Atoms /2.

Electron structure of atoms
Valence electrons
X-rays

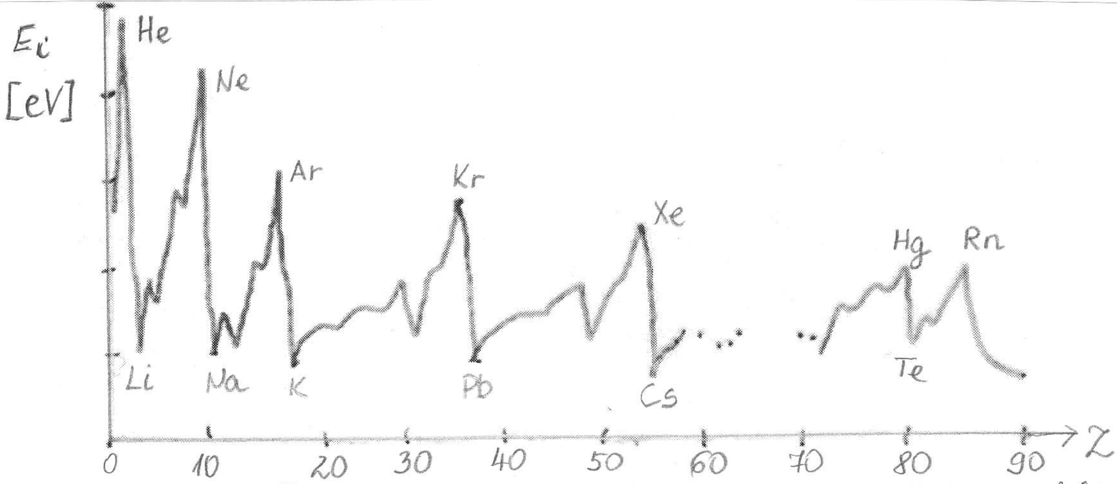
Electron structure of atoms

Independent particle model + Pauli principle

Elements: periodicities in the physical and chemical properties

Periods $Z = 2, 10, 18, 36, 54, 86$ He, Ne, Ar, Kr, Xe Rn

Ionization energies:



(deviation at transition metals, rear earth metals)

Question: for any n, l state how many m_l, m_s combinations? This gives for n, l state the maximum number of coexisting electrons

$\forall l \rightarrow 2(2l+1)$ kind of m_l and m_s $(m_s = \pm \frac{1}{2})$

$n, l \rightarrow 2(2l+1)$ electrons can coexist

configuration number $x = 2(2l+1)$

notation: nl^x e.g.: He ground state

$1s^2$

Let us build up the atoms of the elements from Z = 1
New electron is always added to the lowest energy state allowed by the exclusion principle

States with n, l filled – a shell is filled
Additional electron → to new shell

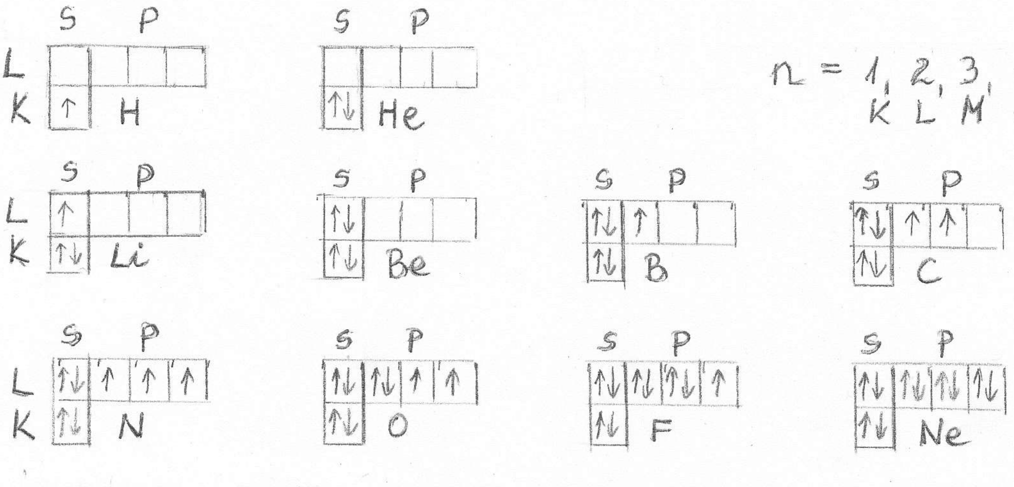
Shells: large energy difference between them

Full shells:
Z = 2, 10, 18, 36, 54
noble gases

	s	p	d	f	g
l =	0	1	2	3	4
2(2l+1) =	2	6	10	14	18

Levels	No. of electrons in the shell (2(2l+1))		Shell completely filled
7p, 6d, 5f, 7s	6, 10, 14, 2	32	118 (?)
6p, 5d, 4f, 6s	6, 10, 14, 2	32	86 (Rn)
5p, 4d, 5s	6, 10, 2	18	54 (Xe)
4p, 3d, 4s	6, 10, 2	18	36 (Kr)
3p, 3s	6, 2	8	18 (Ar)
2p, 2s	6, 2	8	10 (Ne)
1s	2	2	2 (He)

Build up of the first 10 elements



n = 1, 2, 3, 4...
K L M N...

