The Shapes of Molecules

10.1 Depicting Molecules and Ions with Lewis Structures

10.2 Valence-Shell Electron-Pair Repulsion (VSEPR) Theory

10.3 Molecular Shape and Molecular Polarity
Figure 10.1 The steps in converting a molecular formula into a Lewis structure.

Step 1: Place atom with lowest EN in center.

Step 2: Add A-group numbers.

Step 3: Draw single bonds, and subtract 2e⁻ for each bond.

Step 4: Give each atom 8e⁻ (2e⁻ for H).
Example: NF₃

N has a lower EN than F, so N is placed in the center.

\[ 1 \times N = 1 \times 5 = 5e^- \]
\[ 3 \times F = 3 \times 7 = 21 e^- \]
Total = 28 e^-
Sample Problem 10.1 Writing Lewis Structures for Molecules with One Central Atom

PROBLEM: Write a Lewis structure for CCl$_2$F$_2$, one of the compounds responsible for the depletion of stratospheric ozone.

SOLUTION:

Step 1: Carbon has the lowest EN and is the central atom. The other atoms are placed around it.

Step 2: $[1 \times C(4e^-)] + [2 \times F(7e^-)] + [2 \times Cl(7e^-)]$

= 32 valence e$^-$

Step 3-4: Add single bonds, then give each atom a full octet.
Sample Problem 10.2  Writing Lewis Structures for Molecules with More than One Central Atom

PROBLEM:  Write the Lewis structure for methanol (molecular formula CH₄O), an important industrial alcohol that is being used as a gasoline alternative in car engines.

SOLUTION:

Step 1: Place the atoms relative to each other. H can only form one bond, so C and O must be central and adjacent to each other.

Step 2: \([1 \times C(4e^-)] + [1 \times O(6e^-)] + [4 \times H(1e^-)]\)

= 14 valence e⁻

Step 3-4: Add single bonds, then give each atom (other than H) a full octet.
Multiple Bonds

If there are not enough electrons for the central atom to attain an octet, a multiple bond is present.

*Step 5*: If the central atom does not have a full octet, change a lone pair on a surrounding atom into another bonding pair to the central atom, thus forming a multiple bond.
Sample Problem 10.3  Writing Lewis Structures for Molecules with Multiple Bonds

PROBLEM: Write Lewis structures for the following:

(a) Ethylene (C\textsubscript{2}H\textsubscript{4}), the most important reactant in the manufacture of polymers

(b) Nitrogen (N\textsubscript{2}), the most abundant atmospheric gas

PLAN: After following steps 1 to 4 we see that the central atom does not have a full octet. We must therefore add step 5, which involves changing a lone pair to a bonding pair.

SOLUTION:

(a) C\textsubscript{2}H\textsubscript{4} has 2(4) + 4(1) = 12 valence e\textsuperscript{-}. H can have only one bond per atom.
Sample Problem 10.3

(b) \( \text{N}_2 \) has \( 2(5) = 10 \) valence e\(^-\).
Resonance Structures

O₃ can be drawn in 2 ways:

These are two different reasonable Lewis structures for the *same* molecule.

Neither structure depicts O₃ accurately, because in reality the O-O bonds are identical in length and energy.
The structure of $\text{O}_3$ is shown more correctly using both Lewis structures, called *resonance structures*.

A two-headed resonance arrow is placed between them.

Resonance structures have the same relative placement of atoms but different locations of bonding and lone electron pairs.
The Resonance Hybrid

A species like $\text{O}_3$, which can be depicted by more than one valid Lewis structure, is called a resonance hybrid.

Resonance forms are not real bonding depictions. $\text{O}_3$ does not change back and forth between its two resonance forms.

The real structure of a resonance hybrid is an average of its contributing resonance forms.
A mule is a genetic mix, a hybrid, of a horse and a donkey. It is not a horse one instant and a donkey the next. Likewise, a resonance hybrid has a single structure although it retains characteristics of its resonance forms.
Electron Delocalization

Lewis structures depict electrons as *localized* either on an individual atom (lone pairs) or in a bond between two atoms (shared pair).

In a resonance hybrid, electrons are *delocalized*: their density is “spread” over a few adjacent atoms.
Fractional Bond Orders

Resonance hybrids often have *fractional bond orders* due to partial bonding.

