A molecule is a discrete chemical entity, in which atoms are held together by the electrostatic attractions of covalent bonds. In previous chemistry courses, you used Lewis structures to represent the bonding in simple molecules. In a Lewis structure, you assume that each of the atoms in the molecule achieves a noble gas configuration through the sharing of electrons in single, double, or triple bonds. This section introduces you to a systematic approach to drawing Lewis structures for a broader range of molecules and for polyatomic ions. You will see that, in some cases, there are exceptions to the octet rule. Afterwards, you will use bonding theory to help you predict the shapes of various molecules. From the shapes of these molecules (and the electronegativity difference of their atoms), you will determine the polarity of the substances that are comprised of these molecules.

Why is polarity important? It explains why, for example, water is a liquid at room temperature, rather than a gas. In other words, it helps explain why Earth is capable of supporting life! You will explore the significance of molecular polarity in greater detail in section 4.3.

**Lewis Structures for Molecules and Polyatomic Ions**

You can use the procedure outlined below to draw the Lewis structures for molecules and ions that have a central atom, with other atoms around it. The Sample Problems and additional text that follow show how to apply these steps for several molecules and polyatomic ions that obey the octet rule. Afterwards, use Practice Problems 9 to 13 to practice drawing Lewis structures.

**How To Draw Lewis Structures for Simple Molecules and Ions with a Central Atom**

**Step 1** Position the least electronegative atom in the centre of the molecule or polyatomic ion. Write the other atoms around this central atom, with each atom bonded to the central atom by a single bond. Always place a hydrogen atom or a fluorine atom at an end position in the structure.

**Step 2 (a)** Determine the total number of valence electrons in the molecule or ion. For polyatomic ions, pay close attention to the charge. For example, if you are drawing a polyatomic anion such as CO$_3^{2-}$, add two electrons to the total number of valence electrons calculated for the structure CO$_3$. For a polyatomic cation such as NH$_4^+$, subtract one electron from the total number of valence electrons calculated for the structure NH$_4$.

**(b)** Once you have the total number of valence electrons, determine the total number of electrons needed for each atom to achieve a noble gas electron configuration.
Sample Problem

Drawing the Lewis Structure of a Molecule

Problem
Draw the Lewis structure for formaldehyde (methanal), CH₂O.

Solution
The molecular formula, CH₂O, tells you the number of each kind of atom in the molecule. Following steps 1 to 3 from the procedure outlined above:

Step 1 Since H is always placed at the end position and C is less electronegative than O, C should be the central atom. Place the other atoms around C, attached by single bonds.

\[
\begin{array}{c}
\text{O} \\
\text{H—C—H}
\end{array}
\]

Step 2 Determine the total number of valence electrons:
\[
(1 \text{ C atom} \times 4 \text{ e}^{-}/\text{atom}) + (1 \text{ O atom} \times 6 \text{ e}^{-}/\text{atom}) + (2 \text{ H atoms} \times 1 \text{ e}^{-}/\text{atom}) = 4 \text{ e}^{-} + 6 \text{ e}^{-} + 2 \text{ e}^{-} = 12 \text{ e}^{-}
\]

Then, determine the total number of electrons required for each atom in the structure to achieve a noble gas configuration. This would be 8 e⁻ for C and 8 e⁻ for O (to fill their respective valence energy levels) and 2 e⁻ for each H (to fill its 1s orbital). So the total number for CH₂O is:
\[
(2 \text{ atoms} \times 8 \text{ e}^{-}/\text{atom}) + (2 \text{ atoms} \times 2 \text{ e}^{-}/\text{atom}) = 20 \text{ e}^{-}
\]

To find the number of shared electrons, subtract the first total from the second,
\[
20 \text{ e}^{-} - 12 \text{ e}^{-} = 8 \text{ e}^{-}
\]