$K \rightarrow n=1 \rightsquigarrow l=0 \rightarrow s \qquad m_s = \pm\frac{1}{2}$

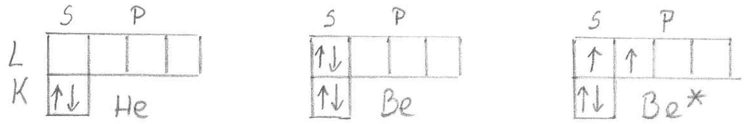
$L \rightarrow n=2 \rightsquigarrow l=0 \rightarrow s \qquad m_s = \pm\frac{1}{2}$

$l=1 \rightarrow p \qquad m_l = +1, 0, -1, \; m_s = \pm\frac{1}{2}$

In the course of filling the shells:
maximum number of parallel spins

Hund's rule: spin of the ground state of atoms is the maximum allowed by the exclusion principle

Reason: ground state ⇒ small repellence between the electrons
⇒ antisymmetric orbital wavefunction
⇒ spin wavefunction is symmetric

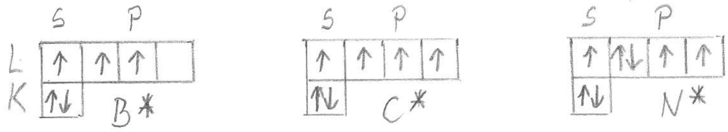


He and Be: completely filled 1s and 2s levels

He – noble gas   Be – is not

Reason: One of the 2s electrons of Be can be easily excited to the 2p level close in energy (differing only due to fine structure

Be* → 2 uncompensated spins
valence = 2



Physical and chemical properties of atoms are determined by the ~~ground~~ electron configurations of the ground state and the closely lying excited states.

E.g.: noble gases: filled shells
large energy difference to the next unfilled energy state.

closed (filled) shell + 1e
e.g. Li, Na, K
the outermost electron is only loosely bound
metallic behaviour

L-S coupling

Complete angular momentum of multielectron atoms

Selection rules

Isolated atom: total angular momentum J = constant

$J^2 = J(J+1)\hbar^2$ $\quad J_z = M\cdot\hbar$ $\quad M = \pm J, \pm(J-1) \dots$

To any given electron configuration: many J-s

(many different wefunctions and energies)

L-S or Russel-Saunders coupling

Full wavefunction is antisymmetric

Individual electrons: n, l, m_l, m_s

$\underline{L} = \sum_i \underline{L}_i$ $\quad L_z = \sum_i L_{zi}$

$L^2 = L(L+1)\hbar^2$ $\quad L_z = M_L\cdot\hbar$ $\quad M_L = \pm L, \pm(L-1)$

Similarly for the spin

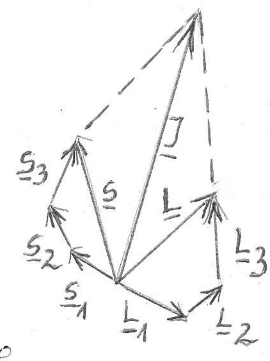
$\underline{S} = \sum_i S_i$ $\quad S_z = \sum_i S_{zi}$

$S^2 = S(S+1)\hbar^2$ $\quad S_z = M_S\hbar$ $\quad M_S = \pm S, \pm(S-1)$

The total angular momentum:

$\underline{J} = \underline{L} + \underline{S}$ $\quad J = L+S, L+S-1, \dots |L-S|$

e.g. for a 3 electron atom $\rightarrow$



In case of the same $\{n_i\}$ configuration different $\underline{L}$ and $\underline{S}$ are possible different energies due to different relative orientations of the motion of the electrons (Coulomb interact.) $\Rightarrow$ Complicated energy level structure

For given L & S $\rightarrow$ different $\{n_i\}$-s (terms)

For given L & S but different J $\rightarrow$ slightly different energies only (due to spin-orbit interaction)

Valence electrons

Completely filled shells form a "kernel": the external electrons feel the nuclear charge shielded by the kernel

For the kernel $L = 0$, $S = 0$

External electrons → valence electrons → they determine the behaviour of the atoms

