Pearson

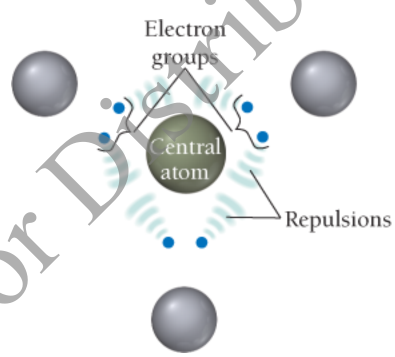
5.7: VSEPR Theory: The Five Basic Shapes

Key Concept Video **VSEPR Theory**

Valence shell electron pair repulsion (VSEPR) theory is based on the simple idea that **electron groups**—which we define as lone pairs, single bonds, multiple bonds, and even single electrons—repel one another through coulombic forces (see Section 3.3). The electron groups, of course, are also attracted to the nucleus (otherwise the molecule would fall apart), but VSEPR theory focuses on the repulsions. According to VSEPR theory, the repulsions between electron groups on *interior atoms* (or the central atom) of a molecule determine the geometry of the molecule (Figure 5.7). The preferred geometry of a molecule is the one in which the electron groups have the maximum separation (and therefore the minimum energy) possible. Consequently, for molecules having just one interior atom (the central atom), molecular geometry depends on (a) the number of electron groups around the central atom and (b) how many of those electron groups are bonding groups and how many are lone pairs. In this section, we first look at the molecular geometries associated with two to six electron groups around the central atom when all of those groups are bonding groups (single or multiple bonds). The resulting geometries constitute the five basic shapes of molecules. We will then consider how these basic shapes are modified if one or more of the electron groups are lone pairs.

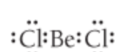
Figure 5.7 Repulsion between Electron Groups

The basic idea of VSEPR theory is that repulsions between electron groups determine molecular geometry.



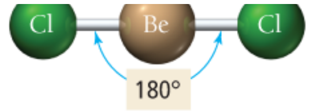
Two Electron Groups: Linear Geometry

Consider the Lewis structure of $BeCl_2$, which has two electron groups (two single bonds) about the central atom:

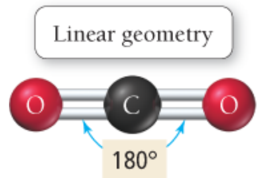


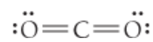
Recall that beryllium often forms incomplete octets, as it does in this structure.

According to VSEPR theory, the geometry of $BeCl_2$ is determined by the repulsion between these two electron groups, which maximize their separation by assuming a 180° bond angle or a **linear geometry**. Experimental measurements of the geometry of $BeCl_2$ indicate that the molecule is indeed linear, as predicted by the theory.



Molecules that form only two single bonds, with no lone pairs, are rare because they do not follow the octet rule. However, the same geometry is observed in all molecules that have two electron groups (and no lone pairs). Consider the Lewis structure of CO_2, which has two electron groups (the double bonds) around the central carbon atom:



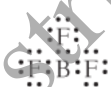


A double bond counts as one electron group.

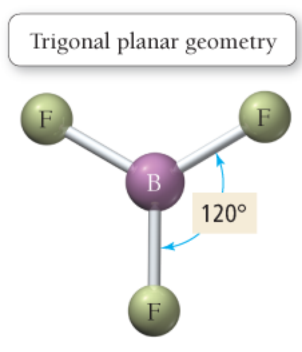
According to VSEPR theory, the two double bonds repel each other (just as the two single bonds in $BeCl_2$ repel each other), resulting in a linear geometry for CO_2. Experimental observations confirm that CO_2 is indeed a linear molecule.

Three Electron Groups: Trigonal Planar Geometry

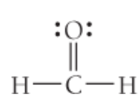
The Lewis structure of BF_3 (another molecule with an incomplete octet) has three electron groups around the central atom:



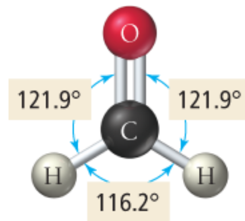
These three electron groups maximize their separation by assuming 120° bond angles in a plane—a **trigonal planar geometry** (see Figure 5.7). Experimental observations of the structure of BF_3 again confirm the predictions of VSEPR theory.



