

**No theory ever solves all the puzzles with which it is confronted at a given time; nor are the solutions already achieved often perfect.**

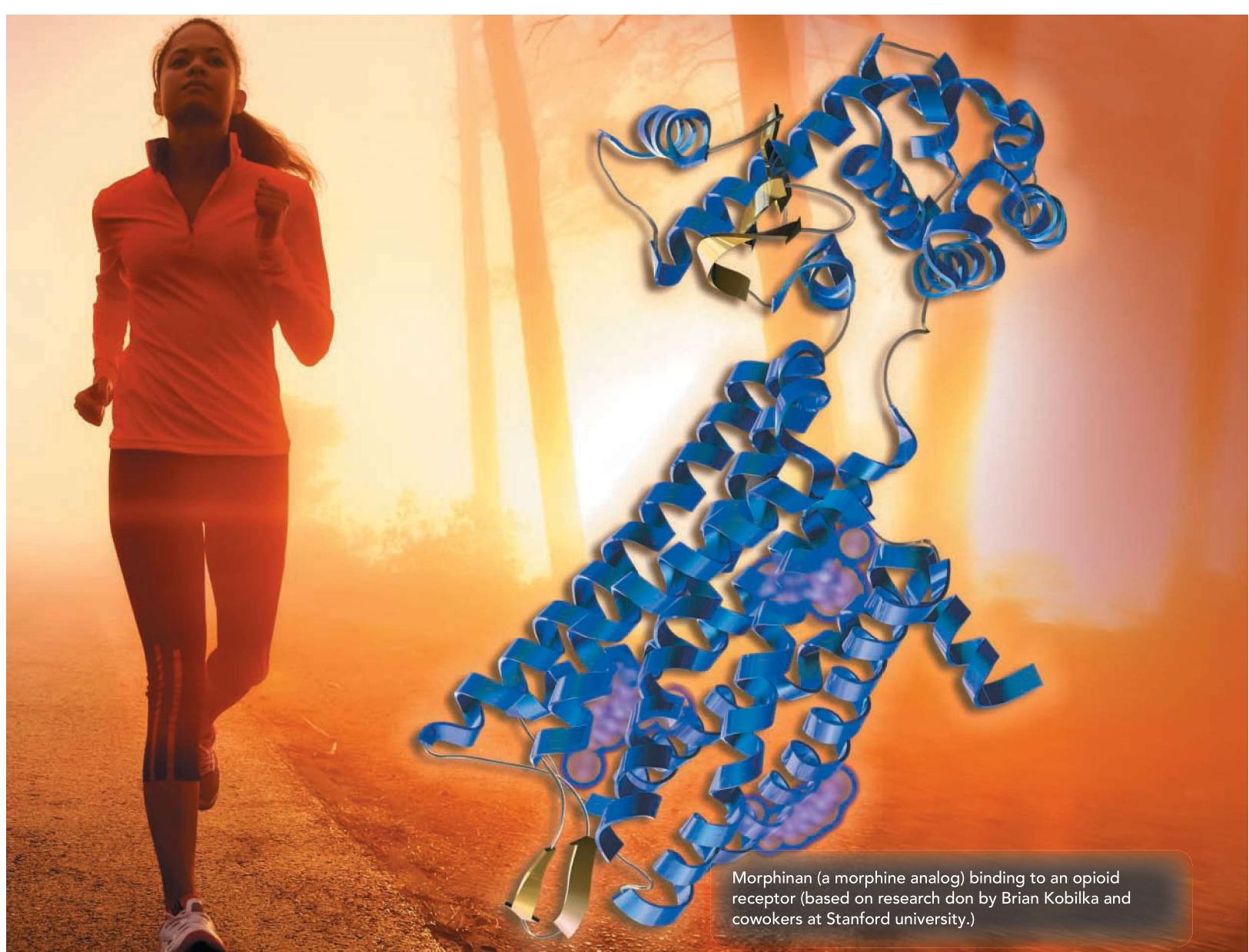
—THOMAS KUHN (1922–1996)

CHAPTER

# 11

## Chemical Bonding II: Molecular Shapes, Valence Bond Theory, and Molecular Orbital Theory

In Chapter 10, we examined a simple model for chemical bonding called the Lewis model. We saw how this model helps us to explain and predict the combinations of atoms that form stable molecules. When we combine the Lewis model with the idea that valence electron groups repel one another—the basis of an approach known as valence shell electron pair repulsion theory—we can predict the general shape of a molecule from its Lewis structure. We address molecular shape and its importance in the first part of this chapter. We then move on to explore two additional bonding theories—called valence bond theory and molecular orbital theory—that are progressively more sophisticated, but at the cost of being more complex, than the Lewis model. As you work through this chapter, our second on chemical bonding, keep in mind the importance of this topic. In our universe, atoms join together to form molecules, and that makes many things possible, including our own existence.



Morphinan (a morphine analog) binding to an opioid receptor (based on research done by Brian Kobilka and coworkers at Stanford university.)

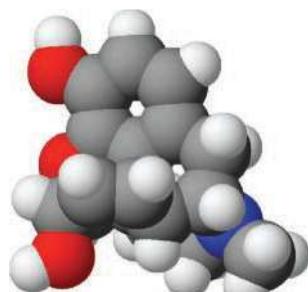
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### **11.1 Morphine: A Molecular Imposter**

Morphine—a drug named after Morpheus, the Greek god of dreams—is the silver bullet in the human arsenal against pain. Morphine is often prescribed after surgery to aid recovery or to alleviate the severe pain associated with illnesses such as cancer. It is also prescribed to patients who have chronic pain toward the end of their lives. For these patients, prescribed morphine provides relief from an otherwise tortuous



Morphine

Proteins are among the most important biological molecules and serve many functions in living organisms.

### WATCH NOW!

#### KEY CONCEPT VIDEO 11.2 VSEPR Theory

existence. Morphine is a natural product derived from the sap of the opium poppy. The effects of opium sap have been known for thousands of years, but morphine itself was not isolated from opium until the early 1800s. Morphine acts by binding to receptors (called opioid receptors) that exist within nerve cells. When morphine binds to an opioid receptor, the transmission of nerve signals is altered, resulting in sedation, less pain, and feelings of euphoria and tranquility.

Why do humans (and other mammals) have receptors within their nerve cells that bind to molecules derived from the sap of a plant? Researchers long suspected that these receptors must also bind other molecules as well; otherwise, why would the receptors exist? In the 1970s, researchers discovered some of these molecules, known as endorphins (short for **endogenous morphine**; endogenous means produced within the organism). Endorphins are the body's natural painkillers. Our bodies naturally produce endorphins during periods of pain such as childbirth or intense exercise. Endorphins are at least partially responsible for the so-called runner's high, a feeling of well-being that often follows an athlete's intense workout.

Morphine binds to opioid receptors because it fits into a special pocket (called the active site) on the opioid receptor protein (just as a key fits into a lock) that normally binds endorphins. Certain parts of the morphine molecule have a similar enough shape to endorphins that they fit the lock (even though they are not the original key). In other words, morphine is a *molecular imposter*, mimicking the action of endorphins because of similarities in shape.

The lock-and-key fit between the active site of a protein and a particular molecule is important not only to our perception of pain, but to many other biological functions as well. Immune response, the sense of smell, the sense of taste, and many types of drug actions depend on shape-specific interactions between molecules and proteins. In fact, our ability to determine the shapes of key biological molecules is largely responsible for the revolution that has occurred in biology over the last 50 years.

In this chapter, we look at ways to predict and account for the shapes of molecules. The molecules we examine are much smaller than the protein molecules we just discussed, but the same principles apply to both. The simple model we examine to account for molecular shape is *valence shell electron pair repulsion* theory, and in this chapter, we use it in conjunction with the Lewis model to make important predictions about the shapes of molecules. We then proceed to explore two additional bonding theories: *valence bond theory* and *molecular orbital theory*. They predict and account for molecular shape as well as other properties of molecules.

## 11.2 VSEPR Theory: The Five Basic Shapes

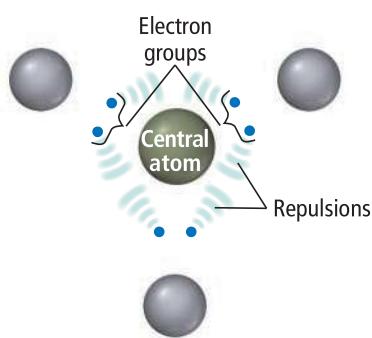
**Valence shell electron pair repulsion (VSEPR) theory** is based on the simple idea that **electron groups**—which we define as lone pairs, single bonds, multiple bonds, and even single electrons—repel one another through coulombic forces. The electron groups are also attracted to the nucleus (otherwise the molecule would fall apart), but VSEPR theory focuses on the repulsions.

According to VSEPR theory, the repulsions between electron groups on *interior atoms* of a molecule determine the geometry of the molecule (Figure 11.1). The preferred geometry of a molecule is the one in which the electron groups have maximum separation (and therefore minimum repulsion energy). For molecules having just one interior atom (the central atom), molecular geometry depends on two factors:

- the number of electron groups around the central atom;
- how many of those electron groups are bonding groups and how many are lone pairs.

We first look at the molecular geometries associated with having two to six electron bonding groups (single or multiple bonds) around the central atom. The resulting geometries constitute the five basic shapes of molecules. We then consider how these basic shapes are modified if one or more of the electron groups are lone pairs.

**▲ FIGURE 11.1** Repulsion between Electron Groups The basic idea of VSEPR theory is that repulsions between electron groups determine molecular geometry.



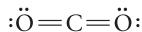
## Two Electron Groups: Linear Geometry

Consider the Lewis structure of  $\text{BeCl}_2$ , which has two electron groups (two single bonds) about the central atom:



According to VSEPR theory, the geometry of  $\text{BeCl}_2$  is determined by the repulsion between these two electron groups, which maximize their separation by assuming a  $180^\circ$  bond angle or a **linear geometry**. Experimental measurements of the geometry of  $\text{BeCl}_2$  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  $\text{CO}_2$ , which has two electron groups (the double bonds) around the central carbon atom:



According to VSEPR theory, the two double bonds repel each other (just as the two single bonds in  $\text{BeCl}_2$  repel each other), resulting in a linear geometry for  $\text{CO}_2$ . Experimental observations confirm that  $\text{CO}_2$  is indeed a linear molecule.

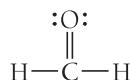
## Three Electron Groups: Trigonal Planar Geometry

The Lewis structure of  $\text{BF}_3$  (another molecule with an incomplete octet) has three electron groups around the central atom:



These three electron groups can maximize their separation by assuming  $120^\circ$  bond angles in a plane—a **trigonal planar geometry**. Experimental observations of the structure of  $\text{BF}_3$  again confirm the predictions of VSEPR theory.

Another molecule with three electron groups, formaldehyde ( $\text{HCHO}$ ), has one double bond and two single bonds around the central atom:



Because formaldehyde has three electron groups around the central atom, we initially predict that the bond angles should also be  $120^\circ$ . However, experimental observations show that the HCO bond angles are  $121.9^\circ$  and the HCH bond angle is  $116.2^\circ$ . These bond angles are close to the idealized  $120^\circ$  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.

## ELECTRON GROUPS AND MOLECULAR GEOMETRY

A central atom in a three-atom molecule forms two double bonds (and has no lone pairs). What is the geometry of the molecule?

- (a) trigonal planar      (b) linear
- (c) Not enough information is given to determine the geometry of the molecule.  
To solve the problem, it is necessary to know how many electron pairs are on the other two atoms.

Beryllium often forms incomplete octets, as it does in this structure.

### Linear geometry

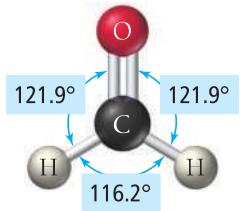
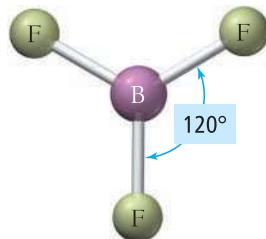


A double bond counts as one electron group.

### Linear geometry



### Trigonal planar geometry



**11.1**

**Cc**

Conceptual Connection

ANSWER NOW!



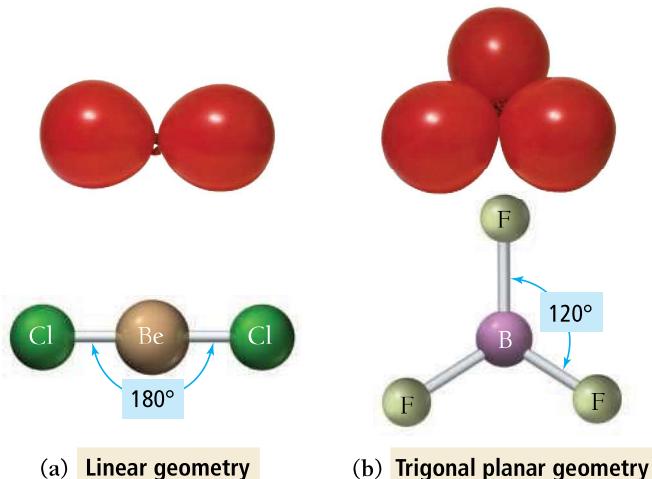
## Four Electron Groups: Tetrahedral Geometry

VSEPR geometries for molecules with two or three electron groups around the central atom are two-dimensional and easy to represent on paper. Molecules with four or more electron groups around a central atom, however, have three-dimensional geometries that are more difficult to imagine and draw. Fortunately, we can understand these basic shapes by analogy to balloons tied together.

**► FIGURE 11.2** Representing Electron Geometry with Balloons

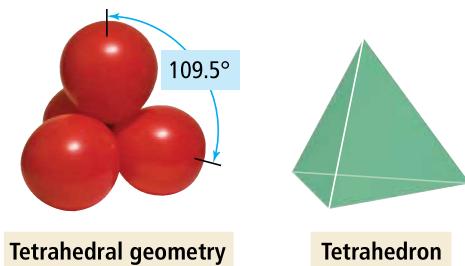
**(a)** The bulkiness of balloons causes them to assume a linear arrangement when two of them are tied together. Similarly, the repulsion between two electron groups produces a linear geometry.

**(b)** Like three balloons tied together, three electron groups adopt a trigonal planar geometry.

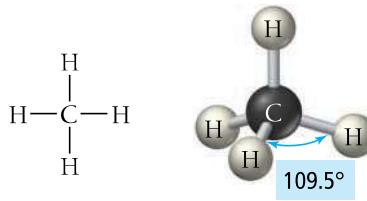


In this analogy, each electron group around a central atom is like a balloon tied to a central point. The bulkiness of the balloons causes them to spread out as much as possible, much as the repulsion between electron groups causes them to position themselves as far apart as possible.

For example, if you tie two balloons together, they assume a roughly linear arrangement, as shown in Figure 11.2(a)▲, analogous to the linear geometry of  $\text{BeCl}_2$  that we just examined. Notice 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 11.2(b)▲, much like the  $\text{BF}_3$  molecule. If you tie *four* balloons together, however, they assume a three-dimensional **tetrahedral geometry** with  $109.5^\circ$  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:



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



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  $\text{CH}_4$  on paper, it may seem that the molecule should be square planar, with bond angles of  $90^\circ$ . However, in three dimensions, the electron groups can get farther away from each other by forming the tetrahedral geometry, as illustrated by our balloon analogy.

## MOLECULAR GEOMETRY

What is the geometry of the HCN molecule? The Lewis structure of HCN is H—C≡N:

- (a) linear
- (b) trigonal planar
- (c) tetrahedral

11.2

Cc

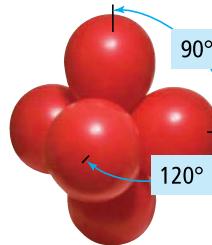
Conceptual Connection

ANSWER NOW!



### Five Electron Groups: Trigonal Bipyramidal Geometry

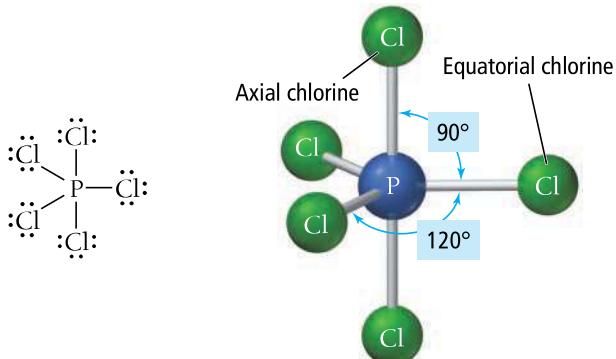
Five electron groups around a central atom assume a **trigonal bipyramidal geometry**, like five balloons tied together. In this structure, three of the groups lie in a single plane, as in the trigonal planar configuration, whereas the other two are positioned above and below this plane. The angles in the trigonal bipyramidal structure are not all the same. The angles between the *equatorial positions* (the three bonds in the trigonal plane) are  $120^\circ$ , whereas the angle between the *axial positions* (the two bonds on either side of the trigonal plane) and the trigonal plane is  $90^\circ$ . PCl<sub>5</sub> is an example of a molecule with five electron groups around the central atom:



Trigonal bipyramidal geometry



Trigonal bipyramidal

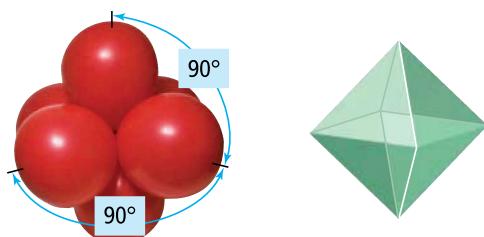


Trigonal bipyramidal geometry

The three equatorial chlorine atoms are separated by  $120^\circ$  bond angles, and the two axial chlorine atoms are separated from the equatorial atoms by  $90^\circ$  bond angles.

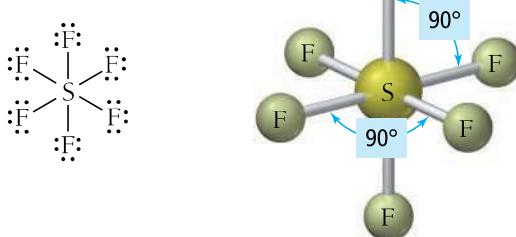
### Six Electron Groups: Octahedral Geometry

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 the sixth below it. The angles in this geometry are all  $90^\circ$ . SF<sub>6</sub> is a molecule with six electron groups around the central atom:



Octahedral geometry

Octahedron



Octahedral geometry

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

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 11.1

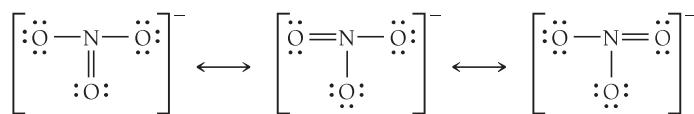
**EXAMPLE 11.1** VSEPR Theory and the Basic ShapesDetermine the molecular geometry of  $\text{NO}_3^-$ .**SOLUTION**

Determine the molecular geometry of  $\text{NO}_3^-$  by counting the number of electron groups around the central atom (N). Begin by drawing a Lewis structure for  $\text{NO}_3^-$ .

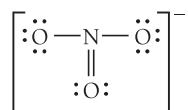
Use any one of the resonance structures to determine the number of electron groups around the central atom.

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

$\text{NO}_3^-$  has  $5 + 3(6) + 1 = 24$  valence electrons. The Lewis structure has three resonance structures:

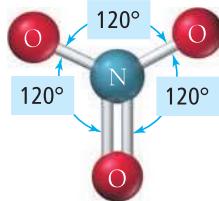


The hybrid structure is intermediate between these three and has three equivalent bonds.



The nitrogen atom has three electron groups: two single bonds and one double bond.

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



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

**FOR PRACTICE 11.1** Determine the molecular geometry of  $\text{CCl}_4$ .

**WATCH NOW!****KEY CONCEPT VIDEO 11.3**

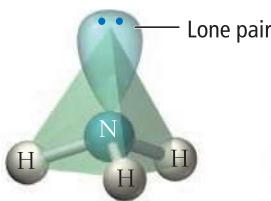
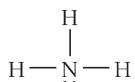
VSEPR Theory: The Effect of Lone Pairs

**11.3****VSEPR Theory: The Effect of Lone Pairs**

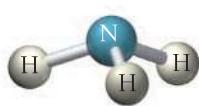
Each of the examples we have just seen has only bonding electron groups around the central atom. What happens in molecules that have lone pairs around the central atom as well? The lone pairs also repel other electron groups, as we see in the examples that follow.

**Four Electron Groups with Lone Pairs**

Consider the Lewis structure of ammonia:



Electron geometry:  
tetrahedral

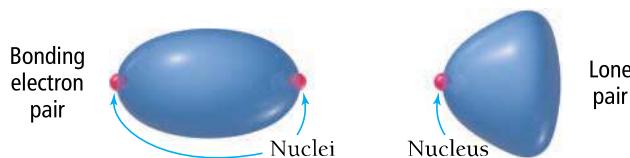


Molecular geometry:  
trigonal pyramidal

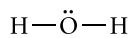
The central nitrogen atom has four electron groups (one lone pair and three bonding pairs) that repel one another. If we do not distinguish between bonding electron groups and lone pairs, we find that the **electron geometry**—the geometrical arrangement of the *electron groups*—is still tetrahedral, as we expect for four electron groups. However, the **molecular geometry**—the geometrical arrangement of the atoms—is **trigonal pyramidal geometry**, as shown here.

Notice that although the electron geometry and the molecular geometry are different, *the electron geometry is relevant to the molecular geometry*. The lone pair exerts its influence on the bonding pairs.

As we noted previously, different kinds of electron groups generally result in different amounts of repulsion. Lone pair electrons typically exert slightly greater repulsions than bonding electrons. If all four electron groups in  $\text{NH}_3$  exerted equal repulsions on one another, the bond angles in the molecule would all be the ideal tetrahedral angle,  $109.5^\circ$ . However, the actual angle between N—H bonds in ammonia is slightly smaller,  $107^\circ$ . A lone electron pair is more spread out in space than a bonding electron pair because a lone pair is attracted to only one nucleus while a bonding pair is attracted to two (Figure 11.3▼). The lone pair occupies more of the angular space around a nucleus, exerting a greater repulsive force on neighboring electrons and compressing the N—H bond angles.



A water molecule's Lewis structure is:



Because water has four electron groups (two bonding pairs and two lone pairs), its *electron geometry* is also tetrahedral, but its *molecular geometry* is **bent geometry**, as shown here.

As in  $\text{NH}_3$ , the bond angles in  $\text{H}_2\text{O}$  are smaller ( $104.5^\circ$ ) than the ideal tetrahedral bond angles because of the greater repulsion exerted by the lone pair electrons. The bond angle in  $\text{H}_2\text{O}$  is even smaller than that in  $\text{NH}_3$  because  $\text{H}_2\text{O}$  has two lone pairs of electrons on the central oxygen atom. These lone pairs compress the  $\text{H}_2\text{O}$  bond angle to a greater extent than in  $\text{NH}_3$ .

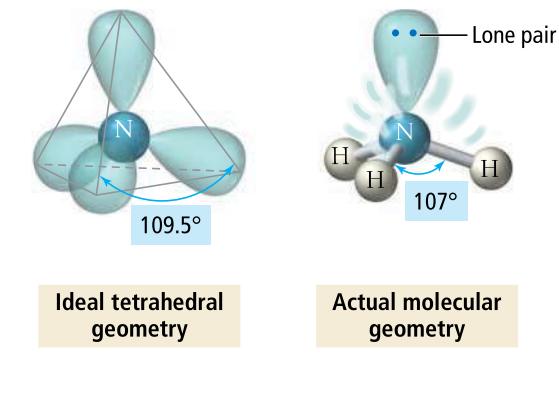
In general, electron group repulsions compare as follows:

Lone pair–lone pair > Lone pair–bonding pair > Bonding pair–bonding pair

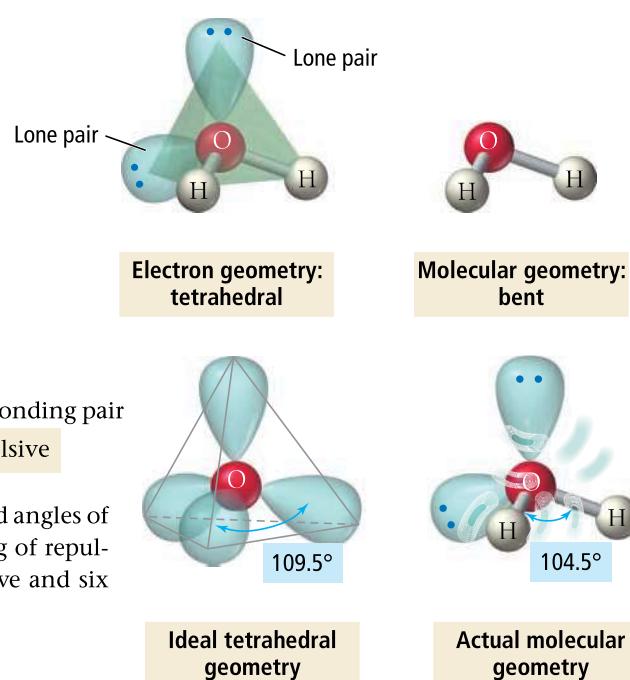
Most repulsive

Least repulsive

We see the effects of this ordering in the progressively smaller bond angles of  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ , shown in Figure 11.4▼. The relative ordering of repulsions also helps to determine the geometry of molecules with five and six electron groups when one or more of those groups are lone pairs.

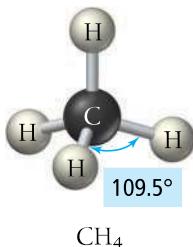


◀ **FIGURE 11.3 Lone Pair versus Bonding Electron Pairs** A lone electron pair occupies more space than a bonding pair.

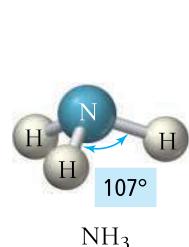


### Effect of Lone Pairs on Molecular Geometry

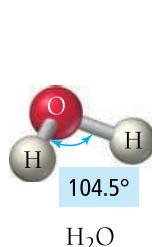
No lone pairs



One lone pair



Two lone pairs



◀ **FIGURE 11.4 The Effect of Lone Pairs on Molecular Geometry** The bond angles get progressively smaller as the number of lone pairs on the central atom increases from zero in  $\text{CH}_4$  to one in  $\text{NH}_3$  to two in  $\text{H}_2\text{O}$ .

ANSWER NOW!



### 11.3 Cc Conceptual Connection

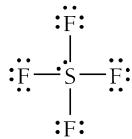
## LONE PAIR ELECTRONS AND MOLECULAR GEOMETRY I

What is the molecular geometry of a molecule whose central atom has three bonding groups and one lone pair?

