Lewis Theory of Shapes and Polarities of Molecules
Lewis Structures and the “Real” 3D-Shape of Molecules

Sulfanilamide

Chemical structure of Sulfanilamide with notes on the interpretation of wedge symbols.
Molecular Shape or Geometry

The way in which atoms of a molecule are arranged in space
The actual position of the nuclei

What influences molecular shape?

The major factor is the tendency of valence electrons to repel each other.

Why is molecular shape important?

Molecular shape influences molecular polarity

Molecular polarity influences such physical properties as melting point, boiling point, and solubility.
Common Molecular Shapes

- **Linear**
- **Bent (angular)**
- **Triangular planar**
- **Tetrahedral**
- **Triangular pyramidal**
Electron Groups and Molecular Shapes

1) The *position of atoms (nuclei)* surrounding a central atom will be determined by where the electron groups are.

2) The *positions of the electron groups* will be determined by trying to minimize repulsions between them.

3) "1" and "2" are not necessarily the same.

*Simply speaking, “Some electron groups are associated with bonding to another atom, and some are not.”*
VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Because of their negative charge electron groups will arrange themselves about a central atom in a way that minimizes repulsion between electrons.

**Electron group:**
a lone pair of electrons
a single bond
a double bond
a triple bond

There are three electron groups around S:

one lone pair
one single bond
one double bond
Predicting Molecular Geometry Using VSEPR Theory

1. Draw a correct **Lewis dot diagram** for the molecule.

2. Determine the total number of **electron groups** around the central atom.

3. Determine the best arrangement of electron groups around the central atom and describe the **electron group geometry**.

4. Determine the **molecular shape** by removing the lone pairs, but retaining their influence on shape.
*Predict the shape of CO$_2$ which has the Lewis structure:*

$$:\ddot{O}=C=\ddot{O}:$$

The geometry of CO$_2$ is determined by the repulsion between the two electron groups (the two double bonds) on the central carbon atom. These two electron groups get as far away from each other as possible, resulting in a bond angle of 180° and a linear geometry for CO$_2$.

*Another example:*
The geometry of H$_2$CO is determined by the repulsion between the three electron groups (the two single bonds and one double bond) on the central carbon atom. These three electron groups get as far away from each other as possible, resulting in a bond angle of 120° and a trigonal planar geometry for CO$_2$.

Another example:
Predict the Shape of CH₄

Because bonds are regions of concentrated negative charge, they repel one another.

Are these bonds as far apart as possible?

Structure diagram
- Bond projects out from page.
- Bond goes back behind page.
- Bond is in plane of page.

Ball-and-stick model emphasizes bonding pattern.

Space-filling model approximates actual molecule shape.
Predicting the Shapes of Molecules with Lone Pairs on the Central Atom
The NH$_3$ molecule has four electron groups (one lone pair and three bonding pairs).

If we look only at the electron groups, the electron geometry—the geometrical arrangement of the electron groups—is tetrahedral.

The molecular geometry—the geometrical arrangement of the atoms—is trigonal pyramidal.
VSEPR Theory

Count all electrons when determining the electron-group geometry.

Treat the lone pairs as invisible when naming the molecule's shape.

Tetrahedral geometry of electron groups

Pyramidal shape of molecule

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

\[
\text{H} \quad \text{N} \quad \text{H}
\]
The H$_2$O molecule has four electron groups (two lone pairs and two bonding pairs).

If we look at the electron groups, the electron geometry—the geometrical arrangement of the electron groups—is tetrahedral.

The molecular geometry—the geometrical arrangement of the atoms—is bent.
Hydrogen Chloride, a Linear Molecule

Ammonia, a Trigonal Pyramidal Molecule

Water, a Bent or Angular Molecule

Methane, a Tetrahedral Molecule

All of these molecular geometries are derived from a tetrahedral arrangement of electron groups.
# Electron and Molecular Geometries

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecule</th>
<th>Electron groups</th>
<th>Bonding groups</th>
<th>Lone pairs</th>
<th>Electron geometry</th>
<th>Molecular geometry</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>linear</td>
<td>linear</td>
<td>180°</td>
</tr>
<tr>
<td>CH₂O</td>
<td></td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>trigonal planar</td>
<td>trigonal planar</td>
<td>120°</td>
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<tr>
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<td></td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>trigonal planar</td>
<td>bent</td>
<td>120°</td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td>4</td>
<td>4</td>
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<td>tetrahedral</td>
<td>tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>NH₃</td>
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<td>trigonal pyramidal</td>
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</tr>
</tbody>
</table>
Bond Polarity

Most bonds have some degree of sharing and some degree of ion formation to them.

