PHYS514

Alkali atoms

Note Title 12/29/2004

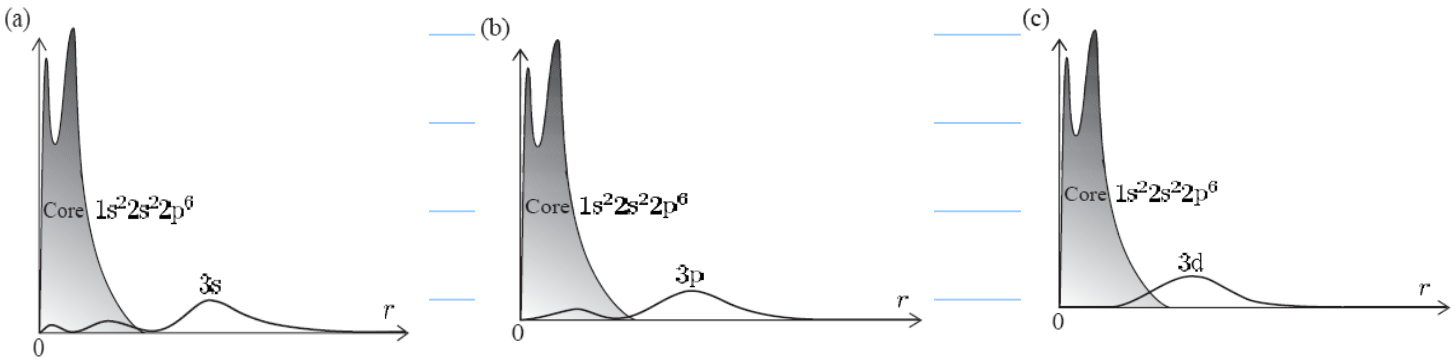
If we try to apply Hydrogen and fine structure theory to alkali atoms, we can't even get close! Why?

Screening!

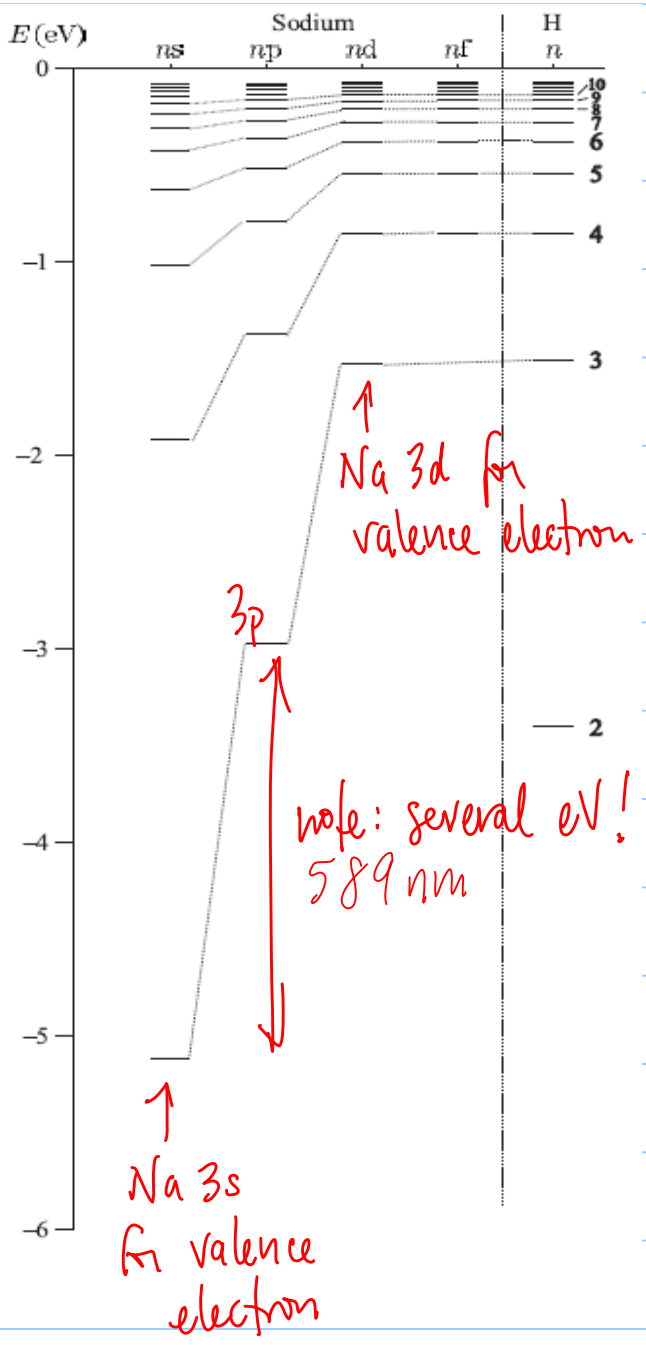
For a many-electron atom, the nuclear charge is shielded by the inner-most electrons

