Outline of algebra for hydrogen fine-structure calculation

The following radial integrals can be proved for the state $|nlm\rangle$

$$\langle r^2 \rangle = \frac{a_0^2 \, n^2}{2} \left(5 \, n^2 + 1 - 3l \, (l+1)\right),$$

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

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0},$$

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

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l \, (l+1/2) \, (l+1) \, n^3 \, a_0^3} \qquad \text{for } l > 0.$$

Relativistic correction to kinetic energy

Relativistic kinetic energy: $KE = \sqrt{(mc^2)^2 + (pc)^2} - mc^2 \approx p^2/2m - p^4/(8m^3c^2)$ so

$$H^{(1)}_{\text{rel.}} = -\frac{p^4}{8m^3c^2} = -\frac{1}{2mc^2}(\hat{H}^{(0)} - V_C(r))^2.$$

So, using $E_n^{(0)} = \frac{1}{2}\alpha^2 mc^2/n^2$, $a_0 = \hbar c/(mc^2\alpha)$ and $V_C(r) = -\hbar c\alpha/r$,

$$
\begin{aligned}
E_{n,l}^{(1)} &= -\frac{1}{2mc^2}\langle nlm|(\hat{H}^{(0)} - V_C(r))^2|nlm\rangle \\
&= -\frac{1}{2mc^2}\langle nlm|(E_n^{(0)} - V_C(r))^2|nlm\rangle \\
&= -\frac{1}{2mc^2}\left((E_n^{(0)})^2 + 2E_n^{(0)}\hbar c\alpha \left\langle \frac{1}{r} \right\rangle + (\hbar c\alpha)^2 \left\langle \frac{1}{r^2} \right\rangle\right) \\
&= -\frac{1}{2mc^2}\left((E_n^{(0)})^2 + 2E_n^{(0)}\hbar c\alpha \frac{1}{n^2 a_0} + (\hbar c\alpha)^2 \frac{1}{(l+1/2) \, n^3 \, a_0^2}\right) \\
&= E_n^{(0)}\alpha^2 \left(\frac{1}{4n^2} - \frac{1}{n^2} + \frac{1}{(l+1/2) \, n}\right) \\
&= -|E_n^{(0)}|\frac{\alpha^2}{n}\left(\frac{1}{(l+1/2)} - \frac{3}{4n}\right).
\end{aligned}
$$

Spin-orbit interaction

$$\hat{H}^{(1)}_{\text{SO}} = \frac{1}{2m^2c^2r}\frac{dV_C}{dr}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{\hbar c\alpha}{4m^2c^2r^3}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$$

So

$$
\begin{aligned}
\langle nljm_j|\hat{H}^{(1)}_{\text{SO}}|nljm_j\rangle &= \frac{\hbar c\alpha}{4m^2c^2}\left\langle \frac{1}{r^3} \right\rangle \hbar^2(j(j+1) - l(l+1) - \tfrac{3}{4}) \\
&= \frac{(\hbar c)^3\alpha}{4(mc^2)^2}\frac{1}{l \, (l+1/2) \, (l+1) \, n^3 \, a_0^3}(j(j+1) - l(l+1) - \tfrac{3}{4}) \\
&= |E_n^{(0)}|\frac{\alpha^2}{2n}\frac{j(j+1) - l(l+1) - \tfrac{3}{4}}{l \, (l+1/2) \, (l+1)}.
\end{aligned}
$$

