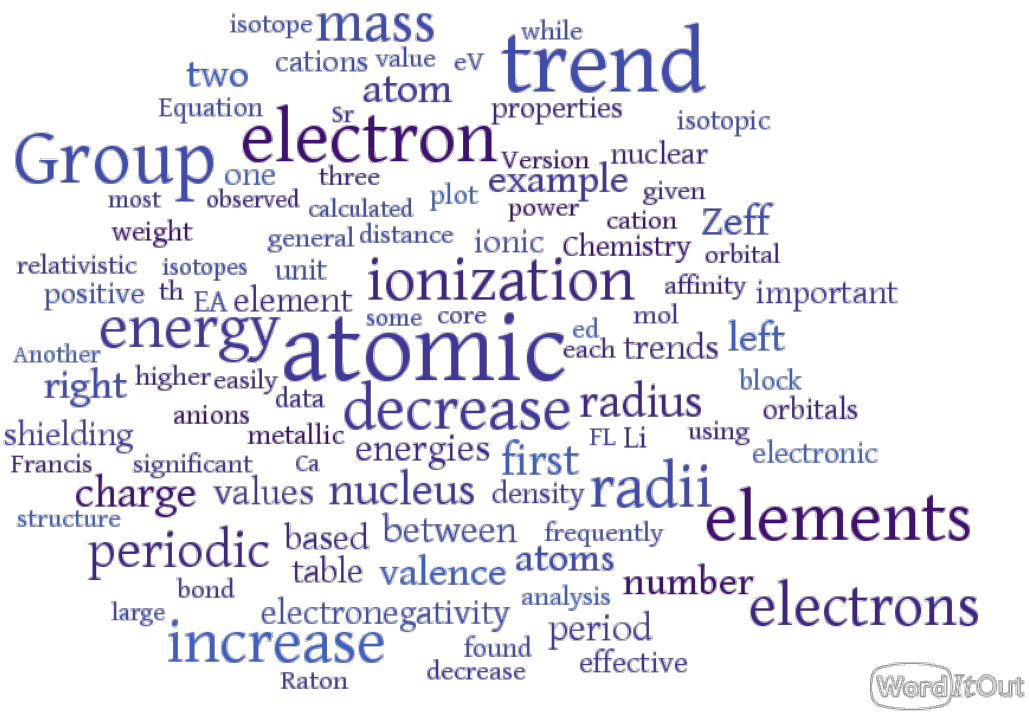
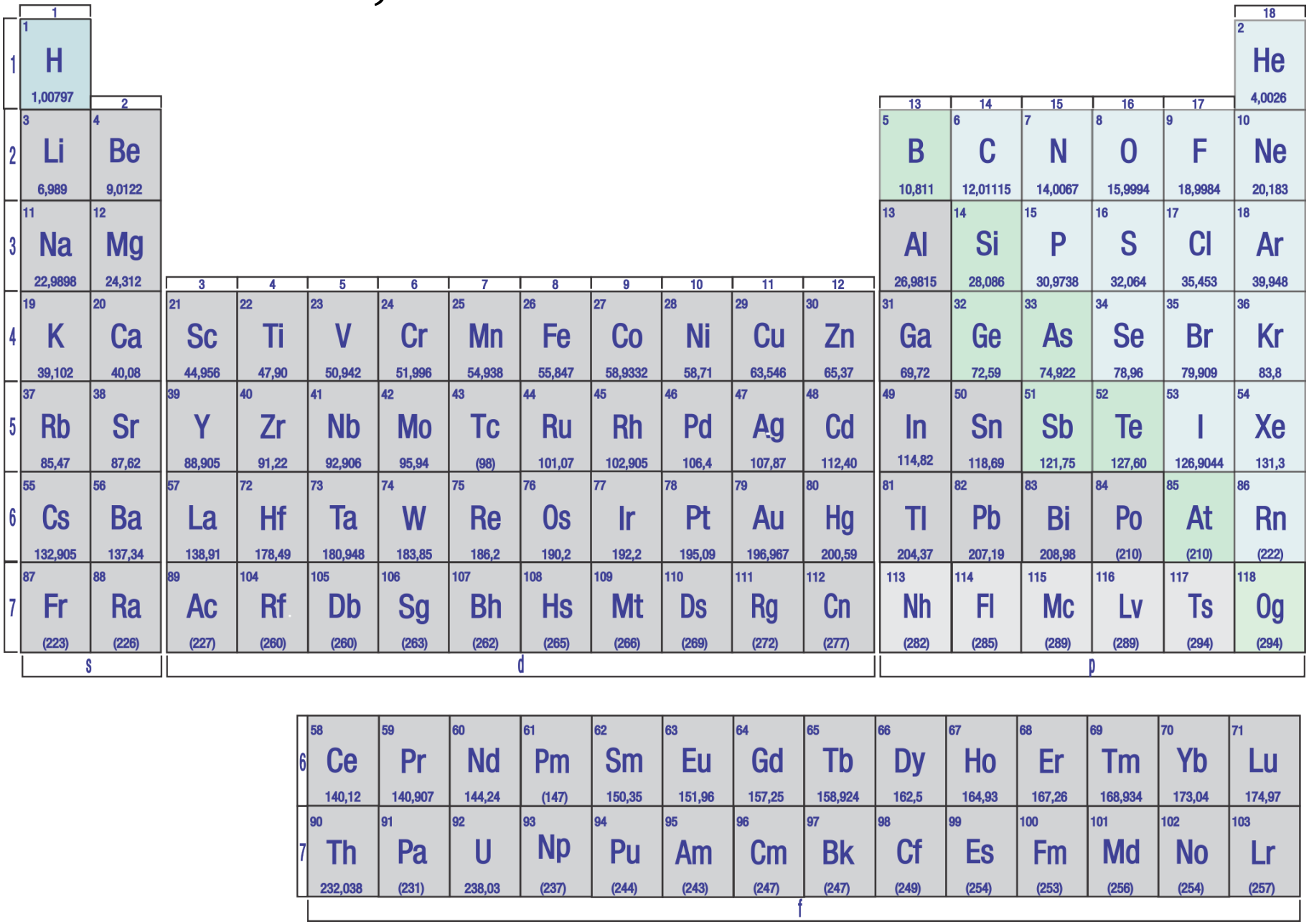
Periodic Trends In Atomic Properties