So, the outer-most, active electrons no longer see a $1/r$ potential, and the energy is dependent on n and ℓ

Foot has a nice cartoon of this for Na:



Much of the 3s wavefunction penetrates the core, experiencing a stronger force from the nucleus. By $l > 2$, the valence electron sees a fully screened nucleus:



Energy can be calculated using a semi-empirical formula:

$$E_{nl} = -hc\frac{R_\infty}{(n-\delta_l)^2} = \frac{-13.6\,eV}{n^{*2}}$$

δ_l (or μ_l in many references) is the "quantum defect"

* quantum defect made sanguine idea - appears in many contexts

note! determining the ionization energy determines n^*:

$$n^* = \sqrt{\frac{13.6\,eV}{IE}}$$

Element	Z	IE (eV)
He	2	24.6
Li	3	5.4
Ne	10	21.6
Na	11	5.1
Ar	18	15.8
K	19	4.3
Kr	36	14.0
Rb	37	4.2
Xe	54	12.1
Cs	55	3.9

more accurate numbers follow

Element	Configuration	n^*	δ_s
Li	2s	1.59	0.41
Na	3s	1.63	1.37
K	4s	1.77	2.23
Rb	5s	1.81	3.19
Cs	6s	1.87	4.13

*note - I.E. roughly the same for all alkalis, so n^* also about the same, but the quantum defect very different

Theorists work on calculating these defects using many-electron theory, but real results are from experiments:

Table 9.2 Parameters of the energy levels of the alkalis.

(a) *quantum defects* ~~$\alpha(l)$~~ δ_ℓ ← more time spent near the nucleus

Atom	$l =$	0	1	2	3
Li		0.40	0.04	0.00	0.00
Na		1.35	0.85	0.01	0.00
K		2.19	1.71	0.25	0.00
Rb		3.13	2.66	1.34	0.01
Cs		4.06	3.59	2.46	0.02

(b) Effective principal quantum numbers n^* for the (n_0s) and (n_0p) levels

Level	Li ($n_0 = 2$)	Na ($n_0 = 3$)	K ($n_0 = 4$)	Rb ($n_0 = 5$)	Cs ($n_0 = 6$)
$(n_0s)^2S_{1/2}$	1.588	1.626	1.771	1.805	1.869
$(n_0p)^2P_{1/2}$	1.966	2.116	2.232	2.280	2.392
$(n_0p)^2P_{3/2}$	1.966	2.117	2.235	2.293	2.362

hint of something important ...

(c) Ionisation potentials of the alkalis

	Li	Na	K	Rb	Cs
I_P (eV)	5.39	5.14	4.34	4.18	3.89

Why do things work out so simply?

Because the central field approximation is very good.

This is a method for solving the quantum many body problem of finding the many-electron wavefunction for heavy atoms.

For alkalis, the closed noble atom-like inner shell mostly has a spherical charge distribution.

The actual Hamiltonian is:

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

We say:

$$H \approx \sum_{i=1}^{N} \left[\frac{-\hbar^2}{2m} \nabla_i^2 + V_{CF}(r_i) \right]$$

this is the central field approximation

sum over electrons

each electron interacts with a spherical distribution formed from itself and all the other electrons

This is separable in the electrons, so we write:

$\psi = \psi_1 \psi_2 \psi_3 \cdots$ as the solution of N equations:

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{CF}(r_i)\right)\psi_i = E_i\psi_i$$

To do this right requires a self consistent solution and getting the wavefunction symmetrized properly

What's V_{CF}? It comes from an electric field:

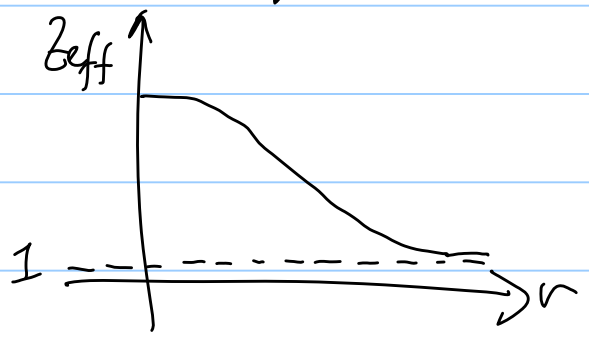
at small r: $\vec{E}(r) = \frac{Ze}{4\pi\varepsilon_0 r^2}\hat{r}$

(an electron sees the whole nucleus)

at large r: $\vec{E} = \frac{e}{4\pi\varepsilon_0 r^2}\hat{r}$

(an electron sees a fully screened nucleus - 1 electron)

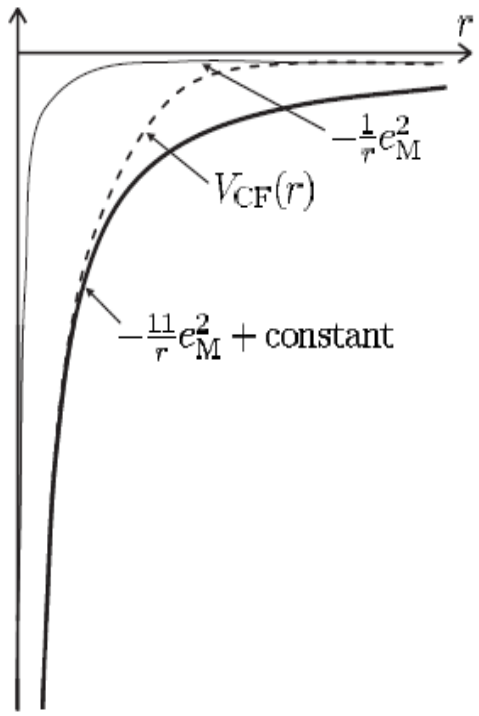
So, we say $\vec{E}_{CF} = \frac{Z_{eff}\, e}{4\pi\varepsilon_0 r^2}\hat{r}$

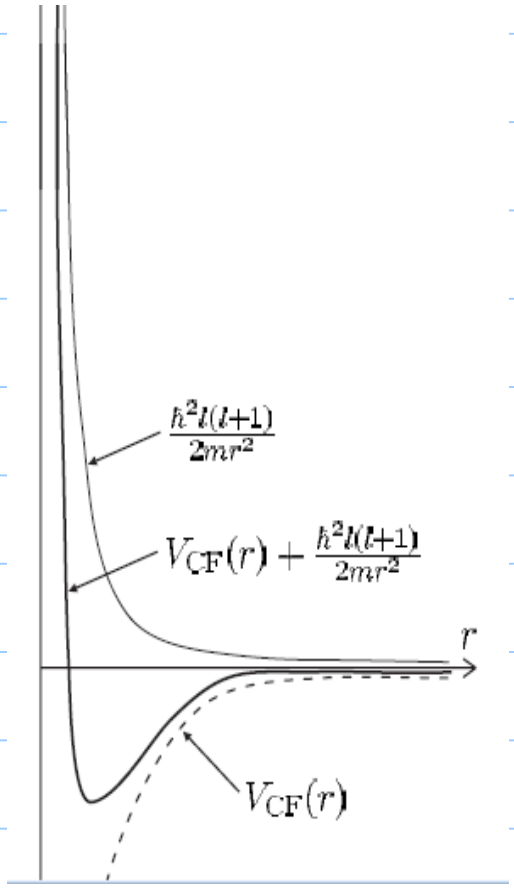


and $V_{CF} = e\int_s^r |\vec{E}_{CF}(r')|\, dr'$

And finding $Z_{eff}(r)$ is part of the optimization problem. You will the the basic idea in your homework!

The centrifugal barrier keeps the high l electrons away from the core and makes them more Hydrogen like.





Why is the central field approximation good?

Let's look at H more carefully —

in atomic units

$$H = \sum_i \left(-\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}$$

write as $H = H_c + H_1$

$$H_c = \sum_i \left[-\tfrac{1}{2}\nabla_i^2 + V_{CF}(r_i) \right]$$

$$H_1 = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i \left(\frac{Z}{r_i} + V_{CF}(r_i) \right)$$

↑ this has all of the non-spherically symmetric stuff in it

Note: $H_1 \ll \sum \frac{1}{r_{ij}}$ because I added and subtracted $\sum V_{CF}(r_i)$

This means that the central field solutions $\psi_i = R^1_{nl}(r_i)\, Y^m_l(\theta_i, \varphi_i)$ are close to correct!

