

## Fine Structure and the Spin-Orbit Effect

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

$$-\frac{e^2}{r} \text{ or even } -\frac{Ze^2}{r}$$

but a more complicated but spherically symmetric

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

This potential  $V_c(r)$  lacks the hidden symmetry of the H-atom and so the energy levels  $E_{nl}$  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

$$E_{nl} > E_{n'l'} \quad \text{if } l > l'.$$

The electric field is

$$\vec{E} = -\frac{1}{e} \nabla V_c(r).$$

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

$$B = -\frac{\vec{v}}{c} \times \vec{E}.$$

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The magnetic moment of the electron is

$$\vec{\mu} = \frac{e \vec{S}}{mc}.$$

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

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

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

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

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

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Now the angular momentum of the electron is

$$\vec{J} = \vec{L} + \vec{S}$$

so

$$J^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

Since

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

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  $|l, s; j, m\rangle$  in the notation of Eqs. (3.7.30). These are the states that diagonalize  $H_{LS}$

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

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

$$= \frac{1}{2m^2c^2} \frac{\hbar^2}{2} \left[ j(j+1) - l(l+1) - \frac{1}{2} \left( \frac{3}{2} \right) \right] \int_0^\infty R_{nl}^2 \frac{1}{r} \frac{dV_c}{dr} r^2 dr \quad (10)$$

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

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

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

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

$$= l^2 - \frac{1}{4} - l^2 - l - \frac{3}{4} = -(l+1) \quad (12)$$

So

$$\langle n, l, s, j, m | H_{L.S.} | n, l, s, j, m \rangle = \frac{\hbar^2}{4m^2c^2} \left\langle \frac{1}{r} \frac{dV_c}{dr} \right\rangle \begin{pmatrix} l \\ -l-1 \end{pmatrix} \begin{matrix} j = l + \frac{1}{2} \\ j = l - \frac{1}{2} \end{matrix}$$

which is Landé's interval rule. Since

$$\left\langle \frac{1}{r} \frac{dV_c}{dr} \right\rangle \sim \frac{ze^2}{a_0^3} \quad (13)$$

the  $j = l + \frac{1}{2}$  states are higher than the  $j = l - \frac{1}{2}$  ones. This L.S. splitting is smaller than the extent that  $V_c$  pushes  $n, p$  states above  $n, s$  states. The  $3p_{3/2}$  state of sodium lies above the  $3s_{1/2}$  state by an amount such that the emitted photon has  $\lambda = 5890 \text{ \AA}$ , while the  $3p_{1/2}$  state's photon is slightly longer at  $\lambda = 5896 \text{ \AA}$ . So

$$E_{3p_{3/2}, 3s_{1/2}} = h\nu = \frac{hc}{\lambda} = \frac{\hbar c 2\pi}{\lambda} = \frac{197.326968 \text{ MeV fm } 2\pi}{5890 \cdot 10^5 \text{ fm}} \quad (14)$$

So

$$E_{3p^{3/2}, 3s^{1/2}} = \frac{197326.968 \text{ eV} \cdot 2\pi}{5890} = \frac{12398.41906 \text{ eV}}{5890}$$

$$= 2.104994747 \text{ eV} \quad (15)$$

while

$$E_{3p^{1/2}, 3s^{1/2}} = 2.102852622 \text{ eV} \quad (16)$$

So the L-S splitting (and the relativistic correction  $-\vec{p}^4/8m^3c^2$ ) is

$$E_{3p^{3/2}, 3s^{1/2}} - E_{3p^{1/2}, 3s^{1/2}} = 2.142 \times 10^{-3} \text{ eV} \quad (17)$$

In general the order of magnitude of the L-S splittings is

$$\Delta E \sim \frac{e^2}{a_0^3} \left( \frac{\hbar}{2mc} \right)^2 (2l+1) \frac{1}{(2l+1)} \quad (18)$$

or since  $a_0 = \frac{\hbar}{me^2}$

$$\Delta E \sim \frac{e^2}{\hbar^3} \frac{m^3 e^6 \hbar^2}{4m^2 c^2} (2l+1) \sim \frac{1}{4} \frac{e^8 m}{\hbar^4 c^2} (2l+1)$$

$$\sim \frac{1}{4} mc^2 \left( \frac{e^2}{\hbar c} \right)^4 (2l+1) = \frac{1}{2} (2l+1) \alpha^2 \left( \frac{mc^2}{2} \alpha^2 \right) \quad (19)$$

$$\text{Now } \frac{mc^2}{2} \alpha^2 = E_I = 13.6 \text{ eV} \quad (20)$$

the ground-state energy of hydrogen.

Estimates (19) & (20) give

$$\Delta E \sim 10^{-3} \text{ eV} \quad (21)$$

which is half the experimental value (17), which includes the relativistic correction  $-p^4/8m^3c^2$ .

This last correction arises from

$$\begin{aligned} \sqrt{m^2c^4 + c^2p^2} &= mc^2 \sqrt{1 + \frac{p^2}{m^2c^2}} \\ &\approx mc^2 \left( 1 + \frac{p^2}{2m^2c^2} - \frac{1}{8} \left( \frac{p^2}{m^2c^2} \right)^2 \right) \\ &\approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \end{aligned}$$

So here

$$\Delta H_{\text{rel}} \approx -\frac{p^4}{8m^3c^2}$$

which gives splitting about as big as L.S. does.