9.5 HYBRID ORBITALS
To account for molecular shape, we consider how the orbitals of one atom mix with one another, or *hybridize,* to create *hybrid orbitals*.

9.6 MULTIPLE BONDS
Atomic orbitals that contribute to covalent bonding in a molecule can overlap in multiple ways to produce *sigma* and *pi* bonds between atoms. Single bonds generally consist of one sigma bond; multiple bonds involve one sigma and one or more pi bonds. We examine the geometric arrangements of these bonds and how they are exemplified in organic compounds.

9.7 MOLECULAR ORBITALS
We examine a more sophisticated treatment of bonding called *molecular orbital theory,* which introduces the concepts of *bonding* and *antibonding molecular orbitals*.

9.8 PERIOD 2 DIATOMIC MOLECULES
We consider how molecular orbital theory is used to construct *energy-level diagrams* for second-row diatomic molecules.

MOLECULAR GEOMETRY AND BONDING THEORIES

WE SAW IN CHAPTER 8 THAT 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.

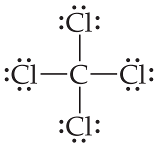
The shape and size of a molecule of a substance, together with the strength and polarity of its bonds, largely determine the properties of that substance. Some of the most dramatic examples of the important roles of molecular architecture are seen in biochemical reactions. For example, the chapter-opening photograph shows a molecular model of diazepam, better known as Valium. In the body, this relatively simple molecule enters into an extraordinary array of biochemical interactions. Valium works by binding to certain important sites in the central nervous system. Its effectiveness is highly dependent on the shape and size of the molecule as well on the charge distributions within it. Even a small modification to molecular shape or size alters the drug's effectiveness.

One of our goals in this chapter is to develop a sense of the shapes of molecules and how those shapes are governed in large measure by the kinds of bonds that exist between the atoms making up the molecules.

Our first goal is to learn the relationship between two-dimensional Lewis structures and three-dimensional molecular shapes. Armed with this knowledge, we can examine 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. Mastering the material in this chapter will help you in later discussions of the physical and chemical properties of substances.

9.1 MOLECULAR SHAPES

In Chapter 8 we used Lewis structures to account for the formulas of covalent compounds. (Section 8.5) 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 CCl_4 tells us only that four Cl atoms are bonded to a central C atom:



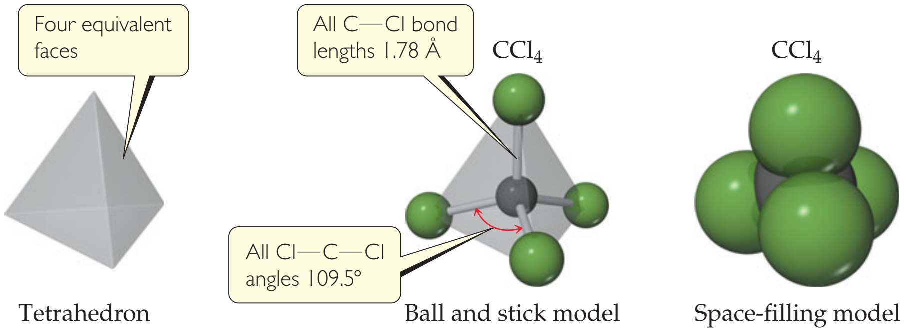
The Lewis structure is drawn with the atoms all in the same plane. As shown in ▼ **FIGURE 9.1**, however, the actual arrangement is the Cl atoms at the corners of a *tetrahedron,* a geometric object with four corners and four faces, each an equilateral triangle.

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 (Section 8.8), 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 CCl_4 and that they all have the same value of 109.5°, the angle size characteristic of a tetrahedron. In addition, all four C—Cl bonds are the same length (1.78 Å). Thus, the shape and size of CCl_4 are completely described by stating that the molecule is tetrahedral with C—Cl bonds of length 1.78 Å.

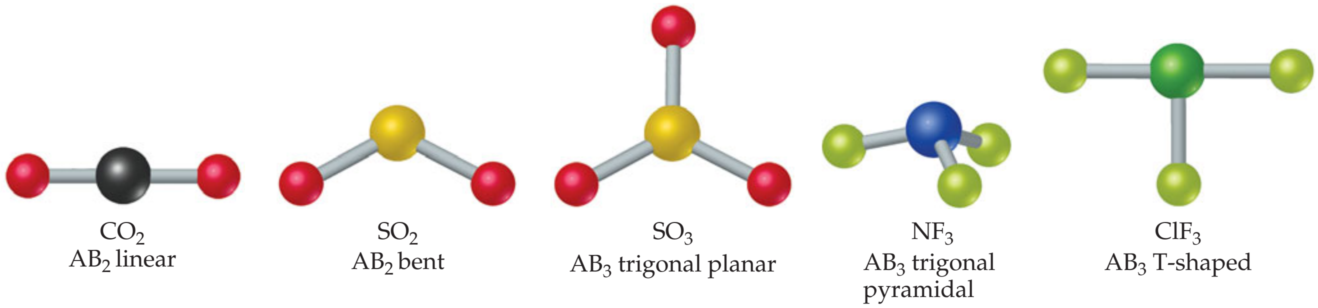
We begin our discussion of molecular shapes with molecules (and ions) that, like CCl_4, have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula AB_n in which the central atom A is bonded to n

