Molecular Geometry: The VSEPR Theory

Lewis structures to help us picture what a molecule might look like. The problem is, this picture is still a bit wrong. After all, we were using Lewis structures that were written on a flat (two-dimensional) piece of paper. Molecules, however, are rarely flat. They generally have a three-dimensional structure to them. In other words, molecules not only have length and width, but they also have depth. Lewis structures do not allow us to picture the depth of a molecule. We must learn something else before we can fully picture what a molecule really looks like.

In order to do this, we must first recall something about Lewis structures. Consider, for example, the Lewis structure for CH₄:

![Lewis structure of CH₄](image)

Remember that the dashes in this Lewis structure represent covalent bonds. Remember also that these covalent bonds are just electron pairs that are shared between two atoms. Well, since each of these covalent bonds is made up of electron pairs, we can easily predict something about their behavior: They will tend to repel one another, because they each have the same type of electrical charge.

If these electron pairs repel each other, it stands to reason that they will try to move as far apart from each other as possible. How will they do that? If the molecule were to stay flat, then the electron pairs could not get any farther apart from each other than what is pictured in the Lewis structure above. In geometry terms, we could say that the largest angle between the chemical bonds would be 90 degrees. On the other hand, if the molecule took advantage of three-dimensional space, the bonds could get farther apart from each other. Figure 9.1 illustrates this phenomenon.
As a flat, two-dimensional structure, the bonds between the C and H cannot get any farther apart from one another than 90 degrees. However, if the molecule takes advantage of three-dimensional space, the bonds can spread out a bit more. It turns out that the bonds can get as far as 109 degrees from each other in a three-dimensional structure. We try to picture this three-dimensional structure by using solid, dashed, and triangular lines. The solid lines represent chemical bonds that are in the plane of the paper. The dashed line, however, is supposed to indicate a bond that goes behind the plane of the paper. Finally, the heavy, triangular line represents a chemical bond that is out in front of the plane of the paper. Thus, the hydrogen atom attached to the dashed line sits behind the paper, while the hydrogen atom attached to the heavy, triangular line is sitting in front of the paper. The other two hydrogens are sitting on the paper. This shape, called a tetrahedron (teh truh he’ drun), is one of the fundamental shapes that a molecule can attain. This shape is easiest to understand by looking at the photograph, where the black sphere represents the carbon atom, and the yellow spheres represent the hydrogen atoms. The wooden sticks represent the bonds between the atoms.

The theory that allows us to predict that CH$_4$ has a tetrahedral shape is called VSEPR theory. VSEPR stands for Valence Shell Electron Pair Repulsion. The VSEPR theory states that molecules will attain whatever shape keeps the valence electrons of the central atom as far apart from one another as possible. Thus, we know that CH$_4$ has a tetrahedral shape because that shape allows carbon's valence electrons to be as far apart from each other as possible.
If you have a hard time picturing all of this in your mind, don't worry too much. Trying to picture three-dimensional shapes can be very difficult for some, while it is perfectly natural for others. As we go through more molecular shapes, I will give them all names. In addition, I will mention the angles that exist between the chemical bonds. All you need to be able to do is learn those two things. It would be nice if you could also picture it in your mind, but I realize that this is a little too hard for some people. Hopefully, you will get the hang of this as we go along.

The tetrahedral shape is not the only shape a molecule might possess. Consider, for example, an ammonia molecule: NH$_3$. The Lewis structure for this molecule, which you have already drawn, is pictured below:

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H
   H---N:
   H
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In trying to determine what kind of three-dimensional shape a molecule attains, we have to look at the electron groups that surround the central atom. In this case, the central atom is nitrogen. How many groups of electrons surround the N? There are a total of four. Three of them are bonds, represented by the dashes in the Lewis diagram. The fourth, however, is a pair of non-bonding electrons. Even though these electrons do not form a bond, we still have to worry about them because they are still electrons and will repel any other electron pair that comes close to them. Thus, the four electron groups will try to get as far away from each other as possible. As we saw above, when four groups of electrons try to get as far away from each other as possible, a tetrahedron is formed. This tetrahedron, however, is a bit misshapen, as shown in Figure 9.2.
In the figure, I took the original Lewis structure and rotated it so that the non-bonding electron pair is on top of the nitrogen atom. This is done simply to make the next drawing a little easier to understand. In that drawing, I tried to illustrate the three-dimensional nature of the molecule. Once again, the dashed line indicates that the bond is behind the plane of the paper, while the heavy, triangular line indicates that the bond lies in front of the plane of the paper. The non-bonding electron pair and the bond indicated by the solid line lie in the plane of the paper.

You may be tempted to call this a tetrahedron as well, because it looks very similar to the situation with CH₄, which I said formed a tetrahedron. However, there is one big difference. The top of the tetrahedron is not a bond in this case. It is a pair of non-bonding electrons. Thus, the top “leg” of the tetrahedron is missing, deforming the tetrahedron. The resulting shape looks a lot like a pyramid, with the H's as the pyramid's base and the N as its apex. Thus, we say that NH₃ has a pyramidal (pih ram' uh dul) shape. This pyramidal shape is easiest to understand by looking at the photograph, where the blue sphere represents the nitrogen atom and the yellow spheres represent hydrogen atoms. Once again, the wooden sticks represent covalent bonds.