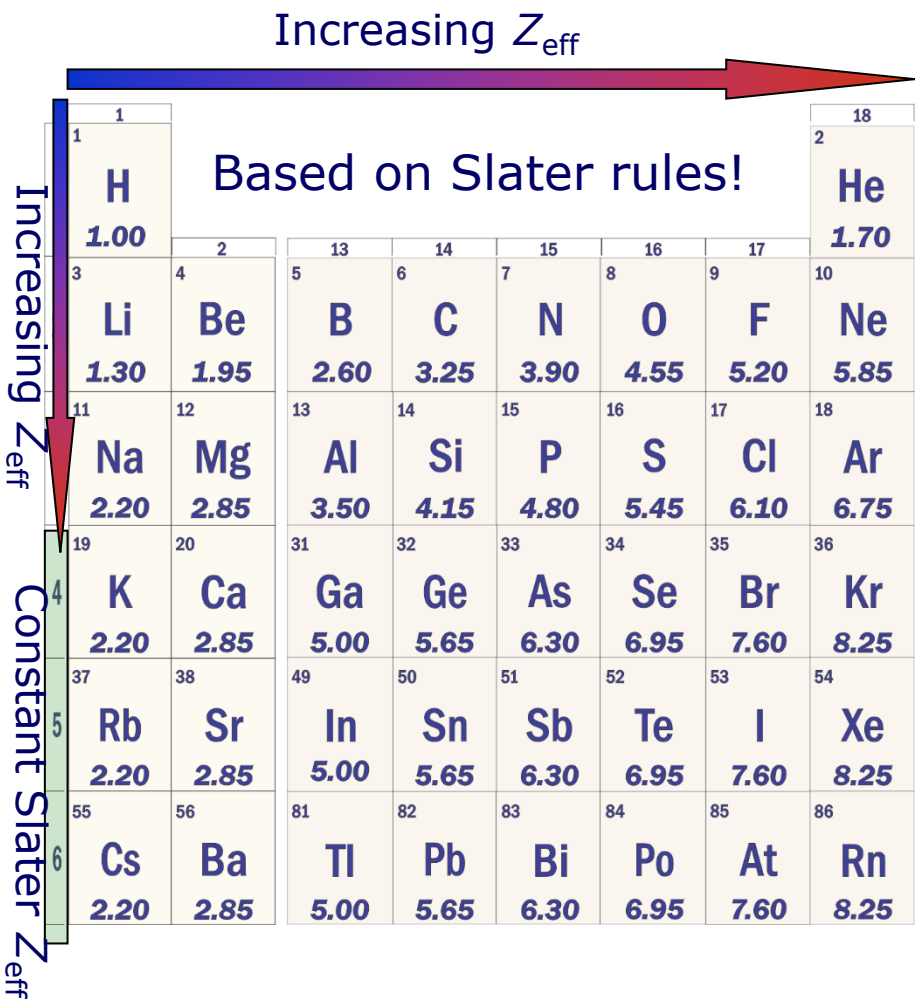
Trends in fundamental physical properties of atoms/elements

