Chapter Nine Learning Objectives

• predict the geometries of simple polyatomic molecules using the VSEPR model
• use electronegativity to predict molecular polarity
• describe single and multiple covalent bonds using valence-bond theory
• use the concept of hybrid orbitals to explain the geometries of simple polyatomic molecules

The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

• The VSEPR model assumes that valence electrons surrounding a central atom are localized into regions called electron domains that repel one another, thus causing covalent compounds to assume specific shapes.
• An electron domain can consist of a single bond, a multiple bond, a lone pair, or a lone electron.
• The best arrangement of a given number of electron domains is the one that minimizes the repulsions between them.
Electron-Domain Geometries

The arrangement of electron domains about a central atom in a covalent compound is referred to as the electron-domain geometry.
The Importance of Lewis Structures

While Lewis structures do not indicate the shapes of covalent compounds, drawing a Lewis structure is the first step in predicting the geometries of simple polyatomic molecules.

Electron-Domain Geometry Versus Molecular Geometry

The number of bonding and nonbonding pairs determines the electron-domain geometry, but the molecular geometry describes the arrangement of only the atoms in a covalent compound.
### Molecular Geometries

<table>
<thead>
<tr>
<th>Bonding Domains</th>
<th>Nonbonding Domains</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>Linear</td>
<td>( \mathrm{O} = \mathrm{C} = \mathrm{O} )</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>Trigonal planar</td>
<td>( \mathrm{BF}_3 )</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td></td>
<td>( \mathrm{NO}_2^- )</td>
</tr>
</tbody>
</table>

### Molecular Geometries

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</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>Tetrahedral</td>
<td>( \mathrm{H}_2\mathrm{O}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td></td>
<td>( \mathrm{NH}_3 )</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>( \mathrm{H}_2\mathrm{O}^- )</td>
</tr>
</tbody>
</table>
Practice Exercise

Use Lewis structures and the VSEPR model to predict the electron-domain and molecular geometries of the following covalent compounds:

(a) $\text{H}_3\text{O}^+$
(b) $\text{CO}_3^{2−}$
(c) $\text{SO}_2$

The Effect of Nonbonding Electrons on Bond Angles
The Effect of Multiple Bonds on Bond Angles

- The electron domains for multiple bonds exert a greater repulsive force on adjacent domains than do electron domains for single bonds.

- What bond angles are predicted for the nitrate ion, NO$_3^-$?

Molecules with Expanded Octets: Five Electron Domains

<table>
<thead>
<tr>
<th>Bonding Domains</th>
<th>Nonbonding Domains</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>Trigonal bipyramidal</td>
<td>PCl$_5$</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td></td>
<td>SF$_4$</td>
</tr>
</tbody>
</table>
Molecules with Expanded Octets:
Five Electron Domains

<table>
<thead>
<tr>
<th>Bonding Domains</th>
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<tbody>
<tr>
<td>3</td>
<td>2</td>
<td></td>
<td>CIF₃</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td></td>
<td>XeF₂</td>
</tr>
</tbody>
</table>

Equatorial Versus Axial Positions:
Five Electron Domains

- The three equatorial electron domains define an equilateral triangle whereas the two axial domains lie above and below the plane of the triangle.

- If a molecule has nonbonding electron domains, then will they occupy equatorial or axial positions?
Molecules with Expanded Octets: Six Electron Domains

<table>
<thead>
<tr>
<th>Bonding Domains</th>
<th>Nonbonding Domains</th>
<th>Molecular Geometry</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>9</td>
<td>Octahedral</td>
<td>$\text{SF}_6$</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td></td>
<td>$\text{BrF}_3$</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td></td>
<td>$\text{XeF}_4$</td>
</tr>
</tbody>
</table>

Key Concept

The VSEPR model can be extended to more complex molecules:
Molecular Polarity

• Most molecules have polar covalent bonds, but the overall molecular polarity depends on how those bonds are positioned relative to one another.

• Which one of the covalent compounds pictured here is a nonpolar molecule?

Molecular Polarity

• A vector of relative magnitude, called a *bond dipole*, points in the direction of the more electronegative atom in a polar covalent bond.

