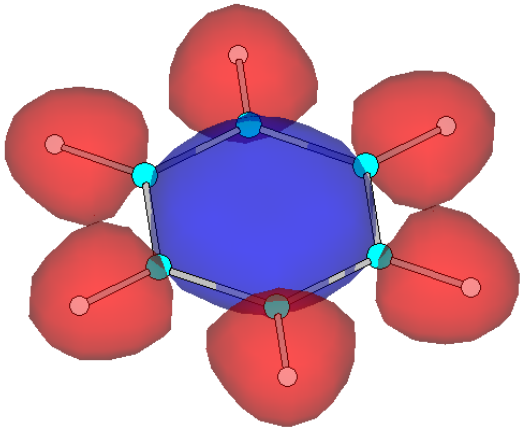
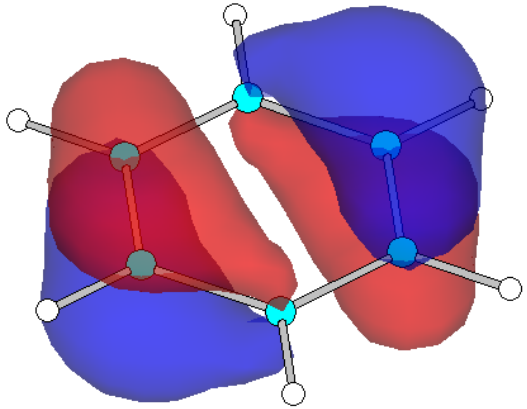
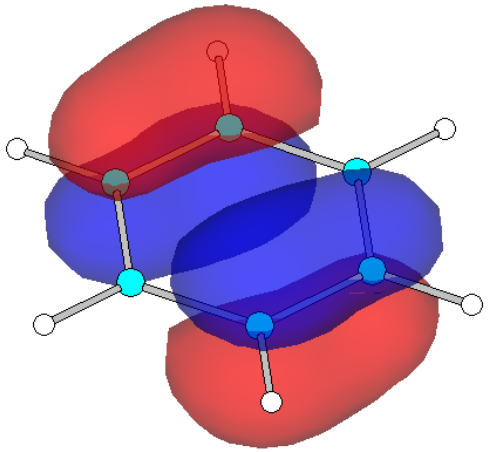




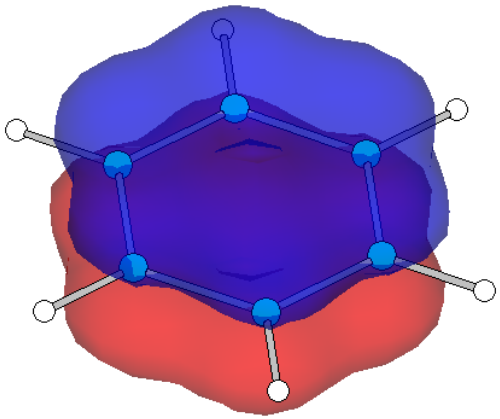
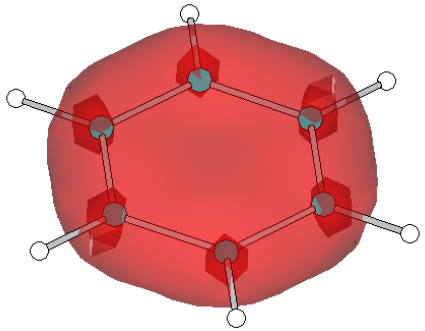
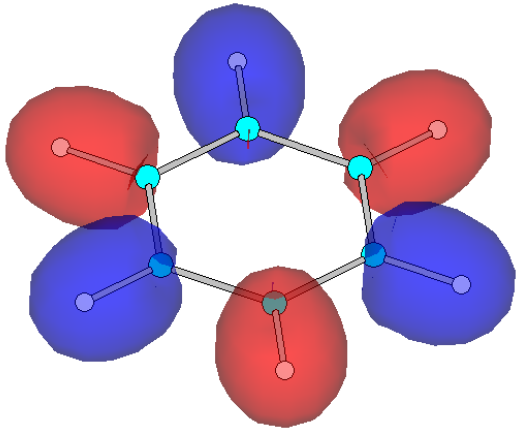
CHEMISTRY 2000

Topic #1: Bonding – What Holds Atoms Together?

