

# **MO Diagrams for Diatomic Molecules**

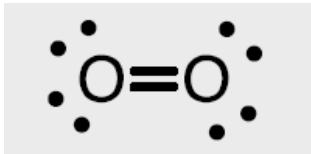
Chapter 5

Friday, October 9, 2015

# Homonuclear Diatomic Molecules

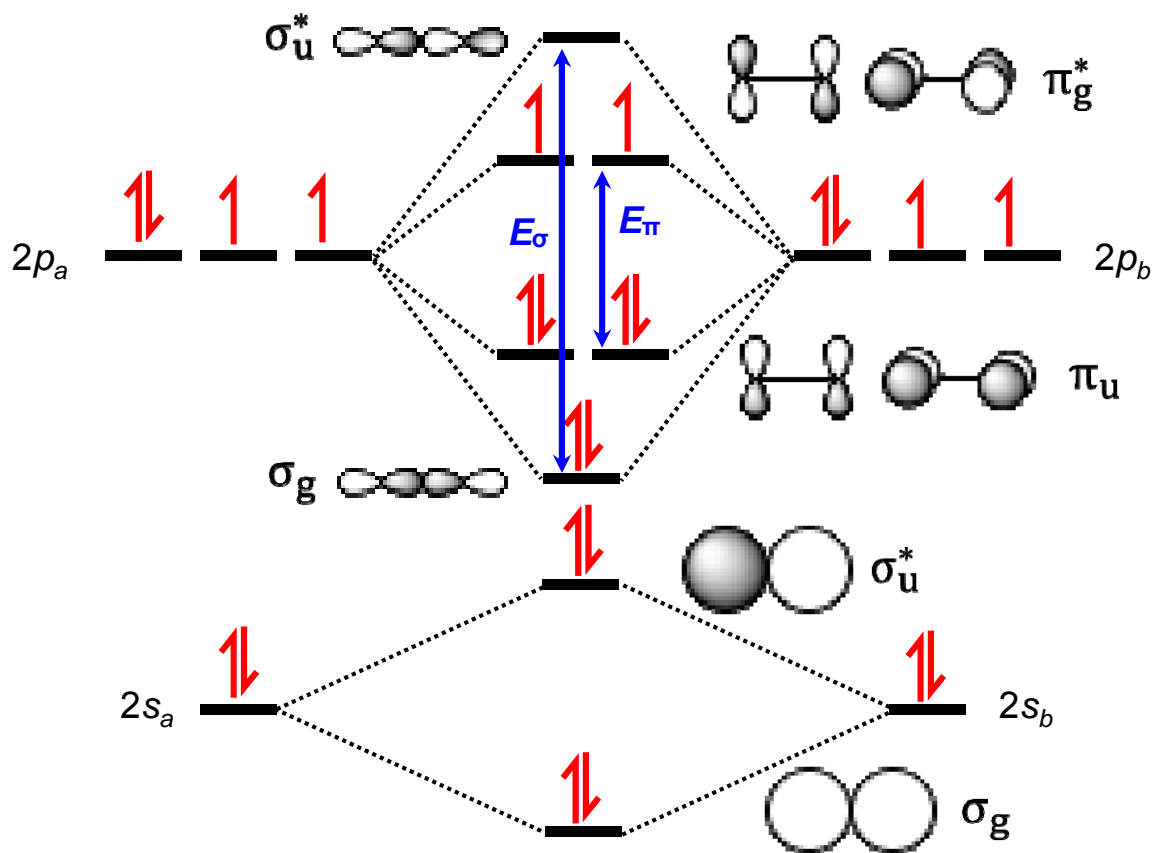
What happens when we move to more complicated systems?  
Consider  $O_2$ .

- The Lewis dot structure famously predicts the wrong electronic structure for  $O_2$



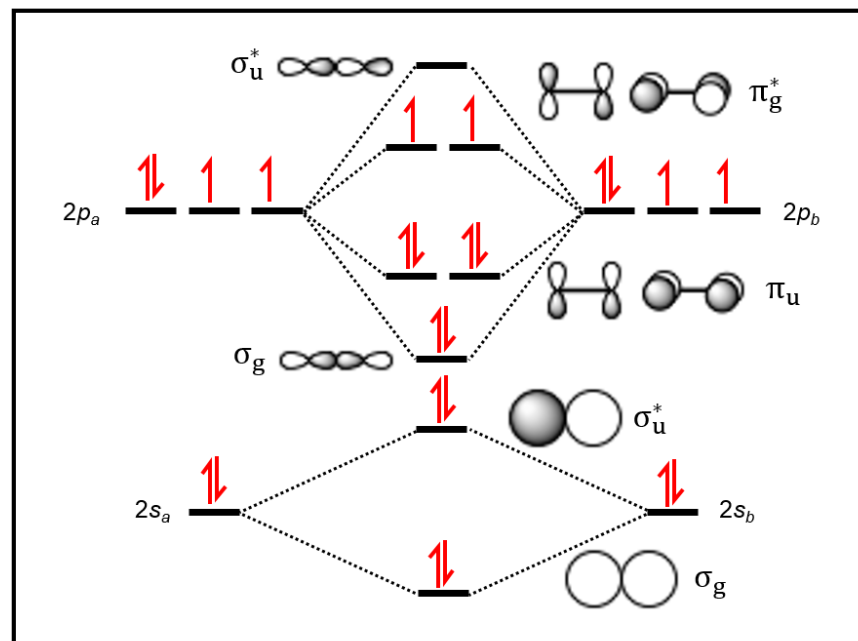
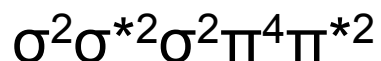
- We can use LCAO-MO theory to get a better picture:

Notice that  
 $E_\sigma > E_\pi$ ,  
because the  
 $\sigma$  bonds have  
more overlap  
than  $\pi$  bonds



# Electron Configurations and Bond Orders

Just as with atoms, we can write a molecular electron configuration for O<sub>2</sub>



We can also calculate the O–O bond order:

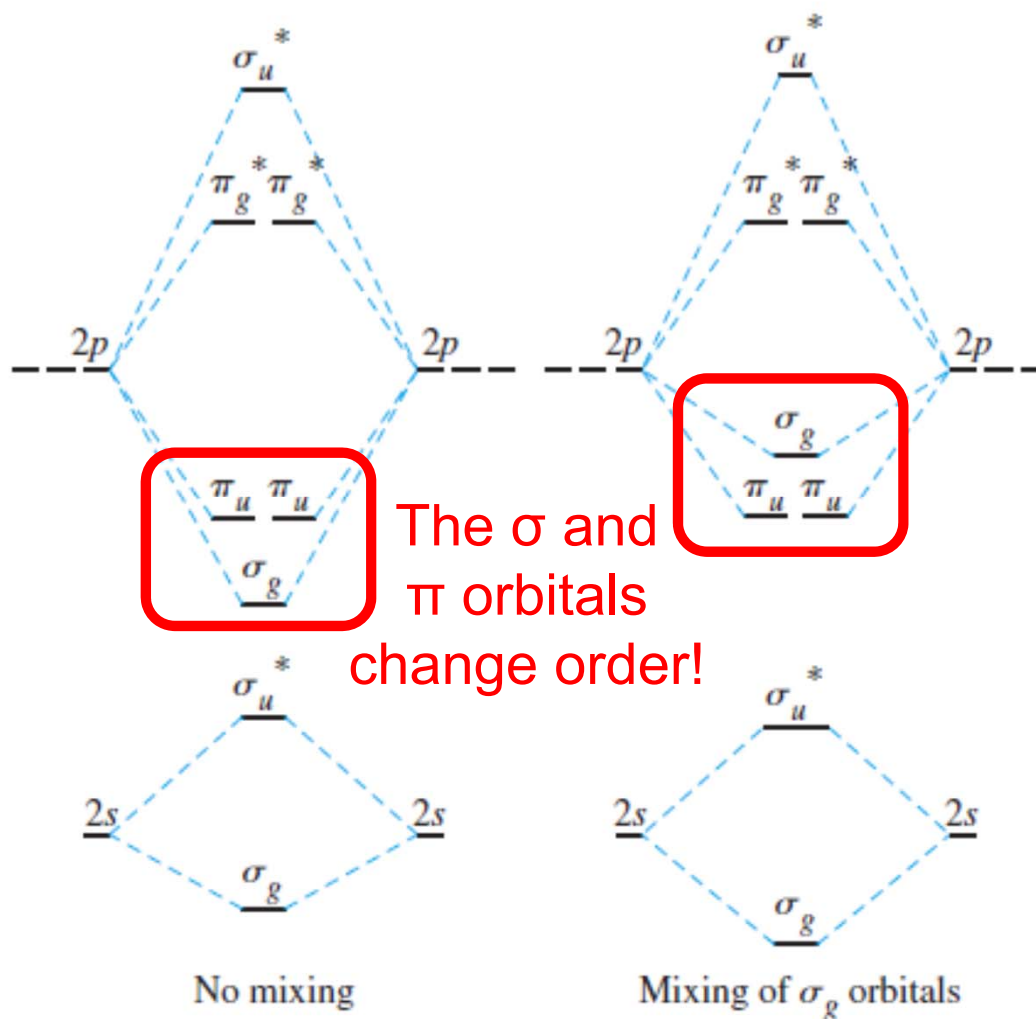
$$\begin{aligned} BO &= \frac{1}{2} [(\# \text{ bonding e}) - (\# \text{ anti-bonding e})] \\ &= \frac{1}{2} [8 - 4] = 2 \end{aligned}$$

LCAO MO theory also predicts (correctly) that O<sub>2</sub> has two unpaired electrons.

