Comparison of Hartree-Fock Results with Other Observables

Another meaningful link of the orbital energies, ε_I to physical properties is to the ionization energy.

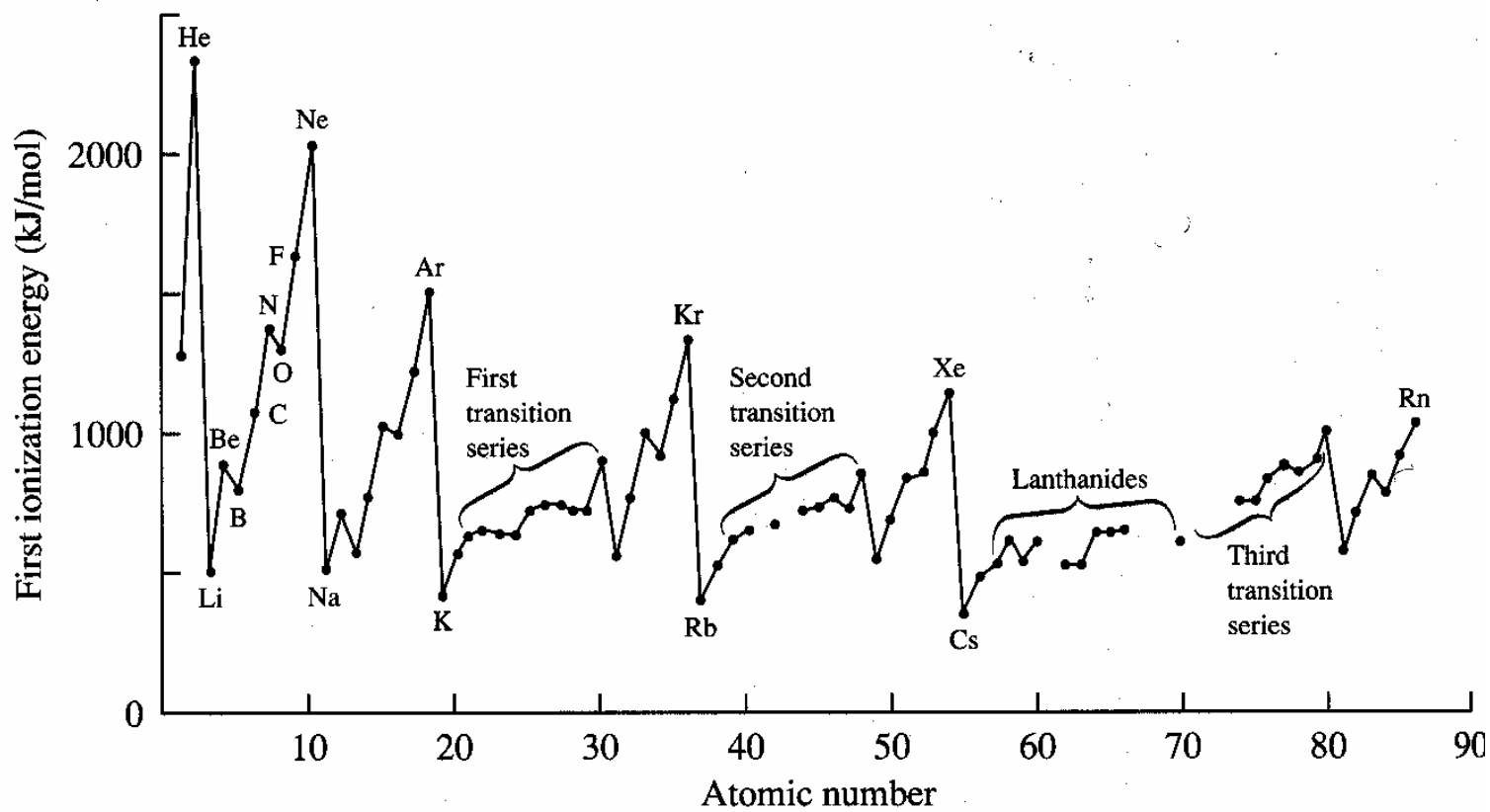To a reasonable approximation
ε_I for the highest occupied orbital $\cong$ the first ionization energy

For example, for the first ionization energy for F, $\Delta \sim 15\%$.
Calculation versus experimental = 19.95 eV : 17.42 eV

Koopmans' theorem

By analogy, ε_I **for the lowest unoccupied orbital $\cong$ the electron affinity**

However, the Hartree–Fock limit results in much less accurate electron affinity e.g., Hartree Fock results in a negative value for the electron affinity for F, meaning F^- is less stable than F, contrary to experiments.

