

Chapter 4 - The Alkalies

In many ways, alkali atoms are the most boring atoms, but they have properties that have made them the most useful in ultra cold experiments.

Atom	Outermost	$E_{np} - E_{ns}$	λ (nm)	$E_{nP_{3/2}} - E_{nP_{1/2}}$
Li	2s	1.85 eV	671	4.2×10^{-5} eV
Na	3s	2.10 eV	590	0.0021 eV
K	4s	1.61 eV	769	0.0071 eV
Rb	5s	1.56 eV	795	0.029 eV
Cs	6s	1.39 eV	895	0.069 eV

The dipole matrix element between the ns and np is roughly what you would expect.

The highly excited states (Rydberg states) have been useful in many Quantum Information Science (QIS) expts.

For highly excited states, the quantum defects, $\mu_{l,j}$ or $\delta_{l,j}$, important concept. These are nearly energy independent parameters that give highly accurate energies

$$E_{n,l,j} = E_{\text{thresh}} - hc \frac{R}{(n - \delta_{l,j}(n))^2}$$

Rb example	$\delta(n) = \delta_0 + \frac{\delta_2}{(n - \delta_0)^2}$	fit to energies
$nS_{1/2}$	$\delta_0 = 3.131 180 4 (10)$	$\delta_2 = 0.178 4 (6)$
$nP_{1/2}$	2.654 884 9 (10)	0.290 0 (6)
$nP_{3/2}$	2.641 673 7 (10)	0.2950 (7)

Don't use outside of range of fit, OK(ish) to go to higher n but can be problematic at lower n.

Typically, μ_l, δ_l decrease with increasing l. The μ_l, δ_l increase with row of periodic table. From book $\delta_0 = 1.35, \delta_1 = 0.86$ for Na (compare to Rb above).

Why this behavior for large n ? Because the $Z-1$ core electrons can be thought of as inert charge that gives a spherically symmetric potential for the outer electron. The potential for the valence electron strongly deviates from hydrogen for r less than $\sim 1 \text{ \AA}$. High n orbitals extend out to $r_{\text{max}} \sim 2a_0(n-\delta_e)^2 \sim 1 \text{ \AA} (n-\delta_e)^2$

In my codes:

Atom	μ_s	μ_p	μ_d	μ_f
Li	0.40	0.048	0.002	
Na	1.35	0.856	0.015	0.006
K	2.184	1.714	0.265	0.0097
Rb	3.14	2.64	1.35	0.016
Cs	4.06	3.57	2.473	0.031

Model the potential as

$$V_{\text{mod}}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \left[1 + (Z-1)e^{-\alpha_1 r} + \alpha_2 r e^{-\alpha_3 r} \right] - \frac{\alpha}{2r^4} \left(1 - e^{-(r/r_c)^3} \right)^2$$

charge distribution
polarizability of core

From my code

Li $Z=3$, $\alpha_1 = \frac{2.8917}{a_0}$, $\frac{2.8964}{a_0}$; $\alpha_2 = \frac{0.9476}{a_0}$, $\frac{3.2052}{a_0}$; $\alpha_3 = \frac{1.9664}{a_0}$, $\frac{4.7130}{a_0}$
 $\alpha = 27.21 \text{ eV} \cdot a_0^4 \cdot 0.189$, $r_c = a_0$

It is possible to accurately solve for the full N -electron wave function for alkali. These are used to get accurate matrix elements for lower n . Using model potentials for Rydberg electrons can be pretty accurate (unless there is lots of cancellation) because so much of the probability is outside of the core region: getting E_{nc} correct means this part is fine.

The book's method for the numerical solution of the radial equation is not how it's done.

Solve:

$$-\frac{\hbar^2}{2m_e} P_{nl}''(r) + \left[V_{\text{mod}}(r) + \frac{\hbar^2 l(l+1)}{2m_e r^2} \right] P_{nl}(r) = E_{nl} P_{nl}(r)$$

$$P_{nl}(r \rightarrow \infty) \rightarrow 0 \quad P_{nl}(r \rightarrow 0) \rightarrow C r^{l+1} \rightarrow 0$$

Low order method $r_j = j \cdot \Delta r$ $j = 0, 1, \dots, N$ $r_{\text{max}} = N \Delta r$
 Define $P_{j, nl} = P_{nl}(r_j)$

Approximate $P_{nl}''(r_j) = (P_{j+1} - 2P_j + P_{j-1}) / \Delta r^2$

$$\underline{H} \begin{pmatrix} P_1 \\ P_2 \\ \vdots \end{pmatrix} = E \begin{pmatrix} P_1 \\ P_2 \\ \vdots \end{pmatrix}$$

$$\underline{H} = \begin{pmatrix} \left(\frac{\hbar^2}{m_e} + V_{\text{eff}}(r_1)\right) & -\frac{\hbar^2}{2m_e} & 0 & 0 & \dots \\ -\frac{\hbar^2}{2m_e} & \left(\frac{\hbar^2}{m_e} + V_{\text{eff}}(r_2)\right) & -\frac{\hbar^2}{2m_e} & 0 & \dots \\ 0 & -\frac{\hbar^2}{2m_e} & \left(\frac{\hbar^2}{m_e} + V_{\text{eff}}(r_3)\right) & -\frac{\hbar^2}{2m_e} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Tridiagonal matrix

Very powerful solvers, for example, only find states in a certain range

Higher order methods can be adapted to a diagonalization scheme.

For Rydberg states, use Numerov's method by propagating inward.

$$P''(r) = -g(r)P(r)$$

$$g(r) = \frac{2m_e}{\hbar^2} [E - V_{\text{eff}}(r)]$$

$$P_{n-1} = [2(1 - \frac{5\Delta r^2}{12} g_n)P_n - (1 + \frac{\Delta r^2}{12} g_{n+1})P_{n+1}] / (1 + \frac{\Delta r^2}{12} g_{n-1})$$

You know energies from quantum defect formula. Start with $P_n = 0$, $P_{n-1} = 10^{-30}$, use the recursion to get $n-1$ then $n-2$ etc.

Will diverge in small region $r \rightarrow 0$. Smoothly set to 0. OK because such a small part of $P(r)$.

The treatment of the spin-orbit splitting is the same as that for hydrogen since the core electrons have $L=0, S=0$

There is an interaction term $V_{so} = F(r) \vec{L} \cdot \vec{S}$

$$\vec{J} = \vec{L} + \vec{S} \Rightarrow \vec{J}^2 \rightarrow \hbar^2 J(J+1) \quad J = l \pm \frac{1}{2}$$

↑ valence ↑

$$E_{\text{neg}} = E_{nl} + \langle \psi_{nlm} | F(r) | \psi_{nlm} \rangle \frac{\hbar^2}{2} [J(J+1) - l(l+1) - s(s+1)]$$

From the first page, the spin orbit splitting increased going from Li to Cs. Why?

Very roughly the spin orbit splitting is (Landé Formula)

$$\Delta E_{fs} \sim \frac{Z_i^2}{(n-\delta)^3 l(l+1)} \propto^2 hc R_{\infty}$$