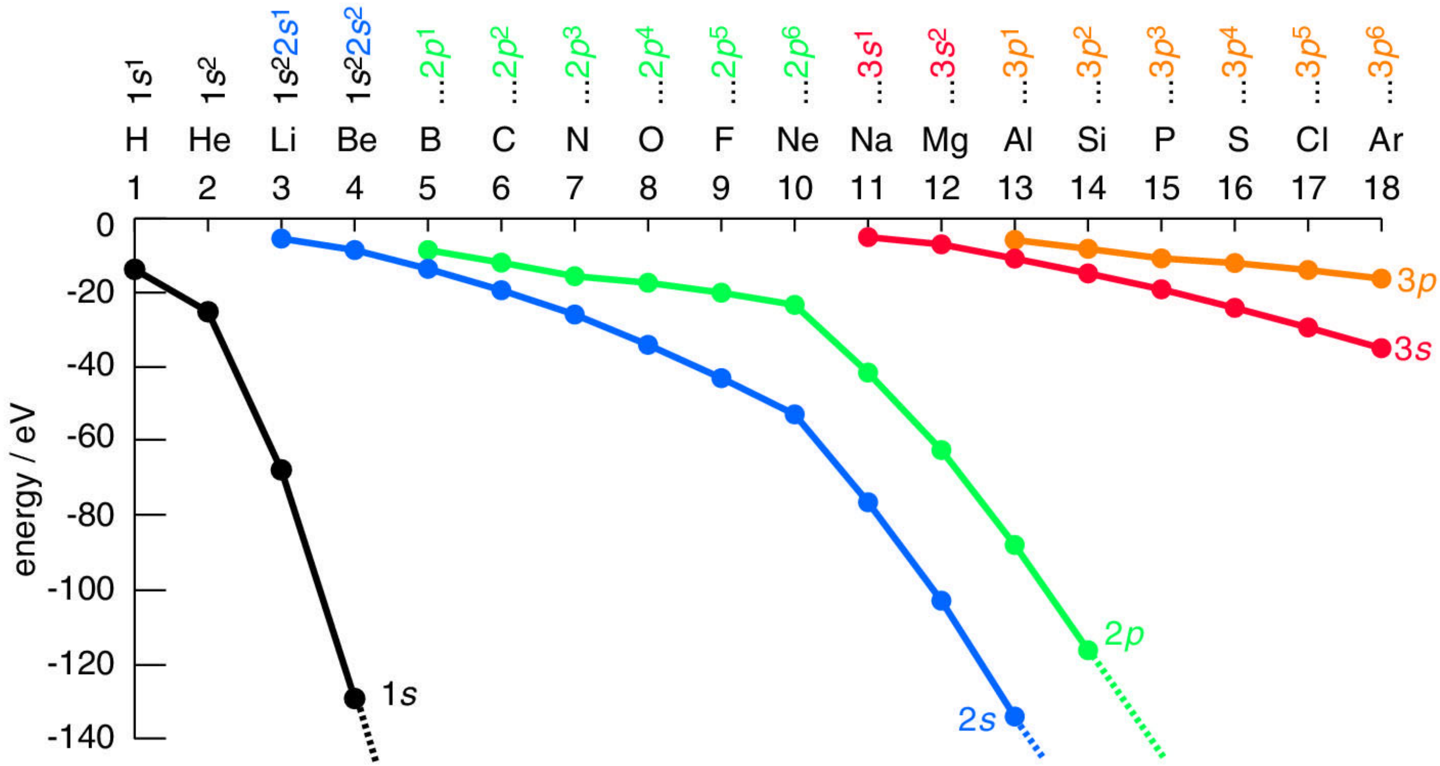
