The Fine Structure of the Hydrogen atom

We previously mentioned that in high resolution spectra of hydrogen, the predicted lines are actually split into multiple lines. This is because of the fine structure of hydrogen.

The Schrödinger equation we have been using until now is non-relativistic. It was extended to the relativistic version by Dirac, hence the relativistic version is called the Dirac equation. However, in the small velocity limit, the Dirac equation tends to the Schrödinger equation, so instead of solving the dirac equation directly, we treat the difference between the two equations as a series of perturbations.

The different perturbations have different names.

Spin Orbit Coupling

The magnetic moment associated with the spin of an electron is given by:

$$\underline{M} = -\frac{ge}{2m}\underline{S} \qquad \text{where } \underline{S} = \pm\frac{\hbar}{2}$$
$$\text{and } g = 2.002319\ldots$$

We know from relativity that what is observed in one inertial frame to only have an electric field will be observed in another reference frame to also have a magnetic field. So in the rest frame of the nucleus, the nucleus only generates an electric field. But in the rest frame of an electron passing the nucleus, the electron also experiences a magnetic field.

The magnetic field is given by: $\underline{B} = \frac{\underline{E} \times \underline{v}}{c^2}$

where $\underline{v}$ is velocity of electron and $\underline{E} = \frac{e\underline{r}}{4\pi\varepsilon_0 r^3}$

$$\therefore \quad \underline{B} = \frac{e}{4\pi\varepsilon_0 c^2 r^3} \underline{r} \times \underline{v}$$

$$= \frac{e}{4\pi\varepsilon_0 c^2 r^3} \underline{r} \times m\underline{v} \times \frac{1}{m} = \frac{e}{4\pi\varepsilon_0 m c^2 r^3} \underline{L}$$

where $\underline{L}$ is orbital angular momentum

A magnetic dipole in the presence of a magnetic field has a energy change $-\underline{M} \cdot \underline{B}$ so:

$$\text{Denergy} = -\underline{M} \cdot \underline{B} = \frac{ge^2}{8\pi\varepsilon_0 m^2 c^2 r^3} \underline{L} \cdot \underline{S}$$

Actually, this isn't quite right. We assumed the electron moves in a straight line past the nucleus but it is actually orbiting. The correction for this is called Thomas precession. So our final perturbation hamiltonian is half this:

$$\hat{H}_p = \frac{ge^2}{16\pi\varepsilon_0 m^2 c^2 r^3} \hat{L} \cdot \hat{S}$$

Let $\hat{J}$ be the total angular momentum operator:

$\hat{J} = \hat{L} + \hat{S}$ Note, we are using slightly different letters to previous chapters. But the end result won't change.

We need this because we are seeking the correct combination of degenerate states to use in the perturbation calculation, since $\hat{L} \cdot \hat{S}$ no longer commutes with the z components $L_z \cdot S_z$.

But $\hat{L}^2$, $\hat{J}^2$ and $\hat{S}^2$ do. So let's see if we can introduce those.

$$\hat{J} = \hat{L} + \hat{S}$$

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

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

so $$\hat{H}_p = \frac{ge^2}{32\pi\varepsilon_0 m^2c^2r^3}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

This now commutes with $\hat{J}^2, \hat{L}^2, \hat{S}^2$ and J_z, L_z, S_z so the new basis states are also eigenstates of these operators.

$$E^{(1)}_{n,j,l,s} = \frac{\hbar^2 ge^2}{32\pi\varepsilon_0 m^2c^2}\frac{1}{(na_0)^3 l(l+\frac{1}{2})(l+1)}\{j(j+1) - l(l+1) - s(s+1)\}$$

which we can write as:

$$E^{(1)}_{njls} = \frac{\alpha^2 g E_n^{(0)}}{4nl(l+\frac{1}{2})(l+1)}\{j(j+1) - l(l+1) - s(s+1)\}$$

where $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$ the fine structure constant.

So we have the spin-orbit coupling correction.

A note on the Term Symbol

We can represent n, j, l and s with one symbol called the term symbol. This is written in the form:

$${}^{2S+1}L_j$$

where $2S+1$ is called the multiplicity.

$^{2S+1}L_j$

The multiplicity is usually given as a number, along with the j value. The L value is the standard letter associated with the angular momentum (the orbital s, p, d). The whole thing is preceded by the value of n, the principle quantum number.

principal quantum no.

So, for an electron in a 2p orbital. we know $s = \frac{1}{2}$ for electron. we know $j = L + S$ and L can be: $L = 0 \ldots n-1$

so $L = 0$ or $L = 1$. if $L = 0$, $j = \frac{1}{2}$ if $L = 1$, $j = \frac{3}{2}$

$$\therefore \quad 2\,{}^2P_{\frac{1}{2}} \quad \text{or} \quad 2\,{}^2P_{3/2}$$

These are our term symbols.

Relativistic Mass Correction

In the SE, the kinetic energy we use is $\frac{p^2}{2m}$ but in relativity, the kinetic energy is actually:

$$\sqrt{p^2c^2 + m^2c^4} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$$ when expanded.

we will only use up to the second term, which is called the relativistic mass correction term, and is used as our perturbation hamiltonian.

This gives us:

$$E^{(1)}_{njLS} = -\frac{\alpha^2}{n^2}\left[\frac{3}{4} - \frac{n}{L+\frac{1}{2}}\right]E^{(0)}_n$$

so we have the relativistic mass correction

Darwin Correction

This correction has no classical analogue and is due to non-classical dynamics of electrons near the nucleus. So we will simply state it for $l=0$ states:

$$E^{(1)}_{nj0S} = -\frac{\alpha^2}{n} E^{(0)}_n$$

Sum of Relativistic Fine Structure Corrections

Summing the effects of spin-orbit coupling, relativistic mass correction and Darwin correction:

$$E^{(1)}_{njLS} = -\frac{\alpha^2}{n^2}\left[\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right] E^{(0)}_n$$

This is our first order energy shift. Adding this to our unperturbed energy lets us find the energy of the shifted line.

Other Effects

However, even Dirac equation doesn't fully describe the hydrogen atom since it treats the electric field as a classical field.

If we use quantum electrodynamics, it turns out states with same j and different l are actually not degenerate.

The energy difference between states is very small, around 1 GHz.

This difference between the states is called Lamb Shift.