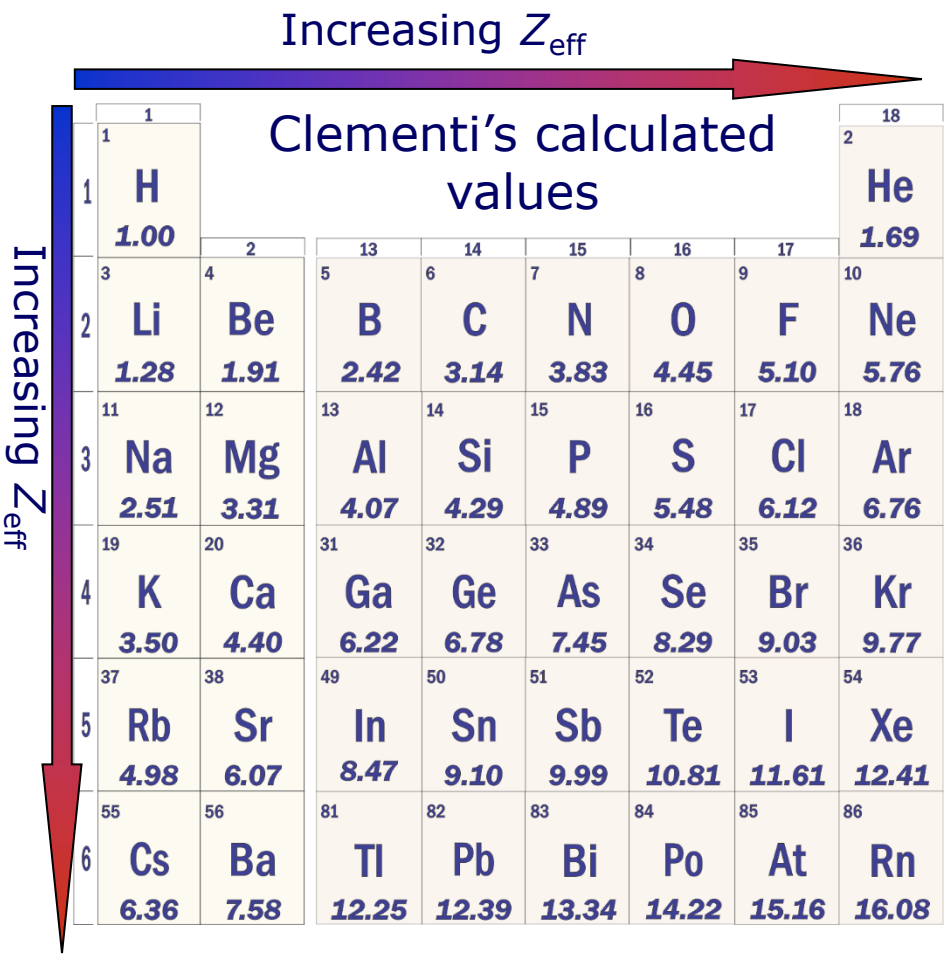


Metals, metalloids and non-metals



Atomic properties 1: Trends in Z_{eff}

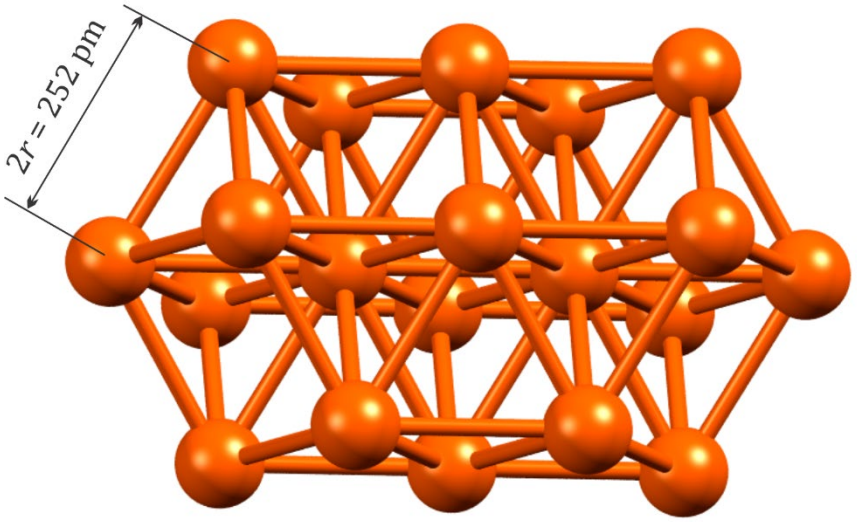




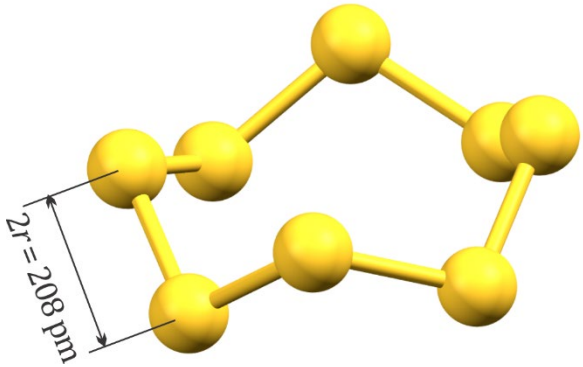
- **General Trend**: from left to right along the period and down a group, both nuclear and effective nuclear charge *increase*

Atomic Properties 2: Atomic radii

- How de we determine atomic radii? (Definition of atomic radii)



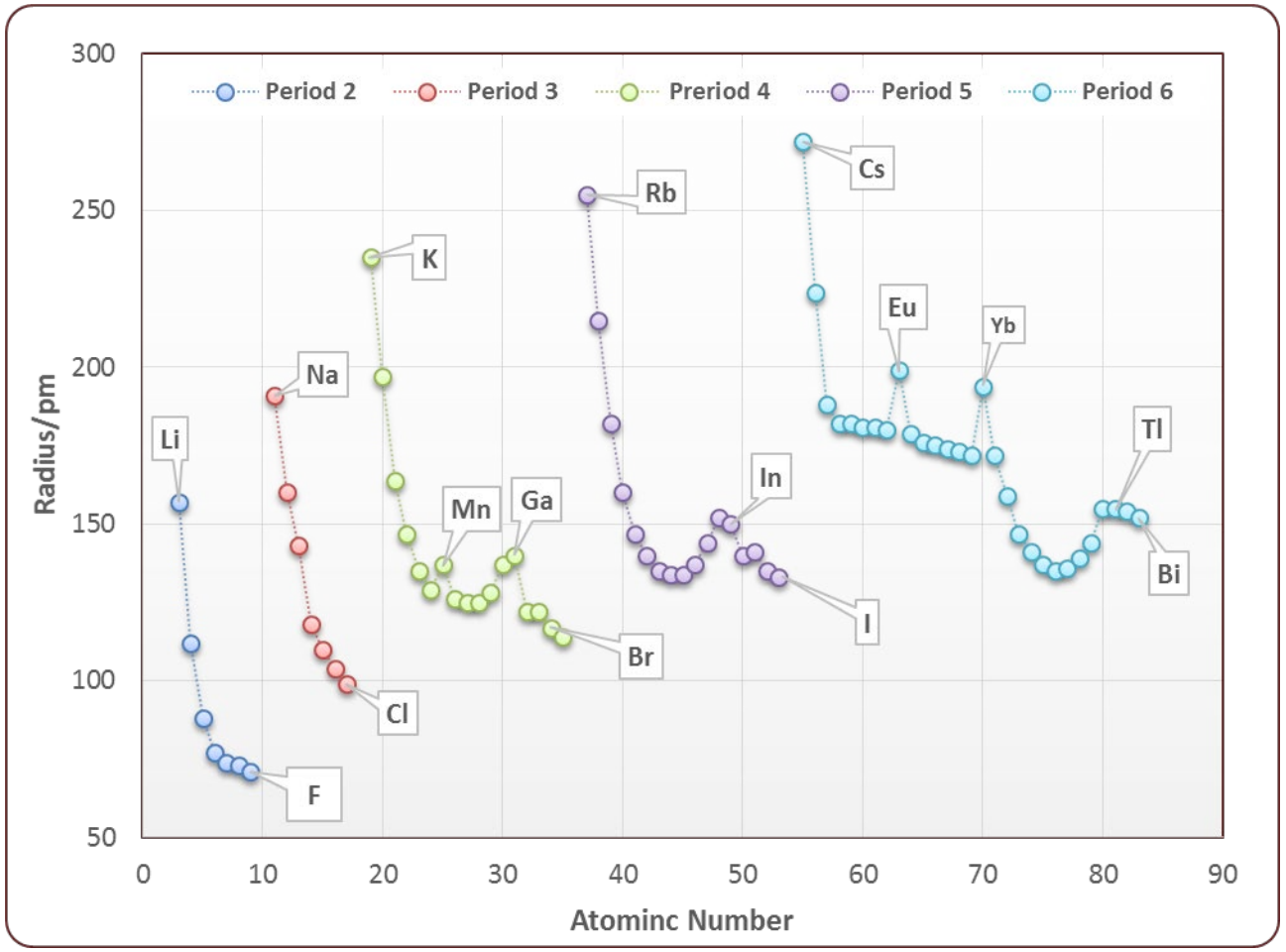
For metallic elements we use *the metallic radius*: half the experimentally determined distance between the centers of nearest neighbor atoms in the solid. Above is the structure of Fe with such a distance indicated.