- (a) linear    (b) trigonal planar    (c) tetrahedral    (d) trigonal pyramidal

### Five Electron Groups with Lone Pairs

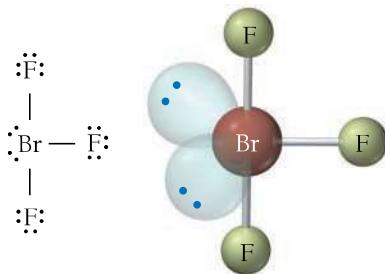
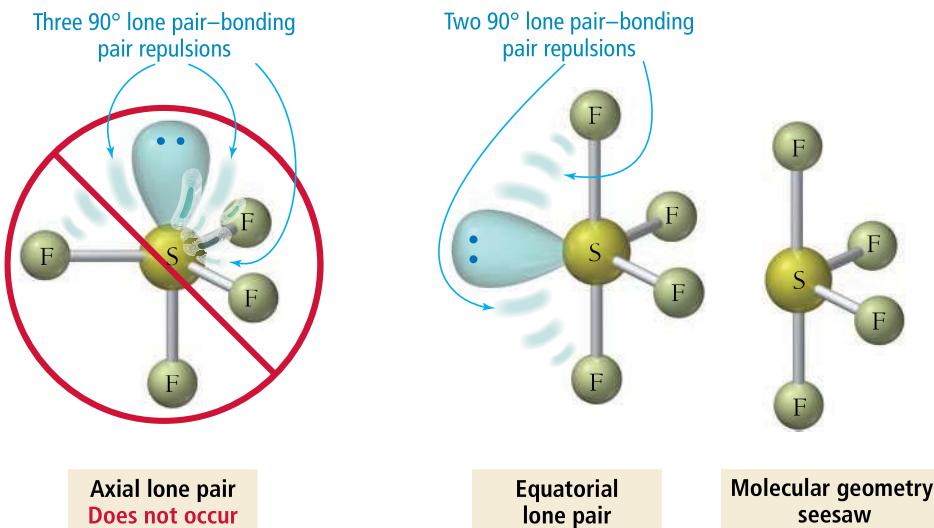
Consider the Lewis structure of  $\text{SF}_4$ :



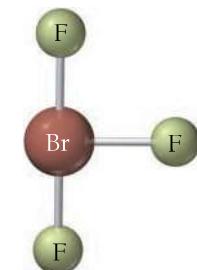
The central sulfur atom has five electron groups (one lone pair and four bonding pairs). The *electron geometry*, due to the five electron groups, is trigonal bipyramidal.

To determine the molecular geometry for sulfur tetrafluoride, notice that the lone pair could occupy either an equatorial position or an axial position within the trigonal bipyramidal electron geometry. Which position is more favorable? To answer this question, recall that, as we have just seen, lone pair–bonding pair repulsions are greater than bonding pair–bonding pair repulsions. Therefore, the lone pair occupies the position that minimizes its interaction with the bonding pairs. If the lone pair were in an axial position, it would have three  $90^\circ$  interactions with bonding pairs. In an equatorial position, however, it has only two  $90^\circ$  interactions. Consequently, the lone pair occupies an equatorial position. The resulting molecular geometry is called **seesaw geometry** because it resembles a seesaw (or teeter-totter).

The seesaw molecular geometry is sometimes called an *irregular tetrahedron*.



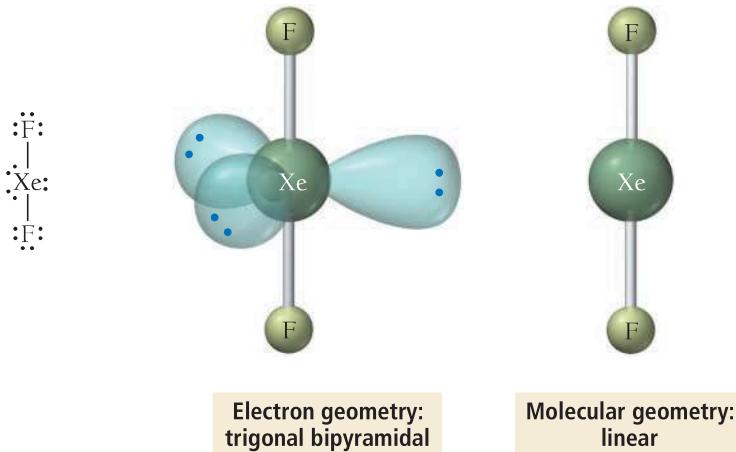
Electron geometry:  
trigonal bipyramidal



Molecular geometry:  
T-shaped

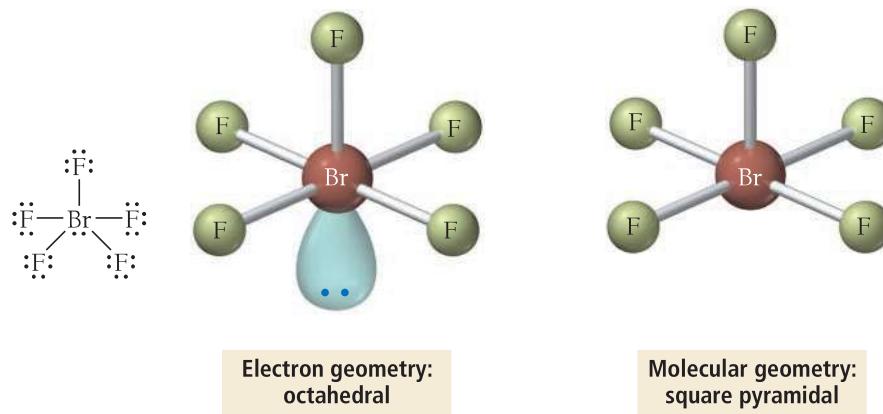
When two of the five electron groups around the central atom are lone pairs, as in  $\text{BrF}_3$ , the lone pairs occupy two of the three equatorial positions—again minimizing  $90^\circ$  interactions with bonding pairs and also avoiding a lone pair–lone pair  $90^\circ$  repulsion. The resulting molecular geometry is **T-shaped**.

When three of the five electron groups around the central atom are lone pairs, as in  $\text{XeF}_2$ , the lone pairs occupy all three of the equatorial positions, and the resulting molecular geometry is linear.

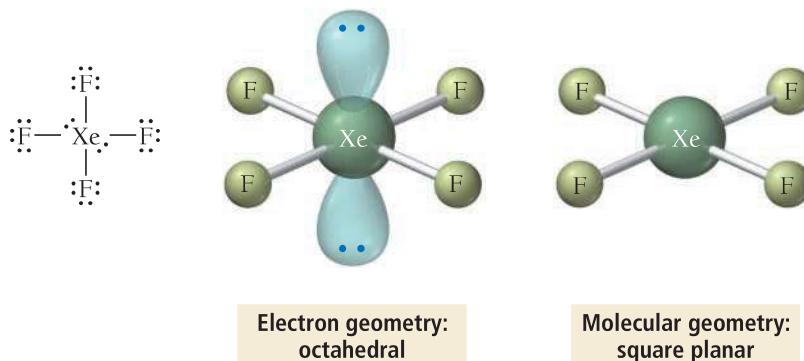


## Six Electron Groups with Lone Pairs

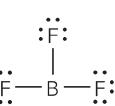
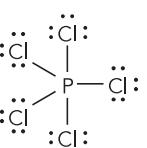
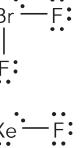
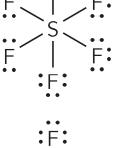
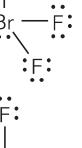
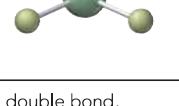
Consider the Lewis structure of  $\text{BrF}_5$  shown here. The central bromine atom has six electron groups (one lone pair and five bonding pairs). The electron geometry, due to the six electron groups, is octahedral. Since all six positions in the octahedral geometry are equivalent, the lone pair can be situated in any one of these positions. The resulting molecular geometry is **square pyramidal geometry**.



When two of the six electron groups around the central atom are lone pairs, as in  $\text{XeF}_4$ , the lone pairs occupy positions across from one another (to minimize lone pair-lone pair repulsions), and the resulting molecular geometry is **square planar geometry**.



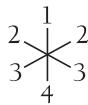
**TABLE 11.1** ■ Electron and Molecular Geometries

| Electron Groups* | Bonding Groups | Lone Pairs | Electron Geometry    | Molecular Geometry   | Approximate Bond Angles            | Example   |
|------------------|----------------|------------|----------------------|----------------------|------------------------------------|---|
| 2                | 2              | 0          | Linear               | Linear               | 180°                               | : $\ddot{\text{O}}$ =C= $\ddot{\text{O}}$ :                              |
| 3                | 3              | 0          | Trigonal planar      | Trigonal planar      | 120°                               | : $\ddot{\text{F}}$ :<br> <br>B—F:<br>                                   |
| 3                | 2              | 1          | Trigonal planar      | Bent                 | <120°                              | : $\ddot{\text{O}}$ =S= $\ddot{\text{O}}$ :                              |
| 4                | 4              | 0          | Tetrahedral          | Tetrahedral          | 109.5°                             | H—C—H<br> <br>H<br>  |
| 4                | 3              | 1          | Tetrahedral          | Trigonal pyramidal   | <109.5°                            | H—N—H<br> <br>H<br>  |
| 4                | 2              | 2          | Tetrahedral          | Bent                 | <109.5°                            | H—O—H<br>  |
| 5                | 5              | 0          | Trigonal bipyramidal | Trigonal bipyramidal | 120° (equatorial)<br>90° (axial)   | : $\ddot{\text{Cl}}$ :<br> <br>P—Cl:<br> <br>: $\ddot{\text{Cl}}$ :<br> |
| 5                | 4              | 1          | Trigonal bipyramidal | Seesaw               | <120° (equatorial)<br><90° (axial) | : $\ddot{\text{F}}$ :<br> <br>S—F:<br> <br>: $\ddot{\text{F}}$ :<br>   |
| 5                | 3              | 2          | Trigonal bipyramidal | T-shaped             | <90°                               | : $\ddot{\text{F}}$ :<br> <br>Br—F:<br> <br>: $\ddot{\text{F}}$ :<br>  |
| 5                | 2              | 3          | Trigonal bipyramidal | Linear               | 180°                               | : $\ddot{\text{F}}$ :<br> <br>Xe—F:<br> <br>: $\ddot{\text{F}}$ :<br>  |
| 6                | 6              | 0          | Octahedral           | Octahedral           | 90°                                | : $\ddot{\text{F}}$ :<br> <br>S—F:<br> <br>: $\ddot{\text{F}}$ :<br>   |
| 6                | 5              | 1          | Octahedral           | Square pyramidal     | <90°                               | : $\ddot{\text{F}}$ :<br> <br>Br—F:<br> <br>: $\ddot{\text{F}}$ :<br>  |
| 6                | 4              | 2          | Octahedral           | Square planar        | 90°                                | : $\ddot{\text{F}}$ :<br> <br>Xe—F:<br> <br>: $\ddot{\text{F}}$ :<br>  |

\*Count only electron groups around the central atom. Each of the following is considered one electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron.

**LONE PAIR REPULSIONS** Imagine that a molecule with six electron groups is confined to two dimensions and therefore has a hexagonal planar electron geometry. If two of the six groups are lone pairs, where are they located?

- (a) positions 1 and 2
- (b) positions 1 and 3
- (c) positions 1 and 4



ANSWER NOW!



### Summarizing VSEPR Theory:

- The geometry of a molecule is determined by the number of electron groups on the central atom (or on all interior atoms, if there is more than one).
- The number of electron groups is determined from the Lewis structure of the molecule. If the Lewis structure contains resonance structures, use any one of the resonance structures to determine the number of electron groups.
- Each of the following counts as a single electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron (as in a free radical).
- The geometry of the electron groups is determined by their repulsions as summarized in Table 11.1. In general, electron group repulsions vary as follows:

Lone pair-lone pair < lone pair-bonding pair < bonding pair-bonding pair

- Bond angles can vary from the idealized angles because double and triple bonds occupy more space than single bonds (they are bulkier even though they are shorter), and lone pairs occupy more space than bonding groups. The presence of lone pairs usually makes bond angles smaller than the ideal angles for the particular geometry.

## MOLECULAR GEOMETRY AND ELECTRON GROUP REPULSIONS

Which statement is *always* true according to VSEPR theory?

- (a) The shape of a molecule is determined only by repulsions among bonding electron groups.
- (b) The shape of a molecule is determined only by repulsions among nonbonding electron groups.
- (c) The shape of a molecule is determined by the polarity of its bonds.
- (d) The shape of a molecule is determined by repulsions among all electron groups on the central atom (or interior atoms, if there is more than one).



ANSWER NOW!

**11.4**

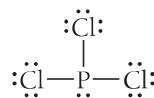
## VSEPR Theory: Predicting Molecular Geometries

To determine the geometry of a molecule, follow the procedure presented on the following page. As in other examples, we provide the steps in the left column and two examples of applying the steps in the center and right columns.

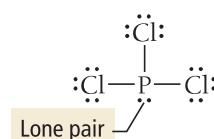
**WATCH NOW!****INTERACTIVE WORKED EXAMPLE VIDEO 11.2****HOW TO:** Predict Molecular Geometries**1. Draw the Lewis structure for the molecule.****EXAMPLE 11.2****Predicting Molecular Geometries**

Predict the geometry and bond angles of  $\text{PCl}_3$ .

$\text{PCl}_3$  has 26 valence electrons.

**2. Determine the total number of electron groups around the central atom.** Lone pairs, single bonds, double bonds, triple bonds, and single electrons each count as one group.

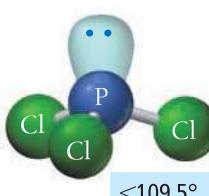
The central atom (P) has four electron groups.

**3. Determine the number of bonding groups and the number of lone pairs around the central atom.** These should sum to your result from step 2. Bonding groups include single bonds, double bonds, and triple bonds.

Three of the four electron groups around P are bonding groups, and one is a lone pair.

**4. Refer to Table 11.1 to determine the electron geometry and molecular geometry.** If no lone pairs are present around the central atom, the bond angles will be that of the ideal geometry. If lone pairs are present, the bond angles may be smaller than the ideal geometry.

The electron geometry is tetrahedral (four electron groups), and the molecular geometry—the shape of the molecule—is *trigonal pyramidal* (three bonding groups and one lone pair). Because of the presence of a lone pair, the bond angles are less than  $109.5^\circ$ .

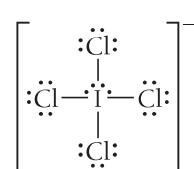
**Trigonal pyramidal**

**FOR PRACTICE 11.2** Predict the molecular geometry and bond angle of  $\text{ClNO}$ .

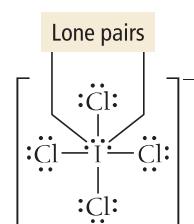
**EXAMPLE 11.3****Predicting Molecular Geometries**

Predict the geometry and bond angles of  $\text{ICl}_4^-$ .

$\text{ICl}_4^-$  has 36 valence electrons.

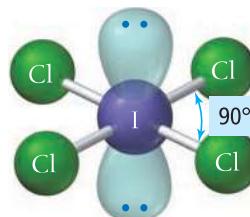


The central atom (I) has six electron groups.



Four of the six electron groups around I are bonding groups, and two are lone pairs.

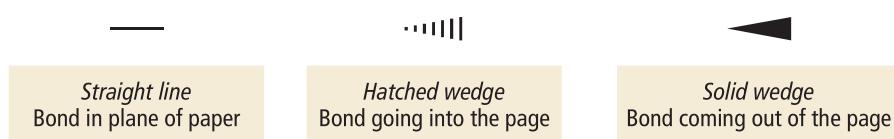
The electron geometry is octahedral (six electron groups), and the molecular geometry—the shape of the molecule—is *square planar* (four bonding groups and two lone pairs). Even though lone pairs are present, the bond angles are  $90^\circ$  because the lone pairs are symmetrically arranged and do not compress the I—Cl bond angles.

**Square planar**

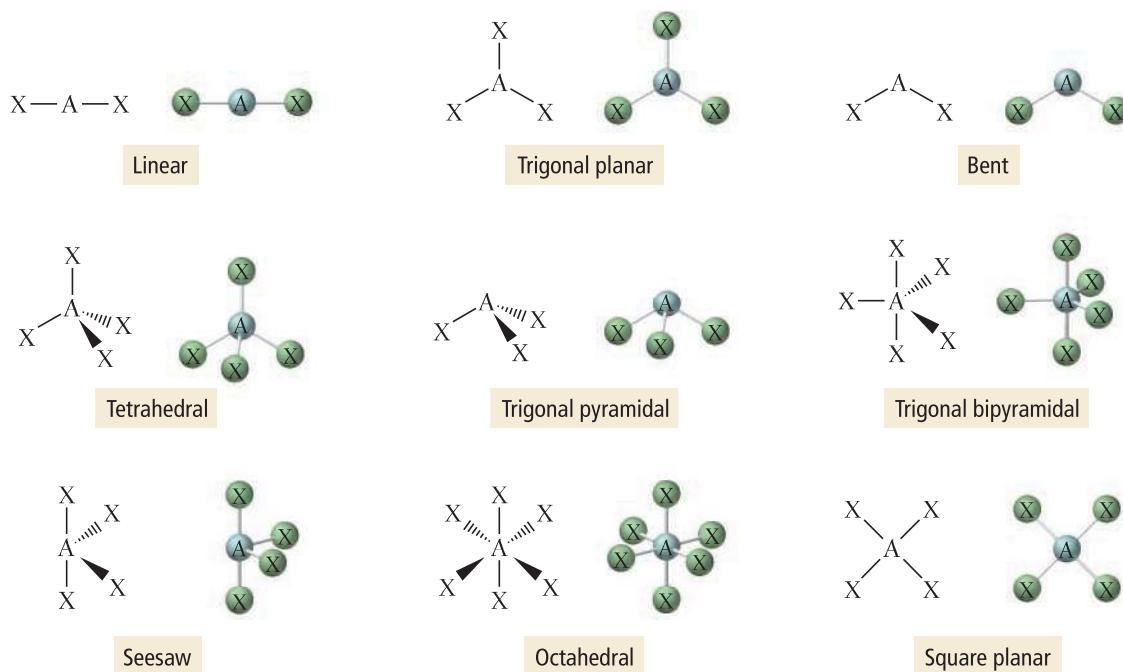
**FOR PRACTICE 11.3** Predict the molecular geometry of  $\text{I}_3^-$ .

## Representing Molecular Geometries on Paper

Since molecular geometries are three-dimensional, they are often difficult to represent on two-dimensional paper. Many chemists use the notation shown here for bonds to indicate three-dimensional structures on two-dimensional paper.

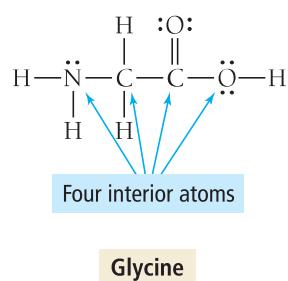


Some examples of the molecular geometries used in this book are shown below using this notation.



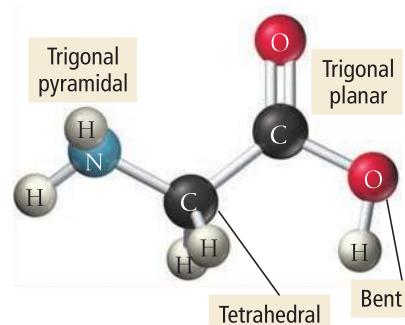
## Predicting the Shapes of Larger Molecules

Larger molecules may have two or more *interior* atoms. When predicting the shapes of these molecules, we apply the principles we just covered to each interior atom. Consider glycine, an amino acid found in many proteins (such as those that act as opioid receptors, discussed in Section 11.1). Glycine, shown in the margin, contains four interior atoms: one nitrogen atom, two carbon atoms, and an oxygen atom. To determine the shape of glycine, we determine the geometry about each interior atom as follows:



| Atom             | Number of Electron Groups | Number of Lone Pairs | Molecular Geometry |
|------------------|---------------------------|----------------------|--------------------|
| Nitrogen         | 4                         | 1                    | Trigonal pyramidal |
| Leftmost carbon  | 4                         | 0                    | Tetrahedral        |
| Rightmost carbon | 3                         | 0                    | Trigonal planar    |
| Oxygen           | 4                         | 2                    | Bent               |

Considering the geometries of each of these, we can determine the entire three-dimensional shape of the molecule as shown here.

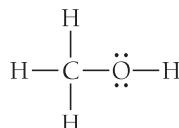


WATCH NOW!

INTERACTIVE WORKED EXAMPLE 11.4

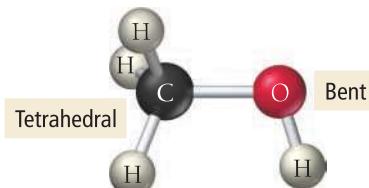
**EXAMPLE 11.4** Predicting the Shape of Larger MoleculesPredict the geometry about each interior atom in methanol ( $\text{CH}_3\text{OH}$ ) and make a sketch of the molecule.**SOLUTION**

Begin by drawing the Lewis structure of  $\text{CH}_3\text{OH}$ .  $\text{CH}_3\text{OH}$  contains two interior atoms: one carbon atom and one oxygen atom. To determine the shape of methanol, determine the geometry about each interior atom as follows:



| Atom   | Number of Electron Groups | Number of Lone Pairs | Molecular Geometry |
|--------|---------------------------|----------------------|--------------------|
| Carbon | 4                         | 0                    | Tetrahedral        |
| Oxygen | 4                         | 2                    | Bent               |

Considering these interior atom geometries, draw a three-dimensional sketch of the molecule:



**FOR PRACTICE 11.4** Predict the geometry about each interior atom in acetic acid

$(\text{H}_3\text{C}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H})$  and make a sketch of the molecule.

ANSWER NOW!



## 11.6 Cc

Conceptual Connection

### THE SHAPE OF LARGER MOLECULES

What is the molecular geometry about nitrogen in  $\text{CH}_3\text{NH}_2$ ?

- (a) trigonal planar      (b) tetrahedral  
 (c) trigonal pyramidal      (d) bent

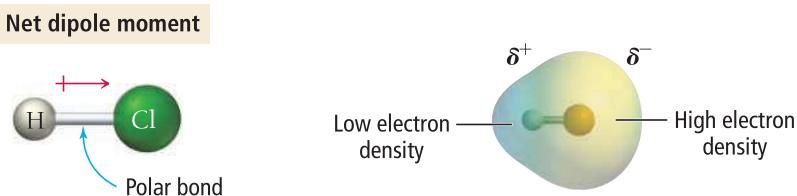
## WATCH NOW!

## KEY CONCEPT VIDEO 11.5

Molecular Shape and Polarity

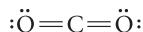
### 11.5 Molecular Shape and Polarity

In Chapter 10, we discussed polar bonds. Entire molecules can also be polar, depending on their shape and the nature of their bonds. For example, if a diatomic molecule has a polar bond, the molecule as a whole is polar:



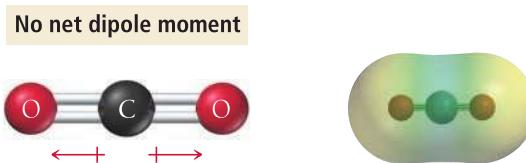
The figure on the right is an electrostatic potential map of  $\text{HCl}$ . In these maps, red areas indicate electron-rich regions in the molecule and the blue areas indicate electron-poor regions. Yellow indicates moderate electron density. Notice that the region around the more electronegative atom (chlorine) is more electron-rich than the region around the hydrogen atom. Thus the molecule itself is polar. If the bond in a diatomic molecule is *nonpolar*, the molecule as a whole is *nonpolar*.

In polyatomic molecules, the presence of polar bonds may or may not result in a polar molecule, depending on the molecular geometry. If the molecular geometry is such that the dipole moments of individual polar bonds sum together to a net dipole moment, then the molecule is polar. But if the molecular geometry is such that the dipole moments of the individual polar bonds cancel each other (that is, sum to zero), then the molecule is nonpolar. It all depends on the geometry of the molecule. Consider carbon dioxide:



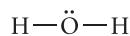
Each C=O bond in CO<sub>2</sub> is polar because oxygen and carbon have significantly different electronegativities (3.5 and 2.5, respectively). However, since CO<sub>2</sub> is a linear molecule, the polar bonds directly oppose one another and the dipole moment of one bond exactly opposes the dipole moment of the other—the two dipole moments sum to zero and the *molecule* is nonpolar.

Dipole moments can cancel each other because they are *vector quantities*; they have both a magnitude and a direction. Think of each polar bond as a vector, pointing in the direction of the more electronegative atom. The length of the vector is proportional to the electronegativity difference between the bonding atoms. In CO<sub>2</sub>, we have two identical vectors pointing in exactly opposite directions—the vectors sum to zero, much as +1 and -1 sum to zero:



Notice that the electrostatic potential map shows regions of moderately high electron density (yellow with slight red) positioned symmetrically on either end of the molecule with a region of low electron density (blue) located in the middle.

In contrast, consider water:



The O—H bonds in water are also polar; oxygen and hydrogen have electronegativities of 3.5 and 2.1, respectively. However, the water molecule is not linear but bent, so the two dipole moments do not sum to zero as they do in carbon dioxide. If we imagine each bond in water as a vector pointing toward oxygen (the more electronegative atom), we see that, because of the angle between the vectors, they do not cancel but sum to an overall vector or a net dipole moment (shown by the dashed arrow):

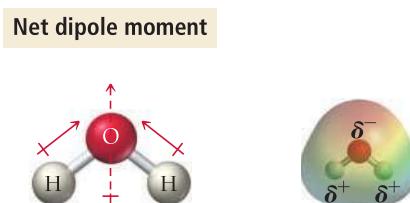


Table 11.2 (on page 453) summarizes common geometries and molecular polarity while the How To... feature summarizes how to determine if a molecule is polar.

### HOW TO: Determine Molecular Shape and Polarity

- **Draw the Lewis structure for the molecule and determine its molecular geometry.**
- **Determine whether the molecule contains polar bonds.** A bond is polar if the two bonding atoms have sufficiently different electronegativities (see Figure 10.8). If the molecule contains polar bonds, superimpose a vector, pointing toward the more electronegative atom, on each bond. Draw the length of the vector proportional to the electronegativity difference between the bonding atoms.
- **Determine whether the polar bonds add together to form a net dipole moment.** Sum the vectors corresponding to the polar bonds together. If the vectors sum to zero, the molecule is nonpolar. If the vectors sum to a net vector, the molecule is polar.

ANSWER NOW!



## 11.7

### CC

Conceptual Connection

## POLARITY OF MOLECULES

A molecule contains three identical polar bonds in a trigonal planar molecular geometry. Is the molecule polar?

- (a) yes
- (b) no
- (c) unable to determine whether the molecule is polar without more information

## Vector Addition

We determine whether a molecule is polar by summing the vectors associated with the dipole moments of all the polar bonds in the molecule. If the vectors sum to zero, the molecule is nonpolar. If they sum to a net vector, the molecule is polar. In this section, we demonstrate how to add vectors together in one dimension and in two or more dimensions.

**Example 1**  $\vec{R} = \vec{A} + \vec{B}$

**Example 2**  $\vec{R} = \vec{A} + \vec{B}$

**Example 3**  $\vec{R} = \vec{A} + \vec{B}$   
(the vectors exactly cancel)

**Example 4**  $\vec{R} = \vec{A} + \vec{B}$

**Example 5**  $\vec{R} = \vec{A} + \vec{B}$

### One Dimension

To add two vectors that lie on the same line, assign one direction as positive. Vectors pointing in that direction have positive magnitudes. Consider vectors pointing in the opposite direction to have negative magnitudes. Then sum the vectors (always remembering to include their signs), as shown in Examples 1–3.

### Two or More Dimensions

To add two vectors in two or more dimensions, draw a parallelogram in which the two vectors form two adjacent sides. Draw the other two sides of the parallelogram parallel to and the same length as the two original vectors. Draw the resultant vector beginning at the origin and extending to the far corner of the parallelogram, as shown in Examples 4 and 5.