For $\text{O}_3$, bond order $= \frac{3 \text{ electron pairs}}{2 \text{ bonded-atom pairs}} = 1\frac{1}{2}$
**Sample Problem 10.4  Writing Resonance Structures**

**PROBLEM:** Write resonance structures for the nitrate ion, NO$_3^-$ and find the bond order.

**PLAN:** Write the Lewis structure, remembering to add 1e$^-$ to the total number of valence e$^-$ for the -1 charge. We apply Step 5 to form multiple bonds. Since multiple bonds can be formed in more than one location, there are resonance forms.

**SOLUTION:**
Nitrate has $[1 \times N(5e^-)] + [3 \times O(6e^-)] + 1e^- = 24$ valence e$^-$

After Steps 1-4:
Step 5. Since N does not have a full octet, we change a lone pair from O to a bonding pair to form a double bond.

Bond order = \frac{4 \text{ shared electron pairs}}{3 \text{ bonded-atom pairs}} = 1\frac{1}{3}
**Formal Charge**

*Formal charge* is the charge an atom would have if all electrons were shared *equally*.

Formal charge of atom =
# of valence e\(^-\) - (# of unshared valence e\(^-\) + \(\frac{1}{2}\) # of shared valence e\(^-\))

For O\(_A\) in resonance form I, the formal charge is given by

6 valence e\(^-\) - (4 unshared e\(^-\) + \(\frac{1}{2}(4\) shared e\(^-\)) = 6 - 4 - 2 = 0
Formal Charge

Formal charges must sum to the actual charge on the species for all resonance forms.

\[
\begin{align*}
O_A [6 - 4 - \frac{1}{2}(4)] & = 0 & O_A [6 - 6 - \frac{1}{2}(2)] & = -1 \\
O_B [6 - 2 - \frac{1}{2}(6)] & = +1 & O_B [6 - 2 - \frac{1}{2}(6)] & = +1 \\
O_C [6 - 6 - \frac{1}{2}(2)] & = -1 & O_C [6 - 4 - \frac{1}{2}(4)] & = 0
\end{align*}
\]

For both these resonance forms the formal charges sum to zero, since \(O_3\) is a neutral molecule.
Choosing the More Important Resonance Form

• Smaller formal charges (positive or negative) are preferable to larger ones.

• The *same* nonzero formal charges on adjacent atoms are not preferred.
  Avoid like charges on adjacent atoms.

• A more negative formal charge should reside on a more electronegative atom.
Example: NCO\textsuperscript{-} has 3 possible resonance forms:

\begin{align*}
+2 & \quad 0 & \quad -1 \\
-1 & \quad 0 & \quad 0 \\
0 & \quad 0 & \quad -1
\end{align*}

Resonance forms with smaller formal charges are preferred. Resonance form I is therefore \textit{not} an important contributor.

A negative formal charge should be placed on a more electronegative atoms, so resonance form III is preferred to resonance form II.

The overall structure of the NCO\textsuperscript{-} ion is still an \textit{average} of all three forms, but resonance form III contributes \textit{most} to the average.
For a **formal charge**, bonding electrons are *shared equally* by the atoms.

The formal charge of an atom may change between resonance forms.

<table>
<thead>
<tr>
<th>Formal charges</th>
<th>0</th>
<th>0</th>
<th>-1</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>-3</th>
<th>+4</th>
<th>-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3</td>
<td>+4</td>
<td>-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-3</td>
<td>+4</td>
<td>-2</td>
</tr>
</tbody>
</table>

**Oxidation numbers**

For an **oxidation number**, bonding electrons are *transferred* to the *more* electronegative atom.

The oxidation number of an atom is the *same* in all resonance forms.
Exceptions to the Octet Rule

Molecules with Electron-Deficient Atoms

B and Be are commonly electron-deficient.

Odd-Electron Species

A molecule with an odd number of electrons is called a free radical.
Exceptions to the Octet Rule

Expanded Valence Shells

An expanded valence shell is only possible for nonmetals from Period 3 or higher because these elements have available d orbitals.
PROBLEM: Write a Lewis structure and identify the octet-rule exception for (a) SClF$_5$; (b) H$_3$PO$_4$ (draw two resonance forms and select the more important); (c) BFCl$_2$. 

PLAN: Draw each Lewis structure and examine it for exceptions to the octet rule. Period 3 elements can have an expanded octet, while B commonly forms electron-deficient species. 

SOLUTION: 

(a) The central atom is S, which is in Period 3 and can have an expanded valence shell.
Sample Problem 10.5

(b) $\text{H}_3\text{PO}_4$ has two resonance forms and formal charges indicate the more important form.

