MOLECULAR ORBITALS

Chapter 5

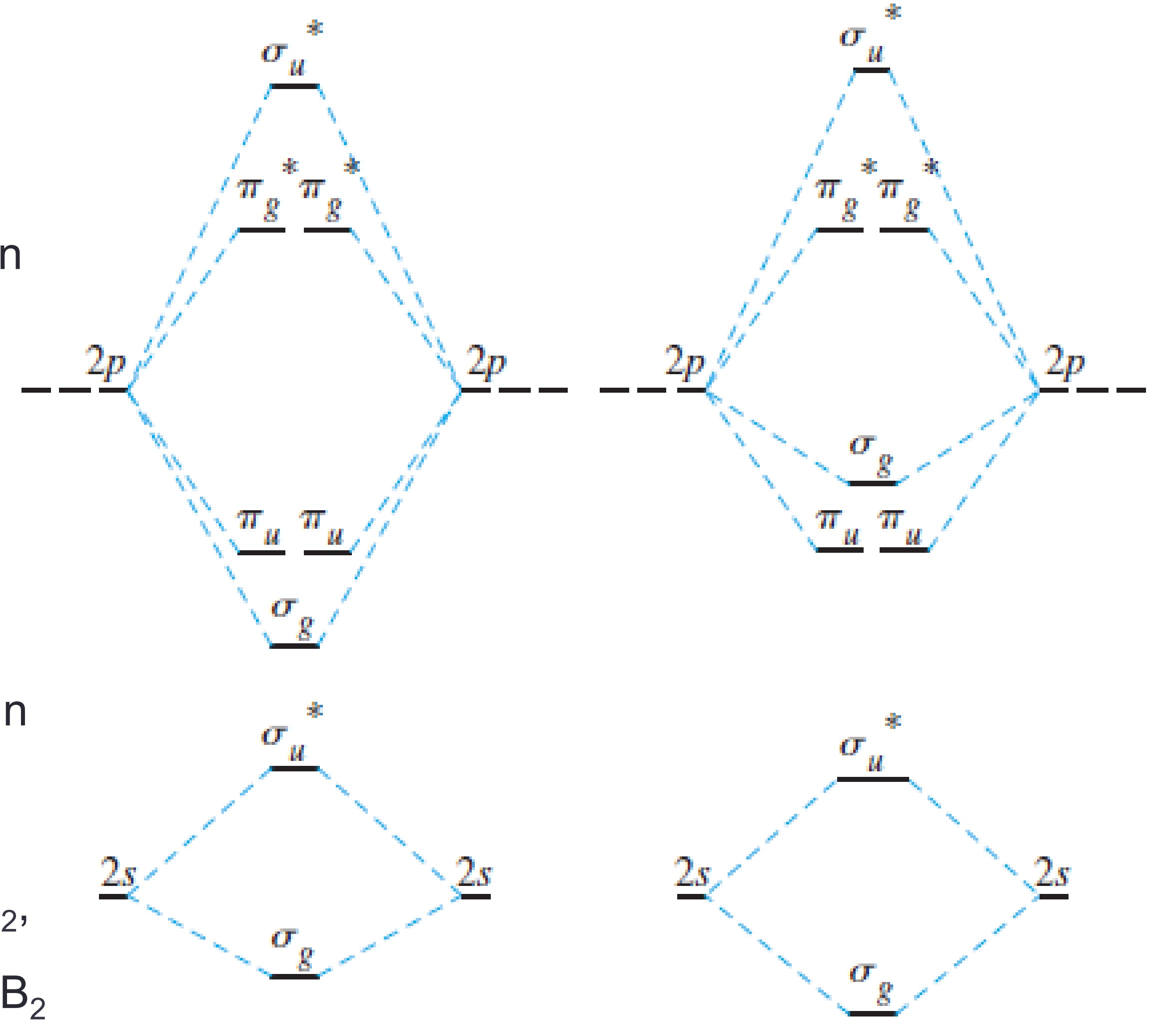
Orbital mixing

- MOs with similar symmetries can ‘mix’, resulting in stabilization of lower energy orbital, destabilization of higher energy orbital-**only has an effect if the two molecular orbitals in question are close enough in energy to have a significant interaction**

- In some molecules, this results in p_z sigma bond being higher in energy that p_x and p_y pi bonds

