Lecture 4: The alkalis

Readings: Foot Chapter 4

Last time: charge screening and energy structure in helium spin configurations in multi-electron atoms

This time: back to ``single’’-electron atoms w/ the alkalis

- unpaired valence electrons

- due to screening from filled inner sub-shell structure, the relevant low-energy (eV-scale) excitations will all be of the valence electron
The alkalis

<table>
<thead>
<tr>
<th>Period</th>
<th>Element</th>
<th>Atomic Number</th>
<th>Mass Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1</td>
<td>1.00808</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>2</td>
<td>4.003</td>
</tr>
</tbody>
</table>

* Lanthanide series

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Mass Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>57</td>
<td>138.91</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>140.12</td>
</tr>
<tr>
<td>Pr</td>
<td>59</td>
<td>140.91</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
<td>144.24</td>
</tr>
<tr>
<td>Pm</td>
<td>61</td>
<td>145.00</td>
</tr>
<tr>
<td>Sm</td>
<td>62</td>
<td>150.36</td>
</tr>
<tr>
<td>Eu</td>
<td>63</td>
<td>151.96</td>
</tr>
<tr>
<td>Gd</td>
<td>64</td>
<td>157.25</td>
</tr>
<tr>
<td>Tb</td>
<td>65</td>
<td>158.93</td>
</tr>
<tr>
<td>Dy</td>
<td>66</td>
<td>162.50</td>
</tr>
<tr>
<td>Ho</td>
<td>67</td>
<td>164.93</td>
</tr>
<tr>
<td>Er</td>
<td>68</td>
<td>167.26</td>
</tr>
<tr>
<td>Tm</td>
<td>69</td>
<td>168.93</td>
</tr>
<tr>
<td>Yb</td>
<td>70</td>
<td>173.04</td>
</tr>
</tbody>
</table>

* Actinide series

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Mass Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>89</td>
<td>227.03</td>
</tr>
<tr>
<td>Th</td>
<td>90</td>
<td>232.04</td>
</tr>
<tr>
<td>Pa</td>
<td>91</td>
<td>231.04</td>
</tr>
<tr>
<td>U</td>
<td>92</td>
<td>238.03</td>
</tr>
<tr>
<td>Np</td>
<td>93</td>
<td>237.04</td>
</tr>
<tr>
<td>Pu</td>
<td>94</td>
<td>244.01</td>
</tr>
<tr>
<td>Am</td>
<td>95</td>
<td>243.04</td>
</tr>
<tr>
<td>Cm</td>
<td>96</td>
<td>247.08</td>
</tr>
<tr>
<td>Bk</td>
<td>97</td>
<td>251.04</td>
</tr>
<tr>
<td>Cf</td>
<td>98</td>
<td>252.04</td>
</tr>
<tr>
<td>Es</td>
<td>99</td>
<td>253.04</td>
</tr>
<tr>
<td>Fu</td>
<td>100</td>
<td>254.04</td>
</tr>
</tbody>
</table>

The periodic table is shown with the alkali metals highlighted. The elements are arranged in order of increasing atomic number.
The alkalis

~ add one electron to the inert gases (He, Ne, Ar, Kr, ...)

quantum degeneracy
laser-cooling / trapping
Screening in the alkalis

How do the electron’s fill up?

We saw that electron screening played a big role for He

Big jump in screening effects as you move up in $n$ or $l$
(big shift in distance of “next” electron from the nucleus)

$1s^2$

- increased $Z$
- screening
Screening in the alkalis

How do the electron’s fill up?

- increased \( Z \)
- screening

\[ kT \ll eV, \text{ so electrons just fill lowest energy levels} \]

\[ E_{2s} = E_{2p} \text{ for hydrogen (1/r potential, } E_n \text{ ind. of } l) \]

\[ V(r) \neq \beta/r \text{ for alkalis (screening, e-e interactions)} \]
Screening in the alkalis

How do the electron’s fill up?

Considering the effects of shielding, which orbital will be most bound (lowest energy)?

a - 3s
b - 3p
c - 3d

$E_{3s} < E_{3p} < E_{3d}$
Screening in the alkalis

How do the electron’s fill up?

\[ 1s^2 2s \]

\[ V(r) \neq \beta / r \] for alkalis (screening, e-e interactions)

\[ E_{2s} = E_{2p} \] for hydrogen (1/r potential, \( E_n \) ind. of \( l \))

\[ kT \ll eV, \text{ so electrons just fill lowest energy levels} \]

- increased \( Z \)
- screening
Screening in the alkalis

How do the electron’s fill up?

