Chapter 9: Molecular Geometries and Bonding Theories

Learning Outcomes:
- Predict the three-dimensional shapes of molecules using the VSEPR model.
- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments.
- Explain the role of orbital overlap in the formation of covalent bonds.
- Determine the hybridization atoms in molecules based on observed molecular structures.
- Sketch how orbitals overlap to form sigma (σ) and pi (π) bonds.
- Explain the existence of delocalized π bonds in molecules such as benzene.
- Count the number of electrons in a delocalized π system.
- Explain the concept of bonding and antibonding molecular orbitals and draw examples of σ and π MOs.
- Draw molecular orbital energy-level diagrams and place electrons into them to obtain the bond orders and electron configurations of diatomic molecules using molecular orbital theory.
- Correlate bond order, bond strength (bond enthalpy), bond length, and magnetic properties with molecular orbital descriptions of molecules.
Molecular Shapes

Common shapes for \( \text{AB}_2 \) and \( \text{AB}_3 \) molecules.

The shape of a molecule plays an important role in its reactivity.

Molecular shapes tend to allow maximum distances between B atoms in \( \text{AB}_n \) molecules.

- By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.
- Additional shapes may be derived from the above shapes.
Two additional shapes may be derived from a tetrahedral shape by removal of corner atoms.

Shape of a Molecule

- Electron pairs, whether they be bonding or nonbonding, repel each other.
- By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.
Electron Domains

- We can refer to the electron pairs as **electron domains**.
- In a *double* or *triple* bond, all electrons shared between those two atoms are on the same side of the central atom; therefore, they count as one electron domain.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

- The table shows the electron-domain geometries for two through six electron domains around a central atom.
- To determine the electron-domain geometry, count the total number of lone pairs, single, double, and triple bonds on the central atom.
Electron-Domain Geometries

- Count the number of electron domains in the Lewis structure.
- The electron domain geometry corresponds to the base geometry with that number of electron domains.
- The electron-domain geometry is often *not* the shape of the molecule, however.
- The molecular geometry is that defined by the positions of *only* the atoms in the molecules, not the nonbonding pairs.

Geometries

The **molecular geometry** is the arrangement of the atoms in space.
- To determine the shape of a molecule we distinguish between *lone pairs* (nonbonding domains) and *bonding pairs* (bonding domains).

**Linear Electron Domain**

<table>
<thead>
<tr>
<th>Number of Electron Domains</th>
<th>Electron-Domain Geometry</th>
<th>Bonding Domains</th>
<th>Nonbonding Domains</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>2</td>
<td>0</td>
<td>Linear</td>
<td>( \overset{\text{O}}{\text{C}} = \overset{\text{O}}{\text{C}} )</td>
</tr>
</tbody>
</table>

- In this domain, there is only one molecular geometry: linear.
- If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.
Trigonal Planar Electron Domain

There are two molecular geometries:
- Trigonal planar, if all the electron domains are bonding
- Bent, if one of the domains is a nonbonding pair.

Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Their repulsions are greater; this tends to decrease bond angles in a molecule.
Multiple Bonds and Bond Angles

- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Therefore, they also affect bond angles.

Tetrahedral Electron Domain

- Three molecular geometries:
  - Tetrahedral, if all are bonding pairs
  - Trigonal pyramidal if one is a nonbonding pair
  - Bent if there are two nonbonding pairs
Expanded Valence Shell: Trigonal bipyramidal

There are four distinct molecular geometries in this domain:
- Trigonal bipyramidal
- Seesaw
- T-shaped
- Linear

<table>
<thead>
<tr>
<th>Number of Electron Domains</th>
<th>Electron-Domain Geometry</th>
<th>Bonding Domain</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Trigonal Bipyramidal</td>
<td>5</td>
<td>Trigonal Bipyramidal</td>
<td>PCl₅</td>
</tr>
<tr>
<td>4</td>
<td>Seesaw</td>
<td>1</td>
<td>Seesaw</td>
<td>Si₂</td>
</tr>
<tr>
<td>3</td>
<td>T-shaped</td>
<td>2</td>
<td>T-shaped</td>
<td>CIF₃</td>
</tr>
<tr>
<td>2</td>
<td>Linear</td>
<td>3</td>
<td>Linear</td>
<td>SO₂</td>
</tr>
</tbody>
</table>
Trigonal Bipyramidal Electron Domain: Deviations from Ideal Bond Angles

Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.