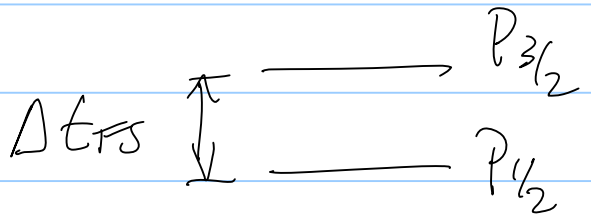
Fine structure in the alkalis

- mostly spin-orbit, recall our equation

$$\Delta E_{LS} = \frac{1}{2mc^2}\frac{Ze^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\frac{\partial V}{\partial r}\right\rangle \left[j(j+1) - l(l+1) - s(s+1)\right]$$

this is the energy shift for any particular state $|\psi_{jl}\rangle$

We would like to know the splitting, for example, between the states $j = l + 1/2$ and $j = l - 1/2$



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

assume this is independent of j — not really true — note that n^* is different for $P_{3/2}$ and $P_{1/2}$ in heavy alkalis which means that spin-orbit interaction modifies the electronic wavefunction

from dealing with j, l, s

In Hydrogen, $\left\langle \frac{1}{r}\frac{\partial V}{\partial r} \right\rangle = \left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_\mu n^3 \ell(\ell+1/2)(\ell+1)}$

So, naively, we'd have $\Delta E_{FS} \propto \frac{Z^4}{n^3 \ell(\ell+1)}$ — but screening strongly effects $\left\langle \frac{1}{r}\frac{\partial V}{\partial r} \right\rangle$

The simplest approach to taking this into account —

$$\left\langle \frac{1}{r}\frac{\partial V}{\partial r} \right\rangle \sim \left\langle \frac{Z_{eff}(r)}{r^3} \right\rangle$$

Using a typical $Z_{eff}(r)$, this ends up producing the "Landé formula"

$$\Delta E_{FS} = \frac{Z_i^2 Z_o^2}{(n^*)^3 \ell(\ell+1)} \alpha^2 hcR \quad \text{, as in Foot}$$

where Z_i is the "inner" Z ($\approx Z$)
and Z_o is the "outer" Z (≈ 1)

Overall scaling is more like Z^2. Unfortunately, this is not useful for much — we have to measure ΔE_{FS} at the precision that is relevant...

Fine structure splittings:

Atom	Li	Na	K	Rb	Cs
n_0	2	3	4	5	6
ΔE	0.337	17.2	57.7	238	554 cm^{-1}
	0.42	21	72	295	687×10^{-4} eV

Sources:

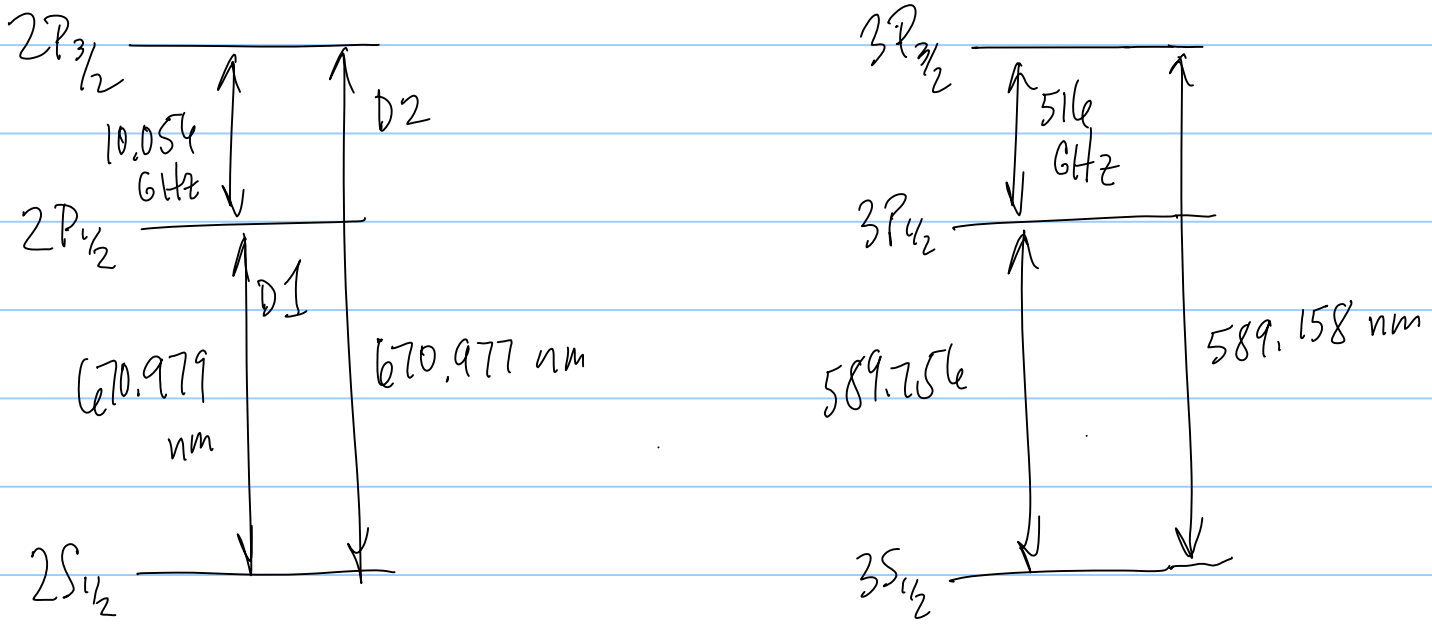
- NIST Atomic spectra database
- journal articles!
- alkalis - Dan Steck - Cs, Na, Rb (see Gehm for Li)

http://physics.nist.gov/cgi-bin/AtData/main_asd
http://steck.us/alkalidata/
http://www.phy.duke.edu/research/photon/qoptics/techdocs/

Alkali atoms

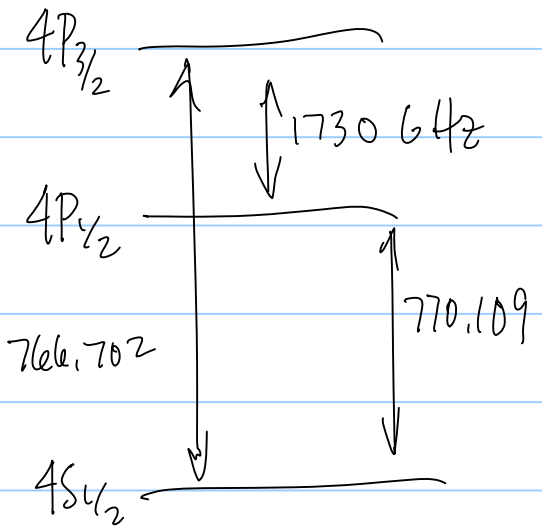
We care about wavelengths to better than 1 MHz — quantum defects not good enough (although handy for estimating quantities like polarizability, etc).

^6Li ^{23}Na

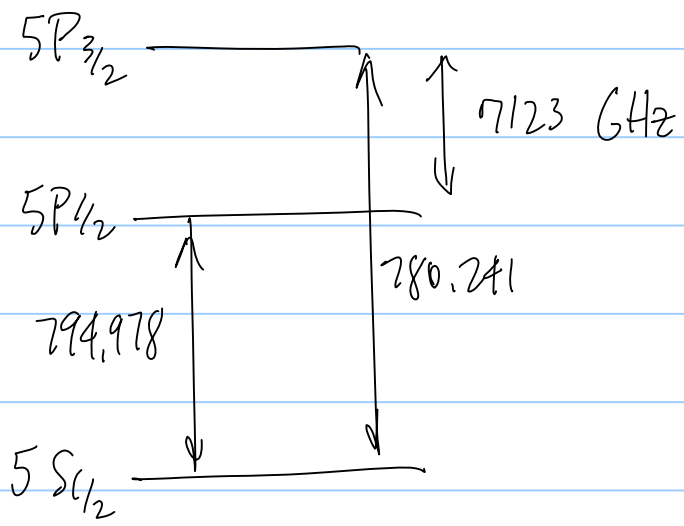


Wavelengths are known at the 100 kHz level, but this is changing because of optical frequency standards and the "femto-comb" — $S_{1/2} \rightarrow D_{5/2}$ transition in Hg^+ now known at 10 Hz level.

^{39}K



^{87}Rb



^{133}Cs