Fine Structure and the Spin-Orbit Effect In Alkali Atoms

The alkali atoms Li, Na, K, Rb, Cs, and Fr all have a single electron outside one or more closed shells of electrons. These atoms are hydrogen-like.

They differ in that the Coulomb potential is not

$$-\frac{Zq^2}{4\pi\epsilon_0}\frac{1}{r} = -\frac{e^2}{r} \quad \text{or even} \quad -\frac{Ze^2}{r}. \qquad 1$$

It is a more complicated but spherically symmetric potential of the form

$$V_c(r) = e\,\phi(r). \quad (e<0). \qquad 2$$

This potential $V_c(r)$ lacks the hidden symmetry of the H-atom and so the energy levels $E_{n\ell}$ are no longer independent of ℓ. The higher ℓ states lie farther from the positive nucleus and are screened by the inner shells of electrons. So

$$E_{n\ell} > E_{n\ell'} \quad \text{if } \ell > \ell'. \qquad 3$$

The electric field is

$$\vec{E} = -\frac{1}{q} \nabla V_c(r) \quad \text{in SI units.} \qquad 4$$

The whizzing electron sees this E-field as an E-field and also as a B-field

$$B = -\frac{\vec{v}}{c^2} \times \vec{E}. \qquad 5$$

The magnetic moment of the electron is

$$\vec{\mu} = \frac{q\vec{S}}{m_e}. \qquad 6$$

With a factor of 2, explained by Thomas and by Dirac, the energy of this "spin-orbit" interaction is

$$H_{LS} = -\frac{1}{2}\mu \cdot B$$

$$= \frac{\vec{\mu}}{2} \cdot \left(\frac{\vec{v}}{c^2} \times \vec{E} \right)$$

$$= \frac{q\vec{S}}{2m} \cdot \left[\frac{\vec{p}}{mc^2} \times \frac{\vec{r}}{r} \frac{1}{(-q)} \frac{dV_c}{dr} \right]$$

$$= \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV_c}{dr} \vec{L} \cdot \vec{S} \qquad 7$$

Now the angular momentum of the electron is

$$J = L + S \qquad 8$$

so

$$J^2 = L^2 + S^2 + 2L\cdot S.$$

Since

$$L\cdot S = \frac{1}{2}\left(\vec{J}^2 - L^2 - S^2\right) \qquad 9$$

it makes sense to use the states that are e-vecs of J^2, L^2, and S^2 as well as of J_3. So we use the states $|\ell, s; j\, m\rangle$ in the notation of Eqs. (3.7.30). These are the states that diagonalize H_{LS}

$$\langle n\ell s; j m | H_{LS} | n\ell s; j m\rangle$$

$$= \frac{1}{2m^2c^2} \langle n\ell s; j m | \frac{1}{r}\frac{dV_c}{dr} L\cdot S | n\ell s; j m\rangle$$

$$= \frac{1}{2m^2c^2}\frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - \tfrac{1}{2}\left(\tfrac{3}{2}\right)\right] \int_0^\infty R_{n\ell}^2 \frac{1}{r}\frac{dV_c}{dr} r^2 dr. \qquad (10)$$

Here $j = \ell \pm \frac{1}{2}$, so if $j = \ell + \frac{1}{2}$, then

$$j(j+1) - \ell(\ell+1) - \frac{3}{4} = \left(\ell + \frac{1}{2}\right)\left(\ell + \frac{3}{2}\right) - \ell(\ell+1) - \frac{3}{4} = \ell \qquad (11)$$

while if $j = \ell - \frac{1}{2}$, then

$$j(j+1) - \ell(\ell+1) - \frac{3}{4} = (\ell-\tfrac{1}{2})(\ell+\tfrac{1}{2}) - \ell(\ell+1) - \frac{3}{4}$$

$$= \ell^2 - \tfrac{1}{4} - \ell^2 - \ell - \tfrac{3}{4} = -(\ell+1). \qquad (12)$$

So

$$\langle n\ell s; jm | H_{L\cdot S} | n\ell s; jm \rangle = \frac{\hbar^2}{4m^2c^2} \left\langle \frac{1}{r}\frac{dV_c}{dr} \right\rangle \begin{pmatrix} \ell \\ -\ell-1 \end{pmatrix} \begin{array}{l} j=\ell+\frac{1}{2} \\ j=\ell-\frac{1}{2} \end{array} \qquad (13)$$

which is Landé's interval rule.

