

## WHAT'S AHEAD

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- 9.2 ► The VSEPR Model
- 9.3 ► Molecular Shape and Molecular Polarity
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# 9

# MOLECULAR GEOMETRY AND BONDING THEORIES

## 9.1 | Molecular Shapes



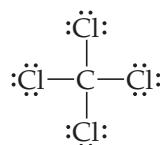
Orchid flowers demonstrate the intimate connection between shape and function. The bee orchid (*ophrys apifera*), for example, has a central labellum that mimics the abdomen of a bee, and is even slightly hairy. The scent of the orchid is similar to that of a female bee. Pollen gets transferred when a male bee attempts to mate with the orchid, to be carried by the unwitting insect to another bee orchid.

In this chapter, our first goal is to understand the relationship between two-dimensional Lewis structures and three-dimensional molecular shapes. We will see the intimate relationship between the number of electrons in a molecule and the overall shape it adopts. Armed with this knowledge, we can examine more closely the nature of covalent bonds. The lines used to depict bonds in Lewis structures provide important clues about the orbitals that molecules use in bonding. By examining these orbitals, we can gain a greater understanding of the behavior of molecules.

By the end of this section, you should be able to

- Recognize the five basic shapes from which geometries of  $\text{AB}_n$  molecules are derived

In Chapter 8, we used Lewis structures to account for the formulas of covalent compounds. Lewis structures, however, do not indicate the shapes of molecules; they simply show the number and types of bonds. For example, the Lewis structure of  $\text{CCl}_4$  tells us only that four Cl atoms are bonded to a central C atom:



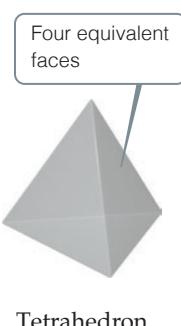
The Lewis structure is drawn with the atoms all in the same plane. As shown in **Figure 9.1**, however, the actual three-dimensional arrangement has the Cl atoms at the corners of a *tetrahedron*, a geometric object with four corners and four faces, each an equilateral triangle.

The shape of a molecule is determined by its **bond angles**, the angles made by the lines joining the nuclei of the atoms in the molecule. The bond angles of a molecule, together with the bond lengths, define the shape and size of the molecule. In Figure 9.1, you should be able to see that there are six Cl—C—Cl bond angles in  $\text{CCl}_4$ , all of which have the same value. That bond angle,  $109.5^\circ$ , is characteristic of a tetrahedron. In addition, all four C—Cl bonds are of the same length (178 pm). Thus, the shape and size of  $\text{CCl}_4$  are completely described by stating that the molecule is tetrahedral with C—Cl bonds of length 178 pm. To draw the three-dimensional structure of a molecule on paper, chemists use a convention shown in Figure 9.1: Regular lines imply the bond is in the plane of the paper, a heavy wedge is used to show that the bond is coming out of the paper toward you, and the dashed line is used to show that the bond is pointing away from you, through the back of the paper.

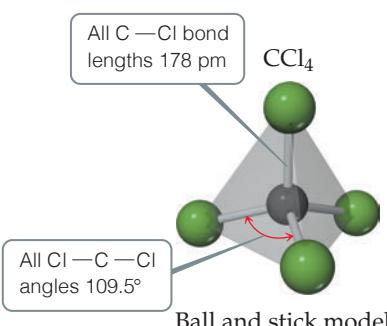


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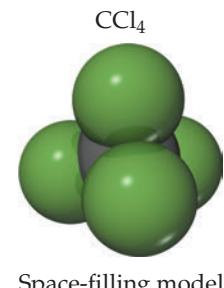
In the space-filling model, what determines the relative sizes of the spheres?



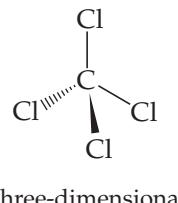
Tetrahedron



Ball and stick model



Space-filling model

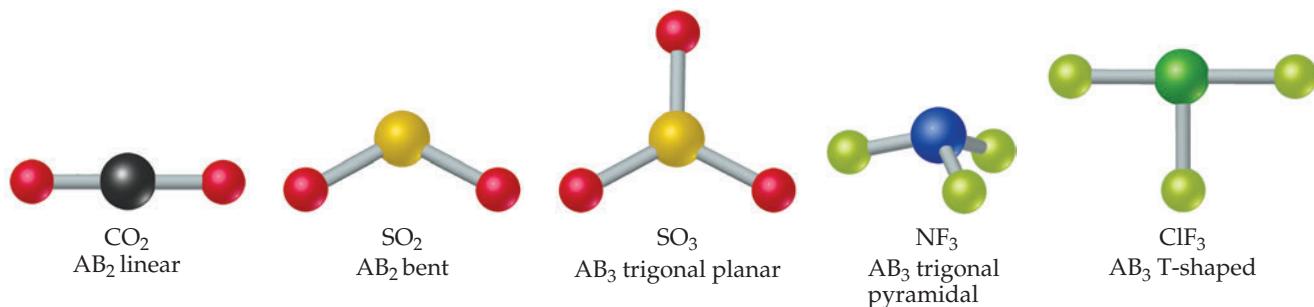


Three-dimensional atomic model

▲ Figure 9.1 Tetrahedral shape of  $\text{CCl}_4$ .

**Go Figure**

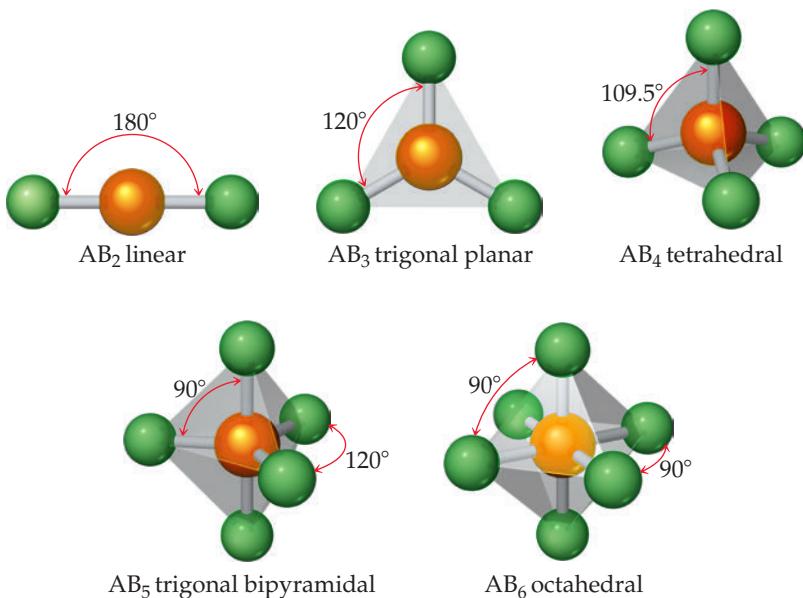
Which of these structures is not planar?

▲ Figure 9.2 Shapes of  $\text{AB}_2$  and  $\text{AB}_3$  molecules.

We begin our discussion of molecular shapes with molecules (and ions) that, like  $\text{CCl}_4$ , have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula  $\text{AB}_n$  in which the central atom A is bonded to  $n$  B atoms. Both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are  $\text{AB}_2$  molecules, for example, whereas  $\text{SO}_3$  and  $\text{NH}_3$  are  $\text{AB}_3$  molecules, and so on.

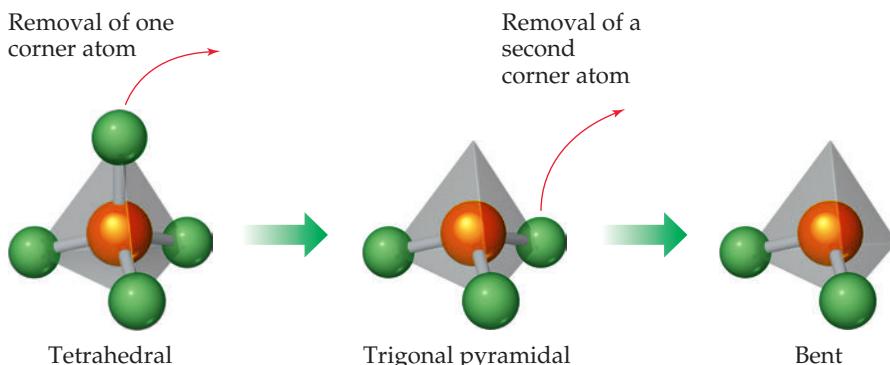
The number of shapes possible for  $\text{AB}_n$  molecules depends on the value of  $n$ . Those commonly found for  $\text{AB}_2$  and  $\text{AB}_3$  molecules are shown in Figure 9.2. An  $\text{AB}_2$  molecule must be either *linear* (bond angle =  $180^\circ$ ) or *bent* (bond angle  $\neq 180^\circ$ ). For  $\text{AB}_3$  molecules, the two most common shapes place the B atoms at the corners of an equilateral triangle. If the A atom lies in the same plane as the B atoms, the shape is called *trigonal planar*. If the A atom lies above the plane of the B atoms, the shape is called *trigonal pyramidal* (a pyramid with an equilateral triangle as its base). Some  $\text{AB}_3$  molecules, such as  $\text{ClF}_3$ , are *T-shaped*, a relatively unusual shape shown in Figure 9.2. The atoms lie in one plane with two B—A—B angles of about  $90^\circ$ , and a third angle close to  $180^\circ$ .

Quite remarkably, the shapes of most  $\text{AB}_n$  molecules can be derived from just five basic geometric arrangements, shown in Figure 9.3. All of these are highly symmetric arrangements of the  $n$  B atoms around the central A atom. We have already seen the first three shapes: linear, trigonal planar, and tetrahedral. The trigonal bipyramidal shape for

**Go Figure**Which of these molecular shapes do you expect for the  $\text{SF}_6$  molecule?▲ Figure 9.3 Shapes allowing maximum distances between B atoms in  $\text{AB}_n$  molecules.


**Go Figure**

In going from the tetrahedral shape to the bent shape, does it matter which two of the atoms we choose to remove?



▲ Figure 9.4 Derivatives of the tetrahedral molecular shape.

$\text{AB}_5$  can be thought of as a trigonal planar  $\text{AB}_3$  arrangement with two additional atoms, one above and one below the equilateral triangle. The octahedral shape for  $\text{AB}_6$  has all six B atoms at the same distance from atom A with  $90^\circ \text{B}—\text{A}—\text{B}$  angles between all neighboring B atoms. Its symmetric shape (and its name) is derived from the *octahedron*, with eight faces, all of which are equilateral triangles.

You may have noticed that some of the shapes we have already discussed are *not* among the five shapes in Figure 9.3. For example, in Figure 9.2, neither the bent shape of the  $\text{SO}_2$  molecule nor the trigonal pyramidal shape of the  $\text{NF}_3$  molecule is among the shapes in Figure 9.3. However, as we soon will see, we can derive additional shapes, such as bent and trigonal pyramidal, by starting with one of our five basic arrangements. Starting with a tetrahedron, for example, we can remove atoms successively from the vertices, as shown in Figure 9.4. When an atom is removed from one vertex of a tetrahedron, the remaining  $\text{AB}_3$  fragment has a trigonal-pyramidal geometry. When a second atom is removed, the remaining  $\text{AB}_2$  fragment has a bent geometry.

Why do most  $\text{AB}_n$  molecules have shapes related to those shown in Figure 9.3? Can we predict these shapes? When A is a representative element (one from the s block or p block of the periodic table), we can answer these questions by using the **valence-shell electron-pair repulsion (VSEPR) model**. Although the name is rather imposing, the model is quite simple. It has useful predictive capabilities, as we will see in Section 9.2.



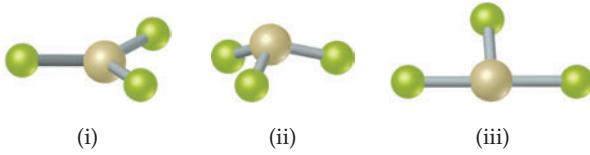
## Self-Assessment Exercise

- 9.1** In addition to tetrahedral, another common shape for  $\text{AB}_4$  molecules is *square planar*. All five atoms lie in the same plane, with the B atoms at the corners of a square and the A atom at the center of the square. Which shape in Figure 9.3 could lead to a square-planar shape upon removal of one or more atoms?
- (a) Tetrahedral  
 (b) Trigonal bipyramidal  
 (c) Octahedral

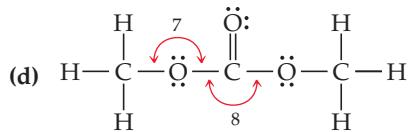
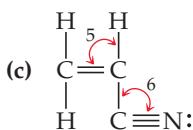
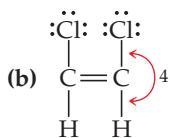
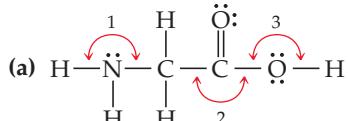
## Exercises

- 9.2** How many nonbonding electron pairs are there in each of the following molecules: (a)  $\text{N}(\text{CH}_3)_3$ , (b)  $\text{CO}$ , (c)  $\text{BF}_3$ , (d)  $\text{SO}_2$ ?
- 9.3** The figure that follows shows ball-and-stick drawings of three possible shapes of an  $\text{AF}_3$  molecule. (a) For each shape, give the electron-domain geometry on which the molecular geometry is based. (b) For each shape, how many nonbonding electron domains are there on atom A? (c) Which of the following elements will lead to an  $\text{AF}_3$  molecule with the

shape in (ii): Li, B, N, Al, P, Cl? (d) Name an element A that is expected to lead to the  $\text{AF}_3$  structure shown in (iii).



- 9.4** Give the approximate values for the indicated bond angles in the following molecules:



9.1 (c)

Answers to Self-Assessment Exercise

## 9.2 | The VSEPR Model



One of the most iconic shapes of a large molecules is the double helix structure of DNA. We instantly recognize it as a three-dimensional object. Less obvious is the association between a formula written on a page and the shape of the substance, yet every compound has a unique size and shape.

Lewis structures help us understand the compositions of molecules and their covalent bonds. However, Lewis structures do not show one of the most important aspects of molecules—their overall shapes. The shape and size of molecules—sometimes referred to as molecular architecture—are defined by the angles and distances between the nuclei of the component atoms.

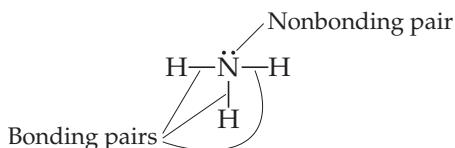
By the end of this section, you should be able to

- Draw and name the predicted three-dimensional shapes of molecules using the VSEPR model.

Imagine tying two identical balloons together at their ends. As shown in **Figure 9.5**, the two balloons naturally orient themselves to point away from each other; that is, they try to “get out of each other’s way” as much as possible. If we add a third balloon, the

balloons orient themselves toward the vertices of an equilateral triangle, and if we add a fourth balloon, they adopt a tetrahedral shape. We see that an optimum geometry exists for each number of balloons.

In some ways, the electrons in molecules behave like these balloons. We have seen that a single covalent bond is formed between two atoms when a pair of electrons occupies the space between the atoms. A *bonding pair* of electrons thus defines a region in which the electrons are most likely to be found. We will refer to such a region as an **electron domain**. Likewise, a *nonbonding pair* (or *lone pair*) of electrons, which was also discussed in Section 8.3, defines an electron domain that is located principally on one atom. For example, the Lewis structure of  $\text{NH}_3$  has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):



Each multiple bond in a molecule also constitutes a single electron domain. Thus, the following resonance structure for  $\text{O}_3$  has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):



In general, *each nonbonding pair, single bond, or multiple bond produces a single electron domain around the central atom in a molecule*.

The VSEPR model is based on the idea that electron domains are negatively charged and therefore repel one another. Like the balloons in Figure 9.5, electron domains try to stay out of one another's way.

*The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.*

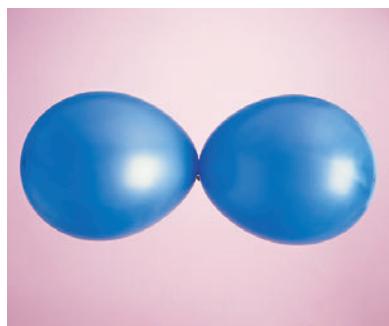
In fact, the analogy between electron domains and balloons is so close that the same preferred geometries are found in both cases. Like the balloons in Figure 9.5, two electron domains orient *linearly*, three domains orient in a *trigonal-planar* fashion, and four orient *tetrahedrally*. These arrangements, together with those for five- and six-electron domains, are summarized in **Table 9.1**. If you compare the geometries in Table 9.1 with those in Figure 9.3, you will see that they are the same.

*The shapes of different  $\text{AB}_n$  molecules or ions depend on the number of electron domains surrounding the central atom.*

The arrangement of electron domains about the central atom of an  $\text{AB}_n$  molecule or ion is called its **electron-domain geometry**. In contrast, the **molecular geometry** is the arrangement of *only the atoms* in a molecule or ion—any nonbonding pairs in the molecule are *not* part of the description of the molecular geometry.

## Applying the VSEPR Model to Determine Molecular Shapes

In determining the shape of any molecule, we first use the VSEPR model to predict the electron-domain geometry. From knowing how many of the domains are due to nonbonding pairs, we can then predict the molecular geometry. When all the electron domains in a molecule arise from bonds, the molecular geometry is identical to the electron-domain geometry. When, however, one or more domains involve nonbonding pairs of electrons, we must remember that *the molecular geometry involves only electron domains due to bonds* even though the nonbonding pairs contribute to the electron-domain geometry.



Two balloons  
linear orientation



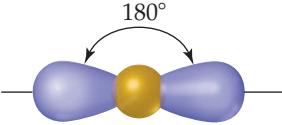
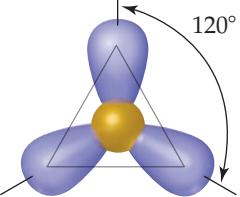
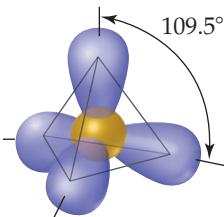
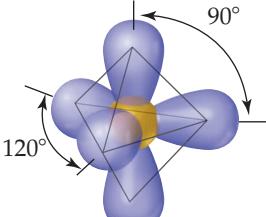
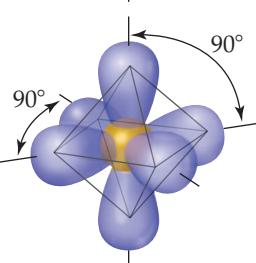
Three balloons  
trigonal-planar orientation



Four balloons  
tetrahedral orientation

▲ **Figure 9.5** A balloon analogy for electron domains.

**TABLE 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains**

Number of Electron Domains*	Arrangement of Electron Domains	Electron Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

\*The number of electron domains is sometimes called the *coordination number* of the atom.

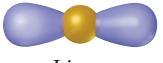
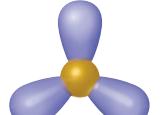
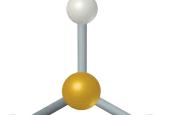
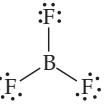
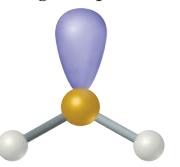
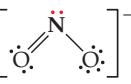
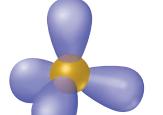
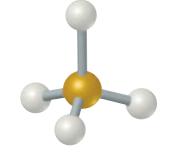
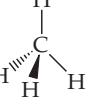
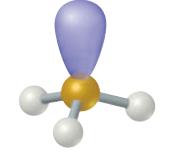
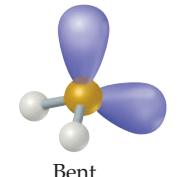
#### How to Predict the Shapes of Molecules and Ions Using the VSEPR Model

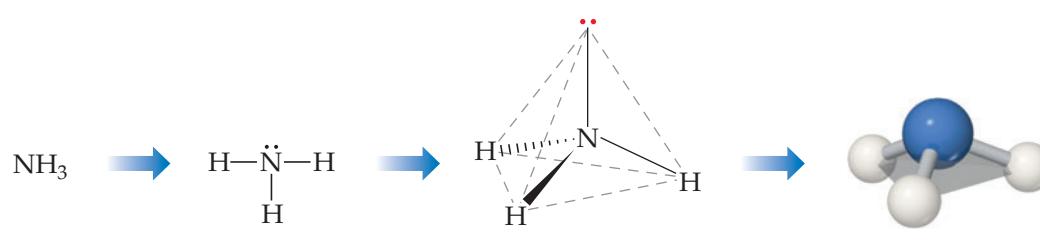
1. Draw the Lewis structure of the molecule or ion, and count the number of electron domains around the central atom. Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as one electron domain.
2. Determine the *electron-domain geometry* by arranging the electron domains about the central atom so that the repulsions among them are minimized, as shown in Table 9.1.
3. Use the arrangement of the bonded atoms to determine the *molecular geometry*.

**Table 9.2** summarizes the possible molecular geometries when an  $\text{AB}_n$  molecule has four or fewer electron domains about A. These geometries are important because they include all the shapes usually seen in molecules or ions that obey the octet rule.

**Figure 9.6** shows how to use the three steps in the VSEPR model to predict the geometry of the  $\text{NH}_3$  molecule. The three bonds and one nonbonding pair in the Lewis

**TABLE 9.2** Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	



◀ **Figure 9.6** Determining the molecular geometry of  $\text{NH}_3$ .

1 Draw Lewis structure.

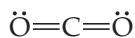
2 Determine electron-domain geometry by counting all electron domains; then use Table 9.1 to determine the appropriate electron domain geometry.

3 Determine molecular geometry by counting only bonding electron domains to see the arrangement of bonded atoms (trigonal pyramidal).

structure tell us we have four electron domains. Thus, from Table 9.1, the electron-domain geometry of  $\text{NH}_3$  is tetrahedral. We know from the Lewis structure that one electron domain is due to a nonbonding pair, which occupies one of the four vertices of the tetrahedron. In determining the molecular geometry, we consider only the three N—H bond domains, which leads to a trigonal pyramidal geometry. The situation is just like the middle drawing in Figure 9.4 in which removing one atom from a tetrahedral molecule results in a trigonal pyramidal molecule. Notice that the tetrahedral arrangement of the four electron domains leads us to predict the trigonal-pyramidal molecular geometry.

Because the trigonal-pyramidal molecular geometry is based on a tetrahedral electron-domain geometry, the ideal bond angles are  $109.5^\circ$ . As we will soon see, bond angles deviate from ideal values when the surrounding atoms and electron domains are not identical.

As one more example, let's determine the shape of the  $\text{CO}_2$  molecule. Its Lewis structure reveals two electron domains (each one a double bond) around the central carbon:



Two electron domains orient in a linear electron-domain geometry (Table 9.1). Because neither domain is a nonbonding pair of electrons, the molecular geometry is also linear, and the O—C—O bond angle is  $180^\circ$ .

## Sample Exercise 9.1

### Using the VSEPR Model



Use the VSEPR model to predict the molecular geometry of (a)  $\text{O}_3$ , (b)  $\text{SnCl}_3^-$ .

#### SOLUTION

**Analyze** We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula  $\text{AB}_n$  and both having a central atom from the *p* block of the periodic table. (Notice that for  $\text{O}_3$ , the A and B atoms are all oxygen atoms.)

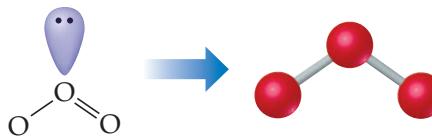
**Plan** To predict the molecular geometries, we draw their Lewis structures and count electron domains around the central atom to get the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

#### Solve

(a) We can draw two resonance structures for  $\text{O}_3$ :

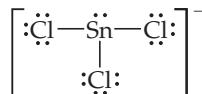


Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures, the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double bond counts as a single electron domain.) The arrangement of three electron domains is trigonal planar (Table 9.1). Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecular geometry is bent with an ideal bond angle of  $120^\circ$  (Table 9.2).

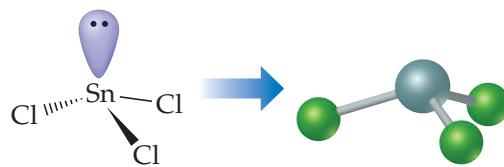


**Comment** As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(b) The Lewis structure for  $\text{SnCl}_3^-$  is:



The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair; thus, we have four electron domains, meaning a tetrahedral electron-domain geometry (Table 9.1) with one vertex occupied by a nonbonding pair of electrons. A tetrahedral electron-domain geometry with three bonding and one nonbonding domains leads to a trigonal-pyramidal molecular geometry (Table 9.2).

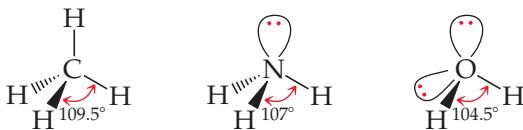


#### ► Practice Exercise

Predict the electron-domain and molecular geometries for (a)  $\text{SeCl}_2$ , (b)  $\text{CO}_3^{2-}$ .

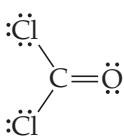
## Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

We can refine the VSEPR model to explain slight distortions from the ideal geometries summarized in Table 9.2. For example, consider methane ( $\text{CH}_4$ ), ammonia ( $\text{NH}_3$ ), and water ( $\text{H}_2\text{O}$ ). All three have a tetrahedral electron-domain geometry, but their bond angles differ slightly:

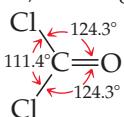


Notice that the bond angles decrease as the number of nonbonding electrons increases. A bonding pair of electrons is attracted by both nuclei of the bonded atoms, but a nonbonding pair is attracted primarily by only one nucleus. Because a nonbonding pair experiences less nuclear attraction, its electron domain is spread out more in space than is the electron domain for a bonding pair (Figure 9.7). Nonbonding electron pairs therefore take up more space than bonding pairs; in essence, they act as larger and fatter balloons in our analogy of Figure 9.5. As a result, *electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles*.

Because multiple bonds contain a higher electronic-charge density than single bonds, multiple bonds also represent enlarged electron domains. Consider the Lewis structure of *phosgene*,  $\text{Cl}_2\text{CO}$ :



Because three electron domains surround the central atom, we might expect a trigonal-planar geometry with  $120^\circ$  bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the  $\text{Cl}—\text{C}—\text{Cl}$  bond angle to  $111.4^\circ$ :



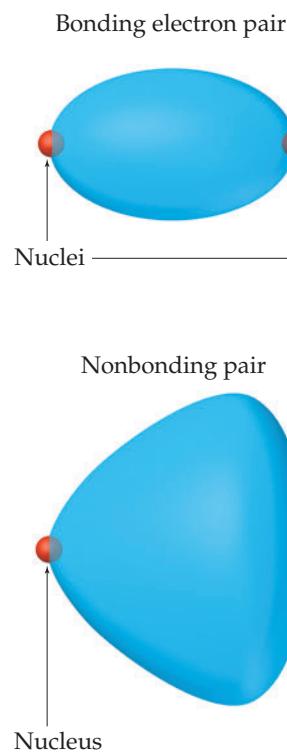
In general, *electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds*.

## Molecules with Expanded Valence Shells

Atoms from Period 3 and beyond may be surrounded by more than four electron pairs. Molecules with five or six electron domains around the central atom have molecular geometries based on either a *trigonal-bipyramidal* (five domains) or *octahedral* (six domains) electron-domain geometry (Table 9.3).

The most stable electron-domain geometry for five electron domains is the trigonal bipyramidal (two trigonal pyramids sharing a base). Unlike the other arrangements we have seen, the electron domains in a trigonal bipyramidal can point toward two geometrically distinct types of positions. Two domains point toward *axial positions*, and three point toward *equatorial positions* (Figure 9.8). Each axial domain makes a  $90^\circ$  angle with any equatorial domain. Each equatorial domain makes a  $120^\circ$  angle with either of the other two equatorial domains and a  $90^\circ$  angle with either axial domain.

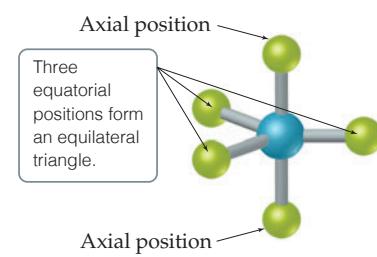
Suppose a molecule has five electron domains, and there are one or more nonbonding pairs. Will the domains from the nonbonding pairs occupy axial or equatorial positions? To answer this question, we must determine which location minimizes repulsion between domains. Repulsion between two domains is much greater when they are situated  $90^\circ$  from each other than when they are at  $120^\circ$ . An equatorial domain is  $90^\circ$  from only two other domains (the axial domains), but an axial domain is  $90^\circ$  from three other domains (the equatorial domains). Hence, an equatorial domain experiences



▲ Figure 9.7 Relative volumes occupied by bonding and nonbonding electron domains.

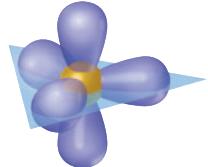
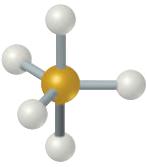
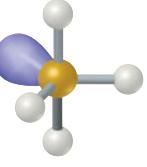
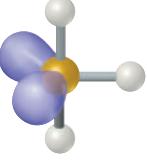
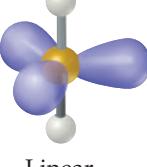
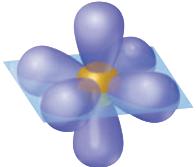
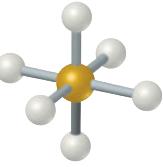
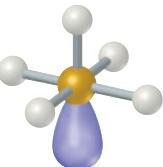
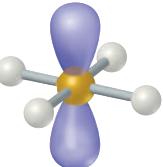
### Go Figure

What is the bond angle formed by an axial atom, the central atom, and any equatorial atom?