1s²2s

kT << eV, so electrons just fill lowest energy levels

E₂s = E₂p for hydrogen (1/r potential, Eₙ ind. of l)

V(r) ≠ β/r for alkalis (screening, e-e interactions)

- increased Z
- increased screening
Screening in the alkalis

How do the electron’s fill up?

1s²2s

$kT \ll eV$, so electrons just fill lowest energy levels

$E_{2s} = E_{2p}$ for hydrogen ($1/r$ potential, $E_n$ ind. of $l$)

$V(r) \neq \beta/r$ for alkalis (screening, e-e interactions)
Screening in the alkalis

1s²2s

1s²2s²2p⁶3s

kT ≪ eV, so electrons just fill lowest energy levels

E₂s = E₂p for hydrogen (1/r potential, Eₙ ind. of l)

V(r) ≠ β/r for alkalis (screening, e-e interactions)
Screening in the alkalis

How do the electron’s fill up?

1s\(^2\)2s

1s\(^2\)2s\(^2\) 2p\(^6\)3s

1s\(^2\)2s\(^2\) 2p\(^6\)3s\(^2\) 3p\(^6\)4s

Note: 4s fill before 3d for potassium
Screening in the alkalis

How do the electron’s fill up?

1s^2 2s

1s^2 2s^2 2p^6 3s

1s^2 2s^2 2p^6 3s^2 3p^6

1s^2 2s^2 2p^6 3s^2 3p^6 3d^10 4s^2 4p^6

1s^2 2s^2 2p^6 3s^2 3p^6 3d^10 4s^2 4p^6 4d^10 5s^2 5p^6

1s^2 2s^2 2p^6 3s^2 3p^6 3d^10 4s^2 4p^6 4d^10 5s^2 5p^6 4f^14 5d^10 6s^2 6s^7
Screening in the alkalis

Some general considerations

1s$^2$2s

It’s pretty easy to rip the valence electron away, these elements can be a bit hard to handle

1s$^2$2s$^2$2p$^6$3s
Some general considerations

It’s pretty easy to rip the valence electron away, these elements can be a bit hard to handle.
Screening in the alkalis

Some general considerations

\[ 1s^22s \]

It’s pretty easy to rip the valence electron away, these elements can be a bit hard to handle

\[ 1s^22s^22p^63s \]
Screening in the alkalis

Some general considerations

$1s^22s$

$1s^22s^22p^63s$

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>IE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2</td>
<td>24.6</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>5.4</td>
</tr>
<tr>
<td>Ne</td>
<td>10</td>
<td>21.6</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>5.1</td>
</tr>
<tr>
<td>Ar</td>
<td>18</td>
<td>15.8</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>4.3</td>
</tr>
<tr>
<td>Kr</td>
<td>36</td>
<td>14.0</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>4.2</td>
</tr>
<tr>
<td>Xe</td>
<td>54</td>
<td>12.1</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Screening in the alkalis

Some general considerations

$$1s^22s$$

$$1s^22s^22p^63s$$

Why not $$3s \rightarrow 3d$$?

Why not $$3s \rightarrow 4s$$?

It’ll cost wayyy more energy to excite inner-shell electrons than the valence electrons. We’ll mostly just care about excitations like:

Na: $$1s^22s^22p^63s \rightarrow 1s^22s^22p^63p, 1s^22s^22p^64p$$, etc.
Quantum defects in the alkali metals

An empirical way to parameterize the effects of shielding

\[ E_{nl} = \frac{hcR_\infty}{(n - \delta_l)^2} = -\frac{13.6 \text{ eV}}{(n^*)^2} \]

