Hydrogen atom

electron has orbital angular momentum $\vec{L}$
and spin angular momentum $\vec{S}$

Total angular momentum $\vec{J} = \vec{L} + \vec{S}$

Product space states $|l, m_l; s, m_s\rangle$ or $|m_l; m_s\rangle$

Direct sum states $|j, m_j\rangle$

l	(Spin l) $\otimes$ (spin $\frac{1}{2}$)	multiplicities	spin $(l+\frac{1}{2}) \oplus$ spin $(l-\frac{1}{2})$	
0 (s)	$\underset{\sim}{1} \otimes \underset{\sim}{2}$	2	$\underset{\sim}{2}$	$S_{\frac{1}{2}}$
1 (p)	$\underset{\sim}{3} \otimes \underset{\sim}{2}$	6	$\underset{\sim}{4} \oplus \underset{\sim}{2}$	$P_{\frac{3}{2}}, P_{\frac{1}{2}}$
2 (d)	$\underset{\sim}{5} \otimes \underset{\sim}{2}$	10	$\underset{\sim}{6} \oplus \underset{\sim}{4}$	$d_{\frac{5}{2}}, d_{\frac{3}{2}}$
3 (f)	$\underset{\sim}{7} \otimes \underset{\sim}{2}$	14	$\underset{\sim}{8} \oplus \underset{\sim}{6}$	$f_{\frac{7}{2}}, f_{\frac{5}{2}}$

$\underbrace{\text{eigenvalues of } L_z, S_z}$ $\qquad$ $\underbrace{\text{(subscript labels } j\text{)}}$ eigenvalue of J^2, J_z

e.g.

	$l=0$	$l=1$			
$n=2$	$2s$	$2p$	$\Rightarrow$	$2s_{1/2}$	$2p_{\frac{1}{2}}$ $\quad$ $2p_{\frac{3}{2}}$
	$1 \otimes 2$	$3 \otimes 2$		$\underset{\sim}{2}$	$\underset{\sim}{2}$ $\quad$ $\underset{\sim}{4}$

The non-relativistic Schrodinger eqn for hydrogen has energy levels $E_n = -\left(\frac{mc^2\alpha^2}{2}\right)\frac{1}{n^2}$, $\alpha = \frac{ke^2}{\hbar c}$ ↑ "fine structure constant"

as well see.

There are relativistic and spin-orbit corrections to the Hamiltonian (see early problem set) (Dirac eqn)

$$\delta E_{rel} = -\frac{p^4}{8m^3c^2}$$

$$\delta E_{s.o.} = \frac{ke^2}{2m^2c^2r^3}\vec{L}\cdot\vec{S} = \frac{mc^2\alpha^4}{2}\left(\frac{a_0}{r}\right)^3\frac{\vec{L}\cdot\vec{S}}{\hbar^2}$$

which give corrections of $O(\alpha^2)$ to the energy levels (called fine structure corrections).

We can't yet calculate the effects of p^4 and $\frac{1}{r}$ ...

Before, we estimated $\vec{L}\cdot\vec{S} \sim \hbar^2$

now do it more carefully

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

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

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

direct sum states are $\perp$ eigenstates of $\vec{L}\cdot\vec{S}$

$$\left[L^2 \otimes 1 + 1 \otimes S^2 + 2\vec{L}\otimes\vec{S}\right]$$

Let $\vec{L}\cdot\vec{S}$ act on states of total angular momentum $|j, m_j\rangle$

$$\vec{L}\cdot\vec{S}\,|j, m_j\rangle = \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\right]|j, m_j\rangle$$

For $j = \ell + \frac{1}{2}$ $\Rightarrow$ $\frac{\hbar^2}{2}\left[\left(\ell+\frac{1}{2}\right)\left(\ell+\frac{3}{2}\right) - \ell(\ell+1) - \frac{3}{4}\right] = \frac{\ell\hbar^2}{2}$

For $j = \ell - \frac{1}{2}$ $\Rightarrow$ $\frac{\hbar^2}{2}\left[\left(\ell-\frac{1}{2}\right)\left(\ell+\frac{1}{2}\right) - \ell(\ell+1) - \frac{3}{4}\right] = (-\ell-1)\frac{\hbar^2}{2}$

