FINE STRUCTURE OF HYDROGEN: SPIN-ORBIT EIGENSTATES AND FINAL FORMULA

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.17.

We've got expressions for the relativistic correction and spin-orbit coupling in the hydrogen atom, so we can combine them to get a formula for the fine structure energies in hydrogen. The relativistic correction is

$$E_{n1} = -\frac{E_{n0}^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right) \tag{1}$$

For the spin-orbit coupling we got only as far as the correction to the hamiltonian:

$$H' = \frac{e^2}{8\pi\varepsilon_0 m^2 c^2 r^3}\mathbf{S}\cdot\mathbf{L} \tag{2}$$

We found that this hamiltonian term commutes with J_z, J^2, L^2 and S^2. This means that the 'special' eigenstates that allow us to use non-degenerate perturbation theory to calculate the energy corrections are eigenstates of these operators, but not eigenstates of L_z or S_z. For example, if we choose $\ell = 2$, $s = \frac{1}{2}$, $j = \frac{3}{2}$ and $j_z = -\frac{1}{2}$, the special eigenstate is a linear combination of $|2,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle$ and $|2,-1\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle$ (first bracket is$|\ell,\ell_z\rangle$, second $|s,s_z\rangle$), where the coefficients are found using Clebsch-Gordan tables:

$$|j,j_z\rangle = \left|\frac{3}{2},-\frac{1}{2}\right\rangle = \sqrt{\frac{2}{5}}\,|2,0\rangle\left|\frac{1}{2},-\frac{1}{2}\right\rangle - \sqrt{\frac{3}{5}}\,|2,-1\rangle\left|\frac{1}{2},\frac{1}{2}\right\rangle \tag{3}$$

This state has eigenvalues of $\ell(\ell+1) = 6$ for L^2, $s(s+1) = \frac{3}{4}$ for S^2, $j(j+1) = \frac{15}{4}$ for J^2 and $j_z = -\frac{1}{2}$, but is not an eigenstate of L_z or S_z.

In the derivation of the relativistic correction, we used the eigenstates of L^2 and L_z (that is, the raw eigenstates of hydrogen) to calculate the first-order correction. Since the relativistic correction does not depend on spin, we can just as well use the same eigenstates as in the spin-orbit correction, since

$$\left\langle \frac{3}{2},-\frac{1}{2}\middle| H'_{rel} \middle|\frac{3}{2},-\frac{1}{2}\right\rangle = \frac{2}{5}\left\langle \ell=2,\ell_z=0\middle| H'_{rel} \middle|\ell=2,\ell_z=0\right\rangle + \frac{3}{5}\left\langle \ell=2,\ell_z=-1\middle| H'_{rel} \middle|\ell=2,\ell_z=-1\right\rangle \tag{4}$$

Since the mean of H'_{rel} does not depend on ℓ_z, both brackets on the RHS give the same result, so the first-order correction calculated this way yields the same answer as when we use the raw eigenstates of hydrogen, as we did in the original derivation.

Using such states, we can write $\mathbf{S}\cdot\mathbf{L}$ as

$$\mathbf{S}\cdot\mathbf{L} = \frac{1}{2}\left((\mathbf{S}+\mathbf{L})^2 - S^2 - L^2\right) \tag{5}$$

$$= \frac{1}{2}\left(J^2 - S^2 - L^2\right) \tag{6}$$

and thus its eigenvalues are $\frac{\hbar^2}{2}\left(j(j+1) - s(s+1) - \ell(\ell+1)\right)$. For hydrogen, $s = \frac{1}{2}$ always, so this reduces to

$$\mathbf{S}\cdot\mathbf{L}\left|j,j_z\right\rangle = \frac{\hbar^2}{2}\left(j(j+1) - \frac{3}{4} - \ell(\ell+1)\right)\left|j,j_z\right\rangle \tag{7}$$

The spin-orbit energy correction is then given by

$$\left\langle j,j_z\middle| H' \middle| j,j_z\right\rangle = \frac{\hbar^2 e^2\left(j(j+1) - \frac{3}{4} - \ell(\ell+1)\right)}{16\pi\varepsilon_0 m^2 c^2}\left\langle j,j_z\middle|\frac{1}{r^3}\middle| j,j_z\right\rangle \tag{8}$$

$$= \frac{\hbar^2 e^2\left(j(j+1) - \frac{3}{4} - \ell(\ell+1)\right)}{16\pi\varepsilon_0 m^2 c^2}\left\langle \frac{1}{r^3}\right\rangle \tag{9}$$

Thus the problem reduces to that of finding $\left\langle \frac{1}{r^3}\right\rangle$. We derive the result using Kramers's relation:

$$\left\langle \frac{1}{r^3}\right\rangle = \frac{1}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)n^3a^3} \tag{10}$$

where a is the Bohr radius. The spin-orbit correction is therefore

$$E_{1,so} = \frac{\hbar^2 e^2\left(j(j+1) - \frac{3}{4} - \ell(\ell+1)\right)}{16\pi\varepsilon_0 m^2 c^2 \ell\left(\ell+\frac{1}{2}\right)(\ell+1)n^3a^3} \tag{11}$$

The unperturbed energies and Bohr radius are

$$E_{n0} = -\frac{m}{2\hbar^2 n^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \tag{12}$$

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \tag{13}$$

so we get

$$E_{1,so} = \left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)^3\left(\frac{\hbar^2e^2}{16\pi\varepsilon_0m^2c^2n^3}\right)\frac{j(j+1)-\frac{3}{4}-\ell(\ell+1)}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)} \tag{14}$$

$$= \frac{nE_{n0}^2}{mc^2}\frac{j(j+1)-\frac{3}{4}-\ell(\ell+1)}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)} \tag{15}$$

The relativistic correction is

$$E_{1,rel} = -\frac{E_{n0}^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}}-3\right) \tag{16}$$

so the total correction is the sum of the two:

$$E_{n1} = E_{1,so}+E_{1,rel} \tag{17}$$

$$= \frac{E_{n0}^2}{mc^2}\left[n\frac{j(j+1)-\frac{3}{4}-\ell(\ell+1)}{\ell\left(\ell+\frac{1}{2}\right)(\ell+1)}-\frac{4n}{2l+1}+\frac{3}{2}\right] \tag{18}$$

We can simplify this result by noting that there are two cases: $j = \ell \pm \frac{1}{2}$. We can substitute both values into this expression and do some tedious algebra (or just use Maple to do it for us, as I did) and find that for both cases, we get

$$E_{n1} = \frac{1}{2}\frac{E_{n0}^2}{mc^2}\frac{-8n+6j+3}{2j+1} \tag{19}$$

$$= \frac{E_{n0}^2}{2mc^2}\left(3-\frac{4n}{j+\frac{1}{2}}\right) \tag{20}$$

In terms of the fine structure constant

$$\alpha \equiv \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137.036} \tag{21}$$

$$E_{n0} = -\frac{\alpha^2}{2n^2}mc^2 \tag{22}$$

$$E_{n1} = -E_{n0}\frac{\alpha^2}{4n^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) \tag{23}$$

The final form for the energies of hydrogen is then

$$E_n = E_{n0}\left[1 - \frac{\alpha^2}{4n^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right)\right] \tag{24}$$

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