

# Chemistry 2000 Slide Set 3: LCAO-MO theory for heteronuclear diatomic molecules

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# Heteronuclear diatomics

Key ideas used in constructing LCAO-MOs of **heteronuclear** diatomics:

① Only valence orbitals of similar energy ( $\pm 1$  Ry) mix to form an MO.

② We can separate AOs into two sets:

$\sigma$ -type AOs:  $s$  and  $p_z$

$\pi$ -type AOs:  $p_x$  and  $p_y$

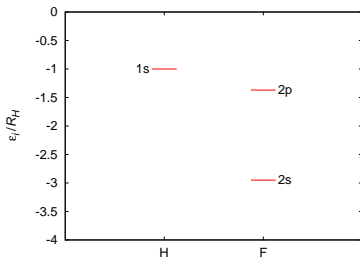
Only  $\sigma$ -type AOs are involved in  $\sigma$  bonding.

Only  $\pi$ -type AOs are involved in  $\pi$  bonding.

③ Number of MOs constructed = number of AOs mixed

# LCAO-MO treatment of HF

Valence AO energies:



Develop MO diagram, compare to Lewis diagram.

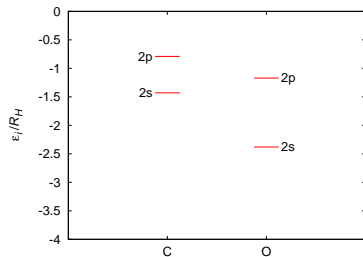
# LCAO-MO treatment of HF (continued)

New elements in the MO diagram:

- We get **nonbonding** (nb) orbitals.
- We generally drop the antibonding labels because this becomes harder to decide from the MO diagram alone.
  - In a simple case like this ( $\sigma$  orbitals arise from mixing **one** AO on each atom), it is generally the case that the lower combination is bonding and the upper is anti-bonding.
  - Otherwise, we need to look at pictures from an MO program like Gaussian, although even that isn't always very clear.
  - Better: look at dependence of orbital energy on distance between nuclei.
    - If the orbital energy increases as the nuclei move apart, the orbital is bonding; decreases, antibonding.
  - Soon: experiments to the rescue!

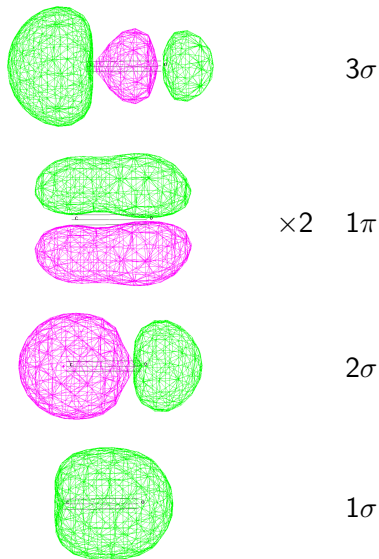
# LCAO-MO treatment of CO

- Valence AO energies:



(Develop MO diagram on board)

# CO molecular orbitals



# LCAO-MO treatment of CO

- The orbitals are **polarized**. As a rule, there is a larger contribution to the MO from the nearest AO in energy.  
Use this to discuss the Lewis acidity of CO.

- The ordering of the  $\sigma$  and  $\pi$  orbitals is not immediately obvious. To determine this, we can use a quantum chemistry program like Gaussian.

We can however take a reasonable guess based on the fact that CO is **isoelectronic** with  $N_2$ : In  $N_2$ , the  $1\pi$  orbitals are below the  $3\sigma$ . This turns out to be the case for CO as well.