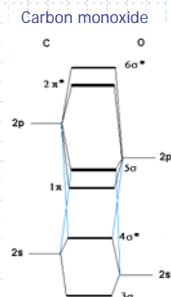


# Physical Chemistry

Lecture 25  
Heteroatomic Diatomic Molecules

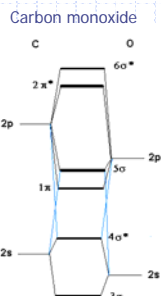
## Heteroatomic molecular orbitals

- ◆ Heteroatomic molecular orbitals
  - Mix atomic orbitals
  - For discussion, treated simplistically as one orbital from each center
    - Often close to correct because a single orbital predominates
  - Must mix orbitals of
    - Similar energy
    - Same symmetry
- ◆ Molecular orbital energies
  - Rough estimation by diagram
  - Calculated with computer simulations



## Example: carbon monoxide

- ◆ Atomic orbitals
  - $2p_C$  similar to  $2p_O$
  - $2s_C$  similar to  $2s_O$
  - Allows an energy diagram similar to homonuclear diatomics
- ◆ Mixing occurs to create bonding and antibonding states
  - Some mixing of  $2s$  states into the  $\sigma$  states from  $2p$
  - Some mixing of  $2p$  states into the  $\sigma$  states from  $2s$
- ◆ Produces a filling order for producing configurations



## Example: carbon monoxide

- ◆ Hartree-Fock calculations give relative energies of states
 

|             |   |               |
|-------------|---|---------------|
| $1\sigma$   | - | 20.58 hartree |
| $2\sigma^*$ | - | 11.32 hartree |
| $3\sigma$   | - | 1.55 hartree  |
| $4\sigma^*$ | - | 0.79 hartree  |
| $1\pi$      | - | 0.64 hartree  |
| $5\sigma$   | - | 0.54 hartree  |
- Calculated with Gaussian
- Not "correct" energies, but gives order of stability
- ◆ Gives a filling order for producing configurations

## Determining configuration and term of carbon monoxide

- ◆ Fill MOs in order
  - Ground configuration
    - $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma^*)^2(1\pi)^4(5\sigma)^2$
  - Total angular momentum = 0
  - Total spin = 0
- ◆ Use term symbols as with homonuclear diatomics
  - Note lack of indication of inversion symmetry

$$1 \Sigma^+$$

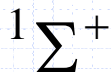
## Example 2: hydrogen fluoride

- ◆ When atoms are of different energies, one must be concerned with the relative energies and symmetries of orbitals
  - Orbitals of same symmetry and approximately similar energy combine most effectively
- ◆ Can estimate approximate HF molecular orbitals
  - Energies calculated with Gaussian
  - Gives filling order of orbitals
 

|             |                                    |   |               |
|-------------|------------------------------------|---|---------------|
| $1\sigma$   | $[\approx 1s_F]$                   | - | 26.11 hartree |
| $2\sigma$   | $[\approx 2s_F]$                   | - | 1.55 hartree  |
| $3\sigma$   | $[\approx C\{2p_{0F} + 1s_H\}]$    | - | 0.71 hartree  |
| $1\pi$      | $[\approx \{2p_{+1F}, 2p_{-1F}\}]$ | - | 0.60 hartree  |
| $4\sigma^*$ | $[\approx D\{2p_{0F} - 1s_H\}]$    |   |               |

## Example 2: hydrogen fluoride

- ◆ Finding ground configuration
  - 10 electrons
- ◆ Fill molecular orbitals in order
 
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$$
- ◆ Eigenvalues with respect to operations
  - $\Lambda = 0$  (all shells filled)
  - $S = 0$  (all shells filled)
  - Even under reflection in vertical plane
- ◆ Term symbol



## Example 2: hydrogen fluoride

- ◆ Bond-order
  - $1\sigma$  is a nonbonding orbital
  - $2\sigma$  is a nonbonding orbital
  - $1\pi$  is a nonbonding orbital
  - $3\sigma$  is a bonding orbital
- ◆ Consider only bonding and antibonding electrons

$$BO_{HF} = \frac{1}{2}(2-0) = 1$$

## Example 3: hydrogen fluoride

- ◆ Excited configuration found by promoting a single electron
 
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^3(4\sigma)^1$$
- ◆ Eigenvalues of operators
  - Treat 3  $\pi$  electrons like 1  $\pi$  electron
    - "The state of a hole is the state of an electron."
  - $\Lambda = 1$
  - $S = 0, 1$  (either paired or unpaired)
- ◆ Terms that arise from this configuration



## Example 4: Nitric oxide, NO

- ◆ Fifteen (15) electrons
- ◆ Use heteroatomic filling order
 
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^1$$
- ◆ Leads to  $\Pi$  term
- ◆  $S = 1/2$
- ◆ Results ground-state term



## Summary

- ◆ Heteroatomic molecules are analyzed in a manner similar to homoatomic molecules
  - Must know MOs
  - Must know filling order
- ◆ MOs are more complex
  - Must involve atomic orbitals of similar energy and symmetry
- ◆ Energies calculated by computer
  - Hartree-Fock calculation relatively straightforward