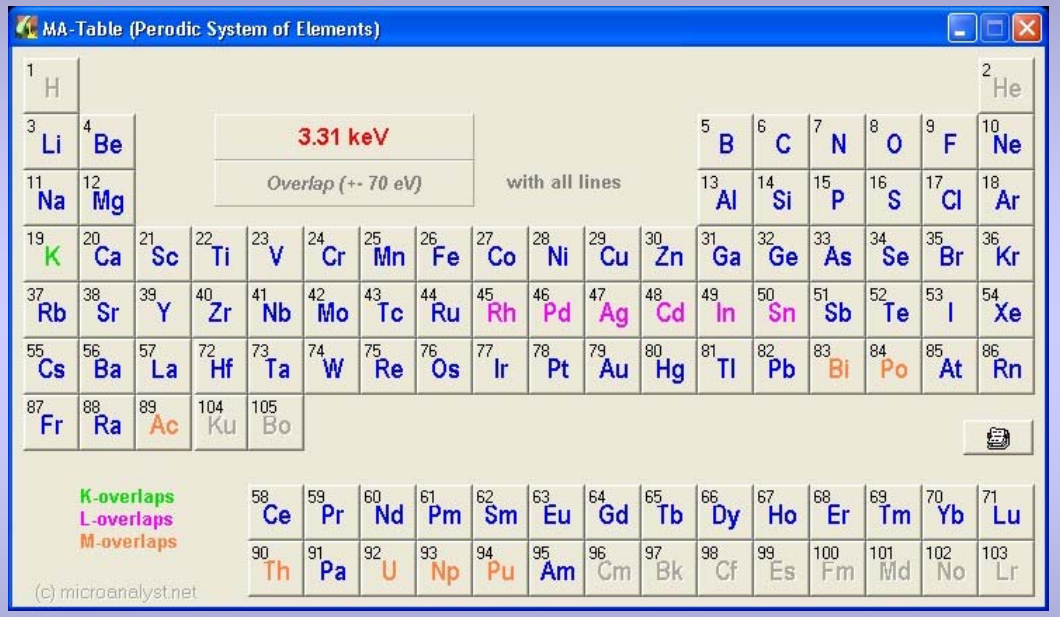
Complex atoms and the Periodic System of the elements

Non-central forces due to electron repulsion

Central field approximation
→electronic orbitals
→lift degeneracy of *l*

$$E_{n\ell} = -\frac{R(hc)}{(n-\delta_\ell)^2}$$



→ "Aufbau" principle

Complex atoms and the central field approximation

The potential energy in a multi-electron atom:

$$V = -\frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{Z}\frac{1}{|\vec{r}_i|} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i<j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

attraction to nucleus — repulsion between electrons

V is a *non*-central potential

Schrödinger equation

$$-\frac{\hbar^2}{2m}\left[\nabla_1^2 + \nabla_2^2 + \cdots + \nabla_Z^2\right]\Psi + V\Psi = E\Psi$$

The wave function depends on 3Z spatial coordinates

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z)$$

CFA:

The overall effect of $V\left(\sum_i \vec{r}_i\right)$ is centrally directed toward the nucleus

$$\longrightarrow V_c(r) \begin{cases} -\dfrac{Ze^2}{4\pi\varepsilon_0 r} & \text{for } r \to 0 \\ -\dfrac{e^2}{4\pi\varepsilon_0 r} & \text{for } r \to \infty \end{cases}$$

Then V can be written in terms of an "effective screened nuclear charge"

$$V_{cfa}(r) = -\frac{Z_{eff}(r)e^2}{4\pi\varepsilon_0 r}$$

Note: $V_{atom} = V_{cfa}(r) + V_{ee'}^{NC}$

Separation of variables in the central field approximation

Product wave function

$$\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_Z)=\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\cdots\psi_Z(\vec{r}_Z)$$

Potential and eigenenergy

$$V=\sum_{i=1}^{Z}V_c(r_i) \qquad E=\sum_{i=1}^{Z}E_i$$

Insertion of trial yields a set of equations:

$$-\frac{\hbar^2}{2m}\nabla_i^2\Psi(\vec{r}_i)+V_c(r_i)\Psi(\vec{r}_i)=E_i\Psi(\vec{r}_i)$$

The potential function is not Coulombic i.e. is *not* 1/r but

$$-\frac{Z_{eff}(r)}{r}$$

1. Angular part of the wave function is the same, hence angular functions

$$Y_{l_i m_i}(\theta_i,\phi_i)$$

2. Radial part of the wave function

$$-\frac{\hbar^2}{2mr}\frac{d}{dr}rR_{nl}+\left[\frac{Z_{eff}(r)}{r}+\frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]R_{nl}=E_{nl}R_{nl}$$

