**Bonding and Molecular Structure: Orbital Hybridization and Molecular Orbitals**

Chapter 8

**Advanced Theories of Chemical Bonding**

**Two Theories of Bonding**

**MOLECULAR ORBITAL THEORY** - Robert Mulliken (1896-1986)

Valence electrons are **delocalized**

Valence electrons are in orbitals (called molecular orbitals) spread over entire molecule.

**VALENCE BOND THEORY** - Linus Pauling

Valence electrons are localized between atoms (or are lone pairs).

Half-filled atomic orbitals overlap to form bonds.

Electrons stabilized by 2 nuclei

**Sigma Bond Formation by Orbital Overlap**

Two s orbitals overlap

One s & one p overlap

Two p orbitals overlap

**Sigma Bond Formation by Orbital Overlap**

Two s orbitals overlap

One s & one p overlap

Two p orbitals overlap
Using VB Theory

Bonding in BF₃

Boron configuration

↑↑↓ ↑↓

2p²s¹s

planar triangle
angle = 120°

How to account for 3 bonds 120° apart using a spherical s orbital and p orbitals that are 90° apart?

Pauling said to modify VB approach with ORBITAL HYBRIDIZATION - mix available orbitals to form a new set of orbitals - HYBRID ORBITALS - that will give the maximum overlap in the correct geometry.

Bonding in BF₃

The three hybrid orbitals are made from 1 s orbital and 2 p orbitals create 3 sp² hybrids.

Now we have 3, half-filled HYBRID orbitals that can be used to form planar B-F σ bonds.

Bonding in CH₄

How do we account for 4 C-H sigma bonds 109° apart?

Need to use 4 atomic orbitals - s, px, py, and pz - to form 4 new hybrid orbitals pointing in the correct direction.
Bonding in a Tetrahedron - Formation of Hybrid Atomic Orbitals

4 C atom orbitals hybridize to form four equivalent $sp^3$ hybrid atomic orbitals.

**Bonding in CH₄**

- **Bonds**
  - 2: linear $sp$
  - 3: trigonal planar $sp^2$
  - 4: tetrahedral $sp^3$
  - 5: trigonal bipyramidal $sp^3d$
  - 6: octahedral $sp^3d^2$

**Orbital Hybridization**

- **REMAINING p orbs?**
  - 2 p
  - 1 p
  - none
  - ---
  - ---

- **see: VSEPR Guide**

**Bonding in Glycine**

- $sp^3$
- $sp^2$
- $sp^3$
- $sp^3$
- $sp^3$

**Arrangement of Hybrid Orbitals**

- **Two electron pairs $sp$**
- **Three electron pairs $sp^2$**
- **Four electron pairs $sp^3$**

**Generic Figure**

- Linear
- Trigonal planar
- Tetrahedral

**Example**

- $H_2O_2$
- $NF_3$

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Multiple Bonds

Consider ethylene, $C_2H_4$

Sigma Bonds in $C_2H_4$

$\sigma$ and $\pi$ Bonding in $C_2H_2$

$C_2H_2$ has a triple bond
Consequences of Multiple Bonding

There is restricted rotation around C=C bond.

Consequences of Multiple Bonding

Restricted rotation around C=C bond.

Molecular Orbital Theory

- Accounts for paramagnetism, color, bonding
- Atomic orbitals delocalize into molecular orbitals
- Bonding, Antibonding and Nonbonding orbitals
- Quite complicated, need computers; we will only look at diatomics (2 atom systems) from the first and second periods only

Advantages of MO Theory

Dioxygen should be electron paired (diamagnetic) by VB Theory, but dioxygen is actually paramagnetic. MO Theory accounts for paramagnetism of O₂

Four Principles of MO Theory

**Principle #1:**
Number of Molecular Orbitals = Number of Atomic Orbitals

When two atomic 1s H orbitals combine, a bonding (σ) and antibonding (σ*) molecular orbital forms

Molecular Orbital Type

Two 1s orbitals from two hydrogen atoms create two molecular orbitals in H₂

Two 1s orbitals and two 2s orbitals from two lithium atoms create four molecular orbitals in Li₂

See Four Principles of MO Handout
Four Principles of MO Theory

**Principle #2:**
Bonding MO lower in energy than the parent orbital
Antibonding MO higher in energy than the parent orbital

**Principle #3:**
Electrons of molecule assigned to successively higher MOs

Use Pauli Exclusion Principle and Hund's Rule when assigning electrons

**MO Diagram for H₂**

Two 1s electrons from two H atoms occupy the σ orbital in H₂

**Bonding MO**

**Antibonding MO**

**MO Diagram for He₂**

Two 1s electrons in σ, Two 1s electrons in σ*

**Bond Order in MO Theory**

Bond Order = \( \frac{1}{2} (\# \text{ bonding } e^- - \# \text{ antibonding } e^-) \)