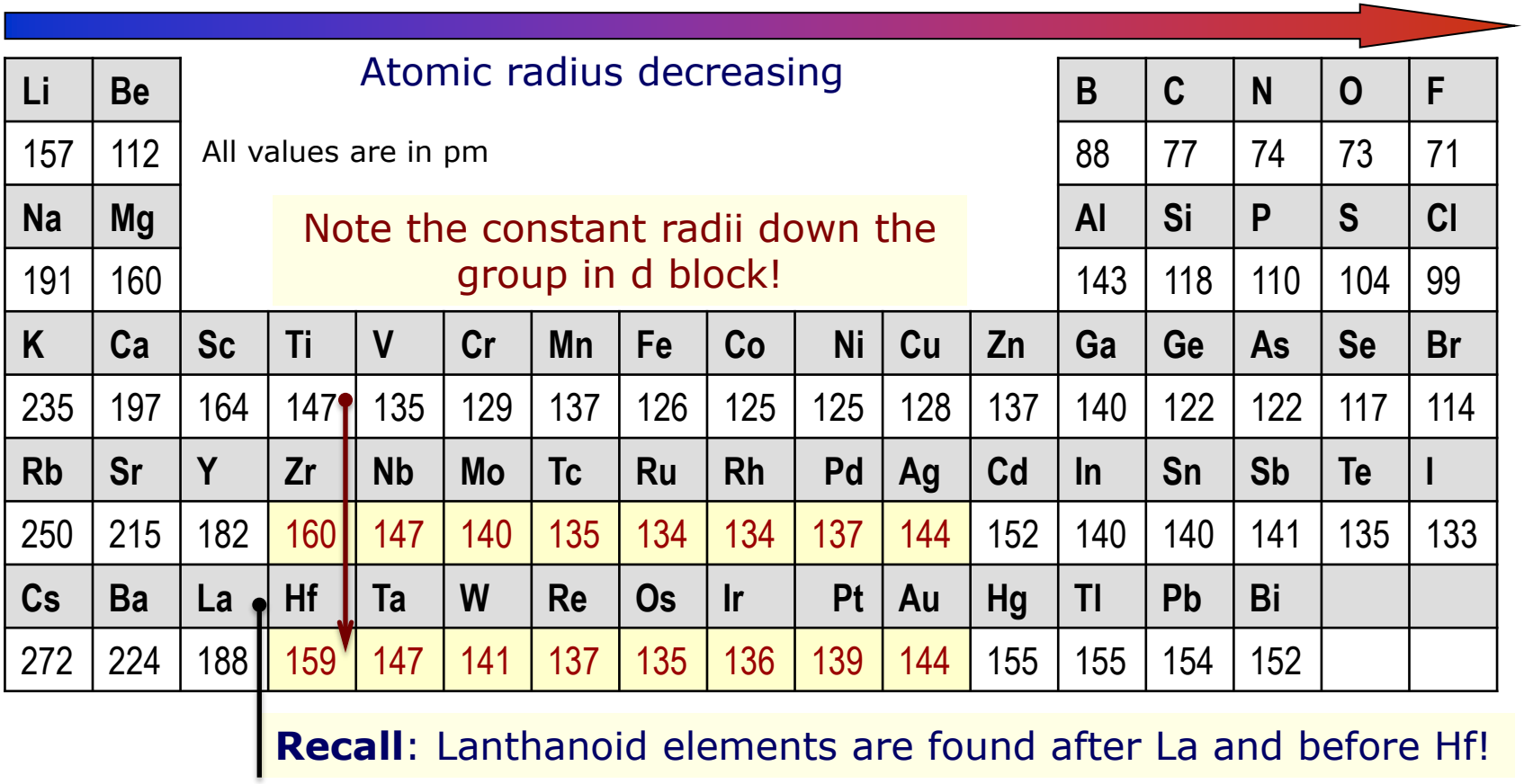
The *covalent radius* is used for non-metallic elements: half the internuclear distance between the covalently bonded atoms of the same element. Above is the structure of S_8 molecule with such a distance indicated.

Atomic properties 2: Trends in atomic radii

- **General Trend**: Atomic radii *increase* down a group and *decrease* from left to right along a period!



Atomic Radii: The Lanthanoid Contraction

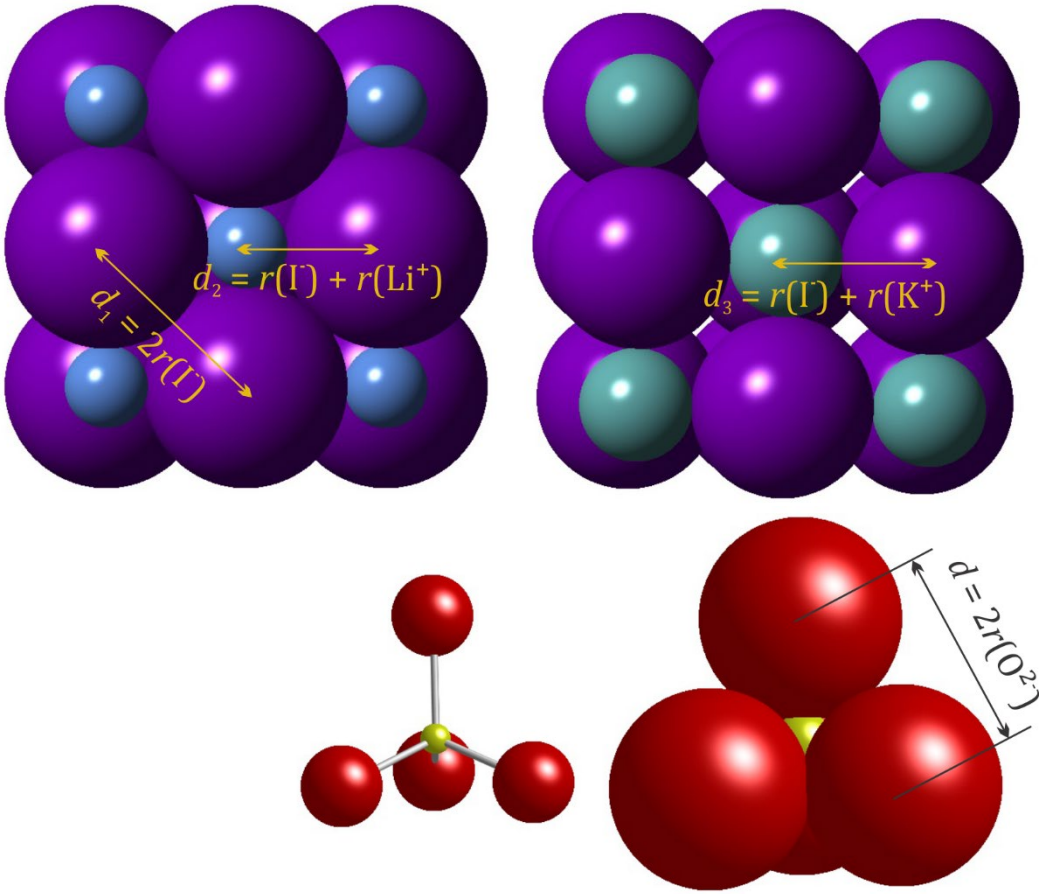


Li	Be											B	C	N	O	F
157	112											88	77	74	73	71
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	140	122	122	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	140	140	141	135	133
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	188	159	147	141	137	135	136	139	144	155	155	154	152		

- The 14 lanthanoids follow the trend: their size decreases from left to right, a trend that continues with Hf and the following elements, Lanthanoids fill weakly shielding f orbitals and Z_{eff} increases in their series!