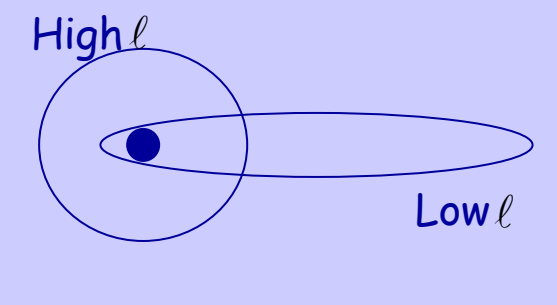
$\longrightarrow$ Energy E_{nl} depends on ℓ

Energy E_{nl} does *not* depend on *m*

Wave functions for single "orbital"

$$\psi_i(\vec{r}_i)=R_{nl}(r_i)Y_{l_i m_i}(\theta_i,\phi_i)\left|\uparrow,\downarrow\right\rangle$$

Screening in the central field approximation

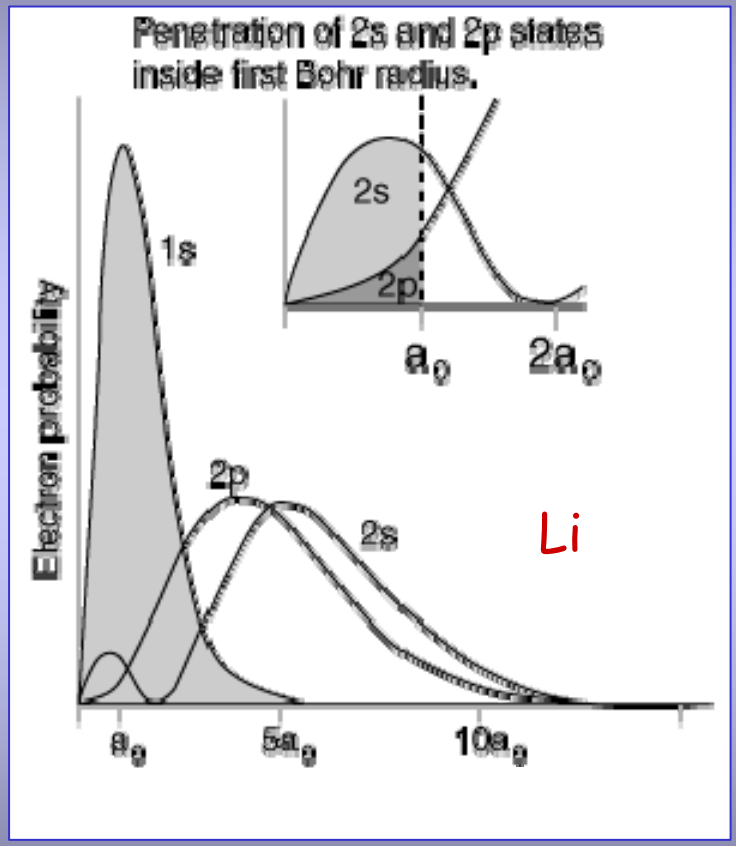


For low ℓ values (and same n)
electron comes closer to the nucleus

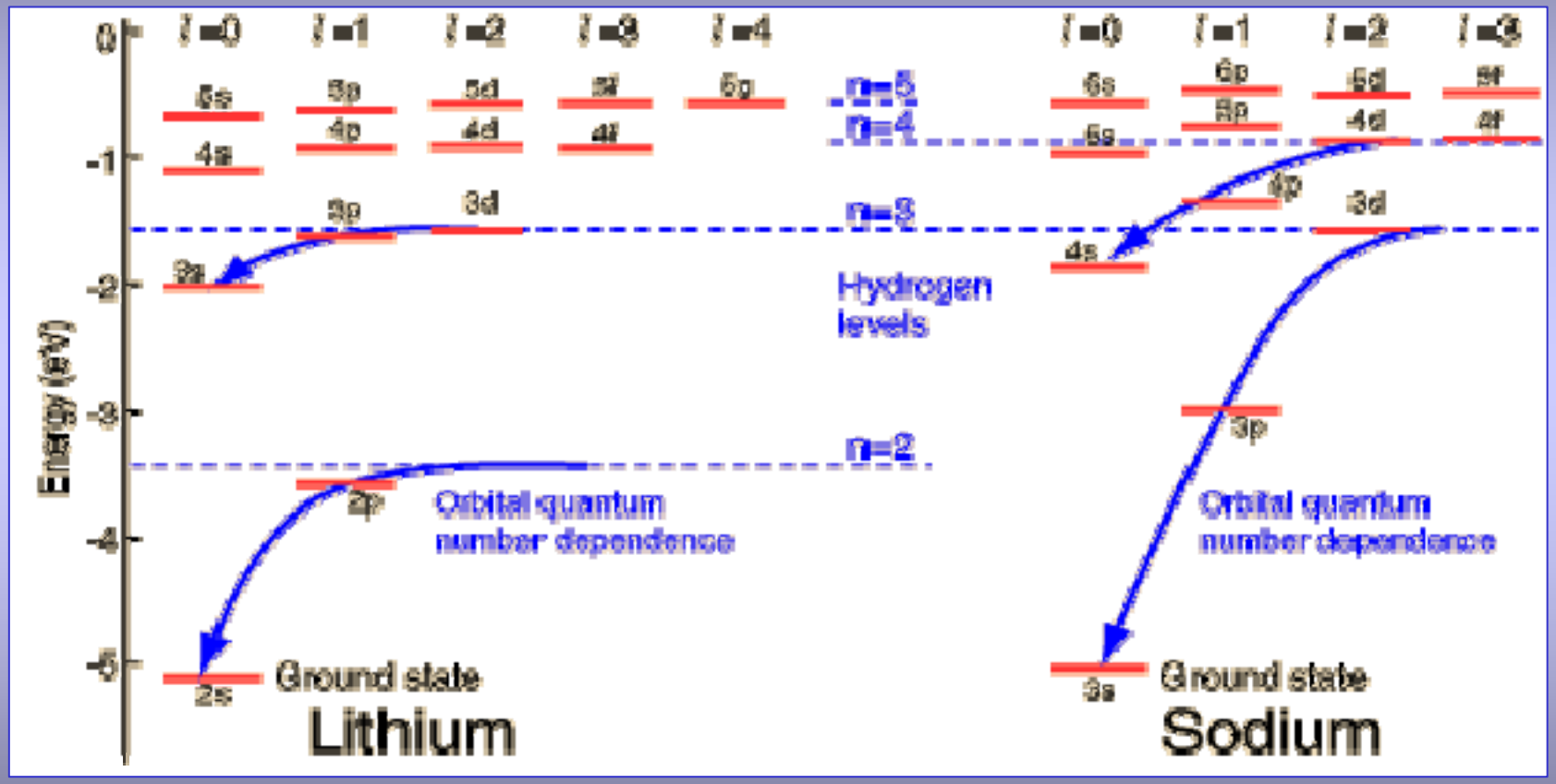
More Coulomb attraction

More binding energy