Now divide the number of shared electrons by two to obtain the number of bonds.
\[
20 \text{ e}^{-} - 12 \text{ e}^{-} = 8 \text{ e}^{-} + 2 = 4 \text{ covalent bonds}
\]

Since there are only three atoms surrounding the central atom, you can infer that one of the bonds is likely a double bond.
Step 3 Determine the number of non-bonding electrons by subtracting the number of shared electrons from the total number of valence electrons:
- 12 valence electrons – 8 shared electrons
- = 4 non-bonding valence electrons (that is, 2 lone pairs)

Since H can only form a single bond, a possible structure is:

\[
\text{H} - \text{C} - \text{H}
\]

Check Your Solution
Each atom has achieved a noble gas electron configuration. Thus, you can be confident that this is a reasonable Lewis structure.

Co-ordinate Covalent Bonds
You know that a covalent bond involves the sharing of a pair of electrons between two atoms; each atom contributes one electron to the shared pair. In some cases, such as the hydronium ion, \( \text{H}_3\text{O}^+ \), one atom contributes both of the electrons to the shared pair. The bond in these cases is called a co-ordinate covalent bond. In terms of the quantum mechanical model, a co-ordinate covalent bond forms when a filled atomic orbital overlaps with an empty atomic orbital. Once a co-ordinate bond is formed, it behaves in the same way as any other single covalent bond. The next Sample Problem involves a polyatomic ion with a co-ordinate covalent bond.

Sample Problem

**Lewis Structures with a Co-ordinate Covalent Bond**

Problem
Draw the Lewis structure for the ammonium ion, \( \text{NH}_4^+ \).

Solution
The formula, \( \text{NH}_4^+ \), tells you the number of each kind of atom in the ion. Following steps 1 to 3 from the procedure outlined above:

Step 1 Since H is always placed at the end position, N is the central atom.

\[
\text{H} - \text{N} - \text{H}
\]

Step 2 Total number of valence electrons:
- \( (1 \text{ N atom} \times 5 \text{ e}^-/\text{N atom}) + (4 \text{ H atom} \times 1 \text{ e}^-/\text{H atom}) - 1 \text{ e}^- = 8 \text{ e}^- \)
- Total number of electrons required for noble gas configuration:
  - \( (1 \text{ atom} \times 8 \text{ e}^-/\text{atom}) + (4 \text{ atoms} \times 2 \text{ e}^-/\text{atom}) = 16 \text{ e}^- \)
Note that the Lewis structure for NH₄⁺ does not indicate which atom provides each shared pair of electrons around the central nitrogen atom. However, the quantum mechanical model of the atom can explain the bonding around this nitrogen atom. The condensed electron configuration for nitrogen is [Ne] 2s²2p³. Each nitrogen atom has only three unpaired 2p electrons in three half-filled orbitals available for bonding. Since there are four covalent bonds shown around nitrogen in the Lewis structure, electrons in one of the bonds must have come from the filled orbitals of nitrogen. Therefore, one of the bonds around the central nitrogen atom must be a co-ordinate covalent bond.

Resonance Structures: More Than One Possible Lewis Structure

Imagine that you are asked to draw the Lewis structure for sulfur dioxide, SO₂. A typical answer would look like this:

\[ :\overset{\cdot}{\ddot{O}} \longrightarrow \ddot{S} \equiv \ddot{O} : \]

This Lewis structure suggests that SO₂ contains a single bond and a double bond. However, experimental measurements of bond lengths indicate that the bonds between the S and each O are identical. The two bonds have properties that are somewhere between a single bond and a double bond. In effect, the SO₂ molecule contains two “one-and-a-half” bonds.

