Valence Bond Theory (hybrid orbitals)

The Orbital Overlap Model of Bonding

\[ \text{End to end overlap} = \text{sigma (} \sigma \text{) bond} \]

Predicted Bonding and VSEPR Geometry for CH₄

\[
\begin{align*}
\text{Lewis Structure} & \quad \text{Electron pairs} \\
\text{around C} & \quad 109.5^\circ
\end{align*}
\]
**Problem:** the available s and p-orbitals are at 90° angles, not at the predicted 109.5°!

New orbitals are constructed from pre-existing s, p, and d-orbitals = hybrid orbitals

1. Hybridize the CENTRAL ATOM ONLY (others as needed)

2. Only use valence shell electrons

3. The number of hybrid orbitals formed = number of atomic orbitals used
For CH₄, we need 4 hybrid orbitals, so 4 atomic orbitals are required as follows: (s + p + p + p) = sp³

Needed to form 4 sigma bonds

Formation of sp³ Hybrid Orbitals
Formation of Covalent Bonds

Fig. 10.8
Hybridization Rules

(will be upgraded as we proceed)

1. Hybrid orbitals get 1 electron for a $\sigma$-bond, 2 electrons for a lone pair.

$\text{sp}^3$ hybridization for H$_2$O

- $2p$ $2p$ $2p$
- $2s$
- isolated O atom

Needed to form 2 sigma bonds and 2 lone pairs
**sp2 Hybridization**

BF$_3$ - trigonal planar according to VSEPR Theory (incomplete octet exception)
For BF$_3$, we need 3 hybrid orbitals, so 3 atomic orbitals are required as follows: \((s + p + p) = sp^2\)

\[
\begin{array}{c}
\text{energy} \\
\downarrow \\
2p \ 2p \ 2p \\
\uparrow \\
2s \\
isolated \text{ B atom}
\end{array}
\]

Needed to form 3 sigma bonds

---

**sp Hybridization**

BeCl$_2$ - linear according to VSEPR Theory

Lewis dot structure  Electron-pair geometry  Molecular geometry
For BeCl₂, we need 2 hybrid orbitals, so 2 atomic orbitals are required as follows: \((s + p) = sp\)

Needed to form 2 sigma bonds

Ex 10.4 Describe the hybridization state of phosphorus in PBr₅
For PBr$_5$, we need 5 hybrid orbitals, so 5 atomic orbitals are required as follows: (s + p + p + p + d) = sp$^3$d

Needed to form 5 sigma bonds

**sp$^3$d$^2$ Hybridization**

e.g. SF$_6$
For SF₆, we need 6 hybrid orbitals, so 6 atomic orbitals are required as follows: \((s + p + p + p + d + d) = sp^3d^2\)

Isolated S atom

Needed to form 6 sigma bonds
Sigma (σ) bonds = end-to-end overlap

(a) $s + p$ sigma overlap

(b) $p + p$ sigma overlap
Pi ($\pi$) bond = side-by-side overlap

$\text{C - C}$ 1 $\sigma$ bond

$\text{C = C}$ 1 $\sigma$ bond
  1 $\pi$ bond

$\text{C≡C}$ 1 $\sigma$ bond
  2 $\pi$ bonds
**Hybridization Rules**

(upgraded – more will be added)

1. Hybrid orbitals get 1 electron for a σ-bond, 2 electrons for a lone pair.

2. Remaining electrons go into unhybridized orbitals = π bonds

DOUBLE BONDS: Ethylene, CH₂CH₂

Lewis Structure:
Apply VSEPR Theory and Determine Hybridization

\[ \begin{array}{c}
\text{H} & \text{C} = \text{C} & \text{H} \\
\text{H} & \text{C} & \text{H}
\end{array} \]

Ethylene, \( \text{C}_2\text{H}_4 \)
sp² hybridization on each C atom -

2p 2p 2p
2s
isolated C atom

sp² hybrids and unhybridized p-orbital
\( \sigma \) bond = end-to-end overlap of the sp\(^2\) hybridized orbitals

1 electron from the sp\(^2\) hybrid on C, the other from the hydrogen 1s orbital

\( \pi \) bond = side-by-side overlap of the unhybridized p-orbitals

Electron from the unhybridized p-orbital on the C atom
Sigma (σ) Bonding in Ethylene

Pi (π) Bonding in Ethylene
**DOUBLE BONDS**: Formaldehyde, CH₂O

Lewis Structure:

Apply VSEPR Theory and Determine Hybridization

\[ \text{H} - \text{C} = \text{O} \]
\[ \text{H} \]
sp² hybridization on C -

2s
isolated C atom

hybridize C orbitals

energy

2p 2p 2p
sp\(^2\) hybridization on O -

energy

\[ \uparrow \uparrow \uparrow \uparrow \]
\[ 2p \ 2p \ 2p \]

\[ \uparrow \downarrow \]
\[ 2s \]

isolated O atom

Sigma (\(\sigma\)) Bonding in Formaldehyde

H

\(sp^2\)

C

\(\sigma\)