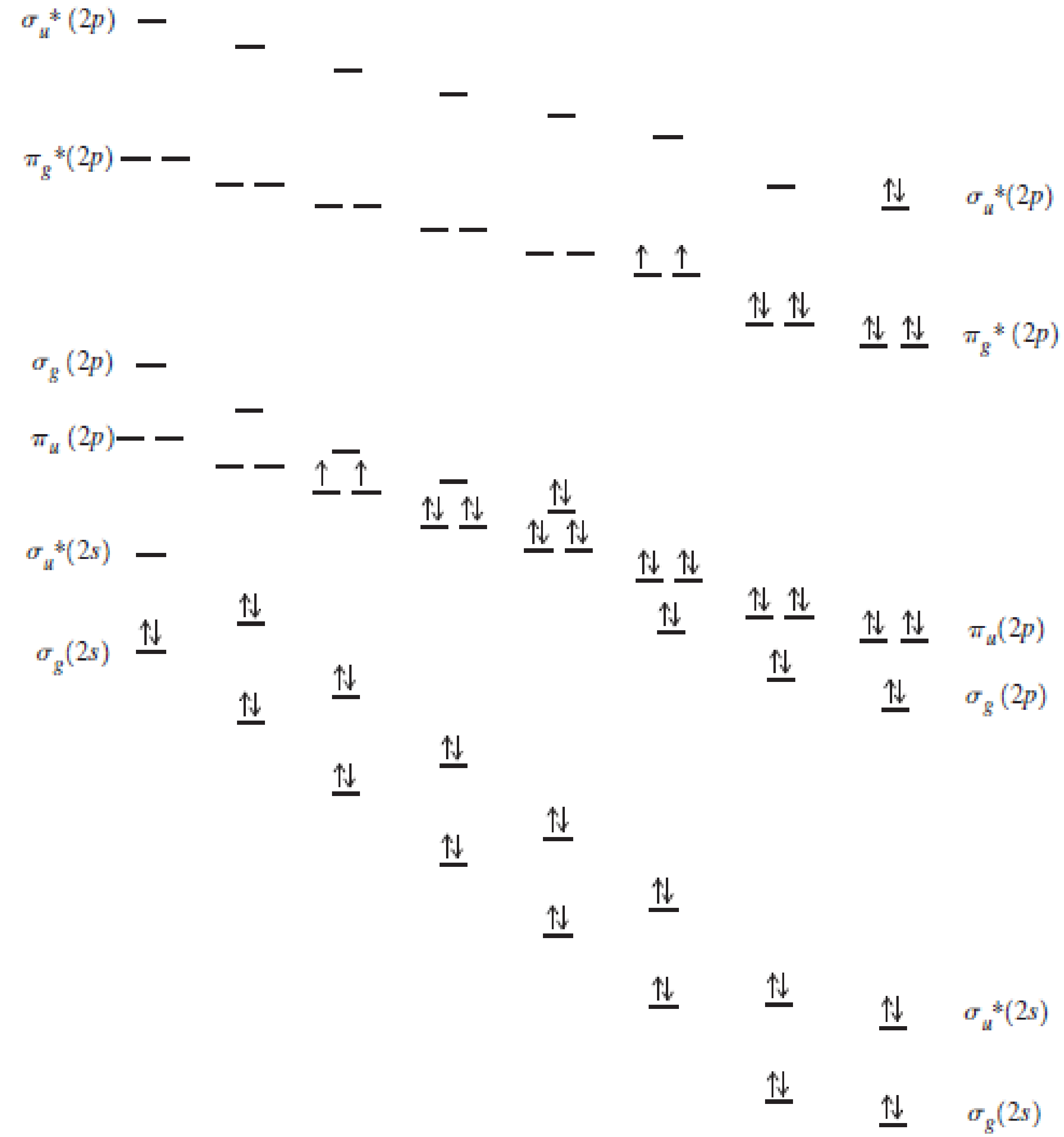
- In n=2, mixing occurs for Li_2, Be_2, B_2, C_2, and N_2: importantly, explains magnetic properties of B_2 and C_2!