Another molecule with three electron groups, formaldehyde, has one double bond and two single bonds around the central atom:



Since formaldehyde has three electron groups around the central atom, we initially predict that the bond angles should also be 120°. However, experimental observations show that the HCO bond angles are 121.9° and that the HCH bond angle is 116.2°. These bond angles are close to the idealized 120° that we originally predicted, but the HCO bond angles are slightly greater than the HCH bond angle because the double bond contains more electron density than the single bond and therefore exerts a slightly greater repulsion on the single bonds. In general, *different types of electron groups exert slightly different repulsions*—the resulting bond angles reflect these differences.



Conceptual Connection 5.5 Electron Groups and Molecular Geometry

Four Electron Groups: Tetrahedral Geometry

The VSEPR geometries of molecules with two or three electron groups around the central atom are two-dimensional and therefore can easily be visualized and represented on paper. For molecules with four or more electron groups around the central atom, the geometries are three-dimensional and are therefore more difficult to imagine and draw. One common way to help visualize these basic shapes is by analogy to balloons tied together. In this analogy, each electron group around a central atom is like a balloon tied to a central point. The bulkiness of the balloons causes them to spread out as much as possible, much as the repulsion between electron groups causes them to position themselves as far apart as possible. For example, if you tie two balloons together, they assume a roughly linear arrangement, as shown in Figure 5.8a, analogous to the linear geometry of $BeCl_2$ that we just examined. Keep in mind that the balloons do not represent atoms, but *electron groups*. Similarly, if you tie three balloons together—in analogy to three electron groups—they assume a trigonal planar geometry, as shown in Figure 5.8b, much like the BF_3 molecule. If you tie *four* balloons together, however, they assume a three-dimensional **tetrahedral geometry** with 109.5° angles between the balloons. That is, the balloons point toward the vertices of a *tetrahedron*—a geometrical shape with four identical faces, each an equilateral triangle, as shown here:

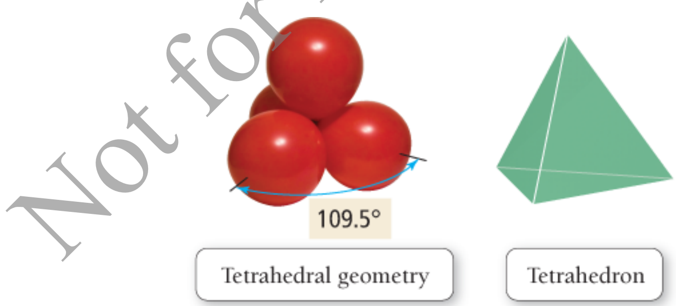
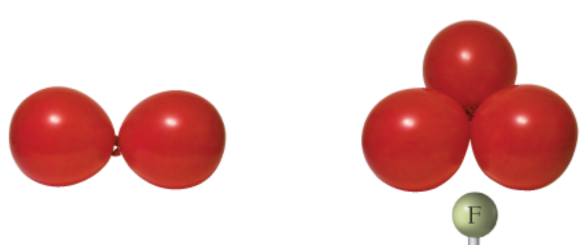


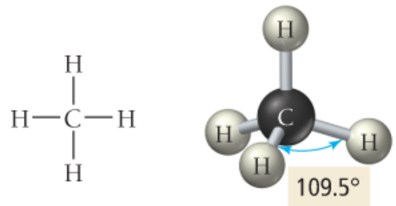
Figure 5.8 Representing Electron Geometry with Balloons

(a) The bulkiness of balloons causes them to assume a linear arrangement when two of them are tied together. Similarly, the repulsion between two electron groups produces a linear geometry. **(b)** Like three balloons tied together, three electron groups adopt a trigonal planar geometry.



(a) Linear geometry (b) Trigonal planar geometry

Methane is an example of a molecule with four electron groups around the central atom:



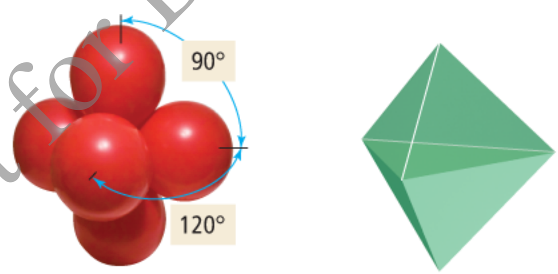
Tetrahedral geometry

For four electron groups, the tetrahedron is the three-dimensional shape that allows the maximum separation among the groups. The repulsions among the four electron groups in the C–H bonds cause the molecule to assume the tetrahedral shape. When we write the Lewis structure of CH_4 on paper, it may seem that the molecule should be square planar, with bond angles of 90°. However, in three dimensions, the electron groups can get farther away from each other by forming the tetrahedral geometry, as illustrated in our balloon analogy.

