Chapter 9: Bonding - Orbitals

1. Molecular Orbitals
2. Valence Bond Theory
3. Molecular Orbital Theory
4. Metals & Semiconductors
What is a Bond?
What is a Molecular Orbital?
9.1 Molecular Orbital Theories

Two Approaches

**Valence Bond (VB) Theory:** Treat bond orbitals as the result of the hybridization of atomic orbitals (s,p,d). Useful for predicting geometries, can not account for all physical properties.

**Molecular Orbital (MO) Theory:** Direct quantum mechanical solution to the multi nucleus wavefunction. Can account for magnetic properties.
9.2 Valence Bond Theory
Hybrid Orbitals

Result From the Mixing of Atomic Orbitals
- linear geometry
- 180° bond angle

-1/2 s & 1/2 p in character,
- note lack of node at nucleus
sp$^2$ Hybrid

- trigonal planar geometry
- 120° bond angle

1/3 s & 2/3 p in character
sp³ Hybrid

- tetrahedral geometry
- 90° bond angle

1/4 s & 3/4 p in character
sp$^{3}$d Hybrid

- trigonal bipyramidal geometry
- $120^\circ$ and $90^\circ$ bond angle

1/5 s, 3/5 p and 1/5 d in character

results in an expanded octet
sp$^3$d$^2$ hybrid

- octahedral geometry
- 90° bond angle

1/6s, 1/2 p & 1/3 d in character
TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

<table>
<thead>
<tr>
<th>Atomic Orbital Set</th>
<th>Hybrid Orbital Set</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp$</td>
<td>Two $sp$</td>
<td>Linear</td>
<td>$\text{BeF}_2$, $\text{HgCl}_2$</td>
</tr>
<tr>
<td>$spp$</td>
<td>Three $sp^2$</td>
<td>Trigonal planar</td>
<td>$\text{BF}_3$, $\text{SO}_3$</td>
</tr>
<tr>
<td>$spp$</td>
<td>Four $sp^3$</td>
<td>Tetrahedral</td>
<td>$\text{CH}_4$, $\text{NH}_3$, $\text{H}_2\text{O}$, $\text{NH}_4^+$</td>
</tr>
<tr>
<td>$spppd$</td>
<td>Five $sp^3d$</td>
<td>Trigonal bipyramidal</td>
<td>$\text{PF}_5$, $\text{SF}_4$, $\text{BrF}_3$</td>
</tr>
<tr>
<td>$spppd$</td>
<td>Six $sp^3d^2$</td>
<td>Octahedral</td>
<td>$\text{SF}_6$, $\text{ClF}_5$, $\text{XeF}_4$, $\text{PF}_6^-$</td>
</tr>
</tbody>
</table>

hybrids
2 Types of Bonds

2 Types of Bonds Result from the Overlap of Adjacent Atomic Orbitals

1. \( \sigma \) bonds - have electron density along the internuclear axis

2. \( \pi \) bonds - have a node on the internuclear axis, result from the overlap of p orbitals which are orthogonal to the internuclear axis
Sigma Bonds

(a) Atoms approach each other

(b) Overlap region

(c) Overlap region

Energy released when bond forms

Energy absorbed when bond breaks

Potential energy (kJ/mol)

Internuclear distance (pm)

Bond length (H₂)

74 pm

-432 kJ/mol
Pi & Double Bonds

Result from overlap of p orbitals

- have node on internuclear axis

Double Bond = 1 $\sigma$ & 1 $\pi$ bond

note: $\sigma$ bond is sp$^2$ hybrid

PREVENT ROTATION
Delocalized Bonding - Benzene

Need Resonance Structures When Describing with Lewis Dot Diagrams (NO$_3^-$)
Triple Bonds

Triple bond = 1 $\sigma$ & 2 $\pi$ bonds

note: $\sigma$ bond is sp$^3$ hybrid
Note: Molecular Geometries Are Determined by the # of Sigma Bonds and Lone Pairs

Pi Bonds Do Not Effect Geometry Which Is Why Multiple Bonds Were Considered As Single Electron Domains in VSEPR Geometric Calculations
9.3 Molecular Orbital (MO) Theory