A better estimate of the electron affinity of F:

$$\text{the electron affinity} \cong E_{total} \text{ of } F - E_{total} \text{ of } F^-$$

Results give an electron affinity of F = .22 V, better, but still short of the experimental value of 3.34V

More accurate calculations need to include **electron correlation**
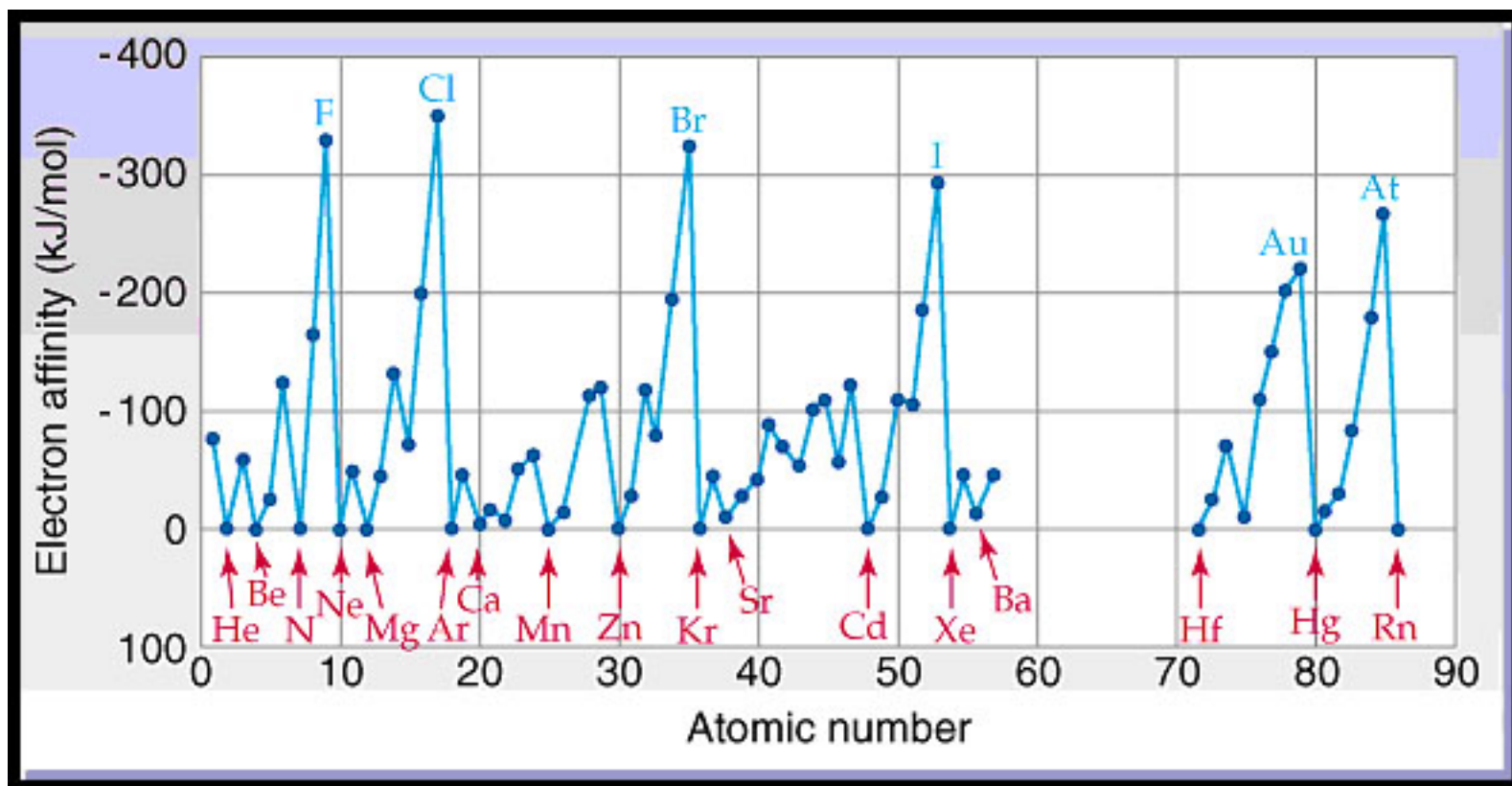
Atomic Sizes and Radii

There is no one way to define the 'size' of an atom, like we can define the size of a billard ball. i.e. there is no single quantum mechanical operator that defines the atomic size.
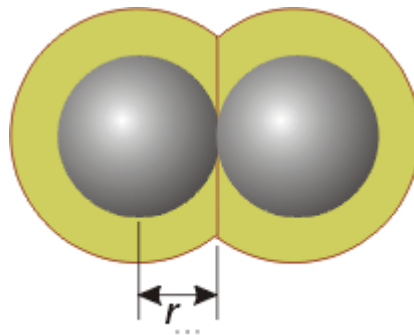
Perhaps the best approach is to choose a method which suites the information that you need. In this course this might include:

- Single–bond covalent radii – radii assigned within a covalent bonding situation.