• The overall dipole moment or polarity of a polyatomic molecule is the vector sum of its individual bond dipoles.
Practice Exercise

Predict whether each of the following molecules is polar or nonpolar:

(a) BF₃
(b) Cl₂CO
(c) SF₄

Practice Exercise

The following molecule, urea, is the primary waste produce excreted in animal urine:

(a) What are the predicted H—N—H and N—C—N bond angles?

(b) Does this molecule have an overall dipole moment (is it a polar molecule)?
Valence-Bond Theory: The Orbital Overlap Model of Bonding

- The valence-bond model applies quantum mechanics to molecular structure, in which overlapping orbitals are involved in covalent bond formation.

- A covalent bond is viewed as the pairing of two electrons with opposing spins in the region of orbital overlap.

Valence-Bond Theory for Methane

- For methane, four orbitals directed to the corners of a tetrahedron are required to match the electron-domain geometry on the central carbon atom.

- While carbon has four valence electrons, how can it form four bonds if two of carbon’s valence electrons are already paired in its 2s orbital?
Valence-Bond Theory for Methane

- The answer is that an electron must be promoted from its 2s orbital to its vacant 2p orbital, giving four singly occupied valence orbitals on the central carbon atom.

- However, if the three 2p orbitals are at 90° to one another, and if the 2s orbital has no directionality, then how can carbon form bonds with angles of 109.5°?

Valence-Bond Theory for Methane: The Importance of Hybrid Orbitals

The bonding in methane and other simple polyatomic molecules can be described using a new set of orbitals, called hybrid orbitals.
Hybrid Orbital Formation

- The number of hybrid orbitals produced is always the same as the number of mathematically combined orbitals.
- The shapes of hybrid orbitals maximize orbital overlap and strengthen the bond.

**sp^3 Hybridization: Four Electron Domains**

The same sp^3 hybridization that describes the bonds to carbon in methane also describes the bonds to nitrogen in ammonia and the bonds to all other atoms that have a tetrahedral electron-domain geometry.
### 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>$\text{BeF}_2, \text{H}_2\text{Cl}_2$</td>
</tr>
<tr>
<td>$sp^3$</td>
<td>Three $sp^3$</td>
<td>Trigonal planar</td>
<td>$\text{BF}_3, \text{SO}_3$</td>
</tr>
<tr>
<td>$sp^3d$</td>
<td>Four $sp^3d$</td>
<td>Tetrahedral</td>
<td>$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$</td>
</tr>
</tbody>
</table>

### TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets (Continued)

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<td>$sp^3d$</td>
<td>Five $sp^3d$</td>
<td>Trigonal bipyramidal</td>
<td>$\text{PF}_5, \text{SF}_4, \text{BrF}_3$</td>
</tr>
<tr>
<td>$sp^3d^2$</td>
<td>Six $sp^3d^2$</td>
<td>Octahedral</td>
<td>$\text{SF}_6, \text{ClF}_6, \text{XeF}_6, \text{PF}_6^-$</td>
</tr>
</tbody>
</table>
Multiple Covalent Bonds: Sigma Bonds Versus Pi Bonds

- A covalent bond formed by the end-to-end overlap of orbitals is called a *sigma* (σ) bond (all single covalent bonds are σ bonds).

- A *pi* (π) bond exhibits overlap above and below the internuclear axis (side-to-side overlap).

Valence-Bond Theory for Ethylene

The presence of unhybridized p orbitals allows for the formation of a π bond.
The rotation about a double bond is severely restricted under ordinary conditions, and as a result, two distinctly different forms exist for many molecules.

A pair of cis and trans isomers are a special type of geometric isomers.

If you know a nonpolar molecule has the chemical formula \( \text{C}_2\text{H}_2\text{Cl}_2 \), then can you determine the structural formula of this molecule?

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Practice Exercise

The following molecule, acrylonitrile, is used as the starting material for manufacturing acrylic fibers:

(a) How many \( \sigma \) and \( \pi \) bonds are there in acrylonitrile?

(b) Do cis and trans isomers exist for acrylonitrile?

(c) What is the hybridization at each C atom in this molecule?