IV. Trends in Atomic Properties

A. Effective Nuclear Charge (Z_{eff})

1. Approximately constant down a group, and approximately equal to the number of valence electrons

   eg Li vs. Na -- Na has 8 more protons, but also 8 more electrons ($2s^2 2p^6$) forming a shell of charge around the nucleus.

2. Increases from left to right across a period

   * Electrons do a poor job of shielding other electrons in the same shell

B. Atomic and Ionic Radii (average size)

$$r \sim \frac{n^2}{Z_{eff}}$$, where n and Z_{eff} refer to the valence (i.e. outermost) shell

1. Across a period, r decreases. (Why?)

2. Down a group, r increases. (Why?)

3. Ionic Radii Examples

$r(Ca) > r(Ca^{2+})$ (compare values of n)

$r(F) < r(F^-)$ (same Zeff plus extra repulsion btwn e^-'s)

$r(Fe^{3+}) < r(Fe^{2+})$ (ditto)

isoelectronic species: $r(F^-) > r(Na^+)$ (compare values of Zeff)

C. Ionization Energies (IE's)

$M_{(g)} \rightarrow M^+_{(g)} + e^- \quad \Delta E_{rxn} \equiv IE_1(M)$

$M^+_{(g)} \rightarrow M^{2+}_{(g)} + e^- \quad \Delta E_{rxn} \equiv IE_2(M)$, etc.

$IE \sim \frac{Z_{eff}^2}{n^2}$ (again, the Zeff and n for the outermost electron(s))

1. Across a period...
   a. IE usually increases...
   b. ...but pairing penalty destabilizes Group 6 (16)
   c. Also remember the unexpectedly high stability of filled and half-filled subshells

2. Down a group, IE decreases

D. Electron Affinities (EA's)

$X_{(g)} + e^- \rightarrow X^-_{(g)}$ $\quad EA \equiv -\Delta E_{rxn}$
(Atkins' convention)

* very rough trends *

1. Down a group, EA decreases (since r increases)

2. Highest for Group 7/17 (give me a full shell!)

3. Second-highest for Group 6/16 (ditto!)

4. Negative EA's for Group 2 and Group 8/18