GO FIGURE

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



▲ **FIGURE 9.1** **Tetrahedral shape of CCl_4.**



CO_2 AB_2 linear

SO_2 AB_2 bent

SO_3 AB_3 trigonal planar

NF_3 AB_3 trigonal pyramidal

ClF_3 AB_3 T-shaped

▲ **FIGURE 9.2** **Shapes of AB_2 and AB_3 molecules.**

B atoms. Both CO_2 and H_2O are AB_2 molecules, for example, whereas SO_3 and NH_3 are AB_3 molecules, and so on.

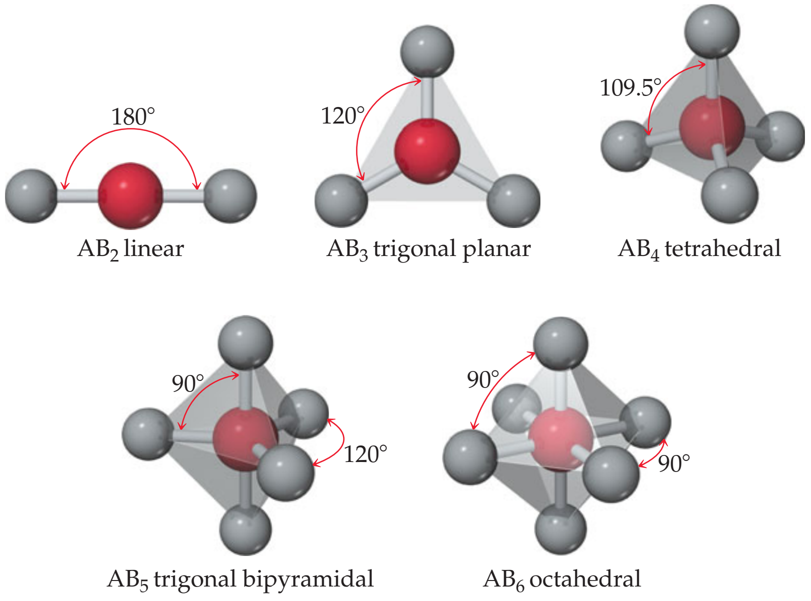
The number of shapes possible for AB_n molecules depends on the value of n. Those commonly found for AB_2 and AB_3 molecules are shown in ▲ **FIGURE 9.2**. An AB_2 molecule must be either linear (bond angle $= 180°$) or bent (bond angle $\neq 180°$). For AB_3 molecules, the two most common shapes place 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 *trigonal planar*. If the A atom lies above the plane of the B atoms, the shape is *trigonal pyramidal* (a pyramid with an equilateral triangle as its base). Some AB_3 molecules, such as ClF_3, are *T-shaped*, the relatively unusual shape shown in Figure 9.2. The atoms lie in one plane, but the angles between them vary as shown.

Compare Figures 9.1 and 9.2 to notice the difference between NF_3 and CCl_4. The CCl_4 molecule is tetrahedral because the four atoms bonded to the carbon are disposed at the four apexes of a tetrahedron around the central atom. The NF_3 molecule is pyramidal because the three atoms bonded to nitrogen lie at the base of a trigonal pyramid.

The shapes that maximize the separation of outer atoms are shown in ▼ **FIGURE 9.3**. In addition to the shapes we have already seen, this figure shows those encountered when there are five or six atoms surrounding a central atom. The trigonal bipyramid can be thought of as two face-to-face trigonal pyramids; the octahedron is like two face-to-face square pyramids.

GO FIGURE

Which of these molecular shapes do you expect for the SF_6 molecule?



