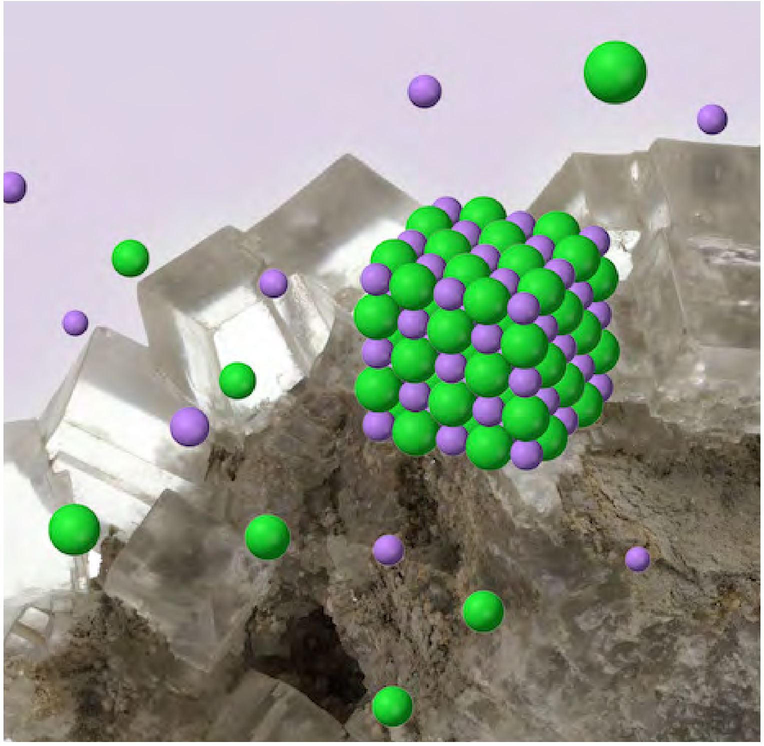
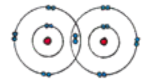


Chapter 6

# How Atoms Bond

THE MAIN IDEA



Atoms bond by exchanging or sharing electrons


6.1 Electron-Dot Structures
6.2 Ion Formation
6.3 Ionic Bonds
6.4 Metallic Bonds
6.5 Covalent Bonds
6.6 Molecular Shape
6.7 Polar Covalent Bonds
6.8 Molecular Polarity

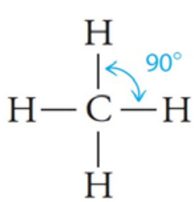

## 6.6 Molecular Shape

Molecules are 3-dimensional entities and therefore best depicted in three dimensions. We can translate the 2-dimensional electron-dot structure representing a molecule into a more accurate 3-dimensional rendering by using the model known as **valence-shell electron-pair repulsion**, also called VSEPR (pronounced ves-per). According to this model, electron pairs in a valence shell arrange themselves to get as far away as possible from all other electron pairs in the shell. This includes nonbonding pairs and any bonding pairs or groups of bonding pairs held together in a double or triple bond. This behavior is the result of simple electrostatic repulsions between the electron pairs.

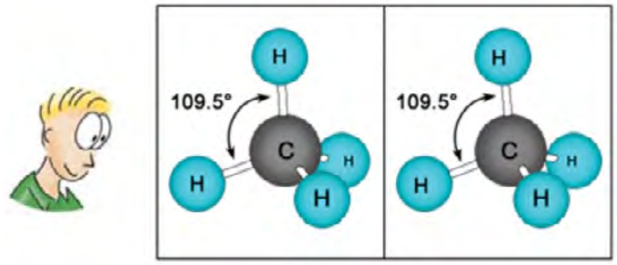
READING CHECK

What do electron pairs, either bonding or nonbonding, tend to do?

