

13.5 Relativistic corrections to momentum

In special relativity, the kinetic energy is given by

$$E^2 = (T + mc^2)^2 = p^2c^2 + m^2c^4$$

$$T + mc^2 = mc^2 \left(1 + \frac{p^2}{m^2c^2}\right)^{1/2} = mc^2 \left(1 + \frac{1}{2} \frac{p^2}{m^2c^2} + \frac{1}{2} \frac{-1}{2} \frac{1}{2!} \left(\frac{p^2}{m^2c^2}\right)^2 + \dots\right)$$

$$T \approx \frac{p^2}{2m} - \frac{1}{8} \frac{p^4}{m^3c^2} = T^0 - (T^0)^2 \frac{4m^2}{8m^3c^2} = T^0 - \frac{1}{2mc^2} (T^0)^2$$

so the lowest order relativistic correction is $H_{rp}^1 = -p^4/(8m^3c^2) = -(T^0)^2/(2mc^2) = -(H^0 - V(r))^2/(2mc^2)$

Each level is $2n^2$ degenerate. But this perturbation commutes (more or less) with H^0 - the perturbation does not act on the spin, and its spherically symmetric so it commutes L^2 and L_z . Hence the degenerate states belonging to E_n^0 are not connected to first order to H_r^1 . so actually we can use non-degenerate perturbation theory (in effect, we have chosen 'good' eigenvectors and eigenvalues by using n, l, m and m_s . so then we have

$$E_n^1 = -\frac{1}{2mc^2} \int \psi_n^{0*} (H^0 - V(r))^2 \psi_n^0 dV$$

we know $H^0 \psi_n^0 dV = E_n^0 \psi_n^0$ so

$$= -\frac{1}{2mc^2} \int \psi_n^* ((H^0) - V(r))(E_n^0 - V(r)) \psi_n dV$$

$$= -\frac{1}{2mc^2} \int \psi_n^* ((E_n^0)^2 - 2E_n^0 V(r) - V(r)^2) \psi_n dV$$

this is just a little bit sleazy, as p^4 is not actually Hermitian for $l = 0$ even though p^2 is!! but it does actually (fortuitously) give the right answer

$$\begin{aligned}
&= -\frac{1}{2mc^2}[(E_n^0)^2 \int \psi_n^* \psi_n dV - 2E_n \int \psi_n^* V(r) \psi_n dV + \int \psi_n^* V(r)^2 \psi_n dV] \\
&= -\frac{1}{2mc^2}[(E_n^0)^2 - 2E_n \int \psi_n^* V(r) \psi_n dV + \int \psi_n^* V(r)^2 \psi_n dV] \\
&= -\frac{1}{2mc^2}[(E_n^0)^2 - 2E_n^0 \langle V(r) \rangle + \langle V(r)^2 \rangle]
\end{aligned}$$

we can get $\langle V \rangle = -e^2/(4\pi\epsilon_0) \langle 1/r \rangle$ and then use the virial theorem to get $\langle 1/r \rangle = 1/na^2$.

similarly (but more difficult, its not the virial theorem any more!) $\langle V^2 \rangle = [-e^2/(4\pi\epsilon_0)]^2 \langle 1/r^2 \rangle$, and

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

and then we also have

$$a = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \text{ so } \frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{am}$$

put it all together and get

$$\begin{aligned}
E^1 &= -\frac{(E_n^0)^2}{2mc^2} \left[1 + \left(\frac{-e^2}{4\pi\epsilon_0} \right) (2/E_n^0) \frac{1}{an^2} + \left(\frac{-e^2}{4\pi\epsilon_0} \right)^2 \frac{(1/(E_n^0)^2)}{a^2 n^3 (l + 1/2)} \right] \\
&= -\frac{(E_n^0)^2}{2mc^2} \left[1 + \frac{\hbar^2}{am} (2/E_n^0) \frac{1}{an^2} + \frac{\hbar^4}{a^2 m^2} \frac{(1/(E_n^0)^2)}{a^2 n^3 (l + 1/2)} \right]
\end{aligned}$$

