(l+\frac{1}{2})(l+1)}$$

so

$$E'_{n,j,l} = E_n + \frac{e^2}{4\pi\epsilon_0 a} \left( \frac{\hbar}{m_e c a} \right)^2 \frac{1}{4} \frac{(j(j+1) - l(l+1) - \frac{3}{4})}{n^3 l(l+\frac{1}{2})(l+1)}$$

note that it depends on  $n, j$  and  $l$

$$\begin{array}{c} \nearrow \\ mc^2 \alpha^2 \\ \text{or } -2E_1 \end{array} \quad \begin{array}{c} \uparrow \\ \alpha^2 \end{array}$$

shift

Note that this is the same order of magnitude as the relativistic KE correction (as we expected)

$$E_1 \alpha^2 \left( -\frac{3}{4n^4} + \frac{1}{n^3(l+\frac{1}{2})} \right)$$

So adding them together

$$E'_{nj\ell} = E_n + E_1 \alpha^2 \left\{ \frac{-3}{4n^4} + \frac{1}{n^3(\ell + \frac{1}{2})} - \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{2n^3 \ell(\ell + \frac{1}{2})(\ell+1)} \right\}$$

$$= E_n + E_1 \alpha^2 \left\{ \frac{-3}{4n^4} - \frac{1}{2n^3} \frac{j(j+1) - 3\ell(\ell+1) - \frac{3}{4}}{\ell(\ell + \frac{1}{2})(\ell+1)} \right\}$$

shifts all levels with given  $n$  by the same amount

leads to fine structure  
- splitting of levels with same  $n$  but different  $j$

→ Two cases:

$$\underline{j = \ell + \frac{1}{2}}$$

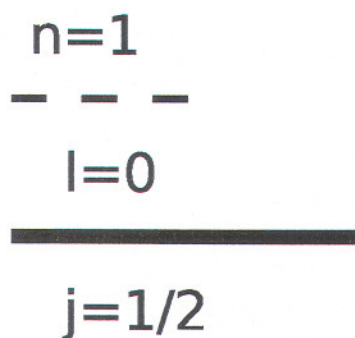
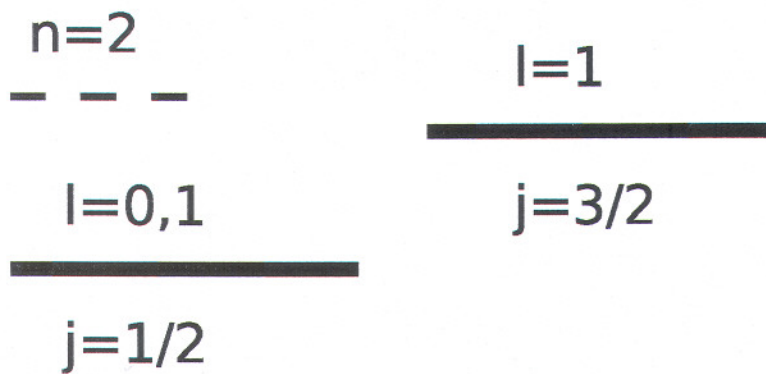
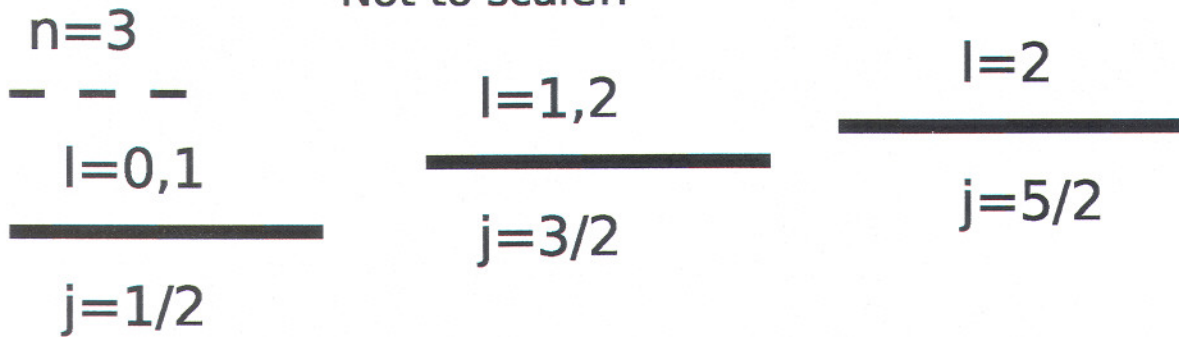
$$\begin{aligned} & \frac{j(j+1) - 3(j - \frac{1}{2})(j + \frac{1}{2}) - \frac{3}{4}}{(j - \frac{1}{2})j(j + \frac{1}{2})} \\ &= \frac{-2j^2 + j}{(j - \frac{1}{2})j(j + \frac{1}{2})} \\ &= \frac{-2}{j + \frac{1}{2}} \end{aligned}$$

$$\underline{j = \ell - \frac{1}{2}}$$

$$\begin{aligned} & \frac{j(j+1) - 3(j + \frac{1}{2})(j + \frac{3}{2}) - \frac{3}{4}}{(j + \frac{1}{2})(j+1)(j + \frac{3}{2})} \\ &= \frac{-2j^2 - 5j - 3}{(j + \frac{1}{2})(j+1)(j + \frac{3}{2})} = -\frac{2}{j + \frac{1}{2}} \quad \text{again} \end{aligned}$$

# Hydrogen Spectrum 2

Not to scale!!