(c) $\text{BFCl}_2$ is an electron-deficient molecule. $\text{B}$ has only six electrons surrounding it.
Valence-Shell Electron-Pair Repulsion Theory (VSEPR)

Each group of valence electrons around a central atom is located as far as possible from the others, to minimize repulsions.

A “group” of electrons is any number of electrons that occupies a localized region around an atom. A single bond, double bond, triple bond, lone pair, or single electron all count as a single group.
Figure 10.2  Electron-group repulsions and molecular shapes.

- **linear**
  - 180°

- **trigonal planar**
  - 120°

- **tetrahedral**
  - 109.5°

- **trigonal bipyramidal**
  - 90°

- **octahedral**
  - 90°
Electron-group Arrangement vs Molecular Shape

The *electron-group arrangement* is defined by both bonding and nonbonding electron groups.

The *molecular shape* is the three-dimensional arrangement of nuclei joined by the bonding groups. This is defined only by the relative positions of the nuclei.

Molecular shape is classified using the designation

\[ AX_mE_n \]

- A = central atom
- X = surrounding atom
- E = nonbonding valence-electron group
- \( m \) and \( n \) are integers
Bond Angle

The *bond angle* is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom.

The angles shown in Figure 10.2 are *ideal* bond angles, determined by basic geometry alone. Real bond angles deviate from the ideal value in many cases.
Figure 10.3  The single molecular shape of the linear electron-group arrangement.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

AX₂
Linear

Examples:
CS₂, HCN, BeF₂

This key refers to Figures 10.3 through 10.8.
Figure 10.4 The two molecular shapes of the trigonal planar electron-group arrangement.

**AX$_3$**
- Trigonal planar
- Examples: SO$_2$, O$_3$, PbCl$_2$, SnBr$_2$

**AX$_2$E**
- Bent (V shaped)
- Examples: SO$_3$, BF$_3$, NO$_3^-$, CO$_3^{2-}$
Factors Affecting Bond Angles

Nonbonding (Lone) Pairs

A lone pair repels bonding pairs more strongly than bonding pairs repel each other. This decreases the angle between the bonding pairs.

Double Bonds

A double bond has greater electron density than a single bond, and repels the single bond electrons more than they repel each other.
The three molecular shapes of the tetrahedral electron-group arrangement.

**AX₄**
- Examples: \( \text{CH}_4, \text{SiCl}_4, \text{SO}_4^{2-}, \text{ClO}_4^- \)

**AX₃E**
- Examples: \( \text{NH}_3, \text{PF}_3, \text{ClO}_3^-, \text{H}_3\text{O}^+ \)

**AX₂E₂**
- Examples: \( \text{H}_2\text{O}, \text{OF}_2, \text{SCl}_2 \)

Tetrahedral

Trigonal pyramidal

Bent (V shaped)
Figure 10.6  Lewis structures do not indicate molecular shape.

Twist to the right

Twist to the left
Figure 10.7  The four molecular shapes of the trigonal bipyramidal electron-group arrangement.

- **AX$_5$**
  - Examples: PF$_5$, AsF$_5$, SOF$_4$
  - Trigonal bipyramidal

- **AX$_4$E**
  - Examples: SF$_4$, XeO$_2$F$_2$, IF$_4^+$, IO$_2$F$_2^-$
  - Seesaw

- **AX$_3$E$_2$**
  - Examples: ClF$_3$, BrF$_3$
  - T shaped

- **AX$_2$E$_3$**
  - Examples: XeF$_2$, I$_3^-$, IF$_2^-$
  - Linear
Axial and Equatorial Positions

A five electron-group system has two different positions for electron groups, and two ideal bond angles.

Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

Where possible, lone pairs in a five electron-group system occupy equatorial positions.
Figure 10.8 The three molecular shapes of the octahedral electron-group arrangement.

Examples:
- SF$_6$, IOF$_5$
- XeOF$_4$
- XeF$_4$, ICl$_4^-$
Figure 10.9 Molecular shapes for central atoms in Period 2 and in higher periods.
Figure 10.10  A summary of common molecular shapes with two to six electron groups.