- There is no mixing for O_2, F_2, Ne_2



No mixing

Mixing of σ_g orbitals



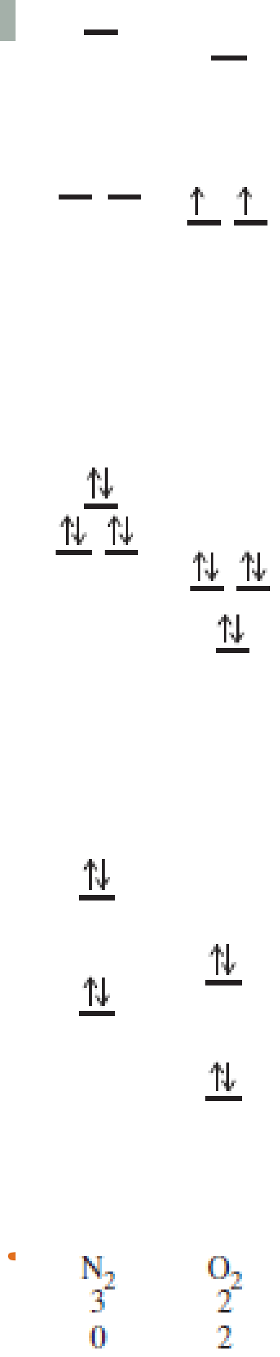
	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	0	1	2	3	2	1	0
Unpaired e^-	0	0	2	0	0	2	0	0

Paramagnetism vs diamagnetism

- **Diamagnetic:** molecule has no unpaired electrons, is slightly repelled by a magnetic field
- **Paramagnetic**: molecule has unpaired electrons, is attracted to a magnetic field

- Paramagnetism of O_2 (vs. diamagnetism of N_2)

