Molecular Shapes

- In order to predict molecular shape, we assume the valence electrons repel each other. Therefore, the molecule adopts whichever 3D geometry minimized this repulsion.
- We call this process **Valence Shell Electron Pair Repulsion (VSEPR)** theory.
- There are simple shapes for \( \text{AB}_2 \) and \( \text{AB}_3 \) molecules.
- When considering the geometry about the central atom, we consider all electrons (lone pairs and bonding pairs).
- When naming the molecular geometry, we focus only on the positions of the atoms.
To determine the electron pair geometry:
• draw the Lewis structure,
• count the total number of electron pairs around the central atom,
• arrange the electron pairs in one of the above geometries to minimize e⁻-e⁻ repulsion, and count multiple bonds as one bonding pair.

### VSEPR Model

#### Table 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

<table>
<thead>
<tr>
<th>Number of Electron Domains</th>
<th>Arrangement of Electron Domains</th>
<th>Electron-Domain Geometry</th>
<th>Predicted Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>Linear</td>
<td>180°</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Trigonal bipyramidal</td>
<td>120°, 90°</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Octahedral</td>
<td>90°</td>
</tr>
</tbody>
</table>

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles
VSEPR Model

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

- By experiment, the H-X-H bond angle decreases on moving from C to N to O:

\[
\begin{align*}
\text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
& \quad 109.5^\circ
\end{align*}
\]

\[
\begin{align*}
\text{N} & \quad \text{H} \\
\text{H} & \quad \text{N} \quad \text{H} \\
& \quad 107^\circ
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{H} & \quad \text{O} \quad \text{H} \\
& \quad 104.5^\circ
\end{align*}
\]

- Since electrons in a bond are attracted by two nuclei, they do not repel as much as lone pairs.
- Therefore, the bond angle decreases as the number of lone pairs increase.
- Similarly, electrons in multiple bonds repel more than electrons in single bonds.

\[
\begin{align*}
\text{Cl} & \quad \text{C} = \text{O} \\
& \quad 111.4^\circ
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{C} = \text{O} \\
& \quad 124.3^\circ
\end{align*}
\]

Molecules with Expanded Valence Shells

- To minimize $e^-e^-$ repulsion, lone pairs are always placed in equatorial positions.
<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></td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>3</td>
<td>0</td>
<td>Trigonal planar</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>4</td>
<td>0</td>
<td>Tetrahedral</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>5</td>
<td>0</td>
<td>Trigonal bipyramidal</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Seesaw</td>
<td>4</td>
<td>1</td>
<td>Seesaw</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CIF₃</td>
<td>3</td>
<td>2</td>
<td>CIF₃</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>XeF₂</td>
<td>2</td>
<td>3</td>
<td>XeF₂</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>6</td>
<td>0</td>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>BrF₅</td>
<td>5</td>
<td>1</td>
<td>BrF₅</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>XeF₄</td>
<td>4</td>
<td>2</td>
<td>XeF₄</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 9.3** Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

<table>
<thead>
<tr>
<th>Total 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>5</td>
<td>Trigonal bipyramidal</td>
<td>5</td>
<td>0</td>
<td>Trigonal bipyramidal</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Seesaw</td>
<td>4</td>
<td>1</td>
<td>Seesaw</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CIF₃</td>
<td>3</td>
<td>2</td>
<td>CIF₃</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>XeF₂</td>
<td>2</td>
<td>3</td>
<td>XeF₂</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>6</td>
<td>0</td>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>BrF₅</td>
<td>5</td>
<td>1</td>
<td>BrF₅</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>XeF₄</td>
<td>4</td>
<td>2</td>
<td>XeF₄</td>
<td></td>
</tr>
</tbody>
</table>

**Example:**
- **PCl₅:** 5 bonding domains, 0 nonbonding domains, trigonal bipyramidal geometry.
- **SF₄:** 4 bonding domains, 1 nonbonding domain, trigonal bipyramidal geometry.
- **CIF₃:** 3 bonding domains, 2 nonbonding domains, T-shaped geometry.
- **XeF₂:** 2 bonding domains, 3 nonbonding domains, linear geometry.
Molecular Shape and Molecular Polarity

