Outline of algebra for hydrogen fine-structure calculation

The following radial integrals can be proved for the state $|n, l, m_l\rangle$

$$\begin{aligned}
\langle r^2 \rangle &= \frac{a_0^2\, n^2}{2}\left(5\, n^2 + 1 - 3l\,(l+1)\right), \\
\langle r \rangle &= \frac{a_0}{2}\left(3n^2 - l\,(l+1)\right), \\
\left\langle \frac{1}{r} \right\rangle &= \frac{1}{n^2 a_0}, \\
\left\langle \frac{1}{r^2} \right\rangle &= \frac{1}{(l+1/2)\, n^3\, a_0^2}, \\
\left\langle \frac{1}{r^3} \right\rangle &= \frac{1}{l\,(l+1/2)\,(l+1)\, n^3\, a_0^3} \qquad \text{for } l > 0.
\end{aligned}$$

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 $V_C(r) = -\hbar c\alpha/r$,

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

Spin-orbit interaction

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

So

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

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

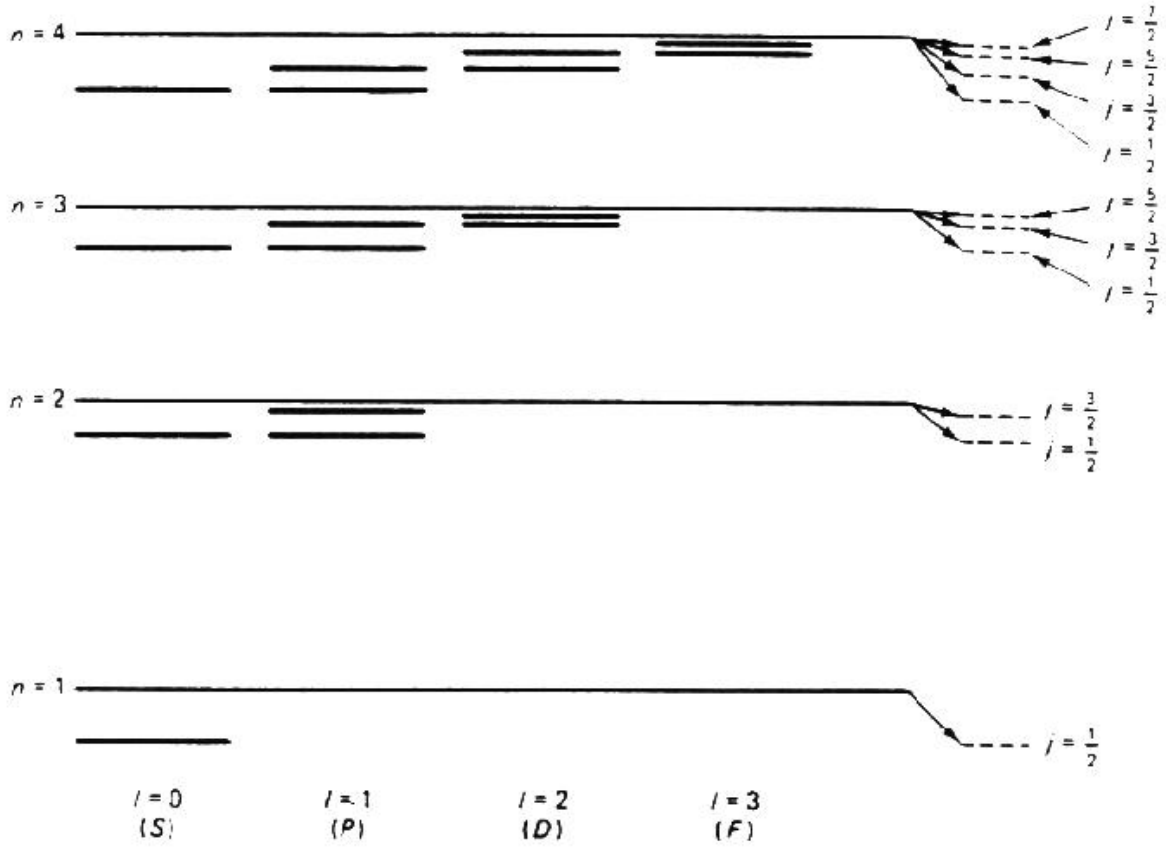
$$\begin{aligned}
\langle n, l; j, m_j | \hat{H}^{(1)}_{\rm SO} | n, l; j, m_j \rangle &= |E^{(0)}_n| \, \frac{\alpha^2}{2n(l+1/2)} \times \begin{cases} 1/(l+1) & \text{if } j = l + \frac{1}{2}, \\ -1/l & \text{if } j = l - \frac{1}{2}. \end{cases} \\
&= |E^{(0)}_n| \, \frac{\pm \alpha^2}{2n(l+1/2)(j+1/2)} \qquad \text{for } j = l \pm \tfrac{1}{2} \\
&= |E^{(0)}_n| \, \frac{\alpha^2}{n} \left(\frac{1}{l+1/2} - \frac{1}{j+1/2} \right).
\end{aligned}$$

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

$$\langle n, l; j, m_j | \hat{H}^{(1)}_{\rm SO+rel} | n, l; j, m_j \rangle = |E^{(0)}_n| \, \frac{\alpha^2}{n} \left(\frac{3}{4n} - \frac{1}{j+1/2} \right),$$

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; the far right of the diagram shows the energy levels without separating them by l.