Now we use $j = l \pm \frac{1}{2}$ and treat the two cases separately, so for instance $j(j+1) - l(l+1) = l + \frac{3}{4}$ or $-l - \frac{1}{4}$ respectively; so
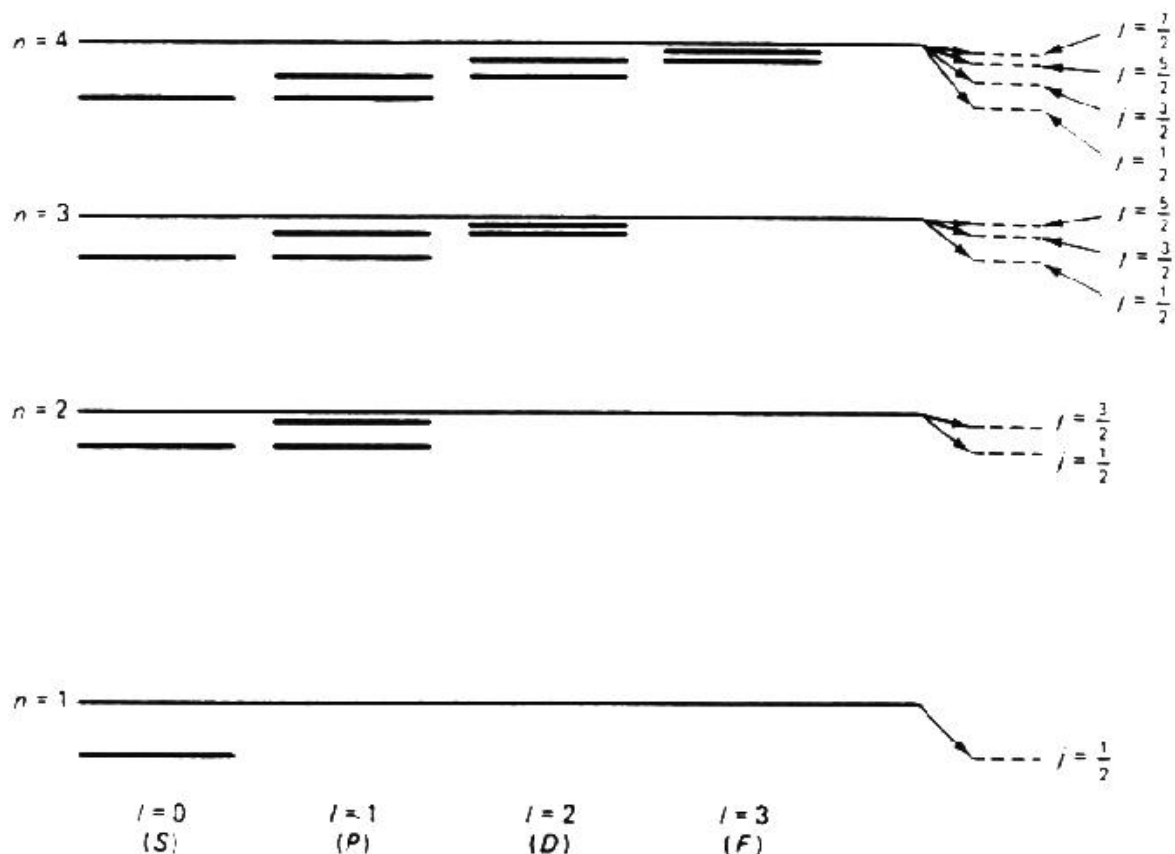
$$\langle nljm_j | \hat{H}_{\text{SO}}^{(1)} | nljm_j \rangle = |E_n^{(0)}| \frac{\alpha^2}{2n(l+1/2)} \times \begin{cases} 1/(l+1) & \text{if } j = l + \frac{1}{2}, \\ -1/l & \text{if } j = l - \frac{1}{2}. \end{cases}$$

$$= |E_n^{(0)}| \frac{\pm \alpha^2}{2n(l+1/2)(j+1/2)} \qquad \text{for } j = l \pm \frac{1}{2}$$

$$= |E_n^{(0)}| \frac{\alpha^2}{n} \left(\frac{1}{l+1/2} - \frac{1}{j+1/2} \right).$$

In the last two lines, we have used $j + \frac{1}{2} = l + 1$ or l, and then $\pm 1 = 2(j - l)$.

Adding the two contributions to the fine structure, we get

$$\langle nljm_j | \hat{H}_{\text{SO+rel}}^{(1)} | nljm_j \rangle = |E_n^{(0)}| \frac{\alpha^2}{n} \left(\frac{3}{4n} - \frac{1}{j+1/2} \right),$$

which is independent of l. Note that $j + \frac{1}{2} \leq n$ and so the fine structure lowers the energy of all states, but within a shell the states of lowest j will lie lowest. The nth shell is split into n discrete levels.

Source: D. Griffiths, Introduction to Quantum Mechanics, 2nd edition, fig 6.5