Physical Chemistry

Lecture 25
Heteroatomic Diatomic Molecules

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

Determining configuration and term of carbon monoxide
- Fill MOs in order:
  - Ground configuration:
    - $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2$
    - 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:
    - $1\sigma$ = $1s_x$  $-26.11$ hartree
    - $2\sigma$ = $2s$  $-11.32$ hartree
    - $3\sigma$ = $C^-(2p_{xy} + 1s_y)$  $-1.55$ hartree
    - $4\pi$ = $2p_{xy}$  $-0.79$ hartree
    - $5\sigma$ = $1s_y$  $-0.64$ hartree
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
  \[1\Sigma^+\]

Bond-order
- \(1\pi\) 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
  \[BO_{BO} = \frac{1}{2}(2 - 0) = 1\]

Example 3: hydrogen fluoride

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

Summary

- Heteroatomic molecules are analyzed in a manner similar to homonuclear 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

Example 4: Nitric oxide, NO

- Fifteen (15) electrons
- Use heteroatomic filling order
  \[(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\pi)^2(2\pi)^1\]
- Leads to \(\Pi\) term
- \(S = \frac{1}{2}\)
- Results ground-state term
  \[2\Pi\]