but we can write

$$E_n^0 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} = -\frac{m}{2\hbar^2} \frac{\hbar^4}{m^2 a^2} \frac{1}{n^2} = -\frac{\hbar^2}{2ma^2} \frac{1}{n^2}$$

so put that in the equation and get

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

13.6 total correction

add the terms (carefully) all together and we get

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

we can also write E_n^0 in another way

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

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) = 1/137$ is the dimensionless fine structure constant. So then E_n^0 is of order α^2 , and E_{nj}^1 is of order α^4 . Lets see this explicitly

$$\begin{aligned} E_{nj} &= E_n^0 + E_n^0 \alpha^2 \frac{mc^2}{2n^2 2mc^2} \left[-3 + \frac{4n}{(j+1/2)} \right] \\ &= E_n^0 \left(1 + \frac{\alpha^2}{n^2} \left[\frac{n}{(j+1/2)} - \frac{3}{4} \right] \right) \end{aligned}$$

so we can see instantly that these corrections are of order $\alpha^2 \sim 10^4 \times$ smaller than the unperturbed energy.

13.6.1 Ground state of Hydrogen

The ground state of hydrogen has $l = 0, j = |l - s|$ and $j = l + s$ so there is only one $j = 1/2$. Hence there is a correction to the ground state energy of

$$\frac{\Delta E_1}{E_1^0} = \frac{\alpha^2}{n^2} \left[\frac{n}{j + 1/2} - \frac{3}{4} \right] = \alpha^2 \left(1 - \frac{3}{4} \right) = \frac{\alpha^2}{4}$$

hence $\Delta E_1 = E_1^0 \alpha^2 / 4 = 1.33 \times 10^{-5} E_1^0 = -1.81 \times 10^{-4} \text{ eV}$. So the ground state energy is SLIGHTLY lower, at $-13.6 - 1.81 \times 10^{-4} \text{ eV}$

13.7 Quantum number sets

Our unperturbed energy levels were labelled with n, l, m, m_s i.e. the quantum numbers corresponding to operators H^0, L^2, L_z, S_z (there is S^2 as well but this has quantum numbers $s(s+1)\hbar^2 = 3/4\hbar^2$ for all electrons so its not very useful!!)

our new quantum number sets label the wavefunctions which follow all these fine structure perturbations. and these are n, l, j, m_j corresponding to H^0, L^2, J^2, J_z (again, we have S^2 as well but its not very useful!)

$\underline{J} = \underline{L} + \underline{S}$ ie its a sum of orbital and spin angular momentum of the electron. as such, its another angular momentum so by definition J^2 has eigenvalues $j(j+1)\hbar^2$ and J_z has eigenvalues $m_j\hbar$.

from the initial vector sum definition, $\underline{J} = \underline{L} + \underline{S}$ then j should take values from $|l - 1/2|$ to $l + 1/2$ in integer steps, so j can take 2 values in general, $l - 1/2$ and $l + 1/2$ except for $l = 0$ where $j = 1/2$. so then m_j can take any value from $-j \dots j$ in integer steps.

13.8 Balmer line energies

the Balmer line transition is $n = 3$ to $n = 2$. In the analytic solution of the Schrodinger equation we had $E_n = -13.6/n^2$ eV so the line has energy

$$E_3 - E_2 = -13.6 \left(\frac{1}{3^2} - \frac{1}{2^2} \right) = 1.889 \text{ eV}$$

but now we have an energy which depends on j as well as n . so the $n = 3$ level splits. and we can either just keep track by using n, l, j, m_j (safe) or write it like the chemists and get confused! they label levels with n , and a LETTER for l such that $l = 0, 1, 2, 3..$ is s,p,d,f (smart physicists don't fail) and then the value of j as a subscript.