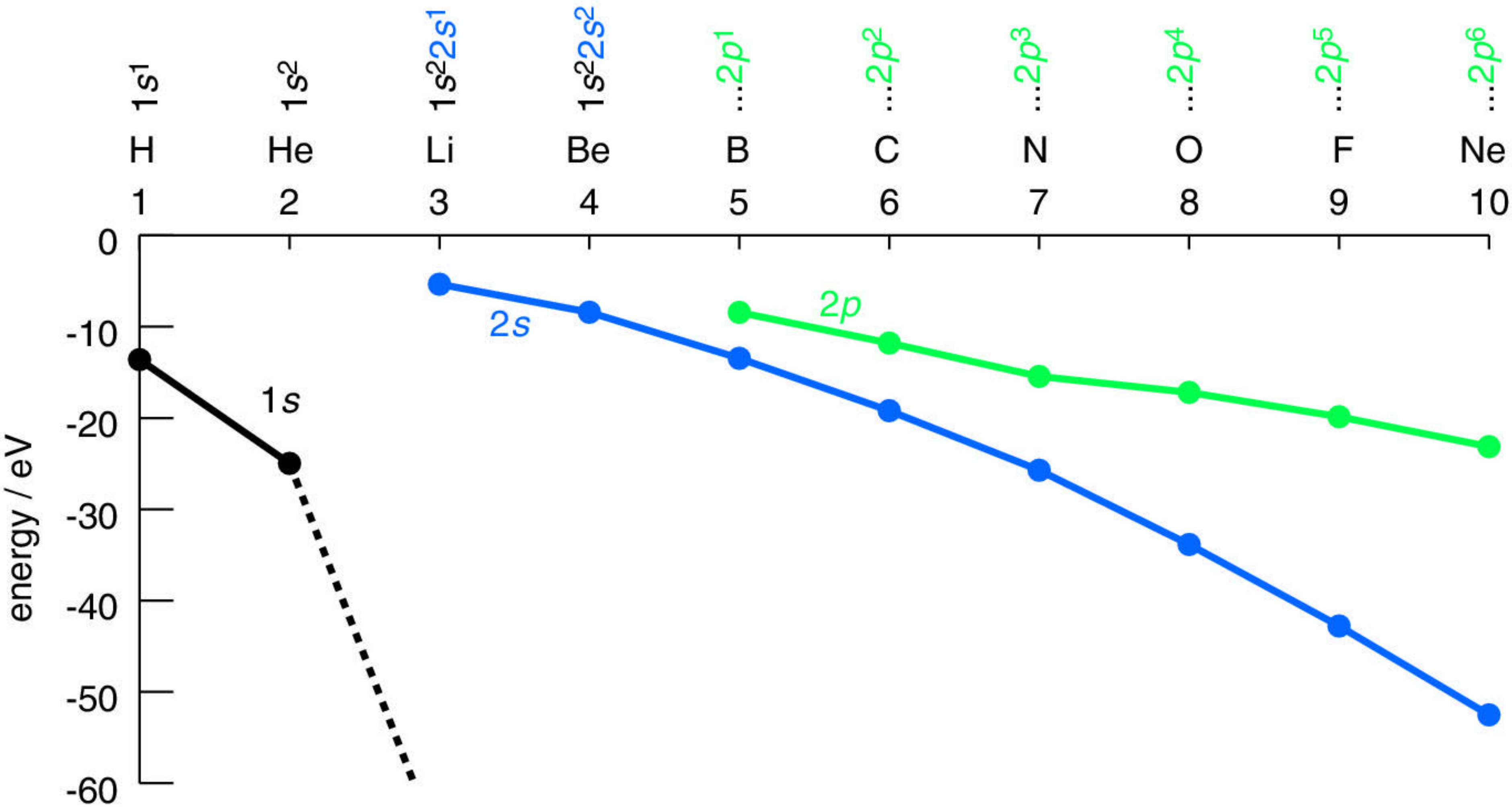
Orbital Energy: Trends, Degeneracies



