

Lecture 6

Alkali-metal atoms. Alkaline-earth metal atoms & their singly-charged ions. The central-field approximation. Self - consistent solutions.

Periodic Table of Elements

1	2																	3	4	5	6	7	8	9	10
1	IA H	IIA																	0 He						
2	3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne	
3	11 Na	12 Mg	IIIB	IVB	VB	VIB	VIB	VII	IB	IB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar									
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr							
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe							
6	55 Cs	56 Ba	*La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn							
7	87 Fr	88 Ra	+Ac	104 Rf	105 Ha	106	107	108	109	110															

* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

+ Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Legend - click to find out more...

H - gas

Li - solid

Br - liquid

Tc - synthetic



Non-Metals



Transition Metals



Rare Earth Metals



Halogens



Alkali Metals



Alkali Earth Metals



Other Metals

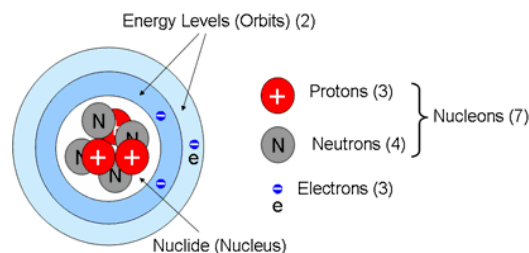
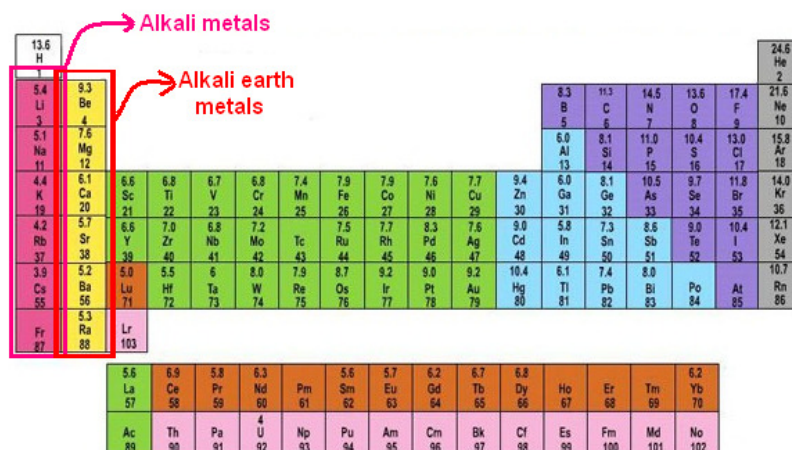


Inert Elements

Which atoms are the best suited for precision experiments?

Considerations:	1) electronic structure
	2) lifetimes of states: availability of metastable (long-lived) states
	3) wavelengths of relevant transitions (convenience, available laser power, etc.)
	4) special considerations that enhance the effect to be studied, for example, some effects are enhanced for heavy atoms (need large Z) or for accidentally close energy levels
	5) nuclear properties (nuclear spin, availability of stable isotopes, availability of several isotopes), is the isotope bosonic or fermionic?
	6) special considerations for quantum control - minimization of decoherence.
	7) availability, material considerations, toxicity, radioactivity

1. Very light atoms and corresponding ions (H, He).
2. Atoms with the simplest electronic structure - alkali-metal atoms, alkaline-earth metal atoms and their singly-charged ions, similar systems (Al⁺, Yb⁺, Yb, etc.)

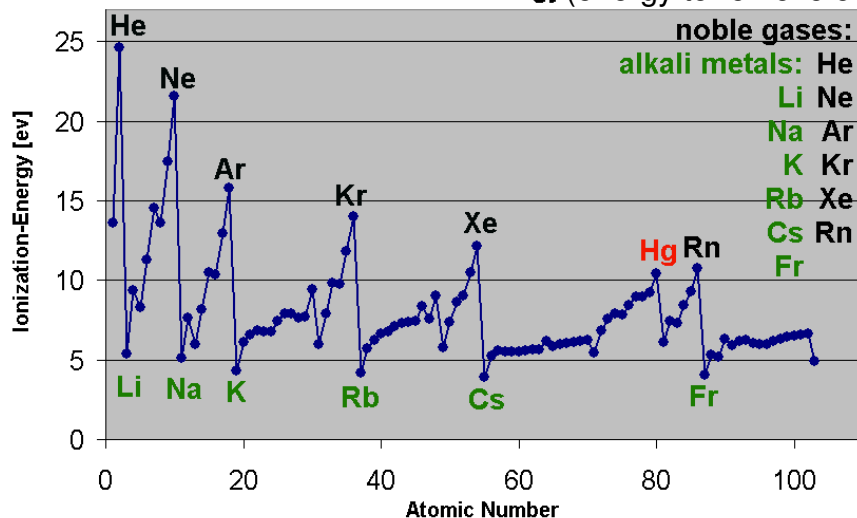


Atomic Structure (Lithium Atom - ${}^7_3\text{Li}$)
Bosonic isotope - total integer spin