▲ Figure 9.8 In a trigonal-bipyramidal geometry, there are two types of positions for the outer atoms.

**TABLE 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom**

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5		5	0		$\text{PCl}_5$
	Trigonal bipyramidal			Trigonal bipyramidal	
					$\text{SF}_4$
		4	1	Seesaw	
					$\text{ClF}_3$
		3	2	T-shaped	
					$\text{XeF}_2$
		2	3	Linear	
6		6	0		$\text{SF}_6$
	Octahedral			Octahedral	
					$\text{BrF}_5$
		5	1	Square pyramidal	
					$\text{XeF}_4$
		4	2	Square planar	

less repulsion than an axial domain. Because the domains from nonbonding pairs exert larger repulsions than those from bonding pairs, nonbonding domains *always* occupy the equatorial positions in a trigonal bipyramidal.

The most stable electron-domain geometry for six electron domains is the *octahedron*. An octahedron is a polyhedron with six vertices and eight faces, each an equilateral triangle. An atom with six electron domains around it can be visualized as being at the center of the octahedron with the electron domains pointing toward the six vertices, as shown in Table 9.3. All the bond angles are  $90^\circ$ , and all six vertices are equivalent. Therefore, if an atom has five bonding electron domains and one nonbonding domain, we can put the nonbonding domain at any of the six vertices of the octahedron. The result is always a *square-pyramidal* molecular geometry. When there are two nonbonding electron domains, however, their repulsions are minimized by pointing them toward opposite sides of the octahedron, producing a *square-planar* molecular geometry, as shown in Table 9.3.

## Sample Exercise 9.2

### Molecular Geometries of Molecules with Expanded Valence Shells

Use the VSEPR model to predict the molecular geometry of (a)  $\text{SF}_4$ , (b)  $\text{IF}_5$ .

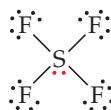
#### SOLUTION

**Analyze** The molecules are of the  $\text{AB}_n$  type with a central  $p$ -block atom.

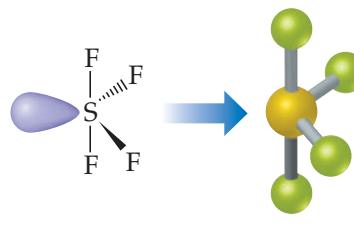
**Plan** We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.

#### Solve

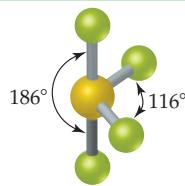
(a) The Lewis structure for  $\text{SF}_4$  is:



The sulfur has five electron domains around it: four from the  $\text{S}-\text{F}$  bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramidal. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as seesaw-shaped:

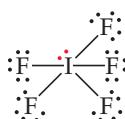


**Comment** The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial  $\text{S}-\text{F}$  bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are “pushed” by the nonbonding domain, which exerts a greater repulsion (Figure 9.7).

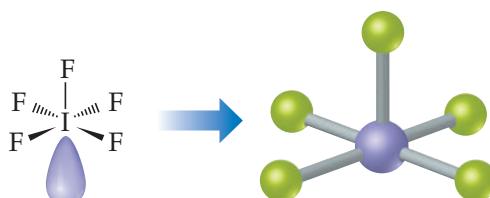


#### Solve

(b) The Lewis structure of  $\text{IF}_5$  is:



The iodine has six electron domains around it, one of which is nonbonding. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair, and the molecular geometry is *square pyramidal* (Table 9.3):



**Comment** Because the nonbonding domain is larger than the bonding domains, we predict that the four F atoms in the base of the pyramid will be tipped up slightly toward the top F atom.

atom. Experimentally, we find that the angle between the base atoms and the top F atom is  $82^\circ$ , smaller than the ideal  $90^\circ$  angle of an octahedron.

► **Practice Exercise**

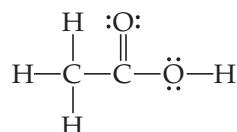
A certain  $\text{AB}_4$  molecule has a square-planar molecular geometry. Which of the following statements about the molecule is or are true?

- The molecule has four electron domains about the central atom A.
- The  $\text{B}-\text{A}-\text{B}$  angles between neighboring B atoms are  $90^\circ$ .
- The molecule has two nonbonding pairs of electrons on atom A.

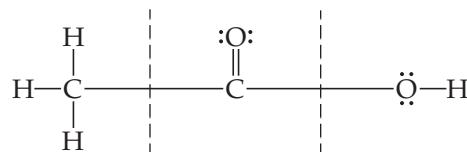
- Only one of the statements is true.
- Statements (i) and (ii) are true.
- Statements (i) and (iii) are true.
- Statements (ii) and (iii) are true.
- All three statements are true.

## Shapes of Larger Molecules

Although the molecules and ions we have considered contain only a single central atom, the VSEPR model can be extended to more complex molecules. Consider the acetic acid molecule:



We can use the VSEPR model to predict the geometry about each carbon atom and the oxygen atom:



Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	$109.5^\circ$	$120^\circ$	$109.5^\circ$

The C on the left has four electron domains (all bonding), so the electron-domain and molecular geometries around that atom are both tetrahedral. The central C has three electron domains (counting the double bond as one domain), making both the electron-domain and the molecular geometries trigonal planar. The O on the right has four electron domains (two bonding, two nonbonding), so its electron-domain geometry is tetrahedral and its molecular geometry is bent. The bond angles about the central C atom and the O atom are expected to deviate slightly from the ideal values of  $120^\circ$  and  $109.5^\circ$  because of the spatial demands of multiple bonds and nonbonding electron pairs.

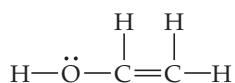
Our analysis of the acetic acid molecule is shown in [Figure 9.9](#).



## Sample Exercise 9.3

### Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule *vinyl alcohol*:



Predict the approximate values for the  $\text{H}-\text{O}-\text{C}$  and  $\text{O}-\text{C}-\text{C}$  bond angles in vinyl alcohol.

**SOLUTION**

**Analyze** We are given a Lewis structure and asked to determine two bond angles.

**Plan** To predict a bond angle, we determine the number of electron domains surrounding the middle atom in the angle. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

**Solve** In H—O—C, the O atom has four electron domains (two bonding, two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5°. The H—O—C angle is compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5°.

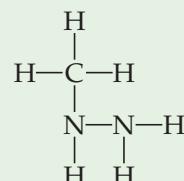
To predict the O—C—C bond angle, we examine the middle atom in the angle. In the molecule, there are three atoms bonded to this C atom and no nonbonding pairs, so it has three

electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120°. Because of the larger size of the C=C domain, the bond angle should be slightly greater than 120°.

**► Practice Exercise**

The atoms of the compound methylhydrazine,  $\text{CH}_6\text{N}_2$ , which is used as a rocket propellant, are connected as follows (note that lone pairs are not shown):

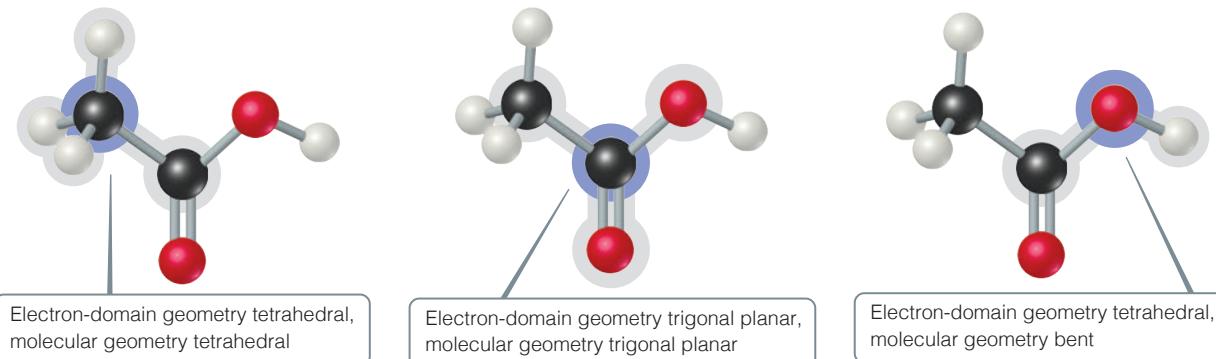
What do you predict for the ideal values of the C—N—N and H—N—H angles, respectively?



- (a) 109.5° and 109.5° (b) 109.5° and 120° (c) 120° and 109.5° (d) 120° and 120° (e) None of these

**Go Figure**

In the actual structure of acetic acid, which bond angle is expected to be the smallest?



▲ Figure 9.9 The electron-domain and molecular geometries around the three central atoms of acetic acid,  $\text{CH}_3\text{COOH}$ .

**Self-Assessment Exercise**

**9.5** What is the O—S—O bond angle in sulfur trioxide,  $\text{SO}_3$ ?

- (a) 90°  
(b) 109.5°

(c) 120°

(d) 180°

**Exercises**

**9.6** (a) An  $\text{AB}_2$  molecule is linear. How many nonbonding electron pairs are around the A atom from this information? (b) How many nonbonding electrons surround the Xe in  $\text{XeF}_2$ ? (c) Is  $\text{XeF}_2$  linear?

**9.7** (a) An  $\text{AB}_6$  molecule has no lone pairs of electrons on the A atom. What is its molecular geometry? (b) An  $\text{AB}_4$  molecule has two lone pairs of electrons on the A atom (in addition to the four B atoms). What is the electron-domain geometry around the A atom? (c) For the  $\text{AB}_4$  molecule in part (b), predict the molecular geometry.

**9.8** In which of these molecules or ions does the presence of nonbonding electron pairs produce an effect on molecular shape? (a)  $\text{CO}_2$ , (b)  $\text{CH}_2\text{Br}_2$ , (c)  $\text{OF}_2$ , (d)  $\text{BCl}_3$ , (e)  $\text{SF}_6$ .

**9.9** Give the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom: (a) four bonding domains and no nonbonding domains, (b) three bonding domains and two nonbonding domains, (c) five bonding domains and one nonbonding domain, (d) four bonding domains and two nonbonding domains.

- 9.10** Give the electron-domain and molecular geometries for the following molecules and ions: (a)  $\text{BeF}_2$ , (b)  $\text{AsCl}_5$ , (c)  $\text{NO}_2^-$ , (d)  $\text{CS}_2$ , (e)  $\text{SF}_4$ , (f)  $\text{BrF}_5$ .
- 9.11** Ammonia,  $\text{NH}_3$ , reacts with incredibly strong bases to produce the amide ion,  $\text{NH}_2^-$ . Ammonia can also react with acids to produce the ammonium ion,  $\text{NH}_4^+$ . (a) Which species (amide ion, ammonia, or ammonium ion) has the largest

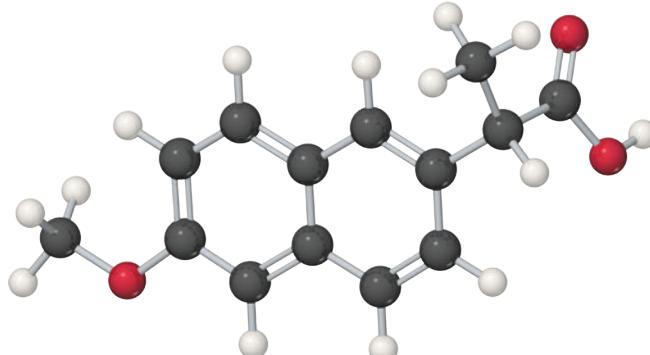
H—N—H bond angle? (b) Which species has the smallest H—N—H bond angle?

- 9.12** (a) Explain why  $\text{BrF}_4^-$  is square planar, whereas  $\text{BF}_4^-$  is tetrahedral. (b) How would you expect the H—X—H bond angle to vary in the series  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ? Explain. (Hint: The size of an electron pair domain depends in part on the electronegativity of the central atom.)

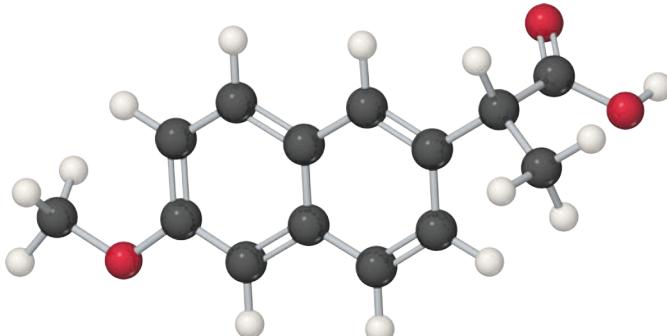
9.5 (c)

Answers to Self-Assessment Exercise

## 9.3 | Molecular Shape and Molecular Polarity



(S)-naproxen



(R)-naproxen

The shape and size of a molecule of a substance, together with the strength and polarity of its bonds, largely determine the properties of that substance. Some of the most dramatic examples of the important roles of molecular architecture are seen in biochemical reactions. Drugs are examples of molecules in which small changes in the three-dimensional arrangement of atoms have huge consequences. In the image, we see two different molecules: their trade names are (S)-naproxen and (R)-naproxen. They have the same chemical formula and even the same number of the same kind of chemical bonds; but if you look closely, the positions of an H and a  $\text{CH}_3$  group are reversed in one compared to the other. The (S) compound is prescribed to treat patients who experience the pain of arthritis; the (R) compound has no beneficial effects in humans and, in fact, causes liver poisoning. These compounds belong to a special class of structural isomers called *enantiomers* that we will learn more about later in the book. Much effort in the pharmaceutical industry goes into making, separating, and purifying one isomer of a compound from other isomers.

By the end of this section, you should be able to

- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments.

Now that we have a sense of the shapes that molecules adopt and why they do so, we will return to some topics that we first discussed in Section 8.4, namely, *bond polarity* and *dipole moments*. Recall that bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond. As the difference in electronegativity between the two atoms increases, so does the bond polarity. We saw that the dipole moment of a diatomic molecule is a measure of the amount of charge separation in the molecule.

For a molecule consisting of more than two atoms, *the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule*. For each bond in the molecule, we consider the **bond dipole**, which is the dipole moment due only to the two atoms in that bond. Consider the linear  $\text{CO}_2$  molecule, for example. As shown in **Figure 9.10(a)**, each  $\text{C}=\text{O}$  bond is polar, and because the  $\text{C}=\text{O}$  bonds are identical, the bond dipoles are equal in magnitude. A plot of the molecule's electron density clearly shows that the individual bonds are polar, but what can we say about the *overall* dipole moment of the molecule?

Bond dipoles and dipole moments are *vector quantities*; that is, they have both a magnitude and a direction. The dipole moment of a polyatomic molecule is the vector sum of its bond dipoles. Both the magnitudes *and* the directions of the bond dipoles must be considered when summing vectors. The two bond dipoles in  $\text{CO}_2$ , although equal in magnitude, are opposite in direction. Adding them is the same as adding two numbers that are equal in magnitude but opposite in sign, such as  $100 + (-100)$ . The bond dipoles, like the numbers, "cancel" each other. Therefore, the dipole moment of  $\text{CO}_2$  is zero, even though the individual bonds are polar. The geometry of the molecule dictates that the overall dipole moment be zero, making  $\text{CO}_2$  a *nonpolar* molecule.

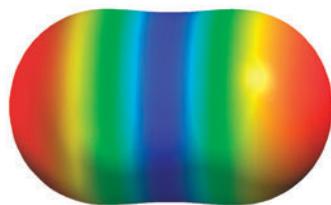
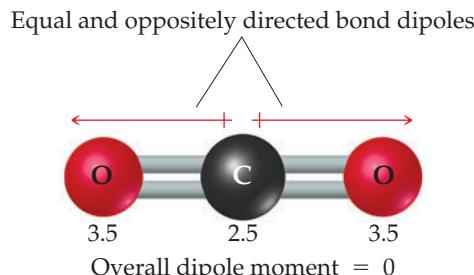
Now let's consider  $\text{H}_2\text{O}$ , a bent molecule with two polar bonds (**Figure 9.10(b)**). Again, the two bonds are identical, and the bond dipoles are equal in magnitude. Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel. Hence, the  $\text{H}_2\text{O}$  molecule has an overall nonzero dipole moment (measured dipole moment,  $\mu = 1.85 \text{ D}$ ) and is therefore a *polar* molecule. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge, as shown in Figure 9.10(b).



### Go Figure

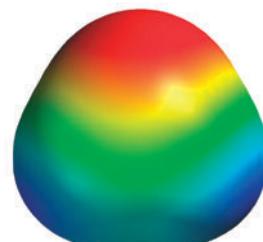
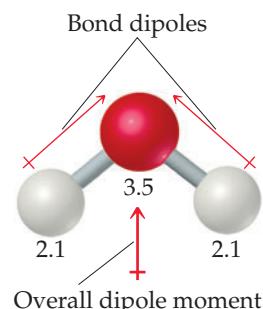
What is the sum of the two red vectors at the top of the left figure?

$\text{CO}_2$ , nonpolar



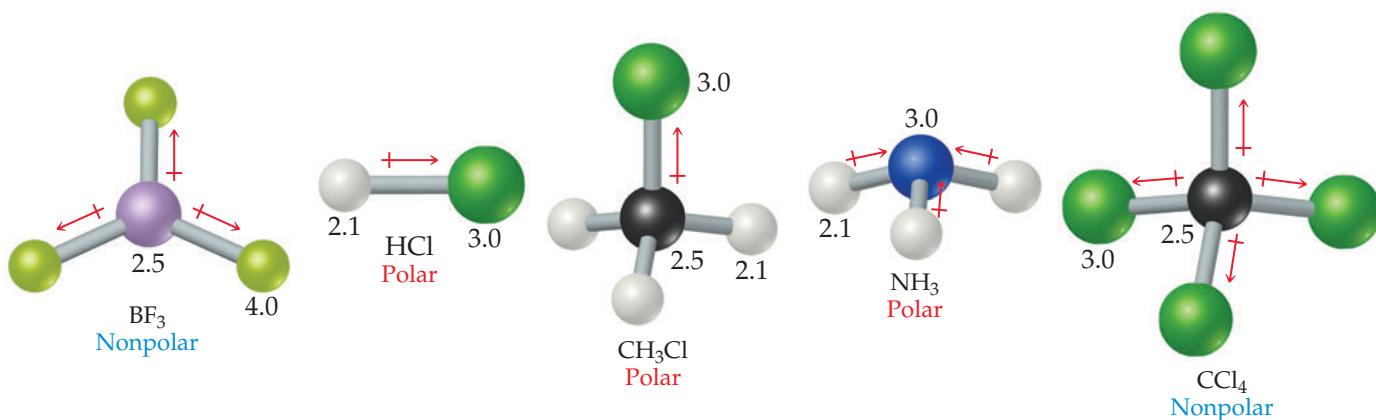
(a)

$\text{H}_2\text{O}$ , polar



(b)

▲ **Figure 9.10**  $\text{CO}_2$ , a nonpolar molecule, and  $\text{H}_2\text{O}$ , a polar molecule. The numbers are electronegativity values for these two atoms.



▲ **Figure 9.11** Polar and nonpolar molecules containing polar bonds. The numbers are electronegativity values.

**Figure 9.11** shows some examples of polar and nonpolar molecules, all with polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms ( $\text{BF}_3$  and  $\text{CCl}_4$ ) are nonpolar. For  $\text{AB}_n$  molecules in which all the B atoms are the same, certain symmetrical shapes—linear ( $\text{AB}_2$ ), trigonal planar ( $\text{AB}_3$ ), tetrahedral and square planar ( $\text{AB}_4$ ), trigonal bipyramidal ( $\text{AB}_5$ ), and octahedral ( $\text{AB}_6$ )—must lead to nonpolar molecules even though the individual bonds might be polar.

## Sample Exercise 9.4

### Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (a)  $\text{BrCl}$ , (b)  $\text{SO}_2$ , (c)  $\text{SF}_6$ .

#### SOLUTION

**Analyze** We are given three molecular formulas and asked to predict whether the molecules are polar.

**Plan** A molecule containing only two atoms is polar if the atoms differ in electronegativity. The polarity of a molecule containing three or more atoms depends on both the molecular geometry and the individual bond polarities. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry. We then use electronegativity values to determine the direction of the bond dipoles. Finally, we see whether the bond dipoles cancel to give a nonpolar molecule or reinforce each other to give a polar one.

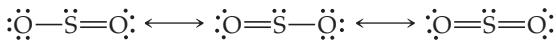
#### Solve

(a) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently,  $\text{BrCl}$  is polar, with chlorine carrying the partial negative charge:

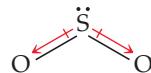


The measured dipole moment  $\mu$  of  $\text{BrCl}$  is 0.57 D.

(b) Because oxygen is more electronegative than sulfur,  $\text{SO}_2$  has polar bonds. Three resonance forms can be written:

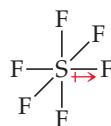


For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:



Experimentally, the dipole moment  $\mu$  of  $\text{SO}_2$  is 1.63 D.

(c) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. For clarity, only one S—F dipole is shown. The six S—F bonds are arranged octahedrally around the central sulfur:



Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that  $\mu = 0$ .

#### ► Practice Exercise

Consider an  $\text{AB}_3$  molecule in which A and B differ in electronegativity. You are told that the molecule has an overall dipole moment of zero. Which of the following could be the molecular geometry of the molecule?  
(a) Trigonal pyramidal (b) Trigonal planar  
(c) T-shaped (d) Tetrahedral  
(e) More than one of these options

## Self-Assessment Exercise

**9.13** Is phosphorus pentachloride,  $\text{PCl}_5$ , polar or nonpolar?

- (a) Polar
- (b) Nonpolar

## Exercises

**9.14** Consider a molecule with formula  $\text{AX}_2$ . Supposing the  $\text{A} - \text{X}$  bond is polar, how would you expect the dipole moment of the  $\text{AX}_2$  molecule to change as the  $\text{X} - \text{A} - \text{X}$  bond angle decreases from  $180^\circ$  to  $100^\circ$ ?

**9.15** (a) Does  $\text{CS}_2$  have a dipole moment? If so, in which direction does the net dipole point? (b) Does  $\text{SO}_2$  have a dipole moment? If so, in which direction does the net dipole point?

**9.16** (a) Is the molecule  $\text{BF}_3$  polar or nonpolar? (b) If you react  $\text{BF}_3$  to make the ion  $\text{BF}_3^{2-}$ , is this ion planar? (c) Does the molecule  $\text{BF}_2\text{Cl}$  have a dipole moment?

**9.17** Predict whether each of the following molecules is polar or nonpolar: (a)  $\text{IF}$ , (b)  $\text{CS}_2$ , (c)  $\text{SO}_3$ , (d)  $\text{PCl}_3$ , (e)  $\text{SF}_6$ , (f)  $\text{IF}_5$ .

**9.18** Dichloroethylene ( $\text{C}_2\text{H}_2\text{Cl}_2$ ) has three forms (isomers), each of which is a different substance. (a) Draw Lewis structures of the three isomers, all of which have a carbon–carbon double bond. (b) Which of these isomers has a zero dipole moment? (c) How many isomeric forms can chloroethylene,  $\text{C}_2\text{H}_3\text{Cl}$ , have? Would they be expected to have dipole moments?

9.13 (b)

Answers to Self-Assessment Exercise

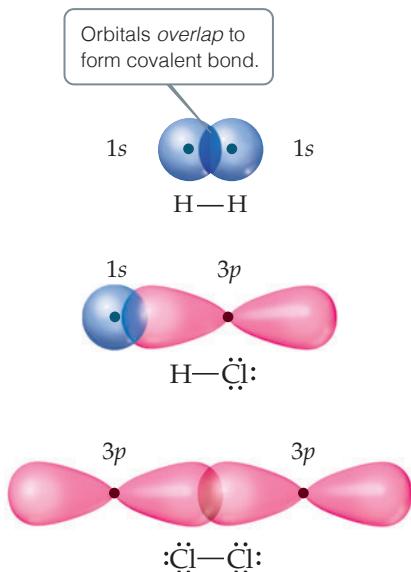
## 9.4 | Covalent Bonding and Orbital Overlap



Electron orbitals overlap to form a chemical bond much as the two parts of a zipper come together to form a secure fastening. A compatible size and shape of the two components is necessary in both cases! By the end of this section, you should be able to

- Appreciate the role of orbital overlap in a chemical bond

The VSEPR model provides a simple means for predicting molecular geometries but does not explain why bonds exist between atoms. In developing theories of covalent bonding, chemists have approached the problem from another direction, using



▲ Figure 9.12 Covalent bonds in  $\text{H}_2$ ,  $\text{HCl}$ , and  $\text{Cl}_2$  result from overlap of atomic orbitals.

quantum mechanics. How can we use atomic orbitals to explain bonding and to account for molecular geometries? The marriage of Lewis's notion of electron-pair bonds and the idea of atomic orbitals leads to a model of chemical bonding, called **valence-bond theory**, in which bonding electron pairs are concentrated in the regions between atoms, and nonbonding electron pairs lie in directed regions of space. By extending this approach to include the ways in which atomic orbitals can mix with one another, we obtain an explanatory picture that corresponds to the VSEPR model.

In Lewis theory, covalent bonding occurs when atoms share electrons because the sharing concentrates electron density between the nuclei. In valence-bond theory, we visualize the buildup of electron density between two nuclei as occurring when a valence atomic orbital of one atom shares space, or *overlaps*, with a valence atomic orbital of another atom. The overlap of orbitals allows two electrons of opposite spin to share the space between the nuclei, forming a covalent bond.

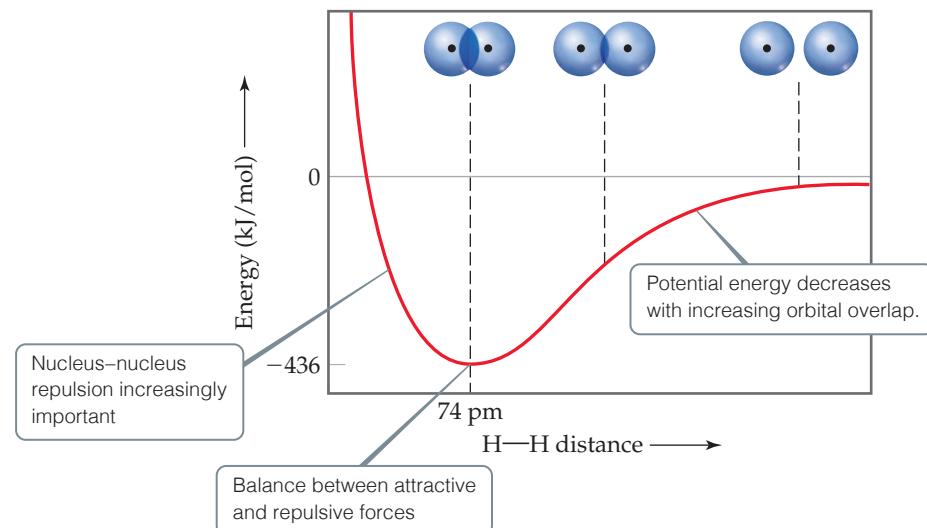
**Figure 9.12** shows three examples of how valence-bond theory describes the coming together of two atoms to form a molecule. In the example of the formation of  $\text{H}_2$ , each hydrogen atom has a single electron in a 1s orbital. As the orbitals overlap, electron density is concentrated between the nuclei. Because the electrons in the overlap region are simultaneously attracted to both nuclei, they hold the atoms together, forming a covalent bond.

The idea of orbital overlap producing a covalent bond applies equally well to other molecules. In  $\text{HCl}$ , for example, chlorine has the electron configuration  $[\text{Ne}]3s^23p^5$ . All the valence orbitals of chlorine are full except one 3p orbital, which contains a single electron. This 3p electron pairs with the single 1s electron of H to form the covalent bond that holds  $\text{HCl}$  together (Figure 9.12). Because the other two chlorine 3p orbitals are already each filled with a pair of electrons, they do not participate in the bonding to hydrogen. Likewise, we can explain the covalent bond in  $\text{Cl}_2$  in terms of the overlap of the singly occupied 3p orbital of one Cl atom with the singly occupied 3p orbital of another.

There is always an optimum distance between the two nuclei in any covalent bond. **Figure 9.13** shows how the potential energy of a system consisting of two H atoms changes as the atoms come together to form an  $\text{H}_2$  molecule. When the atoms are infinitely far apart, they do not "feel" each other and so the energy approaches zero. As the distance between the atoms decreases, the overlap between their 1s orbitals increases. Because of the resulting increase in electron density between the nuclei, the potential energy of the system decreases. That is, the strength of the bond increases, as shown by the decrease in

### Go Figure

From this graph, what are the bond length and bond strength in the  $\text{H}_2$  molecule?



▲ Figure 9.13 Formation of the  $\text{H}_2$  molecule as atomic orbitals overlap.

the potential energy of the two-atom system. However, Figure 9.13 also shows that the energy increases sharply when the distance between the two hydrogen nuclei is less than 74 pm. The increase in potential energy of the system, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance at the minimum of the potential-energy curve (in this example, at 74 pm) corresponds to the bond length of the molecule. The potential energy at this minimum corresponds to the bond strength. Thus, the observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron–electron and nucleus–nucleus).

## Self-Assessment Exercise

- 9.19** What atomic orbitals are expected to overlap in the bonding of F and Cl in FCl?
- (a) F 2s and Cl 2s  
(b) F 2s and Cl 3s  
(c) F 2p and Cl 2p  
(d) F 2p and Cl 3p

## Exercises

- 9.20** Draw sketches illustrating the overlap between the following orbitals on two atoms: (a) the 2s orbital on each atom, (b) the 2p<sub>z</sub> orbital on each atom (assume both atoms are on

the z-axis), (c) the 2s orbital on one atom and the 2p<sub>z</sub> orbital on the other atom.