- The 2s has lower energy than 2p and hence it is filled up first
- Although an orbital in a multi-electron atom is the wave function of one electron, its energy is influenced by all the other electrons due to the electron-electron repulsion energy



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Understanding Screening/Sheilding

$$E_n = -\frac{Z^2 R_H}{n^2}$$

$He \Rightarrow 2e^-$

$1s$

Case I

$Z = +2$ · e#2 · e#1

$\Rightarrow$ Energy of e#1

charge e#1 will encounter will be +1 since one +1 charge will be neutralized by e#2

$$E(e\#1) = -\frac{1^2 R_H}{1^2} = -13.6\,eV$$

Case II

· e#2

$Z = +2$ · e#1

$\Rightarrow$ e#1 will encounter charge of +2

$$E(e\#1) = -\frac{2^2 R_H}{1^2} = -54.4\,eV$$

True energy of e#1 will be between the two extremes $\Rightarrow -24.5\,eV$ actual value

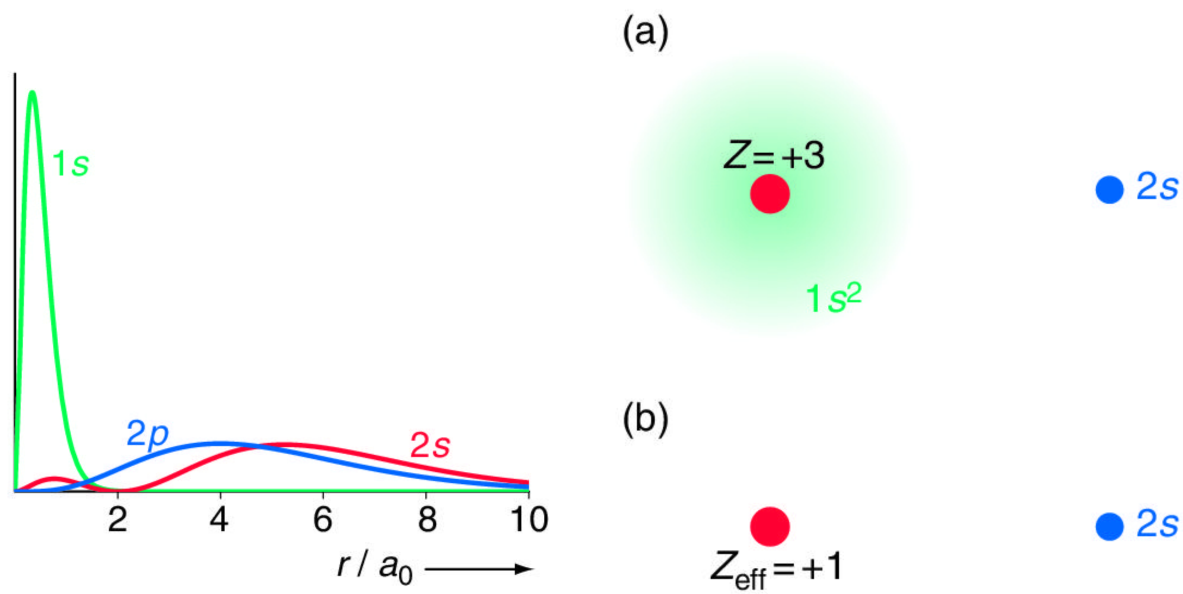
$$E_n = -\frac{Z_{eff}^2 R_H}{n^2}$$

Effective Nuclear Charges: Z_{eff}

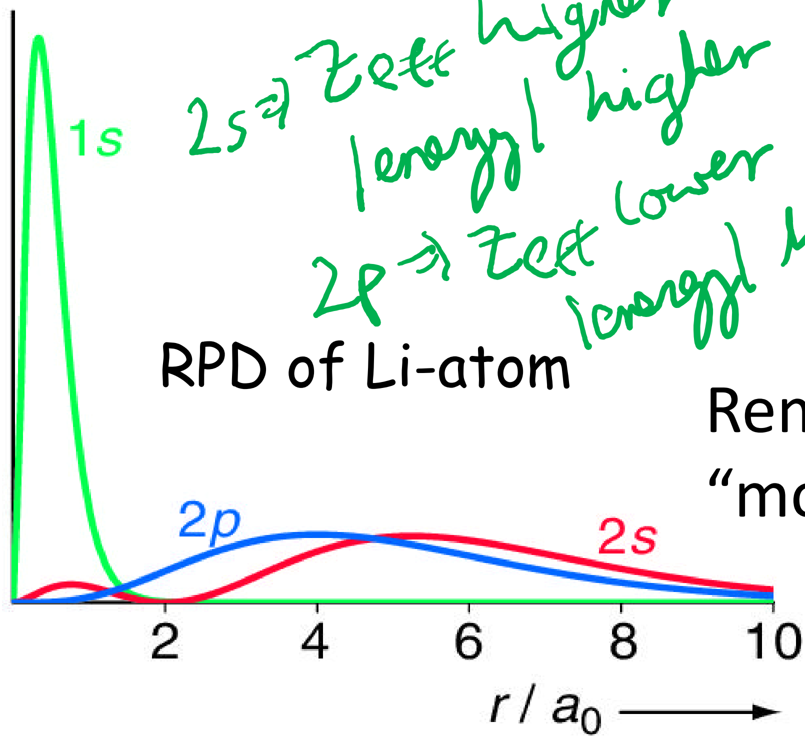
One useful way to quantify the extent of screening/shielding is to use the effective nuclear charge Z_{eff} (we just change Z to Z_{eff})

$$E_n = -\frac{Z_{eff}^2 R_H}{n^2}$$

$$Z_{eff} = \sqrt{-\frac{n^2\ E_n}{R_H}}$$



- For energy of the electron in 2s orbital of Li (Z=3), the Z_{eff} will 1.23 from the given equation (binding energy is -5.34 eV)
- This shows that the screening is not perfect: the 2 electrons in 1s has not been able to completely screen 2s



2s ⇒ Z_{eff} higher
|energy| higher
2p ⇒ Z_{eff} lower
|energy| lower

Penetration

Remember: 1s electron
"more penetrating than 2s"

E
0
— 2p −11
— 2s −13

|Energy| 2s > |Energy| 2p
But in absolute values
2s lower energy than 2p

- Most of electron density of 2s and 2p orbitals is outside the region occupied by 1s
- However small amount to 2s and 2p electron density appears under 1s
- For 2s, the subsidiary maximum of 2s (at $r = 0.7a_0$) is mostly inside the region occupied by 1s, whereas for 2p only the tail of the RDP is inside
- The 2s has more possibility of being inside the 1s screen and on average experiences a greater effective nuclear charge
- Overall energy of 2s is lower than 2p