Conceptual Connection 5.6 Molecular Geometry

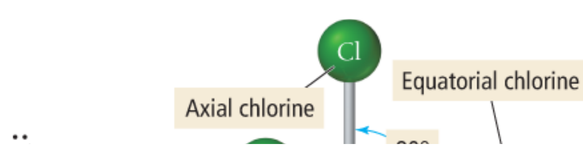
Interactive

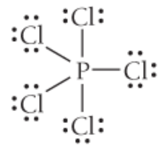
Five Electron Groups: Trigonal Bipyramidal Geometry

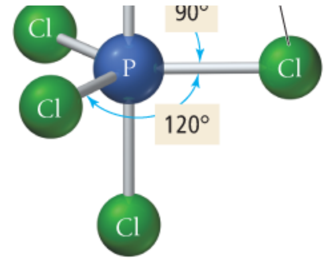


Trigonal bipyramidal geometry Trigonal bipyramid

Five electron groups around a central atom assume a **trigonal bipyramidal geometry**, like five balloons tied together. In this structure, three of the groups lie in a single plane, as in the trigonal planar configuration, while the other two are positioned above and below this plane. The angles in the trigonal bipyramidal structure are not all the same. The angles between the *equatorial positions* (the three bonds in the trigonal plane) are 120°, while the angle between the *axial positions* (the two bonds on either side of the trigonal plane) and the trigonal plane is 90°. As an example of a molecule with five electron groups around the central atom, consider PCl_5:



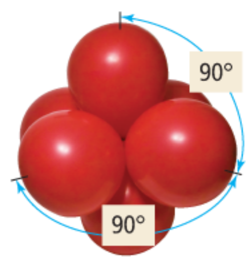




Trigonal bipyramidal geometry

The three equatorial chlorine atoms are separated by 120° bond angles, and the two axial chlorine atoms are separated from the equatorial atoms by 90° bond angles.

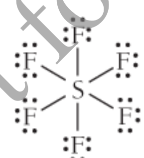
Six Electron Groups: Octahedral Geometry

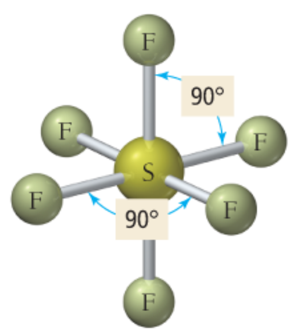


Octahedral geometry

Octahedron

Six electron groups around a central atom assume an **octahedral geometry**, like six balloons tied together. In this structure—named after the eight-sided geometrical shape called the octahedron—four of the groups lie in a single plane, with a fifth group above the plane and another below it. The angles in this geometry are all 90°. As an example of a molecule with six electron groups around the central atom, consider SF_6:





Octahedral geometry

The structure of this molecule is highly symmetrical; all six bonds are equivalent.

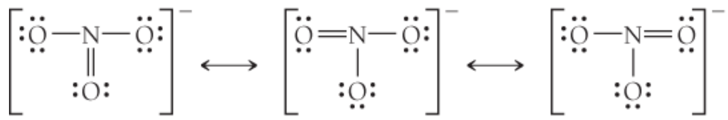
Example 5.9 **VSEPR Theory and the Basic Shapes**

Determine the molecular geometry of NO_3^-.

SOLUTION

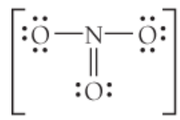
The molecular geometry of NO_3^- is determined by the number of electron groups around the central atom (N). Begin by drawing the Lewis structure of NO_3^-.

NO_3^- has $5 + 3(6) + 1 = 24$ valence electrons. The Lewis structure is as follows:



The hybrid structure is intermediate between these three and has three equivalent bonds.

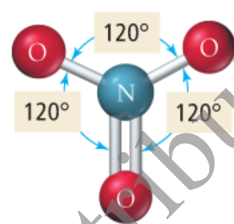
Use any one of the resonance structures to determine the number of electron groups around the central atom.



The nitrogen atom has three electron groups.

Based on the number of electron groups, determine the geometry that minimizes the repulsions between the groups.

The electron geometry that minimizes the repulsions between three electron groups is trigonal planar.



Since the three bonds are equivalent (because of the resonance structures), they each exert the same repulsion on the other two and the molecule has three equal bond angles of 120°.

FOR PRACTICE 5.9 Determine the molecular geometry of CCl_4.