9.19 (d)

Answers to Self-Assessment Exercises

## 9.5 | Hybrid Orbitals



A hybrid car is one that has two different energy sources for its propulsion—electricity and petrol. These energy sources remain separable and distinct from one another. In biology, however, a hybrid is a blend of characteristics from two different species. For example, a mule is a cross between a donkey and a horse, having more strength than the

former and being smaller than the latter. In chemistry, when we talk of hybrid orbitals, we mean a blend that displays some of the shape and size characteristics of the contributing orbitals.

By the end of this section, you should be able to

- Determine the hybridization of atoms in molecules based on observed molecular structures.

The VSEPR model, simple as it is, does a surprisingly good job at predicting molecular shape, despite the fact that it has no obvious relationship to the filling and shapes of atomic orbitals. For example, we would like to understand how to account for the tetrahedral arrangement of C—H bonds in methane in terms of the 2s and 2p orbitals of the central carbon atom, which are not directed toward the apices of a tetrahedron. How can we reconcile the notion that covalent bonds are formed from overlap of atomic orbitals with the molecular geometries that come from the VSEPR model?

To begin with, we recall that atomic orbitals are mathematical functions that come from the quantum-mechanical model for atomic structure. To explain molecular geometries, we often assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called **hybrid orbitals**. The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called **hybridization**. The total number of atomic orbitals on an atom remains constant, so the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

As we examine the common types of hybridization, notice the connection between the type of hybridization and some of the molecular geometries predicted by the VSEPR model: linear, bent, trigonal planar, and tetrahedral.

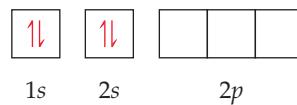
## sp Hybrid Orbitals

To illustrate the process of hybridization, consider the  $\text{BeF}_2$  molecule, which has the Lewis structure

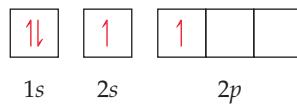


The VSEPR model predicts that  $\text{BeF}_2$  is linear with two identical Be—F bonds, in accord with experiment. How can we use valence-bond theory to describe the bonding? The electron configuration of F ( $1s^2 2s^2 2p^5$ ) indicates an unpaired electron in a 2p orbital. This electron can be paired with an unpaired Be electron to form a polar covalent bond. Which orbitals on the Be atom, however, overlap with those on the F atoms to form the Be—F bonds?

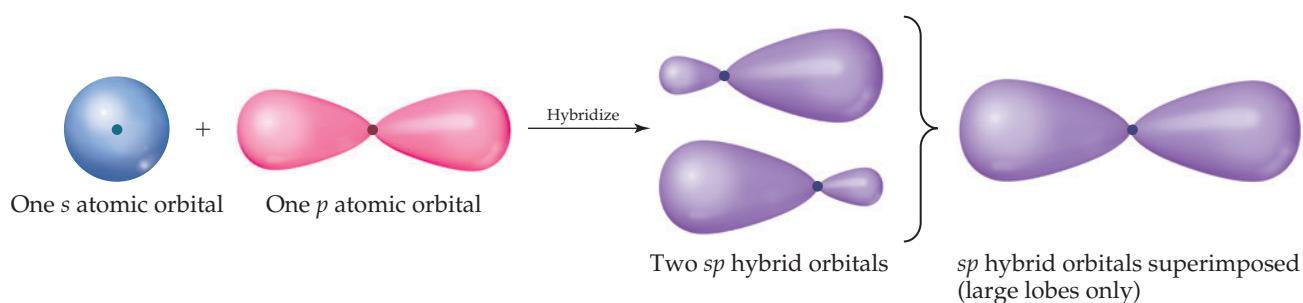
The orbital diagram for a ground-state Be atom is



Because it has no unpaired electrons, the Be atom in its ground state cannot bond with the fluorine atoms. The Be atom could form two bonds, however, by envisioning that we “promote” one of the 2s electrons to a 2p orbital:



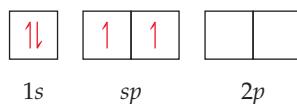
The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with F atoms. The two bonds would not be identical, however, because a 2s orbital would be used to form one of the bonds and a 2p orbital would be used to form the other. Therefore, although the promotion of an electron allows two Be—F bonds to form, we still have not explained the structure of  $\text{BeF}_2$ .



▲ Figure 9.14 Formation of *sp* hybrid orbitals.

We can solve this dilemma by “mixing” the  $2s$  orbital with one  $2p$  orbital to generate two new orbitals, as shown in Figure 9.14. Like  $p$  orbitals, each new orbital has two lobes. Unlike  $p$  orbitals, however, one lobe is much larger than the other. The two new orbitals are identical in shape, but their large lobes point in opposite directions. These two new orbitals, which are shown in purple in Figure 9.14, are hybrid orbitals. Because we have hybridized one  $s$  and one  $p$  orbital, we call each hybrid an *sp* hybrid orbital. *According to the valence-bond model, a linear arrangement of electron domains implies sp hybridization.*

For the Be atom of  $\text{BeF}_2$ , we write the orbital diagram for the formation of two *sp* hybrid orbitals as

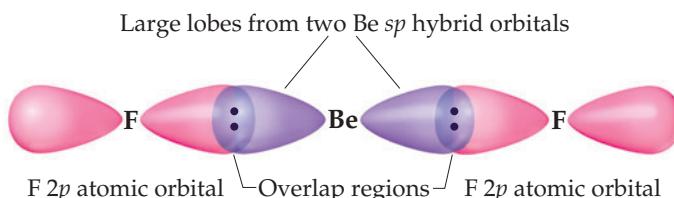


The electrons in the *sp* hybrid orbitals can form bonds with the two fluorine atoms (Figure 9.15). Because the *sp* hybrid orbitals are equivalent but point in opposite directions,  $\text{BeF}_2$  has two identical bonds and a linear geometry. We have used one of the  $2p$  orbitals in making the hybrids; the remaining two  $2p$  atomic orbitals of Be remain unhybridized and are vacant. Remember also that each fluorine atom has two other valence  $p$  atomic orbitals, each containing one nonbonding electron pair. Those atomic orbitals are omitted from Figure 9.15 to keep the illustration simpler.

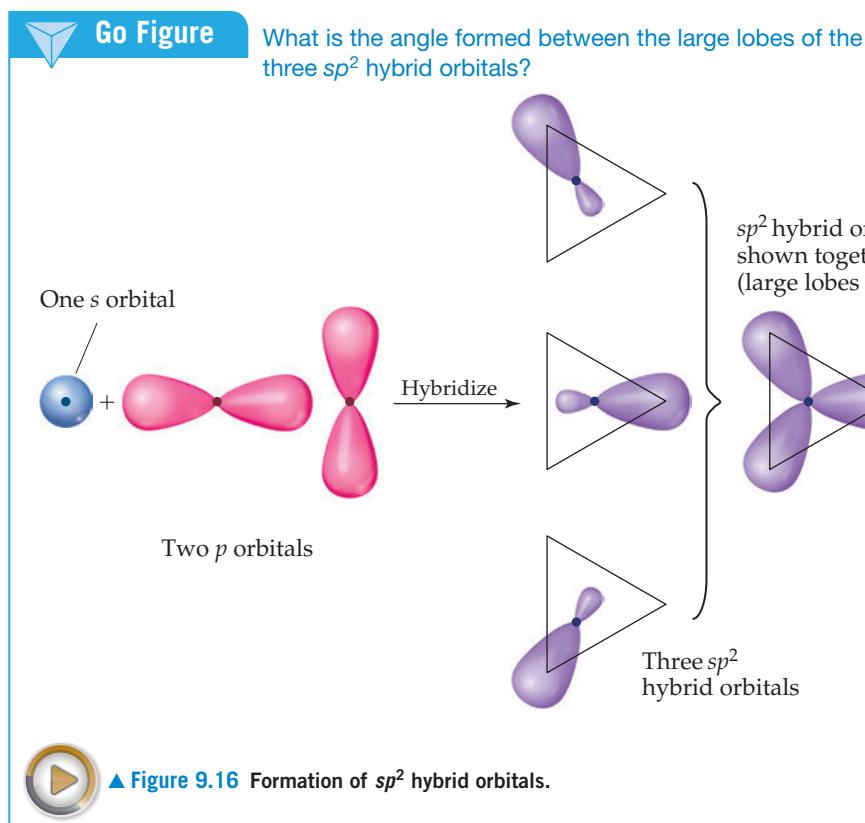
### *sp*<sup>2</sup> and *sp*<sup>3</sup> Hybrid Orbitals

Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each hybrid orbital is equivalent to the others but points in a different direction. Thus, mixing one  $2s$  and one  $2p$  atomic orbital yields two equivalent *sp* hybrid orbitals that point in opposite directions (Figure 9.14). Other combinations of atomic orbitals can be hybridized to obtain different geometries, such as *sp*<sup>2</sup> and *sp*<sup>3</sup>.

In  $\text{BF}_3$ , for example, mixing the  $2s$  and two of the  $2p$  atomic orbitals yields three equivalent *sp*<sup>2</sup> (pronounced “*s-p-two*”) hybrid orbitals (Figure 9.16). The three *sp*<sup>2</sup> hybrid orbitals lie in the same plane,  $120^\circ$  apart from one another. They are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal-planar molecular geometry of  $\text{BF}_3$ . Notice that an unfilled  $2p$  atomic orbital remains unhybridized; it is oriented perpendicular to the plane defined by the three *sp*<sup>2</sup> hybrid orbitals, with one lobe above and one below the plane. This unhybridized orbital will be important when we discuss double bonds in Section 9.6.



◀ Figure 9.15 Formation of two equivalent Be—F bonds in  $\text{BeF}_2$ .



An  $s$  atomic orbital can mix with all three  $p$  atomic orbitals in the same subshell. For example, the carbon atom in  $\text{CH}_4$  forms four equivalent bonds with the four hydrogen atoms. We envision this process as resulting from the mixing of the  $2s$  and all three  $2p$  atomic orbitals of carbon to create four equivalent  $sp^3$  (pronounced “ $s$ - $p$ -three”) hybrid orbitals. Each  $sp^3$  hybrid orbital has a large lobe that points toward one vertex of a tetrahedron (Figure 9.17). These hybrid orbitals can be used to form two-electron bonds by overlap with the atomic orbitals of another atom, such as H. Using valence-bond theory, we can describe the bonding in  $\text{CH}_4$  as the overlap of four equivalent  $sp^3$  hybrid orbitals on C with the  $1s$  orbitals of the four H atoms to form four equivalent bonds.

The idea of hybridization is also used to describe the bonding in molecules containing nonbonding pairs of electrons. In  $\text{H}_2\text{O}$ , for example, the electron-domain geometry around the central O atom is approximately tetrahedral (Figure 9.18). Thus, the four electron pairs can be envisioned as occupying  $sp^3$  hybrid orbitals. Two of the hybrid orbitals contain nonbonding pairs of electrons, and the other two form bonds with the hydrogen atoms.

## Hypervalent Molecules

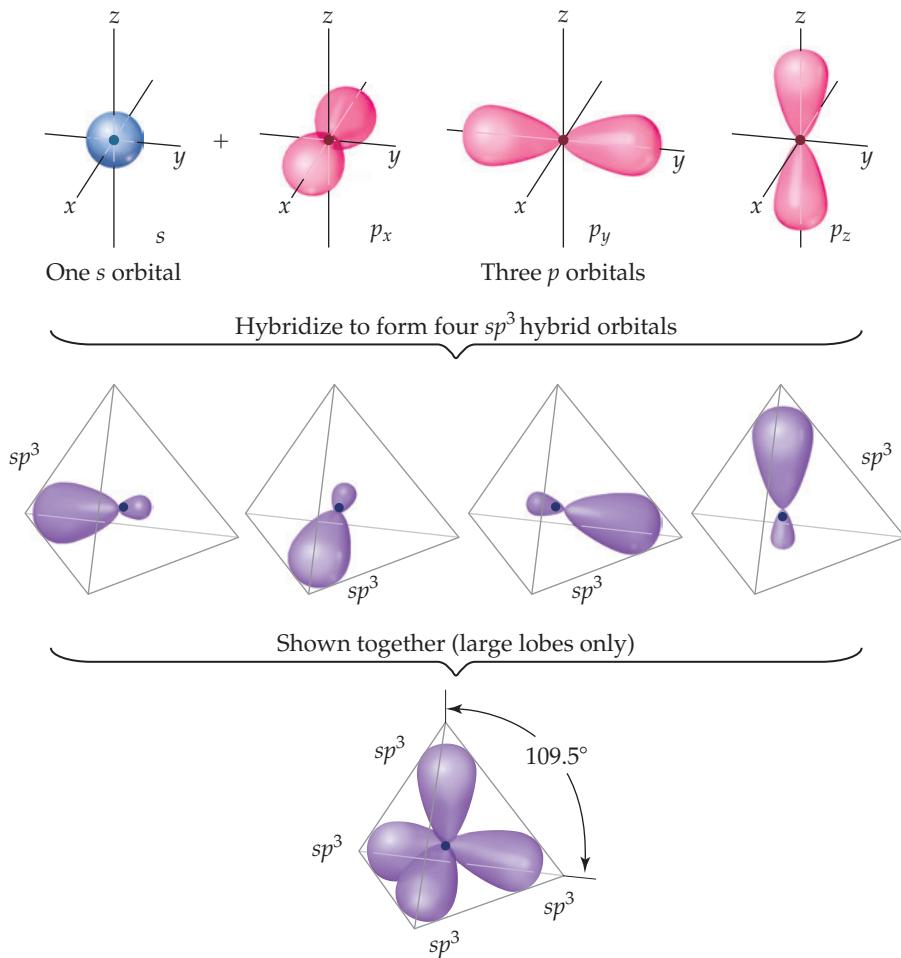
So far our discussion of hybridization has extended only to Period 2 elements, specifically carbon, nitrogen, and oxygen. The elements of Period 3 and beyond introduce a new consideration because in many of their compounds these elements are **hypervalent**—they have more than an octet of electrons around the central atom. We saw in Section 9.2 that the VSEPR model works well to predict the geometries of hypervalent molecules such as  $\text{PCl}_5$ ,  $\text{SF}_6$ , or  $\text{BrF}_5$ . But can we extend the use of hybrid orbitals to describe the bonding in these molecules? In short, the answer is no; hybrid orbitals should not be used for hypervalent molecules. Let’s examine the reasons.

The valence-bond model we developed for Period 2 elements works well for compounds of Period 3 elements so long as we have no more than an octet of electrons in the valence-shell orbitals. Thus, for example, it is appropriate to discuss the bonding in  $\text{PF}_3$  or  $\text{H}_2\text{Se}$  in terms of hybridized  $s$  and  $p$  orbitals on the central atom.

For compounds with more than an octet, we could imagine increasing the number of hybrid orbitals formed by including valence-shell  $d$  orbitals. For example, for  $\text{SF}_6$  we

 Go Figure

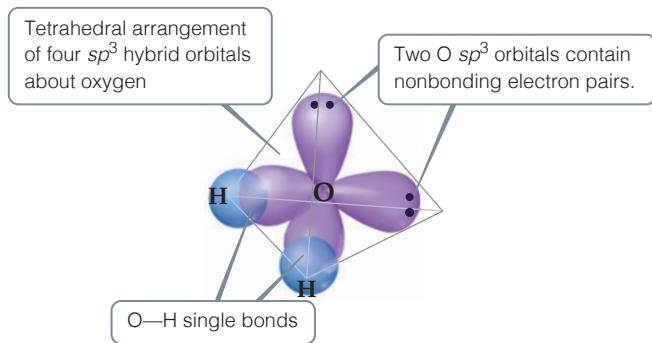
Which of the  $p$  orbitals do you think contributes the most in the mixing that leads to the right-most  $sp^3$  hybrid orbital in the second row of the figure?



 ▲ Figure 9.17 Formation of  $sp^3$  hybrid orbitals.

 Go Figure

Does it matter which of the two  $sp^3$  hybrid orbitals are used to hold the two nonbonding electron pairs?



▲ Figure 9.18 Hybrid orbital description of  $\text{H}_2\text{O}$ .

could envision mixing in two sulfur  $3d$  orbitals in addition to the  $3s$  and three  $3p$  orbitals to make a total of six hybrid orbitals. However, the sulfur  $3d$  orbitals are substantially higher in energy than the  $3s$  and  $3p$  orbitals, so the amount of energy needed to form the six hybrid orbitals is greater than the amount returned by forming bonds with the six fluorine atoms. Theoretical calculations suggest that the sulfur  $3d$  orbitals do not participate to a significant degree in the bonding between sulfur and the six fluorine atoms, and that it would not be valid to describe the bonding in  $\text{SF}_6$  in terms of six hybrid orbitals. The more detailed bonding model needed to discuss the bonding in  $\text{SF}_6$  and other hypervalent molecules requires a treatment beyond the scope of a general chemistry text. Fortunately, the VSEPR model, which explains the geometrical properties of such molecules in terms of electrostatic repulsions, does a good job of predicting their geometries.

This discussion reminds us that models in science are not reality but rather are our attempts to describe aspects of reality that we have been able to measure, such as bond distances, bond energies, molecular geometries, and so on. A model may work well up to a certain point but not beyond it, as is the case for hybrid orbitals. The hybrid orbital model for Period 2 elements has proven very useful and is an essential part of any modern discussion of bonding and molecular geometry in organic chemistry. When it comes to molecules such as  $\text{SF}_6$ , however, we encounter the limitations of the model.

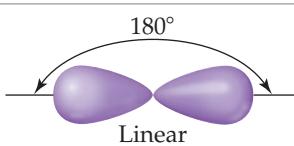
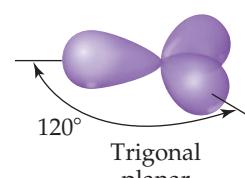
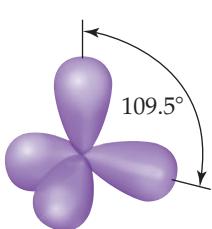
### Hybrid Orbital Summary

Overall, hybrid orbitals provide a convenient model for using valence-bond theory to describe covalent bonds in molecules that have an octet or less of electrons around the central atom and in which the molecular geometry conforms to the electron-domain geometry predicted by the VSEPR model. While the concept of hybrid orbitals has limited predictive value, when we know the electron-domain geometry, we can employ hybridization to describe the atomic orbitals used by the central atom in bonding.

#### *How to Describe the Hybrid Orbitals Used by an Atom in Bonding*

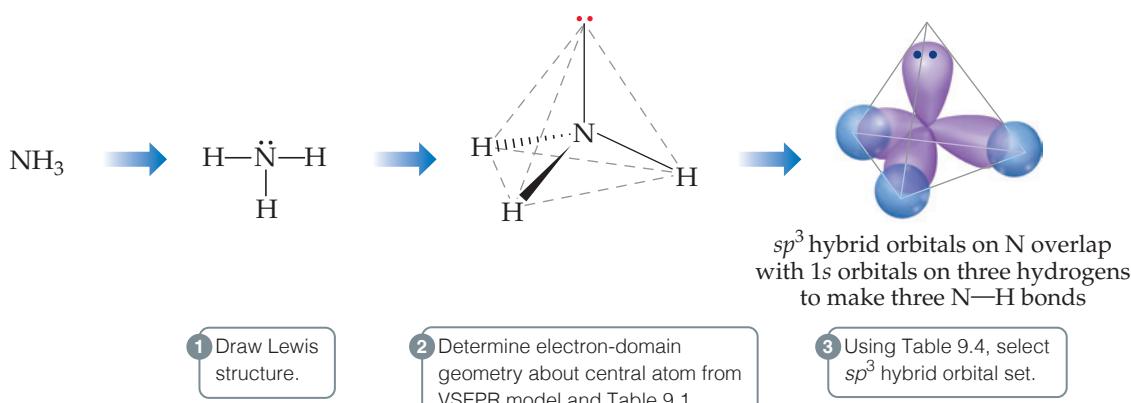
1. Draw the *Lewis structure* for the molecule or ion.
2. Use the VSEPR model to determine the electron-domain geometry around the central atom.
3. Specify the *hybrid orbitals* needed to accommodate the electron pairs based on their geometric arrangement (**Table 9.4**).

**TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets**

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
$s, p$	Two $sp$	 Linear $180^\circ$	$\text{BeF}_2, \text{HgCl}_2$
$s, p, p$	Three $sp^2$	 Trigonal planar $120^\circ$	$\text{BF}_3, \text{SO}_3$
$s, p, p, p$	Four $sp^3$	 Tetrahedral $109.5^\circ$	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

**Go Figure**

How would we modify the figure if we were looking at  $\text{PH}_3$  rather than  $\text{NH}_3$ ?



▲ **Figure 9.19** Hybrid orbital description of bonding in  $\text{NH}_3$ . Note the comparison with Figure 9.6. Here we focus on the hybrid orbitals used to make bonds and to hold nonbonding electron pairs.

These steps are illustrated in **Figure 9.19**, which shows how the hybridization at N in  $\text{NH}_3$  is determined.



### Sample Exercise 9.5

#### Describing the Hybridization of a Central Atom

Describe the orbital hybridization around the central atom in  $\text{NH}_2^-$ .

#### SOLUTION

**Analyze** We are given the chemical formula for a polyatomic anion and asked to describe the type of hybrid orbitals surrounding the central atom.

**Plan** To determine the central atom hybrid orbitals, we must know the electron-domain geometry around the atom. Thus, we draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model.

**Solve** The Lewis structure is



Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is  $sp^3$  (Table 9.4). Two of the  $sp^3$  hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.

#### ► Practice Exercise

For which of the following molecules or ions does the following description apply? “The bonding can be explained using a set of  $sp^2$  hybrid orbitals on the central atom, with one of the hybrid orbitals holding a nonbonding pair of electrons.”

- (a)  $\text{CO}_2$
- (b)  $\text{H}_2\text{S}$
- (c)  $\text{O}_3$
- (d)  $\text{CO}_3^{2-}$
- (e) More than one of these

### Self-Assessment Exercise

**9.21** What is the orbital hybridization around boron in  $\text{BH}_4^-$ ?

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

### Exercises

**9.22** For each statement, indicate whether it is true or false. (a) The greater the orbital overlap in a bond, the weaker the bond. (b) The greater the orbital overlap in a bond, the shorter the bond.

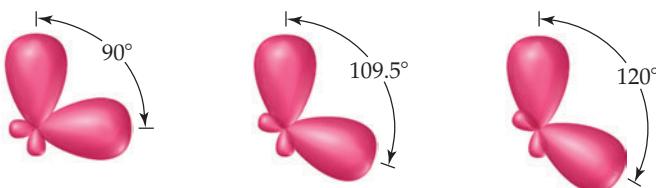
(c) To create a hybrid orbital, you could use the *s* orbital on one atom with a *p* orbital on another atom. (d) Nonbonding electron pairs cannot occupy a hybrid orbital.

**9.23** Consider the molecule  $\text{BF}_3$ . **(a)** What is the electron configuration of an isolated B atom? **(b)** What is the electron configuration of an isolated F atom? **(c)** What hybrid orbitals should be constructed on the B atom to make the B-F bonds in  $\text{BF}_3$ ? **(d)** What valence orbitals, if any, remain unhybridized on the B atom in  $\text{BF}_3$ ?

**9.24** Indicate the hybridization of the central atom in **(a)**  $\text{H}_2\text{S}$ , **(b)**  $\text{SeF}_6$ , **(c)**  $\text{P}(\text{OH})_3$ , **(d)**  $\text{AlI}_3$ .

**9.25** Shown here are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type of

hybridization, if any, that could lead to hybrid orbitals at the specified angle.



9.21 (c)

ANSWERS TO SELF-ASSESSMENT EXERCISE



## 9.6 | Multiple Bonds



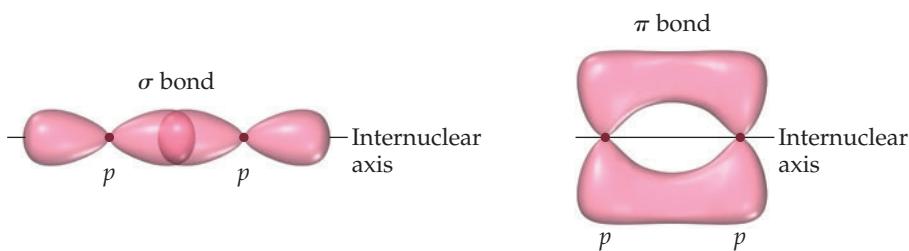
Vision begins when light is focused by the lens of the eye onto the retina, the layer of cells lining the interior of the eyeball. The retina contains photoreceptor cells called rods and cones. The rods are sensitive to dim light and are used in night vision. The cones are sensitive to colors. The tops of the rods and cones contain a molecule called *rhodopsin*, which consists of a protein, *opsin*, bonded to a reddish purple pigment called *retinal*.

Our vision depends on the rigidity of double bonds in retinal. In its normal form, retinal is held rigid by its double bonds. Light entering the eye is absorbed by rhodopsin, and it is the energy of that light that is used to break the  $\pi$ -bond portion of the double bond. Breaking the double bond allows rotation around the bond axis, changing the geometry of the retinal molecule. The retinal then separates from the opsin, triggering the reactions that produce a nerve impulse that the brain interprets as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus, only five photons of light are necessary to stimulate the eye.

At the end of this section, you should be able to

- Recognize orbital arrangements in single, double, and triple bonds.
- Identify where delocalization of  $\pi$ -electrons occurs.

In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the *internuclear axis*). The line joining the



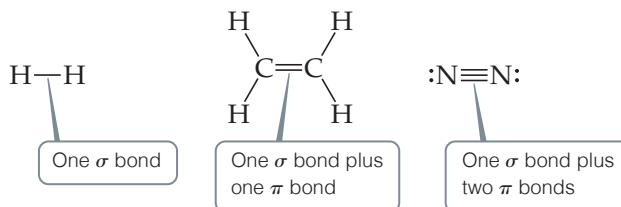
▲ **Figure 9.20** Comparison of  $\sigma$  and  $\pi$  bonds. Note that the two regions of overlap in the  $\pi$  bond, above and below the internuclear axis, constitute a single  $\pi$  bond.

two nuclei passes through the middle of the overlap region, forming a type of covalent bond called a **sigma ( $\sigma$ ) bond**. Examples of sigma bond formation include:

- the overlap of two s orbitals; one from each H in  $\text{H}_2$  (Figure 9.12),
- the overlap of an H s orbital and a Cl  $p$  orbital in  $\text{HCl}$  (Figure 9.12),
- the overlap of two  $p$  orbitals; one from each Cl in  $\text{Cl}_2$  (Figure 9.12),
- the overlap of an F  $p$  orbital and a Be  $sp$  hybrid orbital in  $\text{BeF}_2$  (Figure 9.15).

To describe multiple bonding, we must consider a second kind of bond, this one the result of overlap between two  $p$  orbitals oriented perpendicularly to the internuclear axis (Figure 9.20). The sideways overlap of  $p$  orbitals produces what is called a **pi ( $\pi$ ) bond**. A  $\pi$  bond is one in which the overlap regions lie above and below the internuclear axis. Unlike a  $\sigma$  bond, in a  $\pi$  bond the electron density is not concentrated on the internuclear axis. Although it is not evident in Figure 9.20, the sideways orientation of  $p$  orbitals in a  $\pi$  bond makes for weaker overlap. As a result,  $\pi$  bonds are generally weaker than  $\sigma$  bonds.

In almost all cases, single bonds are  $\sigma$  bonds. A double bond consists of one  $\sigma$  bond and one  $\pi$  bond, and a triple bond consists of one  $\sigma$  bond and two  $\pi$  bonds:

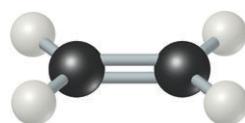


Consider ethene ( $\text{C}_2\text{H}_4$ ), which has a  $\text{C}=\text{C}$  double bond. As illustrated by the ball-and-stick model of Figure 9.21, the three bond angles about each carbon are all approximately  $120^\circ$ , suggesting that each carbon atom uses  $sp^2$  hybrid orbitals (Figure 9.16) to form  $\sigma$  bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after  $sp^2$  hybridization one electron in each carbon remains in the *unhybridized 2p* orbital. Note that this unhybridized  $2p$  orbital is directed perpendicular to the plane that contains the three  $sp^2$  hybrid orbitals.