AB_2 linear

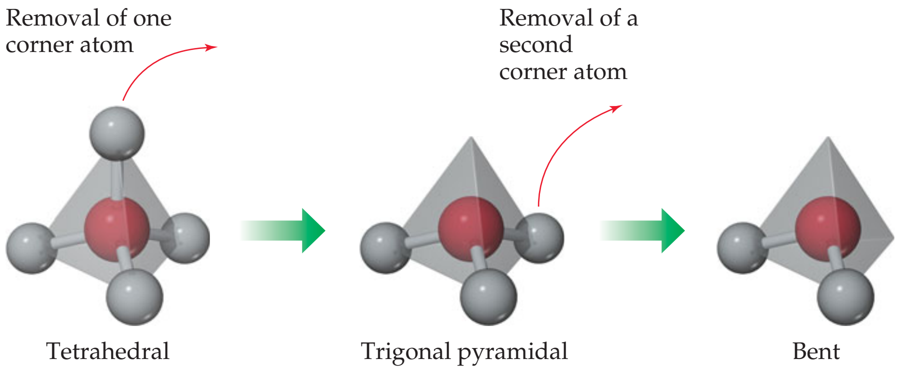
AB_3 trigonal planar

AB_4 tetrahedral

AB_5 trigonal bipyramidal

AB_6 octahedral

◀ **FIGURE 9.3** **Shapes allowing maximum distances between atoms in AB_n molecules.**



▶ **FIGURE 9.4 Derivatives of the tetrahedral molecular shape.**

Some molecules have shapes other than those shown in Figure 9.3, but we can usually derive the shape of those molecules from Figure 9.3. Neither trigonal pyramidal nor bent is shown in Figure 9.3, for instance, but ▲ **FIGURE 9.4** shows how we can arrive at these shapes by removing atoms from the tetrahedral shape.

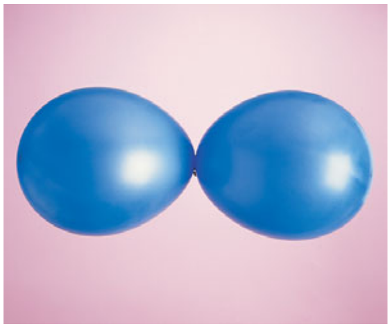
Why do so many AB_n molecules have shapes related to those shown in Figure 9.3, and can we predict these shapes? When A is a representative element (one from the *s* block or *p* block of the periodic table), we can answer these questions by using the **valence-shell electron-pair repulsion (VSEPR) model**.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

GIVE IT SOME THOUGHT

In addition to tetrahedral, another common shape for 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?

9.2 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.



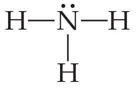
Two balloons
linear orientation

Three balloons
trigonal-planar orientation

Four balloons
tetrahedral orientation

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

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. (Section 8.3) 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 defines an electron domain that is located principally on one atom. For example, the Lewis structure of 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):



$$\begin{array}{c}\text{H}-\ddot{\text{N}}-\text{H}\\ |\\ \text{H}\end{array}$$

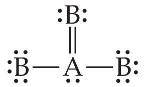
Each multiple bond in a molecule also constitutes a single electron domain. Thus, the resonance structure for O_3 has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):

$$:\underset{..}{\ddot{\text{O}}}-\ddot{\text{O}}=\underset{..}{\ddot{\text{O}}}$$

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

GIVE IT SOME THOUGHT

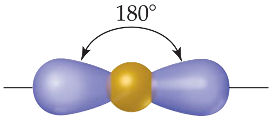
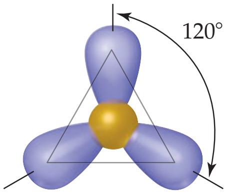
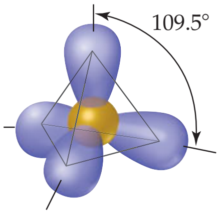
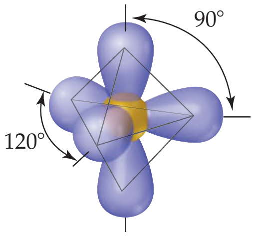
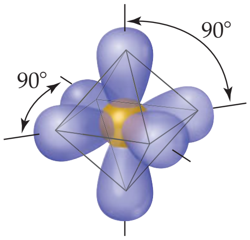
Suppose a particular AB_3 molecule has the resonance structure



Does this structure follow the octet rule? How many electron domains are there around the A atom?

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,

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°

you will see that they are the same. *The shapes of different 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 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.

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 to ignore those domains when talking about molecular shape.

