"Fine Structure" of Hydrogen like atoms.

Lets first recall the spectrum of the Hamiltonian $H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$ which corresponds to non-relativistic hydrogen atom. The eigenstates are labelled as $|n\, l\, m_l\rangle \otimes |m_s\rangle$ where 'n' is the principle quantum number, $l = 0, 1, \ldots n-1$ is the orbital angular momentum, 'm_l' is the z-component of the orbital angular momentum ($m_l = -l, -l+1, \ldots, +l$) and $m_s = \pm\frac{1}{2}$ is the z-component of the intrinsic spin.

The eigenenergy of state $|n l m_l\rangle|m_s\rangle$ depends <u>only</u> on 'n' and is given by $E^0_{nlm m_s} = -\dfrac{mc^2\alpha^2}{2n^2}$ where

$\alpha = \left[\dfrac{e^2}{\hbar c}\right] \simeq \dfrac{1}{137}$ is the fine-structure constant, and $mc^2 \simeq 0.5$ MeV is the rest mass energy of the electron.

Therefore, the energy levels are hugely degenerate. For example, when $n=2$, there are six levels corresponding to $|n=2\ l=1\ m_l\rangle \otimes |m_s\rangle$ and two levels corresponding to $|n=2\ l=0\ m_l=0\rangle \otimes |m_s\rangle$, yielding a degeneracy of eight.

Since $\alpha \approx \frac{1}{137}$ is a small number, one can imagine perturbations to H_0 that are proportional to various subleading powers of α, compared to H_0. It turns out that at the leading order, relativistic corrections are of order α^4. A satisfactory treatment requires studying quantum electrodynamics (QED) / Dirac equation. Here we will only pursue a heuristic treatment.

There are two separate corrections of $O(\alpha^4)$, one due to relativistic dispersion, and other due to spin-orbit coupling.

(a) α^4 correction due to relativistic dispersion:

The relativistic Hamiltonian, ignoring spin, is $H = \sqrt{p^2c^4 + m^2c^4} - mc^2 - \frac{e^2}{r}$

$$\simeq \underbrace{\frac{p^2}{2m} - \frac{e^2}{r}}_{H_0} \underbrace{- \frac{p^4}{8m^3c^2}}_{\Delta H_1} .$$

Therefore, the correction to the energy of a level $|n\, l\, m_l\rangle \otimes |m_s\rangle$ is given by

$$\delta E^{(1)}_{n l m_l m_s} = - \langle n\, l\, m_l\, m_s | \frac{p^4}{8m^3c^2} | n\, l\, m_l\, m_s\rangle$$

To evaluate this expectation value, one may rewrite it as

$$\delta E^{(1)}_{n l m_l m_s} = \frac{-1}{2mc^2} \left\langle \left(\frac{p^2}{2m}\right)^2 \right\rangle$$

where $\langle \quad \rangle$ denotes expectation value w.r.t. $|n l m_l m_s\rangle$

$$= \frac{-1}{2mc^2} \left\langle \left(\frac{e^2}{r} + H_0\right)^2 \right\rangle$$

$$= \frac{-1}{2mc^2} \left\langle H_0^2 + H_0 \frac{e^2}{r} + \frac{e^2}{r} H_0 + \frac{e^4}{r^2} \right\rangle$$

$$= \frac{-1}{2mc^2} \left[(E_n^0)^2 + 2E_n^0 \left\langle \frac{e^2}{r} \right\rangle + e^4 \left\langle \frac{1}{r^2} \right\rangle \right]$$

One may use virial theorem to show $\left\langle \frac{e^2}{r} \right\rangle = -2E_n^0$.

finally $\left\langle \frac{e^4}{r^2} \right\rangle = \frac{4n (E^0_n)^2}{l + \frac{1}{2}}$

[see Gottfried (Shankar for details].

Combining everything,

$$\delta E_{nlmm_s} = -\frac{1}{2mc^2} \left[-3 (E^0_n)^2 + \frac{4n (E^0_n)^2}{l + \frac{1}{2}} \right]$$

Using $E^0_n = -\frac{\alpha^2 mc^2}{2n^2}$

$$\Rightarrow \delta E^{(1)}_{nlm_lm_s} = -\frac{mc^2}{2} \alpha^4 \left[-\frac{3}{4n^4} + \frac{1}{n^3 (l + \frac{1}{2})} \right]$$

(b) α^4 correction due to spin-orbit coupling:

Classically, the electron experiences a magnetic field due to relative motion w.r.t. the proton:

$$\vec{B} = -\frac{e}{c}\frac{\vec{v}\times\vec{r}}{r^3}$$

Since electron carries an intrinsic magnetic moment $\vec{\mu}$ ($\propto \vec{S}$ where $\vec{S}$ is the intrinsic spin), the coupling between $\vec{B}$ and $\vec{\mu}$ leads to a correction to H_0 of the form:

$$\Delta H_2 = -\vec{\mu}\cdot\vec{B}$$

$$= \frac{e\,\vec{\mu}\cdot(\vec{p}\times\vec{r})}{mcr^3}$$

$$= \frac{-e \vec{\mu} \cdot \vec{L}}{m c r^3}$$

where $\vec{L} = \vec{r} \times \vec{p}$ is the orbital angular momentum. Classically, the proportionality constant between $\vec{\mu}$ and $\vec{S}$ is given as $\vec{\mu} = \frac{-e}{mc} \vec{S}$ (see, e.g. Griffiths Electrodynamics Chapter 5). However, quantum mechanically there is an additional factor of $1/2$ which can be derived using Dirac equation. Putting everything together,

$$\Delta H_2 = \frac{e^2}{2m^2 c^2 r^3} \vec{S} \cdot \vec{L}$$

Within degenerate level perturbation theory, $H_{eff} = H_0 + \frac{e^2}{2m^2c^2r^3} \vec{S}\cdot\vec{L}$
+ higher order terms

and therefore, one needs to diagonalize the perturbation $\vec{S}\cdot\vec{L}$. Since

$$\vec{S}\cdot\vec{L} = \frac{1}{2}\left[(\vec{S}+\vec{L})^2 - S^2 - \vec{L}^2\right],$$

the eigenstates of $\vec{S}\cdot\vec{L}$ are labelled by $\vec{J}^2 = (\vec{S}+\vec{L})^2$, $\vec{L}^2 = l(l+1)$ and $J_z = L_z + S_z$.

Using angular momentum addition rules, there are only two possibilities: $\vec{J}^2 = j(j+1)$ with

$$j = l + \frac{1}{2} \quad \text{or} \quad j = l - \frac{1}{2}$$

when $j = l + \frac{1}{2}$,

$$H_{eff} = H_0 + \frac{e^2}{2m^2c^3r^3}\left[\left(l+\frac{1}{2}\right)\left(l+\frac{3}{2}\right) - l(l+1) - \frac{3}{4}\right]$$

$$= H_0 + \frac{e^2}{2m^2c^3}\frac{l}{r^3}$$

when $j = l - \frac{1}{2}$,

$$H_{eff} = H_0 + \frac{e^2}{2m^2c^3r^3}\left[\left(l-\frac{1}{2}\right)\left(l+\frac{1}{2}\right) - l(l+1) - \frac{3}{4}\right]$$

$$= H_0 + \frac{e^2}{2m^2c^3r^3}\left[-l-1\right]$$

The correction to eisenerergy will be $\delta E^{(2)} = \langle n\, l\, m_l\, m_s | \frac{1}{r^3} | n\, l\, m_l\, m_s \rangle$

$$\times \frac{e^2}{2m^2c^3 r^3} \times \begin{cases} l & \text{when } j = l + \frac{1}{2} \\ -l-1 & \text{when } j = l - \frac{1}{2} \end{cases}$$

One can show,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3\, n^3\, l(l+1)(l+\frac{1}{2})}$$

where a_0 is the Bohr radius.

$\Rightarrow$ The total correction to the eisenerersy at $O(\alpha^4)$ is given by

$\delta E = \delta E^{(1)}$ {due to relativistic kinetic energy}

$+ \delta E^{(2)}$ {due to spin-orbit interaction} when $j = l + \frac{1}{2}$:

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

$$+ \frac{mc^2}{4}\frac{\alpha^4}{n^3(l+\frac{1}{2})(l+1)}$$

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

$$= -\frac{mc^2}{2n^3}\alpha^4\left[-\frac{3}{4n} + \frac{1}{l+1}\right]$$

when $j = l - \frac{1}{2}$:

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

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

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

$$= -\frac{mc^2}{2n^3}\alpha^4\left[-\frac{3}{4n}+\frac{1}{l}\right]$$

Therefore, in both cases $(j = l \pm \frac{1}{2})$,

$$\delta E = -\frac{mc^2}{2n^3}\alpha^4\left[-\frac{3}{4n}+\frac{1}{j+\frac{1}{2}}\right]$$

Although we assumed that $l \neq 0$ (otherwise $\langle L \cdot S \rangle = 0$), the above expression is true even when $l = 0$ (so that $j = s = \frac{1}{2}$).