# Orbital Mixing

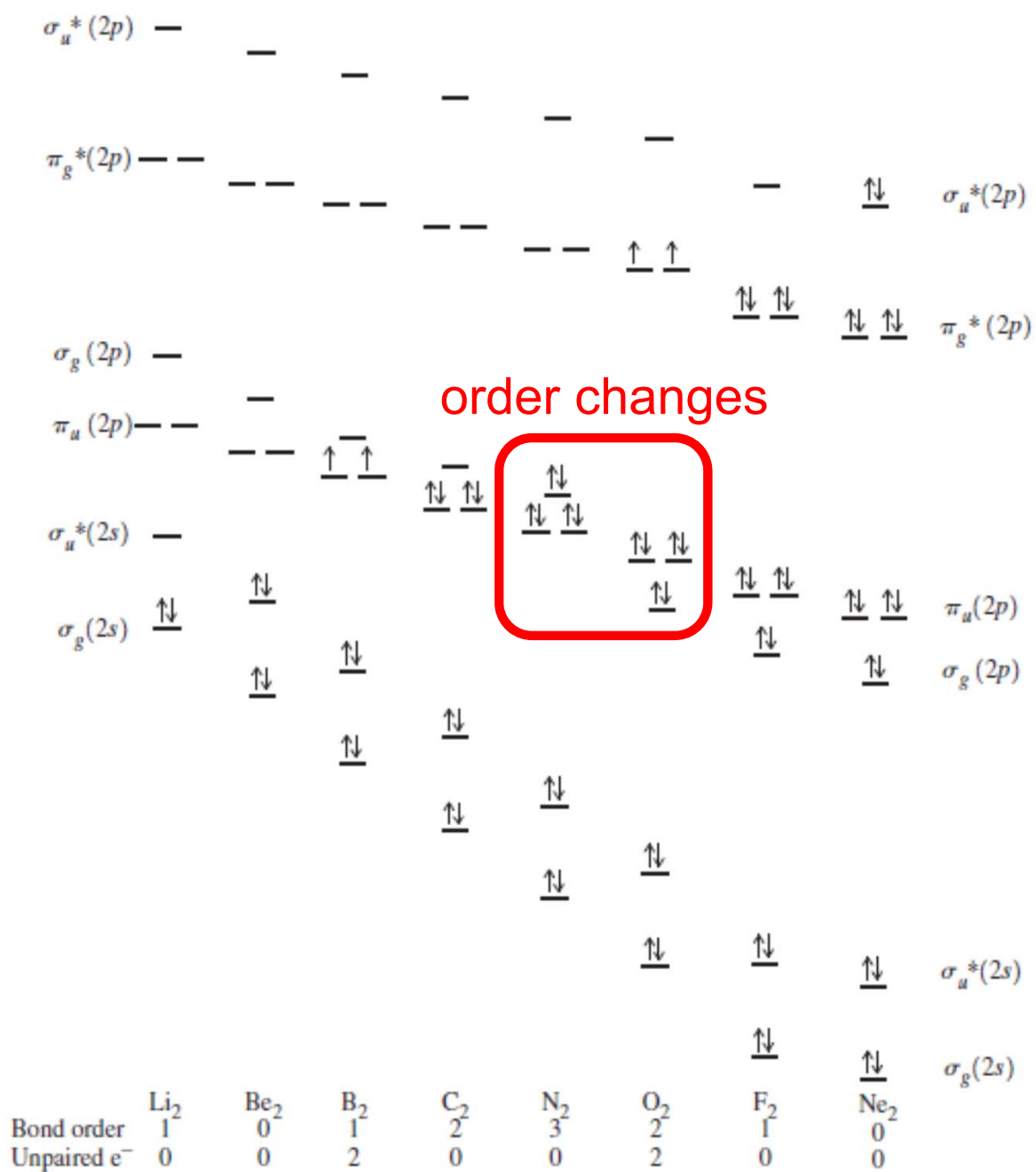
Orbitals of similar but unequal energies can interact if they have the same symmetry

The  $2s$  and  $2p_z$  orbitals form MOs with the same symmetry ( $\sigma_g$  and  $\sigma_u$ ). *sp mixing* causes the  $\sigma_g$  and  $\sigma_u$  MOs to be pushed apart in energy:

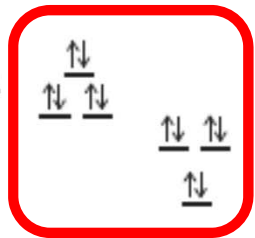


# Orbital Mixing

The size of the effect depends on the 2s-2p energy difference.