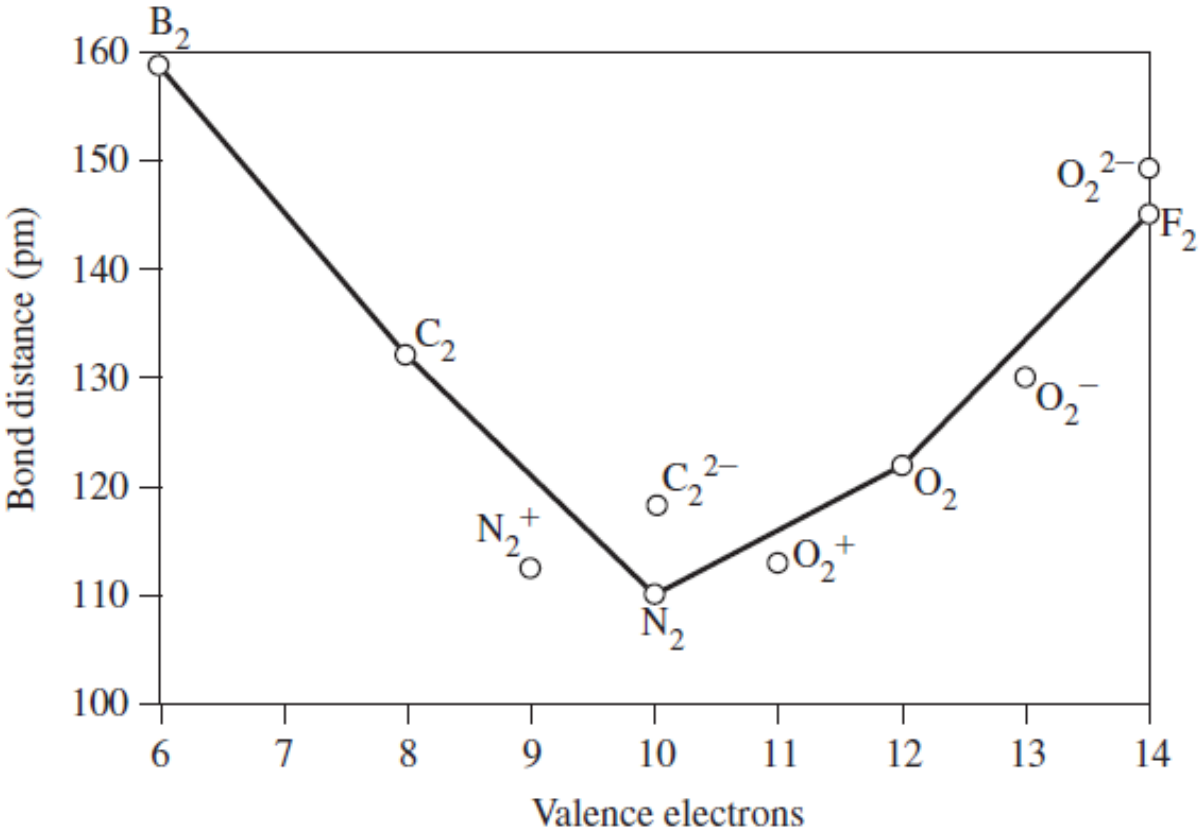
https://youtu.be/QN391RkUHnQ



Bond order

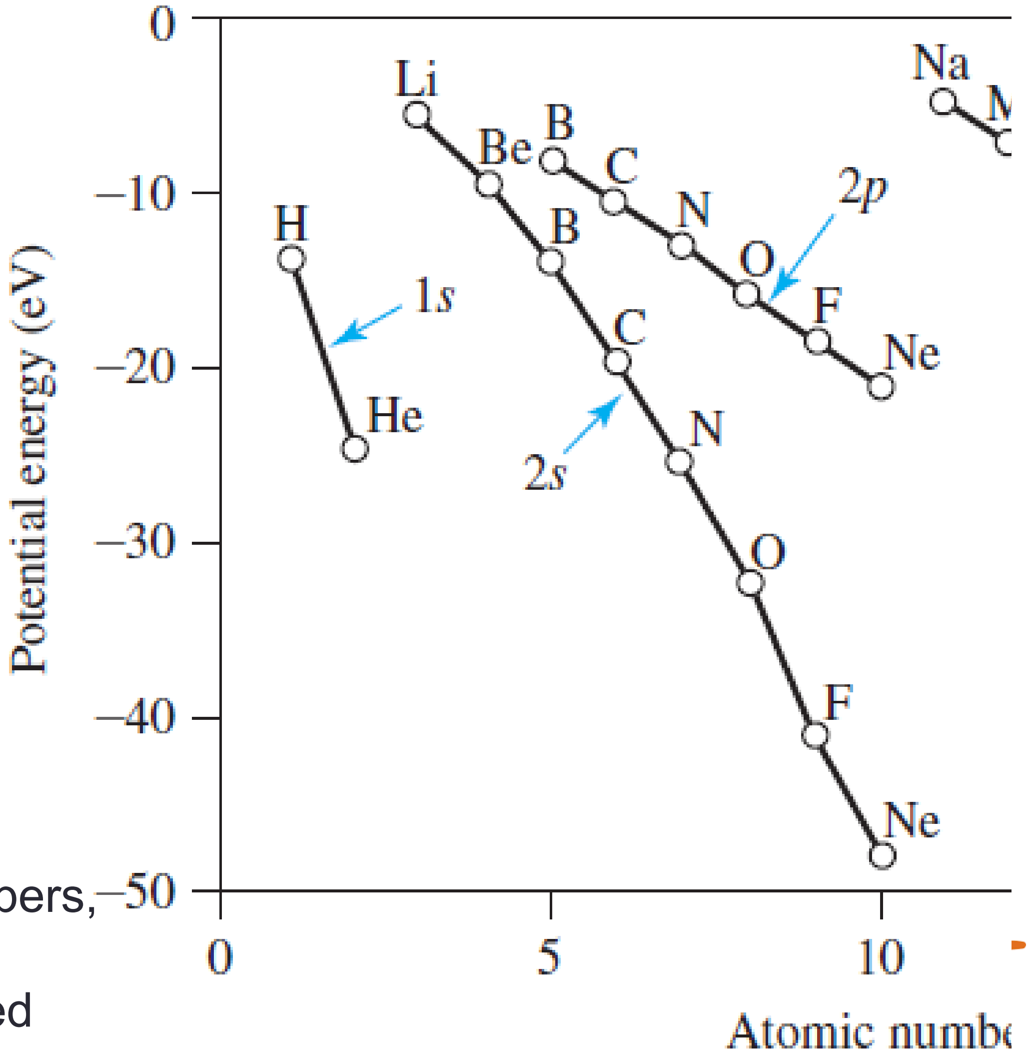
Bond order =

(# of e⁻s in bonding orbitals - # of e⁻s in antibonding orbitals)/2



Heteronuclear diatomic molecules

- Different elements have different orbital potential energies (measured as a function of attraction between electrons and atomic nuclei →similar to trends governed by Z_{eff})
- More electronegative elements will have lower orbital energies