Bonds are classified as **covalent** if the amount of electron transfer is insufficient for the material to display the classic properties of ionic compounds.

If the sharing is unequal enough to produce a dipole in the bond, the bond is classified as **polar covalent**.
Polar Covalent Bonding

Covalent bonding between unlike atoms
Unequal sharing of the electrons

1) one atom pulls the electrons in the bond closer to its side
2) one end of the bond has larger electron density than the other
Electronegativity

The ability of an atom to attract bonding electrons to itself

Increases across period (➡)  Decreases down group (⬇)

1) fluorine is the most electronegative element
2) francium is the least electronegative element
3) noble gas atoms are not assigned values
4) opposite of atomic size trend
Electronegativity Scale
Bond Polarity - Usually Expressed as $\Delta EN$

- **Pure Covalent**
  
  $EN_{Cl} = 3.0$
  
  $3.0 - 3.0 = 0$
  
  Pure Covalent

- **Polar Covalent**
  
  $EN_{Cl} = 3.0$
  
  $EN_H = 2.1$
  
  $3.0 - 2.1 = 0.9$
  
  Polar Covalent

- **Ionic**
  
  $EN_{Cl} = 3.0$
  
  $EN_{Na} = 0.9$
  
  $3.0 - 0.9 = 2.1$
  
  Ionic

$\Delta EN$
Molecular Polarity
When describing the polarity of a molecule, we must consider bond polarities as **VECTOR QUANTITIES** quantities with magnitude and direction.
Polar Bonds and Polar Molecules

Does the presence of one or more polar bonds in a molecule always result in a polar molecule?

A *polar molecule* is one with polar bonds that add together—they do not cancel each other—to form a *net dipole moment*. 
Polar Covalent Bond

When a diatomic molecule contains a polar bond, then the molecule is polar.
Consider carbon dioxide:

Each bond is polar because the difference in electronegativity between oxygen and carbon is 1.0.

$\text{CO}_2$ has a linear geometry, the dipole moment of one bond completely cancels the dipole moment of the other, and the molecule is nonpolar.
Consider water ($H_2O$): each bond is polar because the difference in electronegativity between oxygen and hydrogen is 1.4.

*Each bond is polar* because the difference in electronegativity between oxygen and hydrogen is 1.4.

Water has two dipole moments that do not cancel, and *the molecule is polar*. 
Nonpolar
The molecules all assume the same orientation between the charged plates, meaning H₂O must be polar.

The molecules are oriented randomly, meaning C₂Cl₂ must be nonpolar.
stream of water attracted to a charged glass rod

stream of hexane not attracted to a charged glass rod
**TABLE 10.3** Common Cases of Adding Dipole Moments to Determine Whether a Molecule Is Polar

<table>
<thead>
<tr>
<th>Nonpolar</th>
<th>Polar</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Nonpolar Diagram" /></td>
<td><img src="image2.png" alt="Polar Diagram" /></td>
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**Nonpolar**

Two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.

**Nonpolar**

Three identical polar bonds at 120° from each other will not cancel. The molecule is nonpolar.

**Polar**

Three polar bonds in a trigonal pyramidal arrangement (109.5°) will not cancel. The molecule is polar.

**Polar**

Two polar bonds with an angle of less than 180° between them will not cancel. The molecule is polar.
Common Cases of Adding Dipole Moments to Determine Whether a Molecule is Polar

- **Nonpolar**
  - Two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.
  - Example: A molecule with two identical polar bonds arranged symmetrically will be nonpolar.

- **Polar**
  - Three polar bonds in a trigonal pyramidal arrangement (109.5°) will not cancel. The molecule is polar.
  - Example: A molecule with three polar bonds arranged at 109.5° to each other will be polar.

- **Nonpolar**
  - Three identical polar bonds at 120° from each other will cancel. The molecule is nonpolar.
  - Example: A molecule with three identical polar bonds arranged at 120° to each other will be nonpolar.

- **Polar**
  - Two polar bonds with an angle of less than 180° between them will not cancel. The molecule is polar.
  - Example: A molecule with two polar bonds arranged at an angle less than 180° will be polar.
No net dipole
Some molecules are inherently **polar** because of the atoms which they contain and the arrangement of these atoms in space.
Other molecules are considered **nonpolar**