To add three or more vectors in two or more dimensions, add two of them together first, and then add the third vector to the result as shown in Examples 6 and 7.

**Example 6**  $\vec{R} = \vec{A} + \vec{B}$

$$\begin{aligned}\vec{R}' &= \vec{R} + \vec{C} \\ &= \vec{A} + \vec{B} + \vec{C}\end{aligned}$$

**Example 7**  $\vec{R} = \vec{A} + \vec{B}$

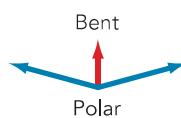
$$\begin{aligned}\vec{R}' &= \vec{R} + \vec{C} \\ &= \vec{A} + \vec{B} + \vec{C}\end{aligned}$$

$\vec{R}' = \text{Zero}$   
(the vectors exactly cancel)

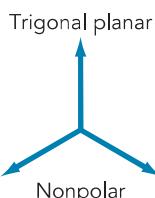
**TABLE 11.2 ■ Common Cases of Adding Dipole Moments to Determine Whether a Molecule Is Polar**



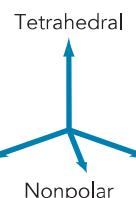
The dipole moments of two identical polar bonds pointing in opposite directions cancel. The molecule is nonpolar.



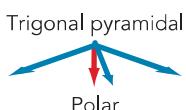
The dipole moments of two polar bonds with an angle of less than 180° between them do not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.



The dipole moments of three identical polar bonds at 120° from each other cancel. The molecule is nonpolar.



The dipole moments of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) cancel. The molecule is nonpolar.



The dipole moments of three polar bonds in a trigonal pyramidal arrangement do not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.

Note: In all cases in which the dipoles of two or more polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.

### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 11.5

#### EXAMPLE 11.5 Determining Whether a Molecule Is Polar

Determine whether NH<sub>3</sub> is polar.

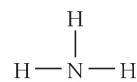
##### SOLUTION

**Draw the Lewis structure for the molecule and determine its molecular geometry.**



### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 11.5



The Lewis structure has three bonding groups and one lone pair about the central atom. Therefore, the molecular geometry is trigonal pyramidal.



The electronegativities of nitrogen and hydrogen are 3.0 and 2.1, respectively. Therefore, the bonds are polar.



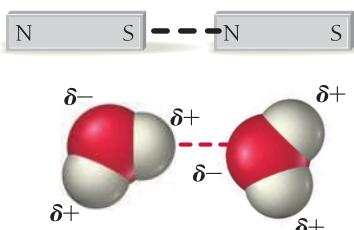
The three dipole moments sum to a net dipole moment. The molecule is polar.

**Determine whether the molecule contains polar bonds.** Sketch the molecule and superimpose a vector for each polar bond. The relative length of each vector is proportional to the electronegativity difference between the atoms forming each bond. The vectors point in the direction of the more electronegative atom.

**Determine whether the polar bonds add together to form a net dipole moment.** Examine the symmetry of the vectors (representing dipole moments) and determine whether they cancel each other or sum to a net dipole moment.

**FOR PRACTICE 11.5** Determine whether CF<sub>4</sub> is polar.

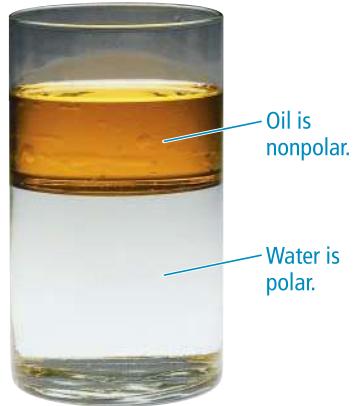
Opposite magnetic poles attract one another.



Opposite partial charges on molecules attract one another.

**▲ FIGURE 11.5 Interaction of Polar Molecules** The north pole of one magnet attracts the south pole of another magnet. In an analogous way, the positively charged end of one molecule attracts the negatively charged end of another (although the forces involved are different). As a result of this electrical attraction, polar molecules interact strongly with one another.

Polar and nonpolar molecules have different properties. Water and oil do not mix, for example, because water molecules are polar and the molecules that compose oil are generally nonpolar. Polar molecules interact strongly with other polar molecules because the positive end of one molecule is attracted to the negative end of another, just as the south pole of a magnet is attracted to the north pole of another magnet (Figure 11.5 ▲). A mixture of polar and nonpolar molecules is similar to a mixture of small magnetic particles and nonmagnetic ones. The magnetic particles (which are like polar molecules) clump together, excluding the nonmagnetic particles (which are like nonpolar molecules) and separating into distinct regions.



▲ Oil and water do not mix because water molecules are polar and the molecules that compose oil are nonpolar.



▲ A mixture of polar and nonpolar molecules is analogous to a mixture of magnetic marbles (opaque) and nonmagnetic marbles (transparent). As with the magnetic marbles, mutual attraction causes polar molecules to clump together, excluding the nonpolar molecules.



## CHEMISTRY IN YOUR DAY

### How Soap Works

Imagine eating a greasy cheeseburger with both hands without a napkin. By the end of the meal, grease and oil coat your hands. If you try to wash them with only water, they remain greasy. However, if you add a little soap, the grease washes away. Why? As we just learned, water molecules are polar and the molecules that compose grease and oil are nonpolar. As a result, water and grease do not mix.

The molecules that compose soap, however, have a special structure that allows them to interact strongly with both water and grease. One end of a soap molecule is polar and the other end is nonpolar.

The nonpolar end is a long hydrocarbon chain. Hydrocarbons are always nonpolar because the electronegativity difference between carbon and hydrogen is small and because the tetrahedral arrangement about each carbon atom tends to cancel any small dipole moments of individual bonds. The polar head of a soap molecule—usually, though not always, ionic—strongly attracts water molecules, while the nonpolar tail interacts more strongly with grease and oil molecules (we examine the nature of these interactions in Chapter 12). Thus, soap acts as a sort of molecular liaison, one end interacting with water and the other end interacting with grease. Soap allows water and grease to mix, removing the grease from your hands and washing it down the drain.



Polar head  
attracts water.

Nonpolar tail  
interacts with grease.



**QUESTION** Consider the detergent molecule shown at right. Which end do you think is polar? Which end is nonpolar?



## 11.6

# Valence Bond Theory: Orbital Overlap as a Chemical Bond

In the Lewis model, we use dots to represent electrons. We know from quantum-mechanical theory, however, that such a treatment is an oversimplification. More advanced bonding theories treat electrons in a quantum-mechanical manner. These theories are actually extensions of quantum mechanics, applied to molecules. Although a detailed quantitative treatment of these theories is beyond the scope of this book, we introduce them in a *qualitative* manner in the sections that follow. Keep in mind, however, that modern *quantitative* approaches to chemical bonding using these theories accurately predict many of the properties of molecules—such as bond lengths, bond strengths, molecular geometries, and dipole moments—that we discuss in this book.

The simpler of the two more advanced bonding theories is **valence bond theory**. According to valence bond theory, electrons reside in quantum-mechanical orbitals localized on individual atoms. In many cases, these orbitals are simply the standard s, p, d, and f atomic orbitals that we learned about in Chapter 8. In other cases, these orbitals are *hybridized atomic orbitals*, a kind of blend or combination of two or more standard atomic orbitals.

When two atoms approach each other, the electrons and nucleus of one atom interact with the electrons and nucleus of the other atom. In valence bond theory, we calculate how these interactions affect the energies of the electrons in the atomic orbitals. If the energy of the system is lowered because of the interactions, then a chemical bond forms. If the energy of the system is raised by the interactions, then a chemical bond does not form.

The interaction energy is usually calculated as a function of the internuclear distance between the two bonding atoms. For example, Figure 11.6▼ shows the calculated interaction energy between two hydrogen atoms as a function of the distance between them. The y-axis of the graph is the potential energy of the interaction between the electron and nucleus of one hydrogen atom and the electron and nucleus of the other hydrogen atom. The x-axis is the separation (or internuclear distance) between the two atoms. As we can see from the graph, when the atoms are far apart (right side of the graph, labeled 1), the interaction energy is nearly zero because the two atoms do not interact to any significant extent. As the atoms get closer (labeled 2 and 3 on the graph), the interaction energy becomes negative. The lowering of the interaction energy is a net stabilization that attracts one hydrogen atom to the other. If the atoms get too close

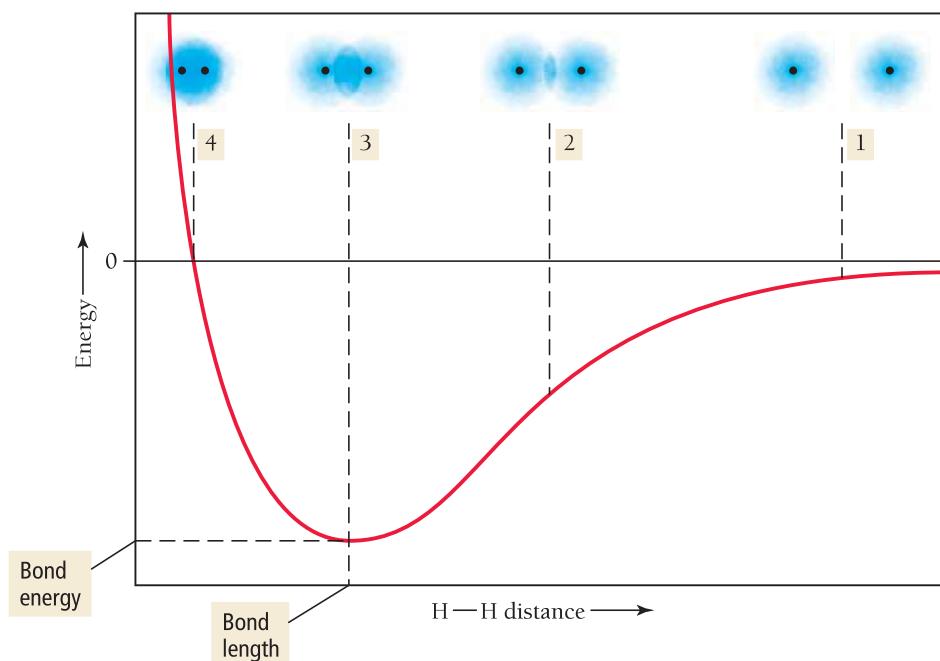
## WATCH NOW!

### KEY CONCEPT VIDEO 11.6

Valence Bond Theory

Valence bond theory is an application of a general quantum-mechanical approximation method called *perturbation theory*. In perturbation theory, a complex system (such as a molecule) is viewed as a simpler system (such as two atoms) that is slightly altered or perturbed by some additional force or interaction (such as the interaction between the two atoms).

### Interaction Energy of Two Hydrogen Atoms



**◀ FIGURE 11.6** Interaction Energy Diagram for  $\text{H}_2$  The potential energy of two hydrogen atoms is lowest when they are separated by a distance that allows their 1s orbitals a substantial degree of overlap without too much repulsion between their nuclei. This distance, at which the system is most stable, is the bond length of the  $\text{H}_2$  molecule (labeled 3 on this graph).

(labeled 4 on the graph), however, the interaction energy begins to rise, primarily because of the mutual repulsion of the two positively charged nuclei. The most stable point on the curve occurs at the minimum of the interaction energy—this is the equilibrium bond length (labeled 3 on the graph). At this distance, the two atomic 1s orbitals have a significant amount of overlap, and the electrons spend time in the internuclear region where they can interact with both nuclei. The value of the interaction energy at the equilibrium bond distance is the bond energy.

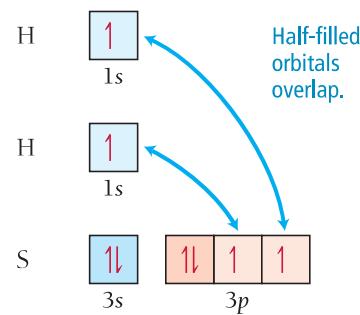
When we apply valence bond theory to a number of atoms and their corresponding molecules, we arrive at the following general observation: *the interaction energy is usually negative (or stabilizing) when the interacting atomic orbitals contain a total of two electrons that can spin-pair (orient with opposing spins)*. Most commonly, the two electrons come from two half-filled orbitals, but in some cases, the two electrons come from one filled orbital overlapping with a completely empty orbital (this is called a coordinate covalent bond, and we will cover it in more detail in Chapter 26). In other words, when two atoms with half-filled orbitals approach each other, the half-filled orbitals *overlap*—parts of the orbitals occupy the same space—and the electrons occupying them align with opposite spins. This results in a net energy stabilization that constitutes a covalent chemical bond. The resulting geometry of the molecule emerges from the geometry of the overlapping orbitals.

When completely filled orbitals overlap, the interaction energy is positive (or destabilizing) and no bond forms.

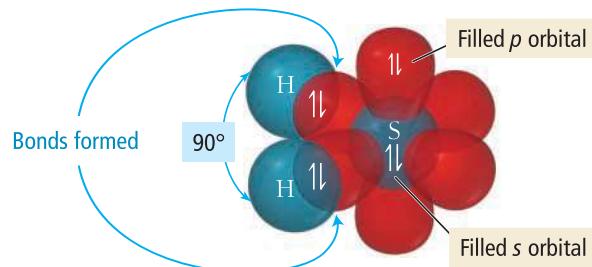
#### **Summarizing Valence Bond Theory:**

- The valence electrons of the atoms in a molecule reside in quantum-mechanical atomic orbitals. The orbitals can be the standard  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals, or they may be hybrid combinations of these.
- A chemical bond results from the overlap of two half-filled orbitals with spin-pairing of the two valence electrons (or less commonly the overlap of a completely filled orbital with an empty orbital).
- The geometry of the overlapping orbitals determines the shape of the molecule.

We can apply the general concepts of valence bond theory to explain bonding in hydrogen sulfide,  $\text{H}_2\text{S}$ . The valence electron configurations of the atoms in the molecule are as follows:



The hydrogen atoms each have one half-filled orbital, and the sulfur atom has two half-filled orbitals. The half-filled orbitals on each hydrogen atom overlap with the two half-filled orbitals on the sulfur atom, forming two chemical bonds:



To show the spin-pairing of the electrons in the overlapping orbitals, we superimpose a half-arrow for each electron in each half-filled orbital to indicate that, within a bond, the electrons are spin-paired (one half-arrow is pointing up and the other is pointing

down). We also superimpose paired half-arrows in the filled sulfur *s* and *p* orbitals to represent the lone pair electrons in those orbitals. (Since those orbitals are full, they are not involved in bonding.)

A quantitative calculation of H<sub>2</sub>S using valence bond theory yields bond energies, bond lengths, and bond angles. In our qualitative treatment, we simply show how orbital overlap leads to bonding and make a rough sketch of the molecule based on the overlapping orbitals. Notice that, because the overlapping orbitals on the central atom (sulfur) are *p* orbitals and because *p* orbitals are oriented at 90° to one another, the predicted bond angle is 90°. The actual bond angle in H<sub>2</sub>S is 92°. In the case of H<sub>2</sub>S, a simple valence bond treatment matches well with the experimentally measured bond angle (in contrast to VSEPR theory, which predicts a bond angle of less than 109.5°).

**WHAT IS A CHEMICAL BOND? PART I** The answer to the question “What is a chemical bond?” depends on the bonding model. What is a chemical bond according to valence bond theory?

- (a) lone electron pair
- (b) the overlap between half-filled atomic orbitals on two atoms
- (c) the overlap between filled atomic orbitals on two atoms
- (d) a shared electron pair between two atoms

## 11.8 Cc

Conceptual Connection

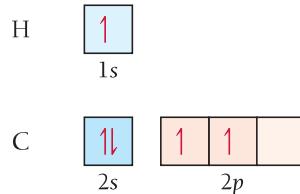
ANSWER NOW!



### 11.7

## Valence Bond Theory: Hybridization of Atomic Orbitals

Although the overlap of half-filled *standard* atomic orbitals adequately explains the bonding in H<sub>2</sub>S, it cannot adequately explain the bonding in many other molecules. For example, suppose we try to explain the bonding between hydrogen and carbon using the same approach. The valence electron configurations of H and C are as follows:



Carbon has only two half-filled orbitals and should therefore form only two bonds with two hydrogen atoms. We would therefore predict that carbon and hydrogen should form a molecule with the formula CH<sub>2</sub> and with a bond angle of 90° (corresponding to the angle between any two *p* orbitals).

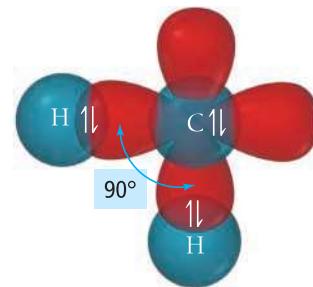
However, from experiments, we know that the stable compound formed from carbon and hydrogen is CH<sub>4</sub> (methane), which has bond angles of 109.5°. The experimental reality is different from our simple prediction in two ways. First, carbon forms bonds to four hydrogen atoms, not two. Second, the bond angles are much larger than the angle between two *p* orbitals. Valence bond theory accounts for the bonding in CH<sub>4</sub> and many other polyatomic molecules by incorporating an additional concept called *orbital hybridization*.

So far, we have assumed that the overlapping orbitals that form chemical bonds are simply the standard *s*, *p*, or *d* atomic orbitals. Valence bond theory treats the electrons in a molecule as if they occupied these standard atomic orbitals, but this is a major oversimplification. The concept of hybridization in valence bond theory is essentially a step toward recognizing that *the orbitals in a molecule are not necessarily the same as the orbitals in an atom*. **Hybridization** is a mathematical procedure in which the standard atomic orbitals are combined to form new atomic orbitals called **hybrid orbitals** that

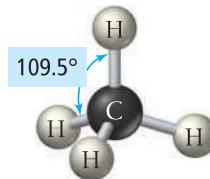
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#### KEY CONCEPT VIDEO 11.7

Valence Bond Theory:  
Hybridization



Theoretical prediction



Observed reality

In Section 11.8, we examine another theory called *molecular orbital theory*, which treats electrons in a molecule as occupying orbitals that belong to the molecule as a whole.

As we saw in Chapter 10, the word *hybrid* comes from breeding. A *hybrid* is an offspring of two animals or plants of different standard races or breeds. Similarly, a hybrid orbital is a product of mixing two or more standard atomic orbitals.

In a more nuanced treatment, hybridization is not an all-or-nothing process—it can occur to varying degrees that are not always easy to predict. We saw earlier, for example, that sulfur does not hybridize very much in forming H<sub>2</sub>S.

correspond more closely to the actual distribution of electrons in chemically bonded atoms. Hybrid orbitals are still localized on individual atoms, but their shapes and energies differ from those of standard atomic orbitals.

Why do we hypothesize that electrons in some molecules occupy hybrid orbitals? In valence bond theory, a chemical bond is the overlap of two orbitals that together contain two electrons. The greater the overlap, the stronger the bond and the lower the energy. In hybrid orbitals, the electron probability density is more concentrated in a single directional lobe, allowing greater overlap with the orbitals of other atoms. Hybrid orbitals *minimize* the energy of the molecule by *maximizing* the orbital overlap in a bond.

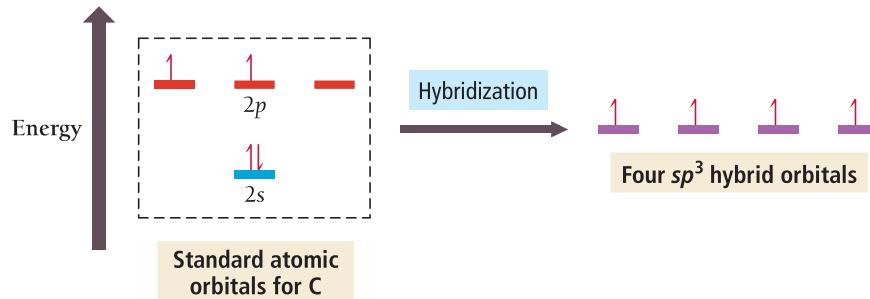
Hybridization, however, is not a free lunch—in most cases it actually costs some energy. So hybridization occurs only to the degree that the energy payback through bond formation is large. In general, therefore, the more bonds that an atom forms, the greater the tendency of its orbitals to hybridize. Central or interior atoms, which form the most bonds, have the greatest tendency to hybridize. Terminal atoms, which form the fewest bonds, have the least tendency to hybridize. *In this book, we focus on the hybridization of interior atoms and assume that all terminal atoms—those bonding to only one other atom—are unhybridized.* Hybridization is particularly important in carbon, which tends to form four bonds in its compounds and therefore always hybridizes.

Although we cannot examine the procedure for obtaining hybrid orbitals in mathematical detail here, we can make the following general statements regarding hybridization:

- The *number of standard atomic orbitals* added together always equals the *number of hybrid orbitals* formed. The total number of orbitals is conserved.
- The *particular combination* of standard atomic orbitals added together determines the *shapes and energies* of the hybrid orbitals formed.
- The *particular type of hybridization that occurs* is the one that yields the *lowest overall energy for the molecule*. Since actual energy calculations are beyond the scope of this book, we use electron geometries as determined by VSEPR theory to predict the type of hybridization.

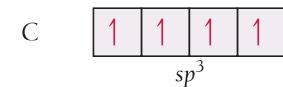
## *sp*<sup>3</sup> Hybridization

We can account for the tetrahedral geometry in CH<sub>4</sub> by the hybridization of the one 2s orbital and the three 2p orbitals on the carbon atom. The four new orbitals that result, called *sp*<sup>3</sup> hybrids, are shown in the following energy diagram:



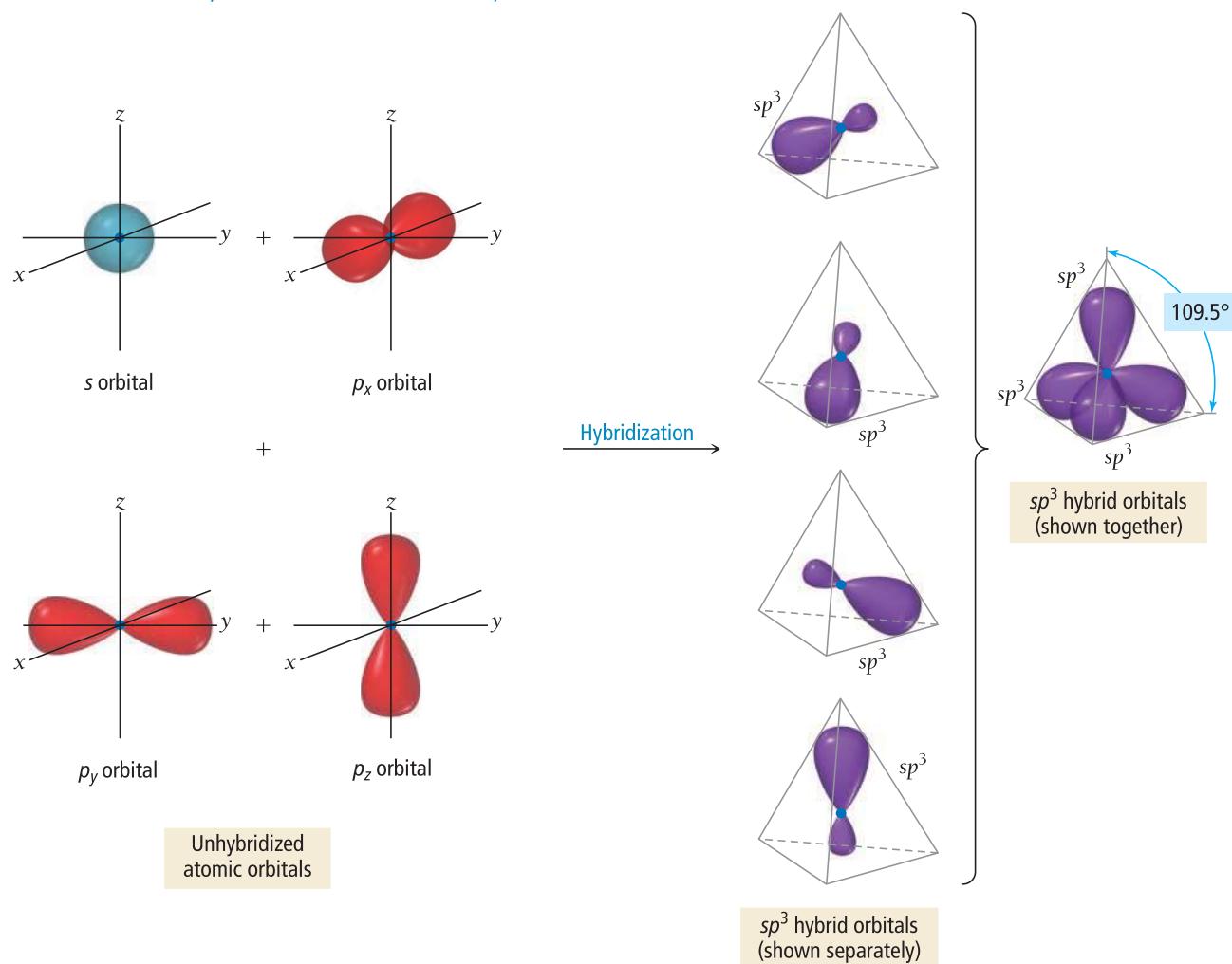
The notation *sp*<sup>3</sup> indicates that the hybrid orbitals are mixtures of one s orbital and three p orbitals. Notice that the hybrid orbitals all have the same energy—they are degenerate. The shapes of the *sp*<sup>3</sup> hybrid orbitals are shown in Figure 11.7▶. The four hybrid orbitals are arranged in a tetrahedral geometry with 109.5° angles between them.

We can write an orbital diagram for carbon using these hybrid orbitals:



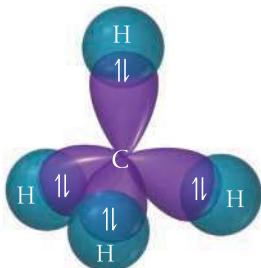
## Formation of $sp^3$ Hybrid Orbitals

One  $s$  orbital and three  $p$  orbitals combine to form four  $sp^3$  orbitals.



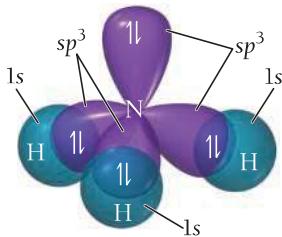
▲ FIGURE 11.7  $sp^3$  Hybridization

Carbon's four valence electrons occupy the orbitals singly with parallel spins as dictated by Hund's rule. With this electron configuration, carbon has four half-filled orbitals and can form four bonds with four hydrogen atoms:



The geometry of the *overlapping orbitals* (the hybrids) is tetrahedral, with angles of 109.5° between the orbitals, so the *resulting geometry of the molecule* is tetrahedral, with 109.5° bond angles. This agrees with the experimentally measured geometry of CH<sub>4</sub> and with the predicted VSEPR geometry.

Hybridized orbitals readily form chemical bonds because they tend to maximize overlap with other orbitals. However, if the central atom of a molecule contains lone pairs, hybrid orbitals can also accommodate them. For example, the nitrogen orbitals in ammonia are  $sp^3$  hybrids. Three of the hybrids are involved in bonding with three hydrogen atoms, but the fourth hybrid contains a lone pair. The presence of the lone pair lowers the tendency of nitrogen's orbitals to hybridize. (Remember that the tendency to hybridize increases with the number of bonds formed.) Therefore the bond angle in  $\text{NH}_3$  is  $107^\circ$ , a bit closer to the unhybridized  $p$  orbital bond angle of  $90^\circ$ .