order changes



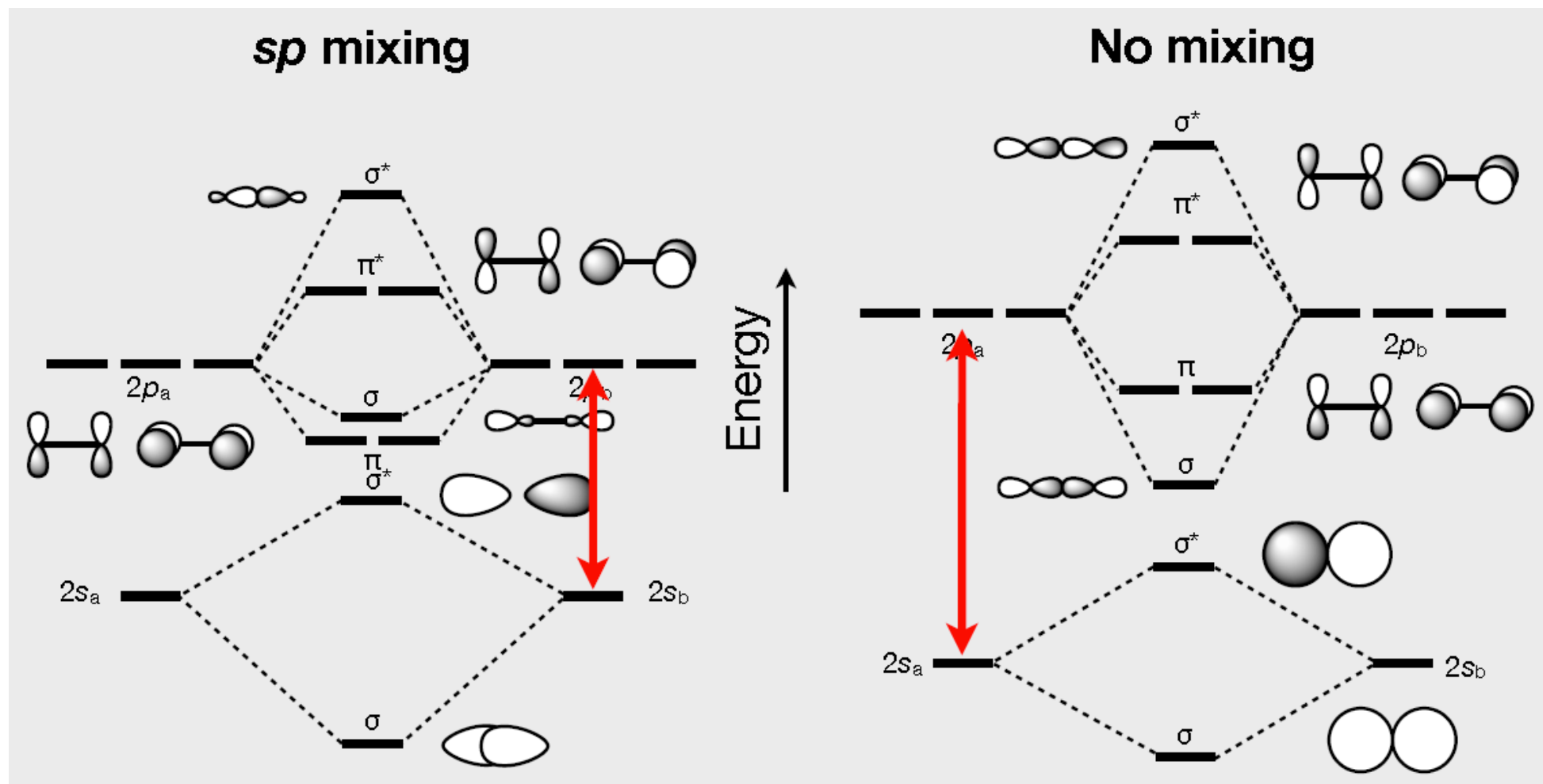
small  $Z_{\text{eff}}$  =  
small energy  
difference =  
large  $sp$  mixing

large  $Z_{\text{eff}}$  =  
large energy  
difference =  
small  $sp$  mixing



# MOs of Homonuclear Diatomic Molecules

The MO picture of homonuclear diatomic molecules depends on the amount of *sp* mixing.