O
Pi (\(\pi\)) Bonding in Formaldehyde

Electron from the unhybridized
\(p\)-orbitals

TRIPLE BONDS: Acetylene, \(\text{C}_2\text{H}_2\)

Lewis Structure:
Apply VSEPR Theory and Determine Hybridization

H - C ≡ C - H

sp hybridization on each C atom -

2s
isolated C atom

2p 2p 2p

hybridize C orbitals
sp hybrids and unhybridized p-orbitals

Sigma (σ) Bonding in Acetylene
Pi ($\pi$) Bonding in Acetylene

Explain the Bonding Using Valence Bond Theory

$\text{CO}_2$
Sigma Bonding in CO$_2$

Pi Bonding in CO$_2$

sigma bond (1 pair of electrons)  pi bond (1 pair of electrons)  pi bond (1 pair of electrons)
VSEPR Theory - electron pair repulsions influence molecular shape

Valence Bond Theory - atoms form bonds by overlapping atomic and/or hybrid orbitals

Applied to $O_2$ - $2(6) = 12$ valence electrons or 6 pairs

This prediction is WRONG! Since all of the electrons are paired up, the molecule should be diamagnetic, but experiments prove that it is PARAMAGNETIC!

An additional refinement in bonding theory is necessary =

\[ \textcolor{red}{\text{Molecular Orbital Theory}} \]
Molecular Orbitals - Preliminary Ideas

Don’t forget that electrons behave like WAVES, and there are WAVE FUNCTIONS ($\psi$) that describe the electron position in space = ATOMIC ORBITALS ($\psi^2$)

Waves (electrons) can interfere with each other, either CONSTRUCTIVELY or DESTRUCTIVELY
Molecular Orbitals - destructive and constructive interference of atomic orbitals

Sigma bond formation involving p-orbitals
Principles of Molecular Orbital Theory

1. The total number of molecular orbitals = total number of atomic orbitals contributed by the bonding atoms

2. Bonding MO’s are lower in energy (more stable) than antibonding MO’s

3. Electrons occupy molecular orbitals following the Pauli Exclusion Principle (spins pair up) and Hund’s Rule (remain unpaired as long as an empty orbital is available of the same energy)
Energy Levels of Molecular Orbitals for Homonuclear Diatomics - H₂, O₂, etc

Molecular orbitals

Atomic orbitals

2p 2p

\( \sigma_{1s} \) \( \sigma_{2s} \) \( \sigma_{1s}^* \)

2s 2s

\( \pi_{2p} \) \( \pi_{2p} \) \( \sigma_{2s} \) \( \sigma_{2s}^* \)

1s 1s

\( \sigma_{2p} \) \( \sigma_{2p} \) \( \sigma_{2p} \) \( \sigma_{2p} \)

Molecular Orbital Electron Configurations

e.g. O₂
**Bond Order**

Order = \( \frac{1}{2} [\text{# electrons bonding MO’s} - \text{# electrons antibonding MO’s}] \)

1. The greater the bond order, the more stable the molecule
2. A high bond order means higher bond energies and shorter bond lengths.
3. Fractional bond orders are possible

\[ \text{Bond order } = \quad \text{Bond order } = \]
Homonuclear Diatomic Molecules of Second Row Elements

*the inner MO’s formed from overlap of the 1s orbitals aren’t shown*

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<th>B₂</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
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<th>Two</th>
<th>Three</th>
<th>Two</th>
<th>One</th>
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<td>620</td>
<td>946</td>
<td>498</td>
<td>159</td>
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<tr>
<td>Bond distance (pm)</td>
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<td>131</td>
<td>110</td>
<td>121</td>
<td>143</td>
</tr>
<tr>
<td>Observed magnetic behavior (paramagnetic or diamagnetic)</td>
<td>Para</td>
<td>Dia</td>
<td>Dia</td>
<td>Para</td>
<td>Dia</td>
</tr>
</tbody>
</table>
Let’s take a look at the molecule ozone - O$_3$

Lewis structure: 3(6) = 18 or 9 pairs

\[\text{sp}^2\text{ hybridization of the central oxygen} -
\]

unhybridized $p$ orbital used for $\pi$ bonding

three $sp^2$ hybrid orbitals
sp\(^2\) hybridization of the terminal oxygens -

Sigma Bonding in O\(_2\)
Explain using Valence Bond Theory
Pi Bonding in $\text{O}_3$

Combine 3 p-orbitals = 3 molecular orbitals

\begin{align*}
\text{Antibonding } \pi \text{ MO} \\
\text{Nonbonding } \pi \text{ MO} \\
\text{Bonding } \pi \text{ MO}
\end{align*}

Pi Bonding in $\text{O}_3$

\begin{align*}
\text{Antibonding } \pi \text{ orbital} \\
\text{Nonbonding } \pi \text{ orbital}
\end{align*}
Electrons in the bonding MO are free to move along the length of the molecule = delocalization

Bonding $\pi$ orbital

Another example - NO$_3^-$

Hybridize all of the atoms to sp$^2$ and combine the unused p-orbitals into molecular orbitals.
Benzene - $C_6H_6$

sp$^3$ hybridize the C atoms and combine the unused p-orbitals into molecular orbitals.