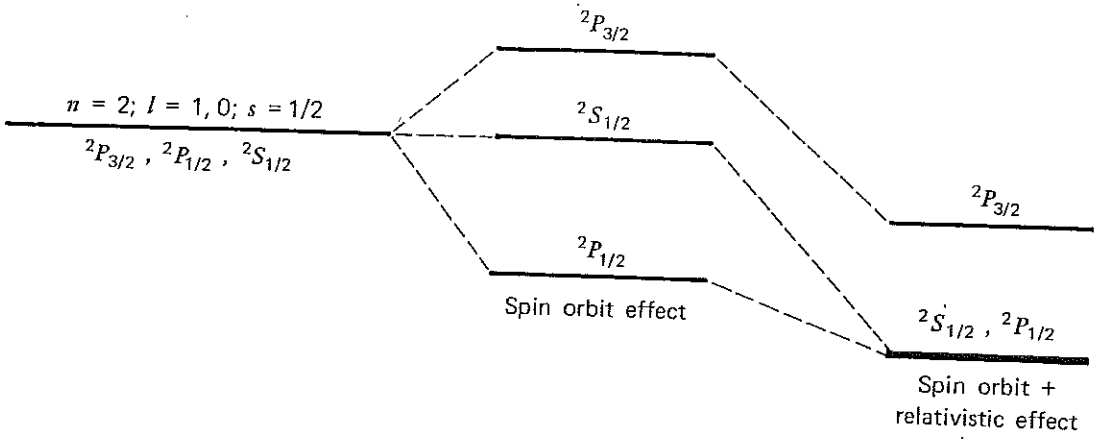
$$\delta E_{s.o.} = \frac{mc^2\alpha^4}{4}\left(\frac{a_0}{r}\right)^3 \begin{cases} \ell & \text{for } j = \ell + \frac{1}{2} \\ -\ell - 1 & \text{for } j = \ell - \frac{1}{2} \end{cases}$$

Spin-orbit effects

$S_{\frac{1}{2}}$ state is unchanged

$P_{\frac{1}{2}}$ state goes down

$P_{\frac{3}{2}}$ state goes up


$n = 2;\ l = 1, 0;\ s = 1/2$
$^2P_{3/2}$, $^2P_{1/2}$, $^2S_{1/2}$
$^2P_{3/2}$
$^2S_{1/2}$
$^2P_{1/2}$
Spin orbit effect
$^2P_{3/2}$
$^2S_{1/2}$, $^2P_{1/2}$
Spin orbit + relativistic effect

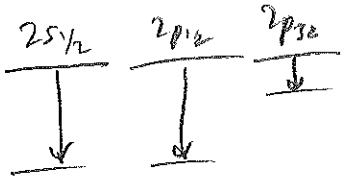
The full fine structure correction

$$\delta E = \delta E_{s.o.} + \delta E_{rel}$$

$$\left[\begin{array}{c}\text{A long} \\ \text{calculation} \\ \text{gives}\end{array}\right] = \frac{mc^2\alpha^4}{2}\left[\frac{3}{4n^4} - \frac{1}{n^3(j+\frac{1}{2})}\right]$$

$2s_{1/2}, 2p_{1/2}$: $\frac{3}{4(2)^4} - \frac{1}{(2)^3(1)} = \frac{3}{64} - \frac{8}{64} = -\frac{5}{64}$ goes down

$2p_{3/2}$ $\frac{3}{4(2)^4} - \frac{1}{(2)^3 2} = \frac{3}{64} - \frac{4}{64} = -\frac{1}{64}$ goes down less



apparent

$$\delta E_{3/2} - \delta E_{1/2} = \frac{mc^2\alpha^4}{2}\left[-\frac{1}{64} - \left(-\frac{5}{64}\right)\right] = \frac{mc^2\alpha^2}{2}\left(\frac{\alpha^2}{16}\right)$$

$$= (13.6\,eV)(3.\times 10^{-6})$$

$$= 4.5\times 10^{-5}\,eV$$

[Lamb shift $\delta E_{p_{1/2}} - \delta E_{s_{1/2}} = 4.3\times 10^{-6}\,eV$]