Fall 2020

Dr. Susan Findlay

See Exercises 3.1 and 3.2

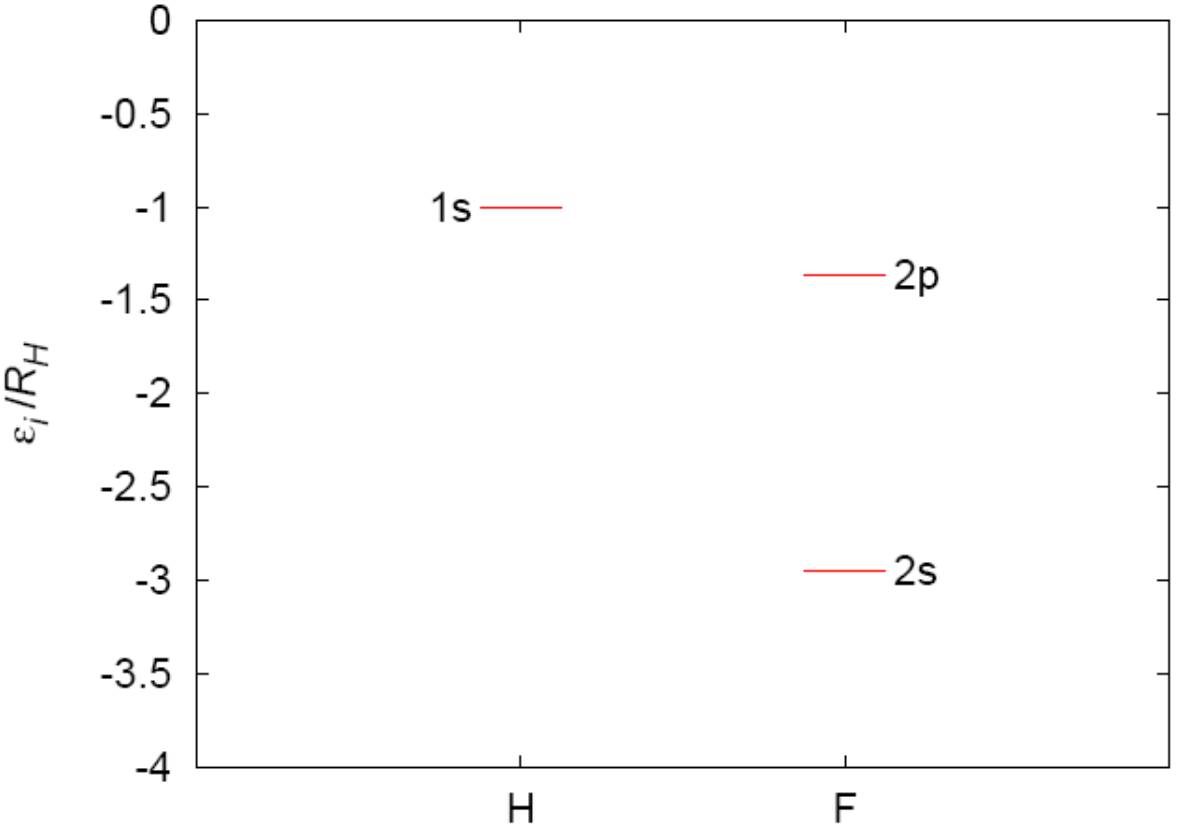




Molecular Orbitals of Heteronuclear Diatomics

- The molecular orbitals of heteronuclear diatomics (HF, CO, CN^-, etc.) can be predicted using the same principles that we used to construct the molecular orbitals of homonuclear diatomics:
  - Ignore the core electrons
  - Total number of MOs = Total number of AOs
  - Only AOs of **similar energy** combine to make LCAO-MOs
  - Only AOs of **compatible symmetry** combine to make LCAO-MOs:
    - σ-type AOs (*s* and p_z orbitals) make σ MOs
    - π-type AOs (p_x and p_y orbitals) make π MOs

Molecular Orbitals for HF

- Consider the valence atomic orbitals of hydrogen and fluorine:



- Which AOs will combine to make MOs?
- Which AOs will not mix (and therefore still look like an AO)?