He 1s ⇒ −24.5eV

Ionization Energies

$$A(g) \longrightarrow A^{+}(g) + e^{-}.$$

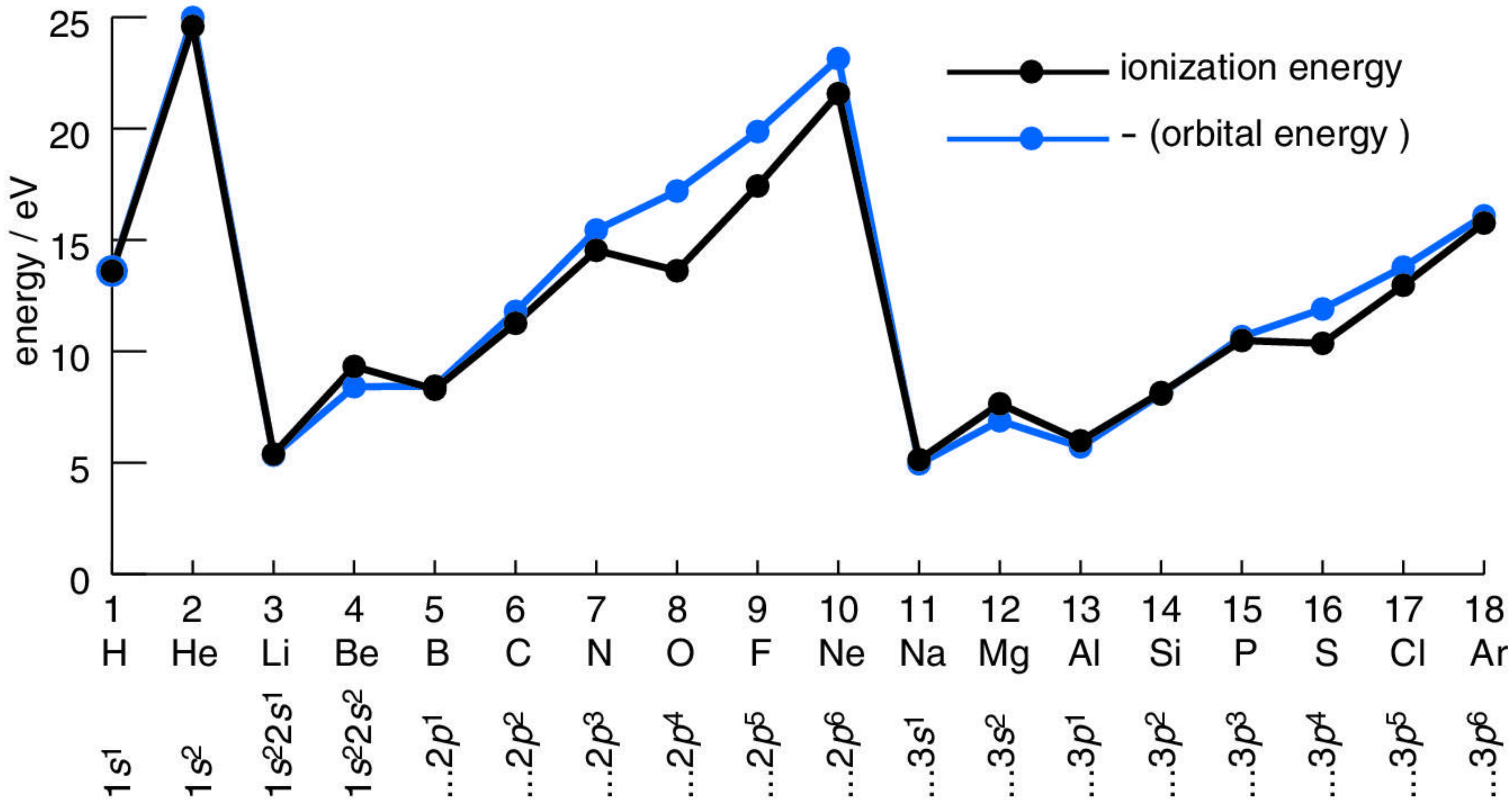
$$IE = \text{energy of } A^{+} - \text{energy of } A.$$

For the H-atom:

$$\begin{aligned} IE_n &= \text{energy of } A^{+} - \text{energy of } A \\ &= 0 - \left(-\frac{R_H Z^2}{n^2}\right) \\ &= \frac{R_H Z^2}{n^2}. \end{aligned}$$

For 1 electron: IE = - orbital energy

Koopmans theorem



For Li: OE is -5.34 eV, IE is 5.30 eV

Deviation for p^4, p^5 and p^6

The RPD of Na orbitals: Screening