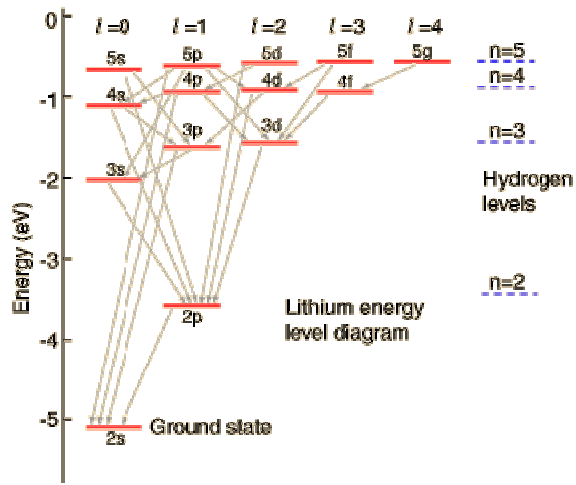
Alkali-metal atoms

		Z	Configuration	Stable isotopes
Lithium	Li	3	$1s^2 2s$	${}^6\text{Li}$, ${}^7\text{Li}$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s$	${}^{23}\text{Na}$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$	${}^{39}\text{K}$, ${}^{40}\text{K}$, ${}^{41}\text{K}$
Rubidium	Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$	${}^{85}\text{Rb}$, ${}^{87}\text{Rb}$
Cesium	Cs	55	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s$	${}^{133}\text{Cs}$
Francium	Fr	87	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s$	none

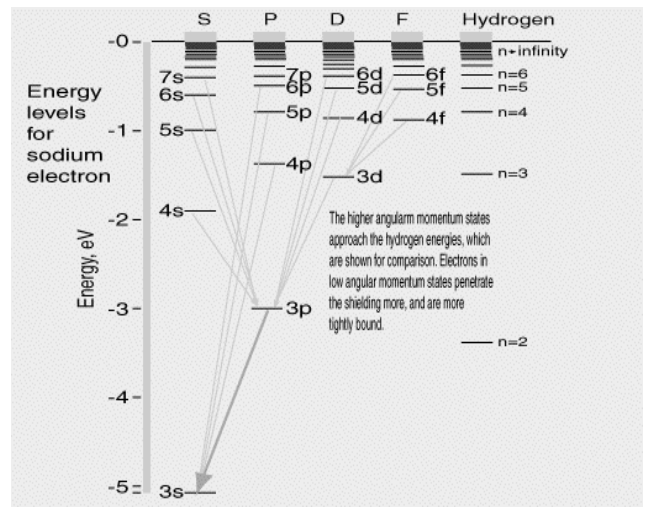
Ionization-Energy (energy to remove one electron)



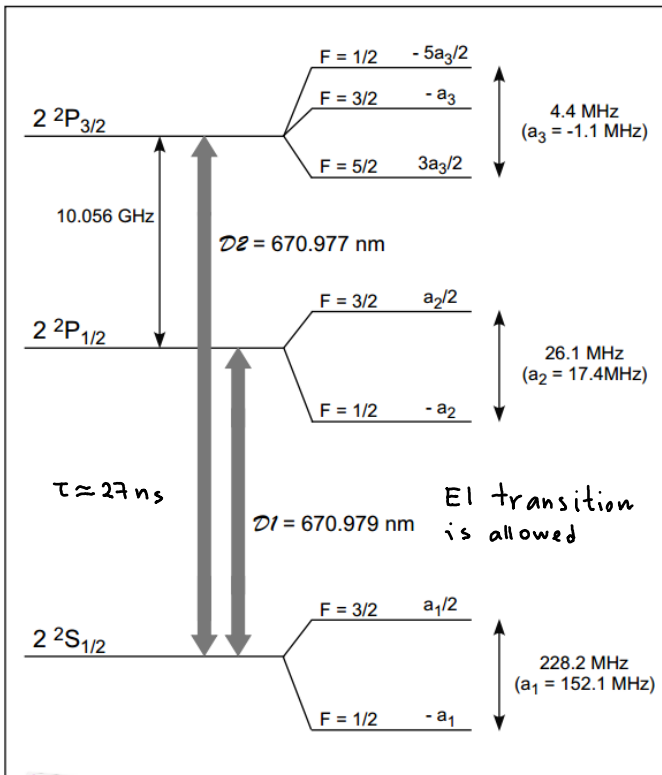
<http://commons.wikimedia.org/wiki/File:IonizationEnergyAtomicWeight.PNG>