Molecular Orbitals for HF

- Using symmetry and energy as our guide, we predict that we will make LCAO-MOs that look something like:

- There can be no π bonding in HF. Why not?

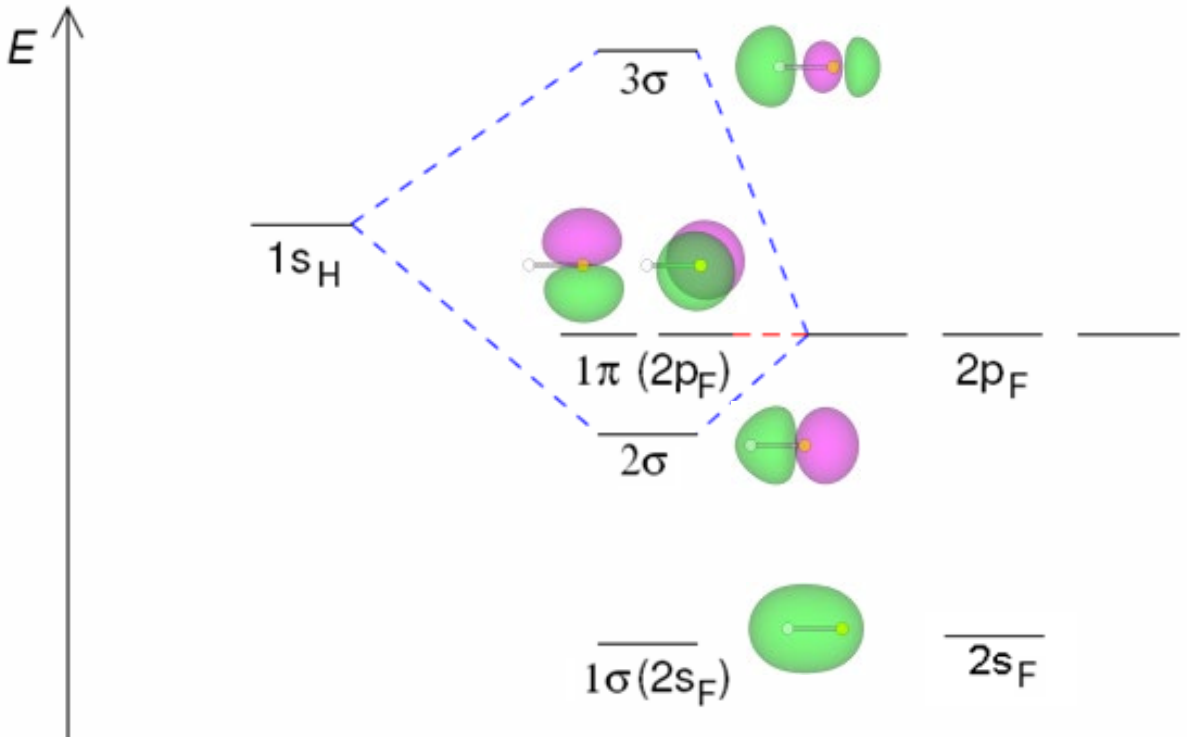
- There will still be orbitals with π symmetry in HF. Which ones?

Molecular Orbitals for HF

- Putting all that information together, we can sketch a molecular orbital energy level diagram for HF:

Molecular Orbitals for HF

- Or use software like HyperChem to do it for us:



Molecular Orbitals for HF

- Write the valence orbital occupancy for HF.
- Draw a Lewis structure for HF, and compare the bond order obtained by the Lewis method to the bond order obtained by MO.
- How is the MO diagram on the previous page consistent with other features of your Lewis structure?

Molecular Orbitals for HF

- What is the **H**ighest **O**ccupied **M**olecular **O**rbital (HOMO) for HF?

- If HF donated electrons to another species, they would come from the HOMO; however, HF is admittedly not a very good Lewis base (electron pair donor). What does our MO diagram tell us about how HF would donate electrons if it encountered a strong enough Lewis acid?