ANSWER NOW!

## 11.9 Cc

Conceptual Connection



### NUMBER OF HYBRID ORBITALS

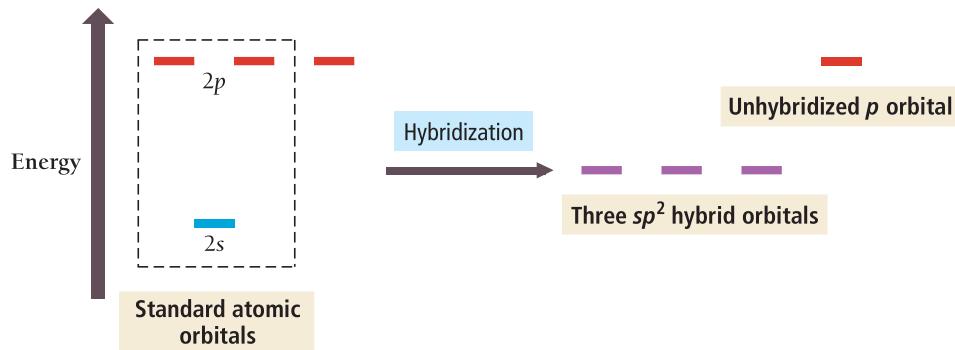
How many  $sp^3$  hybrid orbitals result from the hybridization of one  $s$  and three  $p$  orbitals?

- (a) 1      (b) 2  
(c) 3      (d) 4

In valence bond theory, the particular hybridization scheme to follow  $sp^2$  versus  $sp^3$ , for example, for a given molecule is determined computationally, which is beyond the scope of this text. In this book, we determine the particular hybridization scheme from the VSEPR geometry of the molecule, as shown later in this section.

### $sp^2$ Hybridization and Double Bonds

Hybridization of one  $s$  and two  $p$  orbitals results in three  $sp^2$  hybrids and one leftover unhybridized  $p$  orbital:



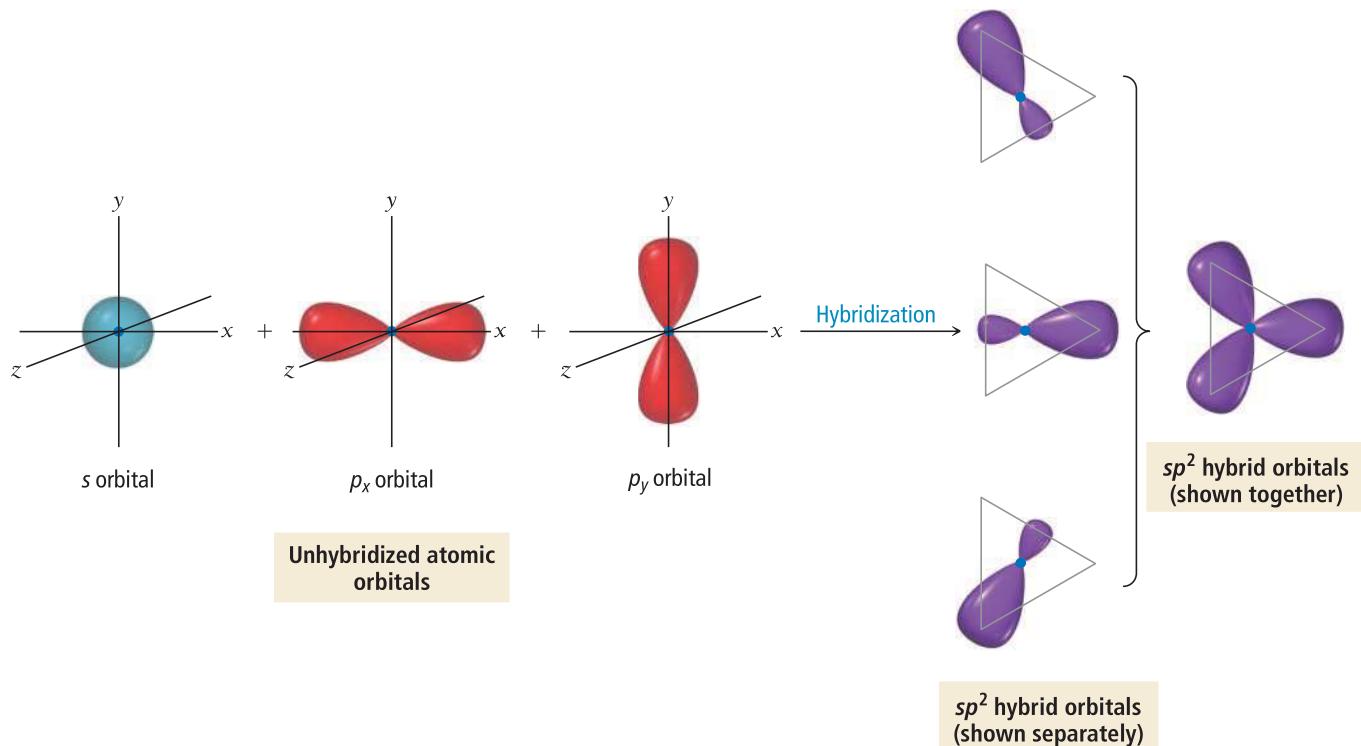
The notation  $sp^2$  indicates that the hybrids are mixtures of one  $s$  orbital and two  $p$  orbitals. Figure 11.8► illustrates the shapes of the  $sp^2$  hybrid orbitals. Notice that the three hybrid orbitals have a trigonal planar geometry with  $120^\circ$  angles between them. The unhybridized  $p$  orbital is perpendicular to the three hybridized orbitals.

As an example of a molecule with  $sp^2$  hybrid orbitals, consider  $\text{H}_2\text{CO}$ . The unhybridized valence electron configurations of each of the atoms are as follows:

|   |    |            |
|---|----|------------|
| H | 1  | 1s         |
| O | 11 | 2s      2p |
| C | 11 | 2s      2p |

## Formation of $sp^2$ Hybrid Orbitals

One  $s$  orbital and two  $p$  orbitals combine to form three  $sp^2$  orbitals.

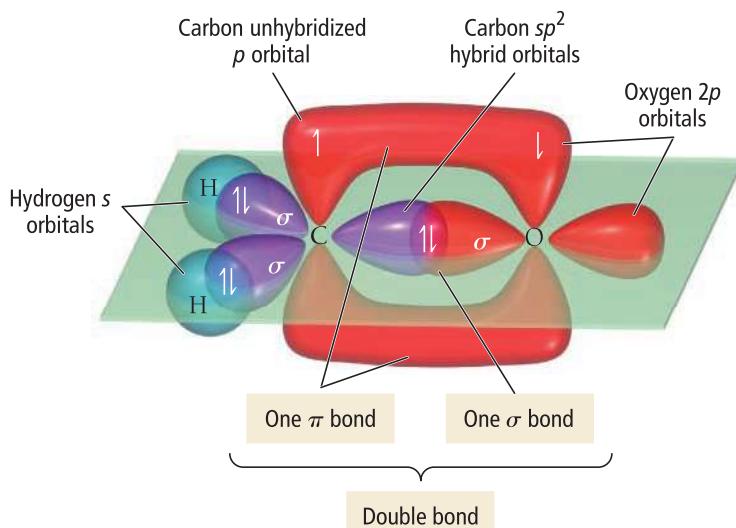


Carbon is the central atom, and the hybridization of its orbitals is  $sp^2$ :



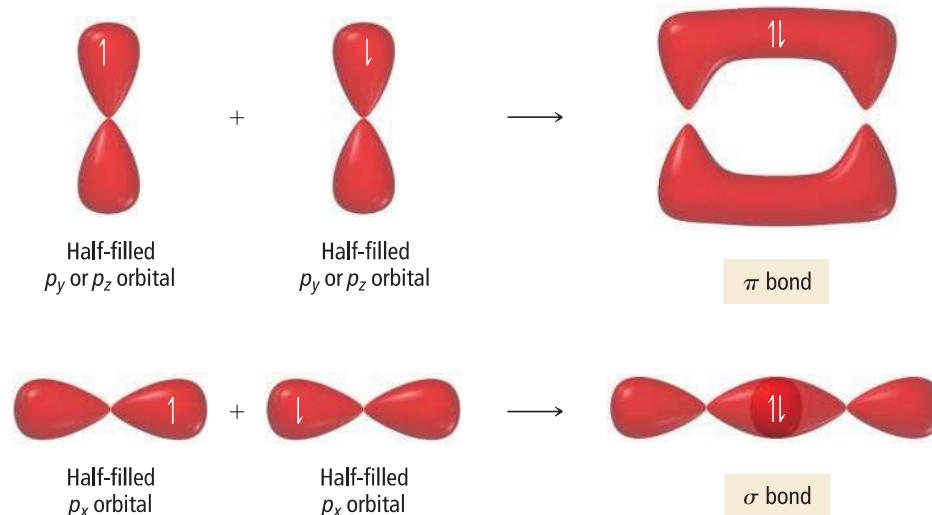
**▲ FIGURE 11.8  $sp^2$  Hybridization** When  $sp^2$  hybrid orbitals form, one  $p$  orbital (not shown) remains unhybridized.

Each of the  $sp^2$  orbitals is half filled. The remaining electron occupies the leftover  $p$  orbital, even though it is slightly higher in energy. We can now see that the carbon atom has four half-filled orbitals and can therefore form four bonds: two with two hydrogen atoms and two (a double bond) with the oxygen atom. We draw the molecule and the overlapping orbitals as follows:

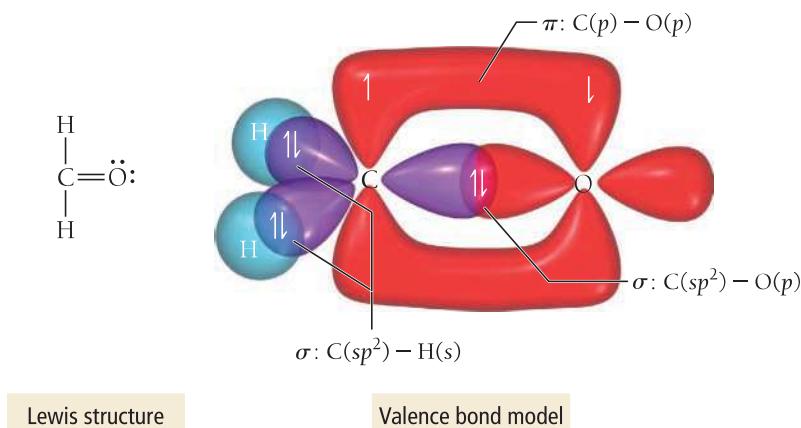


### ► FIGURE 11.9 Sigma and Pi

**Bonding** When orbitals overlap side by side, the result is a pi ( $\pi$ ) bond. When orbitals overlap end to end, they form a sigma ( $\sigma$ ) bond. Two atoms can form only one sigma bond. A single bond is a sigma bond, a double bond consists of a sigma bond and a pi bond, and a triple bond consists of a sigma bond and two pi bonds.



Notice the overlap between the half-filled  $p$  orbitals on the carbon and oxygen atoms. When  $p$  orbitals overlap this way (side by side), the resulting bond is a **pi ( $\pi$ ) bond**, and the electron density is above and below the internuclear axis. When orbitals overlap end to end, as is the case in all of the rest of the bonds in the molecule, the resulting bond is a **sigma ( $\sigma$ ) bond** (Figure 11.9▲). Even though we represent the two electrons in a  $\pi$  bond as two half-arrows in the upper lobe, they are actually spread out over both the upper and lower lobes (this is one of the limitations we encounter when we try to represent electrons with arrows). We can label all the bonds in the molecule using a notation that specifies the type of bond ( $\sigma$  or  $\pi$ ) as well as the type of overlapping orbitals. We have included this notation, as well as the Lewis structure of  $\text{H}_2\text{CO}$  for comparison, in the bonding diagram for  $\text{H}_2\text{CO}$ :



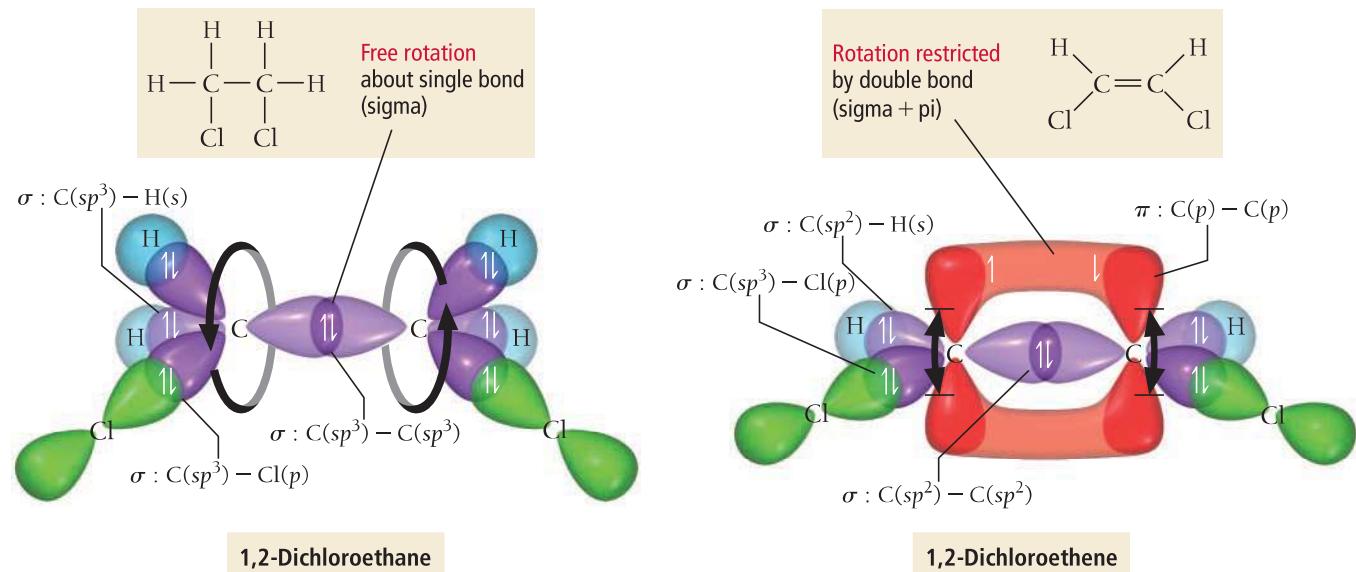
Notice the correspondence between valence bond theory and the Lewis model. In both models, the central carbon atom forms four bonds: two single bonds and one double bond. However, valence bond theory gives us more insight into the bonds. The double bond between carbon and oxygen according to valence bond theory consists of two different kinds of bonds—one  $\sigma$  and one  $\pi$ —whereas in the Lewis model the two bonds within the double bond appear identical. *A double bond in the Lewis model always corresponds to one  $\sigma$  and one  $\pi$  bond in valence bond theory.* In general,  $\pi$  bonds are weaker than  $\sigma$  bonds because side-to-side orbital overlap tends to be less efficient than end-to-end orbital overlap. Consequently, the  $\pi$  bond in a double bond is generally easier to break than the  $\sigma$  bond. Valence bond theory, as you can see, gives us more insight into the nature of a double bond than the Lewis model.

One—and only one— $\sigma$  bond forms between any two atoms. Additional bonds must be  $\pi$  bonds.

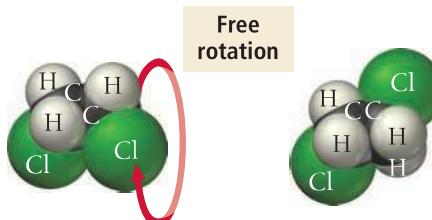
Valence bond theory shows us the types of orbitals involved in the bonding and their shapes. For example, in  $\text{H}_2\text{CO}$ , the  $sp^2$  hybrid orbitals on the central atom are trigonal planar with  $120^\circ$  angles between them, so the resulting predicted geometry of the molecule is trigonal planar with  $120^\circ$  bond angles. The experimentally measured bond angles in  $\text{H}_2\text{CO}$ , as discussed previously, are  $121.9^\circ$  for the HCO bond and  $116.2^\circ$  for the HCH bond angle, close to the predicted values.

Valence bond theory allows us to see why the rotation about a double bond is severely restricted. Because of the side-by-side overlap of the  $p$  orbitals, the  $\pi$  bond must essentially break for rotation to occur (see *Chemistry in Your Day: The Chemistry of Vision*).

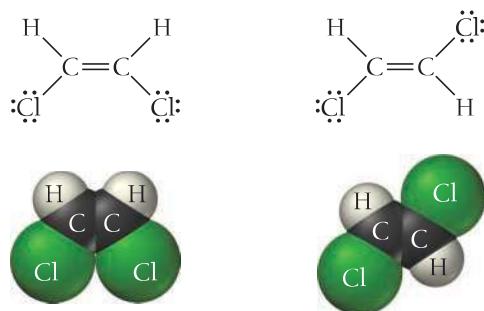
Although rotation about a double bond is highly restricted, rotation about a single bond is relatively unrestricted. Consider, for example, the structures of two chlorinated hydrocarbons, 1,2-dichloroethane and 1,2-dichloroethene:



The hybridization of the carbon atoms in 1,2-dichloroethane is  $sp^3$ , resulting in relatively free rotation about the sigma single bond. Consequently, there is no difference between the following two structures at room temperature because they quickly interconvert:



In contrast, rotation about the double bond (one  $\sigma$  and one  $\pi$  bond) in 1,2-dichloroethene is restricted; therefore at room temperature, 1,2-dichloroethene exists in two forms:



*cis*-1,2-Dichloroethene

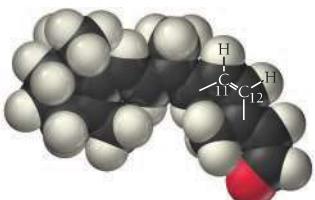
*trans*-1,2-Dichloroethene



## CHEMISTRY IN YOUR DAY

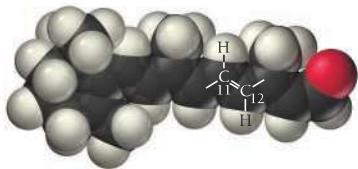
### The Chemistry of Vision

In the human eye, light is detected by a chemical switch involving the breaking and re-forming of a  $\pi$  bond. The back portion of the eye, the retina, is coated with millions of light-sensitive cells called rods and cones. Each of these cells contains proteins that bind a compound called 11-cis-retinal, which has the following structure:



1-cis-Retinal

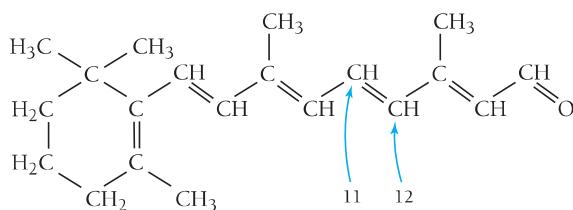
When a photon of sufficient energy strikes a rod or cone, it causes the isomerization of 11-cis-retinal to all-trans-retinal:



all-trans-Retinal

The isomerization occurs because visible light contains enough energy to break the  $\pi$  bond between the eleventh and twelfth carbon atom in 11-cis-retinal. The  $\sigma$  bond, which is stronger, does not break, allowing the molecule to freely rotate about that bond. The  $\pi$  bond then re-forms with the molecule in the trans conformation. The different shape of the resultant all-trans-retinal causes conformational changes in the protein to which it is bound. These changes cause an electrical signal to be transmitted to the brain.

**QUESTION** What is the hybridization of the eleventh and twelfth carbon atoms in retinal?



ANSWER NOW!

**11.10**  
**Cc**  
Conceptual Connection



These two forms of 1,2-dichloroethene are different compounds with different properties. We distinguish between them with the designations *cis* (meaning “same side”) and *trans* (meaning “opposite sides”). Compounds such as these, with the same molecular formula but different structures or different spatial arrangement of atoms, are called *isomers*. Nature can—and does—make different compounds out of the same atoms by arranging the atoms in different ways. Isomerism is common throughout chemistry and is especially important in organic chemistry, as we will discuss in Chapter 22.

**SINGLE AND DOUBLE BONDS** In Section 10.10, we learned that double bonds are stronger and shorter than single bonds. For example, a C—C single bond has an average bond energy of 347 kJ/mole, whereas a C=C double bond has an average bond energy of 611 kJ/mole. According to valence bond theory, why is a double bond *not* simply twice as strong as a single bond?

- (a) Because according to valence bond theory, a double bond is actually composed of two different kinds of bonds, one  $\sigma$  and one  $\pi$ .
- (b) Because according to valence bond theory, a double bond is the sharing of two electron pairs.
- (c) The C=C double bond is an exception. According to valence bond theory, a double bond is generally twice as strong as a single bond.

### sp Hybridization and Triple Bonds

Hybridization of one s and one p orbital results in two *sp* hybrid orbitals and two leftover unhybridized p orbitals:

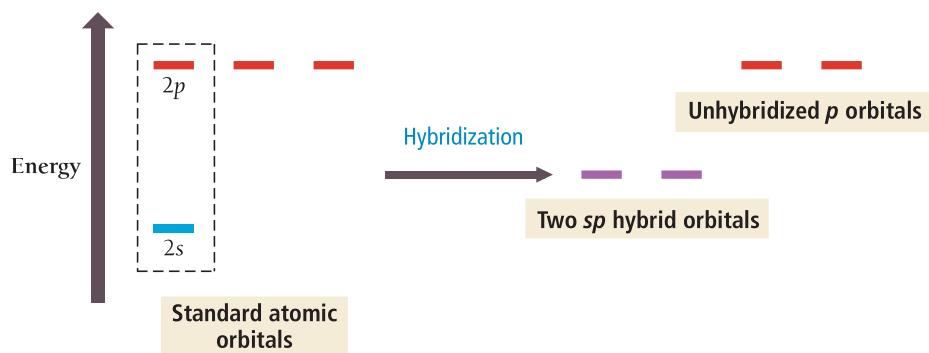
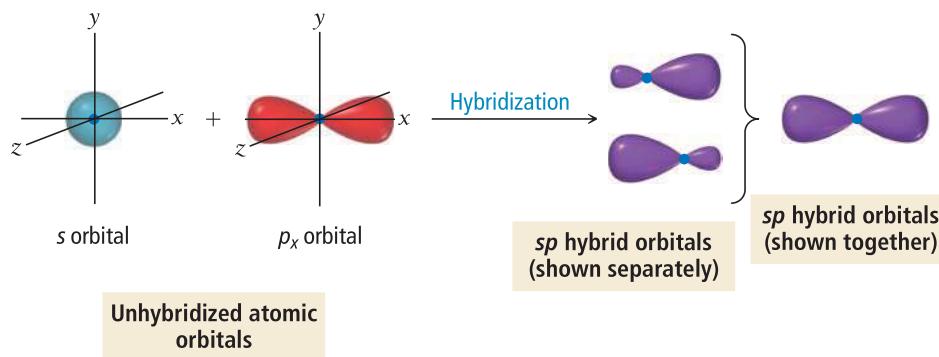


Figure 11.10 shows the shapes of the *sp* hybrid orbitals. Notice that the two *sp* hybrid orbitals are arranged in a linear geometry with a 180° angle between them. The unhybridized *p* orbitals are oriented in the plane that is perpendicular to the hybridized *sp* orbitals.

### Formation of *sp* Hybrid Orbitals

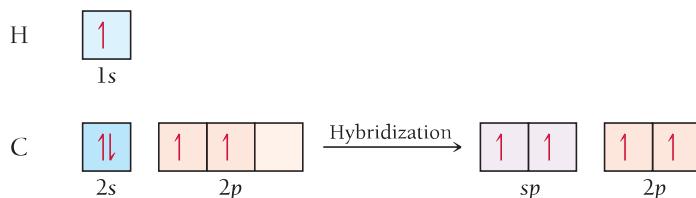
One *s* orbital and one *p* orbital combine to form two *sp* orbitals.



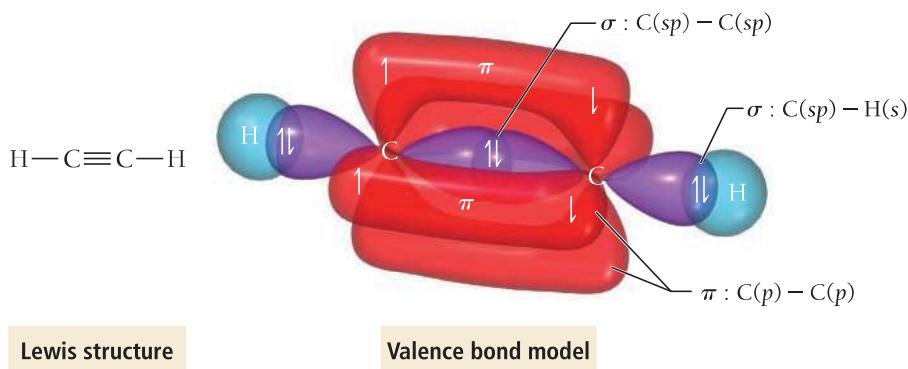
◀ FIGURE 11.10

**sp Hybridization** When *sp* hybrid orbitals form, two *p* orbital (not shown) remain unhybridized.

The acetylene molecule, HC≡CH, has *sp* hybrid orbitals. The four valence electrons of carbon distribute themselves among the two *sp* hybrid orbitals and the two *p* orbitals:



Each carbon atom then has four half-filled orbitals and can form four bonds: one with a hydrogen atom and three (a triple bond) with the other carbon atom. We draw the molecule and the overlapping orbitals as follows:



Notice that the triple bond between the two carbon atoms consists of two  $\pi$  bonds (overlapping  $p$  orbitals) and one  $\sigma$  bond (overlapping  $sp$  orbitals). The  $sp$  orbitals on the carbon atoms are linear with  $180^\circ$  between them, so the resulting geometry of each carbon on the molecule is linear with  $180^\circ$  bond angles, in agreement with the experimentally measured geometry of  $\text{HC}\equiv\text{CH}$ , and also in agreement with the prediction of VSEPR theory.

ANSWER NOW!

