Hydrogen Fine Structure I

Now we are in a position to calculate the effects on the hydrogen energy levels of the perturbations we discussed a ~~couple of~~ few lectures ago.

A. The KE correction

$$h = -\frac{1}{2m c^2}\left(\frac{p^2}{2m}\right)^2$$

The most general matrix element which can turn up in perturbation theory calculations is

$$\langle n', l', m' | \, h \, | n, l, m \rangle$$

This looks as though it could be pretty nasty to calculate – after all h contains four derivatives, and the wavefunctions ϕ_{nlm} are quite complicated. But there is a way through; we know that

$$\left(\frac{p^2}{2m} + V(r)\right) | n, l, m \rangle = E_n | n, l, m \rangle$$

Coulomb potential $-\frac{e^2}{4\pi\varepsilon_0 r}$

so

$$\frac{p^2}{2m} | n, l, m \rangle = \left(E_n - V(r)\right) | n, l, m \rangle$$

and therefore

$$\langle n', l', m' | \left(\frac{p^2}{2m}\right)^2 | n, l, m \rangle = \langle n', l', m' | \overleftarrow{\frac{p^2}{2m}} \; \overrightarrow{\frac{p^2}{2m}} | n, l, m \rangle$$

$$= \langle n', l', m' | \left(E_{n'}^* - V(r)\right)\left(E_n - V(r)\right) | n, l, m \rangle$$

$$= E_n^2 \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

$$- (E_n + E_{n'}) \langle n', l', m' | V(r) | n, l, m \rangle$$

$$+ \langle n', l', m' | (V(r))^2 | n, l, m \rangle$$

Because $V(r)$ is a function of r only, these remaining matrix elements are only non-zero if $l = l'$ and $m = m'$: in terms of overlap integrals we have $\int d\Omega \, Y^*_{l'm'} \, Y_{l,m} = \delta_{ll'} \delta_{mm'}$. So

$$\langle n', l', m' | \left(\frac{p^2}{2m}\right)^2 | n, l, m \rangle$$

$$= \delta_{ll'} \delta_{mm'} \Big\{ E_n^2 \delta_{nn'}$$

$$- (E_n + E_{n'}) \langle n', l, m | V(r) | n, l, m \rangle$$

$$+ \langle n', l, m | (V(r))^2 | n, l, m \rangle \Big\}$$

We can now make an important observation

Degenerate states have same n, different ℓ and/or m

so the matrix elements between degenerate states always vanish. Thus we can use non-degenerate perturbation theory and the first order energy shift is

$$\Delta E_{n,\ell,m} = \frac{-1}{2mc^2} \langle n,\ell,m| \left(\frac{p^2}{2m}\right)^2 |n,\ell,m\rangle$$

$$= -\frac{1}{2mc^2} \left\{ E_n^2 - 2E_n \left(\frac{-e^2}{4\pi\epsilon_0}\right) \left\langle \frac{1}{r} \right\rangle_{n,\ell} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \left\langle \frac{1}{r^2} \right\rangle_{n,\ell} \right\}$$

where

$$\left\langle \frac{1}{r^k} \right\rangle_{n,\ell} = \int_0^\infty r^2 R_{n,\ell}^2 \frac{1}{r^k} \, dr \qquad k = 1, 2$$

It's easy to calculate these for the ground state

$$= \int_0^\infty r^{2-k} \frac{4}{a^3} e^{-2r/a} \, dr$$

set $r = a/2 \, x$ to get

$$= \frac{4}{a^3} \left(a/2\right)^{3-k} \underbrace{\int_0^\infty x^{2-k} e^{-x} \, dx}_{= 1 \text{ for } k = 1, 2}.$$

$$= \frac{1}{a^k} 2^{k-1}$$

So

$$\Delta E_{1,0,0} = \frac{-1}{2mc^2}\left\{ E_1^2 + 2E_1 \frac{e^2}{4\pi\epsilon_0 a} + 2\left(\frac{e^2}{4\pi\epsilon_0 a}\right)^2 \right\}$$

but $E_1 = -\frac{mc^2}{2}\alpha^2$

$$a = \frac{\hbar c}{mc^2 \alpha}$$

so $\frac{e^2}{4\pi\epsilon_0 a} = \frac{e^2}{4\pi\epsilon_0 \hbar c} mc^2\alpha = mc^2\alpha^2$

$$\Delta E_{1,0,0} = -\frac{1}{2mc^2}(mc^2)^2\alpha^4\left\{\frac{1}{4} - 1 + 2\right\}.$$

$$= -\frac{5}{4}\frac{mc^2}{2}\alpha^4$$

$$= +\frac{5}{4}\alpha^2 E_1$$

This is entirely consistent with our earlier estimate that the K.E. correction should be of order α^2 times the original energy. However, <u>this is a real calculation</u> and in due course (when we've done the other $O(\alpha^2)$ terms) we'll be able to compare it with the experimental results.

For general states the expectation values $\left\langle \frac{1}{r^k} \right\rangle_{n,l}$ are a little more tiresome to calculate, although there are some tricks which minimise the effort involved.