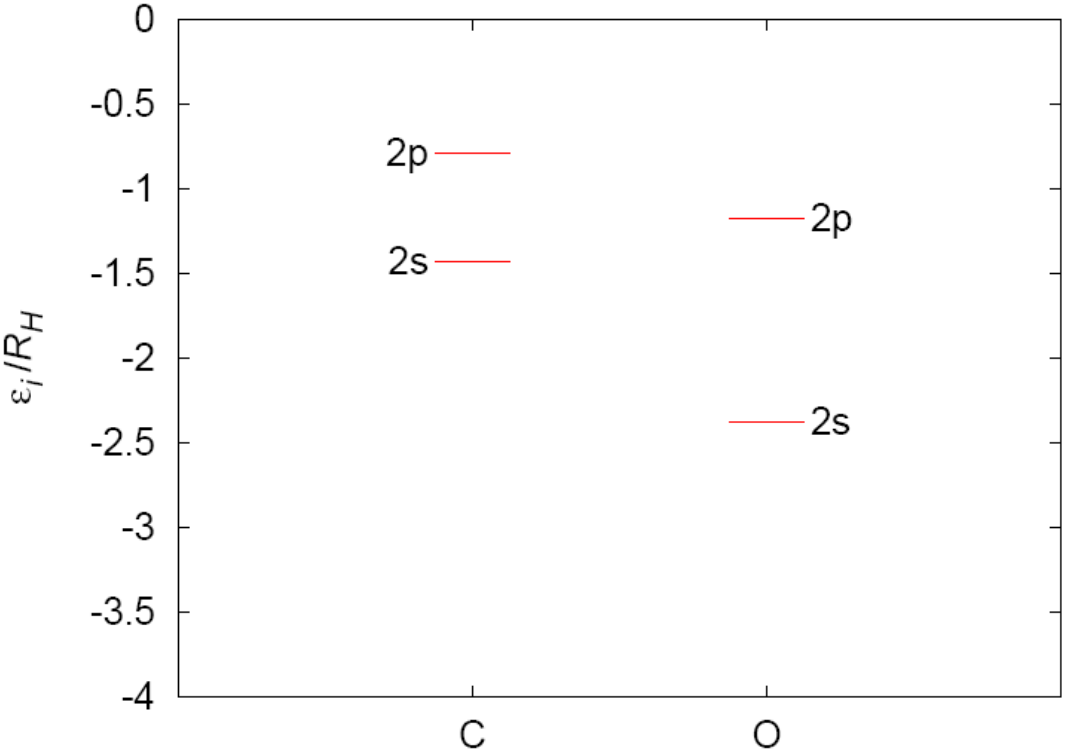
Molecular Orbitals for HF

- What is the **L**owest **U**noccupied **M**olecular **O**rbital (LUMO) for HF?

- If HF accepted electrons from another species, they would go into the LUMO. HF may not be a good base, but it is a good acid. What happens when a base donates an electron pair to HF? Write a reaction equation (with curly arrows to show electron movement) and relate what you've drawn to the LUMO of HF.

Molecular Orbitals for CO

- Consider the valence atomic orbitals of carbon and oxygen:



- Which AOs will combine to make MOs?

Molecular Orbitals for CO

- Using symmetry and energy as our guide, it is possible to predict what the MOs of CO look like.

- Use LCAO to predict the shapes and relative energies of the π MOs of CO:

Molecular Orbitals for CO

- Use LCAO to predict the shapes and relative energies of the σ MOs of CO:

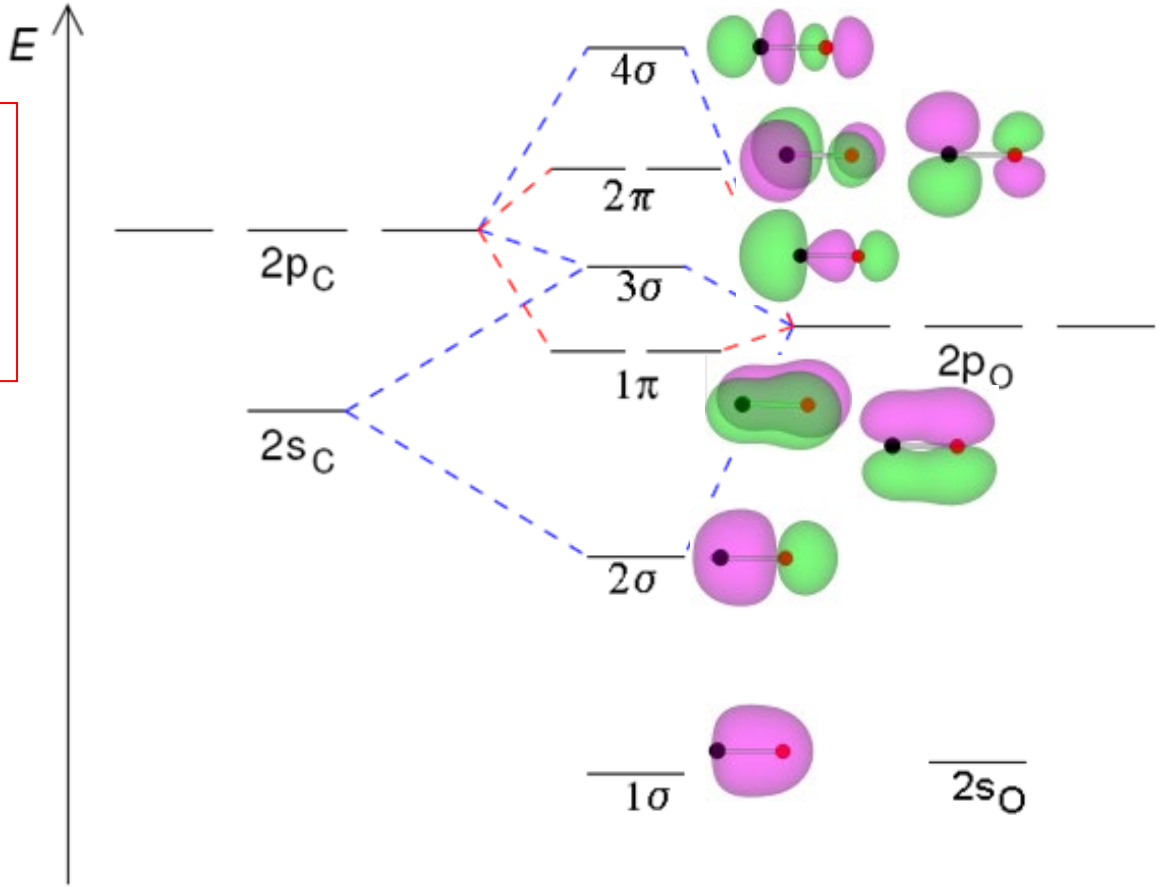
Molecular Orbitals for CO

- We rank these MOs from lowest to highest energy to the best of our ability; however, at this point, we are estimating for a few of the σ MOs.

Molecular Orbitals for CO

- HyperChem shows us the exact energies and shapes of the MOs:

Can you identify each valence molecular orbital in CO as bonding , nonbonding or antibonding (with respect to the C-O bond)?



The MO diagram for CO has the orbitals in the same order as N_2 (verified experimentally). Why does this make sense?

Molecular Orbitals for CO

- Write the valence orbital occupancy for CO.

- Draw a Lewis structure for CO, and compare the bond order obtained by the Lewis method to the bond order obtained by MO.

Molecular Orbitals for CO

- What is the **H**ighest **O**ccupied **M**olecular **O**rbital (HOMO) for CO?

- If CO donated electrons to another species, they would come from the HOMO. As we saw in CHEM 1000, CO is quite a good Lewis base. What happens when CO donates an electron pair to a Lewis acid (e.g. Fe^{3+}) Write a reaction equation (with curly arrows to show electron movement) and relate what you've drawn to the HOMO of CO.

Molecular Orbitals for CO

- What is the **L**owest **U**noccupied **M**olecular **O**rbital (LUMO) for CO?

- If CO accepted electrons from another species, they would go into the LUMO. Looking at the LUMO, what would you expect to happen if a Lewis base donated an electron pair to CO? Write a reaction equation (with curly arrows to show electron movement) and relate what you've drawn to the LUMO of CO.