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

$$-\frac{ze^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{r} \text{ or even } -\frac{2e^2}{r}. $$

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

$$V_e(r) = e\phi(r), \quad (e < 0).$$

This potential $V_e(r)$ lacks the hidden symmetry of the H-atom and so the energy levels $E_n$ 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

$$E_n > E_{n'} \quad \text{if} \quad l > l'. $$
The electric field is
\[ \vec{E} = -\frac{1}{q_0} \nabla V_e(r) \text{ in SI units}. \]

The whizzing electron sees this $E$-field as an $E$-field and also as a $B$-field
\[ \vec{B} = -\frac{\vec{V}_e^2}{c^2} \times \vec{E}. \]

The magnetic moment of the electron is
\[ \vec{\mu} = \frac{q_0 \vec{S}}{m_e}. \]

With a factor of $\sqrt{2}$, explained by Thomas and by Dirac, the energy of this "spin-orbit" interaction is
\[ H_{\mu S} = -\frac{1}{2} \mu \cdot \vec{B} \]
\[ = \frac{\hbar^2}{2m} \left[ \frac{1}{m c^2} \times \frac{\vec{r}}{r} \frac{1}{n} \frac{dV_e}{dn} \right] \]
\[ = \frac{1}{2m^2 c^2} \frac{1}{n} \frac{dV_e}{dn} \vec{\mu} \cdot \vec{S}. \]
Now the angular momentum of the electron is

\[ J = L + S \]

so

\[ J^2 = L^2 + S^2 + 2L \cdot S. \]

Since

\[ L \cdot S = \frac{1}{2} \left( J^2 - L^2 - S^2 \right) \]

it makes sense to use the states that are eigenstates of \( J^2, L^2, \) and \( S^2 \) as well as of \( J_3. \) So we use the states \( \{ n, s, j, m \} \) in the notation of Eqs. (3.7.30). These are the states that diagonalize \( H_{LS} \)

\[ \langle ms; j, m | H_{LS} | n s; j, m \rangle \]

\[ = \frac{1}{2m^2c^2} \langle ms; j, m | \frac{1}{r} \frac{dV}{dr} L \cdot S | n s; j, m \rangle \]

\[ = \frac{1}{2m^2c^2} \frac{k^2}{2} \left[ j(j+1) - l(l+1) - \frac{1}{2} \left( \frac{3}{2} \right) \right] \int \rho^2_n \frac{1}{r} \frac{dV}{dr} r^2 dr. \]

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

\[ j(j+1) - l(l+1) - \frac{3}{4} = (\ell + \frac{1}{2}) \left( \ell + \frac{3}{2} \right) - \ell (\ell + 1) - \frac{3}{4} = \ell - \frac{1}{2}. \]
while \( j = \ell - \frac{1}{2} \), then
\[
j(l+1) - l(l+1) - \frac{3}{4} = (\ell - \frac{1}{2})(\ell + \frac{1}{2}) - l(l+1) - \frac{3}{4} = \ell^2 - \frac{1}{4} - \ell^2 - \ell - \frac{3}{4} = -l - 1.
\]
So
\[
\langle n\ell \delta; j = \ell + \frac{1}{2} | \hat{H}_{LS} | n\ell \delta; j = \ell - \frac{1}{2} \rangle = \frac{\hbar^2}{4m^2c^2} \left[ \frac{1}{\ell} \frac{dV_c}{d\ell} \right]_{\ell = \ell} = \frac{\hbar^2}{4m^2c^2} \left[ \frac{1}{\ell} \frac{dV_c}{d\ell} \right]_{\ell = \ell} \tag{13}
\]
which is Landé's interval rule.

Now
\[
\left[ \frac{1}{\ell} \frac{dV_c}{d\ell} \right] \sim \frac{Z q^2}{4 \pi \varepsilon_0 a_0^3} = \frac{Z e^2}{a_0^3} > 0 \tag{14}
\]
since
\[
V_C \sim -\frac{Z q^2}{4 \pi \varepsilon_0 r} \tag{15}
\]
and
\[
\left[ \frac{1}{\ell} \frac{dV_c}{d\ell} \right] \sim \frac{Z e^2}{4 \pi \varepsilon_0 r^2} > 0 \tag{16}
\]
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 \( \langle r^- V_c \rangle \) is positive, as shown by (14), we see that
\[
E_j = \ell + \frac{1}{2} > E_j = \ell - \frac{1}{2} \tag{17}
\]
The energy splitting (3) due to the screening of the Coulomb potential of the nucleus raises the energies \( E_{nl} \) 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 \( 1s^2 2s^2 2p^6 \), 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 2 eV 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

\[
E_{3p^{3/2}} - E_{3s^{1/2}} = h\nu = 2\pi Fc \frac{2}{\lambda} = 2 \frac{197.32696}{589} \text{ eV} \text{nm} = 2.10499 \text{ eV}
\]

and

(18)
\[ E_{3p^{1/2}} - E_{3s^{1/2}} = 2.10285 \text{ eV}. \]  \hspace{1cm} \text{(19)}

So the splitting of the \( M_0 \) D lines is:

\[ E_{3p^{3/2}} - E_{3p^{1/2}} = 2.142 \times 10^{-3} \text{ eV}. \]  \hspace{1cm} \text{(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:

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

\[ \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \cdots. \hspace{1cm} \text{(21)} \]

One drops the constant \( mc^2 \), and the kinetic energy \( p^2/2m \) goes into \( M_0 \). We are left with the relativistic correction:

\[ V_K = -\frac{p^4}{8m^3c^2}. \]  \hspace{1cm} \text{(22)}

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

\[ \Delta E_L \approx \left( \frac{\hbar}{2mc} \right)^2 \frac{Ze^2}{a_0^3} (2I+1). \]  \hspace{1cm} \text{(23)}
The Bohr radius \( a_0 \) is \( a_0 = \frac{\hbar^2}{mc^2} \).

So,

\[ \Delta E_{ls} \sim \left( \frac{\hbar}{2mc} \right)^2 \frac{Z e^2 (me^2)^3}{\hbar^6} (2l+1) \]

where \( x = \frac{e^2}{\hbar c} = 1/137,036 = 7.3 \times 10^{-3} \).

Now \( mc^2 a_0^2/2 \) is the ground-state energy of atomic hydrogen or 13.6 eV.

So,

\[ \Delta E_{ls} \sim (l+\frac{1}{2})(13.6 \text{ eV}) 5 \times 10^{-5} \]

\[ \sim 2(l+\frac{1}{2}) \cdot 6.8 \times 10^{-4} \]  

For \( Z = 11 \) and \( l = 1 \), this estimate gives

\[ \Delta E_{ls} \sim 11 \times 10^{-3} \text{ eV}, \]  
which must cut \( Z \) down to about 4 giving

\[ \Delta E_{ls} \sim 4 \times 10^{-3} \text{ eV}. \]  

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