Octahedral Electron Domain

All positions are equivalent in the octahedral domain.

Three molecular geometries can be derived from the octahedral electron domain geometry:
- Octahedral
- Square pyramidal
- Square planar
Larger Molecules

In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.

<table>
<thead>
<tr>
<th>Number of electron domains</th>
<th>Tetrahedral</th>
<th>Trigonal planar</th>
<th>Tetrahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron-domain geometry</td>
<td>H--C--H</td>
<td>:O:--C--O</td>
<td>Ò--H</td>
</tr>
<tr>
<td>Predicted bond angles</td>
<td>109.5°</td>
<td>120°</td>
<td>109.5°</td>
</tr>
</tbody>
</table>

Polarity of Molecules

- Previously we discussed bond dipoles.
- But just because a molecule possesses polar bonds does not mean the molecule as a whole will be polar.
Polarity of Molecules

By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.

\[ \sum x = 0 \quad \sum y \neq 0 \]

overall \(\sum \neq 0\)

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**Polarity of Molecules**

For nonionic molecules, determine if the BONDS polar? (Do they have a bond dipole?)

a. **NO**: The molecule is NONPOLAR!

b. **YES**: Continue—Do the AVERAGE position of \(\delta^+\) and \(\delta^-\) coincide? (Is the overall dipole moment equal to ZERO?)

1) **YES**: The molecule is NONPOLAR.

2) **NO**: The molecule is POLAR.

**NOTE**: Different atoms attached to the central atom have different polarity of bonds.

<table>
<thead>
<tr>
<th>Pauling electronegativity difference</th>
<th>Type of bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.4</td>
<td>nonpolar covalent</td>
</tr>
<tr>
<td>0.4-1.7</td>
<td>polar covalent</td>
</tr>
<tr>
<td>&gt; 1.7</td>
<td>ionic</td>
</tr>
</tbody>
</table>
Polarity

It is possible for a molecule with polar bonds to be either polar or nonpolar.

Examine each structure independently to determine if a molecule or ion is polar or nonpolar.

Example: Polarity of Molecules

Draw the Lewis structure and determine the molecular geometry to determine if a molecular is polar.
Valence Bond Theory: Overlap and Bonding

- **Covalent bonds** form when orbitals on two adjacent atoms overlap.
- The shared region of space between the orbitals is called the *orbital overlap*.
- There are two electrons (usually one from each atom) of opposite spin in the orbital overlap.

Overlap and Bonding

- Increased overlap brings the atoms together until a balance is reached between the like charge repulsions and the electron-nucleus attraction.
- Atoms can’t get too close because the internuclear repulsions get too great.
VSEPR and Hybrid Orbitals

VSEPR predicts shapes of molecules very well.

How does that fit with orbitals?
- Let’s use H₂O as an example:
- If we draw the best Lewis structure to assign VSEPR, it becomes bent.
- If we look at oxygen, its electron configuration is \(1s^22s^22p^4\). If it shares two electrons to fill its valence shell, they should be in \(2p\).
- Wouldn’t that make the angle 90°? Why is it 104.5°?

Hybrid Orbitals

But it’s hard to imagine tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize.

- **Hybrid orbitals** form by “mixing” of atomic orbitals to create new orbitals of equal energy, called degenerate orbitals.
- This process is called **hybridization**.
- When two orbitals “mix” they create two hybrid orbitals; when three orbitals mix, they create three hybrid orbitals.
Hybrid Orbitals – \( sp \) hybrid

Beryllium & \( \text{BeF}_2 \):
- In its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals.
- But if it absorbs the small amount of energy needed to promote an electron from the \( 2s \) to the \( 2p \) orbital, it can form two bonds.

Hybrid Orbitals - \( sp \)

Mixing the \( s \) and \( p \) orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
- These \( sp \) hybrid orbitals have two lobes like a \( p \) orbital.
- One of the lobes is larger and more rounded as is the \( s \) orbital.