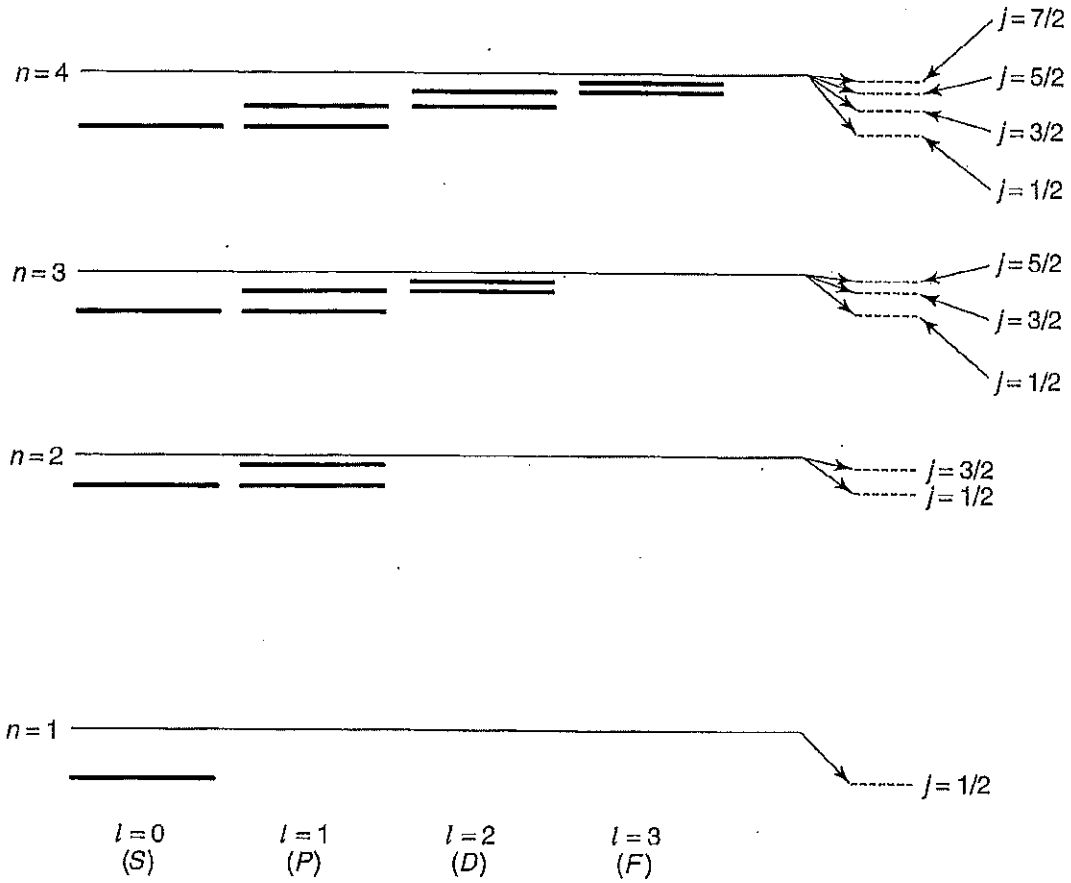


FIGURE 6.9: Energy levels of hydrogen, including fine structure (not to scale).

OLD NOTES

Let's estimate these.

Recall in Bohr model, typical value of $\frac{v}{c}$ is $\alpha \sim \frac{1}{137}$

so typical $p = mv$ is $mc\alpha$

and typical r is Bohr radius $a_0 = \frac{\hbar}{mc\alpha}$ (from $mva_0 = \hbar$)

and typical L or S is $\hbar$ so

$$\delta E = \frac{Ke^2\hbar^2}{2m^2c^2a_0^3}\left(\frac{a_0}{r}\right)^3 \frac{\vec{L}\cdot\vec{S}}{\hbar^2} \sim \frac{(mc\alpha)^4}{8m^3c^2}\left(\frac{p}{mc\alpha}\right)^4$$

$$= \frac{mc^2\alpha^4}{2}\left(\frac{a_0}{r}\right)^3\left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right) - \frac{mc^2\alpha^4}{8}\left(\frac{p}{mc\alpha}\right)^4$$

← done in HW

∴ both corrections are of order $mc^2\alpha^4$

& suppressed by factor $\alpha^2 \sim 10^{-4}$ wrt. leading term.

These are called fine-structure corrections

& α = fine-structure constant [see Griffiths]

Using Schrödinger eqn wavefunctions → one finds derived later in the semester

$$\left(\frac{a_0}{r}\right)^3 = \frac{1}{n^3 l(l+\frac{1}{2})(l+1)}$$

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

OLD NOTES

~~12~~ 3/4

Including both corrections we have

$$\delta E = \frac{mc^2\alpha^4}{4n^3 l(l+\frac{1}{2})(l+1)} \begin{Bmatrix} l \\ -l-1 \end{Bmatrix} - \frac{mc^2\alpha^4}{8}\left[\frac{4}{n^3(l+\frac{1}{2})} - \frac{3}{n^4}\right]$$

all levels go down

[see diagram from Gasiorowicz]

Observe that now $S_{\frac{1}{2}}$ and $P_{\frac{1}{2}}$ have same energy

ie energy depends on j but not l. [for hydrogen]

This is general. w/ some algebra

$$\delta E = \delta E_{s.o} + \delta E_{rel.}$$

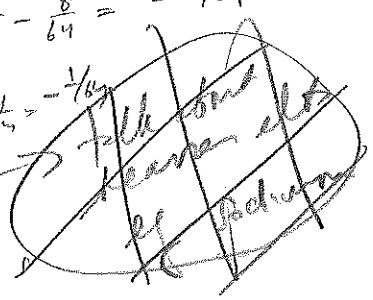
$$\delta E = \frac{mc^2\alpha^4}{2}\left[\frac{3}{4n^4} - \frac{1}{n^3(j+\frac{1}{2})}\right]$$

A long calculation gives

$$\frac{3}{4(2)^4} - \frac{1}{(2)^3(1)} = \frac{3}{64} - \frac{8}{64} = -\frac{5}{64}$$

$$\frac{3}{4(2)^4} - \frac{1}{(2)^3 2} = \frac{3}{64} - \frac{4}{64} = -\frac{1}{64}$$

$2S_{\frac{1}{2}}$ $2P_{\frac{1}{2}}$ $2P_{\frac{3}{2}}$



Ethereal splitting between $nP_{3/2}$ and $nP_{1/2}$

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

fractional shift

$$n=2 \Rightarrow (13.6\,eV)\left(\frac{\alpha^2}{16}\right) = 4.5\times10^{-5}\,eV$$

[Lamb shift $2S_{\frac{1}{2}}, 2P_{\frac{1}{2}} \Rightarrow 4.3\times10^{-6}\,eV$]