In a tetrahedron, the legs are 109° apart. In this shape, the legs are slightly closer together because the non-bonding electron pair tends to repel the bonds just a little more than the bonds repel one another. As a result, the bonds stay a little farther away from the non-bonding electron pair and a little closer to one another. Thus, the bond angle in this case is about 107°.
As you might imagine, we aren't done looking at the different shapes that a molecule can have. Next, we turn our attention to water:

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

According to VSEPR theory, we must look at the electrons surrounding the central atom and determine what shape will allow the electron groups to stay as far apart from each other as possible. Once again, there are four groups of electrons around the central oxygen atom. Two of the groups are chemical bonds, while the other two are non-bonding electron pairs. Since a tetrahedron allows the four electron groups to stay as far apart from each other as possible, the basic shape of this molecule is also a tetrahedron. Once again, however, since two of the groups are non-bonding electron pairs, the tetrahedron is deformed.

![Figure 9.3: How H₂O Gets Its Bent Shape](image)

It is easier to understand water's molecular shape if you first rotate the Lewis structure. When that is done, we once again put each group of electrons on a leg of the tetrahedron. In the second drawing above, the H's are each on a leg that is in the plane of the paper. One of the non-bonding electron pairs is on the tetrahedron leg that juts out in front of the paper, while the other is on the leg that sticks out behind the paper. Since these two non-bonding electron pairs are in the molecule, the tetrahedron looks like it is missing those two legs. What is left, then, is a shape that looks bent. As I mentioned with NH₃, non-bonding electron pairs tend to repel more than bonding electron pairs. As a result, the two bonds in the water molecule are closer together than they would be in a tetrahedron or a pyramidal shape, so the bond angle is about 105°.
The three shapes we have considered so far are all built on the framework of a tetrahedron. The pyramidal shape is just a tetrahedron with one leg removed, while the bent shape is a tetrahedron with two legs removed. This tetrahedron framework exists because in the three molecules we have considered so far, the central atom has four groups of electrons around it. However, four groups of electrons around the central atom is not the only possibility in a Lewis structure. As a result, we have more shapes to consider.

Let's look at a more complicated Lewis structure. In the previous module, you constructed the Lewis structure for CH$_2$O:

![Lewis structure for CH$_2$O]

Notice that in this molecule, there are only three groups of electrons around the central carbon atom. There are two single bonds linking the H's to the C. That's two groups of electrons. There is also one double bond linking the O to the C. Although a double bond represents four electrons, it is still only one group of electrons. After all, a double bond is really only one bond; it is simply twice as strong as a single bond. Thus, in this molecule, there are only three groups of electrons surrounding the central carbon: two single bonds and one double bond. What happens in a situation like this?

![FIGURE 9.4](image)

The Trigonal Shape of CH$_2$O

Now remember, the guiding principle behind the VSEPR theory is that the groups of electrons try to get as far apart from one another as possible. Well, the farthest that three groups of electrons can get from each other is 120°. Thus, the shape of this molecule is triangular, with the hydrogen and oxygen atoms each occupying a vertex of the triangle. We'll call this a trigonal (trg' uh nul) shape. Since all of the atoms lie in the same plane, it is sometimes called a “trigonal planar” shape. The picture shows a
model of this geometry, with the black sphere representing carbon, the red sphere representing oxygen, and the yellow spheres representing hydrogen atoms. Notice that the model uses two springs to represent the double bond that exists between oxygen and carbon. You will see that again in the next figure.

Believe it or not, there is really only one more molecular shape that we are going to consider. There are, in fact, several more shapes that molecules can take, but the ones we are covering here are the most popular. If you take another year of chemistry, you will learn additional molecular shapes then. For right now, we have only one more shape to consider: linear. It turns out that there are two ways for a molecule to become linear. The first should be pretty obvious. If a molecule consists of only two atoms, the molecule must be linear. After all, with only two points, there is no other shape possible than a line. Thus, a molecule like F₂:

![F₂ molecule](image)

must be linear. However, there is another way that a molecule might attain a linear shape. Figure 9.5 illustrates how this can happen.

![Figure 9.5: Carbon Dioxide is Also a Linear Molecule](image)

In this molecule, there are only two groups of electrons around the central atom. Even though it looks like there are four bonds around the carbon, there are not. As I said before, a double bond is really only one bond; it is simply twice as strong as a single bond. Thus, even though there are four dashes around the central carbon, there are really only two bonds. That means there are two groups of electrons. Two groups will get as far away from each other as possible when they form a straight line. Thus, this is a linear shape, with a bond angle of 180°.

As I said before, if you are having trouble visualizing all of this, don't worry. I will give you a set of rules that will help you determine these molecular shapes. Thus, you need not be able to visualize this
in order to solve the problems. You will be better off, however if you are able to visualize the molecules. It will help you as you go to the last section of this module. In addition, much of the chemistry of life is based on molecular shape. Thus, if you wish to pursue chemistry as it applies to living creatures (i.e., organic chemistry, biochemistry, or pharmaceutical chemistry), you will need to be able to “see” the shapes of molecules in your head.

To determine the shape of a molecule:

**Determine the Lewis structure of the molecule.**

If there are only two atoms in the molecule or if there are only two groups of electrons around the central atom, then the molecule must be linear and have a bond angle of 180°.

If there are three groups of electrons around the central atom, then the shape is trigonal with a bond angle of 120°.

If none of the above-listed conditions exists, then there must be four groups of electrons around the central atom, so the basic shape of the molecule is a tetrahedron.

For every non-bonding pair of electrons, you must take a “leg” of the tetrahedron away. Thus, if there are no non-bonding electrons around the central atom, the shape is tetrahedral with a bond angle of 109°.

If the central atom has one pair of non-bonding electrons, then you have a tetrahedron with one leg removed. This results in a pyramidal shape, with a bond angle of about 107°.

If two non-bonding electron pairs surround the central atom, then two legs of the tetrahedron are missing. This ends up giving the molecule a bent shape with a bond angle of approximately 105°.