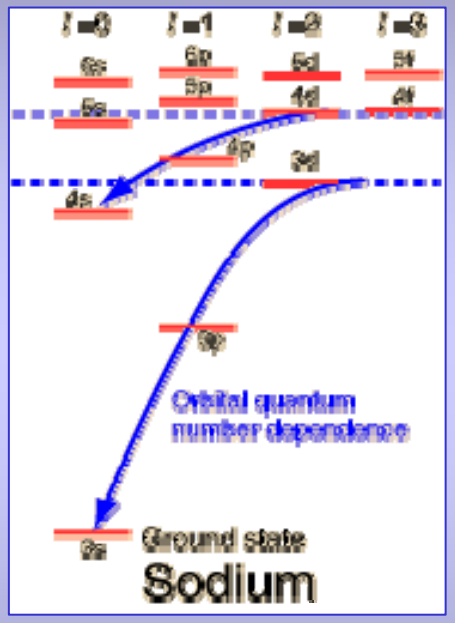
Lower ℓ states → lower energy



Lowering of low ℓ quantum states as an effect of screening



Screening and the quantum defect



Levels described with:

$$E_{nl} = -\frac{R_{Na}}{(n-\delta_\ell)^2}$$

With quantum defects:

δ_s = 1.35

δ_p = 0.86

δ_d = 0.01

δ_f = 0.00

Aufbau principle for multi-electron atoms

Eigenfunctions in multi-electron atom

$$\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_Z)=\psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\cdots\psi_Z(\vec{r}_Z)$$