The 2-dimensional electron-dot structure for methane, $CH_4$,




In this structure, the bonding electron pairs (shown as straight lines representing two electrons each) are set 90° apart because that is the farthest apart they can be shown in two dimensions. When we extend the view to three dimensions, however, we can create a more accurate rendering, in which the four bonding pairs are 109.5° apart:

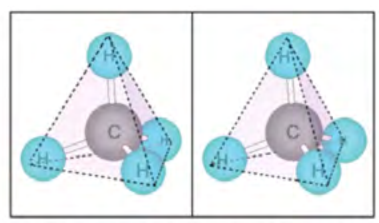



Stereo image

These two renderings of methane are *stereo images*—you can see them in three dimensions by looking at them cross-eyed so that they appear to overlap. To get the images to overlap, you can also try touching your nose to the page and then slowly pulling the book away from your face. If neither of these techniques works, try building these structures with gumdrops and toothpicks.

You can think of this 3-dimensional structure as follows: the central carbon atom has one hydrogen atom sticking out of its top and is supported on a tripod whose legs are formed by the three lower C–H bonds.

Draw the four triangles defined by the hydrogen atoms in the above stereo image of $CH_4$ (one triangle being the base, the other three being the three upright faces) and you'll see that the shape of the methane molecule is a pyramid that has a triangular base supporting three other triangles that meet at the pyramid's apex. In geometry, a pyramid that has a triangular base is given the special name *tetrahedron*, and so chemists say that the methane molecule is tetrahedral:



Stereo image of tetrahedral methane molecule

The VSEPR model allows us to use electron-dot structures to predict the 3-dimensional geometry of simple molecules. This geometry is determined by considering the number of atoms or nonbonding electron pairs surrounding the centrally located atom. Chemists refer to any atom or nonbonding electron pair surrounding a central atom as a **substituent**. They use this fancy term the same way people commonly use the word appendage

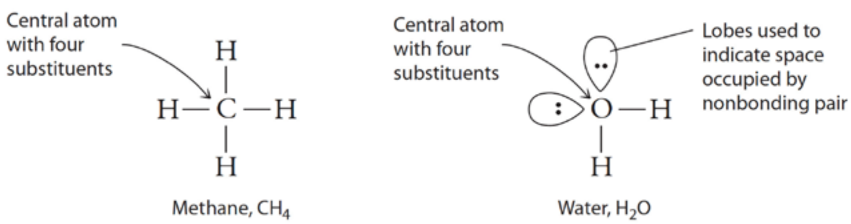
CONCEPT **CHECK**

Why are the two oxygen atoms in carbon dioxide, $CO_2$, spaced 180° apart?

**CHECK YOUR ANSWER**

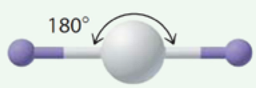
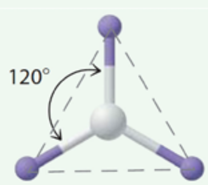
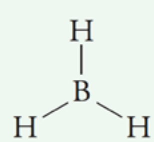
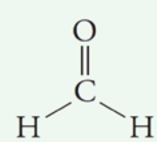
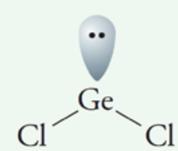
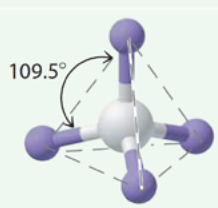
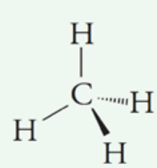
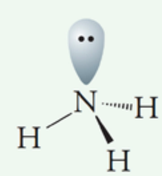
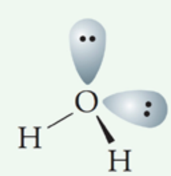
If the two oxygen atoms were on the same side of the carbon atom, the bonding electrons would be relatively close to each other. Because electron pairs repel one another, this is not a stable situation. Instead, the oxygen atoms position themselves so that the bonding pairs of the two double bonds are as far from each other as possible, which is on opposite sides of the carbon atom, 180° apart, as shown in Table 6.2.