<table>
<thead>
<tr>
<th>e⁻ Group arrangement (no. of groups)</th>
<th>Molecular shape (class)</th>
<th>No. of bonding groups</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear (2)</td>
<td>Linear (AX₂)</td>
<td>2</td>
<td>180°</td>
</tr>
<tr>
<td>Trigonal planar (3)</td>
<td>Trigonal planar (AX₃)</td>
<td>3</td>
<td>120°</td>
</tr>
<tr>
<td>V shaped or bent (AX₂E)</td>
<td>V shaped or bent (AX₂E)</td>
<td>2</td>
<td>&lt;120°</td>
</tr>
<tr>
<td>Tetrahedral (4)</td>
<td>Tetrahedral (AX₄)</td>
<td>4</td>
<td>109.5°</td>
</tr>
<tr>
<td>Trigonal pyramidal (AX₃E)</td>
<td>V shaped or bent (AX₂E₂)</td>
<td>3</td>
<td>&lt;109.5°</td>
</tr>
<tr>
<td>V shaped or bent (AX₂E₂)</td>
<td></td>
<td>2</td>
<td>&lt;109.5°</td>
</tr>
</tbody>
</table>
Figure 10.10 continued

<table>
<thead>
<tr>
<th>e⁻ Group arrangement (no. of groups)</th>
<th>Molecular shape (class)</th>
<th>No. of bonding groups</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal bipyramidal (AX₅)</td>
<td>Trigonal bipyramidal (AX₅)</td>
<td>5</td>
<td>90° (ax) 120° (eq)</td>
</tr>
<tr>
<td>Seesaw (AX₄E)</td>
<td>Seesaw (AX₄E)</td>
<td>4</td>
<td>&lt;90° (ax) &lt;120° (eq)</td>
</tr>
<tr>
<td>T shaped (AX₃E₂)</td>
<td>T shaped (AX₃E₂)</td>
<td>3</td>
<td>&lt;90° (ax)</td>
</tr>
<tr>
<td>Linear (AX₂E₃)</td>
<td>Linear (AX₂E₃)</td>
<td>2</td>
<td>180°</td>
</tr>
<tr>
<td>Octahedral (AX₆)</td>
<td>Octahedral (AX₆)</td>
<td>6</td>
<td>90°</td>
</tr>
<tr>
<td>Square pyramidal (AX₅E)</td>
<td>Square pyramidal (AX₅E)</td>
<td>5</td>
<td>&lt;90°</td>
</tr>
<tr>
<td>Square planar (AX₄E₂)</td>
<td>Square planar (AX₄E₂)</td>
<td>4</td>
<td>90°</td>
</tr>
</tbody>
</table>
Figure 10.11  The four steps in converting a molecular formula to a molecular shape

**Molecular Formula**

**Step 1**  Draw Lewis structure.

**Lewis structure**

**Step 2**  Count all $e^-$ groups around central atom (A).

**Electron-group arrangement**

**Step 3**  Note positions of any lone pairs and double bonds.

**Step 4**  Count bonding and nonbonding $e^-$ groups separately.

**Bond angles**

**Molecular shape**  

$(AX_mE_n)$
Sample Problem 10.6  Examining Shapes with Two, Three, or Four Electron Groups

**PROBLEM:** Draw the molecular shape and predict the bond angles (relative to the ideal bond angles) of (a) PF$_3$ and (b) COCl$_2$.

**SOLUTION:**

(a) For PF$_3$, there are 26 valence electrons. The Lewis structure is

There are four electron groups around P, giving a tetrahedral electron-group arrangement. **The ideal bond angle is therefore 109.5°.**

There is one lone pair and three bonding pairs, so the actual bond angle will be **less than 109.5°.**
Sample Problem 10.6

The molecular shape for PF$_3$ is **trigonal pyramidal** (AX$_3$E).
Sample Problem 10.6

(b) For COCl₂ there are 24 valence e⁻. The Lewis structure is

There are three electron groups around C, giving a trigonal planar electron-group arrangement. The ideal bond angle is 120°, but the double bond will compress the Cl-C-Cl angle to less than 120°.
Sample Problem 10.7

Examining Shapes with Five or Six Electron Groups

PROBLEM: Draw the molecular shapes and predict the bond angles (relative to the ideal bond angles) of (a) SbF$_5$ and (b) BrF$_5$.

SOLUTION:

(a) SbF$_5$ has 40 valence e\textsuperscript{\textendash}. The Lewis structure is

There are five electron groups around Sb, giving a trigonal bipyramidal electron-group arrangement. The ideal bond angles are 120° between equatorial groups and 90° between axial groups.
Sample Problem 10.7

(b) BrF$_5$ has 42 valence e$^-$. The Lewis structure is

There are six electron groups around Br, giving an octahedral electron-group arrangement. The ideal bond angles are 90$^\circ$. There is one lone pair, so the bond angles will be less than 90$^\circ$ and the molecular shape is square pyramidal.
Figure 10.12  The tetrahedral shapes around the central atoms and the overall shapes of ethane (A) and ethanol (B).