Atomic properties 3: Ionic radii

- How de we determine ionic radii? (Definition of ionic radii)

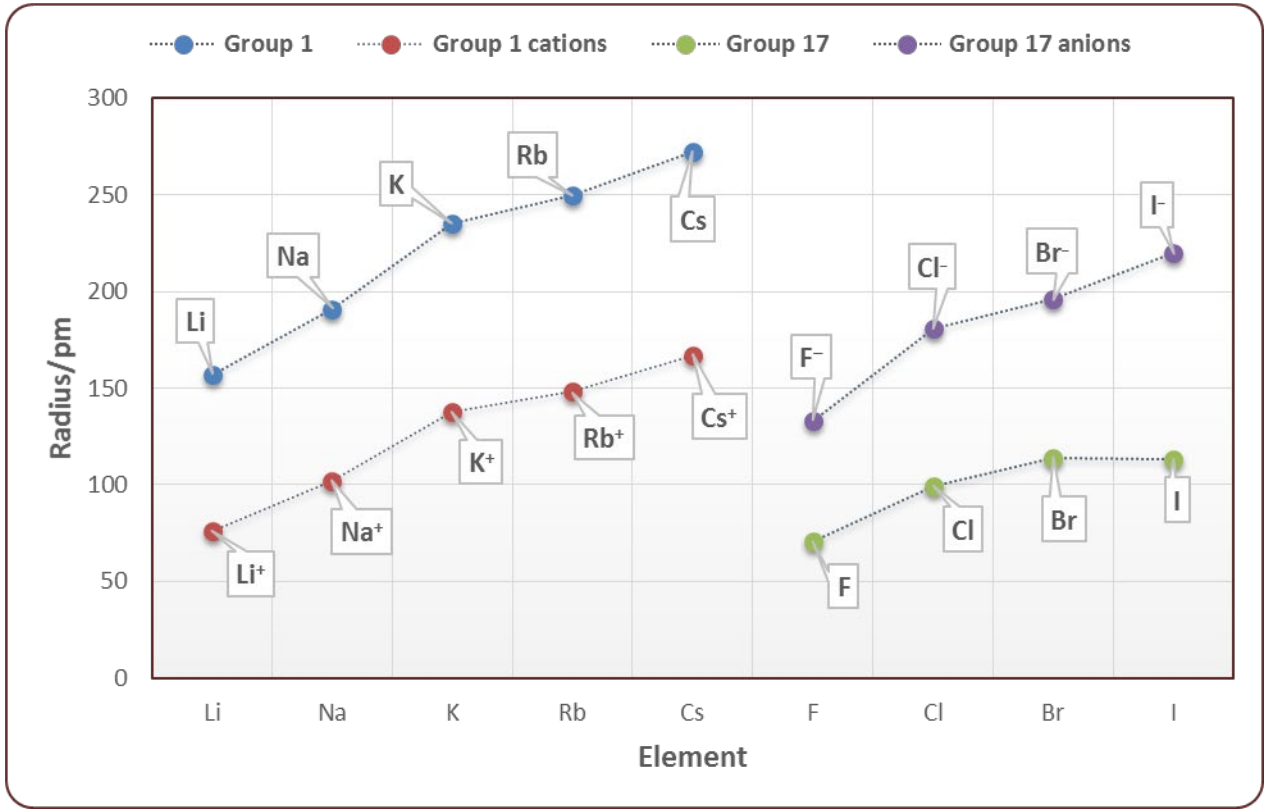


Ionic radii are calculated based on experimentally determined radii for anions. From these, the radii of cations can be determined as $r_+ = r_{total} - r_-$. For example, Lande's method assumes that anions are in contact when combined with small cations (LiI, as above). Other methods use oxide as a reference (as shown left using SiO_4^{4-} as example).

- All tabulated (or plotted) values of both atomic and ionic radii are average values of many measurements and calculations.

Atomic properties 3: Trends in ionic radii

- **General Trend**: Cations are smaller while anions are larger than their parent, neutral atoms!



A final note: Neither atoms or ions have a precise, finite radius.