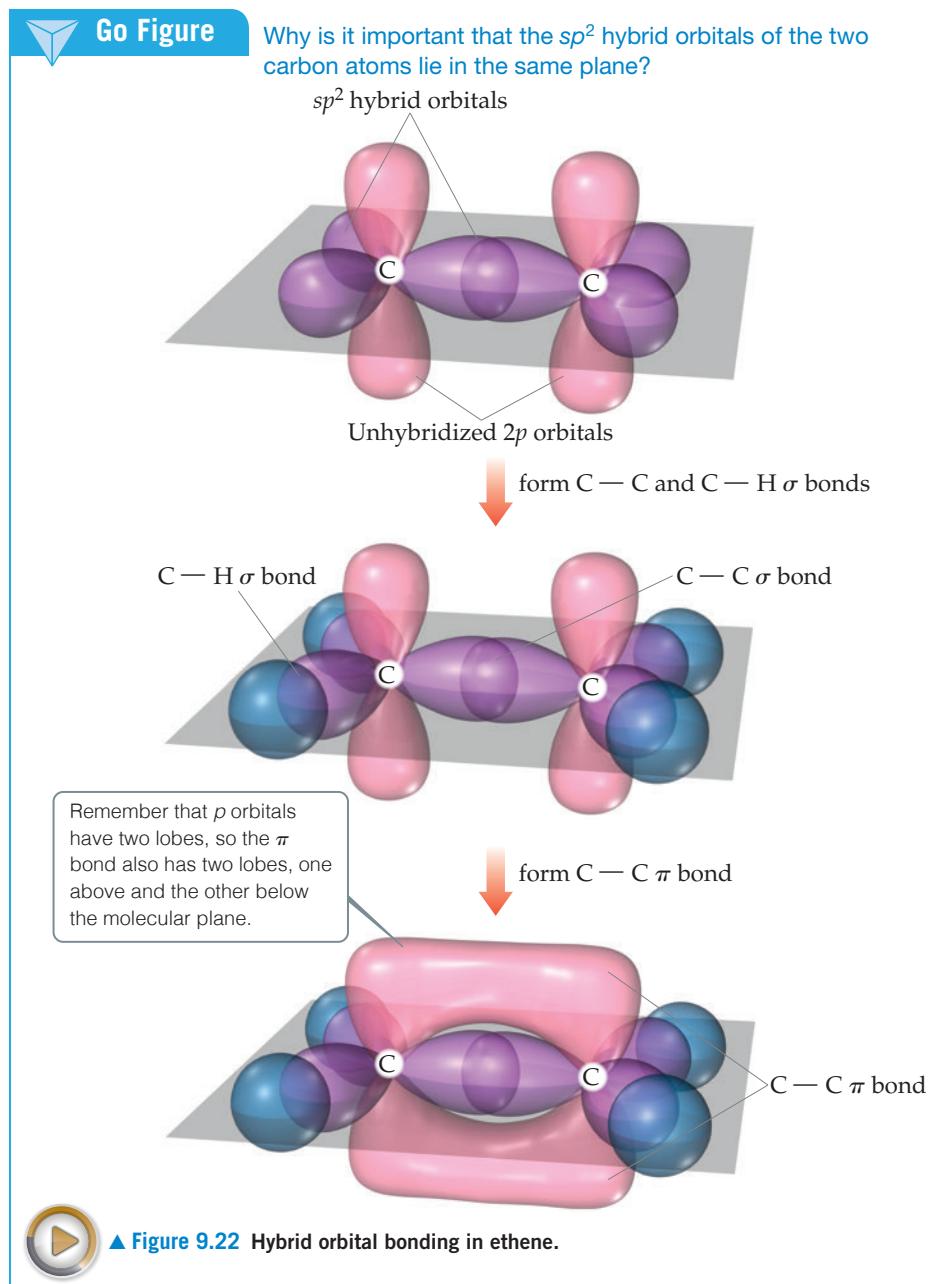
Let's go through the steps of building the bonds in the ethene molecule. Each  $sp^2$  hybrid orbital on a carbon atom contains one electron. Figure 9.22 shows how we can first envision forming the  $\text{C}-\text{C}$   $\sigma$  bond by the overlap of two  $sp^2$  hybrid orbitals, one on each carbon atom. Two electrons are used in forming the  $\text{C}-\text{C}$   $\sigma$  bond. Next, the  $\text{C}-\text{H}$   $\sigma$  bonds are formed by overlap of the remaining  $sp^2$  hybrid orbitals on the C atoms with the  $1s$  orbitals on each H atom. We use eight more electrons to form these four  $\text{C}-\text{H}$  bonds. Thus, 10 of the 12 valence electrons in the  $\text{C}_2\text{H}_4$  molecule are used to form five  $\sigma$  bonds.

The remaining two valence electrons reside in the unhybridized  $2p$  orbitals, one electron on each carbon. These two orbitals can overlap sideways with each other, as shown in Figure 9.22. The resulting electron density is concentrated above and below the  $\text{C}-\text{C}$  bond axis: It is a  $\pi$  bond (Figure 9.20). Thus, the  $\text{C}=\text{C}$  double bond in ethene consists of one  $\sigma$  bond and one  $\pi$  bond.

Although we cannot experimentally observe a  $\pi$  bond directly (all we can observe are the positions of the atoms), the structure of ethene provides strong support for



▲ **Figure 9.21** Trigonal-planar molecular geometry of ethene. The double bond is made up of one  $\text{C}-\text{C}$   $\sigma$  bond and one  $\text{C}-\text{C}$   $\pi$  bond.



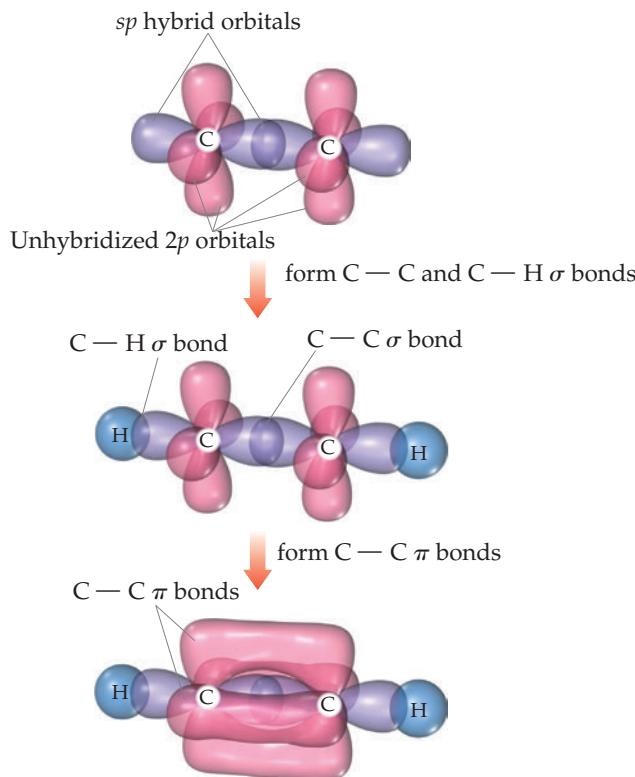
its presence. First, the  $C - C$  bond length in ethene (134 pm) is much shorter than in compounds with  $C - C$  single bonds (154 pm), consistent with the presence of a stronger  $C = C$  double bond. Second, all six atoms in  $C_2H_4$  lie in the same plane. The  $p$  orbitals on each C atom that make up the  $\pi$  bond can achieve a good overlap only when the two  $CH_2$  fragments lie in the same plane. Because  $\pi$  bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.

Triple bonds can also be explained using hybrid orbitals. Ethyne ( $C_2H_2$ ), for example, is a linear molecule containing a triple bond:  $H - C \equiv C - H$ . The linear geometry suggests that each carbon atom uses  $sp$  hybrid orbitals to form  $\sigma$  bonds with the other carbon and one hydrogen. Each carbon atom thus has two unhybridized  $2p$  orbitals at right angles to each other and to the axis of the  $sp$  hybrid set (Figure 9.23). Thus, there are two  $p$  orbitals remaining on an  $sp$ -hybridized carbon atom. These  $p$  orbitals overlap to form a pair of  $\pi$  bonds. The triple bond in ethyne therefore consists of one  $\sigma$  bond and two  $\pi$  bonds.

Although it is possible to make  $\pi$  bonds from  $d$  orbitals, the only  $\pi$  bonds we will consider are those formed by the overlap of  $p$  orbitals. These  $\pi$  bonds can form only if

 Go Figure

Based on the models of bonding in ethene and ethyne, which molecule should have the greater carbon–carbon bond strength?



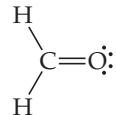
 ▲ Figure 9.23 Formation of two  $\pi$  bonds in ethyne, C<sub>2</sub>H<sub>2</sub>.

unhybridized *p* orbitals are present on the bonded atoms. Therefore, only atoms having *sp* or *sp*<sup>2</sup> hybridization can form  $\pi$  bonds. Further, double and triple bonds (and hence  $\pi$  bonds) are more common in molecules made up of Period 2 atoms, especially C, N, and O. Larger atoms, such as S, P, and Si, form  $\pi$  bonds less readily.

 Sample Exercise 9.6

### Describing $\sigma$ and $\pi$ Bonds in a Molecule

Methanal has the Lewis structure



Describe how the bonds in methanal are formed in terms of overlaps of hybrid and unhybridized orbitals.

**SOLUTION**

**Analyze** We are asked to describe the bonding in methanal in terms of hybrid orbitals.

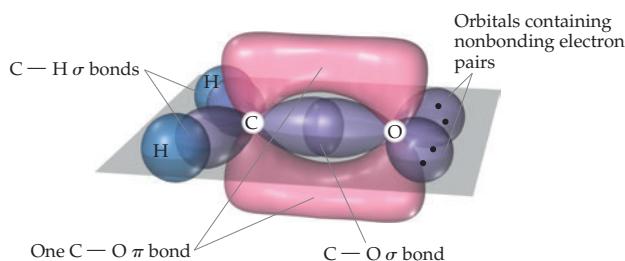
**Plan** Single bonds are  $\sigma$  bonds, and double bonds consist of one  $\sigma$  bond and one  $\pi$  bond. The ways in which these bonds form can be deduced from the molecular geometry, which we predict using the VSEPR model.

**Solve** The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about

120°. This geometry implies *sp*<sup>2</sup> hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C–H and one C–O  $\sigma$  bonds to C. There remains an unhybridized 2p orbital on carbon, perpendicular to the plane of the three *sp*<sup>2</sup> hybrids.

The O atom also has three electron domains around it, and so we assume it has *sp*<sup>2</sup> hybridization as well. One of these hybrid orbitals participates in the C–O  $\sigma$  bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has a *p* orbital that is perpendicular to the plane of the molecule. The two *p* orbitals overlap to form a C–O  $\pi$  bond (Figure 9.24).

*Continued*



▲ Figure 9.24 Formation of  $\sigma$  and  $\pi$  bonds in methanol,  $\text{H}_2\text{CO}$ .

#### ► Practice Exercise

We have just arrived at a bonding description for the methanol molecule. Which of the following statements about the molecule is or are true?

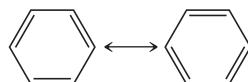
- (i) Two of the electrons in the molecule are used to make the  $\pi$  bond in the molecule.

- (ii) Six of the electrons in the molecule are used to make the  $\sigma$  bonds in the molecule.
- (iii) The C—O bond length in methanol should be shorter than that in methanol,  $\text{H}_3\text{COH}$ .
- (a) Only one of the statements is true.
- (b) Statements (i) and (ii) are true.
- (c) Statements (i) and (iii) are true.
- (d) Statements (ii) and (iii) are true.
- (e) All three statements are true.

## Resonance Structures, Delocalization, and $\pi$ Bonding

In the molecules we have discussed thus far in this section, the bonding electrons are *localized*. By this we mean that the  $\sigma$  and  $\pi$  electrons are associated totally with the two atoms that form the bond. In many molecules, however, we cannot adequately describe the bonding as being entirely localized. This situation arises particularly in molecules that have two or more resonance structures involving  $\pi$  bonds.

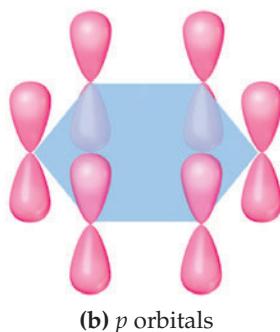
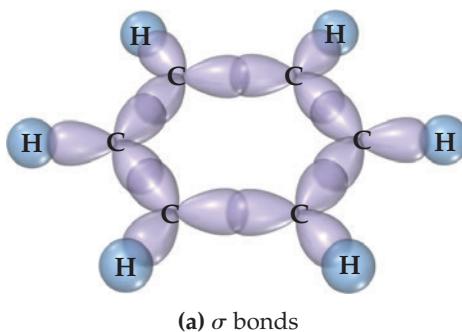
One molecule that cannot be described with localized  $\pi$  bonds is benzene ( $\text{C}_6\text{H}_6$ ), which has two resonance structures:



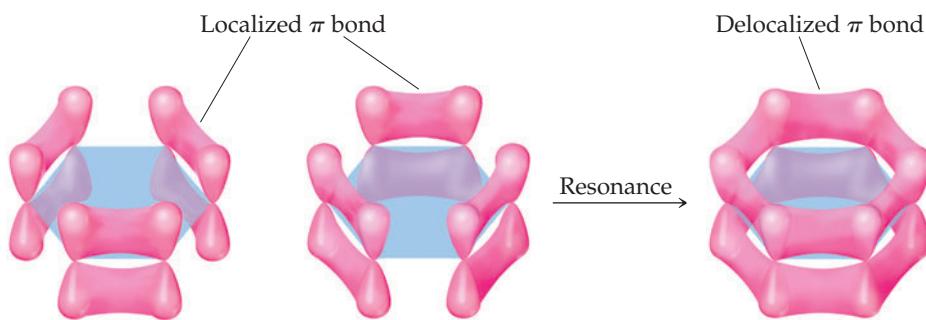
Benzene has a total of 30 valence electrons. To describe the bonding in benzene using hybrid orbitals, we first choose a hybridization scheme consistent with the geometry of the molecule. Because each carbon is surrounded by three atoms at  $120^\circ$  angles, the appropriate hybrid set is  $sp^2$ . Six localized C—C  $\sigma$  bonds and six localized C—H  $\sigma$  bonds are formed from the  $sp^2$  hybrid orbitals, as shown in Figure 9.25(a). Thus, 24 of the valence electrons are used to form the  $\sigma$  bonds in the molecule.

#### Go Figure

What are the two kinds of  $\sigma$  bonds found in benzene?



▲ Figure 9.25  $\sigma$  and  $\pi$  bond networks in benzene,  $\text{C}_6\text{H}_6$ . (a) The  $\sigma$  bond framework. (b) The  $\pi$  bonds are formed from overlap of the unhybridized  $2p$  orbitals on the six carbon atoms.



◀ Figure 9.26 Delocalized  $\pi$  bonds in benzene.

Because the hybridization at each C atom is  $sp^2$ , there is one  $p$  orbital on each C atom, each oriented perpendicular to the plane of the molecule. The situation is very much like that in ethene except we now have six  $p$  orbitals arranged in a ring [Figure 9.25(b)]. The remaining six valence electrons occupy these six  $p$  orbitals, one per orbital.

We could envision using the  $p$  orbitals to form three localized  $\pi$  bonds. As shown in Figure 9.26, there are two equivalent ways to make these localized bonds, each corresponding to one resonance structure. However, a representation that reflects *both* resonance structures has the six  $\pi$  electrons “smeared out” among all six carbon atoms, as shown on the right in Figure 9.26.

This model leads us to predict that all the carbon–carbon bond lengths will be identical, with a bond length between that of a C–C single bond (154 pm) and that of a C=C double bond (134 pm). This prediction is consistent with the observed carbon–carbon bond length in benzene (140 pm).

Because we cannot describe the  $\pi$  bonds in benzene as individual bonds between neighboring atoms, we say that benzene has a six-electron  $\pi$  system **delocalized** among the six carbon atoms. Delocalization of the electrons in its  $\pi$  bonds gives benzene a special stability. Electron delocalization in  $\pi$  bonds is also responsible for the color of many organic molecules. A final important point to remember about delocalized  $\pi$  bonds is the constraint they place on the geometry of a molecule. For optimal overlap of the  $p$  orbitals, all the atoms involved in a delocalized  $\pi$  bonding network should lie in the same plane. This restriction imparts a certain rigidity to the molecule that is absent in molecules containing only  $\sigma$  bonds (see the “Chemistry and Life” box on vision).

## Sample Exercise 9.7

### Delocalized Bonding

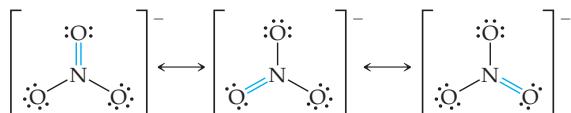
Describe the bonding in the nitrate ion,  $\text{NO}_3^-$ . Does this ion have delocalized  $\pi$  bonds?

#### SOLUTION

**Analyze** Given the chemical formula for a polyatomic anion, we are asked to describe the bonding and determine whether the ion has delocalized  $\pi$  bonds.

**Plan** Our first step is to draw Lewis structures. Multiple resonance structures involving the placement of the double bonds in different locations would suggest that the  $\pi$  component of the double bonds is delocalized.

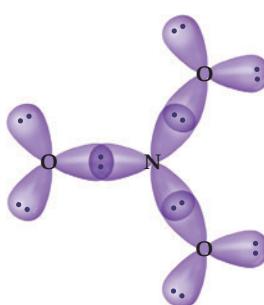
**Solve** In Section 8.6 we saw that  $\text{NO}_3^-$  has three resonance structures:



In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies  $sp^2$  hybridization of the N atom. It is helpful when considering delocalized  $\pi$  bonding to consider atoms with lone pairs that are bonded to the central atom to be  $sp^2$  hybridized as well. Thus, we can envision that each of the O atoms in the anion has three  $sp^2$  hybrid orbitals in the plane of the

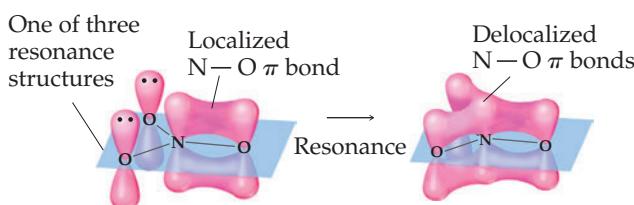
ion. Each of the four atoms has an unhybridized  $p$  orbital oriented perpendicular to the plane of the ion.

The  $\text{NO}_3^-$  ion has 24 valence electrons. We can first use the  $sp^2$  hybrid orbitals on the four atoms to construct the three N–O  $\sigma$  bonds. That uses all of the  $sp^2$  hybrids on the N atom and one  $sp^2$  hybrid on each O atom. Each of the two remaining  $sp^2$  hybrids on each O atom is used to hold a nonbonding pair of electrons. Thus, for any of the resonance structures, we have the following arrangement in the plane of the ion:



Continued

Notice that we have accounted for a total of 18 electrons—6 in the three N—O  $\sigma$  bonds, and 12 as nonbonding pairs on the O atoms. The remaining six electrons will reside in the  $\pi$  system of the ion. The four  $p$  orbitals—one on each of the four atoms—are used to build the  $\pi$  system. For any one of the three resonance structures shown, we might imagine a single localized N—O  $\pi$  bond formed by the overlap of the  $p$  orbital on N and a  $p$  orbital on one of the O atoms. The remaining two O atoms have nonbonding pairs in their  $p$  orbitals. Thus, for each of the resonance structures, we have the situation shown in **Figure 9.27**. Because each resonance structure contributes equally to the observed structure of  $\text{NO}_3^-$ , however, we represent the  $\pi$  bonding as delocalized over the three N—O bonds, as shown in the figure. We see that the  $\text{NO}_3^-$  ion has a six-electron  $\pi$  system delocalized among the four atoms in the ion.



**▲ Figure 9.27** Localized and delocalized representations of the six-electron  $\pi$  system in  $\text{NO}_3^-$ .

### ► Practice Exercise

How many electrons are in the  $\pi$  system of the ozone molecule,  $\text{O}_3$ ?

- (a) 2 (b) 4 (c) 6 (d) 14 (e) 18

## General Conclusions about $\sigma$ and $\pi$ Bonding

On the basis of the examples we have seen, we can draw a few helpful conclusions for using hybrid orbitals to describe molecular structures:

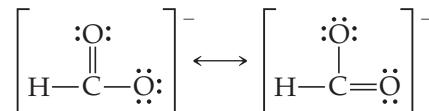
- Every pair of bonded atoms shares one or more pairs of electrons. Each bond line we draw in a Lewis structure represents two shared electrons. In every  $\sigma$  bond one pair of electrons is localized in the space between the atoms. The appropriate set of hybrid orbitals used to form the  $\sigma$  bonds between an atom and its neighbors is determined by the observed geometry of the molecule. The correlation between the set of hybrid orbitals and the geometry about an atom is given in Table 9.4.
- Because the electrons in  $\sigma$  bonds are localized in the region between two bonded atoms, they do not make a significant contribution to the bonding between any other two atoms.
- When atoms share more than one pair of electrons, one pair is used to form a  $\sigma$  bond; the additional pairs form  $\pi$  bonds. The centers of charge density in a  $\pi$  bond lie above and below the internuclear axis.
- Molecules can have  $\pi$  systems that extend over more than two bonded atoms. Electrons in extended  $\pi$  systems are said to be “delocalized.” We can determine the number of electrons in the  $\pi$  system of a molecule using the procedures we discussed in this section.

## Self-Assessment Exercises

**9.26** Draw one resonance structure of the carbonate ion,  $\text{CO}_3^{2-}$ . How many  $\sigma$ - and  $\pi$ -bonds are present in  $\text{CO}_3^{2-}$ ?

- (a) 3 $\sigma$  bonds  
 (b) 3 $\sigma$  bonds and 1 $\pi$  bond  
 (c) 3 $\sigma$  bonds and 2 $\pi$  bonds  
 (d) 4 $\sigma$  bonds

**9.27** Is the  $\pi$ -bond in the  $\text{HCO}_2^-$  ion shown here localized or delocalized?

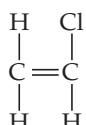


- (a) Localized  
 (b) Delocalized

## Exercises

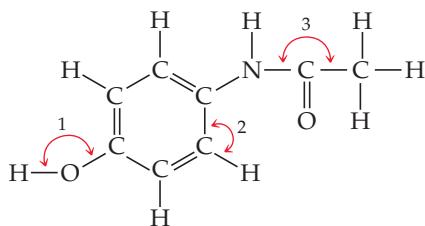
**9.28** (a) Draw a picture showing how two  $p$  orbitals on two different atoms can be combined to make a  $\sigma$  bond. (b) Sketch a  $\pi$  bond that is constructed from  $p$  orbitals. (c) Which is generally stronger, a  $\sigma$  bond or a  $\pi$  bond? Explain. (d) Can two  $s$  orbitals combine to form a  $\pi$  bond? Explain.

**9.29** Vinyl chloride,  $C_2H_3Cl$ , is a gas that is used to form the important polymer called polyvinyl chloride (PVC). Its Lewis structure is



(a) What is the total number of valence electrons in the vinyl chloride molecule? (b) How many valence electrons are used to make  $\sigma$  bonds in the molecule? (c) How many valence electrons are used to make  $\pi$  bonds in the molecule? (d) How many valence electrons remain in nonbonding pairs in the molecule? (e) What is the hybridization at each carbon atom in the molecule?

**9.30** Acetaminophen, better known as paracetamol, has the following Lewis structure:

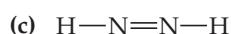
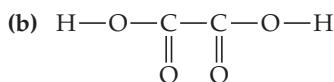
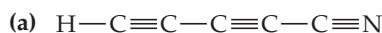


(a) What are the approximate values of the bond angles labelled 1, 2, and 3? (b) What hybrid orbitals are used about the central atom of each of these angles? (c) How many  $\sigma$  bonds are in the molecule?

**9.31** (a) What is the difference between a localized  $\pi$  bond and a delocalized one? (b) How can you determine whether a molecule or ion will exhibit delocalized  $\pi$  bonding? (c) Is the  $\pi$  bond in  $NO_2^-$  localized or delocalized?

**9.32** In the sulfate ion,  $SO_4^{2-}$ , the sulfur atom is the central atom with the other 4 oxygen atoms attached to it. (a) Draw a Lewis structure for the sulfate ion. (b) What hybridization is exhibited by the S atom? (c) Are there multiple equivalent resonance structures for the ion? (d) How many electrons are in the  $\pi$  system of the ion?

**9.33** Predict the molecular geometry of each of the following molecules:



9.26 (b) 9.27 (b)

Answers to Self-Assessment Exercises

## 9.7 | Molecular Orbitals



At the very northern tip of Denmark lies the city of Skagen and Grenen beach, a long sandbar that reaches into the sea. What is remarkable is that it lies at the meeting of two seas—the Skagerrak (part of the North Sea) and the Kattegat (part of the Baltic sea). Where these two seas meet, the water is ‘confused’, the waves of one sea meeting those of the other, sometimes to reinforce one another, sometimes to cancel one another.

In this section, we look at a model of bonding in which the electrons are treated as waves that can interact, reinforce, or cancel one another.

By the end of this section, you should be able to

- Understand the molecular orbitals formed from two 1s atomic orbitals.

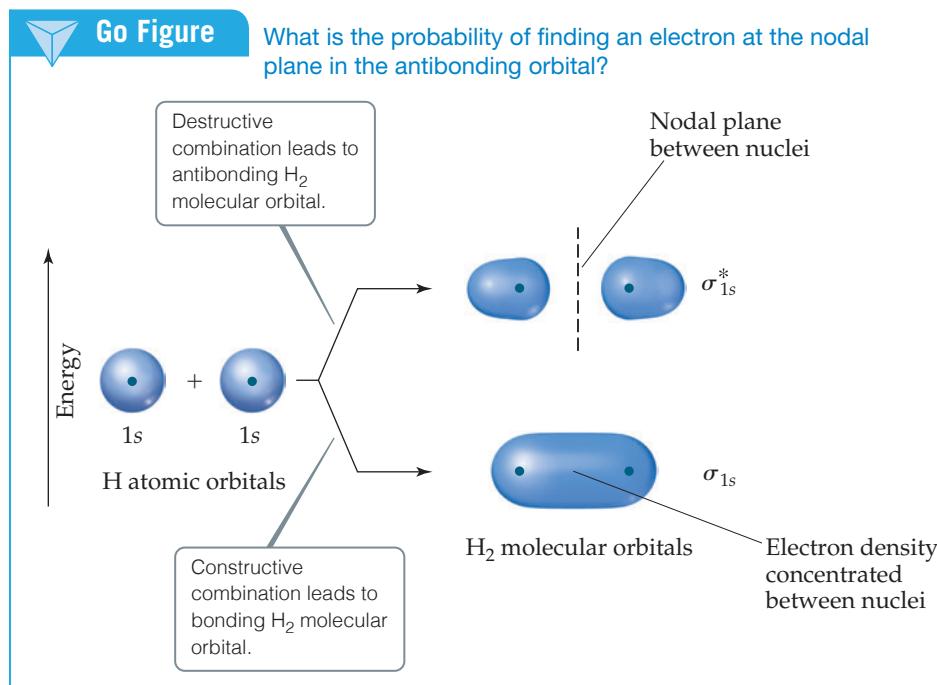
While valence-bond theory helps explain some of the relationships among Lewis structures, atomic orbitals, and molecular geometries, it does not explain all aspects of bonding. It is not successful, for example, in describing the excited states of molecules, which we must understand to explain how molecules absorb light, giving them color.

Some aspects of bonding are better explained by a more sophisticated model called **molecular orbital theory**. In Chapter 6, we saw that electrons in atoms can be described by wave functions, which we call atomic orbitals. In a similar way, molecular orbital theory describes the electrons in molecules by using specific wave functions, each of which is called a **molecular orbital (MO)**.

Molecular orbitals have many of the same characteristics as atomic orbitals. For example, an MO can hold a maximum of two electrons (with opposite spins), it has a definite energy, and we can visualize its electron-density distribution by using a contour representation, as we did with atomic orbitals. Unlike atomic orbitals, however, MOs are associated with an entire molecule, not with a single atom.

### Molecular Orbitals of the Hydrogen Molecule

We begin our study of MO theory with the hydrogen molecule,  $H_2$ . We will use the two 1s atomic orbitals (one on each H atom) to construct molecular orbitals for  $H_2$ . *Whenever two atomic orbitals overlap, two molecular orbitals form.* Thus, the overlap of the 1s orbitals of two hydrogen atoms to form  $H_2$  produces two MOs. The first MO, which is shown at the bottom right of [Figure 9.28](#), is formed by adding the wave functions for the two 1s orbitals. We refer to this as *constructive combination*. The energy of the resulting MO is lower



▲ **Figure 9.28** The two molecular orbitals of  $H_2$ , one a bonding MO and one an antibonding MO.

in energy than the two atomic orbitals from which it was made. It is called the **bonding molecular orbital**.

The second MO is formed by what is called *destructive combination*: combining the two atomic orbitals in a way that causes the electron density to be canceled in the central region where the two overlap. The process is discussed more fully in the “Closer Look” box later in the chapter. The energy of the resulting MO, referred to as the **antibonding molecular orbital**, is higher than the energy of the atomic orbitals. The antibonding MO of H<sub>2</sub> is shown at the top right in Figure 9.28.

As illustrated in Figure 9.28, in the bonding MO electron density is concentrated in the region between the two nuclei. This sausage-shaped MO results from summing the two atomic orbitals so that the atomic orbital wave functions combine in the region between the two nuclei. Because an electron in this MO is attracted to both nuclei, the electron is more stable (it has lower energy) than it is in the 1s atomic orbital of an isolated hydrogen atom. Further, because this bonding MO concentrates electron density between the nuclei, it holds the atoms together in a covalent bond.

By contrast, the antibonding MO has very little electron density between the nuclei. Instead of combining in the region between the nuclei, the atomic orbital wave functions cancel each other in this region, leaving the greatest electron density on opposite sides of the two nuclei. Thus, an antibonding MO excludes electrons from the very region in which a bond must be formed. Antibonding orbitals invariably have a *plane* in the region between the nuclei where the electron density is zero. This plane is called a **nodal plane** of the MO. (The nodal plane is shown as a dashed line in Figure 9.28 and subsequent figures.) An electron in an antibonding MO is repelled from the bonding region and is therefore less stable (it has higher energy) than it is in the 1s atomic orbital of a hydrogen atom.