1) Electrons fill the one-electron orbitals

$$\psi_i(\vec{r}_i)=R_{nl}(r_i)\mathrm{Y}_{l_i m_i}(\theta_i,\phi_i)\left|\uparrow,\downarrow\right\rangle$$

into a "configuration": $\prod_i \psi_i(\vec{r}_i)$

2) Pauli principle dictates: single occupancy

3) For filled shells

$$\sum_{shell} m_{\ell\, i}=0 \Rightarrow \vec{L}_{tot}=0$$

$$\sum_{shell} s_{\ell\, i}=0 \Rightarrow \vec{S}_{tot}=0$$

Degeneracy $2n^2$ structures the Periodic System

Note:
this is about ground states of the atoms

Ground state orbital configurations for multi-electron atoms

Noble gases

He configuration $(1s)^2$; closed shell

Ne conf. $(1s)^2(2s)^2(2p)^6$; closed shell

Ar conf. $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$; closed shell

Alkali metals

Li $(1s)^2(2s)$ one open shell electron

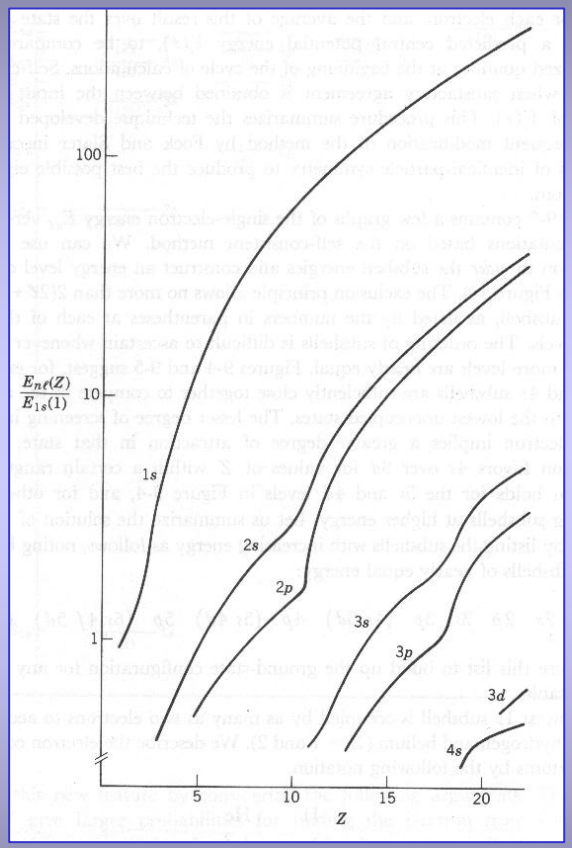
Na $(1s)^2(2s)^2(2p)^6(3s)$ one open shell electron

K $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)$ ....