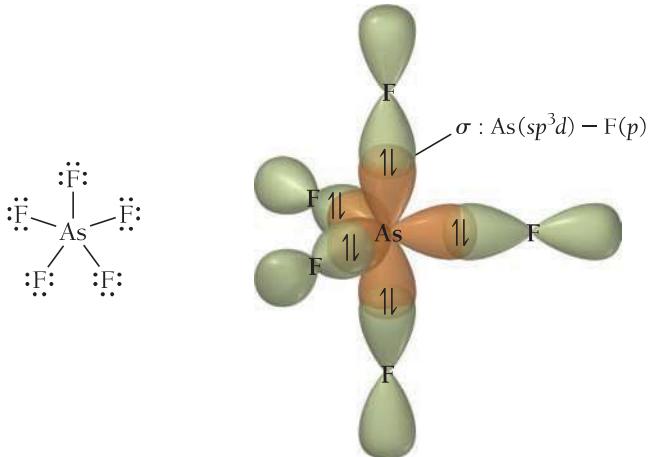
## 11.11


**Cc**  
Conceptual Connection
**HYBRIDIZATION** What is the hybridization of C in  $\text{CO}_2$ ?

- (a)  $sp$   
 (b)  $sp^2$   
 (c)  $sp^3$

 **$sp^3d$  and  $sp^3d^2$  Hybridization**

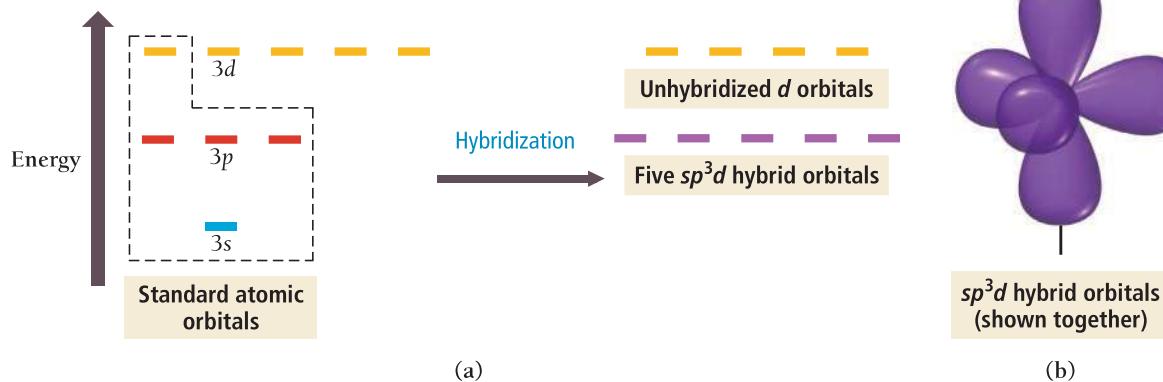
Recall that, according to the Lewis model, elements occurring in the third row of the periodic table (or below) can exhibit expanded octets (see Section 10.9). The equivalent concept in valence bond theory is hybridization involving the  $d$  orbitals. For third-period elements, the  $3d$  orbitals are involved in hybridization because their energies are close to the energies of the  $3s$  and  $3p$  orbitals. The hybridization of one  $s$  orbital, three  $p$  orbitals, and one  $d$  orbital results in  $sp^3d$  hybrid orbitals (Figure 11.11(a)▼). The five  $sp^3d$  hybrid orbitals have a trigonal bipyramidal arrangement (Figure 11.11(b)▼). As an example of  $sp^3d$  hybridization, consider arsenic pentafluoride,  $\text{AsF}_5$ . The arsenic atom bonds to five fluorine atoms by overlap between the  $sp^3d$  hybrid orbitals on arsenic and  $p$  orbitals on the fluorine atoms, as shown here:

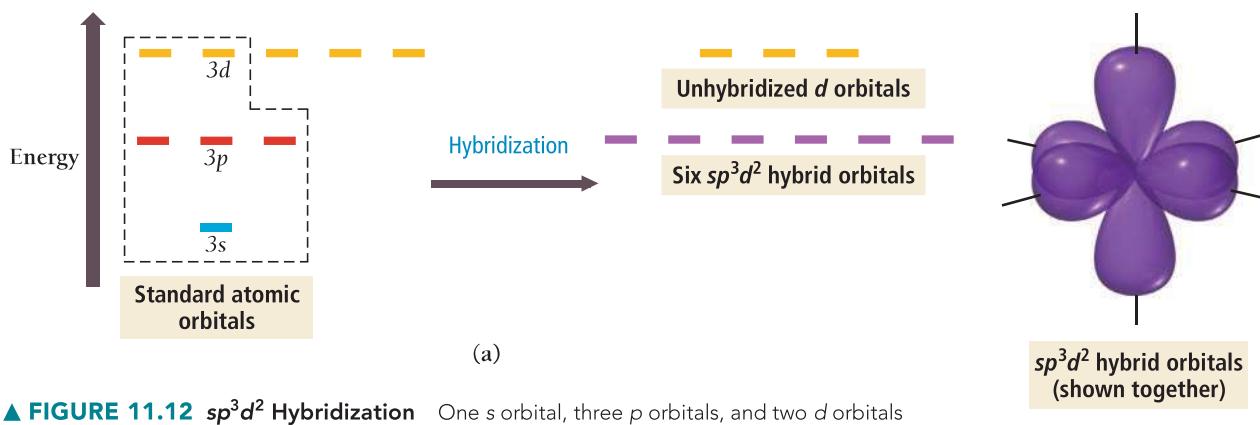
▼ FIGURE 11.11  $sp^3d$ 

**Hybridization** One  $s$  orbital, three  $p$  orbitals, and one  $d$  orbital combine to form five  $sp^3d$  hybrid orbitals.

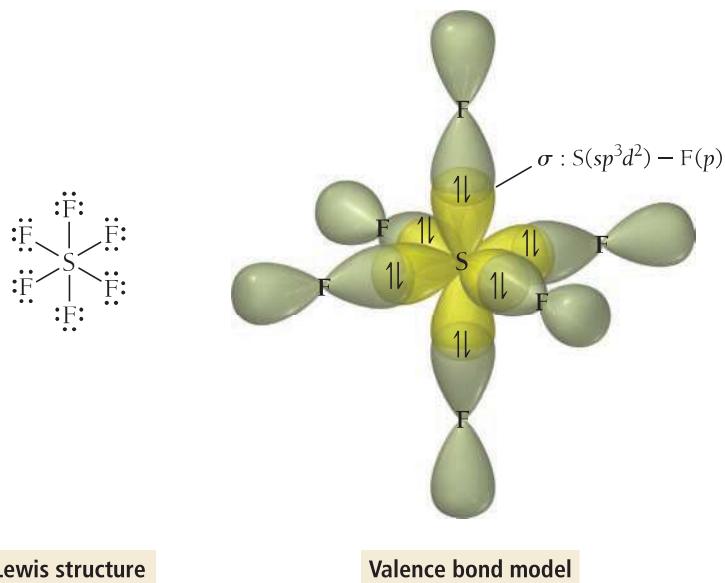
**Lewis structure****Valence bond model**

The  $sp^3d$  orbitals on the arsenic atom are trigonal bipyramidal, so the molecular geometry is trigonal bipyramidal.





The hybridization of one *s* orbital, three *p* orbitals, and *two d* orbitals results in  $sp^3d^2$  hybrid orbitals (Figure 11.12(a)▲). The six  $sp^3d^2$  hybrid orbitals have an octahedral geometry (Figure 11.12(b)▲). As an example of  $sp^3d^2$  hybridization, consider sulfur hexafluoride, SF<sub>6</sub>. The sulfur atom bonds to six fluorine atoms by overlap between the  $sp^3d^2$  hybrid orbitals on sulfur and *p* orbitals on the fluorine atoms:



The  $sp^3d^2$  orbitals on the sulfur atom are octahedral, so the molecular geometry is octahedral, again in agreement with VSEPR theory and with the experimentally observed geometry.

## Writing Hybridization and Bonding Schemes

We have now studied examples of the five main types of atomic orbital hybridization. *But how do we know which hybridization scheme best describes the orbitals of a specific atom in a specific molecule?* In computational valence bond theory, the energy of the molecule is calculated using a computer; the degree of hybridization as well as the type of hybridization are varied to find the combination that gives the molecule the lowest overall energy. For our purposes, we can assign a hybridization scheme from the electron geometry—determined using VSEPR theory—of the central atom (or interior atoms) of

**TABLE 11.3 ■ Hybridization Scheme from Electron Geometry**

| Number of Electron Groups | Electron Geometry (from VSEPR Theory) | Hybridization Scheme |
|---------------------------|---------------------------------------|----------------------|
| 2                         | Linear                                | $sp$                 |
| 3                         | Trigonal planar                       | $sp^2$               |
| 4                         | Tetrahedral                           | $sp^3$               |
| 5                         | Trigonal bipyramidal                  | $sp^3d$              |
| 6                         | Octahedral                            | $sp^3d^2$            |

the molecule. The five VSEPR electron geometries and the corresponding hybridization schemes are shown in Table 11.3. For example, if the electron geometry of the central atom is tetrahedral, then the hybridization is  $sp^3$ , and if the electron geometry is octahedral, then the hybridization is  $sp^3d^2$ , and so on. Although this method of determining the hybridization scheme is not 100% accurate (for example, it predicts that  $H_2S$  should be  $sp^3$  when in fact  $H_2S$  is largely unhybridized), it is the best we can do without more complex computer-based calculations.

We are now ready to put the Lewis model and valence bond theory together to describe bonding in molecules. In the procedure and examples that follow, you will learn how to write a *hybridization and bonding scheme* for a molecule. This involves drawing the Lewis structure for the molecule, determining its geometry using VSEPR theory, determining the hybridization of the interior atoms, drawing the molecule with its overlapping orbitals, and labeling each bond with the  $\sigma$  and  $\pi$  notation followed by the type of overlapping orbitals. As you can see, this procedure involves virtually everything you have learned about bonding in this chapter and Chapter 10. The procedure for writing a hybridization and bonding scheme is shown in the left column, with two examples of how to apply the procedure in the columns to the right.

## HOW TO: Determine Hybridization and Bonding Schemes

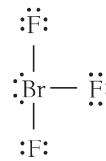
**1. Write the Lewis structure for the molecule.**

### EXAMPLE 11.6 Hybridization and Bonding Scheme

Write a hybridization and bonding scheme for bromine trifluoride,  $\text{BrF}_3$ .

**SOLUTION**

$\text{BrF}_3$  has 28 valence electrons and the following Lewis structure:

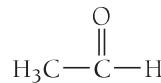


**2. Use VSEPR theory to predict the electron geometry about the central atom (or interior atoms).**

The bromine atom has five electron groups and therefore has a trigonal bipyramidal electron geometry.

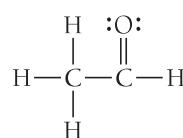
### EXAMPLE 11.7 Hybridization and Bonding Scheme

Write a hybridization and bonding scheme for acetaldehyde,



**SOLUTION**

Acetaldehyde has 18 valence electrons and the following Lewis structure:

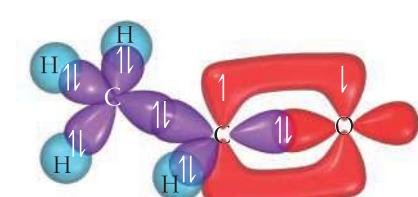
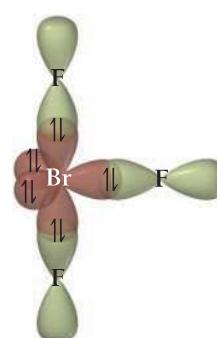


**3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (see Table 11.3).**

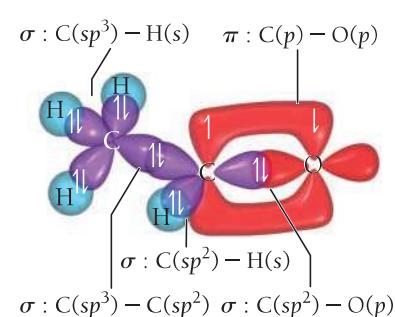
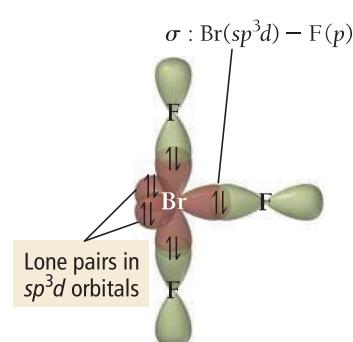
A trigonal bipyramidal electron geometry corresponds to  $sp^3d$  hybridization.

The leftmost carbon atom is  $sp^3$  hybridized, and the rightmost carbon atom is  $sp^2$  hybridized.

**4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms.**



**5. Label all bonds using  $\sigma$  or  $\pi$  notation followed by the type of overlapping orbitals.**



**FOR PRACTICE 11.6** Write the hybridization and bonding scheme for  $\text{XeF}_4$ .

**FOR PRACTICE 11.7** Write the hybridization and bonding scheme for HCN.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 11.8

**EXAMPLE 11.8** Hybridization and Bonding SchemeUse valence bond theory to write a hybridization and bonding scheme for ethene,  $\text{H}_2\text{C}=\text{CH}_2$ .**SOLUTION**

|   |  |
|---|--|
| 1. Write the Lewis structure for the molecule.  | $\begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & =\text{C}-\text{H} \end{array}$  |
| 2. Apply VSEPR theory to predict the electron geometry about the central atom (or interior atoms).  | The molecule has two interior atoms. Because each atom has three electron groups (one double bond and two single bonds), the electron geometry about each atom is trigonal planar. |
| 3. Select the correct hybridization for the central atom (or interior atoms) based on the electron geometry (see Table 11.3).               | A trigonal planar geometry corresponds to $sp^2$ hybridization.  |
| 4. Sketch the molecule, beginning with the central atom and its orbitals. Show overlap with the appropriate orbitals on the terminal atoms. |  |
| 5. Label all bonds using $\sigma$ or $\pi$ notation followed by the type of overlapping orbitals.   |  |

**FOR PRACTICE 11.8** Use valence bond theory to write a hybridization and bonding scheme for  $\text{CO}_2$ .**FOR MORE PRACTICE 11.8** What is the hybridization of the central iodine atom in  $\text{I}_3^-$ ?

## 11.8 Molecular Orbital Theory: Electron Delocalization

Valence bond theory can explain many aspects of chemical bonding—such as the rigidity of a double bond—but it also has limitations. In valence bond theory, we treat electrons as if they reside in the quantum-mechanical orbitals that we calculated *for atoms*. This is a significant oversimplification that we partially compensate for by hybridization. Nevertheless, we can do better.

In Chapter 8, we stated that the mathematical derivation of energies and orbitals for electrons *in atoms* comes from solving the Schrödinger equation for the atom of

interest. For a molecule, we can theoretically do the same thing. The resulting orbitals would be the actual *molecular* orbitals of the molecule as a whole (in contrast to valence bond theory, in which the orbitals are those of individual atoms). As it turns out, however, solving the Schrödinger equation exactly for even the simplest molecules is impossible without making some approximations.

In **molecular orbital (MO) theory**, we do not actually solve the Schrödinger equation for a molecule directly. Instead, we use a trial function, an “educated guess” as to what the solution might be. In other words, rather than mathematically solving the Schrödinger equation, which would give us a mathematical function describing an orbital, we start with a trial mathematical function for the orbital. We then test the trial function to see how well it “works.”

We can understand this process by analogy to solving an algebraic equation. Suppose we want to know  $x$  in the equation  $4x + 5 = 70$  without actually solving the equation. For an easy equation like this one, we might first estimate that  $x = 16$ . We can then determine how well our estimate works by substituting  $x = 16$  into the equation. If the estimate did not work, we could try again until we found the right value of  $x$ . (In this case, we can quickly see that  $x$  must be a little more than 16.)

In MO theory, the estimating procedure is analogous. However, we need to add one more important concept to get at the heart of MO theory. In order to determine how well a trial function for an orbital “works” in MO theory, we calculate its energy. No matter how good our trial function, *we can never do better than nature at minimizing the energy of the orbital*. In other words, we can devise any trial function for an orbital in a molecule and calculate its energy. The energy we calculate for the devised orbital will always be greater than or (at best) equal to the energy of the actual orbital.

How does this help us? The best possible orbital is therefore the one with the minimum energy. In modern MO theory, computer programs are designed to try many different variations of a guessed orbital and compare the energies of each one. The variation with the lowest energy is the best approximation for the actual molecular orbital.

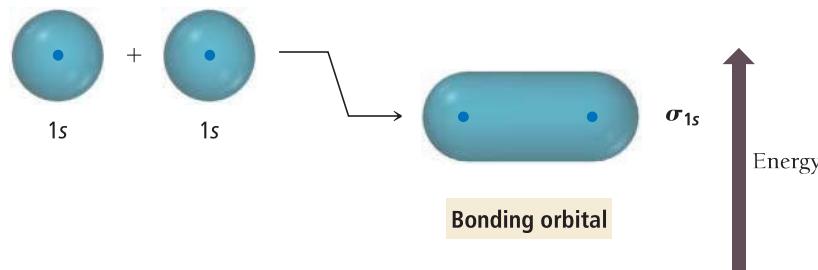
Molecular orbital theory is a specific application of a more general quantum-mechanical approximation technique called the variational method. In the variational method, the energy of a trial function within the Schrödinger equation is minimized.

We calculate the energy of an estimated orbital by substituting it into the Schrödinger equation and solving for the energy.

## Linear Combination of Atomic Orbitals (LCAOs)

The simplest trial functions that work reasonably well in MO theory turn out to be linear combinations of atomic orbitals, or LCAOs. An LCAO molecular orbital is a *weighted linear sum—analogous to a weighted average—of the valence atomic orbitals* of the atoms in the molecule. At first glance, this concept might seem very similar to that of hybridization in valence bond theory. However, in valence bond theory, hybrid orbitals are weighted linear sums of the valence atomic orbitals of a *particular atom*, and the hybrid orbitals remain *localized* on that atom. In MO theory, the molecular orbitals are weighted linear sums of the valence atomic orbitals of *all the atoms* in a molecule, and many of the molecular orbitals are *delocalized* over the entire molecule.

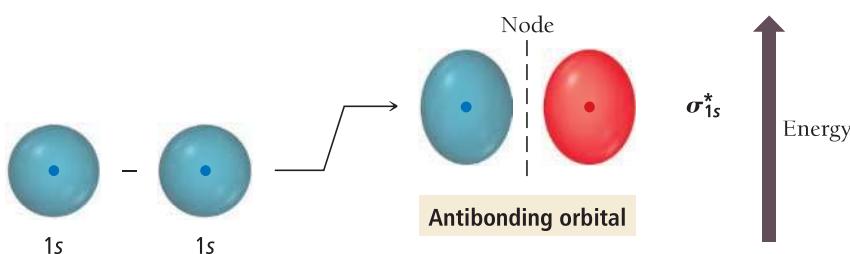
Consider the  $\text{H}_2$  molecule. One of the molecular orbitals for  $\text{H}_2$  is simply an equally weighted sum of the 1s orbital from one atom and the 1s orbital from the other. We represent this pictorially and energetically as follows:



When molecular orbitals are calculated mathematically, it is actually the wave *functions* corresponding to the orbitals that are combined.

The name of this molecular orbital is  $\sigma_{1s}$ . The  $\sigma$  comes from the shape of the orbital, which looks like a  $\sigma$  bond in valence bond theory, and the  $1s$  comes from its formation by a linear sum of  $1s$  orbitals. The  $\sigma_{1s}$  orbital is lower in energy than either of the two  $1s$  atomic orbitals from which it was formed. For this reason, this orbital is called a **bonding orbital**. When electrons occupy bonding molecular orbitals, the energy of the electrons is lower than it would be if they were occupying atomic orbitals.

We can think of a molecular orbital in a molecule in much the same way that we think about an atomic orbital in an atom. Electrons seek the lowest energy molecular orbital available, but just as an atom has more than one atomic orbital (and some may be empty), a molecule has more than one molecular orbital (and some may be empty). The next molecular orbital of  $H_2$  is approximated by summing the  $1s$  orbital on one hydrogen atom with the *negative* (opposite phase) of the  $1s$  orbital on the other hydrogen atom:

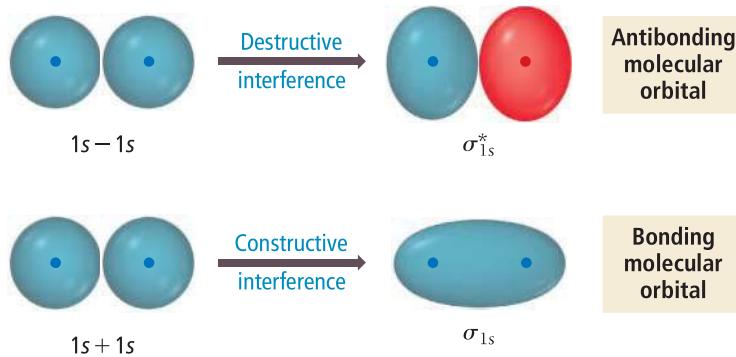


The different phases of the orbitals result in *destructive interference* between them. The resulting molecular orbital therefore has a node between the two atoms. The different colors (red and blue) on either side of the node represent the different phases of the orbital (see Section 8.6). The name of this molecular orbital is  $\sigma_{1s}^*$ . The star indicates that this orbital is an **antibonding orbital**. Electrons in antibonding orbitals have higher energies than they did in their respective atomic orbitals and therefore tend to raise the energy of the system (relative to the unbonded atoms).

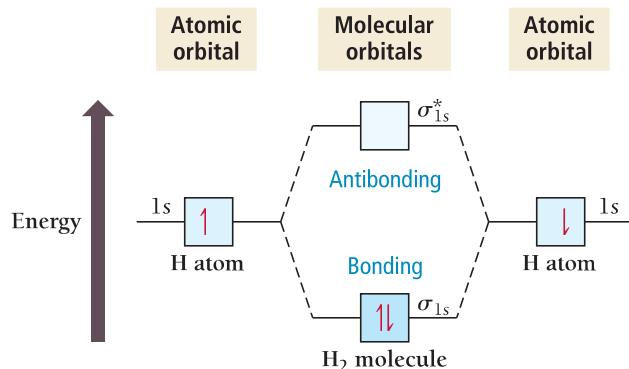
In general, when two atomic orbitals are added together to form molecular orbitals, one of the resultant molecular orbitals is lower in energy (the bonding orbital) than the atomic orbitals and the other is higher in energy (the antibonding orbital). Remember that electrons in orbitals behave like waves. The bonding molecular orbital arises out of constructive interference between the overlapping atomic orbitals because both orbitals have the same phase. The antibonding orbital arises out of destructive interference between the overlapping atomic orbitals because *subtracting* one from the other means the two interacting orbitals have opposite phases (Figure 11.13▼).

For this reason, the bonding orbital has an increased electron density in the internuclear region, whereas the antibonding orbital has a node in the internuclear region. Bonding orbitals have greater electron density in the internuclear region, thereby lowering their energy compared to the orbitals in nonbonded atoms. Antibonding orbitals have less electron density in the internuclear region, and their energies are generally higher than in the orbitals of nonbonded atoms.

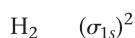
**► FIGURE 11.13** Formation of Bonding and Antibonding Orbitals Constructive interference between two atomic orbitals gives rise to a molecular orbital that is lower in energy than the atomic orbitals. This is the bonding orbital. Destructive interference between two atomic orbitals gives rise to a molecular orbital that is higher in energy than the atomic orbitals. This is the antibonding orbital.



We put all of this together in the molecular orbital energy diagram for H<sub>2</sub>:



We can represent the molecular orbital energy diagram with a molecular orbital electron configuration (which is analogous to the electron configurations we wrote for elements in Section 9.3):



In this notation, the  $\sigma_{1s}$  represents the molecular orbital, and the superscript 2 represents the two electrons in the orbital.

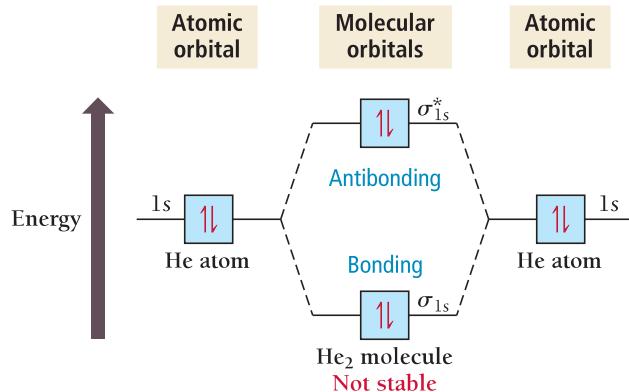
The molecular orbital energy diagram shows that two hydrogen atoms can lower their overall energy by forming H<sub>2</sub> because the electrons can move from higher-energy atomic orbitals into the lower-energy  $\sigma_{1s}$  bonding molecular orbital. In MO theory, we define the **bond order** of a diatomic molecule such as H<sub>2</sub> as follows:

$$\text{Bond order} = \frac{(\text{number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

For H<sub>2</sub>, the bond order is 1:

$$\text{H}_2 \text{ bond order} = \frac{2 - 0}{2} = 1$$

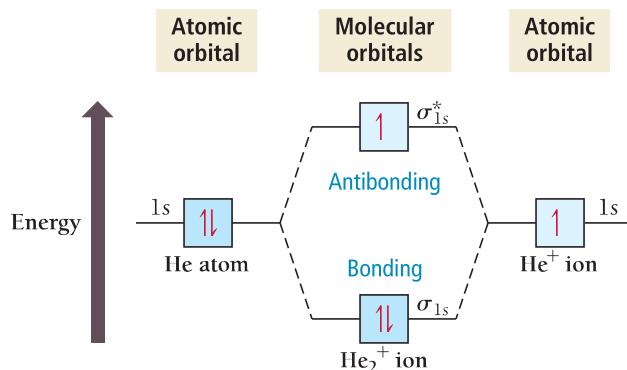
A positive bond order means that there are more electrons in bonding molecular orbitals than in antibonding molecular orbitals. The electrons therefore have lower energy than they did in the orbitals of the isolated atoms, and a chemical bond forms. In general, the higher the bond order, the stronger the bond. A negative or zero bond order indicates that a bond does *not* form between the atoms. For example, consider the MO diagram for He<sub>2</sub>:



Notice that the two additional electrons must go into the higher-energy antibonding orbital. There is no net stabilization by joining two helium atoms to form a helium molecule, as indicated by the bond order:

$$\text{He}_2 \text{ bond order} = \frac{2 - 2}{2} = 0$$

So according to MO theory,  $\text{He}_2$  should not exist as a stable molecule, and in fact it does not. Another interesting case is the helium–helium ion,  $\text{He}_2^+$ , with the following MO diagram:



The bond order is  $\frac{1}{2}$ , indicating that  $\text{He}_2^+$  should exist, and indeed it does.

#### Summarizing LCAO-MO Theory:

- We can approximate MOs as a linear combination of atomic orbitals (AOs). The total number of MOs formed from a particular set of AOs always equals the number of AOs in the set.
- When two AOs combine to form two MOs, one MO is lower in energy (the bonding MO) and the other is higher in energy (the antibonding MO).
- When assigning the electrons of a molecule to MOs, fill the lowest energy MOs first with a maximum of two spin-paired electrons per orbital.
- When assigning electrons to two MOs of the same energy, follow Hund's rule—fill the orbitals singly first, with parallel spins, before pairing.
- The bond order in a diatomic molecule is the number of electrons in bonding MOs minus the number in antibonding MOs divided by two. Stable bonds are associated with a positive bond order (more electrons in bonding MOs than in antibonding MOs).

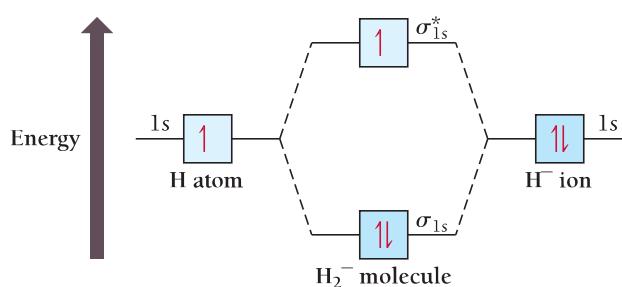
Notice the power of the molecular orbital approach. Every electron that enters a bonding molecular orbital stabilizes the molecule or polyatomic ion, and every electron that enters an antibonding molecular orbital destabilizes it. The emphasis on electron pairs has been removed. One electron in a bonding molecular orbital stabilizes half as much as two, so a bond order of one-half is nothing mysterious.

### EXAMPLE 11.9 Bond Order

Use MO theory to predict the bond order in  $\text{H}_2^-$ . Is the  $\text{H}_2^-$  bond a stronger or weaker bond than the  $\text{H}_2$  bond?