to refer to either an arm or a leg. Thus, to simplify our discussion, we define a substituent as any atom or nonbonding pair of electrons surrounding a centrally located atom. For example, the carbon of a methane molecule has four substituents—the four hydrogen atoms. The oxygen atom of a water molecule also has four substituents—two hydrogen atoms and two nonbonding pairs of electrons:




As shown in **Table 6.2**, when a central atom has only two substituents, the geometry of the molecule is linear, meaning that a single straight line may be drawn passing through both substituents and the central atom. Three substituents arrange themselves in a triangle—the plane of which passes through the central atom—so this geometry is called *triangular planar*. Four substituents form a tetrahedron, as already discussed. Why these geometries? Simply put, these are the geometries that allow the maximum distance between substituents.

**TABLE 6.2** Molecular Geometries

| NUMBER OF SUBSTITUENTS | 3-DIMENSIONAL GEOMETRY | EXAMPLES | | |
|---|---|---|---|---|
| 2 |   Linear | H—Be—H $BeH_2$ | O=C=O $CO_2$ | H—C≡N HCN |
| 3 |   Triangular planar |  $BH_3$ |  $H_2CO$ |  $GeCl_2$ |
| 4 |   Tetrahedral |  $CH_4$ |  $NH_3$ |  $H_2O$ |

## Molecular Shape Is Defined by the Substituent Atoms

When chemists talk about the *shape of a molecule*, they are talking about the relative positions of the atoms of the molecule. How atoms position themselves is spelled out by VSEPR. But from VSEPR, we see that the nonbonding electrons (lone pairs) also affect how atoms within a molecule get positioned.

Figuring out the shape of a molecule is a two-step process. The first step is to use VSEPR to position all substituents, both atoms and nonbonding pairs, around a central atom. The second step is to ignore all nonbonding pairs and decide what 3-dimensional shape the atoms form. Let's work through a few examples from Table 6.2 to see what all this means.

In any molecule in which there are no nonbonding pairs around the central atom, the molecular shape is the same as the VSEPR geometry. Thus, to use the examples from Table 6.2, all the molecules of the first row ($BeH_2$, $CO_2$, HCN) have a linear shape. Two molecules of the second row ($BH_3$ and $H_2CO$) have a triangular planar shape, and the first molecule of the third row ($CH_4$) has a tetrahedral shape.

Now let's look at molecules that have nonbonding pairs, beginning with germanium chloride, $GeCl_2$, and its one nonbonding pair. The VSEPR geometry is triangular planar, but to get the shape of the molecule, we focus only on the atoms. This reveals the germanium and two chlorine atoms held together at an angle—a shape known as *bent*. Similarly, focusing only on the atoms, a water molecule is also seen to have a bent shape. Now you know why water molecule are always depicted with the two hydrogen atoms close to each other, like a set of mouse ears, rather than as far apart as possible on opposite sides of the oxygen atom—two nonbonding pairs are pushing them into this orientation.

Focusing only on the atoms of the ammonia molecule, $NH_3$, in Table 6.2 means the shape is not tetrahedral, because in a tetrahedron, all four corners must be equally distant from the central atom. Ammonia's shape, as shown in **Figure 6.26**, is typically described as *triangular pyramidal*.

The rules for determining the molecular shape of a small molecule are summarized in **Figure 6.27**. The first step is to count the electron pairs surrounding the central atom including both bonding and nonbonding. This determines the geometry. You then count the number of surrounding atoms and this will give you the molecular shape.