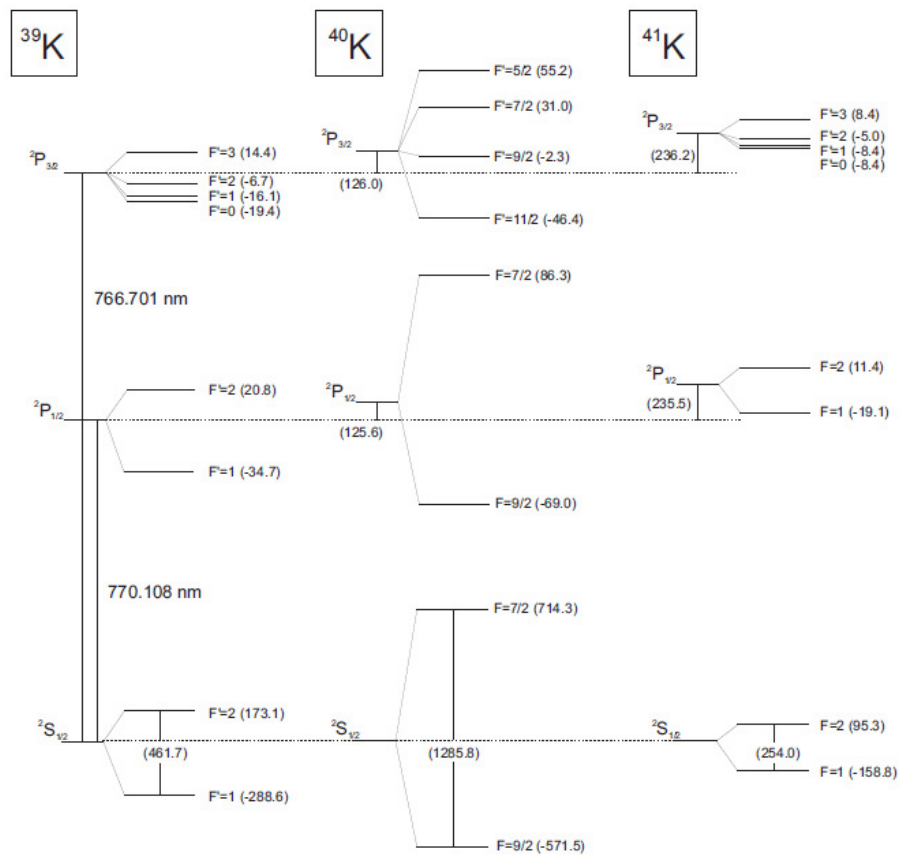
Simplified energy-level diagram for Li



Simplified energy-level diagram for Na



Fine and hyperfine structure for ${}^6\text{Li}$



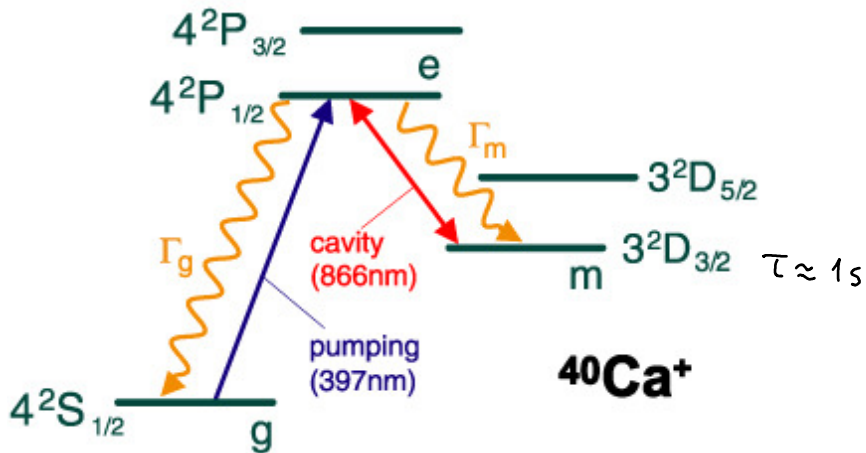
Fine and hyperfine structure for K Isotope shifts

