Important Factoids in Understanding Effective Nuclear Charge

- To understand the concept of effective nuclear charge, we focus on one electron (usually a valence or outer electron) and consider the forces the other charged particles exert on this electron.
- In an atom with more than one electron, each electron will 'feel' both attractive forces from the positive nucleus and repulsive forces from the other electrons.
- Qualitatively, Z_{eff} is the NET (or effective) ATTRACTIVE charge that the electron 'feels', taking into account both the attractive and repulsive forces.
- The attractive part of Z_{eff} is just Z, the positive charge on the nucleus 'pulling' on the electron (i.e. the atomic number)
- The repulsive part, repulsion from the other electrons, is referred to as 'shielding'. It gets this designation because an electron is 'shielded' from the pull of the positive nucleus by the repulsion of the other electrons. To provide shielding an electron must have its probability density closer to the nucleus than the outer electron (and thus partially neutralize the + nuclear charge).
- **Thus $Z_{effective}$=+Z -(shielding of other electrons)**
  [note the + sign for the attractive part and –sign for the repulsive part]
  MORE SHIELDING ⇔ LOWER Z_{eff}
  LESS SHIELDING ⇔ HIGHER Z_{eff}
- In terms of Z_{eff} and the principal quantum number n of the outer electron, the ionization energy and size of an atom can be approximated as:

$$E_{n,Zeff} \approx -\left(2.18\times10^{-18}\,J\right)\frac{Z_{eff}^{\;2}}{n^2} \quad and \quad IE \approx \left(2.18\times10^{-18}\,J\right)\frac{Z_{eff}^{\;2}}{n^2} \quad and \quad r_{avg} \approx \left(5.28\times10^{-11}\,m\right)\frac{n^2}{Z_{eff}}$$

- An approximate Z_{eff} can be obtained empirically from experimental ionization energies:

$$Z_{eff} \approx \left[\frac{n^2\left(IE\right)_{\text{experimental}}}{2.18\times10^{-18}\,J}\right]^{1/2}$$

- The lecture will discuss:
  - ✓ For 1-electron atoms or ions [H, He^+, Li^{2+}, Be^{3+}, etc.] there is no shielding and **Z_{eff}≡Z** [Z=+1, +2, +3, +4, etc.]
  - ✓ For He $1s^2$ the second electron (in the same 1s shell) provides 0.66 shielding *[reduces the pull of the nucleus from Z= +2 to $Z_{eff}\approx1.34$]*
  - ✓ For Li $1s^22s$ each of the two 1s electrons provides 0.84 shielding for the outer 2s electron *[the two reduce the pull of the nucleus from Z=+3 to $Z_{eff}\approx3-2\times0.87=1.26$. **NOTE** an inner shell 1s electron in Li provides more shielding (0.87) than the same shell 1s electron in He (0.66)]*
  - ✓ In B, $1s^22s^22p$ $(Z_{eff})2s > (Z_{eff})2p$
    WHY? Because the 2s orbital with its radial node has a inner peak of electron density that partially **penetrates** the shielding of the $1s^2$ electrons. The 2p orbital does not have this inner peak and thus has greater shielding from $1s^2$ electrons (lower Z_{eff} for 2p).

THIS LEADS TO THE IMPORTANT RESULT: $E_{2s} < E_{2p}$!!
more penetration ⟹ less shielding ⟹ larger Z_{eff} ⟹lower Energy

✓ Similarly for 3s, 3p, 3d orbitals, the 3s (2 radial nodes) has 2 inner peaks of electron density-MOST PENETRATION OF INNER SHIELDING ELECTRONS, the 3p (1 radial node) has 1 inner peak- INTERMEDIATE PENETRATION, and 3d (0 radial nodes) no inner peaks- LEAST PENETRATION
more penetration ⟹ less shielding ⟹ larger Z_{eff} ⟹lower Energy
THUS: $(Z_{eff})3s > (Z_{eff})\ 3p > (Z_{eff})3d$
AND $E_{3s} < E_{3p} < E_{3d}$