Polar

Nonpolar

Nonpolar

Overall dipole moment = 0

Overall dipole moment
Covalent Bonding and Orbital Overlap

- Lewis structures and VSEPR do not explain why a bond forms.
- How do we account for shape in terms of quantum mechanics?
- What are the orbitals that are involved in bonding?
- We use Valence Bond Theory:
  - Bonds form when orbitals on atoms overlap.
  - There are two electrons of opposite spin in the orbital overlap.

Hybrid Orbitals

- Atomic orbitals can mix or hybridize in order to adopt an appropriate geometry for bonding.
- Hybridization is determined by the electron domain geometry.

**sp Hybrid Orbitals**

Two $sp$ hybrid orbitals $sp$ hybrid orbitals shown together (large lobes only)
**Hybrid Orbitals**

**sp² and sp³ Hybrid Orbitals**

- **Important**: when we mix \( n \) atomic orbitals we must get \( n \) hybrid orbitals.
- \( sp² \) hybrid orbitals are formed with one \( s \) and two \( p \) orbitals. (Therefore, there is one unhybridized \( p \) orbital remaining.)
- The large lobes of \( sp² \) hybrids lie in a trigonal plane.
- All molecules with trigonal planar electron pair geometries have \( sp² \) orbitals on the central atom.

\( \text{BF}_3 \)
Hybrid Orbitals

Hybridization Involving d Orbitals

- Since there are only three \( p \)-orbitals, trigonal bipyramidal and octahedral electron domain geometries must involve \( d \)-orbitals.
- Trigonal bipyramidal electron domain geometries require \( sp^3d \) hybridization.
- Octahedral electron domain geometries require \( sp^3d^2 \) hybridization.
- Note the electron domain geometry from VSEPR theory determines the hybridization.

Summary

1. Draw the Lewis structure.
2. Determine the electron domain geometry with VSEPR.
3. Specify the hybrid orbitals required for the electron pairs based on the electron domain geometry.

<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>Linear ( \text{BeF}_2, \text{HgCl}_2 )</td>
</tr>
<tr>
<td>( s,p,p )</td>
<td>Three ( sp^2 )</td>
<td>120°</td>
<td>( \text{BF}_3, \text{SO}_3 )</td>
</tr>
<tr>
<td>( s,p,p,p )</td>
<td>Four ( sp^3 )</td>
<td>109.5°</td>
<td>( \text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+ )</td>
</tr>
<tr>
<td>( s,p,p,d )</td>
<td>Five ( sp^3d )</td>
<td>90°, 120°</td>
<td>( \text{PF}_5, \text{SF}_6, \text{BrF}_3 )</td>
</tr>
<tr>
<td>( s,p,p,d,p,d )</td>
<td>Six ( sp^3d^2 )</td>
<td>90°, 90°</td>
<td>( \text{SF}_6, \text{ClF}_5, \text{XeF}_4, \text{PF}_6^- )</td>
</tr>
</tbody>
</table>
Multiple Bonds

- **σ-Bonds**: electron density lies on the axis between the nuclei.
- All single bonds are σ-bonds.
- **π-Bonds**: electron density lies above and below the plane of the nuclei.
- A double bond consists of one σ-bond and one π-bond.
- A triple bond has one σ-bond and two π-bonds.
- Often, the $p$-orbitals involved in π-bonding come from unhybridized orbitals.

Ethylene, $C_2H_4$, has:
- one σ- and one π-bond;
- both C atoms $sp^2$ hybridized;
- both C atoms with trigonal planar electron pair and molecular geometries.
Consider acetylene, $\text{C}_2\text{H}_2$

- the electron pair geometry of each C is linear;
- therefore, the C atoms are $sp$ hybridized;
- the $sp$ hybrid orbitals form the C-C and C-H $\sigma$-bonds;
- there are two unhybridized $p$-orbitals;
- both unhybridized $p$-orbitals form the two $\pi$-bonds;
- one $\pi$-bond is above and below the plane of the nuclei;
- one $\pi$-bond is in front and behind the plane of the nuclei.