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

ethane
CH₃CH₃

ethanol
CH₃CH₂OH
Sample Problem 10.8  Predicting Molecular Shapes with More Than One Central Atom

PROBLEM: Determine the shape around each of the central atoms in acetone, \((\text{CH}_3)_2\text{CO}\).

PLAN: There are three central C atoms, two of which are in CH$_3$– groups. We determine the shape around one central atom at a time.

SOLUTION:

Step 1: The Lewis structure is

Step 2: Each CH$_3$– group has four electron groups around its central C, so the electron-group arrangement is tetrahedral. The third C atom has three electron groups around it, with a trigonal planar arrangement.
Sample Problem 10.8

Step 3: The H-C-H bond angle in each CH₃– group should be near the ideal value of 109.5°. The C=O double bond will compress the C-C-C angle to less than the ideal angle of 120°.

Step 4: The shape around the C in each CH₃– group is tetrahedral (AX₄). The shape around the middle C is trigonal planar (AX₃).
Molecular Shape and Molecular Polarity

Overall *molecular polarity* depends on both *shape* and *bond polarity*.

The polarity of a molecule is measured by its *dipole moment* ($\mu$), which is given in the unit *debye* (D).

A molecule is polar if
- it contains one or more *polar bonds* and
- the individual bond dipoles *do not cancel*. 
Figure 10.13  The orientation of polar molecules in an electric field.

Molecules are randomly oriented.

B  Electric field off
Molecules are randomly oriented.

C  Electric field on
Molecules become oriented when the field is turned on.
Bond Polarity, Bond Angle, and Dipole Moment

Example: CO$_2$

The $\Delta$EN between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond polar.

CO$_2$ is linear, the bond angle is 180°, and the individual bond polarities therefore cancel. The molecule has no net dipole moment ($\mu = 0$ D).
Example: H$_2$O

The $\Delta$EN between H (EN = 2.1) and O (EN = 3.5) makes each H-O bond polar.

H$_2$O has a V shaped geometry and the individual bond polarities do **not** cancel. This molecule has an **overall molecular polarity**. The O is partially negative while the H atoms are partially positive.
Molecules with the same shape may have different polarities.

\[
\text{CCl}_4 \hspace{2cm} \text{CHCl}_3
\]

Bonds are polar, but individual bond polarities cancel. Bond polarities do not cancel. This molecule is polar (\(\mu = 1.01 \text{ D}\)).
Sample Problem 10.9

Predicting the Polarity of Molecules

PROBLEM: For each of the following use the molecular shape and EN values and trends (Figure 9.20, p. 349) to predict the direction of bond and molecular polarity, if present.

(a) Ammonia, NH₃  
(b) Boron trifluoride, BF₃

(c) Carbonyl sulfide, COS (atom sequence SCO)

PLAN: We draw and name the molecular shape, and mark each polar bond with a polar arrow pointing toward the atom with the higher EN. If bond polarities balance one another, the molecule is nonpolar. If they reinforce each other, we show the direction of overall molecular polarity.
Sample Problem 10.9

SOLUTION:

(a) \( \text{NH}_3 \) has 8 valence e\(^-\) and a trigonal pyramidal molecular shape.

N (EN = 3.0) is more electronegative than H (EN = 2.1) so bond polarities point towards N.

---

Ammonia is polar overall.
Sample Problem 10.9

(b) $\text{BF}_3$ has 24 valence e$^-$ and a trigonal planar molecular shape.

F (EN = 4.0) is more electronegative than B (EN = 2.0) so bond polarities point towards F.

Individual bond polarities balance each other and $\text{BF}_3$ has no molecular polarity.

Boron trifluoride is nonpolar.
Sample Problem 10.9

(c) COS has a linear shape.

C and S have the same EN (2.5) but the C=O bond (ΔEN = 1.0) is quite polar.

Carbonyl sulfide is polar overall.
The Effect of Molecular Polarity on Behavior

Example: The *cis* and *trans* isomers of C$_2$H$_2$Cl$_2$

The *cis* isomer is polar while the *trans* isomer is not. The boiling point of the *cis* isomer boils is 13 °C higher than that of the *trans* isomer.
Figure 10.14  The influence of atomic properties on macroscopic behavior.
Chemical Connections

Figure B10.1 Shapes of some olfactory receptor sites.

Figure B10.2 Different molecules with the same odor.
Chemical Connections

Figure B10.3 Molecular shape and enzyme action.

A. A small sugar molecule is shown near a specific region of an enzyme molecule.
B. When the sugar lands in that region, the reaction begins.