<http://www.physics.ncsu.edu/jet/techdocs/pdf/PropertiesOfLi.pdf>

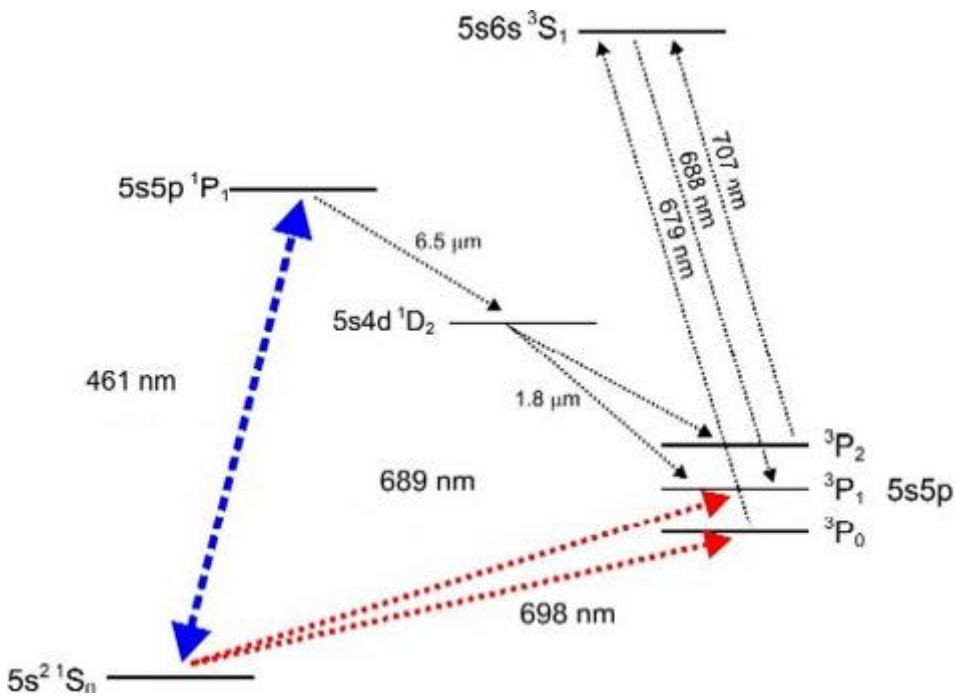
http://staff.science.uva.nl/~walraven/walraven/Publications_files/PotassiumProperties.pdf

Singly-charged ions of alkaline-earth metal atoms

Lowest p and d energy levels exchange places in comparison to alkali
 Result: first excited level becomes metastable (long-lived).



Alkaline-earth metal atoms: lowest excited level is also metastable.



Strontium energy level diagram

The central-field approximation

The Hamiltonian for N electrons in the Ze Coulomb potential is

$$H = \sum_{i=1}^N \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_i} \right\} + \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}}$$

$$r_{ij} = |\vec{r}_i - \vec{r}_j|$$

Kinetic and potential energy for each electron in the Coulomb field

Electrostatic repulsion between two electrons. Sum is taken for $j>i$ to avoid double counting

← Too large to be treated as a perturbation.

Large part of the repulsion between the electrons can be treated as a central potential $S(r)$ since the closed sub-shells within the core have a spherical charge distribution. Therefore, the interaction between the different shells and the valence electron are also spherically symmetric. Then, the total potential energy depends only on the radial coordinate:

$$V_{CF}(r) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + S(r)$$

The Hamiltonian is

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

When the potential is in this form, the N-electron Schrödinger equation

$$H\psi = E_{atom} \psi$$

separates into N one-electron equations

$$\left\{ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{CF}(r_i) \right\} \psi_i = E_i \psi_i \quad i = 1 \dots N$$

$$\psi_{atom} = \psi_1 \psi_2 \dots \psi_N$$

Note that proper antisymmetric wave function has the form of the Slater determinant.