To communicate the bonding in SO₂ more accurately, chemists draw two Lewis structures and insert a double-headed arrow between them. Each of these Lewis structures is called a resonance structure. **Resonance structures** are models that give the same relative position of atoms as in Lewis structures, but show different places for their bonding and lone pairs.

\[ :\overset{\cdot}{\ddot{O}} \longrightarrow \ddot{S} \equiv \ddot{O} : \quad \leftrightarrow \quad :\overset{\cdot}{\ddot{O}} \equiv \ddot{S} \longrightarrow \ddot{O} : \]
Many molecules and ions—especially organic ones—require resonance structures to represent their bonding. It is essential to bear in mind, however, that resonance structures do not exist in reality. For example, SO$_2$ does not shift back and forth from one structure to the other. An actual SO$_2$ molecule is a combination—a hybrid—of its two resonance structures. It is more properly referred to as a resonance hybrid. You could think of resonance hybrids as being like “mutts.” For example, a dog that is a cross between a spaniel and a beagle (a “speagle”) is part spaniel and part beagle. It does not exist as a spaniel one moment and a beagle the next. Instead, a speagle is an average, of sorts, between the two breeds. Similarly, a resonance hybrid is a weighted average between two or more resonance structures.

## Practice Problems

9. Draw Lewis structures for each of the following molecules.
   (a) NH$_3$
   (b) CH$_4$
   (c) CF$_4$
   (d) AsH$_3$
   (e) BrO$^-$
   (f) H$_2$S
   (g) H$_2$O$_2$
   (h) CINO

10. Draw Lewis structures for each of the following ions. (Note: Consider resonance structures.)
   (a) CO$_3^{2-}$
   (b) NO$^+$
   (c) ClO$_3^-$
   (d) SO$_3^{2-}$

11. Dichlorofluoroethane, CH$_3$CFCl$_2$, has been proposed as a replacement for chlorofluorocarbons (CFCs). The presence of hydrogen in CH$_3$CFCl$_2$ markedly reduces the ozone-depleting ability of the compound. Draw a Lewis structure for this molecule.

12. Draw Lewis structures for the following molecules. (Note: Neither of these molecules has a single central atom.)
   (a) N$_2$H$_4$
   (b) N$_2$F$_2$

13. Although Group 18 (VIIIA) elements are inactive, chemists are able to synthesize compounds of several noble gases, including Xe. Draw a Lewis structure for the XeO$_4$ molecule. Indicate if co-ordinate covalent bonding is likely a part of the bonding in this molecule.

### Central Atoms with an Expanded Valence Level

The octet rule allows a maximum of four bonds (a total of eight electrons) to form around an atom. Based upon bond energies, however, chemists have suggested that the bonding in some molecules (and polyatomic ions) is best explained by a model that shows more than eight electrons in the valence energy level of the central atom. This central atom is said to have an **expanded valence energy level**. One example of a molecule with an expanded valence energy level is phosphorus pentachloride, PCl$_5$. This substance is a pungent, pale-yellow powder that is used in the agricultural, pharmaceutical, and dyeing industries. Organic chemists also use reactions with PCl$_5$ to identify compounds that contain hydroxyl groups.
14. Draw Lewis structures for the following molecules.
   (a) SF₆  
   (b) BrF₅

15. Draw Lewis structures for the following molecules.
   (a) XeF₄  
   (b) PF₅

16. How does the arrangement of electrons around the central atom differ in PI₃ and ClI₃? Draw the Lewis structures for these compounds to answer this question.

17. Draw a Lewis structure for the ion, IF₄⁻.

Practice Problems

Shapes and Polarity of Molecules

Up to now, you have represented molecules using Lewis structures. These two-dimensional, formula-like diagrams help you count and keep track of valence electrons, and communicate essential information about the placement and bonding of atoms or ions in a molecule. Chemists often draw Lewis structures in a way that suggests the shape of a molecule. However, this is not their function. It is important to remember that Lewis structures do not communicate any information about a molecule’s shape. To represent the shapes of real molecules, you need a model that depicts them in three-dimensions.