### C. Comparison with Experiment

We have calculated the order  $\alpha^2$  corrections to the Hydrogen energy levels and found

$$E'_{nj} = E_n + E_1 \alpha^2 \left( -\frac{3}{4n^4} + \frac{1}{n^3(j+1/2)} \right)$$

Transparency  $\rightarrow$

Things to note:

1. The energy depends on  $j$  but not on  $l$ . Therefore these corrections we have calculated lift the degeneracy between states of different  $j$ ; but states with the same  $j$  and different  $l$  remain degenerate.
2. The magnitude of the shifts decreases with increasing  $n$ . In fact the calculated shifts agree very well with observations.
3. It turns out that the degeneracy between states of the same  $j$  but different  $l$  is lifted by an effect due to Quantum Electrodynamics called the Lamb Shift.



This is a tiny effect —  
a lot smaller than the fine structure corrections. For example

at  $n = 2, j = \frac{1}{2}$

$l=0$  goes up

$l=1$



$\cdot 0.035 \text{ cm}^{-1}$

$\sim \frac{1}{10}$  of  $j = \frac{1}{2}, j = \frac{3}{2}$

fine structure  
splitting.

- 4. If you have been very wide awake you'll have noticed that when  $l=0$  some of our intermediate expressions blow up and appear not to make sense. Nevertheless our final results work fine for  $l=0$ ! It turns out that, if we do the calculation really properly
- using the Dirac equation, indeed our final answer is right even for  $l=0$ .

## Footnote

We assumed  $[\underline{S}^2, \underline{J}^2] = 0$  and  $[\underline{L}^2, \underline{J}^2] = 0$ . This is easy to prove. Start with

$$\begin{aligned} [\underline{S}^2, J_x] &= [\underline{S}^2, L_x + S_x] \\ &= [\underline{S}^2, L_x] + [\underline{S}^2, S_x] \\ &= 0 + 0 \quad \& \text{ similarly for } J_y, J_z. \end{aligned}$$

so  $\underline{S}^2$  commutes with  $J_x, y, z$  and therefore it commutes with  $\underline{J}^2$ . Similarly  $\underline{L}^2$  does (just swap  $S \leftrightarrow L$  in the above argument).

Finally we can check that  $\underline{J}^2$  does not commute with  $L_z$  or  $S_z$  but only with their sum  $J_z$ . So

$$\begin{aligned} [\underline{J}^2, L_z] &= [\underline{L}^2 + 2\underline{L} \cdot \underline{S} + \underline{S}^2, L_z] = 2 [\underline{L} \cdot \underline{S}, L_z] \\ &= 2 [L_x S_x + L_y S_y + \underbrace{L_z S_z}_0, L_z] \\ &= 2 S_x [L_x, L_z] + 2 S_y [L_y, L_z] \\ &= 2 (S_x (-i\hbar L_y) + 2 S_y i\hbar L_x) \\ &= 2i\hbar (S_y L_x - S_x L_y) \end{aligned}$$

To get  $[\underline{J}^2, S_z]$  just swap  $L \leftrightarrow S$  to get  $[\underline{J}^2, S_z] = 2i\hbar (S_x L_y - S_y L_x) = -[\underline{J}^2, L_z]$

## D. The isotope shift

This is not really part of "fine structure" but we can only be sure that our understanding of it is correct once we have quantified the size of the fine structure.

Remember that in the results for the gross structure

$$E_n = -\frac{1}{2} \frac{m c^2 \alpha^2}{n^2}$$

it is the reduced mass  $m = \frac{m_e m_p}{m_e + m_p}$

that appears. Although most of the material which is chemically hydrogen has a proton for its nucleus a small fraction of that occurring naturally has a deuteron which is a bound state of a proton and a neutron (which is like a proton but with no electric charge). This stuff is called Deuterium The mass of a deuteron is  $m_d = 2 m_p$  so the corresponding reduced mass differs from that for hydrogen

$$\frac{m_D - m_H}{m_H} \approx \frac{m_e m_d}{m_e + m_d} \cdot \frac{m_e + m_p}{m_e m_p} - 1 \approx \frac{1}{2} \frac{m_e}{m_p} \approx \frac{1}{3600}$$

So hydrogen and deuterium have coarse structures which differ by about 1 part in 3600. Now this is substantially bigger than the fine structure. The spectrum from deuterium is a copy of that from hydrogen but "spread out" by a factor of  $\approx 1 + \frac{1}{3600}$ . This is easily detectable (being much bigger than the FS) and is in fact the way deuterium was originally identified by Urey.

Isotopes are atomic nuclei which have a common charge  $Z$  - and hence give atoms which are chemically the same - but different mass. So this effect is called the isotope shift.