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
<th>( n^* )</th>
<th>( \delta_s )</th>
<th>( Z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2s</td>
<td>1.59</td>
<td>0.41</td>
<td>3</td>
</tr>
<tr>
<td>Na</td>
<td>3s</td>
<td>1.63</td>
<td>1.37</td>
<td>11</td>
</tr>
<tr>
<td>K</td>
<td>4s</td>
<td>1.77</td>
<td>2.23</td>
<td>19</td>
</tr>
<tr>
<td>Rb</td>
<td>5s</td>
<td>1.81</td>
<td>3.19</td>
<td>37</td>
</tr>
<tr>
<td>Cs</td>
<td>6s</td>
<td>1.87</td>
<td>4.13</td>
<td>55</td>
</tr>
</tbody>
</table>

Pretty remarkable: all ionization energies (and transition energies) are roughly equal despite \( Z^2 \) scaling of energies without shielding
## Alkalis - wide range of physics to study

Consequently, transitions in a wide range of species (with very different \( Z \) values) can be addressed with roughly the same range of laser wavelengths (within a factor of <2).

<table>
<thead>
<tr>
<th>Stable isotopes</th>
<th>( ^7)Li BEC in 1997, ( ^6)Li DFG in 2001 – very light, very broad Feshbach resonances for both the bosonic and fermionic species</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^6,^7)Li</td>
<td>( ^23)Na BEC in 1995 – stable scattering properties, stable mixtures used to explore spinor physics</td>
</tr>
<tr>
<td>( ^{39,40,41})K</td>
<td>( ^{40})K DFG in 1999, ( ^{39,41})K BECs in early 2000s – fermions, broad feshbach resonances,</td>
</tr>
<tr>
<td>( ^{85,87})Rb</td>
<td>( ^{87})Rb BEC in 1995; ( ^{87})Rb has stable scattering properties, nice Feshbach resonances in ( ^{85})Rb; large spin-orbit splitting allows for state-dependent potentials / Raman-dressing schemes</td>
</tr>
<tr>
<td>( ^{133})Cs</td>
<td>BEC in 2002; nice Feshbach resonances, mostly unstable in spin mixtures and mixtures with other species</td>
</tr>
<tr>
<td>( ^{223})Fr (not really)</td>
<td>Laser cooling and magneto-optical trapping for parity nonconservation studies</td>
</tr>
</tbody>
</table>

Note that the mass number \( A = Z + N \) is written as, e.g., \( ^{87}\)Rb for the rubidium isotope with \( A = 87 \). (atomic number \( Z \) = # of protons) + (\( N \) = # of neutrons). An odd value of \( A \) implies a fermionic isotope for the alkalis (1 “extra” valence electron).
Quantum defect for different orbitals

Foot Fig. 4.1

\[ l = \delta_l \]

Cs: \(1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s\)

Table 9.2  Parameters of the energy levels of the alkalis.

\[
E_{nl} = \frac{hcR_\infty}{(n - \delta_l)^2} = -\frac{13.6 \text{ eV}}{(n^*)^2}
\]

(a) quantum defects \(\delta_l\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>(l = 0)</th>
<th>(l = 1)</th>
<th>(l = 2)</th>
<th>(l = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.40</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Na</td>
<td>1.35</td>
<td>0.85</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>K</td>
<td>2.19</td>
<td>1.71</td>
<td>0.25</td>
<td>0.00</td>
</tr>
<tr>
<td>Rb</td>
<td>3.13</td>
<td>2.66</td>
<td>1.34</td>
<td>0.01</td>
</tr>
<tr>
<td>Cs</td>
<td>4.06</td>
<td>3.59</td>
<td>2.46</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Quantum defects in the alkali metals

\[ 1s^2 2s^2 2p^6 3s \]

Na
Transition energies (wavelengths)

Recall $E_{2p} - E_{1s} \sim 10.2$ eV for hydrogen, relating to $\lambda_{1\rightarrow2} \sim 120$ nm

\[ hc = 1240 \text{ eV nm} \]

Estimate the wavelength related to the Na $3s \rightarrow 4p$ transition

\[ E_{nl} = -\frac{hcR_{\infty}}{(n - \delta_l)^2} = -\frac{13.6 \text{ eV}}{(n^*)^2} \]

Is this the longest wavelength that can be used to excite g.s. sodium?
Quantum defects in the alkali metals

$n \rightarrow n' = n$

transitions are typically in the visible or near-IR

$\sim 2$ eV

$589$ nm

$1s^22s^22p^63s$

$Na$
Solving the many-electron atom

Everything so far has been super empirical, results of experiment

How do you actually tackle the problem for a many-electron atom?