Now

$$\left\langle \frac{1}{r}\frac{dV_c}{dr} \right\rangle \sim \frac{Zq^2}{4\pi\epsilon_0 a_0^3} = \frac{Ze^2}{a_0^3} > 0 \qquad (14)$$

since

$$V_c \sim -\frac{Zq^2}{4\pi\epsilon_0 r} \qquad (15)$$

and

$$\frac{1}{r}\frac{dV_c}{dr} \sim \frac{Zq^2}{4\pi\epsilon_0 r^2} > 0 \qquad (16)$$

where we use (15) and (16) just to get the sign right. The potential V_c is not a simple Coulomb potential. Since the mean value of $\langle r^{-1} V_c' \rangle$ is positive, as shown by (14), we see that

$$E_{j=\ell+\frac{1}{2}} > E_{j=\ell-\frac{1}{2}}. \qquad (17)$$

The energy splitting (3) due to the screening of the Coulomb potential of the nucleus raises the energies $E_{n\ell}$ of higher-ℓ states by an eV or a fraction of an eV. But the spin-orbit splitting described by the Landé interval rule (13) is smaller by 2 to 3 orders of magnitude.

Sodium has $Z = 11$ electrons. The first 10 electrons populate the 1S, 2S, and 2p levels forming the atomic structure of the rare gas neon. The 11th electron is in the $3S_{1/2}$ state when the Na atom is in its ground state.

The 3p level lies about 2eV above the 3S level due to screening (3). The spin-orbit effect (13) splits the 3p level into the $3p_{3/2}$ level and the $3p_{1/2}$ level. An electron in one of these two states can emit a photon of 5890 Å ($3p_{3/2}$) or 5896 Å ($3p_{1/2}$) when going to the ground $3S_{1/2}$ state. These are the yellow sodium D lines. Their energies are

$$E_{3p_{3/2}} - E_{3S_{1/2}} = h\nu = 2\pi\frac{\hbar c}{\lambda} = 2\pi\,\frac{197.32696\ \mathrm{eV\,nm}}{589\ \mathrm{nm}}$$

$$= 2.10499\ \mathrm{eV} \qquad \text{and} \tag{18}$$

$$E_{3p1/2} - E_{3s1/2} = 2.10285 \text{ eV}. \quad (19)$$

So the splitting of the Na D lines is

$$E_{3p3/2} - E_{3p1/2} = 2.142 \times 10^{-3} \text{ eV}. \quad (20)$$

Roughly half of this splitting is due to the L·S effect.

The other half is due to the relativistic correction obtained from the expansion

$$\sqrt{m^2c^4 + c^2p^2} = mc^2 \sqrt{1 + \frac{p^2}{m^2c^2}}$$

$$\approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots. \quad (21)$$

One drops the constant mc^2, and the kinetic energy $p^2/2m$ goes into H_0. We are left with the relativistic correction

$$V_R = -\frac{p^4}{8m^3c^2}. \quad (22)$$

Let's estimate the L·S effect (13) by using the crude estimate (14)

$$\Delta E_{LS} \sim \left(\frac{\hbar}{2mc}\right)^2 \frac{Ze^2}{a_0^3} (2\ell+1). \quad (23)$$

The Bohr radius a_0 is $a_0 = \hbar^2/me^2$.
So

$$\Delta E_{LS} \sim \left(\frac{\hbar}{2mc}\right)^2 \frac{Ze^2(me^2)^3}{\hbar^6}(2\ell+1) \qquad (24)$$

$$\sim \left(\ell+\tfrac{1}{2}\right)\tfrac{1}{2}mc^2\alpha^2 Z\alpha^2 \qquad (25)$$

where $\alpha = e^2/\hbar c = 1/137.036 = 7.3\times10^{-3}$.
Now $mc^2\alpha^2/2$ is the ground-state energy of atomic hydrogen or 13.6 eV.
So

$$\Delta E_{LS} \sim \left(\ell+\tfrac{1}{2}\right)(13.6\,\text{eV})\,5\times10^{-5} Z$$

$$\sim Z\left(\ell+\tfrac{1}{2}\right)6.8\,10^{-4}. \qquad (26)$$

For $Z=11$ and $\ell=1$, this estimate gives $\Delta E_{LS} \sim 11\times10^{-3}$ eV. Screening must cut Z down to about 4 giving

$$\Delta E_{LS} \sim 4\times10^{-3}\ \text{eV}. \qquad (27)$$

The relativistic correction (22) is negative and cuts this ΔE_{LS} back to about 2 meV consistent with the experimental splitting (24) of the sodium D lines.