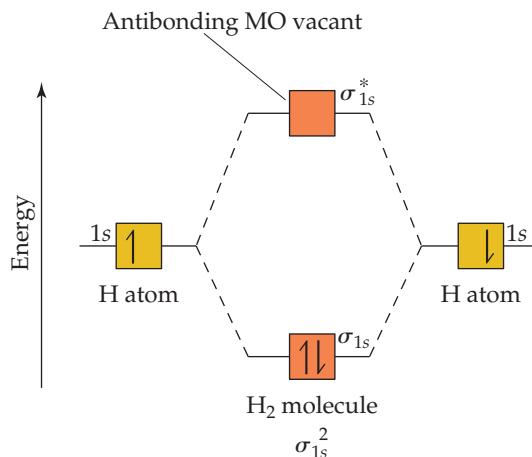
Notice from Figure 9.28 that the electron density in both the bonding MO and the antibonding MO of H<sub>2</sub> is centered about the internuclear axis. MOs of this type are called **sigma ( $\sigma$ ) molecular orbitals** (by analogy to  $\sigma$  bonds). The bonding sigma MO of H<sub>2</sub> is labeled  $\sigma_{1s}$ ; the subscript indicates that the MO is formed from two 1s orbitals. The antibonding sigma MO of H<sub>2</sub> is labeled  $\sigma_{1s}^*$  (read “sigma-star-one-s”); the asterisk denotes that the MO is antibonding.

The relative energies of two 1s atomic orbitals and the molecular orbitals formed from them are represented by an **energy-level diagram** (also called a **molecular orbital diagram**). Such diagrams show the interacting atomic orbitals on the left and right and the MOs in the middle, as shown in Figure 9.29. Like atomic orbitals, each MO can accommodate two electrons with their spins paired (Pauli exclusion principle).



### Go Figure

What would happen to the energy of the  $\sigma_{1s}$  MO if the H atoms in H<sub>2</sub> were pulled apart to a distance twice as long as its normal bond length?



▲ Figure 9.29 Energy-level diagram and electron configuration for H<sub>2</sub>.

As the MO diagram for H<sub>2</sub> in Figure 9.29 shows, each H atom has one electron, so there are two electrons in H<sub>2</sub>. These two electrons occupy the lower-energy bonding ( $\sigma_{1s}$ ) MO, and their spins are paired. Electrons occupying a bonding molecular orbital are called *bonding electrons*. Because the  $\sigma_{1s}$  MO is lower in energy than the H 1s atomic orbitals, the H<sub>2</sub> molecule is more stable than the two separate H atoms.

By analogy with atomic electron configurations, the electron configurations for molecules can be written with superscripts to indicate electron occupancy. The electron configuration for H<sub>2</sub>, then, is  $\sigma_{1s}^2$ .

### Bond Order

In molecular orbital theory, the stability of a covalent bond is related to its **bond order**, defined as half the difference between the number of bonding electrons and the number of antibonding electrons:

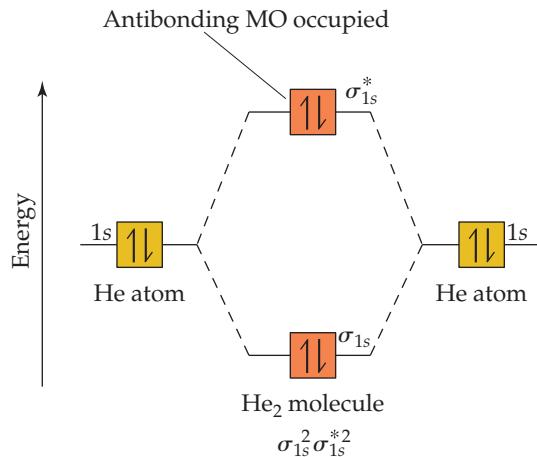
$$\text{Bond order} = \frac{1}{2} (\text{number of bonding electrons} - \text{number of antibonding electrons}) \quad [9.1]$$

We take half the difference because we are used to thinking of bonds as pairs of electrons. A *bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond*. Because MO theory also treats molecules containing an odd number of electrons, bond orders of 1/2, 3/2, or 5/2 are possible.

Let's now consider the bond order in H<sub>2</sub> and He<sub>2</sub>, referring to Figures 9.29 and 9.30. H<sub>2</sub> has two bonding electrons and zero antibonding electrons, so it has a bond order of 1.

**Figure 9.30** shows the energy-level diagram for the hypothetical He<sub>2</sub> molecule, which requires four electrons to fill its molecular orbitals. Because only two electrons can go in the  $\sigma_{1s}$  MO, the other two electrons must go in the  $\sigma_{1s}^*$  MO. The electron configuration of He<sub>2</sub> is thus  $\sigma_{1s}^2\sigma_{1s}^{*2}$ . The energy decrease realized in going from He atomic orbitals to the He bonding MO is offset by the energy increase realized in going from the atomic orbitals to the He antibonding MO.\* Because He<sub>2</sub> has two bonding electrons and two antibonding electrons, it has a bond order of 0. A bond order of 0 means that no bond exists. Molecular orbital theory correctly predicts that hydrogen forms diatomic molecules but helium does not.

► **Figure 9.30** Energy-level diagram and electron configuration for He<sub>2</sub>.



\*Antibonding MOs are slightly more energetically unfavorable than bonding MOs are energetically favorable. Thus, whenever there is an equal number of electrons in bonding and antibonding orbitals, the energy of the molecule is slightly higher than that for the separated atoms. As a result, no bond is formed.

## Sample Exercise 9.8

### Bond Order

What is the bond order of the  $\text{He}_2^+$  ion? Would you expect this ion to be stable relative to the separated He atom and  $\text{He}^+$  ion?

#### SOLUTION

**Analyze** We will determine the bond order for the  $\text{He}_2^+$  ion and use it to predict whether the ion is stable.

**Plan** To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the  $1s$  orbital, and the  $1s$  orbitals combine to give an MO diagram like that for  $\text{H}_2$  or  $\text{He}_2$  (Figure 9.30). If the bond order is greater than 0, we expect a bond to exist, and the ion is stable.

**Solve** The energy-level diagram for the  $\text{He}_2^+$  ion is shown in Figure 9.31. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

Because the bond order is greater than 0, we predict the  $\text{He}_2^+$  ion to be stable relative to the separated He and  $\text{He}^+$ . Formation of  $\text{He}_2^+$  in the gas phase has been demonstrated in laboratory experiments.

#### ► Practice Exercise

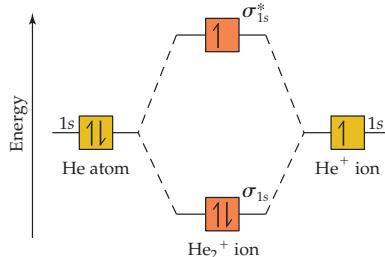
How many of the following molecules and ions have a bond order of  $\frac{1}{2}$ :  $\text{H}_2$ ,  $\text{H}_2^+$ ,  $\text{H}_2^-$ , and  $\text{He}_2^{2+}$ ?

- (a) 0   (b) 1   (c) 2   (d) 3   (e) 4



### Go Figure

What is the electron configuration of the  $\text{He}_2^+$  ion?



▲ Figure 9.31 Energy-level diagram for the  $\text{He}_2^+$  ion.

## Self-Assessment Exercise

**9.34** What is the bond order of  $\text{H}_2^{2+}$ ?

- (a) 0  
(b)  $\frac{1}{2}$   
(c) 1

## Exercises

**9.35** (a) What is the difference between hybrid orbitals and molecular orbitals? (b) How many electrons can be placed into each MO of a molecule? (c) Can antibonding molecular orbitals have electrons in them?

**9.36** Consider the  $\text{H}_2^+$  ion. (a) Sketch the molecular orbitals of the ion and draw its energy-level diagram. (b) How many electrons are there in the  $\text{H}_2^+$  ion? (c) Write the electron configuration of the ion in terms of its MOs. (d) What is the bond order in  $\text{H}_2^+$ ? (e) Suppose that the ion is excited

by light so that an electron moves from a lower-energy to a higher-energy MO. Would you expect the excited-state  $\text{H}_2^+$  ion to be stable or to fall apart? (f) Which of the following statements about part (e) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

9.34 (a)

Answers to Self-Assessment Exercises



## 9.8 | Bonding in Period 2 Diatomic Molecules



Some diatomic molecules are harmless to us, for example  $\text{N}_2$ , others are harmful, for example  $\text{CO}$  and  $\text{CN}^-$ , yet others are essential for life— $\text{O}_2$  and  $\text{NO}$ . Even simple molecules may play a central role in our physiology!

Take the  $\text{NO}$  molecule. It controls several important human physiological functions. Our bodies use it to relax muscles, kill foreign cells, and reinforce memory. The 1998 Nobel Prize in Physiology or Medicine was awarded to three scientists for their research that uncovered the importance of  $\text{NO}$  as a “signaling” molecule in the cardiovascular system.  $\text{NO}$  also functions as a neurotransmitter and is implicated in many other biological pathways. That  $\text{NO}$  plays such an important role in human metabolism was unsuspected before 1987, because  $\text{NO}$  has an odd number of electrons and is highly reactive. In 1992, it was named ‘Molecule of the Year’. Leafy greens and beetroot are rich in nitrates which can be metabolized to  $\text{NO}$  in the body.

In this section, we will focus on a molecular orbital approach to bonding in diatomic molecules. By the end, you should be able to

- Use MO diagrams to describe the bonding in Period 2 diatomic molecules.

In considering the MO description of diatomic molecules other than  $\text{H}_2$ , we will initially restrict our discussion to *homonuclear* diatomic molecules (those composed of two identical atoms) of Period 2 elements.

Period 2 atoms have valence  $2s$  and  $2p$  orbitals, and we need to consider how they interact to form MOs. The following rules summarize some of the guiding principles for the formation of MOs and for how they are populated by electrons:

1. The number of MOs formed equals the number of atomic orbitals combined.
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy.
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap. That is, as the overlap increases, the energy of the bonding MO is lowered and the energy of the antibonding MO is raised.
4. Each MO can accommodate, at most, two electrons, with their spins paired (Pauli exclusion principle).
5. When MOs of the same energy are populated, one electron enters each orbital (with the same spin) before spin pairing occurs (Hund’s rule).

## Molecular Orbitals for $\text{Li}_2$ and $\text{Be}_2$

Lithium has the electron configuration  $1s^22s^1$ . When lithium metal is heated above its boiling point ( $1342^\circ\text{C}$ ),  $\text{Li}_2$  molecules are found in the vapor phase. The Lewis structure for  $\text{Li}_2$  indicates a Li—Li single bond. We will now use MOs to describe the bonding in  $\text{Li}_2$ .

**Figure 9.32** shows that the Li 1s and 2s atomic orbitals have substantially different energy levels. From this, we can assume that the 1s orbital on one Li atom interacts only with the 1s orbital on the other atom (rule 2). Likewise, the 2s orbitals interact only with each other. Notice that combining four atomic orbitals produces four MOs (rule 1).

The Li 1s orbitals combine to form  $\sigma_{1s}$  and  $\sigma_{1s}^*$  bonding and antibonding MOs, as they did for  $\text{H}_2$ . The 2s orbitals interact with one another in exactly the same way, producing bonding ( $\sigma_{2s}$ ) and antibonding ( $\sigma_{2s}^*$ ) MOs. In general, the separation between bonding and antibonding MOs depends on the extent to which the constituent atomic orbitals overlap. Because the Li 2s orbitals extend farther from the nucleus than the 1s orbitals do, the 2s orbitals overlap more effectively. As a result, the energy difference between the  $\sigma_{2s}$  and  $\sigma_{2s}^*$  orbitals is greater than the energy difference between the  $\sigma_{1s}$  and  $\sigma_{1s}^*$  orbitals. The 1s orbitals of Li are much lower in energy than the 2s orbitals; therefore, the energy of the  $\sigma_{1s}^*$  antibonding MO is much lower than the energy of the  $\sigma_{2s}$  bonding MO.

Each Li atom has three electrons, so six electrons must be placed in  $\text{Li}_2$  MOs. As shown in Figure 9.32, these electrons occupy the  $\sigma_{1s}$ ,  $\sigma_{1s}^*$ , and  $\sigma_{2s}$  MOs, each with two electrons. The electron configuration of  $\text{Li}_2$  is therefore  $\sigma_{1s}^2 \sigma_{1s}^* {}^2 \sigma_{2s}^2$ . There are four electrons in bonding orbitals and two in antibonding orbitals, so the bond order is  $\frac{1}{2}(4 - 2) = 1$ . The molecule has a single bond, in agreement with its Lewis structure.

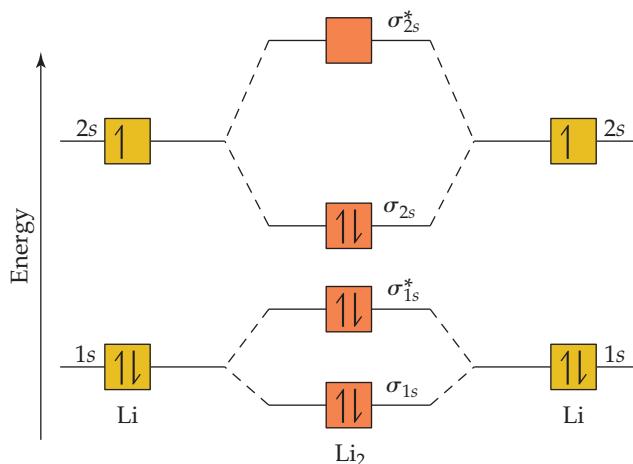
Because both the  $\sigma_{1s}$  and  $\sigma_{1s}^*$  MOs of  $\text{Li}_2$  are completely filled, the 1s orbitals contribute almost nothing to the bonding. The single bond in  $\text{Li}_2$  is due essentially to the interaction of the valence 2s orbitals on the Li atoms. This example illustrates the general rule that *core electrons usually do not contribute significantly to bonding in molecules*. The rule is equivalent to using only the valence electrons when drawing Lewis structures. Thus, we need not consider further the 1s orbitals while discussing the other Period 2 diatomic molecules.

The MO description of  $\text{Be}_2$  follows readily from the energy-level diagram for  $\text{Li}_2$ . Each Be atom has four electrons ( $1s^22s^2$ ), so we must place eight electrons in molecular orbitals. Therefore, we completely fill the  $\sigma_{1s}$ ,  $\sigma_{1s}^*$ ,  $\sigma_{2s}$ , and  $\sigma_{2s}^*$  MOs. With equal numbers of bonding and antibonding electrons, the bond order is zero; thus,  $\text{Be}_2$  does not exist.



### Go Figure

Which of the MOs in the diagram will have nodal planes?

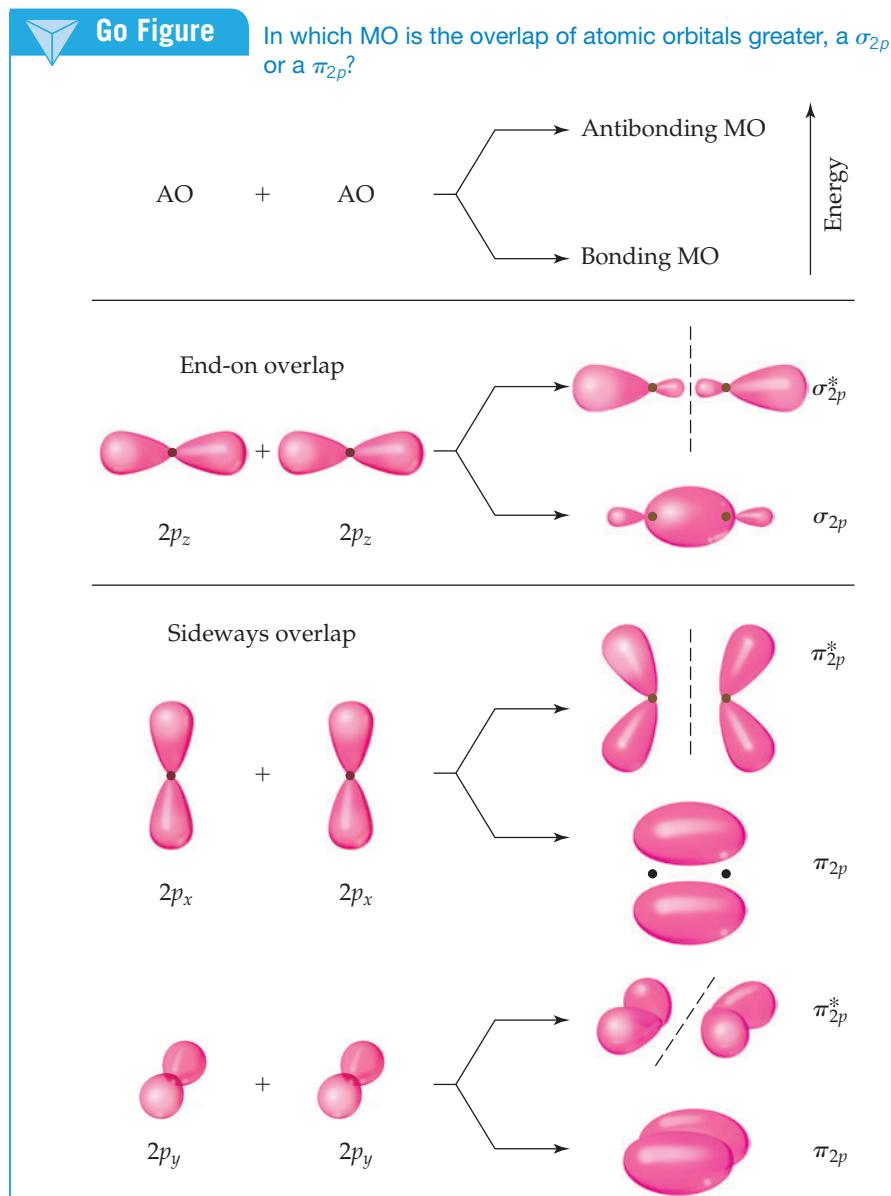


▲ **Figure 9.32** Energy-level diagram for the  $\text{Li}_2$  molecule.

## Molecular Orbitals from $2p$ Atomic Orbitals

Before we can consider the remaining Period 2 diatomic molecules, we must look at the MOs that result from combining  $2p$  atomic orbitals. The interactions between  $p$  orbitals are shown in **Figure 9.33**, where we have arbitrarily chosen the internuclear axis to be the  $z$ -axis. The  $2p_z$  orbitals face each other head to head. Just as with  $s$  orbitals, we can combine  $2p_z$  orbitals in two ways. One combination concentrates electron density between the nuclei and is, therefore, a bonding molecular orbital. The other combination excludes electron density from the bonding region and so is an antibonding molecular orbital. In both MOs, the electron density lies along the internuclear axis, so they are  $\sigma$  molecular orbitals:  $\sigma_{2p}$  and  $\sigma_{2p}^*$ .

The other  $2p$  orbitals overlap sideways and thus concentrate electron density above and below the internuclear axis. MOs of this type are called **pi ( $\pi$ ) molecular orbitals** by analogy to  $\pi$  bonds. We get one  $\pi$  bonding MO by combining the  $2p_x$  atomic orbitals and another from the  $2p_y$  atomic orbitals. These two  $\pi_{2p}$  molecular orbitals have the same energy; in other words, they are degenerate. Likewise, we get two degenerate  $\pi_{2p}^*$  antibonding MOs that are perpendicular to each other like the  $2p$  orbitals from which



▲ Figure 9.33 Contour representations of the molecular orbitals formed by  $2p$  orbitals.

they were made. These  $\pi_{2p}^*$  orbitals have four lobes, pointing away from the two nuclei, as shown in Figure 9.33.

The  $2p_z$  orbitals on two atoms point directly at each other. Hence, overlap of two  $2p_z$  orbitals is greater than that of two  $2p_x$  or  $2p_y$  orbitals. We therefore expect the  $\sigma_{2p}$  MO to be lower in energy (more stable) than the  $\pi_{2p}$  MOs. Similarly, the  $\sigma_{2p}^*$  MO should be higher in energy (less stable) than the  $\pi_{2p}^*$  MOs.

### A CLOSER LOOK Phases in Atomic and Molecular Orbitals

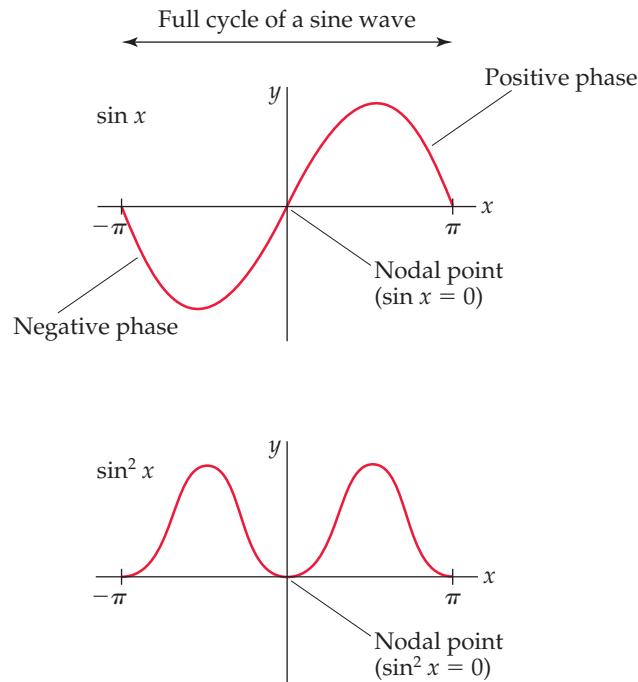
Our discussion of atomic orbitals in Chapter 6 and molecular orbitals in this chapter highlights some of the most important applications of quantum mechanics in chemistry. In the quantum-mechanical treatment of electrons in atoms and molecules, we are mainly interested in determining two characteristics of the electrons—their energies and their distribution in space. Recall that solving Schrödinger's wave equation yields the electron's energy,  $E$ , and wave function,  $\psi$ , but that  $\psi$  does not have a direct physical meaning. The contour representations of atomic and molecular orbitals we have presented thus far are based on  $\psi^2$  (the *probability density*), which gives the probability of finding the electron at a given point in space.

Because probability densities are squares of functions, their values must be nonnegative (zero or positive) at all points in space. However, the functions themselves can have negative values. The situation is like that of the sine function plotted in Figure 9.34. In the top graph, the sine function is negative for  $x$  between 0 and  $-\pi$  and positive for  $x$  between 0 and  $+\pi$ . We say that the *phase* of the sine function is negative between 0 and  $-\pi$  and positive between 0 and  $+\pi$ . If we square the sine function (bottom graph), we get two peaks that are symmetrical about the origin. Both peaks are positive because squaring a negative number produces a positive number. In other words, *we lose the phase information of the function upon squaring it*.

Like the sine function, the more complicated wave functions for atomic orbitals can also have phases. Consider, for example, the representations of the  $1s$  orbital in Figure 9.35. Note that here we plot this orbital a bit differently from what is shown in Section 6.6. The origin is the point where the nucleus resides, and the wave function for the  $1s$  orbital extends from the origin out into space. The plot shows the value of  $\psi$  for a slice taken along the  $z$ -axis. A contour representation of the  $1s$  orbital is shown after the plot. Notice that the value of the  $1s$  wave function is always a positive number (we show positive values in red in Figure 9.35). Thus, it has only one phase. Notice also that the wave function approaches zero only at a long distance from the nucleus. It therefore has no nodes, as we saw in Figure 6.21.

In the graph for the  $2p_z$  orbital in Figure 9.35, the wave function changes sign when it passes through  $z = 0$ . Notice that the two halves of the wave have the same shape except that one has positive (red) values and the other negative (blue) values. Analogously to the sine function, the wave function changes phase when it passes through the origin. Mathematically, the  $2p_z$  wave function is equal to zero whenever  $z = 0$ . This corresponds to any point on the  $xy$  plane, so we say that the  $xy$  plane is a *nodal plane* of the  $2p_z$  orbital. The wave function for a  $p$  orbital is much like a sine function because it has two equal parts that have opposite phases. Figure 9.35 gives a typical representation used by chemists of the wave function for a  $p_z$  orbital.\* The red and blue lobes indicate the different phases of the orbital.

\*The mathematical development of this three-dimensional function (and its square) is beyond the scope of this book, and, as is typically done by chemists, we have used lobes that are the same shape as in Figure 9.35.

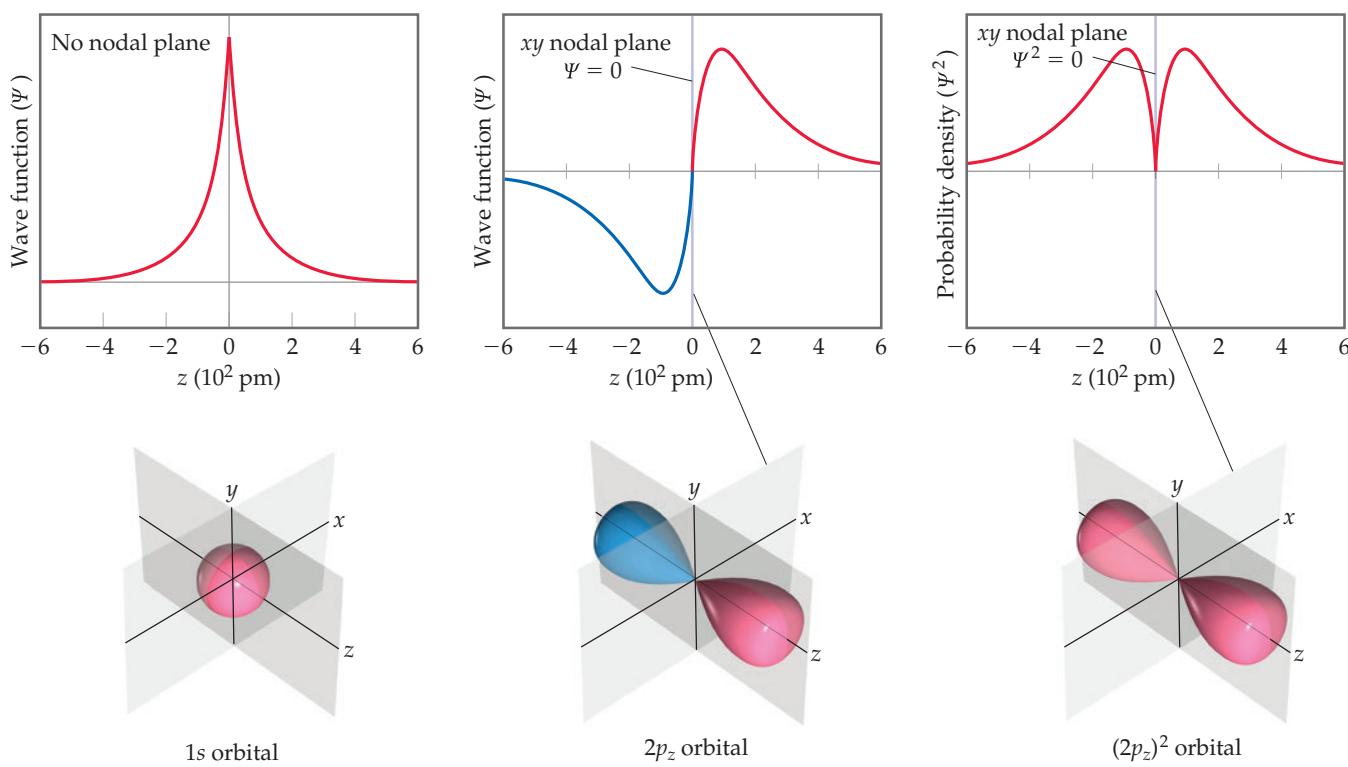


▲ Figure 9.34 Graphs for a sine function and the same function squared.

(Note: The colors do *not* represent charge, as they did in the plots in Figures 9.10 and 9.11.) As with the sine function, the origin is a node.

The third graph in Figure 9.35 shows that when we square the wave function of the  $2p_z$  orbital, we get two peaks that are symmetrical about the origin. Both peaks are positive because squaring a negative number produces a positive number. Thus, *we lose the phase information of the function upon squaring it* just as we did for the sine function. When we square the wave function for the  $p_z$  orbital, we get the probability density for the orbital, which is given as a contour representation in Figure 9.35. This is what we saw in the earlier presentation of  $p$  orbitals. For this squared wave function, both lobes have the same phase and therefore the same sign. We use this representation throughout most of this book because it has a simple physical interpretation: The square of the wave function at any point in space represents the electron density at that point.

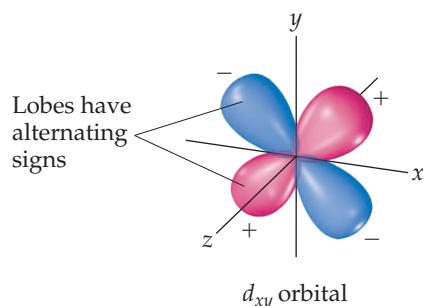
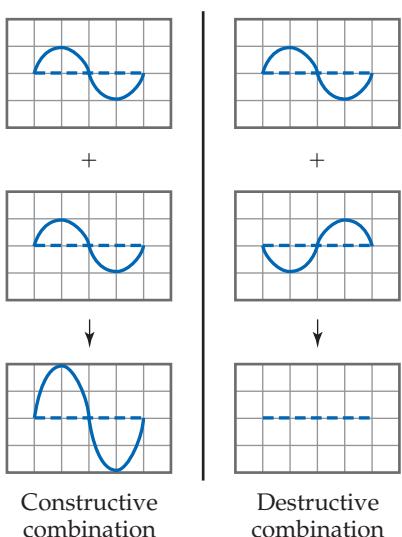
The lobes of the wave functions for the  $d$  orbitals also have different phases. For example, the wave function for a  $d_{xy}$  orbital has four lobes, with the phase of each lobe opposite the phase of its nearest neighbors (Figure 9.36). The wave functions for the



▲ Figure 9.35 Phases in wave functions of  $s$  and  $p$  atomic orbitals. Red shading means a positive value for the wave function, and blue shading means a negative value.

other  $d$  orbitals likewise have lobes in which the phase in one lobe is opposite that in an adjacent lobe.