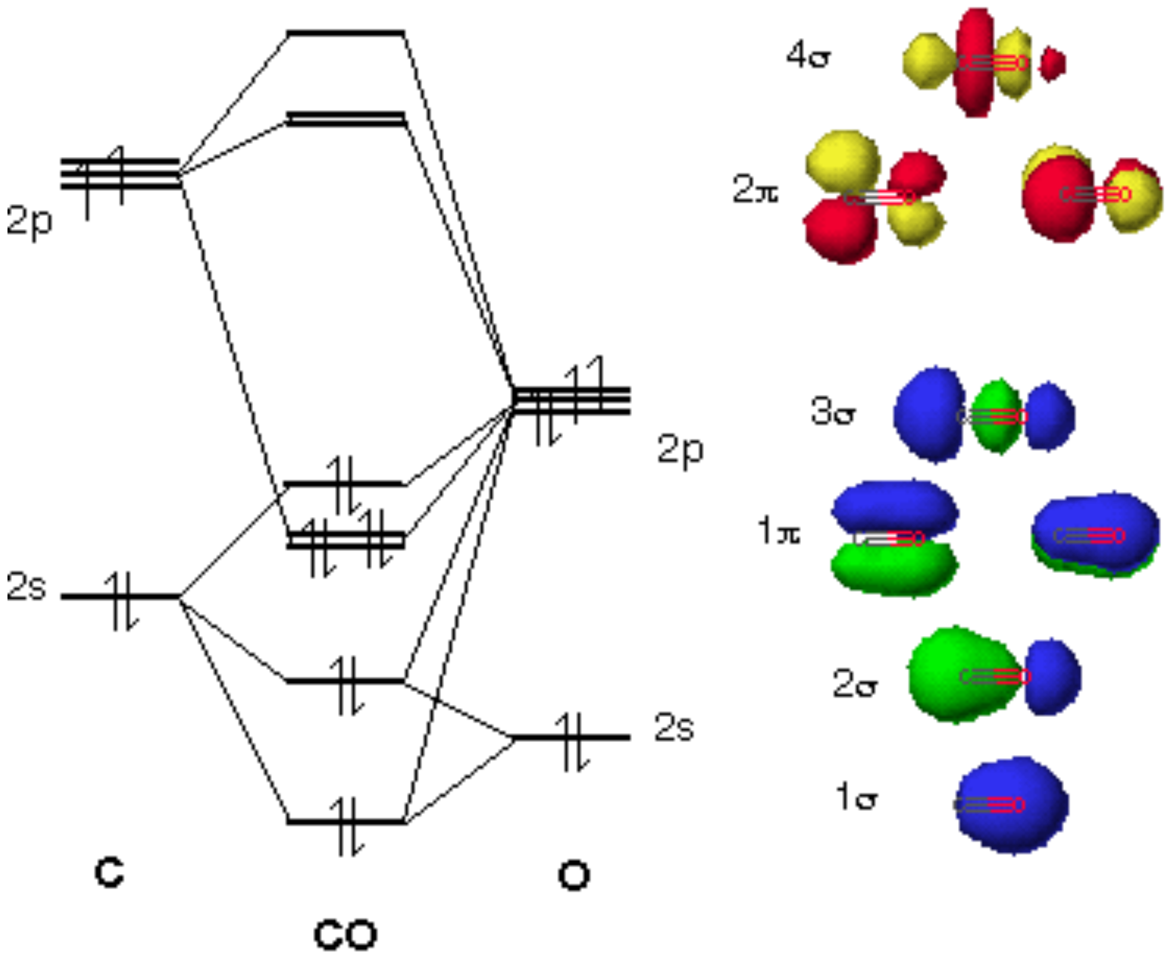


You do not need to memorize these numbers, just know the trend. If energy values are needed for a problem, you will be provided them

Heteronuclear diatomic molecules

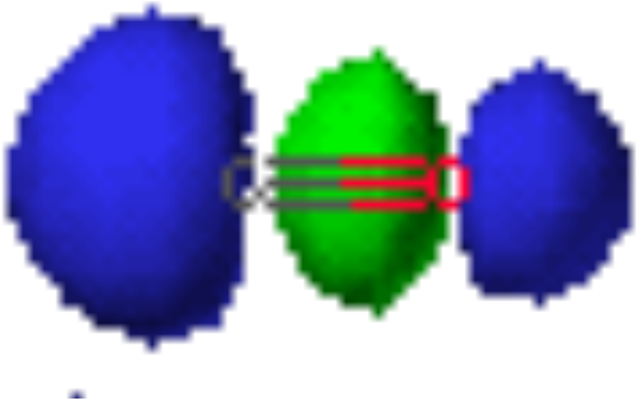
- The difference in orbital energies in heternuclear diatomic molecules makes their MOs *slightly* more complicated