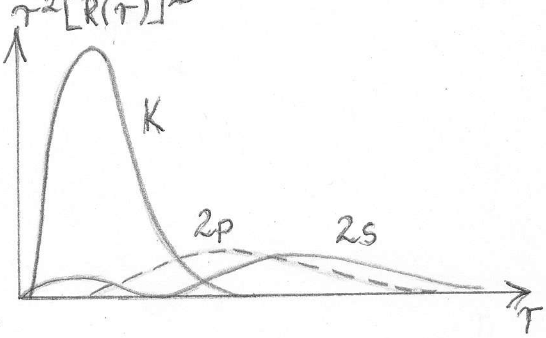
Excitations: primarily the valence electrons

- 1 valence electron

  e.g. Li $Z = 3$

  kernel: 2 electrons + 1 valence electron

  The shielding effect of the kernel depends on the orbit (state) of the valence electron



First approxim.: $+3e$ nuclear charge

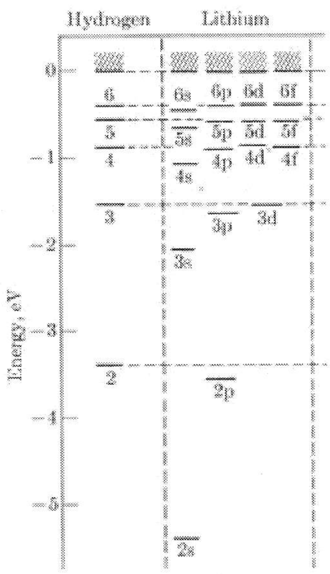
$-2e$ kernel –"–

$+e$ effective charge

H-like

But for the states with small l the valence electrons penetrates the kernel → The energies depend on l!

When n and l are large less penetration more H-like levels



- 2 valence electrons

  He like energy levels

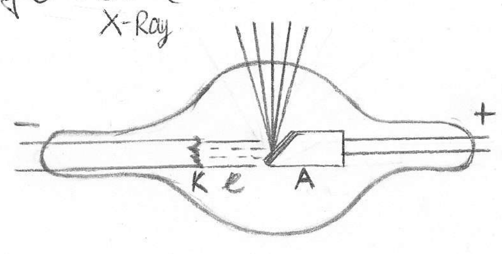
  e.g. Be, Mg, Ca

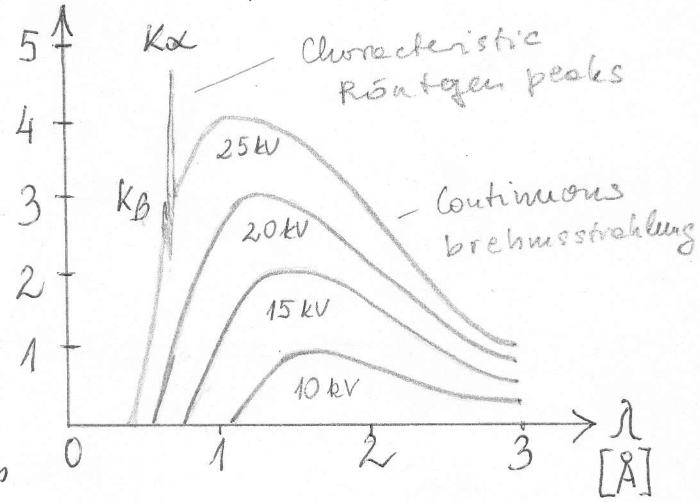
  Two groups of energy levels $S = 0$ singlet, $S = 1$ triplet

  Strong l dependence

X-rays (Röntgen)

Based on excitation of electrons in the completely filled kernel





Radiation spectrum for Molibdenum anode at different accelerating voltages →

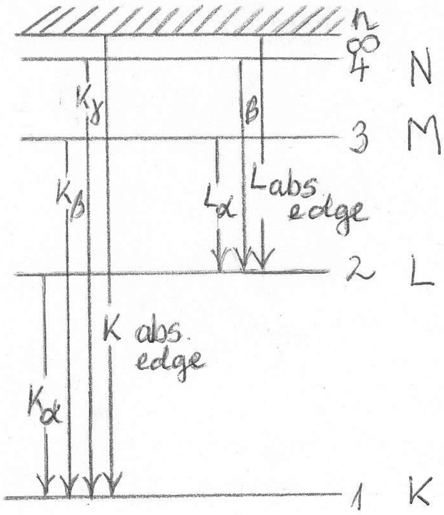
K series excitation potential > 20,1 kV

Sharp peaks : λ peak depends on the anode material

Accelerated electron collides with the atoms of the electrode
  kicks out an electron from the kernel
  e.g. from the K shell (n=1) – an empty state
    (so called "hole") remains

From a higher energy level (from the shell, or a valence electron, or a free electron) falls into the hole

From the L, M, N shell → Kα, Kβ, Kγ



X ray spectrum

It can be generated by creation of a "hole", otherwise no electron can return to a closed shell due to the exclusion principle

Fine structure → the l of the kicked out electron

– Auger effect : the generated X ray does not exit, but it excites one of the external electrons of the atom by photoelectric effect → Auger electron spectroscopy