![Diagram of hybrid orbitals](image-url)
Hybrid Orbitals

- Two degenerate orbitals align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.

Hybrid Orbitals – \( sp^2 \)

Using a similar model for boron leads to...

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32
Hybrid Orbitals – $sp^3$

With carbon we get...

$\begin{align*}
2s & \quad 2p \\
\text{Promote} & \quad \rightarrow \\
\text{Hybridize} & \quad \rightarrow \\
\text{One } s \text{ orbital} & \quad \text{Three } p \text{ orbitals} \\
\text{Hybridize to form four } sp^3 \text{ hybrid orbitals} & \\
\text{Shown together (large lobes only)} & \\
\end{align*}$

$H_2O$

Tetrahedral arrangement of four $sp^3$ hybrid orbitals about oxygen

Two $sp^3$ orbitals contain nonbonding electron pairs.

$NH_3$

$sp^3$ hybrid orbitals on N overlap with 1s orbitals on three hydrogens to make three N–H bonds

1. Draw Lewis structure.
2. Determine electron-domain geometry about central atom from VSEPR model and Table 9.1.
3. Using Table 9.4, select $sp^3$ hybrid orbital set.
Hybrid Orbitals

Once you know the electron-domain geometry, you know the hybridization state of the atom.

<table>
<thead>
<tr>
<th>Atomic Orbital Set</th>
<th>Hybrid Orbital Set</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>s, p</td>
<td>Two sp</td>
<td>180°</td>
<td>BeF₂, HgCl₂</td>
</tr>
<tr>
<td>s, p, p</td>
<td>Three sp²</td>
<td>120°</td>
<td>BF₃, SO₃</td>
</tr>
<tr>
<td>s, p, p, p</td>
<td>Four sp³</td>
<td>109.5°</td>
<td>CH₄, NH₃, H₂O, NH₄⁺</td>
</tr>
</tbody>
</table>

Multiple Bonds

Sigma (σ) bonds are characterized by
- Head-to-head overlap.
- Cylindrical symmetry of electron density about the internuclear axis.

Pi (π) bonds are characterized by
- Side-to-side overlap.
- Electron density above and below the internuclear axis.
Multiple Bonds

In a multiple bond one of the bonds is a $\sigma$ bond and the rest are $\pi$ bonds.

- In $\text{C}_2\text{H}_4$ an $sp^2$ orbital on each carbon overlaps in $\sigma$ fashion with the corresponding orbital on the other carbon and two hydrogens.
- The unhybridized $p$ orbitals overlap in $\pi$ fashion.
Multiple Bonds: acetylene

In triple bonds, as in acetylene, two $sp$ orbitals form a $\sigma$ bond between the carbons, and two pairs of $p$ orbitals overlap in $\pi$ fashion to form the two $\pi$ bonds.

Multiple Bonds: formaldehyde

Orbitals containing nonbonding electron pairs

One C—O $\pi$ bond
**Resonance in Benzene**

The organic molecule benzene has six $\sigma$ bonds and a $p$ orbital on each carbon atom.

- The $\pi$ electrons in benzene are not localized, but **delocalized**.
- The even distribution of the $\pi$ electrons in benzene makes the molecule unusually stable.

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**Delocalized Electrons: Resonance**

- In reality, each of the four atoms in the nitrate ion has a $p$ orbital.
- The $p$ orbitals on all three oxygens overlap with the $p$ orbital on the central nitrogen.
- This means the $\pi$ electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.
Example

Which of the following molecules or ions will exhibit delocalized bonding: $\text{SO}_3$, $\text{SO}_3^{2-}$, $\text{H}_2\text{CO}$, $\text{O}_3$, $\text{NH}_4^+$?

Limitation of Valence Bond Theory

Though valence bond theory effectively conveys most observed properties of ions and molecules, there are some concepts better represented by molecular orbitals.
Molecular Orbital (MO) Theory

- In MO theory, we invoke the wave nature of electrons.
- If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.
- If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.

A nodal plane occurs where electron density equals zero.