In H₂,
Bond Order = \( \frac{1}{2} (2 - 2) = 0 \);
stable molecule

In He₂,
Bond Order = \( \frac{1}{2} (2 - 0) = 1 \);
unstable molecule

∴ He₂ does not exist

**Four Principles of MO Theory**

**Principle #4:**
Atomic orbitals combine to give molecular orbitals only when the atomic orbitals are of similar energy

Similar energy = better overlap

\[ \begin{align*}
1s + 1s &= \text{good MO} \\
1s + 2s &= \text{poor MO} \\
2s + 2s &= \text{good MO} \\
2s + 2p &= \text{poor MO} \\
3s + 2s &= \text{poor MO} \\
&\quad \ldots \text{ etc.} \ldots
\end{align*} \]
Example: Dilithium, Li₂

Note: no overlap between 1s and 2s
Bond Order = \( \frac{1}{2} (4 - 2) = 1 \)
Stable molecule

Would you expect Be₂ to exist? Why?

p orbitals and \( \pi \) bonds

Three possible p orbitals on each atom - six total p MO orbitals
Two p orbitals create 2 \( \sigma \) MO bonds
Four remaining p orbitals create 4 \( \pi \) MO bonds

Four p atomic orbitals create four \( \pi \) molecular orbitals,
\( \pi = \text{bonding} (2) \)
\( \pi^* = \text{antibonding} (2) \)

... but there's a catch!

p orbitals and \( \pi \) bonds

For B, C and N,
\( \pi \) orbitals lower energy than \( \sigma \) orbital
\( \pi^* \) orbitals lower energy than \( \sigma^* \) orbital

Example: B₂
Bond Order = 1

See MO Diagram (B₂ - N₂) Handout

p orbitals and \( \pi \) bonds

For O, F and Ne,
\( \sigma \) orbital lower energy than \( \pi \) orbitals
\( \pi^* \) orbitals lower energy than \( \sigma^* \) orbital

\( \sigma^* \)
\( \pi^* = \text{antibonding} (2) \)

Example: O₂
Bond Order = 2

See MO Diagram (O₂ - Ne₂) Handout

Paramagnetism

Paramagnetism exists when unpaired electrons in MO diagram

\( O₂ \) is paramagnetic; unpaired electrons in two \( \pi^* \) orbitals
**Paramagnetism**

Paramagnetism exists when unpaired electrons in MO diagram

N₂ is diamagnetic; all electrons paired

**Molecular Orbital Notation**

Used to abbreviate the MO diagrams

- Ignore core electrons
- Write in order of increasing energy

For N₂:

\[
[\text{core electrons}] (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p})^4 (\sigma_{2p})^2
\]

**Sigma and Pi Bonds**

Determine sigma and pi bonds using:

\[
\# \sigma \text{ bonds} = \frac{1}{2} (\# \sigma \text{ bonding e}^- - \# \sigma \text{ antibonding e}^-)
\]

\[
\# \pi \text{ bonds} = \frac{1}{2} (\# \pi \text{ bonding e}^- - \# \pi \text{ antibonding e}^-)
\]

and

\[
\# \sigma \text{ bonds} + \# \pi \text{ bonds} = \text{bond order}
\]

For N₂:

\[
[\text{core electrons}] (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p})^4 (\sigma_{2p})^2
\]

\[
\# \sigma \text{ bonds} = \frac{1}{2}(4 - 2) = 1 \sigma \text{ bond}
\]

\[
\# \pi \text{ bonds} = \frac{1}{2}(4 - 0) = 2 \pi \text{ bonds}
\]

**MO Diagram for Diatomics**

Changes in MO diagrams due to s-p mixing and/or electron repulsion

**Ionic Diatomic Molecules**

Predicting Ionic Diatomic MO diagrams simple

*Use Hund and Pauli*

**Example: O₂⁺**

Remove electron from \(\pi_{2p}\) orbital

Check bond order, paramagnetism

**Example: O₂⁻**

Using the O₂ diagram on the right, where would you place the extra electron? Is O₂⁻ more or less stable than O₂? Why?
Application: Vision

Molecular Orbital Theory helps to describe the process of vision - photochemistry

Application: Band Theory

In metallic bonding, electrons delocalized over metallic lattice - a sea of electrons
MO energies identical, excellent overlap
Helps explain conductivity, malleability, more

End of Chapter 8

See:
- Chapter Eight Study Guide
- Chapter Eight Concept Guide

MO Diagram for Mo(CO)5=CH2