

13.2 Adding angular momenta

We saw that electrons have a quantum magnetic moment, kind of like you'd expect if it had spin. And that this magnetic moment interacts with the magnetic field caused by the proton if the electron has angular momentum, giving an additional contribution to the potential of $H'_{so} \propto \underline{S} \cdot \underline{L} = S_X L_X + S_y L_Y + S_Z L_Z$. So this DOES NOT COMMUTE with S_z and L_z since we can only know one of the components of any angular momentum at once. So the perturbation doesn't commute with the original operators L_z, S_z so the original wavefunctions are not the 'good' wavefunctions, so we have to do the full matrix of degenerate perturbation theory....

OR DO WE?? Turns out that if we make a total angular momentum $\underline{J} = \underline{L} + \underline{S}$, then this total J^2, J_z does commute with all our original operators AND with the perturbation! (you'll prove this in next weeks homework! $[J_z, \underline{S} \cdot \underline{L}] = 0$). Here we'll prove that $[J^2, \underline{L} \cdot \underline{S}] = 0$

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

as $S \cdot L = L \cdot S$ since S and L commute. so

$$\begin{aligned} [J^2, \underline{L} \cdot \underline{S}] &= [L^2 + S^2 + 2\underline{L} \cdot \underline{S}, \underline{L} \cdot \underline{S}] \\ &= [L^2, L_x S_x + L_y S_y + L_z S_z] + [S^2, L_x S_x + L_y S_y + L_z S_z] + [2\underline{L} \cdot \underline{S}, \underline{L} \cdot \underline{S}] \\ &= S_x [L^2, L_x] + S_y [L^2, L_y] + S_z [L^2, L_z] + L_x [S^2, S_x] + L_y [S^2, S_y] + L_z [S^2, S_z] + 0 \\ &= 0 \end{aligned}$$

as all components of an angular momentum commute with total square of that angular momentum!

in essence, total angular momentum is conserved, while the component parts of it are not, so instead of going with the component parts, where we have L_z, S_z we replace the problematic S_z, L_z with J^2, J_z so we now think about the set H^0, L^2, J^2, S^2, J_z .

Adding angular momentum is subtle. But if we go back to the vector model we have at least a place to start. $J_z = L_z + S_z$ so this is easy to calculate. L_z has values $m_l \hbar$ where $m_l = -l, -l + 1, \dots, l - 1, l$ and l is the quantum number from the eigenvalues of L^2 which are $l(l + 1)\hbar^2$.

S_z likewise has values $m_s \hbar$ where $m_s = -s, \dots, s$, where s is the quantum number from the eigenvalues of S^2 which are $s(s + 1)\hbar^2$. But here $s = 1/2$ for ALL electrons (in fact all fermions). So $m_s = -1/2$ or $+1/2$.

so the maximum value of J_z is the sum of the maximum values of m_l and s_l i.e. $\max J_z = l + s$. similarly, $\min J_z = -l - s$. In other words, J_z runs from $-l - s, \dots, l + s$ in integer steps, so it must correspond to an value $j = l + s$ of J^2 which has eigenvalues $j(j + 1)\hbar^2$. We can see this by thinking about the vector model of angular momentum - draw \underline{L} as a vector in the L_x, L_y, L_z space. It has length $\sqrt{l(l + 1)\hbar}$, and projection $m_l \hbar$ onto the L_z axis. but it can be oriented anywhere around L_x, L_y forming a cone of possible values for each m_l , so the full sequence can have a cone with $m_l = -l$, another with $m_l = -l + 1$, and so on up to $m_l = l$. so there are $2l + 1$ possible cones, each with their own m_l value, for each l .

Similarly, we can draw \underline{S} in the S_x, S_y, S_z space as a vector of length $\sqrt{s(s + 1)\hbar}$. now there are cones with $S_z = -s$ up to s . So the maximum possible value for \underline{J} is if we take the maximum m_l and m_s and have them aligned as close as possible. this gives a vector \underline{J} of length $\approx (l + s)\hbar$. But the minimum \underline{J} is when we have the maximum m_l and the MINIMUM m_s and have them MISALIGNED as far as possible. This gives a vector \underline{J} of length $\approx |l - s|\hbar$.

So this tells us that when we add orbital and spin angular momenta, to make $\underline{J} = \underline{L} + \underline{S}$ then j can take values $|l - s| < j < l + s$ in integer steps, and for each one then m_j takes values $-j, \dots, j$ in integer steps.

In our specific case, $s = 1/2$ then there is only one integer between $|l - s| <$

m_l	m_s	$m_j = m_l + m_s$
1	1/2	3/2
1	-1/2	1/2
0	1/2	1/2
0	-1/2	-1/2
-1	1/2	-1/2
-1	-1/2	-3/2

Table 1: Possible values of m_j resulting from $l = 1$ and $s = 1/2$

$j < l + s$ so j takes values $|l - 1/2|$ and $l + 1/2$, so in general each of our single state before can take two different values of j , but in the special case of $l = 0$ these are both the same, with $j = 1/2$. for $l \neq 0$ then $j = l - 1/2$ and $l + 1/2$. And since this is a general angular momentum, we also know that J^2 has eigenvalues $j(j + 1)\hbar^2$, and the corresponding $-j < m_j < j$ in integer steps.

lets do an example for $l = 1$ (so this means $n \geq 2$) and $s = 1/2$.