#### SOLUTION

The  $\text{H}_2^-$  ion has three electrons. Assign the three electrons to the molecular orbitals, filling lower-energy orbitals first and proceeding to higher-energy orbitals.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by two.

$$\text{H}_2^- \text{ bond order} = \frac{2 - 1}{2} = +\frac{1}{2}$$

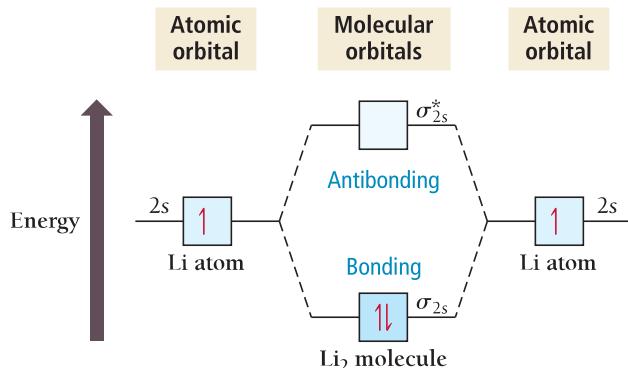
Since the bond order is positive,  $\text{H}_2^-$  should be stable. However, the bond order of  $\text{H}_2^-$  is lower than the bond order of  $\text{H}_2$  (which is 1); therefore, the bond in  $\text{H}_2^-$  is weaker than in  $\text{H}_2$ .

**FOR PRACTICE 11.9** Use MO theory to predict the bond order in  $\text{H}_2^+$ . Is the  $\text{H}_2^+$  bond a stronger or weaker bond than the  $\text{H}_2$  bond?

## Period Two Homonuclear Diatomic Molecules

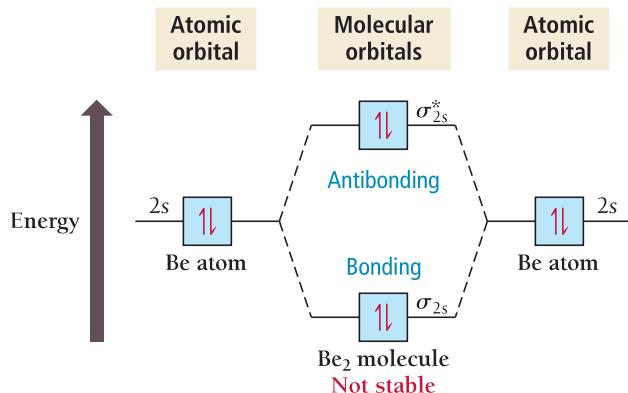
Homonuclear diatomic molecules (molecules made up of two atoms of the same kind) formed from second-period elements have between 2 and 16 valence electrons. To explain bonding in these molecules, we must consider the next set of higher-energy molecular orbitals, which can be approximated by linear combinations of the valence atomic orbitals of the period 2 elements.

We begin with  $\text{Li}_2$ . Even though lithium is normally a metal, we can use MO theory to predict whether or not the  $\text{Li}_2$  molecule should exist in the gas phase. We approximate the molecular orbitals in  $\text{Li}_2$  as linear combinations of the  $2s$  atomic orbitals. The resulting molecular orbitals look much like those of the  $\text{H}_2$  molecule. The MO diagram for  $\text{Li}_2$  therefore looks a lot like the MO diagram for  $\text{H}_2$ :



The core electrons can be ignored (as they are in other models for bonding) because these electrons are held too tightly to individual nuclei to contribute significantly to chemical bonding.

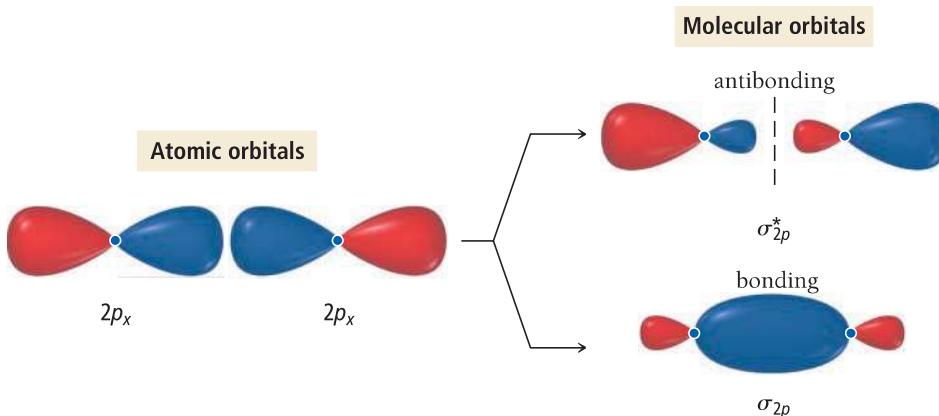
The two valence electrons of  $\text{Li}_2$  occupy a bonding molecular orbital. We would predict that the  $\text{Li}_2$  molecule is stable with a bond order of 1. Experiments confirm this prediction. In contrast, consider the MO diagram for  $\text{Be}_2$ :



The four valence electrons of  $\text{Be}_2$  occupy one bonding MO and one antibonding MO. The bond order is 0; we predict that  $\text{Be}_2$  should not be stable, which is again consistent with experimental findings.

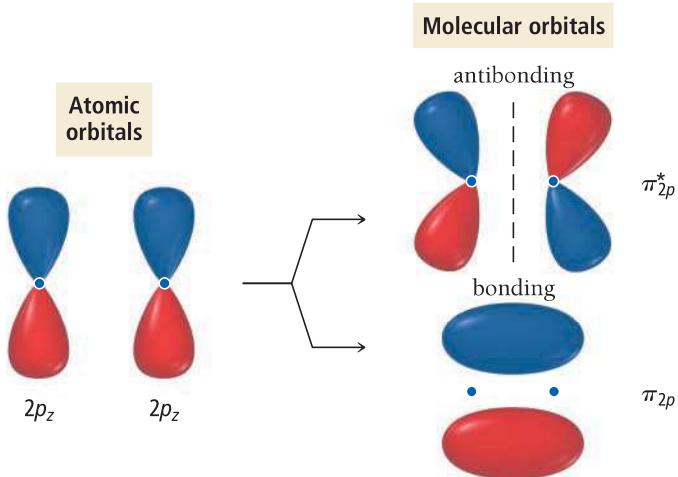
The next homonuclear molecule composed of second-row elements is  $\text{B}_2$ , which has six total valence electrons to accommodate. We can approximate the next

higher-energy molecular orbitals for  $B_2$  and the rest of the period 2 diatomic molecules as linear combinations of the  $2p$  orbitals taken pairwise. Since the three  $2p$  orbitals orient along three orthogonal axes, we must assign similar axes to the molecule. In this book, we assign the internuclear axis to be the  $x$  direction. Then we represent the LCAO-MOs that result from combining the  $2p_x$  orbitals—the ones that lie along the internuclear axis—from each atom as follows:



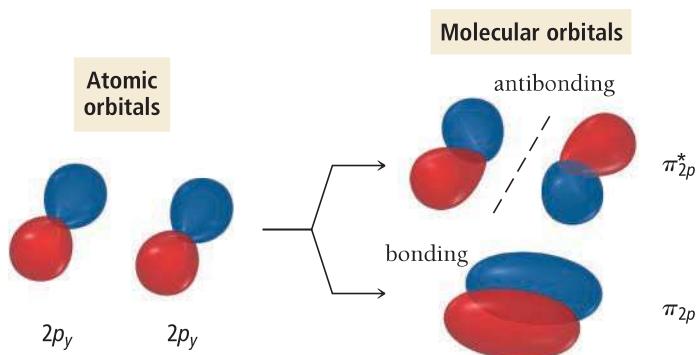
The bonding MO in this pair looks something like candy in a wrapper, with increased electron density in the internuclear region due to constructive interference between the two  $2p$  atomic orbitals. It has the characteristic  $\sigma$  shape (it is cylindrically symmetric about the bond axis) and is therefore called the  $\sigma_{2p}$  bonding orbital. The antibonding orbital, called  $\sigma^*_{2p}$ , has a node between the two nuclei (due to destructive interference between the two  $2p$  orbitals) and is higher in energy than either of the  $2p_x$  orbitals.

The LCAO-MOs that result from combining the  $2p_z$  orbitals from each atom are represented as follows:



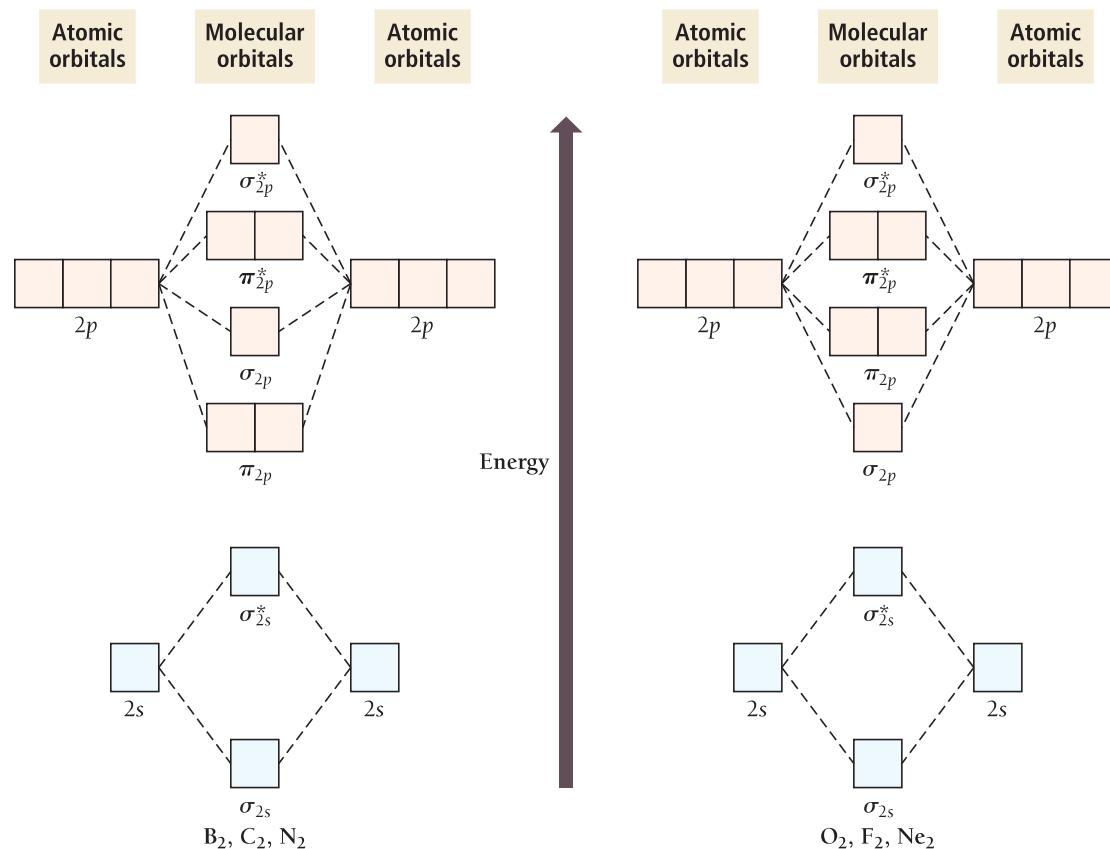
Notice that in this case the  $p$  orbitals are added together in a side-by-side orientation (in contrast to the  $2p_x$  orbitals, which were oriented end to end). The resultant molecular orbitals consequently have a different shape. The electron density in the bonding molecular orbital is above and below the internuclear axis with a nodal plane that includes the internuclear axis. This orbital resembles the electron density distribution of a  $\pi$  bond in valence bond theory. We call this orbital the  $\pi_{2p}$  orbital. The corresponding antibonding orbital has an additional node *between* the nuclei (perpendicular to the internuclear axis) and is called the  $\pi^*_{2p}$  orbital.

The LCAO–MOs that result from combining the  $2p_y$  orbitals from each atom are represented as follows:

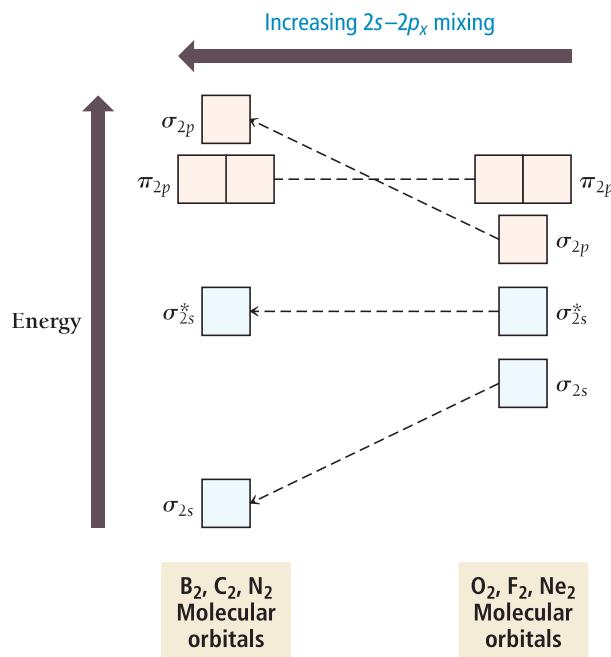


The only difference between the  $2p_y$  and the  $2p_z$  atomic orbitals is a  $90^\circ$  rotation about the internuclear axis. Consequently, the only difference between the resulting MOs is a  $90^\circ$  rotation about the internuclear axis. The energies and the names of the bonding and antibonding MOs obtained from the combination of the  $2p_y$  AOs are identical to those obtained from the combination of the  $2p_z$  AOs.

Before we can draw MO diagrams for  $B_2$  and the other second-period diatomic molecules, we must determine the relative energy ordering of the MOs obtained from the  $2p$  AO combinations. This is not a simple task. The relative ordering of MOs obtained from LCAO–MO theory is usually determined computationally. There is no single order that works for all molecules. For second-period diatomic molecules, computations reveal that the energy ordering for  $B_2$ ,  $C_2$ , and  $N_2$  is slightly different than that for  $O_2$ ,  $F_2$ , and  $Ne_2$  as follows:



▲ Molecular orbital energy diagrams for second-period diatomic molecules show that the energy ordering of the  $\pi_{2p}$  and  $\sigma_{2p}$  molecular orbitals can vary.



**▲ FIGURE 11.14** The Effects of  $2s$ - $2p_x$  Mixing The degree of mixing between two orbitals decreases with increasing energy difference between them. Mixing of the  $2s$  and  $2p_x$  orbitals is therefore greater in  $B_2$ ,  $C_2$ , and  $N_2$  than in  $O_2$ ,  $F_2$ , and  $Ne_2$  because in B, C, and N the energy levels of the atomic orbitals are more closely spaced than in O, F, and Ne. This mixing produces a change in energy ordering for the  $\pi_{2p}$  and  $\sigma_{2p}$  molecular orbitals.

**► FIGURE 11.15** Molecular Orbital Energy Diagrams for Second-Row  $p$ -block Homonuclear Diatomic Molecules

|                      | Large $2s$ - $2p_x$ interaction |       |       | Small $2s$ - $2p_x$ interaction |       |        |
|----------------------|---------------------------------|-------|-------|---------------------------------|-------|--------|
|                      | $B_2$                           | $C_2$ | $N_2$ | $O_2$                           | $F_2$ | $Ne_2$ |
| $\sigma_{2p}^*$      | 1                               | 1     | 1     | 1                               | 1     | 1      |
| $\pi_{2p}^*$         | 2                               | 2     | 2     | 2                               | 2     | 2      |
| $\sigma_{2p}$        | 1                               | 1     | 1     | 1                               | 1     | 1      |
| $\pi_{2p}$           | 1                               | 1     | 1     | 1                               | 1     | 1      |
| $\sigma_{2s}^*$      | 1                               | 1     | 1     | 1                               | 1     | 1      |
| $\sigma_{2s}$        | 1                               | 1     | 1     | 1                               | 1     | 1      |
| Bond order           | 1                               | 2     | 3     | 2                               | 1     | 0      |
| Bond energy (kJ/mol) | 290                             | 620   | 946   | 498                             | 159   | —      |
| Bond length (pm)     | 159                             | 131   | 110   | 121                             | 143   | —      |

ANSWER NOW!



## 11.12 Cc

Conceptual Connection

**BOND ORDER** What is the bond order for a second-period diatomic molecule containing three electrons in antibonding molecular orbitals and six electrons in bonding molecular orbitals?

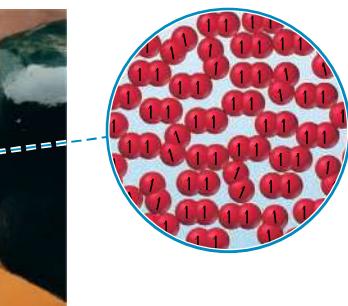
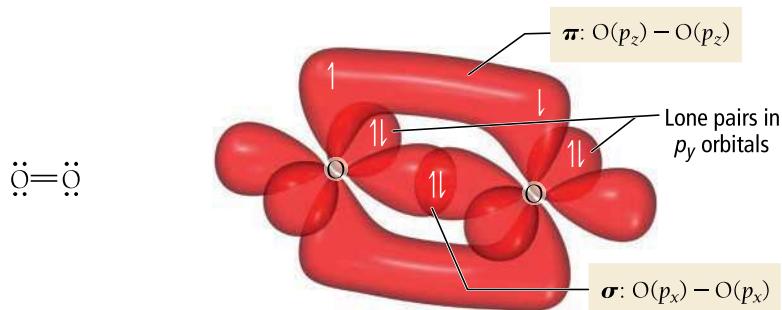
- (a) 1      (b) 1.5      (c) 2      (d) 2.5

The difference in energy ordering can only be explained by revisiting our LCAO-MO model. In our simplified treatment, we assumed that the MOs that result from the second-period AOs could be calculated pairwise. In other words, we took the linear combination of a  $2s$  from one atom with the  $2s$  from another, a  $2p_x$  from one atom with a  $2p_x$  from the other, and so on. However, in a more comprehensive treatment, the MOs are formed from linear combinations that include all of the AOs that are relatively close to each other in energy and of the correct symmetry. Specifically, in a more detailed treatment, the two  $2s$  orbitals and the two  $2p_x$  orbitals should all be combined to form a total of four molecular orbitals. The extent to which we include this type of mixing affects the energy levels of the corresponding MOs, as shown in Figure 11.14◀. The bottom line is that  $s$ - $p$  mixing is significant in  $B_2$ ,  $C_2$ , and  $N_2$  but not in  $O_2$ ,  $F_2$ , and  $Ne_2$ . The result of the mixing is a different energy ordering for some of these diatomic molecules.

Figure 11.15▼ shows the MO energy diagrams for the rest of the second-period homonuclear diatomic molecules, as well as their bond orders, bond energies, and bond lengths. Notice that as bond order increases, the bond gets stronger (greater bond energy) and shorter (smaller bond length). For  $B_2$ , with six electrons, the bond order is 1. For  $C_2$ , the bond order is 2, and for  $N_2$ , the bond order reaches a maximum with a value of 3. Recall that the Lewis structure for  $N_2$  has a triple bond, so both the Lewis model and MO theory predict a strong bond for  $N_2$ , which is experimentally observed.

In  $O_2$ , the two additional electrons occupy antibonding orbitals and the bond order is 2. These two electrons are unpaired—they occupy the  $\pi_{2p}^*$  orbitals *singly with parallel spins*, as indicated by Hund's rule. The presence of unpaired electrons in the molecular orbital diagram of oxygen is significant because oxygen is known from experiment to be *paramagnetic*—it is attracted to a magnetic field (see Section 9.7). The paramagnetism of oxygen can be demonstrated by suspending liquid oxygen between the poles of a magnet. This magnetic property is the direct result of *unpaired electrons*, whose spin and movement around the nucleus (more accurately known as orbital angular momentum) generate tiny magnetic fields. When a paramagnetic substance is placed in an external magnetic field, the magnetic fields of each atom or molecule align with the external field, creating the attraction (much as two magnets attract each other when properly oriented). In contrast, when the electrons in an atom or molecule are all *paired*, the magnetic fields caused by electron spin and orbital angular momentum tend to cancel each other, resulting in diamagnetism. A *diamagnetic* substance is not attracted to a magnetic field (and is, in fact, slightly repelled).

In the Lewis structure of  $O_2$ , as well as in the valence bond model of  $O_2$ , all of the electrons seem to be paired:



▲ Liquid oxygen can be suspended between the poles of a magnet because it is paramagnetic. It contains unpaired electrons (depicted here in the inset) that generate tiny magnetic fields, which align with and interact with the external field.

The s orbital on each oxygen atom contains two electrons, but for clarity neither the s orbitals nor the electrons that occupy them are shown.

In the MO diagram for  $O_2$ , however, we can see the unpaired electrons. MO theory is the more powerful theory in that it can account for the paramagnetism of  $O_2$ —it gives us a picture of bonding that more closely corresponds to what we see in experiments. Continuing along the second-row homonuclear diatomic molecules, we see that  $F_2$  has a bond order of 1 and  $Ne_2$  has a bond order of 0, again consistent with experiment since  $F_2$  exists and  $Ne_2$  does not.

#### WATCH NOW!

#### INTERACTIVE WORKED EXAMPLE 11.10

### EXAMPLE 11.10 Molecular Orbital Theory



Draw an MO energy-level diagram and determine the bond order for the  $N_2^-$  ion. Do you expect the bond in the  $N_2^-$  ion to be stronger or weaker than the bond in the  $N_2$  molecule? Is  $N_2^-$  diamagnetic or paramagnetic?

#### SOLUTION

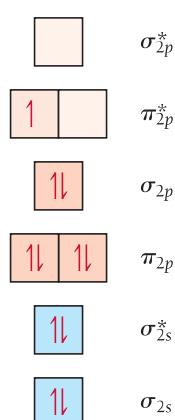
Write an energy-level diagram for the molecular orbitals in  $N_2^-$ . Use the energy ordering for  $N_2$ .

|  |                 |
|--|-----------------|
|  | $\sigma_{2p}^*$ |
|  | $\pi_{2p}^*$    |
|  | $\sigma_{2p}$   |
|  | $\pi_{2p}$      |
|  | $\sigma_{2s}^*$ |
|  | $\sigma_{2s}$   |

—Continued on the next page

*Continued—*

The  $\text{N}_2^-$  ion has 11 valence electrons (five for each nitrogen atom plus one for the negative charge). Assign the electrons to the molecular orbitals beginning with the lowest energy orbitals and following Hund's rule.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by 2.

$$\text{N}_2^- \text{ bond order} = \frac{8 - 3}{2} = +2.5$$

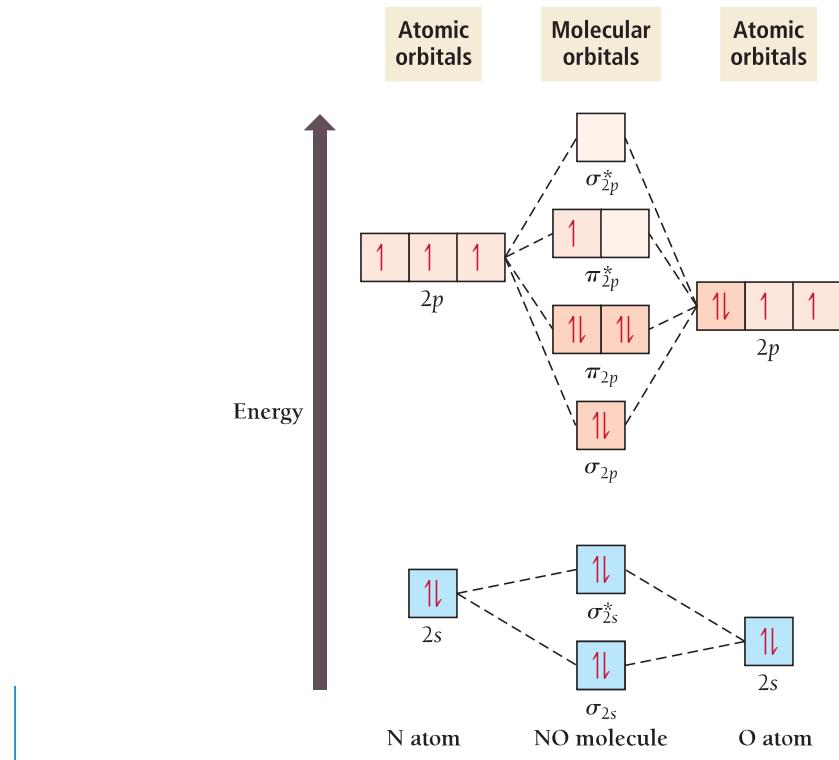
The bond order is 2.5, which is a lower bond order than in the  $\text{N}_2$  molecule (bond order = 3); therefore, the bond is weaker. The MO diagram shows that the  $\text{N}_2^-$  ion has one unpaired electron and is therefore paramagnetic.

**FOR PRACTICE 11.10** Draw an MO energy diagram and determine the bond order for the  $\text{N}_2^+$  ion. Do you expect the bond in the  $\text{N}_2^+$  ion to be stronger or weaker than the bond in the  $\text{N}_2$  molecule? Is  $\text{N}_2^+$  diamagnetic or paramagnetic?

**FOR MORE PRACTICE 11.10** Apply MO theory to determine the bond order of  $\text{Ne}_2$ .

## Second-Period Heteronuclear Diatomic Molecules

We can also apply MO theory to heteronuclear diatomic molecules (two different atoms). For example, we can draw an MO diagram for NO as follows:

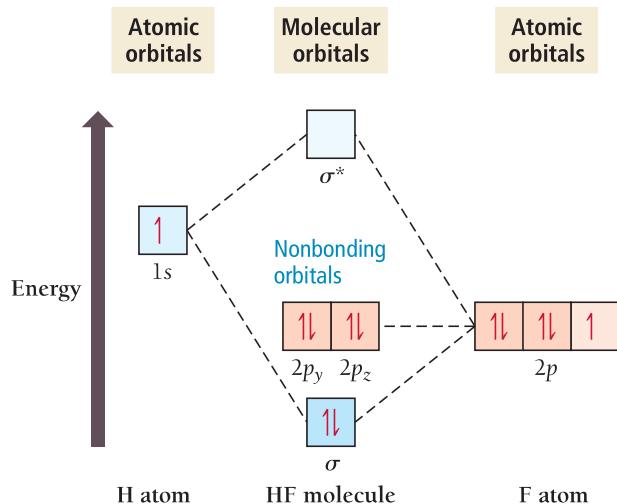


A given orbital will have lower energy in a more electronegative atom. For this reason, electronegative atoms have the ability to attract electrons to themselves.

Oxygen is more electronegative than nitrogen, so its atomic orbitals are lower in energy than nitrogen's atomic orbitals. When two atomic orbitals are identical and of equal energy, the weighting of each orbital in forming a molecular orbital is identical.

However, when two atomic orbitals are different, the weighting of each orbital in forming a molecular orbital may be different. More specifically, when a molecular orbital is approximated as a linear combination of atomic orbitals of different energies, the lower-energy atomic orbital makes a greater contribution to the bonding molecular orbital and the higher-energy atomic orbital makes a greater contribution to the antibonding molecular orbital. For example, notice that the  $\sigma_{2s}$  bonding orbital is closer in energy to the oxygen  $2s$  orbital than to the nitrogen  $2s$  orbital. We can also see this unequal weighting in the shape of the resultant molecular orbital, in which the electron density is concentrated on the oxygen atom, as shown in Figure 11.16►.

