

Outline of algebra for hydrogen fine-structure calculation

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

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

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

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

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

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

So

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

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

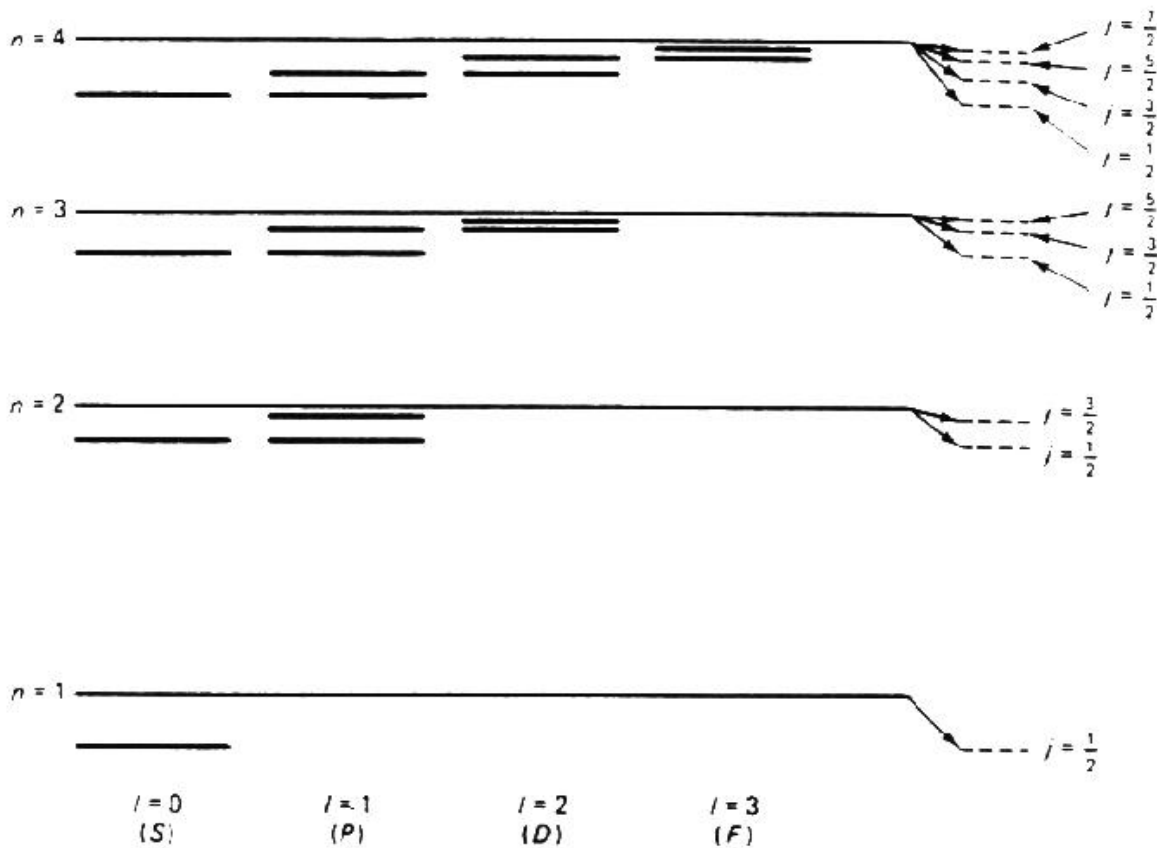
$$\begin{aligned} \langle nlm_j | \widehat{H}_{\text{SO}}^{(1)} | nlm_j \rangle &= |E_n^{(0)}| \frac{\alpha^2}{2n(l+1/2)} \times \begin{cases} 1/(l+1) & \text{if } j = l + \frac{1}{2}, \\ -1/l & \text{if } j = l - \frac{1}{2}. \end{cases} \\ &= |E_n^{(0)}| \frac{\pm \alpha^2}{2n(l+1/2)(j+1/2)} \quad \text{for } j = l \pm \frac{1}{2} \\ &= |E_n^{(0)}| \frac{\alpha^2}{n} \left(\frac{1}{l+1/2} - \frac{1}{j+1/2} \right). \end{aligned}$$

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

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

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 n th shell is split into n discrete levels.



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