Plan of attack

- We will look at some hypothetical molecules (Hₙ molecules) to familiarize you with the rules for MO construction.
- We will consider the delocalized MOs for a few basic molecules.
- Relationships to more familiar local bonding schemes will be discussed.
- Some discussion of how the MO picture relates to experimental measurements - i.e., photoelectron spectroscopy.
- Some coverage of this material in text, Sec 3-6.

H₃ - Linear and Cyclic

for both cases we will break these into two fragments, H₂ and H:

Linear H₃ : Building with symmetry

- Step 1: Set up symmetry adapted basis orbitals.
- Step 2: Interact basis orbitals - mix orbitals of the same symmetry.
Triangular H$_3$ : Do it Again

- Step 1: Set up symmetry adapted basis orbitals
- Step 2: Interact basis orbitals - mix orbitals of the same symmetry

Triangular to Linear

MOs for H$_2$O

Step 1: Set up symmetry adapted basis orbitals
Step 2: Interact basis orbitals - mix orbitals of the same symmetry
MOs for NH₃

MOs for BH₃ and a Walsh Diagram for D₃h to C₃v

• The procedure for constructing a MO diagram for BH₃ is very similar to NH₃.
• A correlation diagram (Walsh diagram) helps to rationalize the planar (D₃h) to pyramidal (C₃v) switchover for these two systems.

Vibrational Effects on Photoelectron Spectra

Ground State binding curve for neutral molecule

Binding curve for Cation after loss of bonding electron

Binding curve for Cation after loss of nonbonding electron
Photoelectron Spectrum for $\text{H}_2\text{O}$

Photoelectron Spectrum for $\text{NH}_3$
“Partial” MO diagrams

• Even when one restricts attention to the valence electrons, MO diagrams can get complicated as the molecular size increases.
• It is therefore useful to be able to combine simpler ‘localized’ bonding schemes with partial MO treatments. To do this correctly requires some experience, but pays off with (relative) simplicity.
• The separation of $\sigma$ and $\pi$ electrons is probably the type of case most familiar to you.

Examples

1. The formate ion, HCO$_2^-$: We can simplify in two ways: (i) handle $\sigma$ system using local hybridization schemes; (ii) recognize an orbital pattern like one we’ve already seen.
2. Diborane, B$_2$H$_6$: We can treat the two BH$_2$ end fragments by invoking localized B-H bonds and using the “frontier” orbitals (similar to another molecule we’ve already done). Then combine the two bridging H atoms together with the two BH$_2$ end fragments.