- Ionic radii – radii assigned to ions of the elements in predominantly ionic compounds

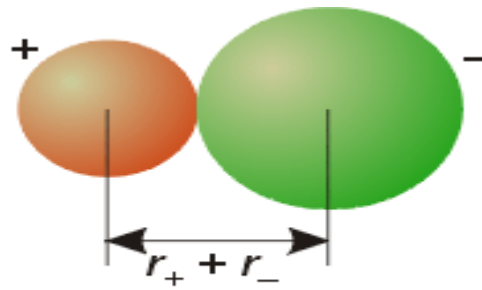- Metallic or van der Waals radii – non–bonded contact distances.
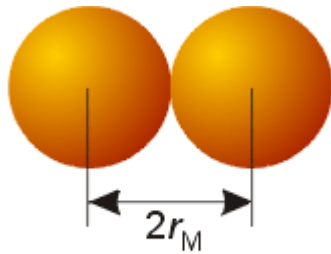
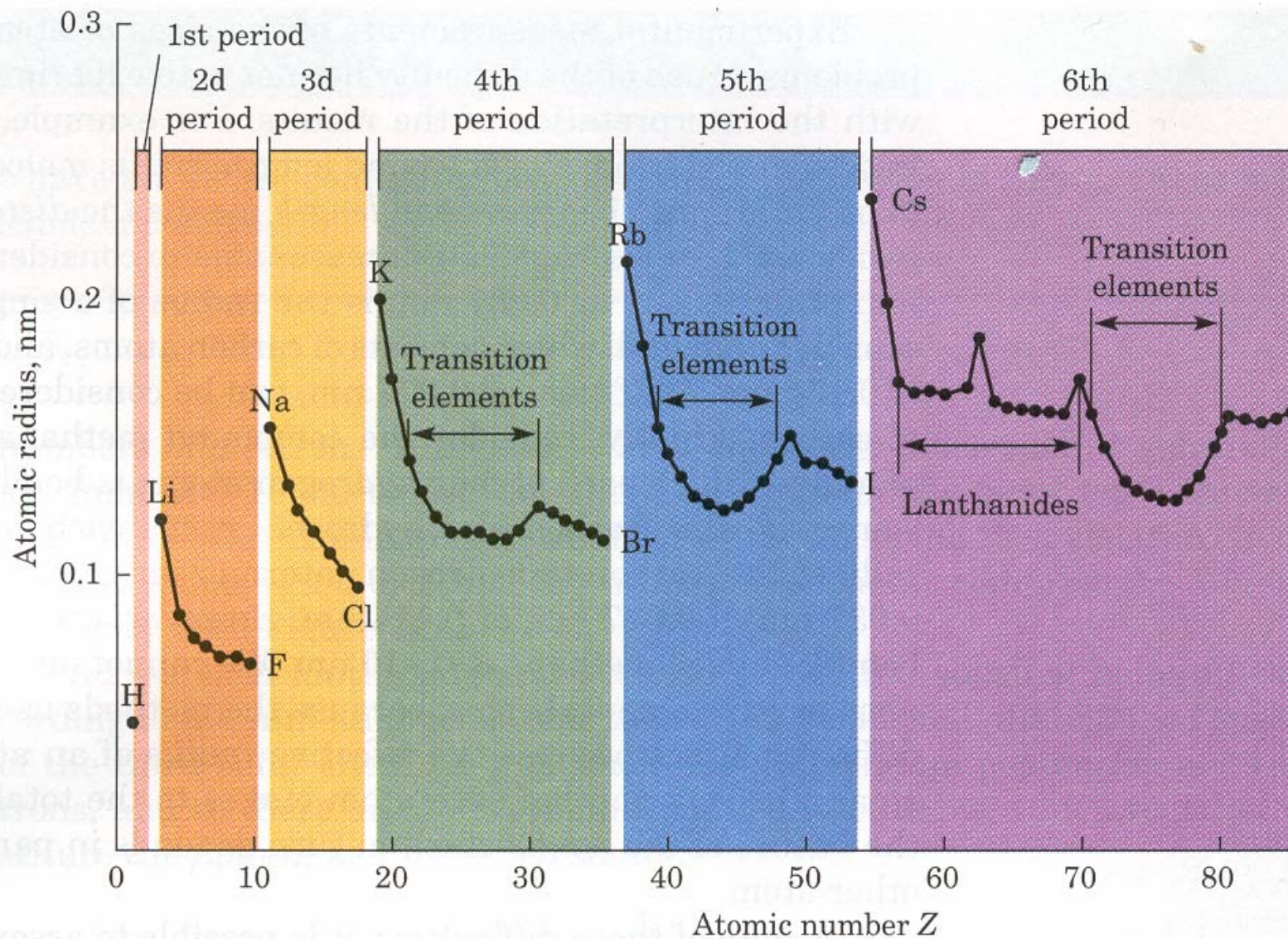Could also be taken as van der Waals radius