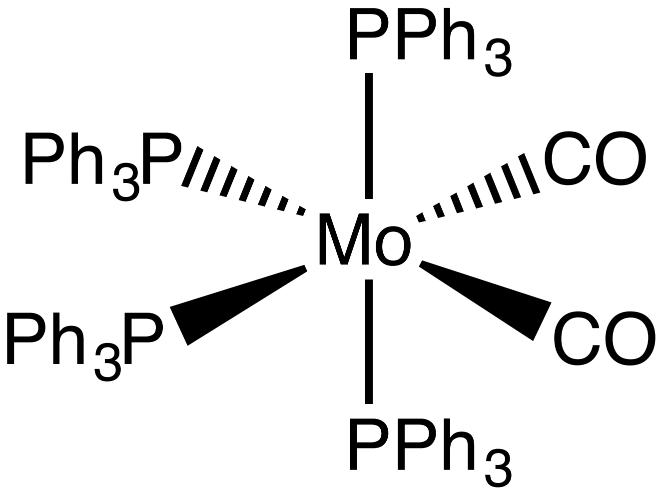
- CO as an example (very important for organometallic M-CO complexes!)



CO interactions with metals is influenced by it’s molecular orbitals

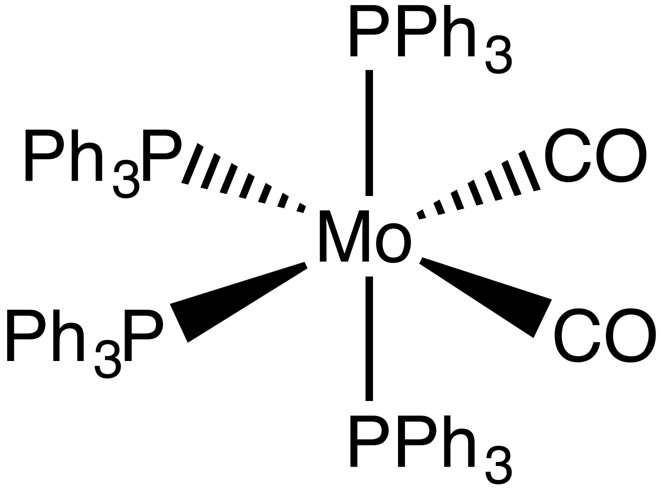
- The **HOMO** of CO (Highest Occupied Molecular Orbital) contains highest probability density on C, thus when metal complexes form with CO, they are C-bound and NOT O-bound.
  - The ligand **HOMO** is the orbital that typically interacts in a σ fashion with metal d orbitals (more later!)





CO interactions with metals is influenced by it’s molecular orbitals

- Further, the **LUMO** of CO (Lowest Unoccupied Molecular Orbital) also can interact strongly with metal, and this also has highest probability density on C
  - The ligand **LUMO** in molecules like CO can interact in a π fashion with metal d orbitals (more later!)



Molecular orbitals for larger molecules

- When molecules contain 3 or more atoms, making molecular orbitals becomes more complicated, for example, what does the MO diagram of H_2O look like? How about ML_6?
- For these molecules, we use **group orbitals** or **symmetry adapted linear combinations (SALCs)** of orbitals to help make the MO diagram
- The number of SALCs = the number of atomic orbitals that make up the SALCs
- FHF^- is a straightforward example to start with

Steps for determining SALCs/group orbitals

1) **Determine the point group of your molecule.** If the molecule is $D_{\infty h}$, use the D_{2h} character table. $C_{\infty v}$, use C_{2v}.

2) **Take stock of the valence orbitals** of both the central and non-central atoms in the molecule

3) **Find $\Gamma_{orbital}$** for all the valence orbitals of the non-central atoms. If they are H's, you only determine Γ_{1s}. If it is a 2nd row p-block element, you calculate Γ_{2s}, Γ_{2pz}, Γ_{2px}, Γ_{2py}

4) **Use the reduction formula** to determine the irreducible representations that make up the $\Gamma_{orbital}$'s

5) **Determine the orbitals on the central atom that match the irreducible representations from 3.** These are the orbitals that can interact with the outer atoms

6) **Determine what the group orbitals look like by matching them with the central atom orbitals determined in 4.**

From SALCs to MO diagrams

1) **You now have a list of all the potential interactions between the central atom and the non-central atoms (previous steps)**

2) **Take a look at the relative energies of the atomic orbitals.** Remember, the most significant interactions will occur between orbitals that are closer in energy

3) **Draw central atom atomic orbitals on one side**, taking into account their relative energies

4) **Draw ligand SALCs on other side**, placing them at the same energy level as their corresponding atomic orbitals

5) **Fill in the bonding and antibonding interactions** based on #1 and on the relative orbitals energies

6) **All other orbitals are essentially nonbonding** though weak interactions within a SALC may stabilize or destabilize the orbitals.