In 1957, an English chemist, Ronald Gillespie, joined Hamilton, Ontario’s McMaster University for a long, distinguished career as a professor of chemistry. Earlier that year, Gillespie, in collaboration with a colleague, Ronald Nyholm, developed a model for predicting the shape of molecules. Like chemistry students around the world since that time, you are about to learn the central features of this model, called the Valence-Shell Electron-Pair Repulsion theory. This is usually abbreviated to VSEPR (pronounced “vesper”) theory. (Note that some chemists use the term “shell” instead of energy level to describe atomic orbitals.)

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

The fundamental principle of the Valence-Shell Electron-Pair Repulsion theory is that the bonding pairs and lone, non-bonding pairs of electrons in the valence level of an atom repel one another. As you know, electron pairs of atoms are localized in orbitals, which are shapes that describe the space in which electrons are most likely to be found around a nucleus. The orbital for each electron pair is positioned as far apart from the other orbitals as possible.
The effect of this positioning minimizes the forces of repulsion between electron pairs. A lone pair (LP) will spread out more than a bond pair. Therefore, the repulsion is greatest between lone pairs (LP—LP). Bonding pairs (BP) are more localized between the atomic nuclei, so they spread out less than lone pairs. Therefore, the BP-BP repulsions are smaller than the LP—LP repulsions. The repulsion between a bond pair and a lone-pair (BP—LP) has a magnitude intermediate between the other two. In other words, in terms of decreasing repulsion:

\[ \text{LP—LP} > \text{LP—BP} > \text{BP—BP}. \]

In Unit 1, you encountered the tetrahedral shape around a single-bonded carbon atom, the trigonal planar shape around a carbon atom with one double bond, and the linear shape around a carbon atom with a triple bond. These shapes result from repulsions between lone pairs and bonding pairs of electrons. Now you will use your understanding of LP and BP repulsions to explain the shapes you learned in Unit 1, and to predict the shapes of other molecules. Figure 4.11 shows the five basic geometrical arrangements that result from the interactions of lone pairs and bonding pairs around a central atom. These arrangements involve up to six electron groups. An electron group is usually one of the following:

- a single bond
- a double bond
- a triple bond
- a lone pair

Each of the electron-group arrangements in Figure 4.11 results in a minimum total energy for the molecule. Variations in these arrangements are possible, depending on whether a bonding pair or a lone pair occupies a specific position. Therefore, it is important to distinguish between electron-group arrangement and molecular shape. Electron-group arrangement refers to the ways in which groups of valence electrons are positioned around the central atom. Molecular shape refers to the relative positions of the atomic nuclei in a molecule. When all the electron groups are bonding pairs, a molecule will have one of the five geometrical arrangements shown in Figure 4.11. If one or more of the electron groups include a lone pair of electrons, variations in one of the five geometric arrangements result.

**Figure 4.11** The five basic electron-group arrangements and their bond angles.
In the following ExpressLab, you will make models of the five electron-group arrangements, and measure their bond angles. Afterwards, you will consider some of the variations in molecular shapes that can occur.

ExpressLab Using Soap Bubbles to Model Molecular Shape

You can use soap bubbles to simulate the molecular shapes that are predicted by VSEPR theory. The soap bubbles represent the electron clouds surrounding the central atom in a molecule.

Safety Precautions

- Ensure that each person uses a clean straw.
- Clean up all spills immediately.

Materials

- soap solution (mixture of 80 mL distilled water, 15 mL detergent, and 5 mL glycerin)
- 100 mL beaker
- straw
- protractor
- hard, flat surface
- paper towels