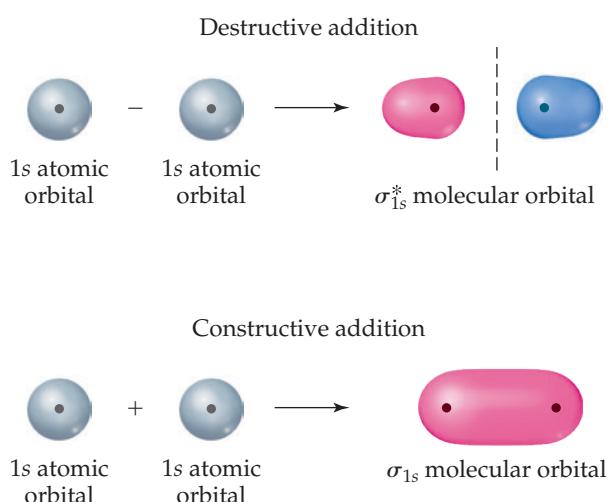
Why do we need to consider the complexity introduced by considering the phase of the wave function? While it is true that the phase is not necessary to visualize the shape of an atomic orbital in an isolated atom, it does become important when we consider overlap of orbitals in molecular orbital theory. Let's use the sine function as an example again. If you add two sine functions having the same phase, they add *constructively*, resulting in increased amplitude:



▲ Figure 9.36 Phases in  $d$  orbitals.

but if you add two sine functions having opposite phases, they add *destructively* and cancel each other.

The idea of constructive and destructive interactions of wave functions is key to understanding the origin of bonding and antibonding molecular orbitals. For example, the wave function of the  $\sigma_{1s}$  MO of  $\text{H}_2$  is generated by adding the wave function for the  $1s$  orbital on one atom to the wave function for the  $1s$  orbital on the other atom, with both orbitals having the same phase. The atomic wave functions overlap *constructively* in this case to increase the electron density between the two atoms (Figure 9.37). The wave function of the  $\sigma_{1s}^*$  MO of  $\text{H}_2$  is generated by subtracting the wave function for a  $1s$  orbital on one atom from the wave function for a  $1s$  orbital on the other atom. The result is that the atomic orbital wave functions overlap *destructively* to create a region of zero electron density between the two atoms—a node. Notice the similarity between this figure and Figure 9.29. In Figure 9.37, we use red and blue shading to denote positive and negative phases in the  $\text{H}$  atomic orbitals.



▲ Figure 9.37 Molecular orbitals from atomic orbital wave functions.

However, chemists may alternatively draw contour representations in different colors, or with one phase shaded and one unshaded, to denote the two phases.

When we square the wave function of the  $\sigma_{1s}^*$  MO, we get the electron density representation which we saw earlier, in Figure 9.29. Notice once again that we lose the phase information when we look at the electron density.

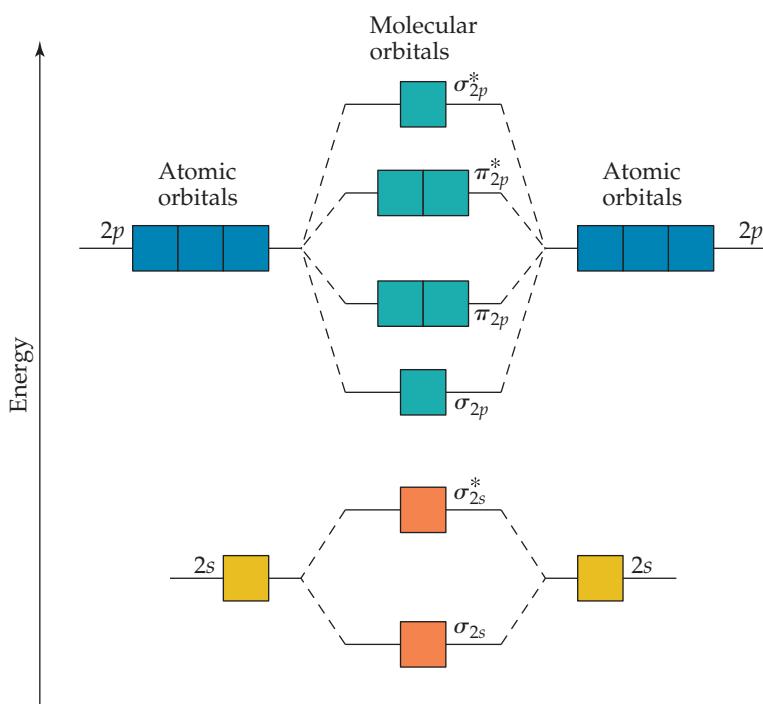
The wave functions of atomic and molecular orbitals are used by chemists to understand many aspects of chemical bonding, spectroscopy, and reactivity.

**Related Exercises:** 9.116, 9.127, 9.129

## Electron Configurations for $B_2$ through $Ne_2$

We can combine our analyses of MOs formed from  $s$  orbitals (Figure 9.29) and from  $p$  orbitals (Figure 9.33) to construct an energy-level diagram (Figure 9.38) for homonuclear diatomic molecules of the elements boron through neon, all of which have valence  $2s$  and  $2p$  atomic orbitals. The following features of the diagram are notable:

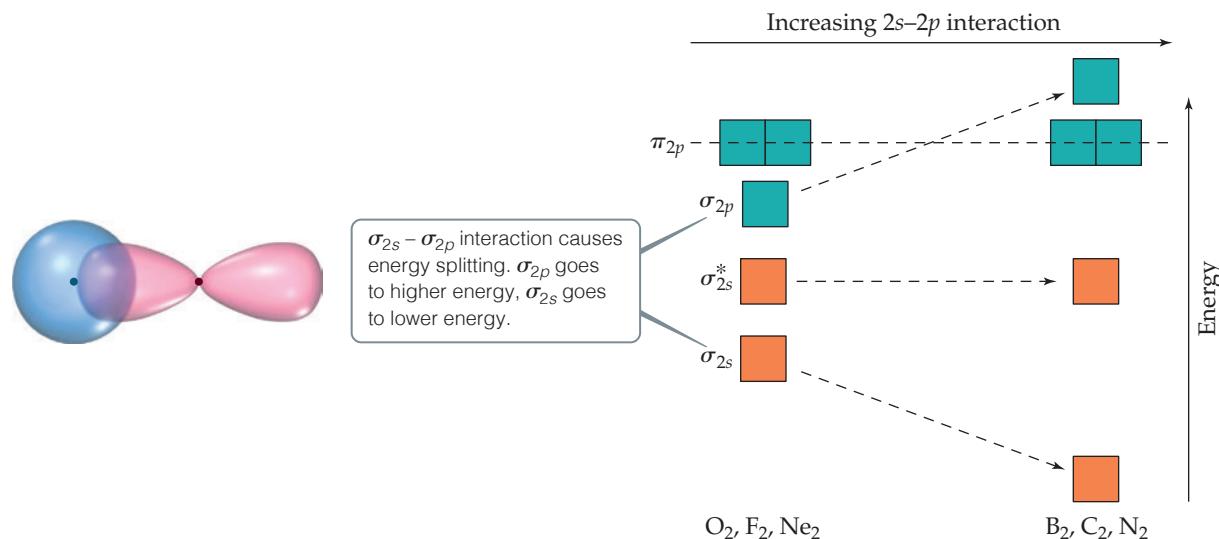
- The  $2s$  atomic orbitals are substantially lower in energy than the  $2p$  atomic orbitals. Consequently, both MOs formed from the  $2s$  orbitals are lower in energy than the lowest-energy MO derived from the  $2p$  atomic orbitals.
- The overlap of the two  $2p_z$  orbitals is greater than that of the two  $2p_x$  or  $2p_y$  orbitals. As a result, the bonding  $\sigma_{2p}$  MO is lower in energy than the  $\pi_{2p}$  MOs, and the antibonding  $\sigma_{2p}^*$  MO is higher in energy than the  $\pi_{2p}^*$  MOs.
- Both the  $\pi_{2p}$  and  $\pi_{2p}^*$  MOs are *doubly degenerate*; that is, there are two degenerate MOs of each type.



◀ Figure 9.38 Energy-level diagram for MOs of Period 2 homonuclear diatomic molecules. The diagram assumes no interaction between the  $2s$  atomic orbital on one atom and the  $2p$  atomic orbitals on the other atom, and experiment shows that it fits only for  $O_2$ ,  $F_2$ , and  $Ne_2$ .

**Go Figure**

Which molecular orbitals have switched relative energy in the group on the right as compared with the group on the left?



▲ **Figure 9.39** The effect of interactions between 2s and 2p atomic orbitals.

Before we can add electrons to Figure 9.38, we must consider one more effect. We have constructed the diagram assuming no interaction between the 2s orbital on one atom and the 2p orbitals on the other. In fact, such interactions can and do take place. **Figure 9.39** shows the overlap of a 2s orbital on one of the atoms with a 2p orbital on the other. These interactions increase the energy difference between the  $\sigma_{2s}$  and  $\sigma_{2p}$  MOs, with the  $\sigma_{2s}$  energy decreasing and the  $\sigma_{2p}$  energy increasing (Figure 9.39). These 2s–2p interactions can be strong enough that the energetic ordering of the MOs can be altered: For  $B_2$ ,  $C_2$ , and  $N_2$ , the  $\sigma_{2p}$  MO is above the  $\pi_{2p}$  MOs in energy. For  $O_2$ ,  $F_2$ , and  $Ne_2$ , the  $\sigma_{2p}$  MO is below the  $\pi_{2p}$  MOs.

Given the energy ordering of the molecular orbitals, it is a simple matter to determine the electron configurations for the diatomic molecules  $B_2$  through  $Ne_2$ . For example, a boron atom has three valence electrons. (Remember that we are ignoring the core 1s electrons.) Thus, for  $B_2$  we must place six electrons in MOs. Four of them fill the  $\sigma_{2s}$  and  $\sigma_{2s}^*$  MOs, leading to no net bonding. The fifth electron goes in one  $\pi_{2p}$  MO, and the sixth goes in the other  $\pi_{2p}$  MO, with the two electrons having the same spin. Therefore,  $B_2$  has a bond order of 1.

Each time we move one element to the right in Period 2, two more electrons must be placed in the energy-level diagram. For example, on moving to  $C_2$ , we have two more electrons than in  $B_2$ , and these electrons are placed in the  $\pi_{2p}$  MOs, completely filling them. The electron configurations and bond orders for  $B_2$  through  $Ne_2$  are given in **Figure 9.40**.

## Electron Configurations and Molecular Properties

The way a substance behaves in a magnetic field can in some cases provide insight into the arrangements of its electrons. Molecules with one or more unpaired electrons are attracted to a magnetic field. The more unpaired electrons in a species, the stronger the attractive force. This type of magnetic behavior is called **paramagnetism**.

Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called **diamagnetism**. The distinction between paramagnetism and diamagnetism is nicely illustrated in an older method for measuring magnetic properties (**Figure 9.41**). It involves weighing the substance in the presence and absence of a magnetic field. A paramagnetic substance appears to weigh more in the magnetic field; a diamagnetic substance appears to weigh less. The magnetic behaviors observed for the Period 2 diatomic molecules agree with the electron configurations shown in Figure 9.40.


**Go Figure**

Which stable molecules have their highest-energy electrons in antibonding orbitals?

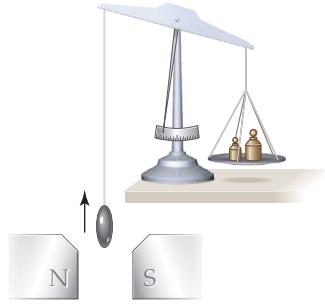
	Large 2s–2p interaction			Small 2s–2p interaction		
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
σ <sub>2p</sub> <sup>*</sup>	□	□	□	σ <sub>2p</sub> <sup>*</sup>	□	□
π <sub>2p</sub> <sup>*</sup>	□□	□□	□□	π <sub>2p</sub> <sup>*</sup>	1 1	1 1
σ <sub>2p</sub>	□	□	1 1	π <sub>2p</sub>	1 1	1 1
π <sub>2p</sub>	1 1	1 1	1 1	σ <sub>2p</sub>	1 1	1 1
σ <sub>2s</sub> <sup>*</sup>	1 1	1 1	1 1	σ <sub>2s</sub> <sup>*</sup>	1 1	1 1
σ <sub>2s</sub>	1 1	1 1	1 1	σ <sub>2s</sub>	1 1	1 1
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (pm)	159	131	110	121	143	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

▲ Figure 9.40 Molecular orbital electron configurations and some experimental data for Period 2 diatomic molecules.

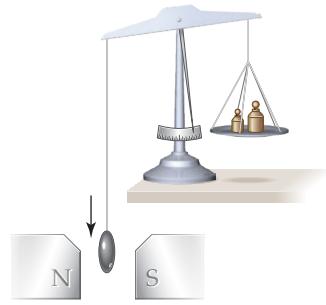
Weigh sample in absence of a magnetic field



A diamagnetic sample appears to weigh less in magnetic field (weak effect)



A paramagnetic sample appears to weigh more in magnetic field



◀ Figure 9.41 Determining the magnetic properties of a sample.

Electron configurations in molecules can also be related to bond distances and bond enthalpies. As bond order increases, bond distances decrease and bond enthalpies increase. N<sub>2</sub>, for example, whose bond order is 3, has a short bond distance and a large bond enthalpy. The N<sub>2</sub> molecule does not react readily with other substances to form nitrogen compounds. The high bond order of the molecule helps explain its exceptional stability. We should also note, however, that molecules with the same bond orders do *not* have the same bond distances and bond enthalpies. Bond order is only one factor influencing these properties. Other factors include nuclear charge and extent of orbital overlap.

Bonding in O<sub>2</sub> provides an interesting test case for molecular orbital theory. The Lewis structure for this molecule shows a double bond and complete pairing of electrons:



The short O—O bond distance (121 pm) and relatively high bond enthalpy (495 kJ/mol) are in agreement with the presence of a double bond. However, Figure 9.40 tells us that

 Go Figure

What would you expect to see if liquid nitrogen were poured between the poles of the magnet?



Because O<sub>2</sub> molecules are paramagnetic ...

... they are attracted into the magnetic field.

▲ **Figure 9.42** Paramagnetism of O<sub>2</sub>. When liquid oxygen is poured through a magnet, it “sticks” to the poles.

the molecule contains two unpaired electrons and should therefore be paramagnetic, a detail not discernible in the Lewis structure. The paramagnetism of O<sub>2</sub> is demonstrated in **Figure 9.42**, which confirms the prediction from MO theory. The MO description also correctly predicts a bond order of 2 as did the Lewis structure.

Going from O<sub>2</sub> to F<sub>2</sub>, we add two electrons, completely filling the π<sub>2p</sub>\* MOs. Thus, F<sub>2</sub> is expected to be diamagnetic and have an F—F single bond, in accord with its Lewis structure. Finally, the addition of two more electrons to make Ne<sub>2</sub> fills all the bonding and antibonding MOs. Therefore, the bond order of Ne<sub>2</sub> is zero, and the molecule is not expected to exist.



### Sample Exercise 9.9

#### Molecular Orbitals of a Period 2 Diatomic Ion

For the O<sub>2</sub><sup>+</sup> ion predict (a) number of unpaired electrons, (b) bond order, (c) bond enthalpy and bond length.

#### SOLUTION

**Analyze** Our task is to predict several properties of the cation O<sub>2</sub><sup>+</sup>.

**Plan** We will use the MO description of O<sub>2</sub><sup>+</sup> to determine the desired properties. We must first determine the number of electrons in O<sub>2</sub><sup>+</sup> and then draw its MO energy diagram. The unpaired electrons are those without a partner of opposite spin. The bond order is one-half the difference between the number of bonding and antibonding electrons. After calculating the bond order, we can use Figure 9.40 to estimate the bond enthalpy and bond length.

#### Solve

(a) The O<sub>2</sub><sup>+</sup> ion has 11 valence electrons, one fewer than O<sub>2</sub>. The electron removed from O<sub>2</sub> to form O<sub>2</sub><sup>+</sup> is one of the two unpaired π<sub>2p</sub>\* electrons (see Figure 9.40). Therefore, O<sub>2</sub><sup>+</sup> has one unpaired electron.

(b) The molecule has eight bonding electrons (the same as O<sub>2</sub>) and three antibonding electrons (one fewer than O<sub>2</sub>). Thus, its bond order is

$$\frac{1}{2}(8 - 3) = 2\frac{1}{2}$$

(c) The bond order of O<sub>2</sub><sup>+</sup> is between that for O<sub>2</sub> (bond order 2) and N<sub>2</sub> (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O<sub>2</sub> and N<sub>2</sub>, approximately 700 kJ/mol and 115 pm. (The experimentally measured values are 625 kJ/mol and 112.3 pm.)

#### ► Practice Exercise

Place the following molecular ions in order from smallest to largest bond order: C<sub>2</sub><sup>2+</sup>, N<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>-</sup>, and F<sub>2</sub><sup>-</sup>.

- (a) C<sub>2</sub><sup>2+</sup> < N<sub>2</sub><sup>-</sup> < O<sub>2</sub><sup>-</sup> < F<sub>2</sub><sup>-</sup>
- (b) F<sub>2</sub><sup>-</sup> < O<sub>2</sub><sup>-</sup> < N<sub>2</sub><sup>-</sup> < C<sub>2</sub><sup>2+</sup>
- (c) O<sub>2</sub><sup>-</sup> < C<sub>2</sub><sup>2+</sup> < F<sub>2</sub><sup>-</sup> < N<sub>2</sub><sup>-</sup>
- (d) C<sub>2</sub><sup>2+</sup> < F<sub>2</sub><sup>-</sup> < O<sub>2</sub><sup>-</sup> < N<sub>2</sub><sup>-</sup>
- (e) F<sub>2</sub><sup>-</sup> < C<sub>2</sub><sup>2+</sup> < O<sub>2</sub><sup>-</sup> < N<sub>2</sub><sup>-</sup>

## Heteronuclear Diatomic Molecules

The principles we have used in developing an MO description of homonuclear diatomic molecules can be extended to *heteronuclear* diatomic molecules—those in which the two atoms in the molecule are not the same. We conclude this section with a fascinating heteronuclear diatomic molecule—nitric oxide, NO.

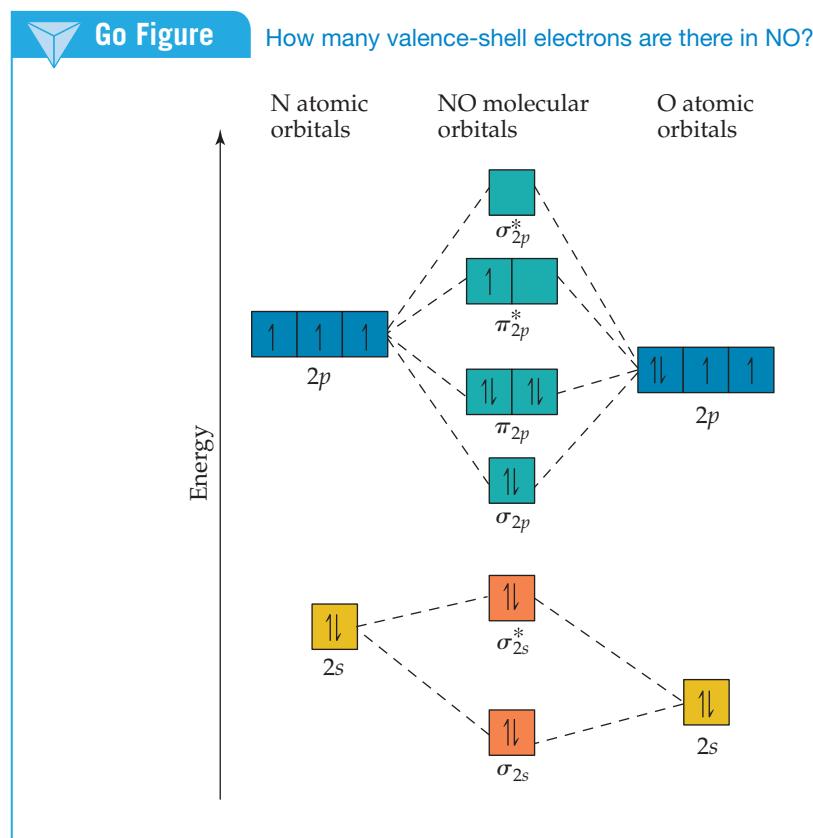
The NO molecule has 11 valence electrons, and two possible Lewis structures can be drawn. The Lewis structure with the lower formal charges places the odd electron on the N atom:



Both structures indicate the presence of a double bond, but when compared with the molecules in Figure 9.40, the experimental bond length of NO (115 pm) suggests a bond order greater than 2. How do we treat NO using the MO model?

If the atoms in a heteronuclear diatomic molecule do not differ too greatly in electronegativities, their MOs resemble those in homonuclear diatomics, with one important modification: The energy of the atomic orbitals of the more electronegative atom is lower than that of the atomic orbitals of the less electronegative element. In **Figure 9.43**, you see that the 2s and 2p atomic orbitals of oxygen are slightly lower in energy than those of nitrogen because oxygen is more electronegative than nitrogen. The MO energy-level diagram for NO is much like that of a homonuclear diatomic molecule—because the 2s and 2p orbitals on the two atoms interact, the same types of MOs are produced.

There is one other important difference in the MOs of heteronuclear molecules. The MOs are still a mix of atomic orbitals from both atoms, but in general an *MO in a heteronuclear diatomic molecule has a greater contribution from the atomic orbital to which it is closer in energy*. In the case of NO, for example, the  $\sigma_{2s}$  bonding MO is closer in energy to the



▲ **Figure 9.43** The energy-level diagram for atomic and molecular orbitals in NO.

O 2s atomic orbital than to the N 2s atomic orbital. As a result, the  $\sigma_{2s}$  MO has a slightly greater contribution from O than from N—the orbital is no longer an equal mixture of the two atoms, as was the case for the homonuclear diatomic molecules. Similarly, the  $\sigma_{2s}^*$  antibonding MO is weighted more heavily toward the N atom because that MO is closest in energy to the N 2s atomic orbital.

We complete the MO diagram for NO by filling the MOs in Figure 9.43 with the 11 valence electrons. Eight bonding and three antibonding electrons give a bond order of  $\frac{1}{2}(8 - 3) = 2\frac{1}{2}$ , which agrees better with experiment than the Lewis structures do. The unpaired electron resides in one of the  $\pi_{2p}^*$  MOs, which have a greater contribution from the N atom. (We could have placed this electron in either the left or right  $\pi_{2p}^*$  MO.) Thus, the Lewis structure that places the unpaired electron on nitrogen (the one preferred on the basis of formal charge) is the more accurate description of the true electron distribution in the molecule.

## CHEMISTRY PUT TO WORK Orbitals and Energy

Asked to identify the major technological challenge for the twenty-first century, you might say “energy,” reasoning that development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. One of the most remarkable sources of clean energy is the Sun, which sends enough energy to power the world for millions of years. Our challenge is to capture enough of this energy in a form that allows us to use it as needed. *Photovoltaic solar cells* convert the light from the Sun into usable electricity, and the development of more efficient solar cells is one way to address Earth’s future energy needs.

How does solar energy conversion work? Fundamentally, we need to be able to use photons from the Sun, especially from the visible portion of the spectrum, to excite electrons in molecules and materials to different energy levels. The brilliant colors around you—those of your clothes, the photographs in this book, the foods you eat—are due to the selective absorption of visible light by chemicals. It is helpful to think of this process in the context of molecular orbital theory: Light excites an electron from a filled molecular orbital to an empty one at higher energy. Because MOs have definite energies, only light of the proper wavelengths can excite electrons.

In discussing light absorption by molecules, we can focus on the two MOs shown in Figure 9.44. The *highest occupied molecular orbital* (HOMO) is the MO of highest energy that has electrons in it. The *lowest unoccupied molecular orbital* (LUMO) is the MO of lowest energy that does not have electrons in it. In N<sub>2</sub>, for example, the HOMO is the  $\sigma_{2p}$  MO and the LUMO is the  $\pi_{2p}^*$  MO (Figure 9.40).

The energy difference between the HOMO and the LUMO—known as the HOMO-LUMO gap—is related to the minimum energy needed to excite an electron in the molecule. Colorless or white substances usually have such a large HOMO-LUMO gap that visible light is not energetic enough to excite an electron to the higher level. The minimum energy needed to excite an electron from the HOMO to the LUMO in N<sub>2</sub> corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. As a result, N<sub>2</sub> cannot absorb visible light and is therefore colorless.

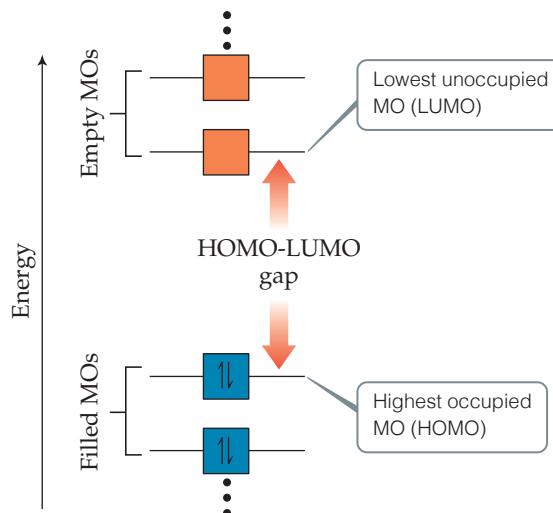
The magnitude of the energy gap between filled and empty electronic states is critical for solar energy conversion. Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy. Titanium dioxide is a readily available material that can be reasonably efficient at converting light directly into electricity. However,

TiO<sub>2</sub> is white and absorbs only a small amount of the Sun’s radiant energy. Scientists are working to make solar cells in which TiO<sub>2</sub> is mixed with highly colored molecules, whose HOMO-LUMO gaps correspond to visible and near-infrared light to absorb more of the solar spectrum. If the HOMO of these molecules is higher in energy than the HOMO of TiO<sub>2</sub>, the excited electrons will flow from the molecules into the TiO<sub>2</sub>, thereby generating electricity when the device is illuminated with light and connected to an external circuit.

Efficient solar energy conversion promises to be one of the most interesting and important areas of both scientific and technological development in our future. Many of you may ultimately end up working in fields that have an impact on the world’s energy portfolio.

### Related Exercises: 9.113, 9.118, 9.128

#### Design an Experiment



▲ **Figure 9.44** Definitions of the highest occupied and lowest unoccupied molecular orbitals. The energy difference between these is the HOMO-LUMO gap.



## Sample Integrative Exercise

### Putting Concepts Together

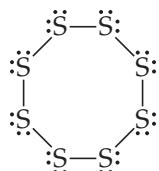
Elemental sulfur is a yellow solid that consists of  $S_8$  molecules. The structure of the  $S_8$  molecule is a puckered, eight-membered ring (see Figure 7.26). Heating elemental sulfur to high temperatures produces gaseous  $S_2$  molecules:



(a) The electron configuration of which Period 2 element is most similar to that of sulfur? (b) Use the VSEPR model to predict the  $S-S-S$  bond angles in  $S_8$  and the hybridization at S in  $S_8$ . (c) Use MO theory to predict the sulfur–sulfur bond order in  $S_2$ . Do you expect this molecule to be diamagnetic or paramagnetic? (d) Use average bond enthalpies (Table 8.3) to estimate the enthalpy change for this reaction. Is the reaction exothermic or endothermic?

### SOLUTION

- (a) Sulfur is a Group 16 element with an  $[Ne]3s^23p^4$  electron configuration. It is expected to be most similar electronically to oxygen (electron configuration,  $[He]2s^22p^4$ ), which is immediately above it in the periodic table.
- (b) The Lewis structure of  $S_8$  is



There is a single bond between each pair of S atoms and two nonbonding electron pairs on each S atom. Thus, we see four electron domains around each S atom and expect a tetrahedral electron-domain geometry corresponding to  $sp^3$  hybridization. Because of the nonbonding pairs, we expect the  $S-S-S$  angles to be somewhat less than  $109.5^\circ$ , the tetrahedral angle. Experimentally, the  $S-S-S$  angle in  $S_8$  is  $108^\circ$ , in good agreement with this prediction. Interestingly, if  $S_8$  were a planar ring, it would have  $S-S-S$  angles of  $135^\circ$ . Instead, the  $S_8$  ring

pucks to accommodate the smaller angles dictated by  $sp^3$  hybridization.

- (c) The MOs of  $S_2$  are analogous to those of  $O_2$ , although the MOs for  $S_2$  are constructed from the  $3s$  and  $3p$  atomic orbitals of sulfur. Further,  $S_2$  has the same number of valence electrons as  $O_2$ . Thus, by analogy with  $O_2$ , we expect  $S_2$  to have a bond order of 2 (a double bond) and to be paramagnetic with two unpaired electrons in the  $\pi_{3p}^*$  molecular orbitals of  $S_2$ .
- (d) We are considering the reaction in which an  $S_8$  molecule falls apart into four  $S_2$  molecules. From parts (b) and (c), we see that  $S_8$  has  $S-S$  single bonds and  $S_2$  has  $S=S$  double bonds. During the reaction, therefore, we are breaking eight  $S-S$  single bonds and forming four  $S=S$  double bonds. We can estimate the enthalpy of the reaction by using Equation 5.33 and the average bond enthalpies in Table 8.3:

$$\begin{aligned}\Delta H_{rxn} &= 8 D(S-S) - 4 D(S=S) \\ &= 8(266 \text{ kJ}) - 4(418 \text{ kJ}) = +456 \text{ kJ}\end{aligned}$$

Recall that  $D(X-Y)$  represents the X–Y bond enthalpy. Because  $\Delta H_{rxn} > 0$ , the reaction is endothermic (Section 5.3). The very positive value of  $\Delta H_{rxn}$  suggests that high temperatures are required to cause the reaction to occur.

