

Alkali metal atoms

Lecture #4
PHYS 598 AC
Fall 2018

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

$$H = \sum_i \left[\frac{-\hbar^2 \nabla_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right] + \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

like for ~~He~~ He, we'll ignore correlations and look for an approx solution to

$$H_{CF} = \sum_i \frac{-\hbar^2 \nabla_i^2}{2m} + V_{CF}(r_i)$$

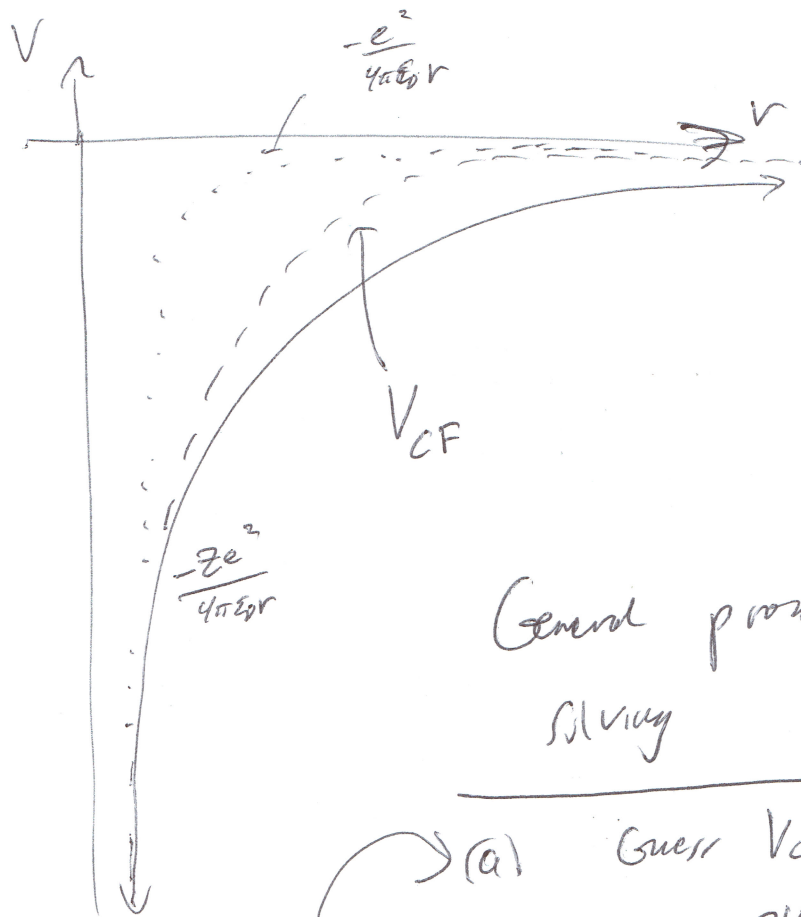
where we imagine an effective, central field

$$\vec{E}_{CF} = \frac{Z_{eff}(r)e}{4\pi\epsilon_0 r^2} \hat{r}$$

$$\text{and } V_{CF}(r) = e \int_{\infty}^r E_{CF}(r') dr'$$



~~The end!~~ The effect of screening modifies the "bare" nuclear potential.



General procedure for actually solving

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- (a) Guess V_{CF}
 - (b) calculate ψ for given V_{CF}
 - (c) calculate new V_{CF}
 - (d) repeat

Spin-orbit coupling/splitting in the alkalis

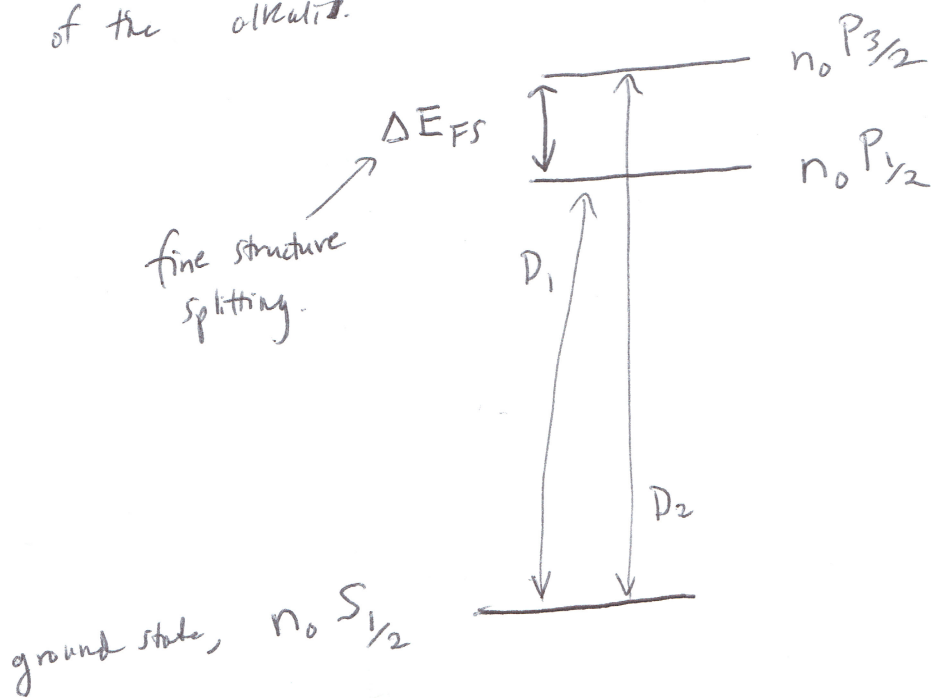
recall from lecture #2, that we found a scaling of the energy shift due to spin-orbit coupling of

$$\Delta E_{LS} = \frac{1}{2mc^2} \frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \frac{\partial V}{\partial r} \right\rangle [j(j+1) - l(l+1) - s(s+1)]$$

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.



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

generally, for the alkalis

$$\Delta E_{FS} \propto \left\langle \frac{1}{r} \frac{\partial V}{\partial r} \right\rangle_{nl} \quad (l + \frac{1}{2})$$

\swarrow
 j -dependence ignored; only really true for the lighter alkalis, where $\Delta E_{FS} \ll E_{gross}$ and the wave functions are essentially independent of j

\searrow comes from plugging in $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ into earlier expression

In the case of hydrogen, where $V \propto \frac{1}{r}$, $\left\langle \frac{1}{r} \frac{\partial V}{\partial r} \right\rangle \propto \left\langle \frac{1}{r^3} \right\rangle$

and we found that $\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0 n^3 l(l + \frac{1}{2})(l + 1)}$, such that

$$\Delta E_{FS} \propto \frac{Z^4}{n^3 l(l + 1)} \quad (\text{true for hydrogen})$$

In the alkalis, screening distorts the potential such that it is not of the form $V \propto \frac{1}{r}$.

One way to account for this, as in the central-field approximation, is to consider a varying $Z_{eff}(r)$. We won't derive it, but this central field approximation produces the "Lande formula"

$$\Delta E_{FS} = \frac{Z_i^2 Z_o^2}{(n^*)^3 l(l + 1)} \alpha^2 h c R_\infty$$

$Z_i \approx Z$ is the "inner" effective Z -value

$Z_o \approx 1$ is the "outer" effective Z -value

scales like Z^2 , much bigger for Cs than Li, e.g.

\rightarrow see slides for comparison between measured splittings and this form.