Procedure

1. Obtain approximately 25 mL of the prepared soap solution in a 100 mL beaker.
   - CAUTION: Clean up any spills immediately.
2. Wet a hard, flat surface, about 10 cm × 10 cm in area, with the soap solution.
3. Dip a straw into the soap solution in the beaker and blow a bubble on the wetted surface.
   - CAUTION: Each person must use a clean straw. Blow a second bubble of the same size onto the same surface to touch the first bubble. Record the shape of this simulated molecule and measure the bond angle between the centres of the two bubbles where the nuclei of the atoms would be located.
4. Repeat step 3 with three bubbles of the same size (to simulate three bonding pairs). Record the shape and the bond angle between the centres of the bubbles.
5. Repeat step 3, but this time make one bubble slightly larger than the other two. This will simulate a lone pair of electrons. Record what happens to the bond angles.
6. On top of the group of three equal-sized bubbles, blow a fourth bubble of the same size that touches the centre. Estimate the angle that is formed where bubbles meet.
7. On top of the group of bubbles you made in step 5, make a fourth bubble that is larger than the other three (to simulate a lone pair). Record what happens to the bond angles.
8. Have five students each blow a bubble of the same size at the same time to join and float in the air. Identify the shape that results. If successful, have six partners join six bubbles in the air and identify the shape.
9. Clean your work area using dry paper towels first. Then wipe the area with wet paper towels.

Analysis

1. What shapes and bond angles were associated with two, three, and four same-sized bubbles? Give an example of a molecule that matches each of these shapes.
2. Give an example of a molecule that matches each of the shapes in steps 5 and 7, where you made one bubble larger than the others.
3. What molecular shapes match the arrangements of the bubbles in step 8?
4. If they are available, use inflated balloons or molecule modeling kits to construct each of the arrangements in Figure 4.11. How do these models compare with your bubble models?
Molecular Geometry

Each of the molecules in Figure 4.12 has four pairs of electrons around the central atom. Observe the differences in the number of bonding and lone pairs in these molecules. Methane, CH₄, has four BPs. Ammonia, NH₃, has three BPs and one LP. Water, H₂O, has two BPs and two LPs. Notice the effect of these differences on the shapes and bond angles of the molecules. Methane, with four BPs, has a molecular shape that is the same as the electron-group arrangement in which four electron groups surround a central atom: tetrahedral. The angle between any two bonding pairs in the tetrahedral electron-group arrangement is 109.5°. This angle corresponds to the most favourable arrangement of electron groups to minimize the forces of repulsion among them.

![Molecular Geometry Diagram](image)

**Figure 4.12** Comparing the bond angles in the molecules of CH₄, NH₃, and H₂O.

When there are 1 LP and 3 BPs around a central atom, there are two types of repulsions: LP—BP and BP—BP. Since LP—BP repulsions are greater than BP—BP repulsions, the bond angle between the bond pairs in NH₃ is reduced from 109.5° to 107.3°. When you draw the shape of a trigonal pyramidal molecule, without the lone pair, you can see that the three bonds form the shape of a pyramid with a triangular base. In a molecule of H₂O, there are two BPs and two LPs. The strong LP—LP repulsions, in addition to the LP—BP repulsions, cause the angle between the bonding pairs to be reduced further to 104.5°. You encountered this variation of the tetrahedral shape in Unit 1: the bent shape around an oxygen atom with 2 LPs and two single bonds.

Table 4.2 summarizes the molecular shapes that commonly occur. The VSEPR notation used for these shapes adopts the letter “A” to represent the central atom, the letter “X” to represent a bonding pair, and the letter “E” to represent a lone pair of electrons. For example, the VSEPR notation for NH₃ is AX₃E. This indicates that ammonia has three BPs around its central atom, and one LP.
<table>
<thead>
<tr>
<th>Number of electron groups</th>
<th>Geometric arrangement of electron groups</th>
<th>Type of electron pairs</th>
<th>VSEPR notation</th>
<th>Name of Molecular shape</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>2 BP</td>
<td>AX₂</td>
<td>X—A—X linear</td>
<td>BeF₂</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>3 BP</td>
<td>AX₃</td>
<td></td>
<td>BF₃</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>trigonal planar</td>
<td>2 BP, 1 LP</td>
<td>AX₂E</td>
<td></td>
<td>SnCl₂</td>
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<td>tetrahedral</td>
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<td>AX₄</td>
<td></td>
<td>CF₄</td>
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</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>3 BP, 1LP</td>
<td>AX₂E</td>
<td></td>
<td>PCl₃</td>
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</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>2 BP, 2LP</td>
<td>AX₂E₂</td>
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<td>H₂S</td>
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<td>5 BP</td>
<td>AX₅</td>
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</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>4 BP, 1 LP</td>
<td>AX₂E</td>
<td></td>
<td>TeCl₄</td>
</tr>
</tbody>
</table>