## Self-Assessment Exercise

- 9.37** What is the bond order of CO?

- (a) 1
- (b) 2
- (c) 3

## Exercises

- 9.38** Draw a picture that shows all three  $2p$  orbitals on one atom and all three  $2p$  orbitals on another atom. (a) Imagine the atoms coming close together to bond. How many  $\sigma$  bonds can the two sets of  $2p$  orbitals make with each other? (b) How many  $\pi$  bonds can the two sets of  $2p$  orbitals make with each other? (c) How many antibonding orbitals, and of what type, can be made from the two sets of  $2p$  orbitals?

- 9.39** (a) What are the relationships among bond order, bond length, and bond energy? (b) According to molecular orbital theory, would either  $Be_2$  or  $Be_2^+$  be expected to exist? Explain.

- 9.40** How would we describe a substance that contains only paired electrons and is weakly repelled by a magnetic field?

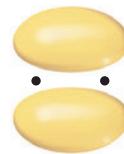
Which of the following ions would you expect to possess similar characteristics:  $H_2^-$ ,  $Ne_2^+$ ,  $F_2$ ,  $O_2^{2+}$ ?

- 9.41** Using Figures 9.32 and 9.40 as guides, draw the molecular orbital electron configuration for (a)  $B_2^+$ , (b)  $Li_2^+$ , (c)  $N_2^+$ , (d)  $Ne_2^{2+}$ . In each case indicate whether the addition of an electron to the ion would increase or decrease the bond order of the species.

- 9.42** Determine the electron configurations for  $CN^+$ ,  $CN$ , and  $CN^-$ . (a) Which species has the strongest C–N bond? (b) Which species, if any, has unpaired electrons?

- 9.43** Consider the molecular orbitals of the  $P_2$  molecule. Assume that the MOs of diatomics from the third row of the periodic

table are analogous to those from the second row. (a) Which valence atomic orbitals of P are used to construct the MOs of  $P_2$ ? (b) The figure that follows shows a sketch of one of the MOs for  $P_2$ . What is the label for this MO? (c) For the  $P_2$  molecule, how many electrons occupy the MO in the figure? (d) Is  $P_2$  expected to be diamagnetic or paramagnetic?



9.37 (c)

Answers to Self-Assessment Exercise



## Chapter Summary and Key Terms

**MOLECULAR SHAPES (INTRODUCTION AND SECTION 9.1)** The three-dimensional shapes and sizes of molecules are determined by their **bond angles** and bond lengths. Molecules with a central atom A surrounded by  $n$  atoms B, denoted  $AB_n$ , adopt a number of different geometric shapes, depending on the value of  $n$  and on the particular atoms involved. In the overwhelming majority of cases, these geometries are related to five basic shapes (linear, trigonal pyramidal, tetrahedral, trigonal bipyramidal, and octahedral).

**THE VSEPR MODEL (SECTION 9.2)** The **valence-shell electron-pair repulsion (VSEPR) model** rationalizes molecular geometries based on the repulsions between **electron domains**, which are regions about a central atom in which electrons are likely to be found. **Bonding pairs** of electrons, which are those involved in making bonds, and **nonbonding pairs** of electrons, also called **lone pairs**, both create electron domains around an atom. According to the VSEPR model, electron domains orient themselves to minimize electrostatic repulsions; that is, they remain as far apart as possible.

Electron domains from nonbonding pairs exert slightly greater repulsions than those from bonding pairs, which leads to certain preferred positions for nonbonding pairs and to the departure of bond angles from idealized values. Electron domains from multiple bonds exert slightly greater repulsions than those from single bonds. The arrangement of electron domains around a central atom is called the **electron-domain geometry**; the arrangement of atoms is called the **molecular geometry**.

**MOLECULAR POLARITY (SECTION 9.3)** The dipole moment of a polyatomic molecule depends on the vector sum of the dipole moments associated with the individual bonds, called the **bond dipoles**. Certain molecular shapes, such as linear  $AB_2$  and trigonal planar  $AB_3$ , lead to cancellation of the bond dipoles, producing a nonpolar molecule, which is one whose overall dipole moment is zero. In other shapes, such as bent  $AB_2$  and trigonal pyramidal  $AB_3$ , the bond dipoles do not cancel and the molecule will be polar (that is, it will have a nonzero dipole moment).

**COVALENT BONDING AND ORBITAL OVERLAP (SECTION 9.4)** **Valence-bond theory** is an extension of Lewis's notion of electron-pair bonds. In valence-bond theory, covalent bonds are formed when atomic orbitals on neighboring atoms overlap one another. The overlap region is one of greater stability for the two electrons because of their simultaneous attraction to two nuclei. The greater the overlap between two orbitals, the stronger the bond that is formed.

**HYBRID ORBITALS (SECTION 9.5)** To extend the ideas of valence-bond theory to polyatomic molecules, we must envision mixing *s* and *p* orbitals to form **hybrid orbitals**. The process of **hybridization** leads to hybrid atomic orbitals that have a large lobe directed to overlap with orbitals on another atom to make

a bond. Hybrid orbitals can also accommodate nonbonding pairs. A particular mode of hybridization can be associated with each of three common electron-domain geometries (linear =  $sp$ ; trigonal planar =  $sp^2$ ; tetrahedral =  $sp^3$ ). The bonding in **hypervalent** molecules—those with more than an octet of electrons—is not as readily discussed in terms of hybrid orbitals.

**MULTIPLE BONDS (SECTION 9.6)** Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called **sigma ( $\sigma$ ) bonds**. Bonds can also be formed from the sideways overlap of *p* orbitals. Such a bond is called a **pi ( $\pi$ ) bond**. A double bond, such as that in  $C_2H_4$ , consists of one  $\sigma$  bond and one  $\pi$  bond; each carbon atom has an unhybridized ***p* orbital**, and these are the orbitals that overlap to form  $\pi$  bonds. A triple bond, such as that in  $C_2H_2$ , consists of one  $\sigma$  and two  $\pi$  bonds. The formation of a  $\pi$  bond requires that molecules adopt a specific orientation; the two  $CH_2$  groups in  $C_2H_4$ , for example, must lie in the same plane. As a result, the presence of  $\pi$  bonds introduces rigidity into molecules. In molecules that have multiple bonds and more than one resonance structure, such as  $C_6H_6$ , the  $\pi$  bonds are **delocalized**; that is, the  $\pi$  bonds are spread among several atoms.

**MOLECULAR ORBITALS (SECTION 9.7)** **Molecular orbital theory** is another model used to describe the bonding in molecules. In this model, the electrons exist in allowed energy states called **molecular orbitals (MOs)**. An MO can extend over all the atoms of a molecule. Like an atomic orbital, a molecular orbital has a definite energy and can hold two electrons of opposite spin. We can build molecular orbitals by combining atomic orbitals on different atomic centers. In the simplest case, the combination of two atomic orbitals leads to the formation of two MOs, one at lower energy and one at higher energy relative to the energy of the atomic orbitals. The lower-energy MO concentrates charge density in the region between the nuclei and is called a **bonding molecular orbital**. The higher-energy MO excludes electrons from the region between the nuclei and is called an **antibonding molecular orbital**. Antibonding MOs exclude electron density from the region between the nuclei and have a **nodal plane**—a place at which the electron density is zero—between the nuclei. Occupation of bonding MOs favors bond formation, whereas occupation of antibonding MOs is unfavorable. The bonding and antibonding MOs formed by the combination of *s* orbitals are **sigma ( $\sigma$ ) molecular orbitals**; they lie on the internuclear axis.

The combination of atomic orbitals and the relative energies of the molecular orbitals are shown by an **energy-level (or molecular orbital) diagram**. When the appropriate number of electrons is put into the MOs, we can calculate the **bond order** of a bond, which is half the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A bond order of 1 corresponds to a single bond, and so forth. Bond orders can be fractional numbers.

### BONDING IN PERIOD 2 DIATOMIC MOLECULES (SECTION 9.8)

Electrons in core orbitals do not contribute to the bonding between atoms, so a molecular orbital description usually needs to consider only electrons in the outermost electron subshells. To describe the MOs of Period 2 homonuclear diatomic molecules, we need to consider the MOs that can form by the combination of  $p$  orbitals. The  $p$  orbitals that point directly at one another can form  $\sigma$  bonding and  $\sigma^*$  antibonding MOs. The  $p$  orbitals that are oriented perpendicular to the internuclear axis combine to form pi ( $\pi$ ) molecular orbitals. In diatomic molecules, the  $\pi$  molecular orbitals occur as a pair of degenerate (same energy) bonding MOs and a pair of degenerate antibonding MOs. The  $\sigma_{2p}$  bonding MO is expected to be lower in energy than the  $\pi_{2p}$  bonding MOs because of larger orbital overlap of

the  $p$  orbitals directed along the internuclear axis. However, this ordering is reversed in  $\text{B}_2$ ,  $\text{C}_2$ , and  $\text{N}_2$  because of interaction between the 2s and 2p atomic orbitals of different atoms.

The molecular orbital description of Period 2 diatomic molecules leads to bond orders in accord with the Lewis structures of these molecules. Further, the model predicts correctly that  $\text{O}_2$  should exhibit **paramagnetism**, which leads to attraction of a molecule into a magnetic field due to the influence of unpaired electrons. Molecules in which all the electrons are paired exhibit **diamagnetism**, which leads to weak repulsion from a magnetic field. The molecular orbitals of heteronuclear diatomic molecules are often closely related to those of homonuclear diatomic molecules.

## Learning Outcomes After studying this chapter, you should be able to:

- Draw and name the predicted three-dimensional shapes of molecules using the VSEPR model. (Section 9.2)  
*Related Exercises: 9.10, 9.63*
- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments. (Section 9.3) *Related Exercises: 9.17, 9.71*
- Explain the role of orbital overlap in the formation of covalent bonds. (Section 9.4) *Related Exercises: 9.22, 9.74*
- Determine the hybridization of atoms in molecules based on observed molecular structures. (Section 9.5) *Related Exercises: 9.24, 9.76*
- Sketch how orbitals overlap to form sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds. (Section 9.6) *Related Exercises: 9.28, 9.78*
- Explain the existence of delocalized  $\pi$  bonds in molecules such as benzene. (Section 9.6) *Related Exercises: 9.31, 9.83*
- Count the number of electrons in a delocalized  $\pi$  system. (Section 9.6) *Related Exercises: 9.32, 9.84*
- Explain the concept of bonding and antibonding molecular orbitals and draw examples of  $\sigma$  and  $\pi$  MOs. (Section 9.7) *Related Exercises: 9.35, 9.86*
- Draw molecular orbital energy-level diagrams and place electrons into them to obtain the bond orders and electron configurations of diatomic molecules using molecular orbital theory. (Sections 9.7 and 9.8) *Related Exercises: 9.36, 9.87*
- Correlate bond order, bond strength (bond enthalpy), bond length, and magnetic properties with molecular orbital descriptions of molecules. (Section 9.8) *Related Exercises: 9.41, 9.91*

## Key Equations

- Bond order =  $\frac{1}{2}$  (number of bonding electrons – number of antibonding electrons) [9.1]

## Exercises

### Visualizing Concepts

**9.44** A certain  $\text{AB}_4$  molecule has a “seesaw” shape



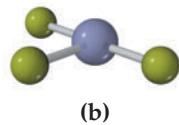
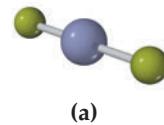
From which of the fundamental geometries shown in Figure 9.3 could you remove one or more atoms to create a molecule having this seesaw shape? [Section 9.1]

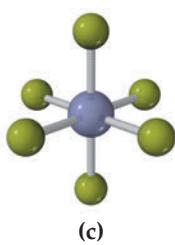
**9.45 (a)** If these three balloons are all the same size, what angle is formed between the red one and the green one? **(b)** If additional air is added to the blue balloon so that it gets larger, will the angle between the red and green balloons increase, decrease, or stay the same? **(c)** Which of the following aspects of the VSEPR model is illustrated by part (b): (i) The

electron-domain geometry for four electron domains is tetrahedral. (ii) The electron domains for nonbonding pairs are larger than those for bonding pairs. (iii) The hybridization that corresponds to a trigonal planar electron-domain geometry is  $sp^2$ . [Section 9.2]

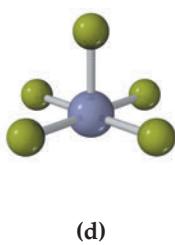


**9.46** For each molecule (a)–(f), indicate how many different electron-domain geometries are consistent with the molecular geometry shown. [Section 9.2]

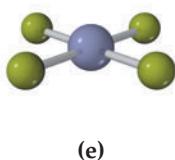




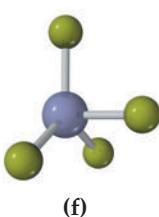
(c)



(d)



(e)

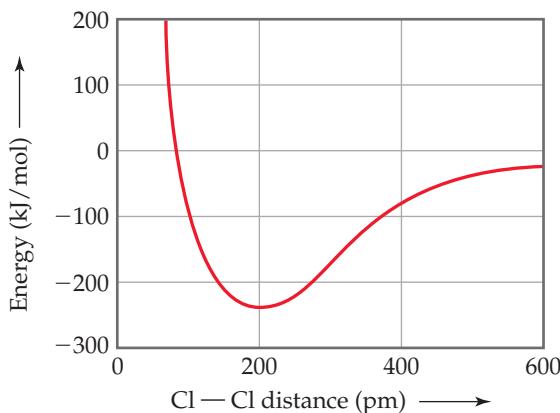


(f)

- 9.47** The molecule shown here is *difluoromethane* ( $\text{CH}_2\text{F}_2$ ), which is used as a refrigerant called R-32. (a) Based on the structure, how many electron domains surround the C atom in this molecule? (b) Would the molecule have a nonzero dipole moment? (c) If the molecule is polar, which of the following describes the direction of the overall dipole moment vector in the molecule: (i) from the carbon atom toward a fluorine atom, (ii) from the carbon atom to a point midway between the fluorine atoms, (iii) from the carbon atom to a point midway between the hydrogen atoms, or (iv) from the carbon atom toward a hydrogen atom? [Sections 9.2 and 9.3]

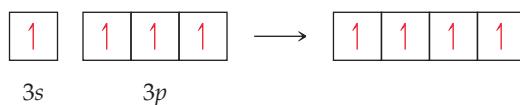


- 9.48** The following plot shows the potential energy of two Cl atoms as a function of the distance between them. (a) If the two atoms are very far away from each other, what is their potential energy of interaction? (b) We know that the  $\text{Cl}_2$  molecule exists. What is the approximate bond length and bond strength for the Cl–Cl bond in  $\text{Cl}_2$  from this graph? (c) If the  $\text{Cl}_2$  molecule is compressed under higher and higher pressure, does the Cl–Cl bond become stronger or weaker?

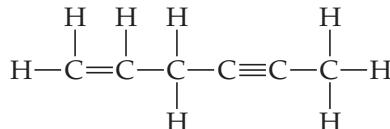


- 9.49** The orbital diagram that follows presents the final step in the formation of hybrid orbitals by a silicon atom. (a) Which of the following best describes what took place before the step pictured in the diagram: (i) Two  $3p$  electrons became unpaired, (ii) An electron was promoted from the  $2p$  orbital to

the  $3s$  orbital, or (iii) An electron was promoted from the  $3s$  orbital to the  $3p$  orbital? (b) What type of hybrid orbital is produced in this hybridization? [Section 9.5]

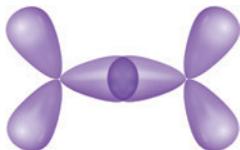


- 9.50** In the hydrocarbon



- (a) What is the hybridization at each carbon atom in the molecule? (b) How many  $\sigma$  bonds are there in the molecule? (c) How many  $\pi$  bonds? (d) Identify all the  $120^\circ$  bond angles in the molecule. [Section 9.6]

- 9.51** This drawing shows the overlap of two hybrid orbitals to form a bond in a hydrocarbon. (a) Which of the following types of bonds is being formed: (i)  $\text{C}=\text{C}\sigma$ , (ii)  $\text{C}=\text{C}\pi$ , or (iii)  $\text{C}=\text{H}\sigma$ ? (b) Which of the following could be the identity of the hydrocarbon: (i)  $\text{CH}_4$ , (ii)  $\text{C}_2\text{H}_6$ , (iii)  $\text{C}_2\text{H}_4$ , or (iv)  $\text{C}_2\text{H}_2$ ? [Section 9.6]

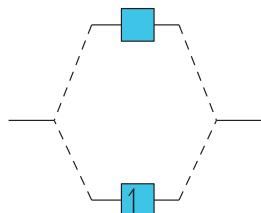


- 9.52** This molecule is called *furan*. It is represented in typical shorthand way for organic molecules, with hydrogen atoms not shown, and each of the 4 vertices representing a carbon atom.

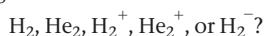


- (a) What is the molecular formula for furan? (b) How many valence electrons are there in the molecule? (c) What is the hybridization at each of the carbon atoms? (d) How many electrons are in the  $\pi$  system of the molecule? (e) The  $\text{C}=\text{C}=\text{C}$  bond angles in furan are much smaller than those in benzene. The likely reason is which of the following: (i) The hybridization of the carbon atoms in furan is different from that in benzene, (ii) Furan does not have another resonance structure equivalent to the one shown here, or (iii) The atoms in a five-membered ring are forced to adopt smaller angles than in a six-membered ring. [Section 9.5]

- 9.53** The following is part of a molecular orbital energy-level diagram for MOs constructed from  $1s$  atomic orbitals.

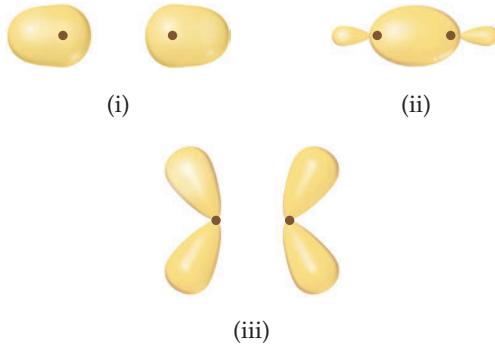


- (a) What labels do we use for the two MOs shown? (b) For which of the following molecules or ions could this be the energy-level diagram:

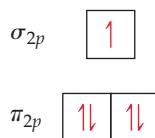


(c) What is the bond order of the molecule or ion? (d) If an electron is added to the system, into which of the MOs will it be added? [Section 9.7]

- 9.54** For each of these contour representations of molecular orbitals, identify (a) the atomic orbitals (*s* or *p*) used to construct the MO (b) the type of MO ( $\sigma$  or  $\pi$ ), (c) whether the MO is bonding or antibonding, and (d) the locations of nodal planes. [Sections 9.7 and 9.8]



- 9.55** The diagram that follows shows the highest-energy occupied MOs of a neutral molecule CX, where element X is in the same row of the periodic table as C. (a) Based on the number of electrons, can you determine the identity of X? (b) Would the molecule be diamagnetic or paramagnetic? (c) Consider the  $\pi_{2p}$  MOs of the molecule. Would you expect them to have a greater atomic orbital contribution from C, have a greater atomic orbital contribution from X, or be an equal mixture of atomic orbitals from the two atoms? [Section 9.8]



### Molecular Shapes; the VSEPR Model (Sections 9.1 and 9.2)

- 9.56** (a) Boron trichloride ( $\text{BCl}_3$ ) and the carbonate ion ( $\text{CO}_3^{2-}$ ) are both described as trigonal. What does this indicate about their bond angles? (b) The  $\text{PCl}_3$  molecule is trigonal pyramidal, while  $\text{ICl}_3$  is T-shaped. Which of these molecules is flat?

- 9.57** How does a trigonal pyramid differ from a tetrahedron so far as molecular geometry is concerned?

- 9.58** Describe the bond angles to be found in each of the following molecular structures: (a) trigonal planar, (b) tetrahedral, (c) octahedral, (d) linear.

- 9.59** Would you expect the nonbonding electron-pair domain in  $\text{NCl}_3$  to be greater or smaller in size than the corresponding one in  $\text{PCl}_3$ ?

- 9.60** In which of the following molecules can you confidently predict the bond angles about the central atom, and for which would you be a bit uncertain? Explain in each case. (a)  $\text{H}_2\text{S}$ , (b)  $\text{BCl}_3$ , (c)  $\text{CH}_3\text{I}$ , (d)  $\text{CBr}_4$ , (e)  $\text{TeBr}_4$ .

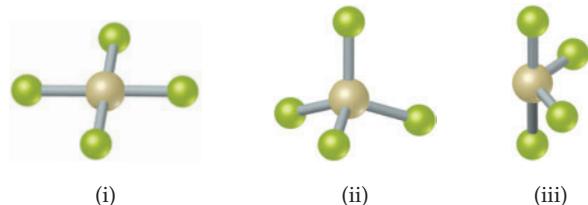
- 9.61** How many electron domains are surrounding the central atoms which adopt the following geometries? (a) linear (b) trigonal planar (c) trigonal pyramidal (d) trigonal bipyramidal.

- 9.62** What are the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom? (a) Three bonding domains and no nonbonding domains, (b) three bonding domains and one nonbonding

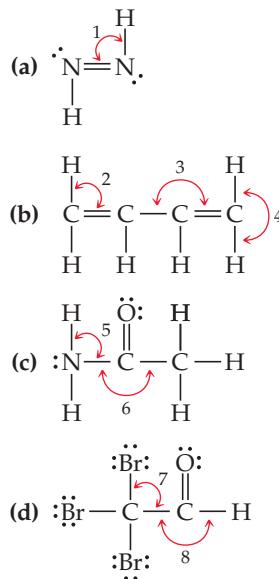
domain, (c) two bonding domains and two nonbonding domains.

- 9.63** Draw the Lewis structure for each of the following molecules or ions, and predict their electron-domain and molecular geometries: (a)  $\text{AsF}_3$ , (b)  $\text{CH}_3^+$ , (c)  $\text{BrF}_3$ , (d)  $\text{ClO}_3^-$ , (e)  $\text{XeF}_2$ , (f)  $\text{BrO}_2^-$ .

- 9.64** The figure that follows contains ball-and-stick drawings of three possible shapes of an  $\text{AF}_4$  molecule. (a) For each shape, give the electron-domain geometry on which the molecular geometry is based. (b) For each shape, how many nonbonding electron domains are there on atom A? (c) Which of the following elements will lead to an  $\text{AF}_4$  molecule with the shape in (iii): Be, C, S, Se, Si, Xe? (d) Name an element A that is expected to lead to the  $\text{AF}_4$  structure shown in (i).



- 9.65** Give the approximate values for the indicated bond angles in the following molecules:



- 9.66** In which of the following  $\text{AF}_n$  molecules or ions is there more than one F—A—F bond angle:  $\text{PF}_6^-$ ,  $\text{SbF}_5$ ,  $\text{SF}_4$ ?

- 9.67** Name the proper three-dimensional molecular shapes for each of the following molecules or ions, showing lone pairs as needed: (a)  $\text{ClO}_2^-$  (b)  $\text{SO}_4^{2-}$  (c)  $\text{NF}_3$  (d)  $\text{CCl}_2\text{Br}_2$  (e)  $\text{SF}_4^{2+}$

### Shapes and Polarity of Polyatomic Molecules (Section 9.3)

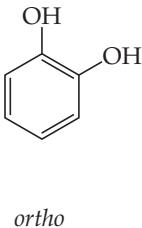
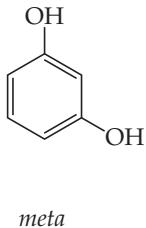
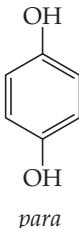
- 9.68** What is the distinction between a bond dipole and a molecular dipole moment?

- 9.69** (a) The  $\text{PH}_3$  molecule is polar. Does this offer experimental proof that the molecule cannot be planar? Explain. (b) It turns out that ozone,  $\text{O}_3$ , has a small dipole moment. How is this possible, given that all the atoms are the same?

- 9.70** (a) Consider the following two molecules:  $\text{PCl}_3$  and  $\text{BCl}_3$ . Which molecule has a nonzero dipole moment? (b) Consider

the following two molecules:  $\text{XeF}_4$  and  $\text{SF}_4$ . Which molecule has a zero dipole moment?

- 9.71** Predict whether each of the following molecules is polar or nonpolar: (a)  $\text{CCl}_4$ , (b)  $\text{NH}_3$ , (c)  $\text{SF}_4$ , (d)  $\text{XeF}_4$ , (e)  $\text{CH}_3\text{Br}$ , (f)  $\text{GaH}_3$ .
- 9.72** Dihydroxybenzene,  $\text{C}_6\text{H}_6\text{O}_2$ , exists in three forms (isomers) called *ortho*, *meta*, and *para*:



Which of these has a nonzero dipole moment?

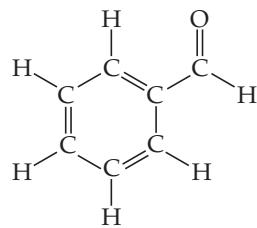
### Orbital Overlap; Hybrid Orbitals (Sections 9.4 and 9.5)

- 9.73** For each statement, indicate whether it is true or false. (a) In order to make a covalent bond, the orbitals on each atom in the bond must overlap. (b) A  $p$  orbital on one atom cannot make a bond to an  $s$  orbital on another atom. (c) Lone pairs of electrons on an atom in a molecule influence the shape of a molecule. (d) The  $1s$  orbital has a nodal plane. (e) The  $2p$  orbital has a nodal plane.
- 9.74** How would you expect the extent of overlap of the bonding atomic orbitals to vary in the series  $\text{IF}$ ,  $\text{ICl}$ ,  $\text{IBr}$ , and  $\text{I}_2$ ? Explain your answer.
- 9.75** Consider the  $\text{SCl}_2$  molecule. (a) What is the electron configuration of an isolated S atom? (b) What is the electron configuration of an isolated Cl atom? (c) What hybrid orbitals should be constructed on the S atom to make the S-Cl bonds in  $\text{SCl}_2$ ? (d) What valence orbitals, if any, remain unhybridized on the S atom in  $\text{SCl}_2$ ?
- 9.76** What is the hybridization of the central atom in (a)  $\text{PBr}_5$ , (b)  $\text{CH}_2\text{O}$ , (c)  $\text{O}_3$ , (d)  $\text{NO}_2$ ?
- 9.77** (a) Which geometry and central atom hybridization would you expect in the series  $\text{BH}_4^-$ ,  $\text{CH}_4$ ,  $\text{NH}_4^+$ ? (b) What would you expect for the magnitude and direction of the bond dipoles in this series? (c) Write the formulas for the analogous species of the elements of Period 3; would you expect them to have the same hybridization at the central atom?

### Multiple Bonds (Section 9.6)

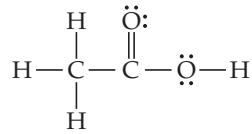
- 9.78** (a) If the valence atomic orbitals of an atom are  $sp$  hybridized, how many unhybridized  $p$  orbitals remain in the valence shell? How many  $\pi$  bonds can the atom form? (b) Imagine that you could hold two atoms that are bonded together, twist them, and not change the bond length. Would it be easier to twist (rotate) around a single  $\sigma$  bond or around a double ( $\sigma$  plus  $\pi$ ) bond, or would they be the same?
- 9.79** (a) Draw Lewis structures for chloromethane ( $\text{CH}_3\text{Cl}$ ), chloroethene ( $\text{C}_2\text{H}_3\text{Cl}$ ), and chloroethyne ( $\text{C}_2\text{HCl}$ ). (b) What is the hybridization of the carbon atoms in each molecule? (c) Predict which molecules, if any, are planar. (d) How many  $\sigma$  and  $\pi$  bonds are there in each molecule?
- 9.80** The oxygen atoms in  $\text{O}_2$  participate in multiple bonding, whereas those in hydrogen peroxide,  $\text{H}_2\text{O}_2$ , do not. (a) Draw Lewis structures for both molecules. (b) What is the hybridization of the oxygen atoms in each molecule? (c) Which molecule has the stronger O—O bond?

- 9.81** Benzaldehyde,  $\text{C}_7\text{H}_6\text{O}$ , is a fragrant substance responsible for the aroma of almonds. Its Lewis structure is



- (a) What is the hybridization at each of the carbon atoms of the molecule? (b) What is the total number of valence electrons in benzaldehyde? (c) How many of the valence electrons are used to make  $\sigma$  bonds in the molecule? (d) How many valence electrons are used to make  $\pi$  bonds? (e) How many valence electrons remain in nonbonding pairs in the molecule?

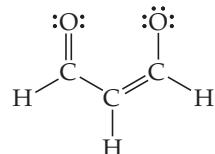
- 9.82** Consider the Lewis structure for acetic acid, which is known as vinegar:



- (a) What are the approximate bond angles about each of the two carbon atoms, and what are the hybridizations of the orbitals on each of them? (b) What are the hybridizations of the orbitals on the two oxygen atoms, and what are the approximate bond angles at the oxygen that is connected to carbon and hydrogen? (c) What is the total number of  $\sigma$  bonds in the entire molecule, and what is the total number of  $\pi$  bonds?