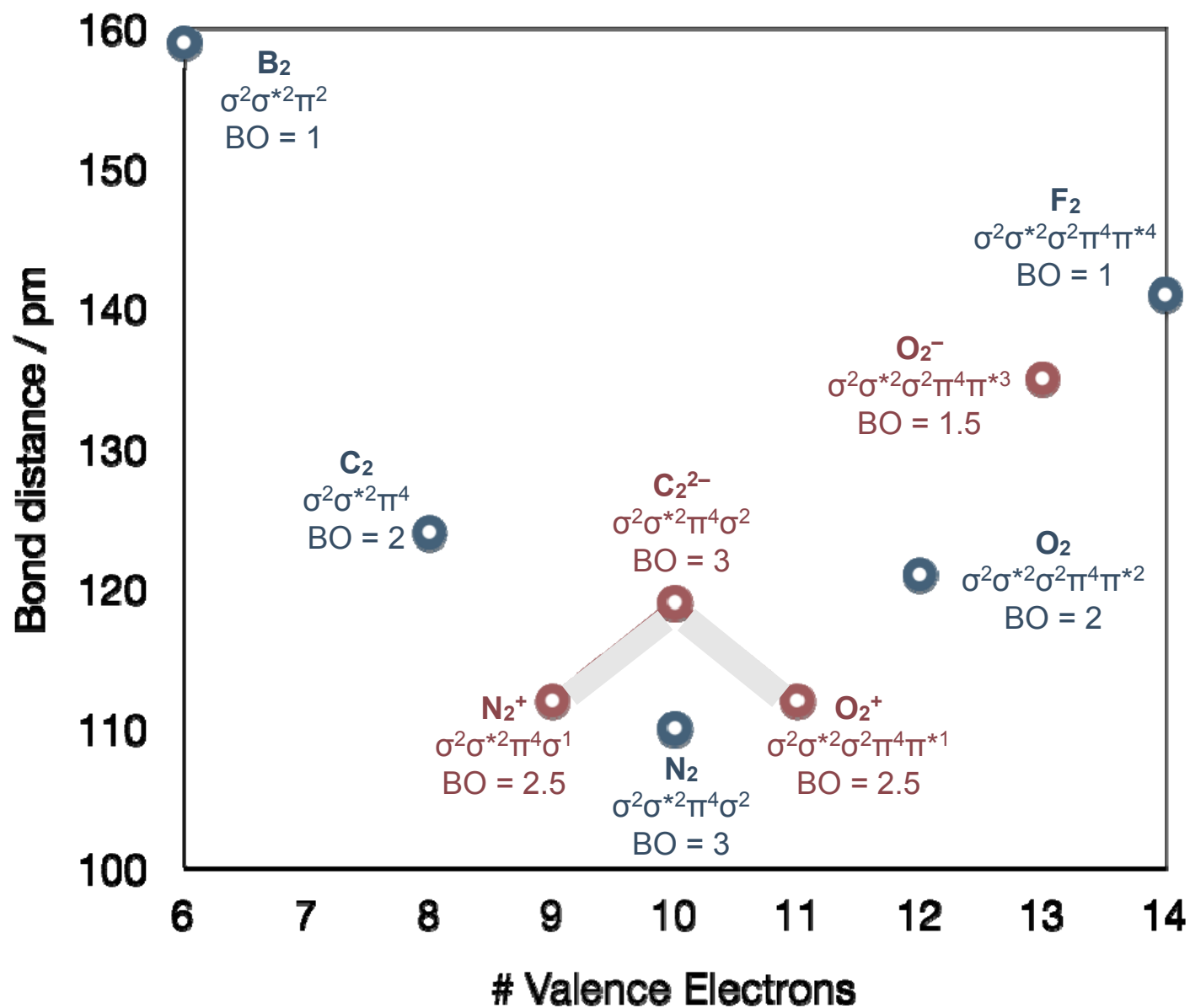


$\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$

$\text{O}_2$ ,  $\text{F}_2$ ,  $\text{Ne}_2$

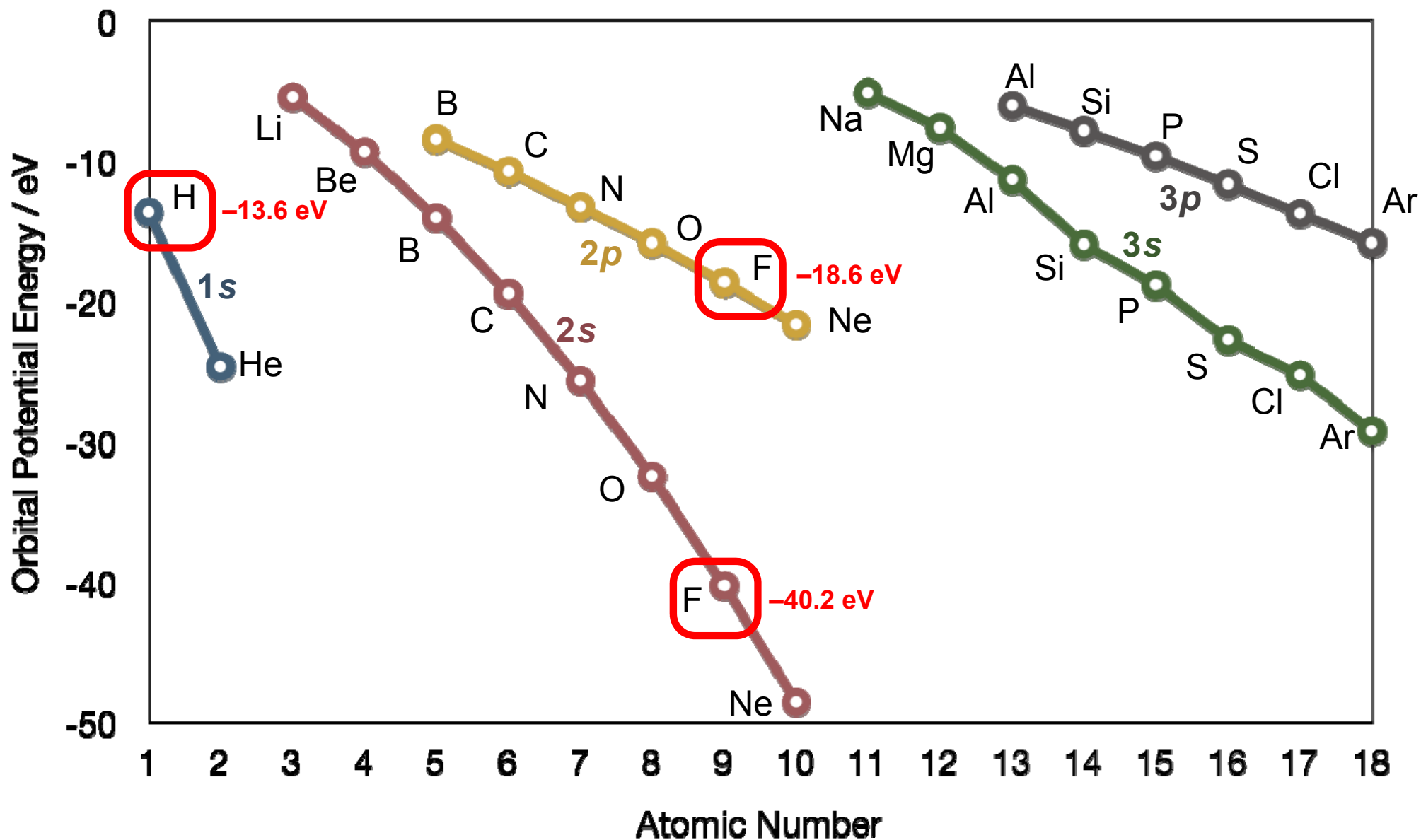
# Bond Order and Bond Distance

The MO bond order