Fine Structure

The effects known as fine structure come from relativistic corrections to the non-relativistic treatment of hydrogen. Fine structure effects are present in all atoms. They are easy to calculate for the case of a one electron atom. Recall from Bohr theory that in hydrogen, the electron's velocity satisfies $v/c \sim \alpha$. As will be seen below, the correction terms in fine structure are $O(v/c)^2$.

LS Coupling The fine structure known as LS coupling is spin-dependent. It arises from the interaction of the electron's magnetic moment with a magnetic field seen in the electron's rest frame. The electron's magnetic moment is proportional to its spin,

$$\vec{\mu} = -\frac{e\hbar}{2mc} g\vec{S},$$

where

$$\vec{S} = \frac{1}{2}\vec{\sigma},$$

and the so-called g factor is very close to 2.

$$g = 2 + O(\alpha) + \ldots$$

The effect can be understood if we go to the electron rest frame. In that frame the electron will experience a magnetic field. The interaction of the magnetic moment with this magnetic field is the origin of the LS term in fine structure.

To derive the effect, we need the formulae for fields in the electron rest frame (prime frame) in terms of field in the lab frame (unprime). Since we are interested only the the first relativistic correction, we only need the field transformation formulae to lowest order in v/c. These are

$$\vec{E}' = \vec{E} + \frac{1}{c}\vec{v} \times \vec{B}$$

$$\vec{B}' = \vec{B} - \frac{1}{c}\vec{v} \times \vec{E}$$

Now in the lab frame, the only field present is the Coulomb field of the nucleus, so the magnetic field we are after is

$$\vec{B}' = -\frac{1}{mc} m\vec{v} \times \vec{E},$$

where

$$E = e\frac{\vec{r}}{r^3}.$$

Rewriting $\vec{B}'$, we have

$$\vec{B}' = \frac{e}{mc}\frac{\vec{r} \times \vec{p}}{r^3} = \frac{e\hbar}{mc}\frac{\vec{L}}{r^3}.$$

This first term in this formula can be regarded as purely classical. Coupling this magnetic field to the magnetic moment of the electron, we have

$$H_{LS} = (\frac{1}{2})(\frac{e\hbar}{mc})^2 \vec{L} \cdot \vec{S}.$$

Again this formula could be regarded as classical if we simply wrote $\vec{\mu}$ for the magnetic moment of the electron, instead of using the formula for $\vec{\mu}$ in terms of the electron spin, and did not pull out $\hbar$ from $\vec{L}$ as we have done. As usual, we take a classical term in the Hamiltonian, and go to quantum mechanics by interpreting the various quantities as quantum operators. Finally, we note that the formula contains a prefactor of 1/2. This comes from so-called "Thomas precession," and arises because the electron is moving in a curved path and tranforming to its rest frame involves velocity transformations in different directions at different times. The derivation of the 1/2 factor is rather tricky- see Jackson's book on Classical Electrodynamics, or google "Thomas Precession" for explanations.

The LS term in fine structure is found by using H_{LS} in lowest order perturbation theory, giving

$$\Delta E_{LS} = \frac{1}{2} < \frac{1}{r^3} >< \vec{L} \cdot \vec{S} > (\frac{e\hbar}{mc})^2.$$

The evaluation of $< \vec{L} \cdot \vec{S} >$ is easy. We use

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

Re-arranging, we have

$$< \vec{L} \cdot \vec{S} >= \frac{1}{2} \left(j(j+1) - l(l+1) - \frac{1}{2}(\frac{3}{2}) \right).$$

It is understood that we have coupled the electron's orbital and spin angular momenta together into states of definite total angular momentum. The possible values of j are $j = l \pm 1/2$. The possible values of $< \vec{L} \cdot \vec{S} >$ are given in the table below.

j	$\vec{L} \cdot \vec{S}$
$l + \frac{1}{2}$	$\frac{l}{2}$
$l - \frac{1}{2}$	$-\frac{l+1}{2}$

Using $\hbar/mc = \alpha a_0$ and going over to atomic units, we have

$$\Delta E_{LS}(a.u.) = \frac{\alpha^2}{4} < \frac{1}{r^3} > \left\{ \begin{array}{cc} l & j = l + \frac{1}{2} \\ -(l+1) & j = l - \frac{1}{2} \end{array} \right\}$$

The evaluation of $< 1/r^3 >$ depends on n and l. The general formula is

$$< \frac{1}{r^3} >_{nl} = \frac{1}{n^3 l(l+1)(l+\frac{1}{2})}.$$

Deriving the general result involves technology of the radial wave functions, but is possible with elementary means for the maximum orbital angular momentum, $l = n - 1$.

We finally have for $\Delta E_{LS}(a.u.)$,

$$\Delta E_{LS}(a.u.) = \frac{\alpha^2}{4} \frac{1}{n^3 l(l+1)(l+\frac{1}{2})} \left\{ \begin{array}{cc} l & j = l + \frac{1}{2} \\ -(l+1) & j = l - \frac{1}{2} \end{array} \right\}$$

Relativistic Correction to Kinetic Energy The kinetic energy contribution to fine structure is less tricky that the LS term, we simply expand the Einstein formula for energy,

$$E = [(mc^2)^2 + (pc)^2]^{1/2} = mc^2[1 + \frac{1}{2}(\frac{p}{mc})^2 - \frac{1}{8}(\frac{p}{mc})^4 + \ldots]$$

$$= mc^2 + \frac{p^2}{2m} - \frac{p^2}{8m}(\frac{p}{mc})^2 + \ldots$$

The expected value of the $O(p^4)$ term gives the term we want. In atomic units, we have

$$\Delta E_K(a.u.) = -\frac{1}{8}\alpha^2 < p^4 > .$$

This term is independent of spin. To evaluate it, we use conservation of energy,

$$\frac{p^2}{2} - \frac{1}{r} = E.$$

Using this formula, we have

$$- < \frac{p^4}{8} > = -\frac{1}{2}(E^2 + 2E < \frac{1}{r} > + < \frac{1}{r^2} >),$$

where

$$E = -\frac{1}{2n^2}$$

The evaluation of the inverse powers of r is again an exercise in using the radial wave functions. It is easy to derive the following for the maximum $l = n - 1$. The general results are:

$$< \frac{1}{r} >_{nl} = \frac{1}{n^2},$$

and

$$< \frac{1}{r^2} >_{nl} = \frac{1}{n^3(l+\frac{1}{2})}$$

Putting it all together, we have for the kinetic energy term in fine structure,

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

The total fine structure energy is

$$\Delta E_{fs} = \Delta E_{LS} + \Delta E_K$$

The final result turns out to depend only on j, and is

$$\Delta E_{fs} = \frac{\alpha^2}{4}[\frac{3}{2n^4} - \frac{2}{n^3(j+\frac{1}{2})}]$$