- 9.83** (a) Write a single Lewis structure for  $\text{N}_2\text{O}$ , and determine the hybridization of the central N atom. (b) Are there other possible Lewis structures for the molecule? (c) Would you expect  $\text{N}_2\text{O}$  to exhibit delocalized  $\pi$  bonding?

- 9.84** Consider this Lewis structure.



- (a) Does the Lewis structure depict a neutral molecule or an ion? If it is an ion, what is the charge on the ion? (b) What hybridization is exhibited by each of the carbon atoms? (c) Are there multiple equivalent resonance structures for the species? (d) How many electrons are in the  $\pi$  system of the species?

- 9.85** What hybridization do you expect for the atom that is underlined in each of the following species? (a)  $\underline{\text{IO}}_2^-$ ; (b)  $\underline{\text{NH}}_4^+$ ; (c)  $\underline{\text{SCN}}^-$ ; (d)  $\underline{\text{BrCl}}_3$

### Molecular Orbitals and Period 2 Diatomic Molecules (Sections 9.7 and 9.8)

- 9.86** (a) If you combine two atomic orbitals on two different atoms to make a new orbital, is this a hybrid orbital or a molecular orbital? (b) If you combine two atomic orbitals on one atom to make a new orbital, is this a hybrid orbital or a molecular orbital? (c) Does the Pauli exclusion principle (Section 6.7) apply to MOs? Explain.

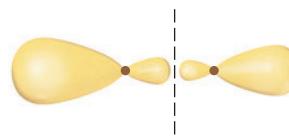
- 9.87** (a) Sketch the molecular orbitals of the  $\text{H}_2^-$  ion and draw its energy-level diagram. (b) Write the electron configuration of

the ion in terms of its MOs. (c) Calculate the bond order in  $\text{H}_2^-$ . (d) Suppose that the ion is excited by light, so that an electron moves from a lower-energy to a higher-energy molecular orbital. Would you expect the excited-state  $\text{H}_2^-$  ion to be stable? (e) Which of the following statements about part (d) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

- 9.88** Indicate whether each statement is true or false. (a)  $p$  orbitals can only make  $\sigma$  or  $\sigma^*$  molecular orbitals. (b) The probability is always 0% for finding an electron in an antibonding orbital. (c) Molecules containing electrons that occupy antibonding orbitals must be unstable. (d) Electrons cannot occupy a nonbonding orbital.
- 9.89** Explain the following: (a) The *peroxide* ion,  $\text{O}_2^{2-}$ , has a longer bond length than the *superoxide* ion,  $\text{O}_2^-$ . (b) The magnetic properties of  $\text{B}_2$  are consistent with the  $\pi_{2p}$  MOs being lower in energy than the  $\sigma_{2p}$  MO. (c) The  $\text{O}_2^{2+}$  ion has a stronger O—O bond than  $\text{O}_2$  itself.
- 9.90** (a) What does the term *paramagnetism* mean? (b) How can one determine experimentally whether a substance is paramagnetic? (c) Which of the following ions would you expect to be paramagnetic:  $\text{O}_2^+$ ,  $\text{N}_2^{2-}$ ,  $\text{Li}_2^+$ ,  $\text{O}_2^{2-}$ ? For those ions that are paramagnetic, determine the number of unpaired electrons.
- 9.91** If we assume that the energy-level diagrams for homonuclear diatomic molecules shown in Figure 9.40 can be applied

to heteronuclear diatomic molecules and ions, predict the bond order and magnetic behavior of (a)  $\text{CC}^-$ , (b)  $\text{NO}^+$ , (c)  $\text{HHe}^+$ , (d)  $\text{ClF}$ .

- 9.92** (a) The nitric oxide molecule,  $\text{NO}$ , readily loses one electron to form the  $\text{NO}^+$  ion. Which of the following is the best explanation of why this happens: (i) Oxygen is more electronegative than nitrogen, (ii) The highest energy electron in  $\text{NO}$  lies in a  $\pi_{2p}^*$  molecular orbital, or (iii) The  $\pi_{2p}^*$  MO in  $\text{NO}$  is completely filled. (b) Predict the order of the N—O bond strengths in  $\text{NO}$ ,  $\text{NO}^+$ , and  $\text{NO}^-$ , and describe the magnetic properties of each. (c) With what neutral homonuclear diatomic molecules are the  $\text{NO}^+$  and  $\text{NO}^-$  ions isoelectronic (same number of electrons)?
- 9.93** The iodine bromide molecule,  $\text{IBr}$ , is an *interhalogen compound*. Assume that the molecular orbitals of  $\text{IBr}$  are analogous to the homonuclear diatomic molecule  $\text{F}_2$ . (a) Which valence atomic orbitals of I and of Br are used to construct the MOs of  $\text{IBr}$ ? (b) What is the bond order of the  $\text{IBr}$  molecule? (c) One of the valence MOs of  $\text{IBr}$  is sketched here. Why are the atomic orbital contributions to this MO different in size? (d) What is the label for the MO sketched here? (e) For the  $\text{IBr}$  molecule, how many electrons occupy the MO sketched here?



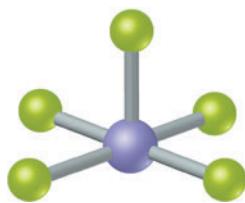
## Additional Exercises

- 9.94** (a) What is the physical basis for the VSEPR model? (b) When applying the VSEPR model, we count a double or triple bond as a single electron domain. Why is this justified?
- 9.95** An  $\text{AB}_2$  molecule is described as having a tetrahedral geometry. (a) How many nonbonding domains are on atom A? (b) Based on the information given, which of the following is the molecular geometry of the molecule: (i) linear, (ii) bent, (iii) trigonal planar, or (iv) tetrahedral?
- 9.96** Consider the following  $\text{XF}_4^-$  ions:  $\text{PF}_4^-$ ,  $\text{BrF}_4^-$ ,  $\text{ClF}_4^+$ , and  $\text{AlF}_4^-$ . (a) Which of the ions have more than an octet of electrons around the central atom? (b) For which of the ions will the electron-domain and molecular geometries be the same? (c) Which of the ions will have an octahedral electron-domain geometry? (d) Which of the ions will exhibit a seesaw molecular geometry?
- 9.97** Consider the molecule  $\text{PF}_4\text{Cl}$ . (a) Draw a Lewis structure for the molecule, and predict its electron-domain geometry. (b) Which would you expect to take up more space, a P—F bond or a P—Cl bond? Explain. (c) Predict the molecular geometry of  $\text{PF}_4\text{Cl}$ . How did your answer for part (b) influence your answer here in part (c)? (d) Would you expect the molecule to distort from its ideal electron-domain geometry? If so, how would it distort?
- 9.98** The vertices of a tetrahedron correspond to four alternating corners of a cube. By using analytical geometry, demonstrate that the angle made by connecting two of the vertices to a point at the center of the cube is  $109.5^\circ$ , the characteristic angle for tetrahedral molecules.
- 9.99** Fill in the blank spaces in the following chart. If the molecule column is blank, find an example that fulfills the conditions of the rest of the row.

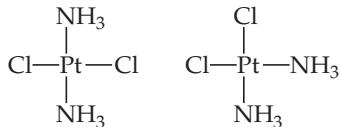
Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
$\text{CO}_2$		$sp^3$	Yes
		$sp^3$	No
	Trigonal planar		No
$\text{SF}_4$	Octahedral		No
		$sp^2$	Yes
	Trigonal bipyramidal		No
$\text{XeF}_2$			

- 9.100** From their Lewis structures, determine the number of  $\sigma$  and  $\pi$  bonds in each of the following molecules or ions: (a) hydrazine,  $\text{N}_2\text{H}_4$ ; (b) hydrogen cyanide,  $\text{HCN}$ ; (c) sulfur trioxide,  $\text{SO}_3$ ; (d) ozone,  $\text{O}_3$ .
- 9.101** Ethyl propanoate,  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ , gives a fruity pineapple-like smell. (a) Draw the Lewis structure for the molecule, assuming that carbon always forms four bonds in its stable compounds. (b) How many  $\sigma$  and how many  $\pi$  bonds are in the molecule? (c) Which CO bond is shortest in the molecule? (d) What is the hybridization of atomic orbitals around the carbon atom associated with that short bond? (e) What are the approximate bond angles around each carbon atom in the molecule?
- 9.102** An  $\text{AB}_5$  molecule adopts the geometry shown here. (a) What is the name of this geometry? (b) Do you think there are any nonbonding electron pairs on atom A? (c) Suppose the

B atoms are halogen atoms. Of which group in the periodic table is atom A a member: (i) Group 15, (ii) Group 16, (iii) Group 17, (iv) Group 18, or (v) More information is needed?



- 9.103** There are two compounds of the formula  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ :



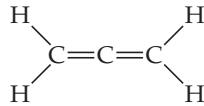
The compound on the right is called *cisplatin*, and the compound on the left is called *transplatin*. (a) Which compound has a nonzero dipole moment? (b) One of these compounds is an anticancer drug, and one is inactive. The anticancer drug works by its chloride ions undergoing a substitution reaction with nitrogen atoms in DNA that are close together, forming a N—Pt—N angle of about  $90^\circ$ . Which compound would you predict to be the anticancer drug?

- 9.104** The O—H bond lengths in the water molecule ( $\text{H}_2\text{O}$ ) are 96 pm, and the H—O—H angle is  $104.5^\circ$ . The dipole moment of the water molecule is  $6.17 \times 10^{-30} \text{ C}\cdot\text{m}$ . (a) In what directions do the bond dipoles of the O—H bonds point? In what direction does the dipole moment vector of the water molecule point? (b) Calculate the magnitude of the bond dipole of the O—H bonds. (Note: You will need to use vector addition to do this.) (c) Compare your answer from part (b) to the dipole moments of the hydrogen halides (Table 8.3). Is your answer in accord with the relative electronegativity of oxygen?

- 9.105** (a) Predict the electron-domain geometry around the central S atom in  $\text{SF}_2$ ,  $\text{SF}_4$ , and  $\text{SF}_6$ . (b) The anion  $\text{IO}_4^-$  has a tetrahedral structure: three oxygen atoms form double bonds with the central iodine atom and one oxygen atom which carries a negative charge forms a single bond. Predict the molecular geometry of  $\text{IO}_6^{5-}$ .

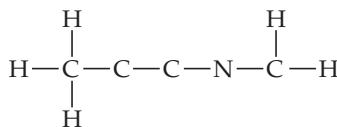
- 9.106** Which of the following statements about hybrid orbitals is or are true? (i) After an atom undergoes  $sp$  hybridization, there is one unhybridized  $p$  orbital on the atom, (ii) Under  $sp^2$  hybridization, the large lobes point to the vertices of an equilateral triangle, and (iii) The angle between the large lobes of  $sp^3$  hybrids is  $109.5^\circ$ .

- 9.107** The Lewis structure for allene is



Make a sketch of the structure of this molecule that is analogous to Figure 9.25. In addition, answer the following three questions: (a) Is the molecule planar? (b) Does it have a nonzero dipole moment? (c) Would the bonding in allene be described as delocalized? Explain.

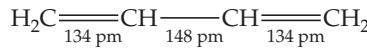
- 9.108** Consider the molecule  $\text{C}_4\text{H}_5\text{N}$ , which has the connectivity shown here. (a) After the Lewis structure for the molecule is completed, how many  $\sigma$  and how many  $\pi$  bonds are there in this molecule? (b) How many atoms in the molecule exhibit (i)  $sp$  hybridization, (ii)  $sp^2$  hybridization, and (iii)  $sp^3$  hybridization?



- 9.109** Sodium azide is a shock-sensitive compound that releases  $\text{N}_2$  upon physical impact. The compound is used in automobile airbags. The azide ion is  $\text{N}_3^-$ . (a) Draw the Lewis structure of the azide ion that minimizes formal charge (it does not form a triangle). Is it linear or bent? (b) State the hybridization of the central N atom in the azide ion. (c) How many  $\sigma$  bonds and how many  $\pi$  bonds does the central nitrogen atom make in the azide ion?

- 9.110** In ozone,  $\text{O}_3$ , the two oxygen atoms on the ends of the molecule are equivalent to one another. (a) What is the best choice of hybridization scheme for the atoms of ozone? (b) For one of the resonance forms of ozone, which of the orbitals are used to make bonds and which are used to hold nonbonding pairs of electrons? (c) Which of the orbitals can be used to delocalize the  $\pi$  electrons? (d) How many electrons are delocalized in the  $\pi$  system of ozone?

- 9.111** Butadiene,  $\text{C}_4\text{H}_6$ , is a planar molecule that has the following carbon–carbon bond lengths:



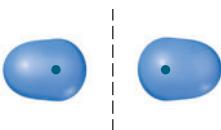
(a) Predict the bond angles around each of the carbon atoms and sketch the molecule. (b) From left to right, what is the hybridization of each carbon atom in butadiene? (c) The middle C—C bond length in butadiene (148 pm) is a little shorter than the average C—C single bond length (154 pm). Does this imply that the middle C—C bond in butadiene is weaker or stronger than the average C—C single bond? (d) Based on your answer for part (c), discuss what additional aspects of bonding in butadiene might support the shorter middle C—C bond.

- 9.112** The structure of *borazine*,  $\text{B}_3\text{N}_3\text{H}_6$ , is a six-membered ring of alternating B and N atoms. There is one H atom bonded to each B and to each N atom. The molecule is planar. (a) Write a Lewis structure for borazine in which the formal charge on every atom is zero. (b) Write a Lewis structure for borazine in which the octet rule is satisfied for every atom. (c) What are the formal charges on the atoms in the Lewis structure from part (b)? Given the electronegativities of B and N, do the formal charges seem favorable or unfavorable? (d) Do either of the Lewis structures in parts (a) and (b) have multiple resonance structures? (e) What are the hybridizations at the B and N atoms in the Lewis structures from parts (a) and (b)? Would you expect the molecule to be planar for both Lewis structures? (f) The six B—N bonds in the borazine molecule are all identical in length at 144 pm. Typical values for the bond lengths of B—N single and double bonds are 151 pm and 131 pm, respectively. Does the value of the B—N bond length seem to favor one Lewis structure over the other? (g) How many electrons are in the  $\pi$  system of borazine?

- 9.113** The highest occupied molecular orbital of a molecule is abbreviated as the HOMO. The lowest unoccupied molecular orbital in a molecule is called the LUMO. Experimentally, one can measure the difference in energy between the HOMO and LUMO by taking the electronic absorption (UV-visible) spectrum of the molecule. Peaks in the electronic absorption spectrum can be labeled as  $\pi_{2p}-\pi_{2p}^*$ ,  $\sigma_{2s}-\sigma_{2s}^*$ , and so on, corresponding to electrons being promoted from one orbital to another. The HOMO-LUMO transition corresponds to molecules going from their ground

state to their first excited state. (a) Write out the molecular orbital valence electron configurations for the ground state and first excited state for  $N_2$ . (b) Is  $N_2$  paramagnetic or diamagnetic in its first excited state? (c) The electronic absorption spectrum of the  $N_2$  molecule has the lowest energy peak at 170 nm. To what orbital transition does this correspond? (d) Calculate the energy of the HOMO-LUMO transition in part (a) in terms of kJ/mol. (e) Is the N—N bond in the first excited state stronger or weaker compared to that in the ground state?

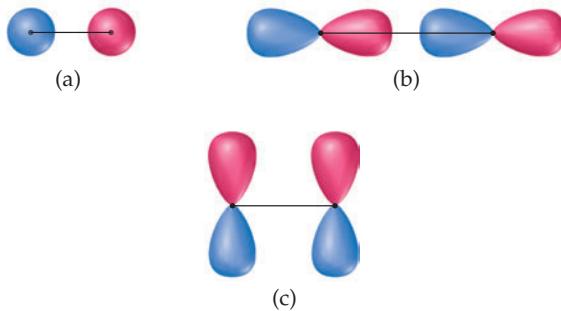
- 9.114** One of the molecular orbitals of the  $H_2^-$  ion is sketched here:



(a) Is the molecular orbital a  $\sigma$  or  $\pi$  MO? Is it bonding or antibonding? (b) In  $H_2^-$ , how many electrons occupy the MO shown here? (c) What is the bond order in the  $H_2^-$  ion? (d) Compared to the H—H bond in  $H_2$ , the H—H bond in  $H_2^-$  is expected to be which of the following: (i) Shorter and stronger, (ii) longer and stronger, (iii) shorter and weaker, (iv) longer and weaker, or (v) the same length and strength?

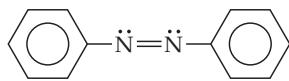
- 9.115** Place the following molecules and ions in order from smallest to largest bond order:  $N_2^{2+}$ ,  $He_2^+$ ,  $Cl_2H_2^-$ ,  $O_2^{2-}$ .

- 9.116** The following sketches show the atomic orbital wave functions (with phases) used to construct some of the MOs of a homonuclear diatomic molecule. For each sketch, determine the type of MO that will result from mixing the atomic orbital wave functions as drawn. Use the same labels for the MOs as in the “Closer Look” box on phases.

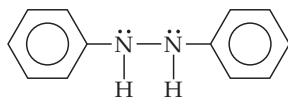


- 9.117** Molecules that are brightly colored have a small energy gap between filled and empty electronic states (the HOMO-LUMO gap; see Exercise 9.113). Suppose you have two samples, one is lycopene which is responsible for the red color in tomato, and the other is curcumin which is responsible for the yellow color in turmeric. Which one has the larger HOMO-LUMO gap?

- 9.118** Azo dyes are organic dyes that are used for many applications, such as the coloring of fabrics. Many azo dyes are derivatives of the organic substance *azobenzene*,  $C_{12}H_{10}N_2$ . A closely related substance is *hydrazobenzene*,  $C_{12}H_{12}N_2$ . The Lewis structures of these two substances are



Azobenzene



Hydrazobenzene

(Recall the shorthand notation used for benzene.) (a) What is the hybridization at the N atom in each of the substances? (b) How many unhybridized atomic orbitals are there on the N and the C atoms in each of the substances? (c) Predict the N—N—C angles in each of the substances. (d) Azobenzene is said to have greater delocalization of its  $\pi$  electrons than hydrazobenzene. Discuss this statement in light of your answers to (a) and (b). (e) All the atoms of azobenzene lie in one plane, whereas those of hydrazobenzene do not. Is this observation consistent with the statement in part (d)? (f) Azobenzene is an intense red-orange color, whereas hydrazobenzene is nearly colorless. Which molecule would be a better one to use in a solar energy conversion device? (See the “Chemistry Put to Work” box for more information about solar cells.)

- 9.119** (a) Using only the valence atomic orbitals of a hydrogen atom and a fluorine atom, and following the model of Figure 9.43, how many MOs would you expect for the HF molecule? (b) How many of the MOs from part (a) would be occupied by electrons? (c) It turns out that the difference in energies between the valence atomic orbitals of H and F are sufficiently different that we can neglect the interaction of the 1s orbital of hydrogen with the 2s orbital of fluorine. The 1s orbital of hydrogen will mix only with one 2p orbital of fluorine. Draw pictures showing the proper orientation of all three 2p orbitals on F interacting with a 1s orbital on H. Which of the 2p orbitals can actually make a bond with a 1s orbital, assuming that the atoms lie on the z-axis? (d) In the most accepted picture of HF, all the other atomic orbitals on fluorine move over at the same energy into the molecular orbital energy-level diagram for HF. These are called “nonbonding orbitals.” Sketch the energy-level diagram for HF using this information and calculate the bond order. (Nonbonding electrons do not contribute to bond order.) (e) Look at the Lewis structure for HF. Where are the nonbonding electrons?

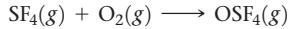
- 9.120** Carbon monoxide, CO, is isoelectronic to  $N_2$ . (a) Draw a Lewis structure for CO that satisfies the octet rule. (b) Assume that the diagram in Figure 9.43 can be used to describe the MOs of CO. What is the predicted bond order for CO? Is this answer in accord with the Lewis structure you drew in part (a)? (c) Experimentally, it is found that the highest energy electrons in CO reside in a  $\sigma$ -type MO. Is that observation consistent with Figure 9.43? If not, what modification needs to be made to the diagram? How does this modification relate to Figure 9.40? (d) Would you expect the  $\pi_{2p}$  MOs of CO to have equal atomic orbital contributions from the C and O atoms? If not, which atom would have the greater contribution?

- 9.121** The energy-level diagram in Figure 9.33 shows that the sideways overlap of a pair of  $p$  orbitals produces two molecular orbitals, one bonding and one antibonding. In ethene there is a pair of electrons in the bonding  $\pi$  orbital between the two carbons. Absorption of a photon of the appropriate wavelength can result in promotion of one of the bonding electrons from the  $\pi_{2p}$  to the  $\pi_{2p}^*$  molecular orbital. (a) Assuming this electronic transition corresponds to the HOMO-LUMO transition, what is the HOMO in ethene? (b) Assuming this electronic transition corresponds to the HOMO-LUMO transition, what is the LUMO in ethene? (c) Is the C—C bond in ethene stronger or weaker in the excited state than in the ground state? Why? (d) Is the C—C bond in ethene easier to twist in the ground state or in the excited state?

## Integrative Exercises

**9.122** A compound composed of 6.7% H, 40.0% C, and 53.3% O has a molar mass of approximately 60 g/mol. (a) What is the molecular formula of the compound? (b) What is its Lewis structure if the two O are bonded to C? (c) What is the geometry and hybridization of the C atom that is bonded to 2 O atoms? (d) How many  $\sigma$  and how many  $\pi$  bonds are there in the molecule?

**9.123** Sulfur tetrafluoride ( $\text{SF}_4$ ) reacts slowly with  $\text{O}_2$  to form sulfur tetrafluoride monoxide ( $\text{OSF}_4$ ) according to the following unbalanced reaction:

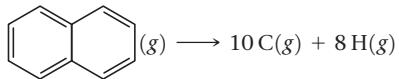


The O atom and the four F atoms in  $\text{OSF}_4$  are bonded to a central S atom. (a) Balance the equation. (b) Write a Lewis structure of  $\text{OSF}_4$  in which the formal charges of all atoms are zero. (c) Use average bond enthalpies (Table 8.3) to estimate the enthalpy of the reaction. Is it endothermic or exothermic? (d) Determine the electron-domain geometry of  $\text{OSF}_4$ , and write two possible molecular geometries for the molecule based on this electron-domain geometry. (e) For each of the molecules you drew in part (d), state how many fluorines are equatorial and how many are axial.

**9.124** The phosphorus trihalides ( $\text{PX}_3$ ) show the following variation in the bond angle X—P—X:  $\text{PF}_3$ , 96.3°;  $\text{PCl}_3$ , 100.3°;  $\text{PBr}_3$ , 101.0°;  $\text{PI}_3$ , 102.0°. The trend is generally attributed to the change in the electronegativity of the halogen. (a) Assuming that all electron domains are the same size, what value of the X—P—X angle is predicted by the VSEPR model? (b) What is the general trend in the X—P—X angle as the halide electronegativity increases? (c) Using the VSEPR model, explain the observed trend in X—P—X angle as the electronegativity of X changes. (d) Based on your answer to part (c), predict the structure of  $\text{PBrCl}_4$ .

**9.125** (a) Compare the bond enthalpies (Table 8.3) of the carbon–carbon single, double, and triple bonds to deduce an average  $\pi$ -bond contribution to the enthalpy. What fraction of a single bond does this quantity represent? (b) Make a similar comparison of nitrogen–nitrogen bonds. What do you observe? (c) Write Lewis structures of  $\text{N}_2\text{H}_4$ ,  $\text{N}_2\text{H}_2$ , and  $\text{N}_2$ , and determine the hybridization around nitrogen in each case. (d) Propose a reason for the large difference in your observations of parts (a) and (b).

**9.126** (a) Use average bond enthalpies (Table 8.3) to estimate  $\Delta H$  for the atomization of naphthalene,  $\text{C}_{10}\text{H}_8$ :

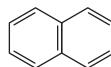


(b) Determine  $\Delta H$  for the atomization of naphthalene using Hess's law and the data in Appendix C. ( $\Delta H_f^\circ$  of solid naphthalene is 77.1 kJ/mol and molar heat of sublimation of naphthalene is 72.9 kJ/mol.) (c) Explain the large discrepancy in the two values.

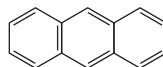
**9.127** Many compounds of the transition-metal elements contain direct bonds between metal atoms. We will assume that the z-axis is defined as the metal–metal bond axis. (a) Which of the  $3d$  orbitals (Figure 6.22) is most likely to

make a  $\sigma$  bond between metal atoms? (b) Sketch the  $\sigma_{3d}$  bonding and  $\sigma_{3d}^*$  antibonding MOs. (c) With reference to the “Closer Look” box on the phases of orbitals, explain why a node is generated in the  $\sigma_{3d}^*$  MO. (d) Sketch the energy-level diagram for the  $\text{Sc}_2$  molecule, assuming that only the  $3d$  orbital from part (a) is important. (e) What is the bond order in  $\text{Sc}_2$ ?

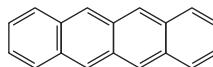
**9.128** The organic molecules shown here are derivatives of benzene in which six-membered rings are “fused” at the edges of the hexagons.



Naphthalene



Anthracene



Tetracene

(a) Determine the empirical formula of benzene and of these three compounds. (b) Suppose you are given a sample of one of the compounds. Could combustion analysis be used to determine unambiguously which of the three it is? (c) Naphthalene, the active ingredient in mothballs, is a white solid. Write a balanced equation for the combustion of naphthalene to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$ . (d) Using the Lewis structure for naphthalene and the average bond enthalpies in Table 8.3, estimate the heat of combustion of naphthalene in kJ/mol. (e) Benzene, naphthalene, and anthracene are colorless, but tetracene is orange. What does this imply about the relative HOMO–LUMO energy gaps in these molecules? See the “Chemistry Put to Work” box on orbitals and energy.

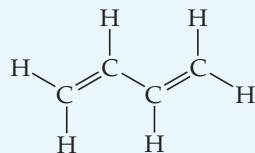
**9.129** Antibonding molecular orbitals can be used to make bonds to other atoms in a molecule. For example, metal atoms can use appropriate  $d$  orbitals to overlap with the  $\pi_{2p}^*$  orbitals of the carbon monoxide molecule. This is called  $d$ - $\pi$  backbonding. (a) Draw a coordinate axis system in which the  $y$ -axis is vertical in the plane of the paper and the  $x$ -axis horizontal. Write “M” at the origin to denote a metal atom. (b) Now, on the  $x$ -axis to the right of M, draw the Lewis structure of a CO molecule, with the carbon nearest the M. The CO bond axis should be on the  $x$ -axis. (c) Draw the CO  $\pi_{2p}^*$  orbital, with phases (see the “Closer Look” box on phases) in the plane of the paper. Two lobes should be pointing toward M. (d) Now draw the  $d_{xy}$  orbital of M, with phases. Can you see how they will overlap with the  $\pi_{2p}^*$  orbital of CO? (e) What kind of bond is being made with the orbitals between M and C,  $\sigma$  or  $\pi$ ? (f) Predict what will happen to the strength of the CO bond in a metal–CO complex compared to CO alone.

**9.130** Methyl isocyanate,  $\text{CH}_3\text{NCO}$ , was made infamous in 1984 when an accidental leakage of this compound from a storage tank in Bhopal, India, resulted in the deaths of about 3800 people and severe and lasting injury to many thousands more. (a) Draw a Lewis structure for methyl isocyanate. (b) Draw a ball-and-stick model of the structure, including estimates of all the bond angles in the compound. (c) Predict all the bond distances in the molecule. (d) Do you predict that the molecule will have a dipole moment? Explain.

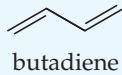
## Design an Experiment

In this chapter, we have seen a number of new concepts, including the delocalization of  $\pi$  systems of molecules and the molecular orbital description of molecular bonding. A connection between these concepts is provided by the field of *organic dyes*, molecules with delocalized  $\pi$  systems that have color. The color is due to the

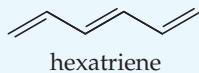
excitation of an electron from the *highest occupied molecular orbital* (HOMO) to the *lowest unoccupied molecular orbital* (LUMO). It is hypothesized that the energy gap between the HOMO and the LUMO depends on the length of the  $\pi$  system. Imagine that you are given samples of the following substances to test this hypothesis:



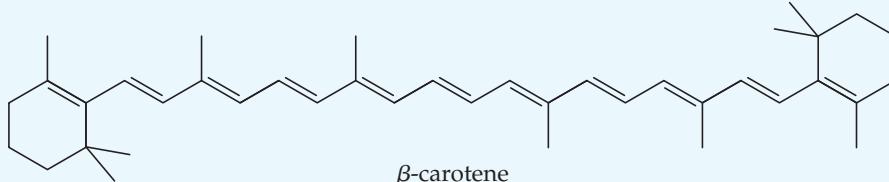
or, in shorthand notation  
for organic molecules



butadiene



hexatriene



$\beta$ -carotene

$\beta$ -Carotene is the substance chiefly responsible for the bright orange color of carrots. It is also an important nutrient for the body's production of retinal. (a) What experiments could you design to determine the amount of energy needed to excite an electron from the HOMO to the LUMO in each of these molecules? (b) How might you graph your data to determine whether a relationship exists between the length of the  $\pi$  system and the excitation energy? (c) What

additional molecules might you want to procure to further test the ideas developed here? (d) How could you design an experiment to determine whether the delocalized systems and not some other molecular features, such as molecular length or the presence of bonds, are important in making the excitations occur in the visible portion of the spectrum? (Hint: You might want to test some additional molecules not shown here.)