Atomic Properties 4: Ionization energies

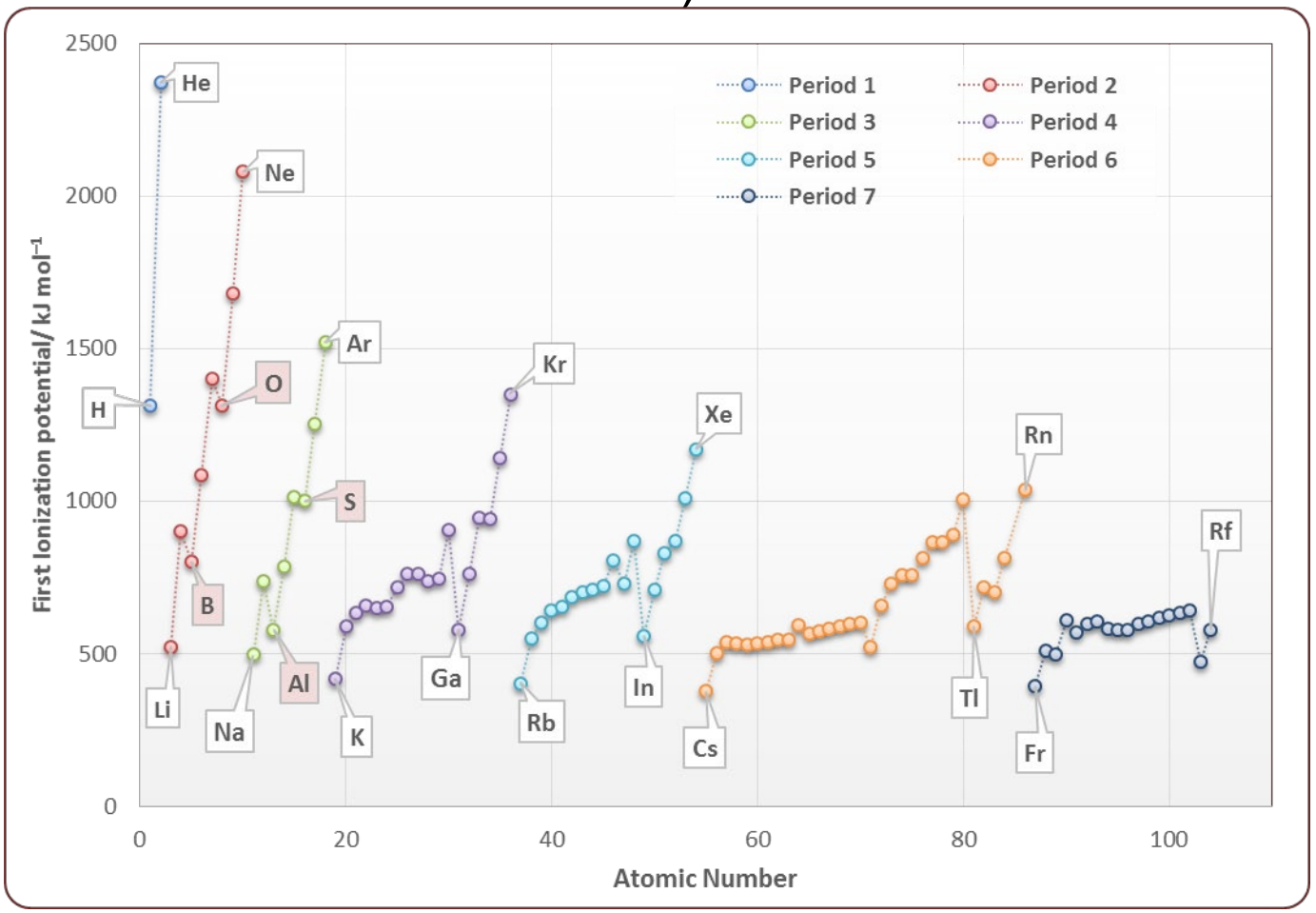
- The energy required to remove one electron from an atom in gas phase is called the *first ionization energy* (potential), I_1.
- Similarly, the energy required to remove one electron from a singly charged cation (M^+) in gas phase is called the *second ionization energy* (potential), I_2 etc.
- Usually given in electronvolts (1eV = 96.485 kJ/mol) at T=0 K
- The first ionization energy can be *approximated* from

$$I_1 = \frac{1312.1 kJ/mol \times Z_{eff}^2}{n^2}$$

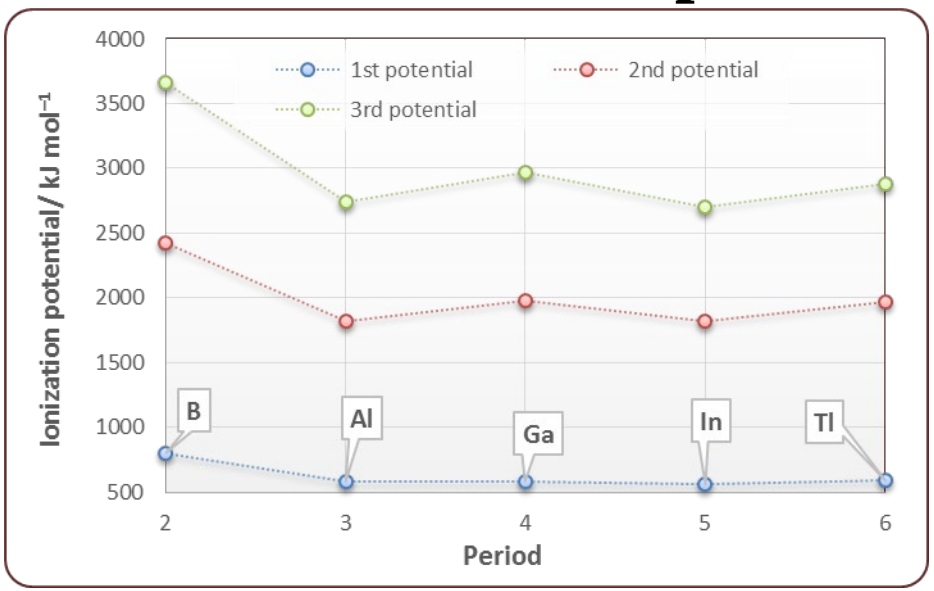
- Note that I_1 depends on *both* Z_{eff} and principal quantum number n
- We can also expect dependence of I on atomic and/or ionic radii: the smaller the radius, the stronger Coulombic attraction.

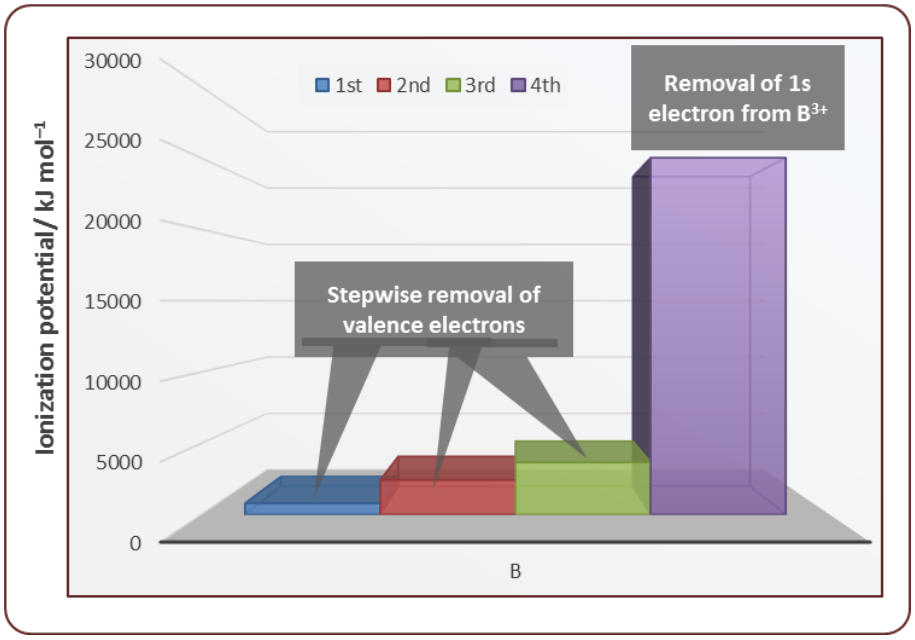
Atomic Properties 4: Trends in ionization energies (potentials)

- **General Trend**: I_1 *Increases* going from left to right in PTE but *decreases* going from top to bottom! (note important deviations from the trend marked in red!)