We'll just quote the answers here

$$\left\langle \frac{1}{r} \right\rangle_{n,l} = \frac{1}{a n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{n,l} = \frac{1}{a^2 n^3 (l+\frac{1}{2})}$$

so we get

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

note that the energy shift depends on l as well as n, but not on m

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

Two points to note here:

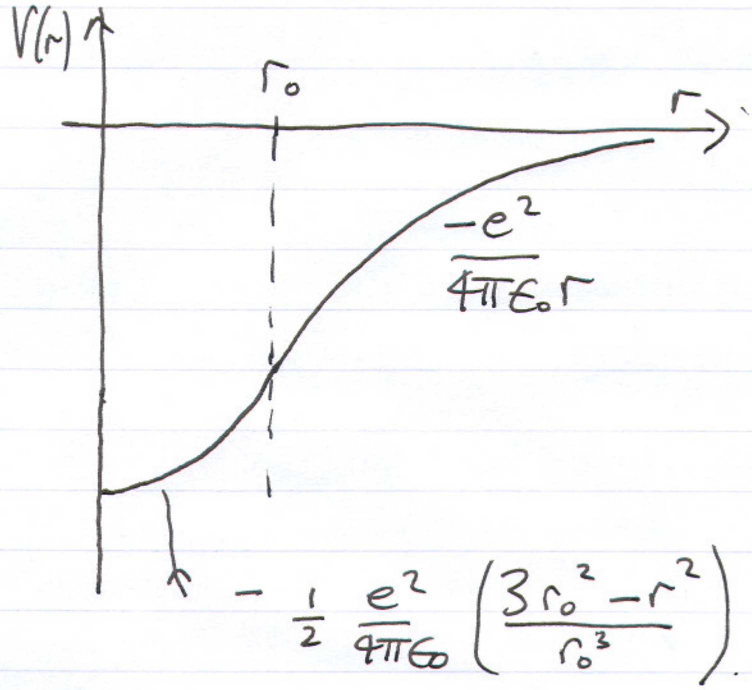
1). The l degeneracy is lifted; we can't yet compare this with experiment because there are more $O(\alpha^2)$ corrections to compute.

2) As n gets large the relative change

$$\frac{\Delta E_{n,l}}{E_n} \sim \frac{\alpha^2}{n(l+\frac{1}{2})}$$

This reflects the fact that large n orbits have "slower" electrons, so relativistic effects are less significant.

B. Finite nuclear volume



so $$h = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\left(\frac{3r_0^2 - r^2}{r_0^3}\right) - \left(\frac{-e^2}{4\pi\epsilon_0 r}\right) \qquad r \leq r_0$$

$$= 0 \qquad r > r_0$$

Because h is just a function of r, and not of θ, ϕ, the reasoning goes just the same as for the relativistic correction and we get

$$\langle n', l', m' | h | n, l, m \rangle = \frac{-e^2}{8\pi\epsilon_0} \delta_{ll'} \delta_{mm'} \times$$

$$\int_0^{r_0} dr\, r^2 (R_{n,l})^2 \left\{ \frac{3}{r_0} - \frac{r^2}{r_0^3} - \frac{2}{r} \right\}$$

Now in this integral we only need $R_{n,l}(r)$ for $r \leq r_0 \ll a$. Remember that

$$R_{n,l} \sim \underbrace{r^l}_{\left(\frac{r_0}{a}\right)^l} \underbrace{\left(1 + O(r/a)\right) e^{-r/an}}_{1 + \underbrace{O(r/a)}_{\sim 10^{-5}}}$$

so by far the largest shift is obtained for $l=0$ states which have a much larger probability of being in the nucleus. For these we get

$$\int_0^{r_0} dr\, r^2 (R_{n,l})^2 \left\{ \frac{3}{r_0} - \frac{r^2}{r_0^3} - \frac{2}{r} \right\}$$

$$= (R_{n,0})^2 \left\{ \frac{r_0^3}{r_0} - \frac{1}{5}\frac{r_0^5}{r_0^3} - r_0^2 \right\} \left(1 + O(10^{-5})\right)$$

$$= - \frac{r_0^2}{5} (R_{n,0})^2$$

$$= - \frac{r_0^2\, C_{n,0}^2}{5 n^3 a^3}$$

$C_{n,0}$ is just a number

$C_{1,0} = 2$

$C_{2,0} = 1/\sqrt{2}$

$C_{3,0} = 2/3^{3/2}$

$\vdots$

so $$\Delta E_{n,0,0} = \frac{1}{5} \frac{e^2}{4\pi\epsilon_0 a} \cdot \left(\frac{r_0}{a}\right)^2 \frac{C_{n,0}^2}{n^3}$$

$$= -\frac{2}{5} E_{n,0,0} \left(\frac{r_0}{a}\right)^2 \frac{C_{n,0}^2}{n}$$

So now we have done a proper calculation and checked that the size of this effect is $\sim \left(\frac{r_0}{a}\right)^2 \sim 10^{-10}$ and much smaller than the $O(\alpha^2)$ effects from relativistic KE and spin-orbit which we'll calculate next time.