-Molecular Orbitals Result Through the Interaction of Atomic Orbitals

Two types of Orbitals Result

1. Bonding Orbitals - result from the complementary overlap of adjacent orbitals
2. Antibonding Orbitals - result from the destructive overlap of adjacent orbitals
Molecular Orbital Theory

2 Factors Influence the Ability of Atomic Orbitals to Combine into Molecular Orbitals

1. **Energy Factor** - the Atomic Orbitals Must Be of Similar Energy
2. **Spatial Factor** - the Atomic Orbitals Must Be in the Same Region of Space
sigma bonds

$\sigma_{2s}$

$\sigma_{2p}$
$\pi$ bonds

(a) $2p_z + 2p_z \rightarrow \sigma^{*}2p$

(b) $2p_x + 2p_x \rightarrow \pi 2p$

(c) $2p_y + 2p_y \rightarrow \pi 2p$
MO Structure of $\text{H}_2$

![Diagram of MO structure of H$_2$ molecule]

What would be the MO structure of He$_2$?
**Bond Order**

\[ \text{BO} = \frac{1}{2} (\text{number electrons in bonding orbitals} - \text{number electrons in antibonding orbitals}) \]

\[ \text{Bond Order} = 0 \]
MO Structure of Li
### 2nd Row Diatomics

<table>
<thead>
<tr>
<th></th>
<th>Large $2s$-$2p$ interaction</th>
<th>Small $2s$-$2p$ interaction</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$B_2$</td>
<td>$C_2$</td>
</tr>
<tr>
<td>$\sigma_{2p}^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi_{2p}^*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_{2p}$</td>
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<tr>
<td>$\pi_{2p}$</td>
<td>1 \uparrow 1</td>
<td>1 \downarrow 1 \downarrow</td>
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<tr>
<td>$\sigma_{2s}^*$</td>
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<tr>
<td>$\sigma_{2s}$</td>
<td>1 \downarrow 1</td>
<td>1 \downarrow 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Bond order</th>
<th>Bond enthalpy (kJ/mol)</th>
<th>Bond length (Å)</th>
<th>Magnetic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>290</td>
<td>1.59</td>
<td>Paramagnetic</td>
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<tr>
<td>$C_2$</td>
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<td>620</td>
<td>1.31</td>
<td>Diamagnetic</td>
</tr>
<tr>
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<td>1.10</td>
<td>Diamagnetic</td>
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<td>495</td>
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<tr>
<td>$F_2$</td>
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<td>155</td>
<td>1.43</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>$Ne_2$</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Magnetic Properties

Diamagnetic: Does not Interact with a Magnetic Field (all electrons are spin paired)

Paramagnetic: Interacts with a Magnetic Field (has unpaired electrons)
10.4 Metals & Semiconductors

**Band Theory:**

- MOs Spread out over huge # of atoms
- # MOs = # AOs mixed (#atoms x # valence orbitals in atom)
- So many orbitals that energies literally overlap forming a “band” of allowable states

- Valence Band = highest occupied Band

**Fermi Level** – Highest occupied orbitals at 0 K
Band Theory & Conductivity

-Metals have vacant valence band orbitals

Electrical conductivity occurs when electrons are excited into vacant orbitals (above fermi level)

-Insulators have filled valence band orbitals and a large energy gap (band gap energy) to conduction band (lowest empty levels)

Semiconductors have filled valence band orbitals and a small band gap energy.
**Doped Semiconductors**

**Intrinsic semiconductors** – (metalloids) have [-] electrons and [+] holes

**Extrinsic semiconductors** – metalloid crystal doped with nearby element of similar size, effectively increasing or decreasing available electrons.

**2 Types**

p-type semiconductor

n-type semiconductor
p-type Semiconductors

- dope Si w/Al or Ge w/Ga

- Valence band is slightly deficient in electrons compared to pure Si but has same number of orbitals.

- Si electrons can occupy these vacant orbitals forming mobile positive holes
n-type Semiconductors

- dope Si w/P or Ge w/As

- Valence band has slight excess electrons than orbitals and so some must occupy conduction band

- Few excess electrons are mobile
Applications of Semiconductors

- Solar Cells
- Transistors (computer chips)
- Rectifiers
- Nanotechnologies