1 Metallic radius

$2r_M$

2 Covalent radius

$r_{...}$

3 Ionic radius

$r_+ + r_-$

\+ −

Relative atomic radii in pm

H
37

Li   Be
152   111

B   C   N   O   F
80   77   74   74   71

Na   Mg
186   160

Al   Si   P   S   Cl
143   118   110   103   99

K   Ca   Sc   Ti   V   Cr   Mn   Fe   Co   Ni   Cu   Zn   Ga   Ge   As   Se   Br
227   197   161   145   131   125   137   124   125   125   128   133   122   123   125   116   114

Rb   Sr   Y   Zr   Nb   Mo   Tc   Ru   Rh   Pd   Ag   Cd   In   Sn   Sb   Te   I
248   215   178   159   143   136   135   133   135   138   145   149   163   141   145   143   133

Cs   Ba   Lu   Hf   Ta   W   Re   Os   Ir   Pt   Au   Hg   Tl   Pb   Bi   Po
265   217   172   156   143   137   137   134   136   139   144   150   170   175   155   118

La   Ce   Pr   Nd   Pm   Sm   Eu   Gd   Tb   Dy   Ho   Er   Tm   Yb
187   183   182   181   181   180   199   179   176   175   174   173   173   194

Ac   Th   Pa   U   Pu   Am
188   180   161   139   151   131

Dmitri Mendeleev: devised
the Periodic Table

Consequences of Neglecting Electron Correlation

Hartree-Fock calculations neglect electron correlation. Therefore, the calculated total energy is larger than the true energy by an amount called the correlation energy

The correlation energy for He = 110 kJ·mol^{-1}.

It increase roughly linearly with the # of electron pairs in the atom

It is a small percentage of the total energy of the atom (~ 1.4% for He)
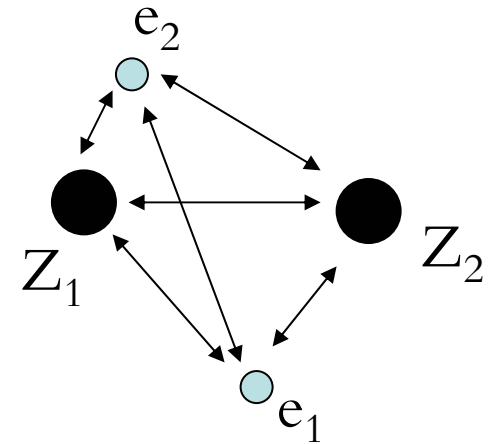However, it can present a problem if we want to apply the Hartree-Fock calculations to chemical problems. In chemical reactions, we are more interested in the difference in the Gibbs energy and enthalpy, not in the total energy, of the reactants and products. The change in the energy in chemical reactions are on the order of 110 kJ·mol^{-1}

However, the error is often similar for the reactants and products, so it cancels out and the effect is less significant than might be expected

Over the years, it has made possible to make corrections for the electron correlation This has made it possible to calculate thermodynamic functions, activation energies for reactions, phase diagrams, etc., for which experimental data are difficult to obtain.

The Molecular Hamiltonian

The full non-relativistic Hamiltonian for a molecular system made up of n_e electrons and N_N nuclei is given by:

$$\hat{H} = -\sum_{I=1}^{N_N} \frac{\hbar^2}{2M_I} \nabla(I)^2 - \sum_{i=1}^{n_e} \frac{\hbar^2}{2m_e} \nabla(i)^2 - \sum_{I=1}^{N_N} \sum_{i=1}^{n_e} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n_e-1} \sum_{j=i+1}^{n_e} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N_N-1} \sum_{J=I+1}^{N_N} \frac{Z_I Z_J e^2}{R_{IJ}}$$

KE of nuclei   KE of e⁻s   e⁻–nuclear attraction   e⁻–e⁻ repulsion   nuclear–nuclear repulsion

Notes on Labeling Conventions (used here but not necessarily by all others)

nuclear coordinates, indices referred to with capital letters, I, J, N_N, R_{IJ}

electron coordinates, indices referred to with lowercase letters, i, j, n_e, r_{ij}

The zero for the potential energy is the state where all electrons and nuclei are an infinite distance apart.