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \dots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \dots & \psi_b(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_x(1) & \psi_x(2) & \dots & \psi_x(N) \end{vmatrix}$$

a, b, \dots, x are possible sets of quantum numbers of individual electrons
 $1, 2, \dots, N$ are electron labels

The total energy of the system is $E_{\text{atom}} = E_1 + E_2 + \dots + E_n$

$$\psi_i = R(r_i) Y_{l,m_i} \gamma_i$$

For $P(r) = rR(r)$ radial equation is

$$\left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{\text{CF}}(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right\} P(r) = EP(r)$$

Small distances: central electric field $\vec{E}(\vec{r}) \rightarrow \frac{Ze}{4\pi\epsilon_0 r^2} \hat{r}$

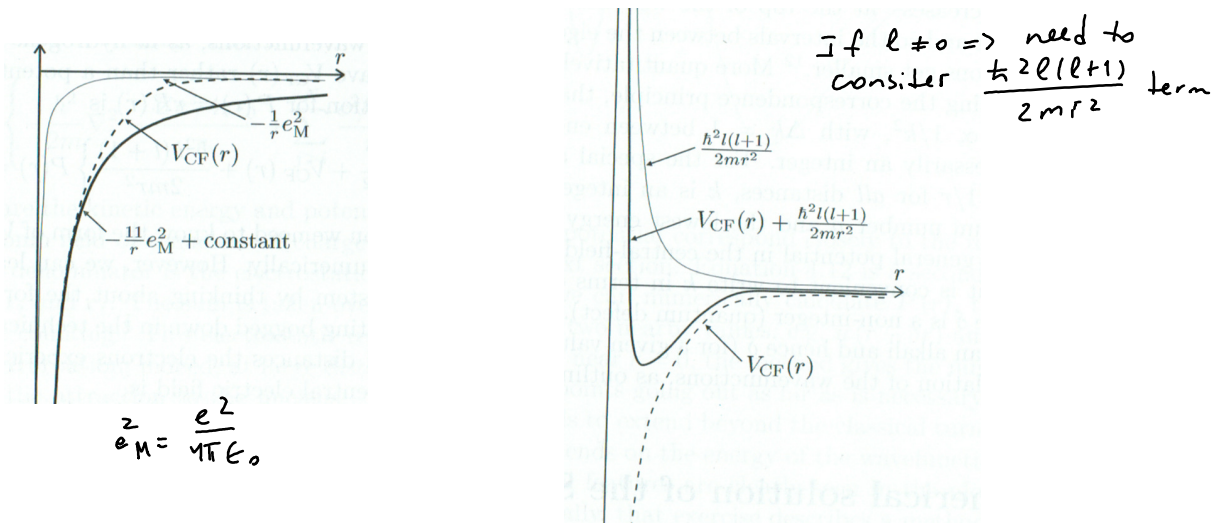
Large distances: most charge is screened by electrons

$$\vec{E}(\vec{r}) \rightarrow \frac{e}{4\pi\epsilon_0 r^2} \hat{r}$$

These two limits may be incorporated by the central potential field of the form

$$\vec{E}_{\text{CF}}(r) \rightarrow \frac{Z_{\text{eff}} e}{4\pi\epsilon_0 r^2} \hat{r} \quad V_{\text{CF}} = e \int_{\infty}^r |E_{\text{CF}}(r')| dr'$$

For Na atom these potentials look as follows (from Atomic Physics, C. J. Foot, p. 66-67)



For more accurate description, one needs to account for effect of the outer electrons on the other electrons and, therefore, central field.

$$N_a: E(1s^2 2s^2 2p^6 3s) = 2E_{1s} + 2E_{2s} + 6E_{2p} + E_{3s} = E_{\text{core}} + E_{3s}$$

One generally measures this binding energy relative to the singly-charged Na^+ ion, which has energy

$$E(1s^2 2s^2 2p^6) = 2E'_{1s} + 2E'_{2s} + 6E'_{2p} = E'_{\text{core}}$$

The ionization energy (the energy to remove 3s electron) is

$$IE = E_{atom} - E_{ion} = (E_{core} - E'_{core}) + E_{3s}$$

core polarization, i.e.
change in the distribution of the charge
in the core due to valence electron.

"Frozen-core" approximation: $E_{core} \approx E'_{core}$

Self-consistent solutions

How do we determine the central-field potential V_{CF} ?

To get the potential we need to know the wave functions, but to get the wave functions we need to know the potential ... going in a circle ...

Procedure (devised by Hartree)

- (a) make initial guess for the potential
- (b) calculate the electron wave function in this potential
- (c) use resulting wave functions to calculate new central-field potential
- (d) repeat until the changes in the wave functions and potential get smaller and converge to self-consistent solution, i.e. solving the radial Schrödinger equation for that central potential gives back the same wave functions within the numerical accuracy.