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

- no analytical solution to this problem
- we’ll walk through one approximate way to treat the effect of many core electrons
Central-field approximation

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

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

One \( V_{CF} \) is assumed, this problem breaks down into \( N \) independent single-particle Schrödinger equations.

For the \( N \) solutions (lowest energy eigenstate wave functions), the total wave function will be of the form

\[ \Psi_{TOT} = \Psi_1 \Psi_2 \Psi_3 \cdots \Psi_N \]

or rather a properly symmetrized version of this (this text goes into more details on the use of Slater determinants to ensure proper w.f. antisymmetrization)
Central-field approximation

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

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

\[ V_{CF}(r) \rightarrow \] an effective, spherically symmetric potential that captures

(1) the static Coulomb potential of the nucleus and

(2) an effectively static, spherically symmetric potential due to the total electron charge distribution

(for product states \( \psi \) this gives a Hartree term like in the He treatment)

> no longer \( 1/r \) potential, so \( E \) depends on \( l \)

> still spherically symmetric, so \( E \) independent of \( m_l \)
**Central-field approximation**

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

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

Basically, an effective electric field \( \vec{E}_{CF}(r) = \frac{Z_{\text{eff}}(r) e}{4\pi\varepsilon_0 r^2} \hat{r} \) exists, of the form and an electron at distance \( r \) will experience the potential

\[
V_{CF}(r) = -e \int_r^\infty E_{CF}(r')dr'
\]
Central-field approximation

As intuition would suggest, the effective potential is unchanged by screening at small $r$, and looks like a $Z = 1$ potential at very large $r$.

The effect of the centrifugal barrier can also be incorporated for $l \neq 0$ solutions.
Solving the many-electron atom

In broad strokes, the basic procedure for obtaining solutions to this problem would look like:

1) Make an initial guess at $\psi$ and $V_{\text{CF}}$
2) Solve the $N$ Schrodinger equations (for $N$ electrons), respecting the necessary antisymmetric nature of $\psi$
3) From the new $\psi$, get a new $V_{\text{CF}}$
4) Iterate

Note: experiments still do the best job at determining state energies (energy differences), up to a part in $10^{18}$ in some cases
Fine structure in the alkalis

An important result that comes from the central-field approximation

Recall from lecture 2 (hydrogen-like atoms with a \(1/r\) potential), that the fine-structure splitting between states with \(j = l + 1/2\) and \(j = l - 1/2\) have the form

\[
\Delta E_{s-o} = \frac{Z^2 \alpha^2}{n l (l+1)} \frac{E_{\text{gross}}(n)}{E_{\text{gross}}(1)} = \frac{Z^4 \alpha^4}{n^3 l (l+1)} mc^2
\]

For the multi-electron atom, which does not follow a \(1/r\) potential, and where \(Z_{\text{eff}}\) varies from \(Z\) to 1 as a function of \(r\), this takes the modified form (the Landé formula):

\[
\Delta E_{s-o} = \frac{Z_i^2 Z_o^2 \alpha^4}{(n^*)^3 l (l+1)} mc^2 \quad \begin{align*} \quad Z_i &\sim Z \\
\quad Z_o &\sim 1 \end{align*}
\]
Fine structure in the alkalis

See how well this scaling works \( \Delta E_{s-o} \propto Z^2 \)

\[
\Delta E_{s-o} / h \\
\begin{array}{|c|c|}
\hline
\text{Li} & 10.056 \text{ GHz} \\
\text{Na} & 516 \text{ GHz} \\
\text{K} & 1730 \text{ GHz} \\
\text{Rb} & 7123 \text{ GHz} \\
\text{Cs} & 16,610 \text{ GHz} \\
\text{Fr} & 50,562 \text{ GHz} \\
\hline
\end{array}
\]

Frequency splitting between “D1” and “D2” lines
What can this splitting be good for?

Control of polarizability by tuning between D1 and D2 optical transitions

Polarizability matching in optical atomic clocks

LeBlanc

Katori, Ye
Why this splitting matters?

Chin

Spin-dependent potentials and Raman-dressing

Spielman

Pan
Fine structure in the alkalis

See how well this scaling works \( \Delta E_{s-o} \propto Z^2 \)