**FOR YOUR INFORMATION**

"Dry cleaning" is the process of washing clothes without water. The most common dry cleaning solvent is perchloroethylene, $C_2Cl_4$. (Can you deduce its chemical structure?) The advantage of dry cleaning is that dirt, grime, and stains are typically more soluble in the dry cleaning solvent, which is also less harsh on the clothing and can do a full load in under 10 minutes. After a washing cycle, the solvent is centrifuged out of the machine, filtered, distilled, and recycled for the next load. Clothes come out of the machine already dried and ready for folding. Perchloroethylene, also known as perc, is mildly carcinogenic and can cause dizziness in those who work with it. An up-and-coming alternative to perc is carbon dioxide, $CO_2$, which at super high pressures forms an unusual liquid-like and gas-like medium, called supercritical fluid, that has remarkable cleaning properties.

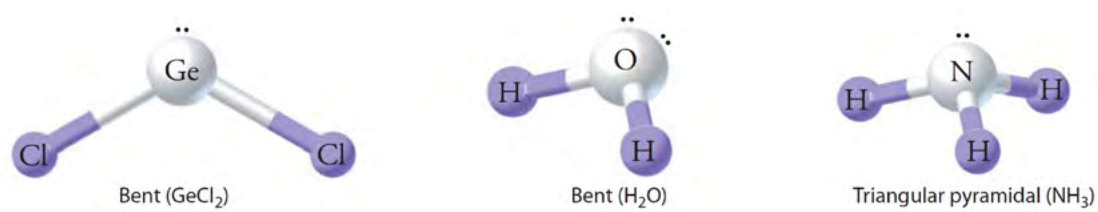
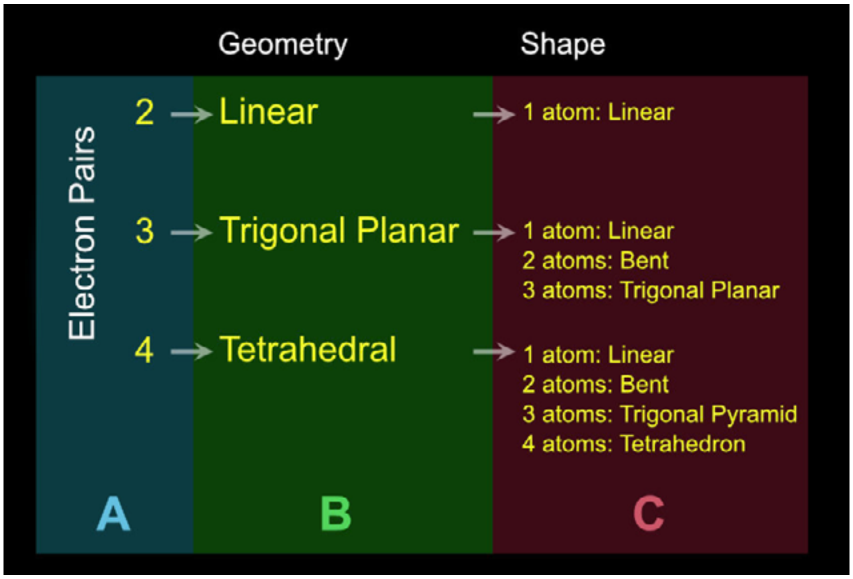



**Figure 6.26**

The shapes of molecules from Table 6.2.

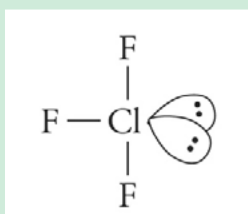



**< Figure 6.27**

A flow chart for determining the shape of a small molecule.

CONCEPT **CHECK**

What is the shape of a chlorine trifluoride molecule, $ClF_3$?




**CHECK YOUR ANSWER**

Describe what you see as you focus only on the atoms (ignoring the nonbonding pairs). For chlorine trifluoride, the shape has all four atoms in the same plane. They form a triangle having a fluorine atom at each corner and the chlorine atom sitting at the midpoint on one side. Call it what you like—most chemists simply call it T-shaped. If you're curious how chlorine is able to form three covalent bonds, you should consider taking a follow-up course in general chemistry.