6.3 The Fine Structure of Hydrogen:

When we studied the hydrogen atom we used what, at first sight, seemed to be the complete Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \qquad \mathbf{p} \rightarrow (\hbar/i)\nabla$$

However, small corrections are still missing. The most important is called fine structure and it is made of a relativistic component and a spin-orbit coupling. These are small corrections that are incorporated by perturbation theory (not possible to solve problem exactly anymore).

Relativity first.
The first term of the Hamiltonian above is the quantum version of:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$$\mathbf{p} \rightarrow (\hbar/i)\nabla$$

We will try to improve the kinetic energy including corrections from relativity:

The full "classical" relativistic formula is:

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2$$

Total energy: $\frac{mc^2}{\sqrt{1-(v/c)^2}}$

Rest energy: mc^2

... and the momentum is:

$$p = \frac{mv}{\sqrt{1-(v/c)^2}}$$

It can be shown (see book) that:

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

Trying to use $\mathbf{p} \rightarrow (\hbar/i)\nabla$ is complicated because of the square root ...

$$T = mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] = mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 \cdots - 1\right]$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots$$

$\sqrt{1+x} \sim 1 + x/2 - x^2/8 + x^3/16 + \ldots$

Then our perturbative correction is:

$$H'_r = -\frac{p^4}{8m^3c^2}$$

To lowest order in perturbation theory the energy correction is:

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3c^2}\langle \psi | p^4 \psi \rangle$$

The "sandwich" is with the unperturbed states of Ch. 4.

From the unperturbed Sch Eq we know that:

$$p^2\psi = 2m(E - V)\psi$$

Unperturbed energies of Ch. 4.

Then we arrive to:

$$E_r^1 = -\frac{1}{2mc^2}\langle(E-V)^2\rangle = -\frac{1}{2mc^2}[E^2 - 2E\langle V\rangle + \langle V^2\rangle]$$

Now specifically for the hydrogen atom potential V= $-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right]$$

It can be shown (no need to verify) that:

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

Then, we arrive to the result:

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{(l + 1/2) n^3 a^2}\right]$$

Using formulas of Ch. 4 for the Bohr radius *a* and for E_n :

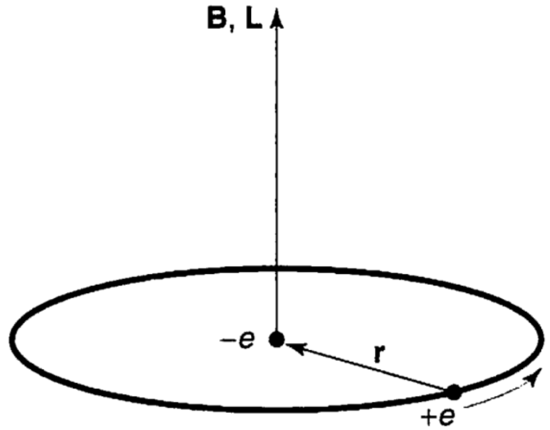
$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \qquad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

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

Example: for ground state use n=1, l=0, E_1 = -13.6 eV, *m* mass of electron, and *c* speed of light. Result ~ 10^{-3} eV (small!).

6.3 Spin-orbit coupling:

From the perspective of the electron, the proton is orbiting around:



From classical electromagnetism a loop of current creates a magnetic field at the center:

$$B = \frac{\mu_0 I}{2r}$$

where the permeability μ_0 of free space and the permittivity of free space ε_0 are related via:

$$c = 1/\sqrt{\epsilon_0 \mu_0}$$

The current relates with the period *T* via:

$$I = e/T$$

v = r ω = r 2π/T

and the period *T* relates with the angular momentum *L* via:

$$L = rmv = 2\pi m r^2/T$$

From study of spins in magnetic fields, Ch. 4, in general:

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}$$

From previous study of spin:

$$\mu_e = -\frac{e}{m}\mathbf{S}$$

From previous page:

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\mathbf{L}$$

Then, overall, classically we obtain the correction called spin-orbit coupling:

$$H = \left(\frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}$$

Repeating via rigorous math (including the fact that the electron inertia system is accelerating, etc.) leads just to a factor 2 difference:

$$H'_{so} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\mathbf{S}\cdot\mathbf{L}$$

Important statement, without proof: Because of the **S.L** term, the Hamiltonian no longer commutes with S_z and L_z, but still commutes with L^2 and S^2 and the total angular momentum J^2 and its projection J_z.

$$\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$$

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

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

Change of basis required: from basis with (l, s, m_l, m_s) as quantum numbers to basis with (l, s, j, m_j) as quantum numbers.

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$$

← Fixed to 3/4

Moreover, the expectation value of $1/r^3$ is:

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

$$\langle H'_{so} \rangle = \langle \left(\frac{e^2}{8\pi\epsilon_0}\right) \frac{1}{m^2c^2r^3} \mathbf{S}\cdot\mathbf{L} \rangle$$

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]$$

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

$$E^1_{so} = \langle H'_{so} \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2c^2} \frac{(\hbar^2/2)[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)n^3a^3}$$

Eqs. From Ch 4 for the Bohr radius *a* and for E_n :

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

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

$$E^1_{so} = \frac{(E_n)^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right\}$$

In spite of their different origins, the relativistic and spin-orbit corrections have the same number in front. I.e. they are of the "same order".