As another example of a heteronuclear diatomic molecule, consider the MO diagram for HF:



Fluorine is so electronegative that all of its atomic orbitals are lower in energy than hydrogen's atomic orbitals. In fact, fluorine's  $2s$  orbital is so low in energy compared to hydrogen's  $1s$  orbital that it does not contribute appreciably to the molecular orbitals. The molecular orbitals in HF are approximated by the linear combination of the fluorine  $2p_x$  orbital and the hydrogen  $1s$  orbital. The other  $2p$  orbitals remain localized on the fluorine and appear in the energy diagram as **nonbonding orbitals**. The electrons in the nonbonding orbitals remain localized on the fluorine atom.

### EXAMPLE 11.11

#### Molecular Orbital Theory Applied to Heteronuclear Diatomic Molecules and Ions

Use MO theory to determine the bond order of the  $\text{CN}^-$  ion. Is the ion paramagnetic or diamagnetic?

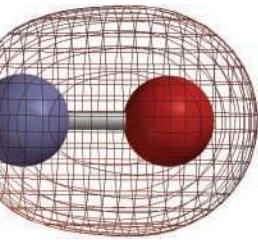
##### SOLUTION

Determine the number of valence electrons in the molecule or ion.

$$\begin{aligned} \text{Number of valence electrons} \\ = 4 \text{ (from C)} + 5 \text{ (from N)} + \\ 1 \text{ (from negative charge)} = 10 \end{aligned}$$

Write an energy-level diagram using Figure 11.15 as a guide. Fill the orbitals beginning with the lowest energy orbital and progressing upward until all electrons have been assigned to an orbital. Remember to allow no more than two electrons (with paired spins) per orbital and to fill degenerate orbitals with single electrons (with parallel spins) before pairing.

|  |                 |
|--|-----------------|
|  | $\sigma_{2p}^*$ |
|  | $\pi_{2p}^*$    |
|  | $\sigma_{2p}$   |
|  | $\pi_{2p}$      |
|  | $\sigma_{2s}^*$ |
|  | $\sigma_{2s}$   |



▲ FIGURE 11.16 Shape of  $\sigma_{2s}$  Bonding Orbital in NO The molecular orbital shows more electron density at the oxygen end of the molecule because the atomic orbitals of oxygen, the more electronegative element, are lower in energy than those of nitrogen. They therefore contribute more to the bonding molecular orbital.

—Continued on the next page

*Continued—*

Calculate the bond order using the appropriate formula:

$$\text{Bond order} = \frac{(\text{number of } e^- \text{ in bonding MOs}) - (\text{number of } e^- \text{ in antibonding MOs})}{2}$$

$$\text{CN}^- \text{ bond order} = \frac{8 - 2}{2} = +3$$

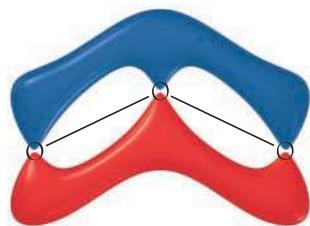
If the MO diagram has unpaired electrons, the molecule or ion is paramagnetic. If the electrons are all paired, the molecule or ion is diamagnetic.

The MO diagram has no unpaired electrons, so the ion is diamagnetic.

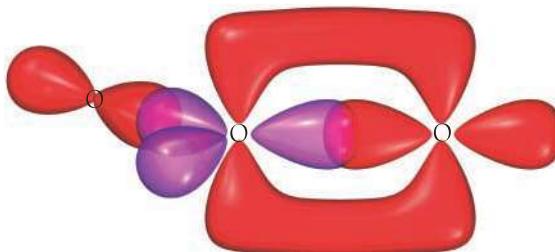
**FOR PRACTICE 11.11** Apply MO theory to determine the bond order of NO. (Use the energy ordering of O<sub>2</sub>.) Is the molecule paramagnetic or diamagnetic?

## Polyatomic Molecules

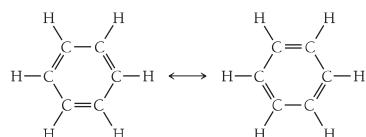
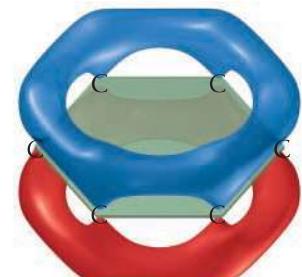
With the aid of computers, MO theory can be applied to polyatomic molecules and ions, yielding results that correlate very well with experimental measurements. These applications are beyond the scope of this text. However, the delocalization of electrons over an entire molecule is an important contribution of MO theory to our basic understanding of chemical bonding. For example, consider the Lewis structure and valence bond diagram of ozone:



Lewis structure



Valence bond model



In MO theory, the  $\pi$  molecular orbitals in benzene are formed from a linear combination of the six carbon  $2p$  orbitals and are delocalized over the entire molecule. The lowest energy  $\pi$  bonding molecular orbital is shown in the left margin.

Benzene is in fact a highly symmetric molecule with six identical carbon–carbon bonds. The best picture of the  $\pi$  electrons in benzene is one in which the electrons occupy roughly circular-shaped orbitals above and below the plane of the molecule, as depicted in the MO theory approach.

## WHAT IS A CHEMICAL BOND? PART II

What is a chemical bond according to MO theory?

- (a) According to MO theory, a chemical bond is the overlap between half-filled atomic orbitals.
- (b) According to MO theory, a chemical bond is a shared electron pair.
- (c) According to MO theory, atoms join together (or bond) when the electrons in the atoms can lower their energy by occupying the molecular orbitals of the resultant molecule.



ANSWER NOW!



QUIZ YOURSELF NOW!

## Self-Assessment Quiz

**Q1.** Determine the molecular geometry of  $\text{CBr}_4$ .**MISSED THIS?** Read Section 11.2; Watch KCV 11.2, IWE 11.1

- a) linear
- b) trigonal planar
- c) tetrahedral
- d) trigonal pyramidal

**Q2.** Determine the molecular geometry of  $\text{SeF}_4$ . **MISSED THIS?**

Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2

- a) tetrahedral
- b) trigonal bipyramidal
- c) T-shaped
- d) seesaw

**Q3.** Predict the relative bond angles in  $\text{BF}_3$  and  $\text{SO}_2$ . **MISSED THIS?**

Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2

- a)  $\text{BF}_3$  bond angles >  $\text{SO}_2$  bond angle
- b)  $\text{SO}_2$  bond angle >  $\text{BF}_3$  bond angles
- c)  $\text{BF}_3$  bond angles =  $\text{SO}_2$  bond angle
- d) Relative bond angles cannot be predicted.

**Q4.** Predict the molecular geometry about nitrogen in the molecule  $\text{CH}_3\text{NHCH}_3$ . **MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.4

- a) linear
- b) trigonal planar
- c) trigonal pyramidal
- d) bent

**Q5.** Which molecule is polar?**MISSED THIS?** Read Section 11.5; Watch KCV 11.5, IWE 11.5

- a)  $\text{SF}_2$
- b)  $\text{BH}_3$
- c)  $\text{PF}_5$
- d)  $\text{CS}_2$

**Q6.** Determine the hybridization about oxygen in  $\text{CH}_3\text{OH}$ .**MISSED THIS?** Read Sections 11.6, 11.7; Watch KCV 11.6, 11.7, IWE 11.8

- a)  $sp$
- b)  $sp^2$
- c)  $sp^3$
- d)  $sp^3d$

**Q7.** Determine the hybridization about carbon in  $\text{H}_2\text{CO}$ . **MISSED THIS?**

Read Sections 11.6, 11.7; Watch KCV 11.6, 11.7, IWE 11.8

- a)  $sp$
- b)  $sp^2$
- c)  $sp^3$
- d)  $sp^3d$

**Q8.** According to valence bond theory, which kind of orbitals overlap to form the P—Cl bonds in  $\text{PCl}_5$ ? **MISSED THIS?**

Read Sections 11.6, 11.7; Watch KCV 11.6, 11.7, IWE 11.8

- a)  $\text{P}(sp^3)\text{-Cl}(p)$
- b)  $\text{P}(sp^3d)\text{-Cl}(s)$
- c)  $\text{P}(sp^3)\text{-Cl}(s)$
- d)  $\text{P}(sp^3d)\text{-Cl}(p)$

**Q9.** Apply MO theory to determine the bond order in  $\text{C}_2$ .**MISSED THIS?** Read Section 11.8; Watch IWE 11.10

- a) 0
- b) 1
- c) 2
- d) 3

**Q10.** Apply MO theory to predict which species has the strongest bond.**MISSED THIS?** Read Section 11.8; Watch IWE 11.10

- a)  $\text{N}_2$
- b)  $\text{N}_2^-$
- c)  $\text{N}_2^+$
- d) All bonds are equivalent according to MO theory.

**Q11.** Apply MO theory to determine which molecule is diamagnetic.**MISSED THIS?** Read Section 11.8; Watch IWE 11.10

- a)  $\text{CO}$
- b)  $\text{B}_2$
- c)  $\text{O}_2$
- d) None of the above (all are paramagnetic)

**Q12.** Which hybridization scheme occurs about nitrogen when nitrogen forms a double bond?**MISSED THIS?** Read Section 11.7; Watch KCV 11.7

- a)  $sp$
- b)  $sp^2$
- c)  $sp^3$
- d)  $sp^3d$

**Q13.** Which molecular geometry results when a central atom has five total electron groups, with three of those being bonding groups and two being lone pairs?**MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2

- a) trigonal bipyramidal
- b) seesaw
- c) T-shaped
- d) bent

**Q14.** Determine the correct molecular geometry (from left to right) about each interior atom in  $\text{CH}_3\text{CH}_2\text{OH}$ .**MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.4

- a) 1st C tetrahedral; 2nd C trigonal planar; O linear
- b) 1st C trigonal planar; 2nd C bent; O linear
- c) 1st C trigonal planar; 2nd C trigonal pyramidal; O bent
- d) 1st C tetrahedral; 2nd C tetrahedral; O bent

**Q15.** The central atom in a molecule has a bent molecular geometry. Determine the hybridization of the orbitals in the atom.**MISSED THIS?** Read Section 11.7; Watch KCV 11.7, IWE 11.4

- a)  $sp$
- b)  $sp^2$
- c)  $sp^3$
- d) Hybridization cannot be determined from the information given.

# CHAPTER 11 IN REVIEW

## TERMS

### Section 11.2

valence shell electron pair repulsion (VSEPR) theory (438)  
electron groups (438)  
linear geometry (439)  
trigonal planar geometry (439)  
tetrahedral geometry (440)  
trigonal bipyramidal geometry (441)  
octahedral geometry (441)

### Section 11.3

electron geometry (442)  
molecular geometry (442)  
trigonal pyramidal geometry (442)  
bent geometry (443)  
seesaw geometry (444)  
T-shaped geometry (444)  
square pyramidal geometry (445)  
square planar geometry (445)

### Section 11.6

valence bond theory (455)

### Section 11.7

hybridization (457)  
hybrid orbitals (457)  
pi ( $\pi$ ) bond (462)  
sigma ( $\sigma$ ) bond (462)

### Section 11.8

molecular orbital (MO) theory (471)  
bonding orbital (472)  
antibonding orbital (472)  
bond order (473)  
nonbonding orbitals (481)

## CONCEPTS

### Molecular Shape and VSEPR Theory (11.1–11.4)

- The properties of molecules are directly related to their shapes. In VSEPR theory, molecular geometries are determined by the repulsions between electron groups on the central atom. An electron group can be a single bond, double bond, triple bond, lone pair, or even a single electron.
- The five basic molecular shapes are linear (two electron groups), trigonal planar (three electron groups), tetrahedral (four electron groups), trigonal bipyramidal (five electron groups), and octahedral (six electron groups).
- When lone pairs are present on the central atom, the *electron* geometry is still one of the five basic shapes, but one or more positions are occupied by lone pairs. The *molecular* geometry is therefore different from the electron geometry. Lone pairs are positioned so as to minimize repulsions with other lone pairs and with bonding pairs.

### Polarity (11.5)

- The polarity of a polyatomic molecule containing polar bonds depends on its geometry. If the dipole moments of the polar bonds are aligned in such a way that they cancel one another, the molecule is not polar. If they are aligned in such a way as to sum together, the molecule is polar.
- Highly symmetric molecules tend to be nonpolar, whereas asymmetric molecules containing polar bonds tend to be polar. The polarity of a molecule dramatically affects its properties.

### Valence Bond Theory (11.6–11.7)

- In contrast to the Lewis model, in which a covalent chemical bond is the sharing of electrons represented by dots, in valence bond theory a chemical bond is the overlap of half-filled atomic orbitals (or in some cases the overlap between a completely filled orbital and an empty one).

- The overlapping orbitals may be the standard atomic orbitals, such as 1s or 2p, or they may be hybridized atomic orbitals, which are mathematical combinations of the standard orbitals on a single atom. The basic hybridized orbitals are  $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ , and  $sp^3d^2$ .
- The geometry of the molecule is determined by the geometry of the overlapping orbitals.
- In our treatment of valence bond theory, we use the electron geometry determined by VSEPR theory to determine the correct hybridization scheme.
- In valence bond theory, we distinguish between two types of bonds,  $\sigma$  (sigma) and  $\pi$  (pi). In a  $\sigma$  bond, the orbital overlap occurs in the region that lies directly between the two bonding atoms. In a  $\pi$  bond, formed from the side-by-side overlap of p orbitals, the overlap occurs above and below the region that lies directly between the two bonding atoms.
- Rotation about a  $\sigma$  bond is relatively free, whereas rotation about a  $\pi$  bond is restricted.

### Molecular Orbital Theory (11.8)

- The simplest molecular orbitals are linear combinations of atomic orbitals (LCAOs), weighted averages of the atomic orbitals of the different atoms in the molecule.
- When two atomic orbitals combine to form molecular orbitals, they form one molecular orbital of lower energy (the bonding orbital) and one of higher energy (the antibonding orbital).
- A set of molecular orbitals fills in much the same way as atomic orbitals.
- The stability of the molecule and the strength of the bond depend on the number of electrons in bonding orbitals compared to the number in antibonding orbitals.

## EQUATIONS AND RELATIONSHIPS

### Bond Order of a Diatomic Molecule (11.8)

$$\text{Bond order} = \frac{(\text{number of electrons in bonding MOs}) - (\text{number of electrons in antibonding MOs})}{2}$$

## LEARNING OUTCOMES

| Chapter Objectives   | Assessment  |
|--|---|
| Predict the basic shapes of molecules according to VSEPR theory ( <b>11.2</b> )                              | Example 11.1 For Practice 11.1 Exercises 31–34  |
| Predict how lone pairs and electron groups affect molecular geometry ( <b>11.3, 11.4</b> )                   | Examples 11.2, 11.3 For Practice 11.2, 11.3 Exercises 35–45   |
| Predict the shape of larger molecules ( <b>11.4</b> )  | Example 11.4 For Practice 11.4 Exercises 46   |
| Predict the polarity of a molecular compound ( <b>11.5</b> )   | Example 11.5 For Practice 11.5 Exercises 47–52  |
| Determine the hybridization and bonding scheme of a molecule using valence bond theory ( <b>11.6, 11.7</b> ) | Examples 11.6, 11.7, 11.8 For Practice 11.6, 11.7, 11.8 For More Practice 11.8 Exercises 53–68      |
| Predict properties of diatomic molecules using molecular orbital theory ( <b>11.8</b> )                      | Examples 11.9, 11.10, 11.11 For Practice 11.9, 11.10, 11.11 For More Practice 11.10 Exercises 69–82 |

## EXERCISES

### REVIEW QUESTIONS

**Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

- Why is molecular geometry important? Cite some examples.
- According to VSEPR theory, what determines the geometry of a molecule?
- Name and sketch the five basic electron geometries, and state the number of electron groups corresponding to each. What constitutes an *electron group*?
- Explain the difference between electron geometry and molecular geometry. Under what circumstances are they not the same?
- Give the correct electron and molecular geometries that correspond to each set of electron groups around the central atom of a molecule.
  - four electron groups overall; three bonding groups and one lone pair
  - four electron groups overall; two bonding groups and two lone pairs
  - five electron groups overall; four bonding groups and one lone pair
  - five electron groups overall; three bonding groups and two lone pairs
  - five electron groups overall; two bonding groups and three lone pairs
  - six electron groups overall; five bonding groups and one lone pair
  - six electron groups overall; four bonding groups and two lone pairs
- How do you apply VSEPR theory to predict the shape of a molecule with more than one interior atom?
- How do you determine whether a molecule is polar? Why is polarity important?
- What is a chemical bond according to valence bond theory?
- In valence bond theory, what determines the geometry of a molecule?
- In valence bond theory, the interaction energy between the electrons and nucleus of one atom with the electrons and nucleus of another atom is usually negative (stabilizing) when \_\_\_\_\_.
- What is hybridization? Why is hybridization necessary in valence bond theory?
- How does hybridization of the atomic orbitals in the central atom of a molecule help lower the overall energy of the molecule?
- How is the *number* of hybrid orbitals related to the number of standard atomic orbitals that are hybridized?
- Sketch each set of hybrid orbitals.
 

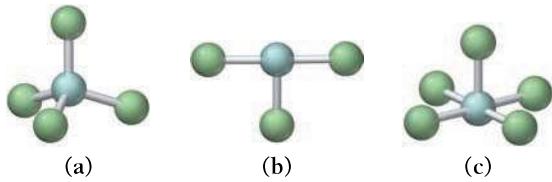
|            |              |           |
|------------|--------------|-----------|
| a. $sp$    | b. $sp^2$    | c. $sp^3$ |
| d. $sp^3d$ | e. $sp^3d^2$ |           |
- In the Lewis model, the two bonds in a double bond look identical. However, valence bond theory shows that they are not. Describe a double bond according to valence bond theory. Explain why rotation is restricted about a double bond but not about a single bond.
- Name the hybridization scheme that corresponds to each electron geometry.
  - linear
  - trigonal planar
  - tetrahedral
  - trigonal bipyramidal
  - octahedral
- What is a chemical bond according to MO theory?
- Explain the difference between hybrid atomic orbitals in valence bond theory and LCAO molecular orbitals in MO theory.
- What is a bonding molecular orbital?
- What is an antibonding molecular orbital?
- What is the role of wave interference in determining whether a molecular orbital is bonding or antibonding?

22. In MO theory, what is bond order? Why is it important?
23. How is the number of molecular orbitals approximated by a linear combination of atomic orbitals related to the number of atomic orbitals used in the approximation?
24. Sketch each molecular orbital.
- $\sigma_{2s}$
  - $\sigma_{2s}^*$
  - $\sigma_{2p}$
  - $\sigma_{2p}^*$
  - $\pi_{2p}$
  - $\pi_{2p}^*$
25. Draw an energy diagram for the molecular orbitals of period 2 diatomic molecules. Show the difference in ordering for  $B_2$ ,  $C_2$ , and  $N_2$  compared to  $O_2$ ,  $F_2$ , and  $Ne_2$ .
26. Why does the energy ordering of the molecular orbitals of the period 2 diatomic molecules change in going from  $N_2$  to  $O_2$ ?
27. Explain the difference between a paramagnetic species and a diamagnetic one.
28. When applying MO theory to heteronuclear diatomic molecules, the atomic orbitals used may be of different energies. If two atomic orbitals of different energies make two molecular orbitals, how are the energies of the molecular orbitals related to the energies of the atomic orbitals? How is the shape of the resultant molecular orbitals related to the shape of the atomic orbitals?
29. In MO theory, what is a nonbonding orbital?
30. Write a short paragraph describing chemical bonding according to the Lewis model, valence bond theory, and MO theory. Indicate how the theories differ in their description of a chemical bond and describe the strengths and weaknesses of each theory. Which theory is correct?

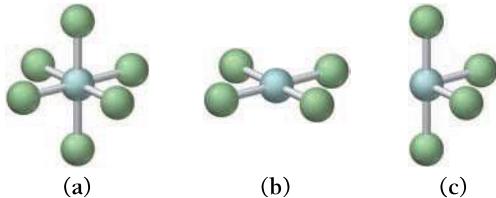
## PROBLEMS BY TOPIC

### VSEPR Theory and Molecular Geometry

31. A molecule with the formula  $AB_3$  has a trigonal pyramidal geometry. How many electron groups are on the central atom (A)?
- MISSED THIS?** Read Section 11.2; Watch KCV 11.2, IWE 11.1
32. A molecule with the formula  $AB_3$  has a trigonal planar geometry. How many electron groups are on the central atom?
33. For each molecular geometry, list the number of total electron groups, the number of bonding groups, and the number of lone pairs on the central atom. **MISSED THIS?** Read Sections 11.2, 11.3; Watch KCV 11.2, 11.3, IWE 11.1, 11.2



34. For each molecular geometry, list the number of total electron groups, the number of bonding groups, and the number of lone pairs on the central atom.



35. Determine the electron geometry, molecular geometry, and idealized bond angles for each molecule. In which cases do you expect deviations from the idealized bond angle?

**MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2

- $PF_3$
- $SBr_2$
- $CHCl_3$
- $CS_2$

36. Determine the electron geometry, molecular geometry, and idealized bond angles for each molecule. In which cases do you expect deviations from the idealized bond angle?

- $CF_4$
- $NF_3$
- $OF_2$
- $H_2S$

37. Which species has the smaller bond angle,  $H_3O^+$  or  $H_2O$ ? Explain.

**MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2

38. Which species has the smaller bond angle,  $ClO_4^-$  or  $ClO_3^-$ ? Explain.

39. Determine the molecular geometry and sketch each molecule or ion using the bond conventions shown in “Representing Molecular Geometries on Paper” in Section 11.4.

**MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2

- $SF_4$
- $ClF_3$
- $IF_2^-$
- $IBr_4^-$

40. Determine the molecular geometry and sketch each molecule or ion, using the bond conventions shown in “Representing Molecular Geometries on Paper” in Section 11.4.

- $BrF_5$
- $SCl_6$
- $PF_5$
- $IF_4^+$

41. Determine the molecular geometry about each interior atom and sketch each molecule.

**MISSED THIS?** Read Section 11.4; Watch IWE 11.4

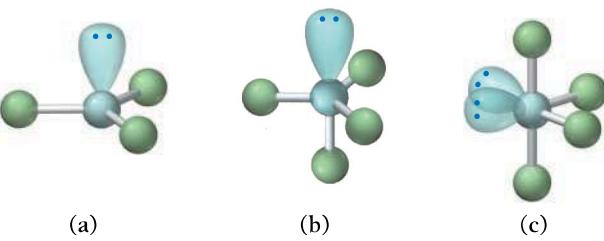
- $C_2H_2$  (skeletal structure  $HC\equiv CH$ )
- $C_2H_4$  (skeletal structure  $CH_2=CH_2$ )
- $C_2H_6$  (skeletal structure  $CH_3CH_3$ )

42. Determine the molecular geometry about each interior atom and sketch each molecule.

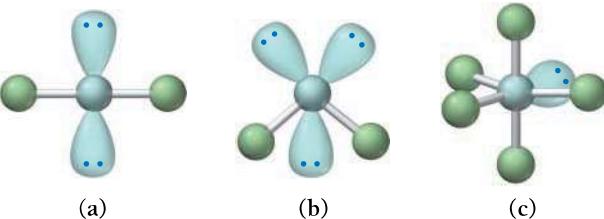
- $N_2$
- $N_2H_2$  (skeletal structure  $HNNH$ )
- $N_2H_4$  (skeletal structure  $H_2NNH_2$ )

43. Each ball-and-stick model shows the electron and molecular geometry of a generic molecule. Explain what is wrong with each molecular geometry and provide the correct molecular geometry, given the number of lone pairs and bonding groups on the central atom.

**MISSED THIS?** Read Sections 11.3, 11.4; Watch KCV 11.3, IWE 11.2



44. Each ball-and-stick model shows the electron and molecular geometry of a generic molecule. Explain what is wrong with each molecular geometry and provide the correct molecular geometry, given the number of lone pairs and bonding groups on the central atom.



45. Determine the geometry about each interior atom in each molecule and sketch the molecule. (Skeletal structure is indicated in parentheses.)

**MISSED THIS?** Read Section 11.4; Watch IWE 11.4

- a.  $\text{CH}_3\text{OH}(\text{H}_3\text{COH})$       b.  $\text{CH}_3\text{OCH}_3(\text{H}_3\text{COCH}_3)$   
c.  $\text{H}_2\text{O}_2(\text{HOOH})$

46. Determine the geometry about each interior atom in each molecule and sketch the molecule. (Skeletal structure is indicated in parentheses.)

- a.  $\text{CH}_3\text{NH}_2(\text{H}_3\text{CNH}_2)$   
b.  $\text{CH}_3\text{CO}_2\text{CH}_3$  ( $\text{H}_3\text{CCOOCH}_3$  one O atom attached to 2nd C atom; the other O atom is bonded to the 2nd and 3rd C atom)  
c.  $\text{NH}_2\text{CO}_2\text{H}$  ( $\text{H}_2\text{NCOOH}$  both O atoms attached to C)

## Molecular Shape and Polarity

47. Explain why  $\text{CO}_2$  and  $\text{CCl}_4$  are both nonpolar, even though they contain polar bonds.

**MISSED THIS?** Read Section 11.5; Watch KCV 11.5, IWE 11.5

48.  $\text{CH}_3\text{F}$  is a polar molecule, even though the tetrahedral geometry often leads to nonpolar molecules. Explain.

49. Determine whether each molecule in Exercise 35 is polar or nonpolar.

**MISSED THIS?** Read Section 11.5; Watch KCV 11.5, IWE 11.5

50. Determine whether each molecule in Exercise 36 is polar or nonpolar.

51. Determine whether each molecule is polar or nonpolar.

**MISSED THIS?** Read Section 11.5; Watch KCV 11.5, IWE 11.5

- a.  $\text{SCl}_2$       b.  $\text{SCl}_4$       c.  $\text{BrCl}_5$

52. Determine whether each molecule is polar or nonpolar.

- a.  $\text{SiCl}_4$       b.  $\text{CF}_2\text{Cl}_2$   
c.  $\text{SeF}_6$       d.  $\text{IF}_5$

## Valence Bond Theory

53. The valence electron configurations of several atoms are shown here. How many bonds can each atom make without hybridization? **MISSED THIS?** Read Section 11.6; Watch KCV 11.6

- a. Be  $2s^2$       b. P  $3s^23p^3$       c. F  $2s^22p^5$

54. The valence electron configurations of several atoms are shown here. How many bonds can each atom make without hybridization?

- a. B  $2s^22p^1$       b. N  $2s^22p^3$       c. O  $2s^22p^4$

55. Write orbital diagrams (boxes with arrows in them) to represent the electron configurations—without hybridization—for all the atoms in  $\text{PH}_3$ . Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of  $93.3^\circ$ ?

**MISSED THIS?** Read Section 11.6; Watch KCV 11.6

56. Write orbital diagrams (boxes with arrows in them) to represent the electron configurations—with hybridization—for all the atoms in  $\text{SF}_2$ . Circle the electrons involved in bonding. Draw a three-dimensional sketch of the molecule and show orbital overlap. What bond angle do you expect from the unhybridized orbitals? How well does valence bond theory agree with the experimentally measured bond angle of  $98.2^\circ$ ?

57. Write orbital diagrams (boxes with arrows in them) to represent the electron configuration of carbon before and after  $sp^3$  hybridization.

