Alkali metal atoms

Screening plays a crucial role in determining the level structure of the alkalis, allowing for convenient optical excitation transitions.

The full Hamiltonian for the many-electron atom looks like

$$H = \sum_{i} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right] + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

Like for He, we'll ignore correlation and look for an approximation.

$$H_{\text{CF}} = \sum_{i} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 \right] + V_{\text{CF}}(r_i)$$

Where we may use an effective central field

$$E_{\text{CF}} = \frac{Ze_{\text{eff}}(r) e}{4\pi\varepsilon_0 r^2}$$

with

$$V_{\text{CF}}(r) = e \int_{0}^{r} E_{\text{CF}}(r') dr'$$
The effect of screening modifies the "bare" nuclear potential.

General procedure for actually solving

(a) Guess $V_{CF}$
(b) Calculate $\Psi$ for given $V_{CF}$
(c) Calculate new $V_{CF}$
(d) repeat
Spin-orbit coupling/splitting in the alkalis

Recall from lecture #2 that we found a scaling of the energy shift due to spin-orbit coupling of

\[ \Delta E_{ls} = \frac{1}{2m^2} \frac{Ze^2}{4\pi\epsilon_0} \left< \frac{1}{r} \frac{\partial V}{\partial r} \right> \left[ j(j+1) - l(l+1) - s(s+1) \right] \]

This is the energy shift for any combination of \((j, l, s)\).

In the alkalis, as in hydrogen, we will have a lone, unpaired outer electron, such that \(s = \frac{1}{2}\) and only the \(j\)-values of \( j = l + \frac{1}{2} \) and \( j = l - \frac{1}{2} \) will be available.

We are interested in the energy splitting between the two lowest-energy excited states, relating to the \(D_2\) and \(D_1\) excitations of the alkalis.

![Energy level diagram]

The fine structure splitting is dominated by spin-orbit contributions in the alkalis.
generally, for the alkalis

\[ \Delta E_{Fs} \propto \left( \frac{1}{r^{3/2}} \right) \left( \frac{1}{r^{1/2}} \right) \left( l + \frac{1}{2} \right) \]

\( \Rightarrow \) comes from plugging in \( j = l+\frac{1}{2} \) and \( j = l-\frac{1}{2} \) into earlier expression

\[ \left( \frac{1}{r^{3/2}} \right) \left( \frac{1}{r^{1/2}} \right) \]

\( j \)-dependence ignored; only

really true for the lighter

alkalis, where \( \Delta E_{Fs} \ll E_{g}\text{max} \)

and the wave functions are

essentially independent of \( j \)

In the case of hydrogen, where \( V = \frac{1}{r} \), \( \langle \frac{1}{r^{3/2}} \rangle \propto \frac{1}{r^{3/2}} \)

and we found that \( \langle \frac{1}{r^{3/2}} \rangle = \frac{Z^3}{a_0^2 \hbar^3 \ell (l+\frac{1}{2})(l+1)} \), such that

\[ \Delta E_{Fs} \propto \frac{Z^4}{\hbar^3 \ell (l+1)} \] (true for hydrogen)

In the alkalis, screening distorts the potential such that it is

not of the form \( V = \frac{1}{r} \), \( \ldots \)

One way to account for this, as in the central-field approximation,

is to consider a varying Zeff (r). We won't derive it but

this central-field approximation produces the "Lande formula"

\[ Z_i \approx Z \] is the "inner" effective Z-value

\( Z_0 = 1 \) is the "outer" effective Z-value

\[ \Delta E_{Fs} = \frac{Z_0^2 Z^2}{(\hbar^3 \ell (l+1)^2) (\hbar^3 \ell (l+1))} \alpha^2 \hbar c R_{\infty} \]

Scales like \( Z^2 \), much bigger for Cs than Li, e.g.

\( \Rightarrow \) see slide for comparison between measured splittings and this form.