We could have $m_l = -1, 0, 1$ and for each state we can have $m_s = \pm 1/2$. so this tells us that the eigenvalues of $J_z = L_z + S_z$ are $m_j \hbar$ where $m_j = m_l + m_s$. so we can write this in a table

And here we see something strange - there are two ways to get $m_j = 1/2$ or $-1/2$ but only 1 way to get $m_j = 3/2$ or $-3/2$. We get more insight on this by writing this out in j as well. we know that $l = 1$ and $s = 1/2$ can give us total $j = |l - s| = 1/2$ or $l + s = 3/2$. so we could have written our table instead like this

so now we see that those 'extra' two states, come from the fact that j can have $j = l + s..|l - s|$ i.e. that $j = 3/2$ OR $1/2$. if we had just stopped with $j = l + s = 3/2$ we wouldn't have had enough!

So we can see that if we start with $l = 1$ and $s = 1/2$ then we have a $4/6 = 2/3$ chance to have $j = 3/2$ and a $1/3$ chance to have $j = 1/2$.

j	m_j
3/2	3/2
3/2	1/2
3/2	-1/2
3/2	-3/2
1/2	1/2
1/2	-1/2

Table 2: Possible values of m_j resulting from $j = |l - s|$ and $j = l + s$

13.3 So what is $\underline{S.L}$

So what we now need to do is understand $\underline{L.S}$. and we get there from considering J^2 .

$$J^2 = (\underline{L} + \underline{S}).(\underline{L} + \underline{S}) = L^2 + S^2 + 2\underline{L.S}$$

as $S.L = L.S$ since S and L commute.

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

so the eigenvalues of $\underline{L.S}$ are eigenvalues of $\frac{1}{2}(J^2 - L^2 - S^2)$

i.e. $\frac{\hbar^2}{2}(j(j+1) - l(l+1) - s(s+1)) = \frac{\hbar^2}{2}(j(j+1) - l(l+1) - 3/4)$

$$E_{n,so}^1 = \langle \psi_n | H'_{so} \psi_n \rangle = \frac{e^2}{8\pi\epsilon_0 c^2 m^2} \frac{\hbar^2}{2} (j(j+1) - l(l+1) - 3/4) \langle \psi_n | r^{-3} \psi_n \rangle$$

we can just look up $\langle 1/r^3 \rangle = 1/[l(l+1/2)(l+1)n^3 a^3]$ so we get:

$$= \frac{e^2 \hbar^2}{16\pi\epsilon_0 c^2 m^2} (j(j+1) - l(l+1) - 3/4) \frac{1}{l(l+1/2)(l+1)n^3 a^3}$$

but we had $e^2/(4\pi\epsilon_0) = \hbar^2/(am)$ so

$$= \frac{\hbar^4}{4a^4n^3m^3c^2} (j(j+1) - l(l+1) - 3/4) \frac{1}{l(l+1/2)(l+1)}$$

and we also have $E_n^0 = -\hbar^2/(2ma^2n^2)$ so $(E_n^0)^2 = \hbar^4/(4m^2a^4n^4)$

$$= (E_n^0)^2 \frac{n}{mc^2} (j(j+1) - l(l+1) - 3/4) \frac{1}{l(l+1/2)(l+1)}$$

$$= \frac{(E_n^0)^2 n (j(j+1) - l(l+1) - 3/4)}{mc^2 l(l+1/2)(l+1)} \quad l \neq 0$$

and its a good job we have $l \neq 0$ from our semi-classical approach (saying we needed to have angular momentum!) as for $l = 0$ the denominator $\rightarrow 0!$ but since we are only discussing here the states with angular momentum, we are OK. and this spin-orbit coupling typically leads to $E_n^1/E_n^0 \sim E_n^0/mc^2$

13.4 Correction to the potential

However, the spin-orbit coupling is NOT the only thing of importance when it comes to getting the energy levels exactly right. there are two more terms which are important at this level.

We assumed the potential was a point source of +ve charge at the centre. but its not - a proton has some (very small) spatial extent. so there is an additional correction to the potential energy if the electron is at the same position as the proton - called the Darwin term - which effectively smears out the charge a bit

$$H_{rv}^1 = \frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} \delta(r-0)$$

this doesn't care about spin, and it commutes with all the angular momentum operators so we can use non-degenerate perturbation theory.

$$E_n^1 = \frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} \int_V \psi_{nlm}^* \delta(r-0) \psi_{nlm} dV$$

This only acts at the origin so it acts only on states which are not zero at the origin - only $l = 0$ have $R_{nl} \neq 0$ at $r = 0$ so it acts only on the $l = 0$ - which must also have $m = 0$ (s-states) wavefunctions.

$$= \frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} |\psi_{n00}(0)|^2$$

at $r = 0$ then all the Laguerre polynomials for $l = 0$ i.e. $L_{n-l-1}^{2l+1}(2r/na)$ are $L_{n-1}^1(0)$ so this is just the constant term in the polynomial and all in all we get $\psi_{n00}(0) = 1/(\pi a^3 n^3)$ and

$$\begin{aligned} E_n^1 &= \frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{\pi a^3 n^3} = \frac{\pi\hbar^2}{2m^2c^2} \frac{\hbar^2}{am} \frac{1}{\pi a^3 n^3} \\ &= \frac{\hbar^4}{2m^3c^2} \frac{1}{a^4 n^3} \end{aligned}$$

but we had $(E_n^0)^2 = \hbar^4/(4m^2a^4n^4)$ so $1/(a^4n^4) = 4m^2(E_n^0)^2/\hbar^4$ and $1/(a^4n^3) = 4m^2n(E_n^0)^2/\hbar^4$ so

$$\begin{aligned} &= \frac{\hbar^4}{2m^3c^2} \frac{4m^2n(E_n^0)^2}{\hbar^4} \\ &= \frac{2}{mc^2} (E_n^0)^2 n \end{aligned}$$