is the main factor controlling the internuclear distance.



# Relative AO Energies for MO Diagrams

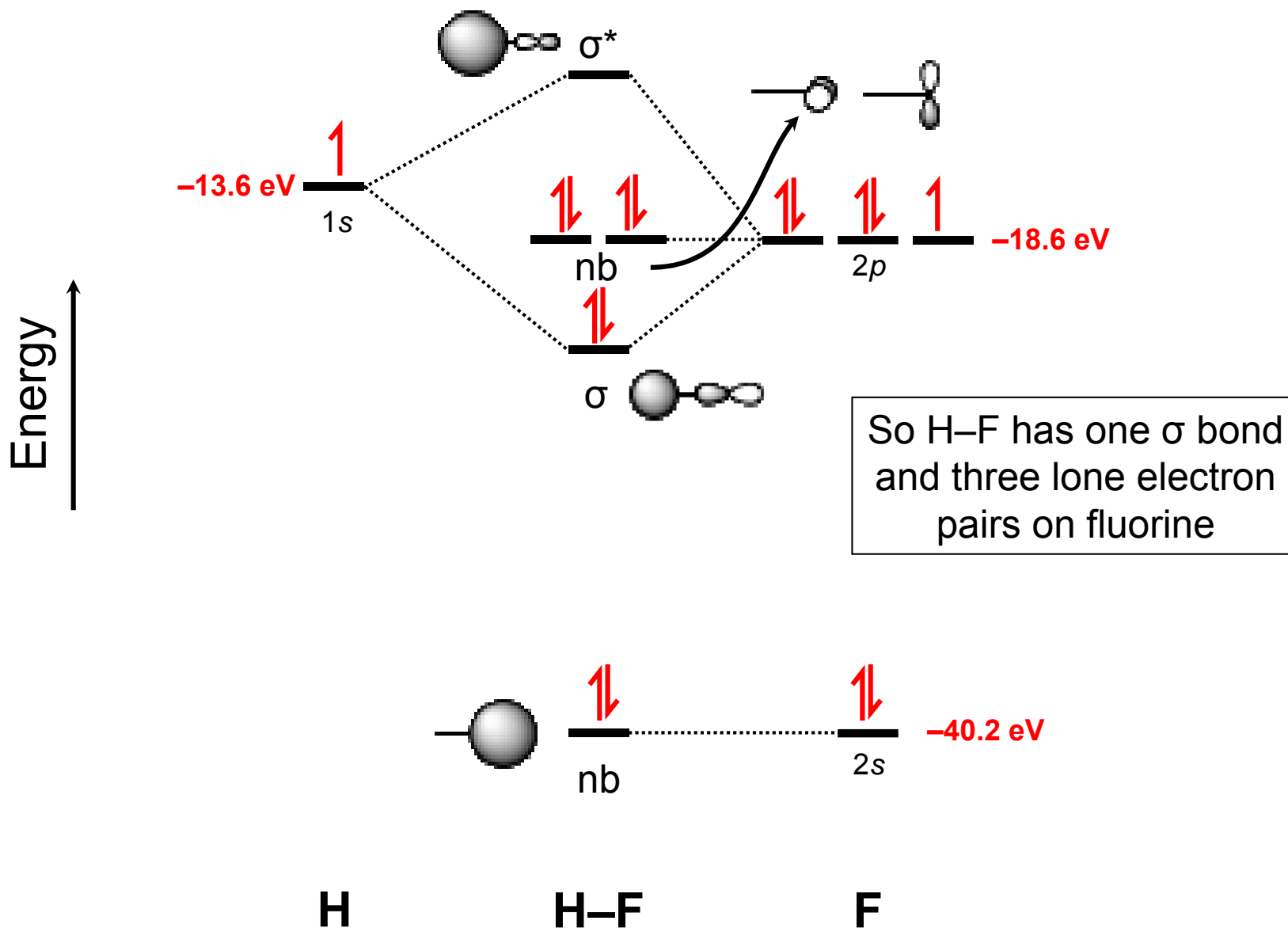
*Photoelectron spectroscopy* gives us a pretty good idea of the relative energies for AOs.