Whenever there is direct overlap of orbitals, forming a bonding and an antibonding orbital, they are called **sigma ($\sigma$) molecular orbitals**. The antibonding orbital is distinguished with an asterisk as $\sigma^*$. Here is an example for the formation of a hydrogen molecule from two atoms.
MO Theory

bond order = \( \frac{1}{2} (\#\text{bonding electrons} - \#\text{antibonding electrons}) \)

\( \frac{1}{2}(2 - 0) = 1 \text{ bond} \)

\( \frac{1}{2}(2 - 2) = 0 \text{ bond} \)

\( \frac{1}{2}(2 - 1) = \frac{1}{2} \)

MO Theory

In the case of He\(_2\), the bond order would be:

\( \frac{1}{2}(2 - 2) = 0 \)

Therefore, He\(_2\) does not exist.

\( \frac{1}{2}(2 - 1) = \frac{1}{2} \)

He\(_2^+\) forms
Guiding Principles for the Formation of Molecular Orbitals

1) The number of MOs formed equals the number of AOs combined.
2) AOs combine with AOs of similar energy.
3) The effectiveness with which two AOs combine is proportional to their overlap.
4) Each MO can accommodate at most two electrons with opposite spin. (They follow the Pauli exclusion principle.)
5) When MOs of the same energy are populated, one electron enters each orbital (same spin) before pairing. (They follow Hund’s rules.)

- \( \text{Li}_2 (g) \) occurs at high temperatures.
- Lewis structure: \( \text{Li} — \text{Li} \).
- The MO diagram is on the right.
- Notice that core electrons don’t play a major part in bonding, so we usually don’t include them in the MO diagram.
MO Theory

For atoms with both \( s \) and \( p \) orbitals, there are two types of interactions:

- The \( s \) and the \( p \) orbitals that face each other overlap in \( \sigma \) fashion.
- The other two sets of \( p \) orbitals overlap in \( \pi \) fashion.

MO Diagram – Second Period

- The resulting MO diagram looks like this for \( \text{O}_2, \text{N}_2, \text{F}_2 \).
- There are both \( \sigma \) and \( \pi \) bonding molecular orbitals and \( \sigma^* \) and \( \pi^* \) antibonding molecular orbitals.
- Early p-block elements in the second period have a sizeable interaction (overlap) between s and p orbitals.
- This changes the order of the σ and π molecular orbitals in B₂, C₂, and N₂ compared to O₂, N₂, and Ne₂.
  - Energy of σ₂p is higher than π₂p for B₂, C₂, and N₂.
  - Energy of π₂p is higher than σ₂p for O₂, F₂, and Ne₂.

**Second Period MO Diagrams**

<table>
<thead>
<tr>
<th>Energy</th>
<th></th>
<th>Large 2s–2p interaction</th>
<th></th>
<th>Small 2s–2p interaction</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>B₂</td>
<td>C₂</td>
<td>N₂</td>
<td>O₂</td>
</tr>
<tr>
<td>σ₁s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>σ₁p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>π₁p</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>π₁2p</td>
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<td></td>
</tr>
<tr>
<td>σ₂s</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>σ₂p</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>π₂p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>π₂2p</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond order</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond enthalpy (kJ/mol)</td>
<td>290</td>
<td>620</td>
<td>944</td>
<td>495</td>
<td>155</td>
<td>—</td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>1.59</td>
<td>1.31</td>
<td>1.10</td>
<td>1.21</td>
<td>1.43</td>
<td>—</td>
</tr>
<tr>
<td>Magnetic behavior</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
<td>Diamagnetic</td>
<td>Paramagnetic</td>
<td>Diamagnetic</td>
<td>—</td>
</tr>
</tbody>
</table>
**Paramagnetic** – has unpaired electrons, attracted to magnetic field.

**Diamagnetic** – has no unpaired electrons, weakly repelled by magnetic field.

Heteronuclear Diatomic Molecules

- The atomic orbitals have different energy, so the interactions change slightly.
- The more electronegative atom has orbitals lower in energy, so the bonding orbitals will more resemble them in energy.

Bond Order

\[
\frac{1}{2}(8-3) = 2.5
\]