$n=3, l=0$ means $j = |l - 1/2|$ to $j = l + 1/2$ so $j=1/2$ ($3s_{1/2}$)

$n=3, l=1$ means $j = 1/2$ and $3/2$ ($3p_{1/2}$ and $3p_{3/2}$)

$n=3, l=2$ means $j = 3/2$ and $5/2$ ($3d_{1/2}$ and $3d_{5/2}$)

then it drops to $n=2$ where we can have

$n=2, l=0$ means $j = |l - 1/2|$ to $j = l + 1/2$ so $j=1/2$ ($2s_{1/2}$)

$n=2, l=1$ means $j = 1/2$ and $3/2$ ($2p_{1/2}$ and $2p_{3/2}$)

so there are 5 different labels for the initial $n = 3$ state but only 3 with distinct n, j values i.e. distinct energies. we started off with the level as $2n^2 = 18$ degenerate - now we have split the 18 possible degenerate states into 3 different energies. but the level is still highly degenerate!

And there are 3 different labels for the final $n = 2$ state but only 2 distinct n, j i.e. only 2 distinct energies. and since this level has degeneracy 8 before we considered the perturbations it is still highly degenerate too!

so there are 6 possible different transition energies

$n=3, j=1/2$ ($l=0$ and 1) $3s_{1/2}$ and $3p_{1/2}$ going to $n=2 j=1/2$ ($l=0$ and 1) $2s_{1/2}$ or $2p_{1/2}$

$n=3, j=1/2$ ($l=0$ and 1) $3s_{1/2}$ and $3p_{1/2}$ going to $n=2, j=3/2$ ($l=1$) $2p_{3/2}$

$n=3, j=3/2$ ($l=1$ and 2) $3p_{3/2}$ and $3d_{3/2}$ going to $n=2, j=1/2$ ($l=0$ and 1) $2s_{1/2}$ or $2p_{1/2}$

$n=3, j=3/2$ ($l=1$ and 2) $3p_{3/2}$ and $3d_{3/2}$ going to $n=2, j=3/2$ ($l=1$) $2p_{3/2}$

$n=3, j=5/2$ ($l=2$) $3d_{5/2}$ going to $n=2, j=1/2$ ($l=0$ and 1) $2s_{1/2}$ or $2p_{1/2}$

$n=3, j=5/2$ ($l=2$) $3d_{5/2}$ going to $n=2, j=3/2$ ($l=1$) $2p_{3/2}$

so there are 6 separate energy levels now which correspond to a transition between $n=3$ and $n=2$. so why do we see only two strong lines?

we know that the photon carries angular momentum of unity so to conserve angular momentum we need to change $\Delta l = \pm 1$ for a radiative transition (ie we see a line!). and this corresponds to $\Delta j = 0, \pm 1$ for allowed transitions (electric dipole radiation!) - others are called forbidden - they do happen but with much much smaller probability

so these selection rules (conservation of angular momentum!) remove some of the possibilities above, leaving only

$3s_{1/2} - 2p_{1/2}$ and $3p_{1/2} - 2s_{1/2}$

$3s_{1/2} - 2p_{3/2}$

$3p_{3/2} - 2s_{1/2}$ and $3d_{3/2} - 2p_{1/2}$

$3d_{3/2} - 2p_{3/2}$

$3d_{5/2} - 2p_{3/2}$

i.e. there are 7 possible labels, but only 5 possible energies i.e distinct combinations of n, j . These are

$3, 1/2$ to $2, 1/2$

$3, 1/2$ to $2, 3/2$

$3,3/2$ to $2,1/2$

$3,3/2$ to $2,3/2$

$3,5/2$ to $2,3/2$

but why then do we have 2 lines?? well, we don;t really - there are 5 lines, but the energy spilt gets smaller and smaller with n so they form 2 sets of lines, $n=3$ to $2,1/2$ (2 lines) and $n=3$ to $2,3/2$ (3 lines) which is why we see this as a doublet.