Earth alkali metals

Mg $(1s)^2(2s)^2(2p)^6(3s)^2$ closed

Ca $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2$



Binding energies of the one-electron orbitals vary with Z: Screening effects

Irregularities and degeneracies

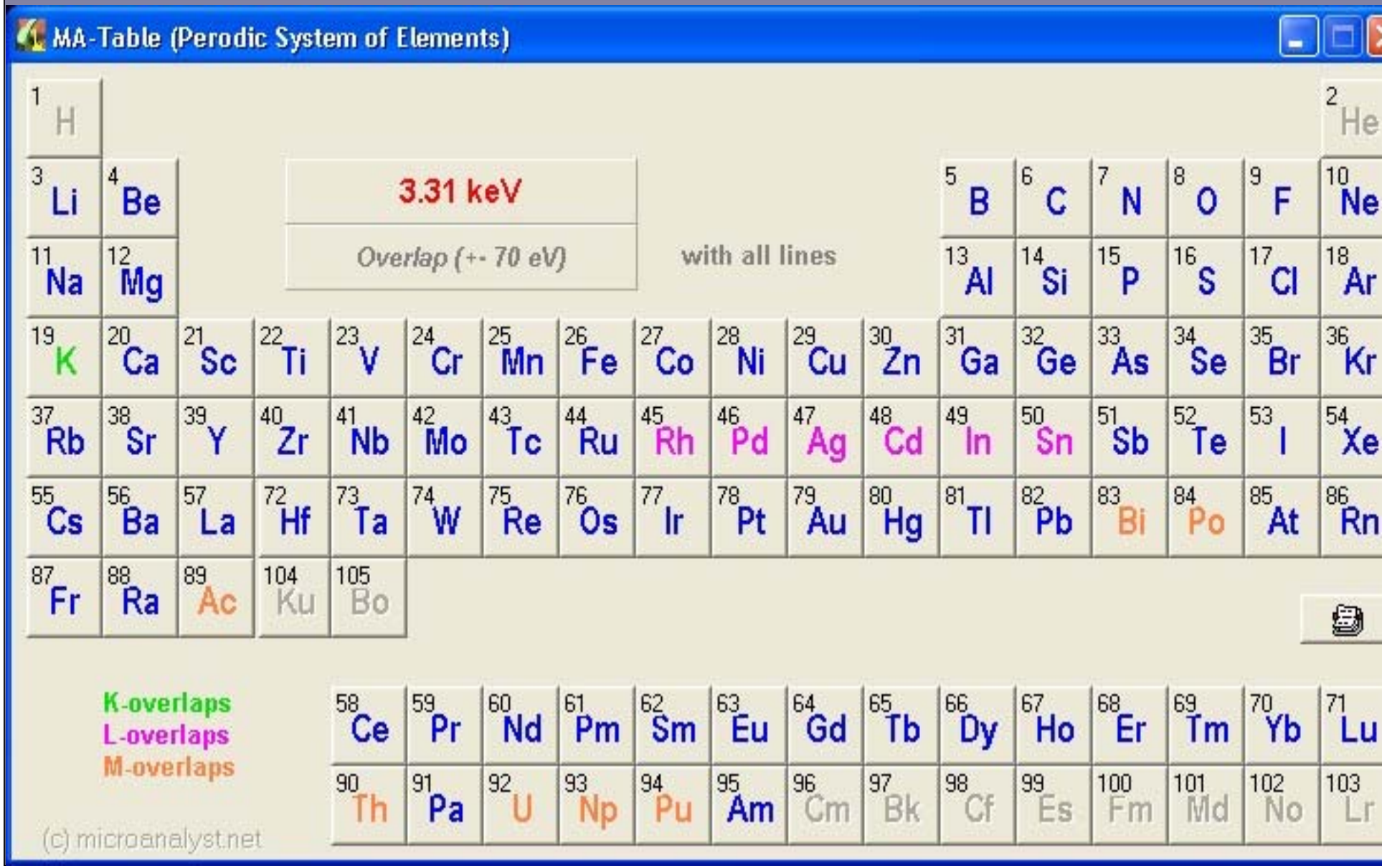
Transition metals; effect of *3d* orbitals:		ground term
Ca	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2$	$^1S_0$
Sc	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)$	$^2D_{3/2}$
Ti	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^2$	$^3F_2$
V	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^3$	$^4F_{3/2}$
Cr	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)(3d)^5$	$^7S_3$
Mn	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^5$	$^6S_{5/2}$
Fe	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^6$	$^5D_4$
Co	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^7$	$^4F_{9/2}$
Ni	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^8$	$^3F_4$
Cu	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)(3d)^{10}$	$^2S_{1/2}$
Zn	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}$	$^1S_0$

Near degeneracy of *3d* and *4s* orbitals

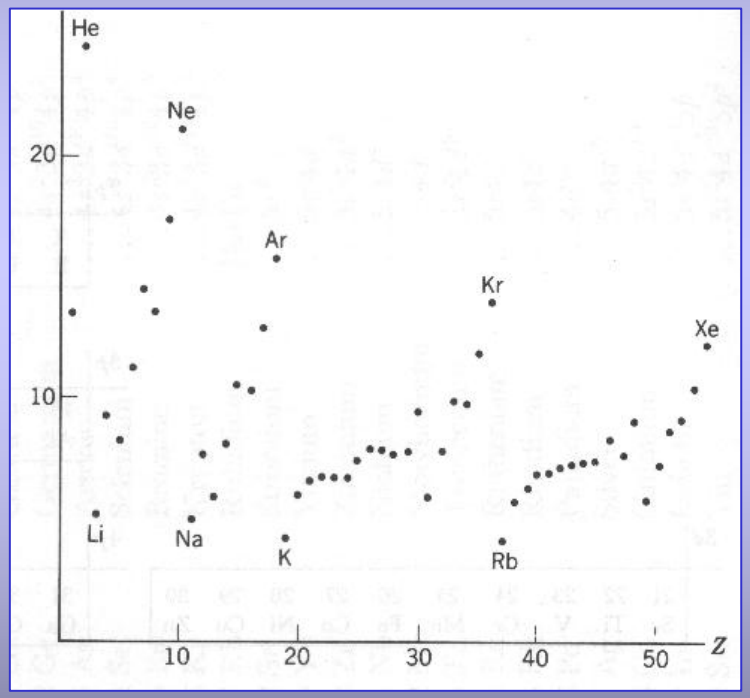
Competition in allocation of electrons

Coupling of the Angular momenta

The periodic system of the elements



Ionization Potentials vary over the periodic structures



-Shell closing for the noble gases;

-Alkali metals
outer electron least binding energy