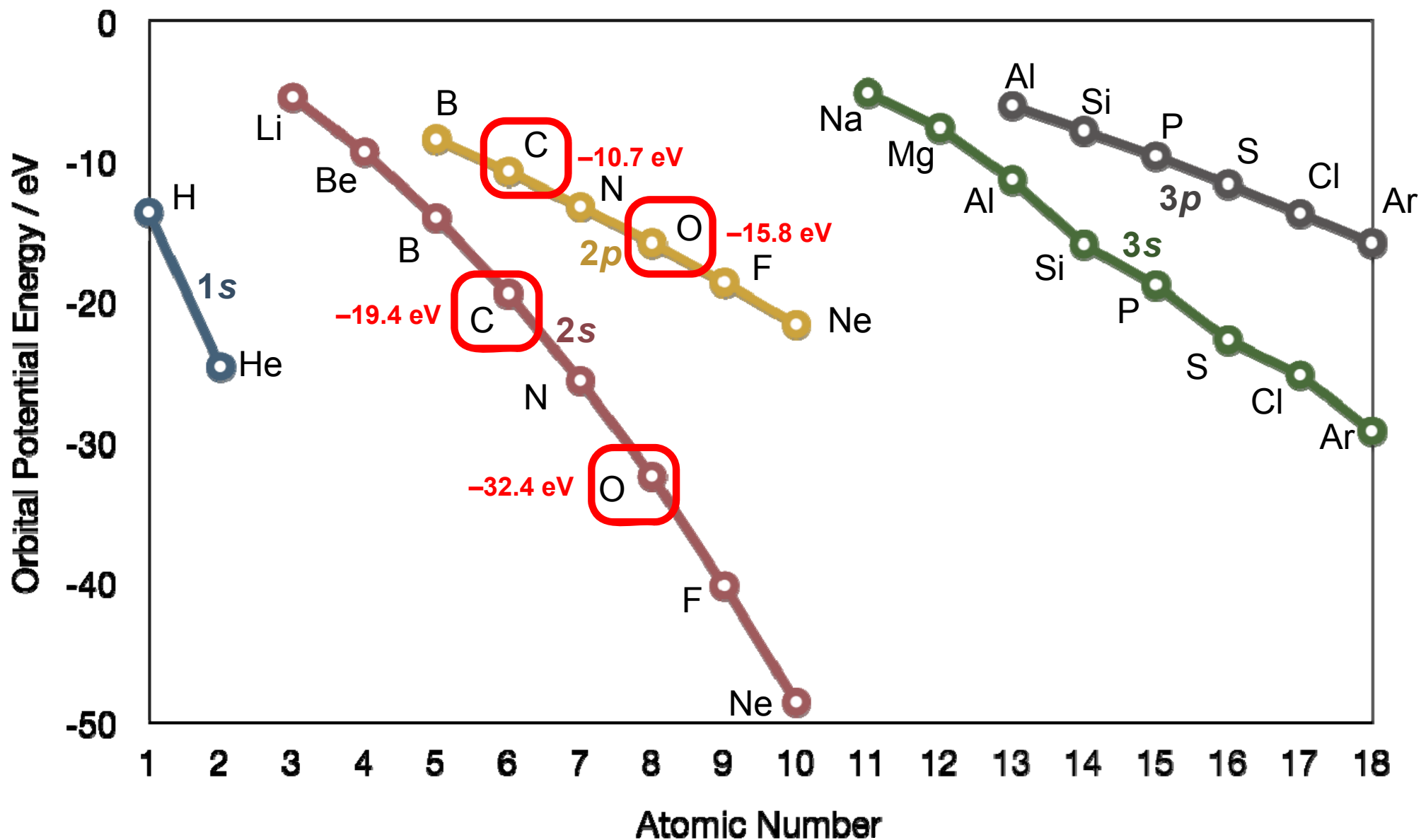
# MO Diagram for HF

The AO energies suggest that the 1s orbital of hydrogen interacts mostly with a 2p orbital of fluorine. The F 2s is nonbonding.



