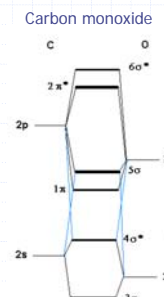


Physical Chemistry

Lecture 25
Heteronuclear Diatomic Molecules

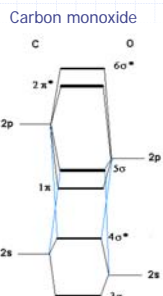
Heteroatomic molecular orbitals

- ◆ 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 σ states from $2p$
 - Some mixing of $2p$ states into the σ states from $2s$
- ◆ Produces a filling order for producing configurations



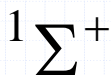
Example: carbon monoxide

- ◆ Hartree-Fock calculations give relative energies of states

1σ	- 20.58 hartree
$2\sigma^*$	- 11.32 hartree
3σ	- 1.55 hartree
$4\sigma^*$	- 0.79 hartree
1π	- 0.64 hartree
5σ	- 0.54 hartree
- ◆ 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



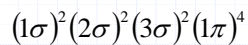
Example 2: hydrogen fluoride

- ◆ 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

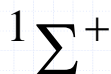
1σ	$[\approx 1s_F]$	- 26.11 hartree
2σ	$[\approx 2s_F]$	- 1.55 hartree
3σ	$[\approx C\{2p_{0F} + 1s_H\}]$	- 0.71 hartree
1π	$[\approx \{2p_{\pm 1F}, 2p_{\pm 1H}\}]$	- 0.60 hartree
$4\sigma^*$	$[\approx D\{2p_{0F} - 1s_H\}]$	

Example 2: hydrogen fluoride

- ◆ Finding ground configuration
 - 10 electrons
- ◆ Fill molecular orbitals in order



- ◆ Eigenvalues with respect to operations
 - $\Lambda = 0$ (all shells filled)
 - $S = 0$ (all shells filled)
 - Even under reflection in vertical plane
- ◆ Term symbol



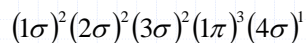
Example 2: hydrogen fluoride

- ◆ Bond-order
 - 1σ is a nonbonding orbital
 - 2σ is a nonbonding orbital
 - 1π is a nonbonding orbital
 - 3σ 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

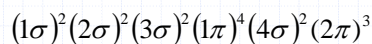


- ◆ Eigenvalues of operators
 - Treat 3 π electrons like 1 π electron
 - "The state of a hole is the state of an electron."
 - $\Lambda = 1$
 - $S = 0, 1$ (either paired or unpaired)
- ◆ Terms that arise from this configuration



Example 4: Nitric oxide, NO

- ◆ Fifteen (15) electrons
- ◆ Use heteroatomic filling order



- ◆ Leads to Π 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