**Table 4.2** Common Molecular Shapes and Their Electron Group Arrangements

- **Number of electron groups**: The number of electron groups around the central atom.
- **Geometric arrangement of electron groups**: The arrangement of electron pairs around the central atom.
- **Type of electron pairs**: The type of electron pairs, either bonding pairs (BP) or lone pairs (LP).
- **VSEPR notation**: The notation used in the Valence Shell Electron Pair Repulsion (VSEPR) theory.
- **Name of Molecular shape**: The shape of the molecule as predicted by the VSEPR theory.
- **Example**: The molecular example that fits the description.
Predicting Molecular Shape

You can use the steps below to help you predict the shape of a molecule (or polyatomic ion) that has one central atom. Refer to these steps as you work through the Sample Problems and the Practice Problems that follow.

1. Draw a preliminary Lewis structure of the molecule based on the formula given.
2. Determine the total number of electron groups around the central atom (bonding pairs, lone pairs and, where applicable, account for the charge on the ion). Remember that a double bond or a triple bond is counted as one electron group.
3. Determine which one of the five geometric arrangements will accommodate this total number of electron groups.
4. Determine the molecular shape from the positions occupied by the bonding pairs and lone pairs.
Sample Problem

Predicting Molecular Shape for a Simpler Compound

**Problem**
Determine the molecular shape of the hydronium ion, $\text{H}_3\text{O}^+$.  

**Plan Your Strategy**
Follow the four-step procedure that helps to predict molecular shape. Use Table 4.2 for names of the electron-group arrangements and molecular shapes.

**Act on Your Strategy**

**Step 1** A possible Lewis structure for $\text{H}_3\text{O}^+$ is:

![Lewis structure of H₃O⁺]

**Step 2** The Lewis structure shows 3 BPs and 1 LP. That is, there are a total of four electron groups around the central O atom.

**Step 3** The geometric arrangement of the electron groups is tetrahedral.

**Step 4** For 3 BPs and 1 LP, the molecular shape is trigonal pyramidal.

**Check Your Solution**
This molecular shape corresponds to the VSEPR notation for this ion, $\text{AX}_3\text{E}$.

---

Sample Problem

Predicting Molecular Shape for a Complex Compound

**Problem**
Determine the shape of $\text{SiF}_6^{2-}$ using VSEPR theory.

**Plan Your Strategy**
Follow the four-step procedure that helps to predict molecular shape apply. Use Table 4.2 for names of the electron group arrangements and molecular shapes.

**Act on Your Strategy**

**Step 1** Draw a preliminary Lewis structure for $\text{SiF}_6^{2-}$.

![Lewis structure of SiF₆²⁻]

This polyatomic ion has six bonds around the central Si atom, an obvious exception to the octet rule, so the central atom needs an expanded valence shell.

Total number of valence electrons

\[
= 1 \text{ Si atom} \times 4 \text{ e}^-/\text{Si atom} + 6 \text{ F atom} \times 7 \text{ e}^-/\text{F atom} + 2 \text{ e}^- \\
= 48 \text{ e}^-
\]
18. Use VSEPR theory to predict the molecular shape for each of the following:
   (a) HCN       (b) SO₂       (c) SO₃       (d) SO₄²⁻

19. Use VSEPR theory to predict the molecular shape for each of the following:
   (a) CH₂F₂       (b) AsCl₅       (c) NH₄⁺       (d) BF₄⁻

20. Use VSEPR theory to predict the molecular shapes of NO₂⁺ and NO₂⁻.