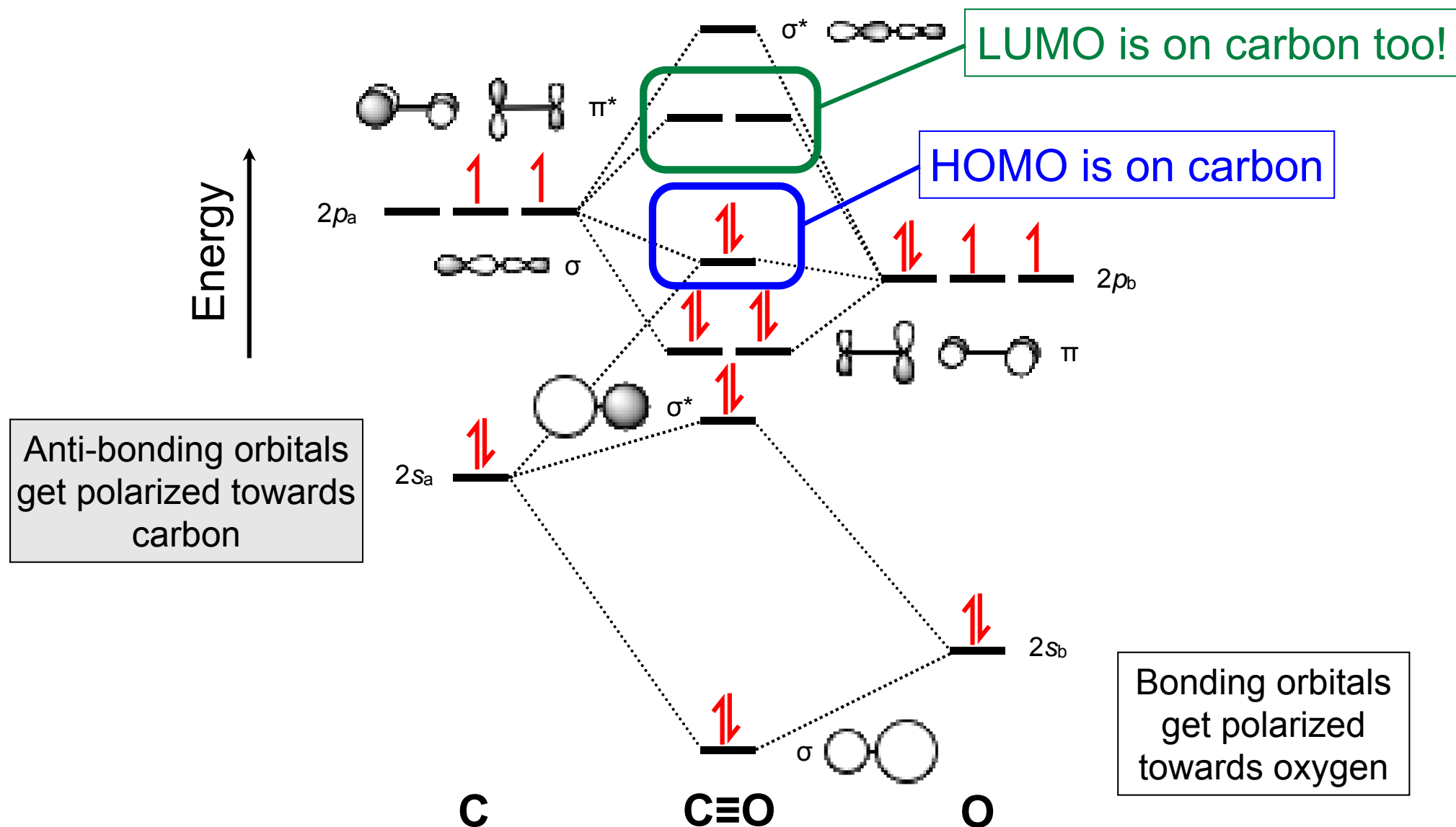
# Relative AO Energies for MO Diagrams

*Photoelectron spectroscopy* gives us a pretty good idea of the relative energies for AOs.



# Heteronuclear Diatomic Molecules: CO

In molecules with more than one type of atom, MOs are formed from AOs that have different energies. Consider CO:



# Summary

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## MO Theory

- **LCAO-MO Theory is a simple method for predicting the approximate electronic structure of molecules.**
- **Atomic orbitals must have the proper symmetry and energy to interact and form molecular orbitals.**
- **Photoelectron spectroscopy provides useful information on the energies of atomic orbitals.**
- **Next we'll see that symmetry will help us treat larger molecules in the LCAO-MO theory framework.**