**MISSED THIS?** Read Section 11.7; Watch KCV 11.7

58. Write orbital diagrams (boxes with arrows in them) to represent the electron configurations of carbon before and after  $sp$  hybridization.

59. Which hybridization scheme allows the formation of at least one  $\pi$  bond? **MISSED THIS?** Read Section 11.7; Watch KCV 11.7

- $sp^3$ ,  $sp^2$ ,  $sp^3d^2$

60. Which hybridization scheme allows the central atom to form more than four bonds?

- $sp^3$ ,  $sp^3d$ ,  $sp^2$

61. Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

**MISSED THIS?** Read Section 11.7; Watch KCV 11.7, IWE 11.8

- a.  $\text{CCl}_4$       b.  $\text{NH}_3$       c.  $\text{OF}_2$       d.  $\text{CO}_2$

62. Write a hybridization and bonding scheme for each molecule. Sketch the molecule, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

- a.  $\text{CH}_2\text{Br}_2$       b.  $\text{SO}_2$       c.  $\text{NF}_3$       d.  $\text{BF}_3$

63. Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

**MISSED THIS?** Read Section 11.7; Watch KCV 11.7, IWE 11.8

- a.  $\text{COCl}_2$  (carbon is the central atom)  
b.  $\text{BrF}_5$       c.  $\text{XeF}_2$       d.  $\text{I}_3^-$

64. Write a hybridization and bonding scheme for each molecule or ion. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

- a.  $\text{SO}_3^{2-}$       b.  $\text{PF}_6^-$   
c.  $\text{BrF}_3$       d.  $\text{HCN}$

65. Write a hybridization and bonding scheme for each molecule that contains more than one interior atom. Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

**MISSED THIS?** Read Section 11.7; Watch KCV 11.7, IWE 11.8

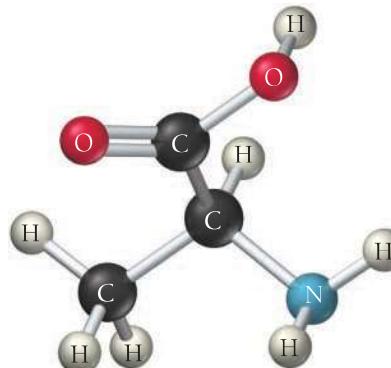
- a.  $\text{N}_2\text{H}_2$  (skeletal structure  $\text{HNNH}_2$ )  
b.  $\text{N}_2\text{H}_4$  (skeletal structure  $\text{H}_2\text{NNH}_2$ )  
c.  $\text{CH}_3\text{NH}_2$  (skeletal structure  $\text{H}_3\text{CNH}_2$ )

66. Write a hybridization and bonding scheme for each molecule that contains more than one interior atom. Indicate the hybridization about each interior atom. Sketch the structure, including overlapping orbitals, and label all bonds using the notation shown in Examples 11.6 and 11.7.

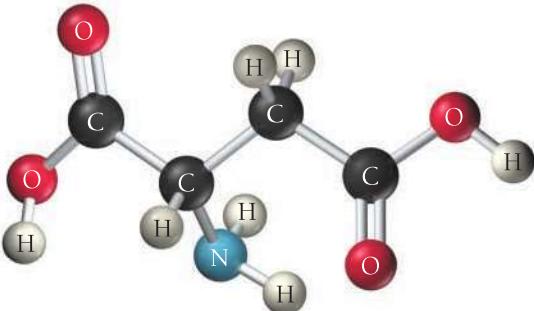
- a.  $\text{C}_2\text{H}_2$  (skeletal structure  $\text{HCCCH}$ )  
b.  $\text{C}_2\text{H}_4$  (skeletal structure  $\text{H}_2\text{CCH}_2$ )  
c.  $\text{C}_2\text{H}_6$  (skeletal structure  $\text{H}_3\text{CCH}_3$ )

67. Consider the structure of the amino acid alanine. Indicate the hybridization about each interior atom.

**MISSED THIS?** Read Section 11.7; Watch KCV 11.7, IWE 11.8



68. Consider the structure of the amino acid aspartic acid. Indicate the hybridization about each interior atom.



### Molecular Orbital Theory

69. Sketch the bonding molecular orbital that results from the linear combination of two 1s orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).

**MISSED THIS?** Read Section 11.8

70. Sketch the antibonding molecular orbital that results from the linear combination of two 1s orbitals. Indicate the region where interference occurs and state the kind of interference (constructive or destructive).

71. Draw an MO energy diagram and predict the bond order of Be<sub>2</sub><sup>+</sup> and Be<sub>2</sub><sup>-</sup>. Do you expect these molecules to exist in the gas phase?

**MISSED THIS?** Read Section 11.8; Watch IWE 11.10

72. Draw an MO energy diagram and predict the bond order of Li<sub>2</sub><sup>+</sup> and Li<sub>2</sub><sup>-</sup>. Do you expect these molecules to exist in the gas phase?

73. Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the 2p<sub>x</sub> atomic orbitals in a homonuclear diatomic molecule. (The 2p<sub>x</sub> orbitals are those whose lobes are oriented along the bonding axis.)

**MISSED THIS?** Read Section 11.8

74. Sketch the bonding and antibonding molecular orbitals that result from linear combinations of the 2p<sub>z</sub> atomic orbitals in a homonuclear diatomic molecule. (The 2p<sub>z</sub> orbitals are those whose lobes are oriented perpendicular to the bonding axis.)

How do these molecular orbitals differ from those obtained from linear combinations of the 2p<sub>y</sub> atomic orbitals? (The 2p<sub>y</sub> orbitals are also oriented perpendicular to the bonding axis but are also perpendicular to the 2p<sub>z</sub> orbitals.)

75. Using the molecular orbital energy ordering for second-row homonuclear diatomic molecules in which the π<sub>2p</sub> orbitals lie at lower energy than the σ<sub>2p</sub>, draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?

**MISSED THIS?** Read Section 11.8; Watch IWE 11.10

- a. 4      b. 6      c. 8      d. 9

76. Using the molecular orbital energy ordering for second-row homonuclear diatomic molecules in which the π<sub>2p</sub> orbitals lie at higher energy than the σ<sub>2p</sub>, draw MO energy diagrams and predict the bond order in a molecule or ion with each number of total valence electrons. Will the molecule or ion be diamagnetic or paramagnetic?

- a. 10      b. 12      c. 13      d. 14

77. Use MO theory to predict if each molecule or ion exists in a relatively stable form.

**MISSED THIS?** Read Section 11.8; Watch IWE 11.10

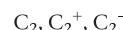
- a. H<sub>2</sub><sup>2-</sup>      b. Ne<sub>2</sub>      c. He<sub>2</sub><sup>2+</sup>      d. F<sub>2</sub><sup>2-</sup>

78. Use MO theory to predict if each molecule or ion exists in a relatively stable form.

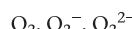
- a. C<sub>2</sub><sup>2+</sup>      b. Li<sub>2</sub>      c. Be<sub>2</sub><sup>2+</sup>      d. Li<sub>2</sub><sup>2-</sup>

79. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?

**MISSED THIS?** Read Section 11.8; Watch IWE 11.10



80. According to MO theory, which molecule or ion has the highest bond order? Highest bond energy? Shortest bond length?



81. Draw an MO energy diagram for CO. (Use the energy ordering of O<sub>2</sub>.) Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.

**MISSED THIS?** Read Section 11.8

82. Draw an energy diagram for HCl. Predict the bond order and make a sketch of the lowest energy bonding molecular orbital.

## CUMULATIVE PROBLEMS

83. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.

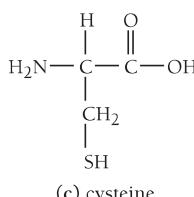
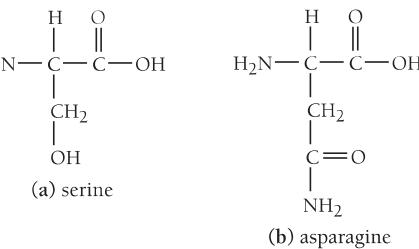
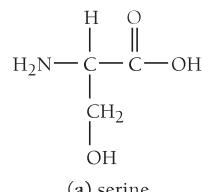
- a. COF<sub>2</sub> (carbon is the central atom)  
b. S<sub>2</sub>Cl<sub>2</sub> (Cl is the central atom)  
c. SF<sub>4</sub>

84. For each compound, draw the Lewis structure, determine the geometry using VSEPR theory, determine whether the molecule is polar, identify the hybridization of all interior atoms, and make a sketch of the molecule, according to valence bond theory, showing orbital overlap.

- a. IF<sub>5</sub>  
b. CH<sub>2</sub>CHCH<sub>3</sub>  
c. CH<sub>3</sub>SH

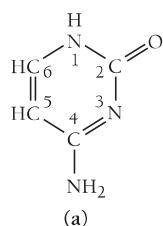
85. Amino acids are biological compounds that link together to form proteins, the workhorse molecules in living organisms. The skeletal structures of several simple amino acids are shown

here. For each skeletal structure, complete the Lewis structure, determine the geometry and hybridization about each interior atom, and make a sketch of the molecule, using the bond conventions of Section 11.4.

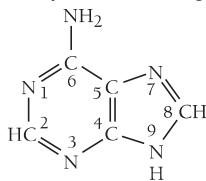


**86.** The genetic code is based on four different bases with the structures shown here. Assign a geometry and hybridization to each interior atom in these four bases.

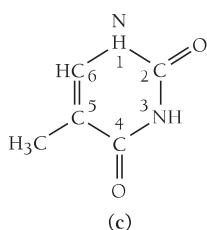
- a. cytosine      b. adenine      c. thymine      d. guanine



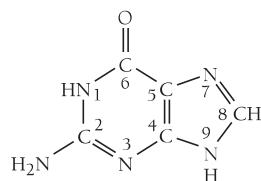
(a)



(b)

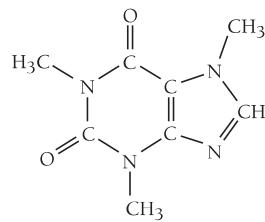


(c)

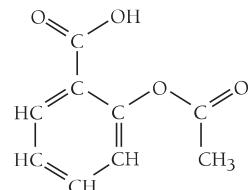


(d)

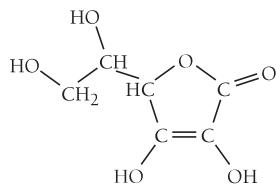
**87.** The structure of caffeine, present in coffee and many soft drinks, is shown here. How many pi bonds are present in caffeine? How many sigma bonds? Insert the lone pairs in the molecule. What kinds of orbitals do the lone pairs occupy?



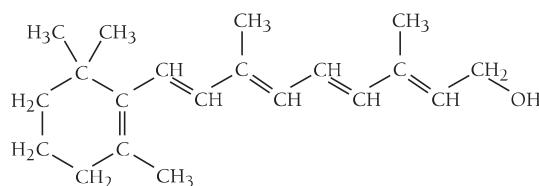
**88.** The structure of acetylsalicylic acid (aspirin) is shown here. How many pi bonds are present in acetylsalicylic acid? How many sigma bonds? What parts of the molecule are free to rotate? What parts are rigid?



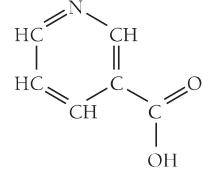
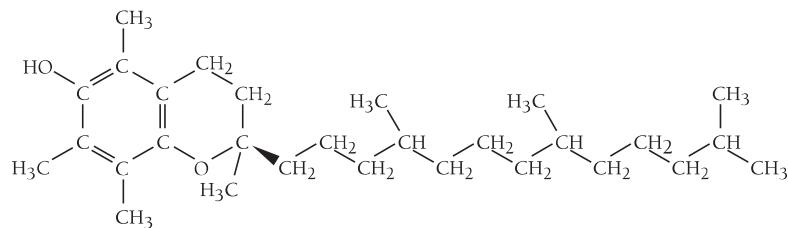
**89.** Most vitamins can be classified as either fat soluble, which results in their tendency to accumulate in the body (so that taking too much can be harmful), or water soluble, which results in their tendency to be quickly eliminated from the body in urine. Examine the structural formulas and space-filling models of these vitamins and determine whether each one is fat soluble (mostly nonpolar) or water soluble (mostly polar).



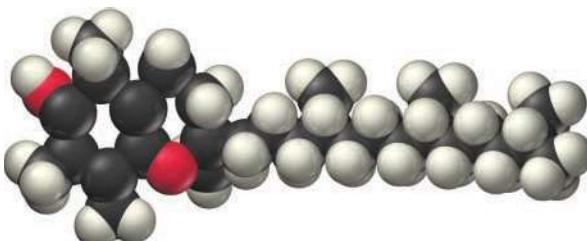
(a) vitamin C



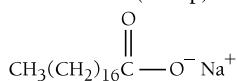
(b) vitamin A

(c) niacin (vitamin B<sub>3</sub>)

(d) vitamin E



90. Water does not easily remove grease from dishes or hands because grease is nonpolar and water is polar. The addition of soap to water, however, allows the grease to dissolve. Study the structure of sodium stearate (a soap) and describe how it works.



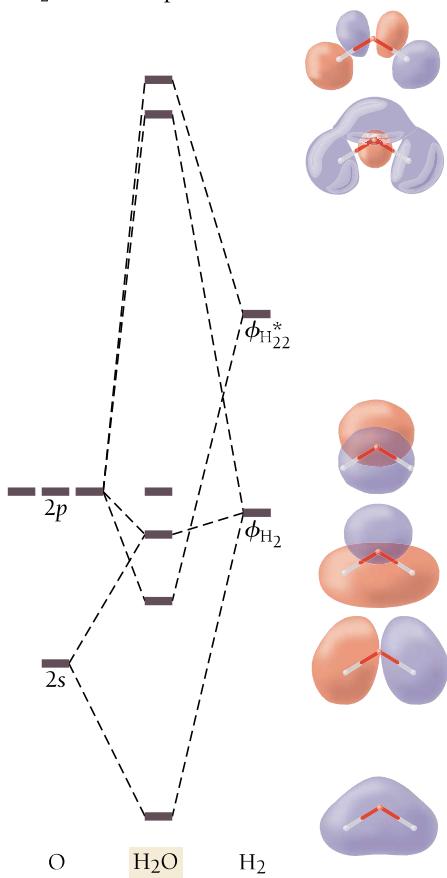
91. Draw a molecular orbital energy diagram for  $\text{ClF}$ . (Assume that the  $\sigma_p$  orbitals are lower in energy than the  $\pi$  orbitals.) What is the bond order in  $\text{ClF}$ ?
92. Draw Lewis structures and MO diagrams for  $\text{CN}^+$ ,  $\text{CN}$ , and  $\text{CN}^-$ . According to the Lewis model, which species is most stable? According to MO theory, which species is most stable? Do the two theories agree?

93. Bromine can form compounds or ions with any number of fluorine atoms from one to five. Write the formulas of all five of these species, assign a hybridization, and describe their electron and molecular geometry.

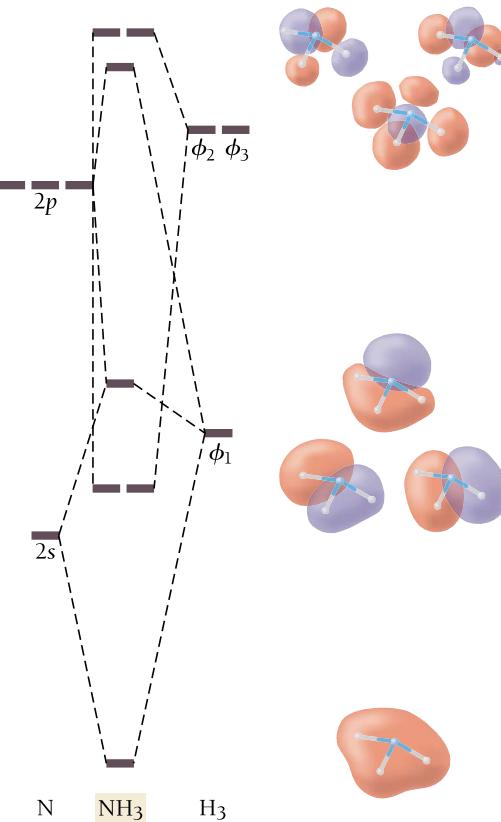
94. The compound  $\text{C}_3\text{H}_4$  has two double bonds. Describe its bonding and geometry, using a valence bond approach.
95. Draw the structure of a molecule with the formula  $\text{C}_4\text{H}_6\text{Cl}_2$  that has a dipole moment of 0.
96. Draw the structures of two compounds that have the composition  $\text{CH}_3\text{NO}_2$  and have all three H atoms bonded to the C. Predict which compound has the larger  $\text{ONO}$  bond angle.
97. How many types of hybrid orbitals do we use to describe each molecule?
- $\text{N}_2\text{O}_5$
  - $\text{C}_2\text{H}_5\text{NO}$  (four C—H bonds and one O—H bond)
  - $\text{BrCN}$  (no formal charges)
98. Indicate which orbitals overlap to form the  $\sigma$  bonds in each molecule.
- $\text{BeBr}_2$
  - $\text{HgCl}_2$
  - $\text{ICN}$

## CHALLENGE PROBLEMS

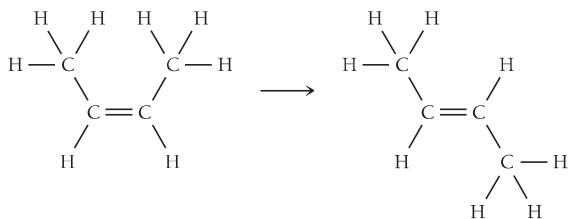
99. In VSEPR theory, which uses the Lewis model to determine molecular geometry, the trend of decreasing bond angles in  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  is accounted for by the greater repulsion of lone pair electrons compared to bonding pair electrons. How would this trend be accounted for in valence bond theory?
100. The results of a molecular orbital calculation for  $\text{H}_2\text{O}$  are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is  $\text{H}_2\text{O}$  stable? Explain.



101. The results of a molecular orbital calculation for  $\text{NH}_3$  are shown here. Examine each of the orbitals and classify them as bonding, antibonding, or nonbonding. Assign the correct number of electrons to the energy diagram. According to this energy diagram, is  $\text{NH}_3$  stable? Explain.



- 102.** *cis*-2-Butene isomerizes to *trans*-2-butene via the reaction shown here.



- a. If isomerization requires breaking the  $\pi$  bond, what minimum energy is required for isomerization in J/mol? In J/molecule?  
 b. If the energy for isomerization came from light, what minimum frequency of light would be required? In what portion of the electromagnetic spectrum does this frequency lie?  
**103.** The species  $\text{NO}_2$ ,  $\text{NO}_2^+$ , and  $\text{NO}_2^-$  in which N is the central atom have very different bond angles. Predict what these bond angles might be with respect to the ideal angles and justify your prediction.

- 104.** The bond angles increase steadily in the series  $\text{PF}_3$ ,  $\text{PCl}_3$ ,  $\text{PBr}_3$ , and  $\text{PI}_3$ . After consulting the data on atomic radii in Chapter 9, provide an explanation for this observation.  
**105.** The ion  $\text{CH}_5^+$  can form under very special high-energy conditions in the vapor phase in a mass spectrometer. Propose a hybridization for the carbon atom and predict the geometry.  
**106.** Neither the VSEPR model nor the hybridization model is able to account for the experimental observation that the F—Ba—F bond angle in gaseous  $\text{BaF}_2$  is  $108^\circ$  rather than the predicted  $180^\circ$ . Suggest some possible explanations for this observation.  
**107.** Draw the Lewis structure for acetamide ( $\text{CH}_3\text{CONH}_2$ ), an organic compound, and determine the geometry about each interior atom. Experiments show that the geometry about the nitrogen atom in acetamide is nearly planar. What resonance structure can account for the planar geometry about the nitrogen atom?  
**108.** Use VSEPR theory to predict the geometry (including bond angles) about each interior atom of methyl azide ( $\text{CH}_3\text{N}_3$ ), and make a sketch of the molecule. Would you expect the bond angle between the two interior nitrogen atoms to be the same or different? Would you expect the two nitrogen–nitrogen bond lengths to be the same or different?

## CONCEPTUAL PROBLEMS

- 109.** Which statement best captures the fundamental idea behind VSEPR theory? Explain what is wrong with each of the other statements.  
 a. The angle between two or more bonds is determined primarily by the repulsions between the electrons within those bonds and other (lone pair) electrons on the central atom of a molecule. Each of these electron groups (bonding electrons or lone pair electrons) will lower its potential energy by maximizing its separation from other electron groups, thus determining the geometry of the molecule.  
 b. The angle between two or more bonds is determined primarily by the repulsions between the electrons within those bonds. Each of these bonding electrons will lower its potential energy by maximizing its separation from other electron groups, thus determining the geometry of the molecule.  
 c. The geometry of a molecule is determined by the shapes of the overlapping orbitals that form the chemical bonds. Therefore, to determine the geometry of a molecule, you must determine the shapes of the orbitals involved in bonding.

- 110.** Suppose that a molecule has four bonding groups and one lone pair on the central atom. Suppose further that the molecule is confined to two dimensions (this is a purely hypothetical assumption for the sake of understanding the principles behind VSEPR theory). Make a sketch of the molecule and estimate the bond angles.  
**111.** How does each of the three major bonding theories (the Lewis model, valence bond theory, and MO theory) define a single chemical bond? A double bond? A triple bond? How are these definitions similar? How are they different?  
**112.** The most stable forms of the nonmetals in groups 4A, 5A, and 6A of the second period are molecules with multiple bonds. Beginning with the third period, the most stable forms of the nonmetals of these groups are molecules without multiple bonds. Propose an explanation for this observation based on valence bond theory.

## QUESTIONS FOR GROUP WORK

Active Classroom Learning

- Discuss these questions with the group and record your consensus answer.  
**113.** In complete sentences, describe why someone might expect the bond angles in methane ( $\text{CH}_4$ ) to be  $90^\circ$  even though the bond angles are actually  $109.5^\circ$ .  
**114.** At least two different numbers of electron groups can result in a linear molecule. What are they? What are the numbers of bonding groups and lone pairs in each case? Provide an example of a linear molecule in each case.  
**115.** Have each member of your group select one of the molecules shown below and complete steps a-d. Each member should then present his or her results to the rest of the group, explaining the reasoning used to determine the answers.

$\text{CS}_2$     $\text{NCl}_3$     $\text{CF}_4$     $\text{CH}_2\text{F}_2$

- a. Draw the Lewis dot structure.  
 b. Determine the molecular geometry and draw it accurately.  
 c. Indicate the polarity of any polar bonds within the structure.  
 d. Classify the molecule as polar or nonpolar.  
**116.** How many atomic orbitals form a set of  $sp^3$  hybrid orbitals? A set of  $sp^2$  hybrid orbitals? A set of  $sp$  hybrid orbitals? What is the relationship between these numbers and the number of electron groups around the central atom?  
**117.** Use MO theory to explain in detail why  $\text{N}_2^+$  and  $\text{N}_2^-$  have similar bond strengths and both are very different from neutral  $\text{N}_2$ .



## DATA INTERPRETATION AND ANALYSIS

### Using Distances between Atoms to Predict Bond Angles

**11.8** The VSEPR model is useful in predicting bond angles for many compounds. However, as we have seen, other factors (such as type of bond and atomic radii) may also influence bond angles. Consider that data for bond angles in related species in the tables and answer the questions.

### Bond Angles in $\text{NO}_2$ and Associated Ions

| Species         | Bond Angle |
|-----------------|------------|
| $\text{NO}_2$   | 134°       |
| $\text{NO}_2^+$ | 180°       |
| $\text{NO}_2^-$ | 115°       |

### Bond Angles in $\text{PX}_3$ Compounds

| Compounds      | Bond Angle |
|----------------|------------|
| $\text{PH}_3$  | 94°        |
| $\text{PF}_3$  | 97°        |
| $\text{PCl}_3$ | 100°       |
| $\text{PI}_3$  | 102°       |

- a. Draw Lewis structures for all of the species in the Bond Angles in  $\text{NO}_2$  and Associated Ions Table.
- b. Use the Lewis structures from part a to explain the observed bond angles in  $\text{NO}_2$  and its associated ions.
- c. Draw Lewis structures for all of the species in the Bond Angles in  $\text{PX}_3$  Compounds Table.
- d. Make your own table showing the atomic radii of H, F, Cl, and I.
- e. Use your answers to parts c and d to explain the observed bond angles in  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{PCl}_3$ , and  $\text{PI}_3$ .



## ANSWERS TO CONCEPTUAL CONNECTIONS

### Electron Groups and Molecular Geometry

**11.1** (b) Two electron groups with no lone pairs on a central atom in a molecule result in a linear geometry.

### Molecular Geometry

**11.2** (a) Linear. HCN has two electron groups (the single bond and the triple bond) resulting in a linear geometry.

### Lone Pairs and Molecular Geometry I

**11.3** (d) Three bonding groups and one lone pair lead to a trigonal pyramidal geometry.

### Lone Pair Repulsions

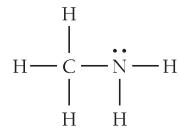
**11.4** (c) Positions 1 and 4 would put the greatest distance between the lone pairs and minimize lone pair-lone pair repulsions.

### Molecular Geometry and Electron Group Repulsions

**11.5** (d) All electron groups on the central atom (or interior atoms, if there is more than one) determine the shape of a molecule according to VSEPR theory.

### The Shape of Larger Molecules

**11.6** (c) The nitrogen atom has four electron groups and one lone pair, as the Lewis structure illustrates; therefore, the molecular geometry about the nitrogen atom is trigonal pyramidal.



### Polarity of Molecules

**11.7** (b) Even though the molecule has polar bonds, the dipole moments of the three bonds cancel out because of the trigonal planar geometry, and the molecule is not polar.

### What Is a Chemical Bond? Part I

**11.8** (b) In valence bond theory, a covalent chemical bond is the overlap of half-filled atomic orbitals.

### Number of Hybrid Orbitals

**11.9** (d) The number of hybrid orbitals that form must always equal the number of orbitals that are combined. Since one  $s$  and three  $p$  orbitals are combined, four hybrid orbitals form. You can also determine the number of hybrid orbitals by summing the superscripts in the hybridization notation. For  $sp^3$ , you add the implied 1 superscript on the  $s$  to the 3 superscript on the  $p$  and you get  $1 + 3 = 4$ .

**Single and Double Bonds**

**11.10** (a) Applying valence bond theory, we see that a double bond is actually composed of two different kinds of bonds, one  $\sigma$  and one  $\pi$ . The orbital overlap in the  $\pi$  bond is side to side between two  $p$  orbitals and consequently different from the end-to-end overlap in a  $\sigma$  bond. Since the bonds are different types, the bond energy of the double bond is not just twice the bond energy of the single bond.

**Hybridization**

**11.11** (a) Because carbon has two electron groups in carbon dioxide (the two double bonds), the geometry is linear and the hybridization is  $sp$ .

**Bond Order**

**11.12** (b) The bond order is 1.5. Remember that bond order is equal to the number of bonding electrons minus the number of antibonding electrons, all divided by two, so you get that the bond order =  $(6 - 3)/2 = 1.5$ .

**What Is a Chemical Bond? Part II**

**11.13** (c) According to MO theory, atoms join together (or bond) when the electrons in the atoms can lower their energy by occupying the molecular orbitals of the resultant molecule. Unlike the Lewis model or valence bond theory, the chemical “bonds” in MO theory are not localized between atoms but are spread throughout the entire molecule.