Delocalized $\pi$ Bonding

(a) $\sigma$ bonds  
(b) $2p$ atomic orbitals  
(c) Delocalized $\pi$ bonds
**Multiple Bonds**

**General Conclusions**

- Every two atoms share at least 2 electrons.
- Two electrons between atoms on the same axis as the nuclei are $\sigma$ bonds.
- $\sigma$-Bonds are always localized.
- If two atoms share more than one pair of electrons, the second and third pair form $\pi$-bonds.
- When resonance structures are possible, delocalization is also possible.

**Molecular Orbitals**

- Some aspects of bonding are not explained by Lewis structures, VSEPR theory and hybridization. (E.g. why does $O_2$ interact with a magnetic field?; Why are some molecules colored?)
- For these molecules, we use **Molecular Orbital (MO)** Theory.
- Just as electrons in atoms are found in atomic orbitals, electrons in molecules are found in molecular orbitals.

**Electron Configurations and Molecular Properties**

- Two types of magnetic behavior:
  - paramagnetism (unpaired electrons in molecule): strong attraction between magnetic field and molecule;
  - diamagnetism (no unpaired electrons in molecule): weak repulsion between magnetic field and molecule.
- Magnetic behavior is detected by determining the mass of a sample in the presence and absence of magnetic field:
**Molecular Orbitals**

**The Hydrogen Molecule**

- Energy level diagram or MO diagram shows the energies and electrons in an orbital.
- The total number of electrons in all atoms are placed in the MOs starting from lowest energy ($\sigma_{1s}$) and ending when you run out of electrons.
  - Note that electrons in MOs have opposite spins.
- $\text{H}_2$ has two bonding electrons.
- $\text{He}_2$ has two bonding electrons and two antibonding electrons.

**Bond Order**

- Define
  - Bond order = 1 for single bond.
  - Bond order = 2 for double bond.
  - Bond order = 3 for triple bond.
  - Fractional bond orders are possible.
- For $\text{H}_2$  
  B.O. = $1/2 (2 - 0) = 1$
- Therefore, $\text{H}_2$ has a single bond.
Second-Row Diatomic Molecules

- We look at homonuclear diatomic molecules (e.g. Li₂, Be₂, B₂ etc.).
- AOs combine according to the following rules:
  - The number of MOs = number of AOs;
  - AOs of similar energy combine;
  - As overlap increases, the energy of the MO decreases;
- Pauli: each MO has at most two electrons;
- Hund: for degenerate orbitals, each MO is first occupied singly.

![Diagram of Li and Li₂ molecules with molecular orbitals]
## Second-Row Diatomic Molecules

<table>
<thead>
<tr>
<th></th>
<th>Large $2s-2p$ interaction</th>
<th>Small $2s-2p$ interaction</th>
</tr>
</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>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi_{2p}$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_{2s}$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_{2s}$</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Bond order
- $B_2$: 1
- $C_2$: 2
- $N_2$: 3
- $O_2$: 2
- $F_2$: 1
- $Ne_2$: 0

### Bond enthalpy (kJ/mol)
- $B_2$: 290
- $C_2$: 620
- $N_2$: 941
- $O_2$: 445
- $F_2$: 155
- $Ne_2$: —

### Bond length (Å)
- $B_2$: 1.59
- $C_2$: 1.31
- $N_2$: 1.10
- $O_2$: 1.21
- $F_2$: 1.43
- $Ne_2$: —

### Magnetic behavior
- $B_2$: Paramagnetic
- $C_2$: Diamagnetic
- $N_2$: Diamagnetic
- $O_2$: Paramagnetic
- $F_2$: Diamagnetic
- $Ne_2$: —

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