Atomic Properties 4: Trends in ionization energies (potentials) (cont.)





☞ Important trend: successive ionizations of an element require increasingly higher energies, i.e.:

$B(g) \rightarrow B(g)^+ ; I_1 = 799$ kJ/mol

$B(g)^+ \rightarrow B(g)^{2+} ; I_2 = 2427$ kJ/mol

$B(g)^{2+} \rightarrow B(g)^{3+} ; I_3 = 3660$ kJ/mol

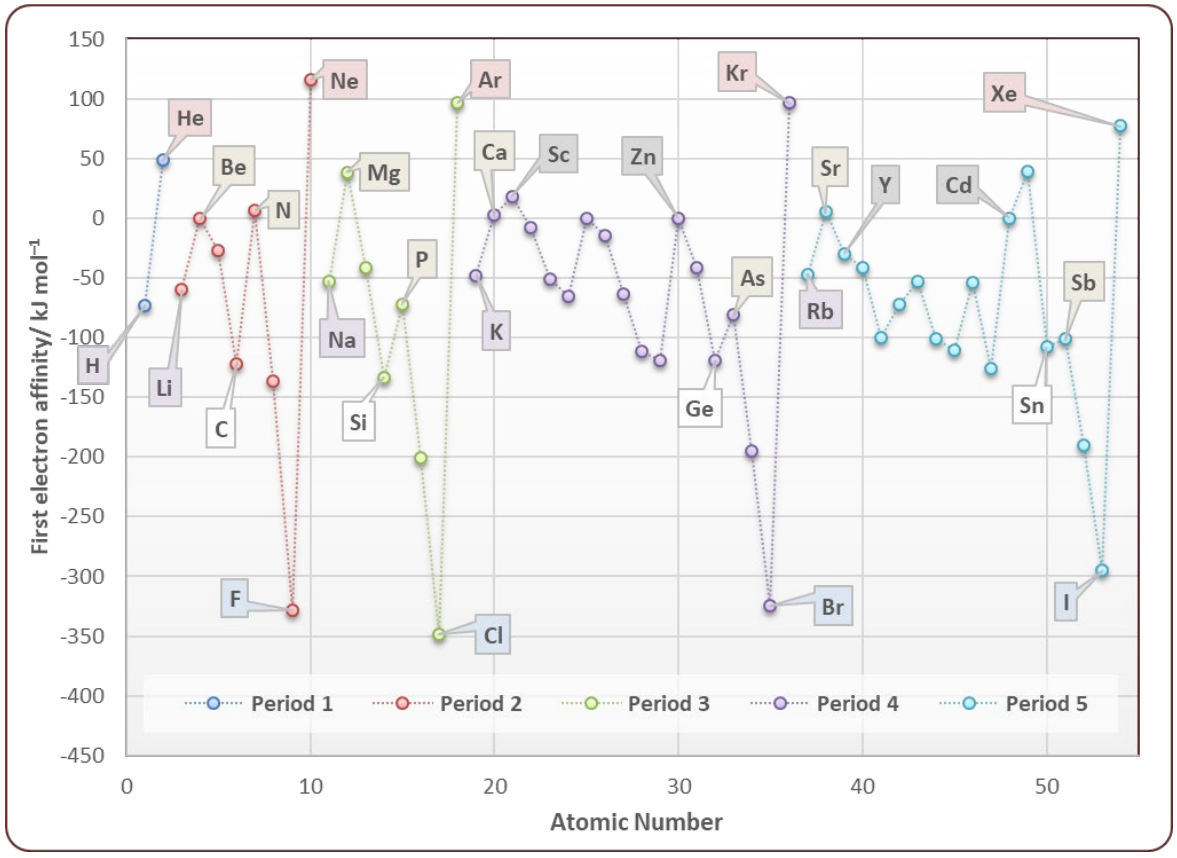
- Once the valence electrons have been removed, the ionization potential undergoes a massive increase

Atomic Properties 5: Electron Affinity

- The *electron affinity* (E_a) is energy change which occurs when an atom in gas phase gains one electron at T = 0 K

$$A(g) + e^- (g) \rightarrow A^- (g); \; E_a = E(A(g)) - E(A^-(g))$$

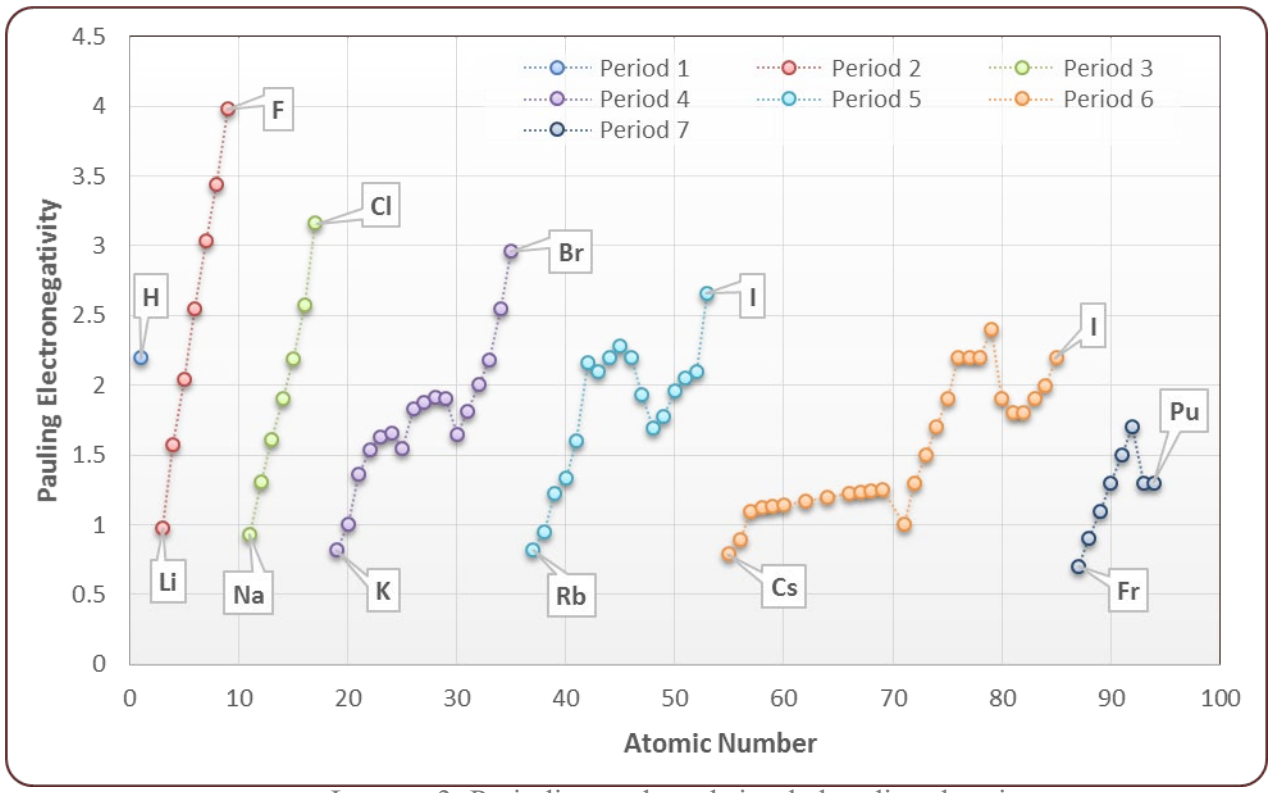
- The trends in E_a are not as clear as with I:



Atomic Properties 6: Electronegativity

- Electronegativity (χ) is the power of an atom of the element to attract electrons to itself when it is a part of a compound
- Three different definitions of electronegativity: **Pauling**, Miliken and Allerd- Rochow

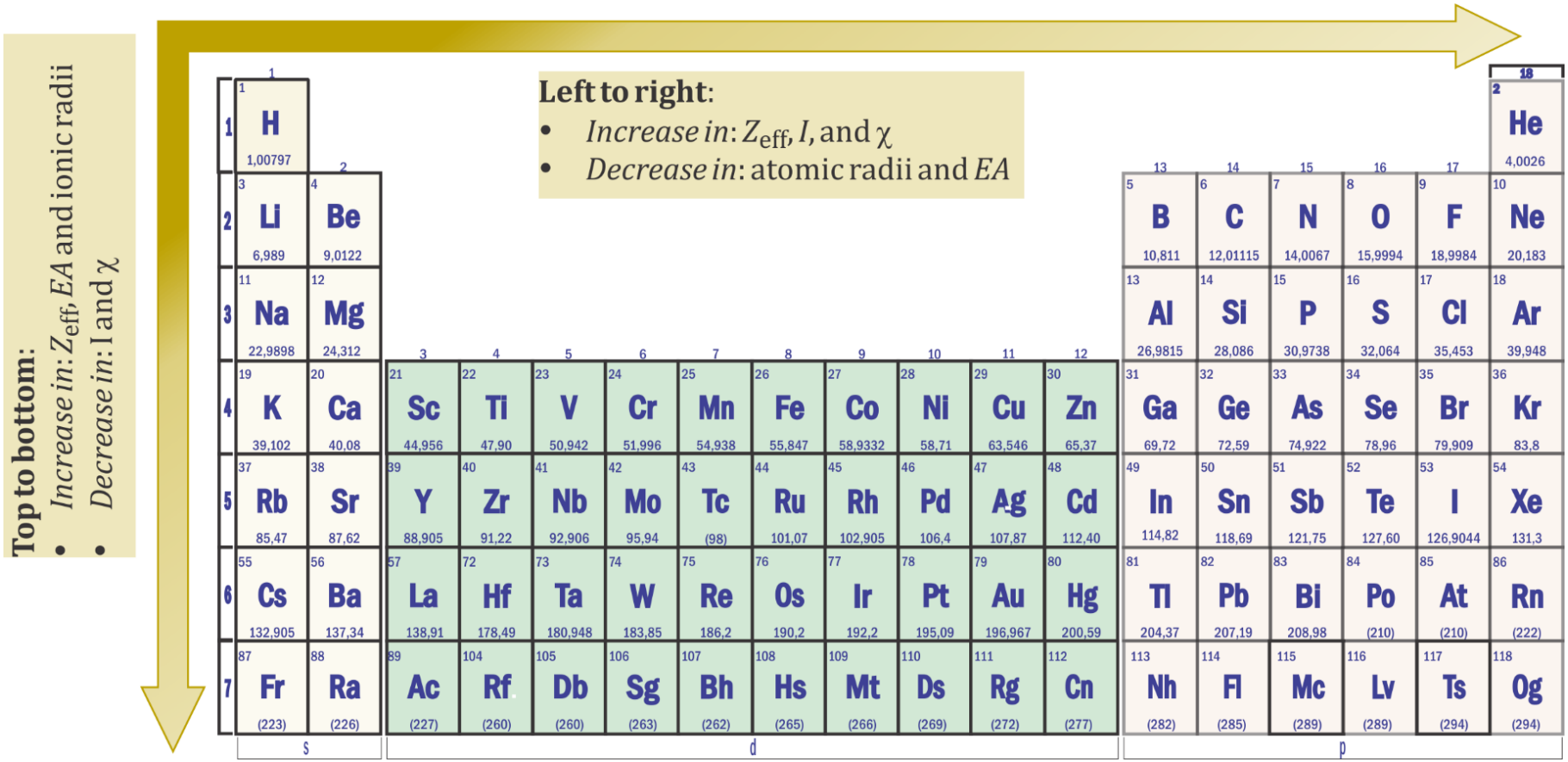
☞ The values differ but the trends are the same for all three: increase from left to right and decrease from top to bottom!



Atomic properties 7: Polarizability

- The **polarizability** (α) of an atom or an ion is its ability to be distorted by an electric field (for example the field of neighboring atom or ion)
- **Fajan's rules**:
  1. Small cations (i.e. Li^+) have polarizing ability (can deform the electronic clouds of other species)
  2. Large anions (I^-) are easily polarized (can be deformed)
  3. Cations that do not have a noble gas configuration (*d*- and *f*- block) are easily polarized
- For example, Li^+ has a higher polarizing ability compared to Cs^+, while I^- is easier to polarize than F^-

Overview of trends in atomic properties



Readings and problems

- ✓ **Readings**:
  - The same for both 6th and 7th edition of the textbook:
    - Remaining part of Chapter 1 from *Shriver's Inorganic Chemistry*
    - Recommended: chapter available on Quercus

- ✓ **Problems**:
- From the 6th edition:
  - Examples and Self-Tests 1.8 – 1.11
  - Exercises: 1.19 – 1.21
- From the 7th edition
  - Examples and Self-Tests: 1.9 – 1.12
  - Exercises: 1.19 – 1.21