We can generalize the steps we follow in using the VSEPR model to predict the shapes of molecules or ions:

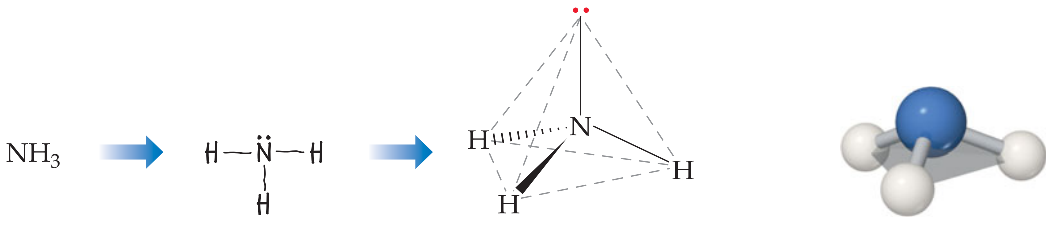
1. Draw the *Lewis structure* of the molecule or ion, and count the number of electron domains around the central atom. Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as one electron domain.
2. Determine the *electron-domain geometry* by arranging the electron 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*.

▼ **FIGURE 9.6** shows how these steps are applied to predict the geometry of the NH_3 molecule. The three bonds and one nonbonding pair in the Lewis structure tell us we have four electron domains. We know from Table 9.1 that the repulsions among four electron domains are minimized when the domains point toward the vertices of a tetrahedron, so the electron-domain geometry of NH_3 is tetrahedral. We know from the Lewis structure that one electron domain holds a nonbonding pair of electrons, which occupies one of the four vertices of the tetrahedron. The bonding arrangement is therefore three atoms bonded to a central atom, with the central atom not in the same plane as the three others. This is just the situation we find in the middle molecule of Figure 9.4. Hence, the molecular geometry of NH_3 is trigonal pyramidal. 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°. As we will soon see, bond angles deviate from ideal values when the surrounding atoms and electron domains are not identical.

GIVE IT SOME THOUGHT

From the standpoint of the VSEPR model, what do nonbonding electron pairs, single bonds, and multiple bonds have in common?



1. Draw Lewis structure

2. Determine electron-domain geometry by counting *all* electron domains, then use Table 9.1 to determine appropriate electron domain geomtry.

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

▶ **FIGURE 9.6 Determining the molecular geometry of NH_3.**

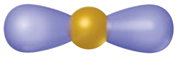
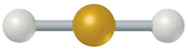
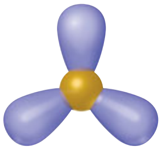
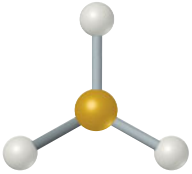
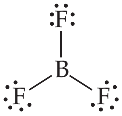
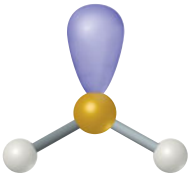
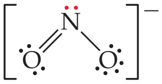
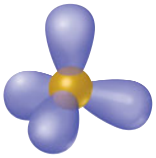
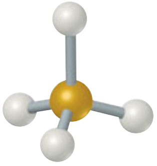
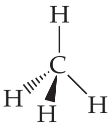
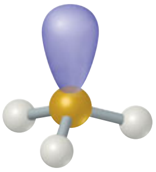
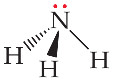
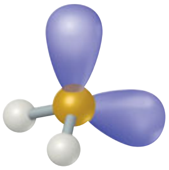
As one more example, let's determine the shape of the CO_2 molecule. Its Lewis structure reveals two electron domains (each one a double bond) around the central carbon:

$$\ddot{\underset{\cdot\cdot}{\text{O}}}=\text{C}=\ddot{\underset{\cdot\cdot}{\text{O}}}$$

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°.

▼ **TABLE 9.2** summarizes the possible molecular geometries when an 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.

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	$\ddot{\underset{\cdot\cdot}{\text{O}}}=\text{C}=\ddot{\underset{\cdot\cdot}{\text{O}}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

SAMPLE EXERCISE 9.1 Using the VSEPR Model

Use the VSEPR model to predict the molecular geometry of **(a)** O_3, **(b)** $SnCl_3^-$.

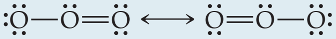
SOLUTION

Analyze We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula AB_n and both having a central atom from the *p* block of the periodic table.

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.

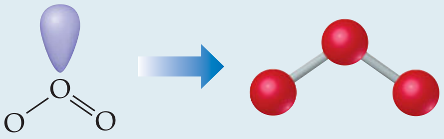
Solve

(a) We can draw two resonance structures for O_3:



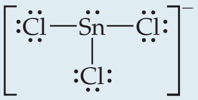
$$:\ddot{\underset{\cdot\cdot}{O}}-\ddot{O}=\ddot{\underset{\cdot\cdot}{O}} \longleftrightarrow \ddot{\underset{\cdot\cdot}{O}}=\ddot{O}-\ddot{\underset{\cdot\cdot}{O}}:$$

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 molecule has a bent shape with an ideal bond angle of 120° (Table 9.2).

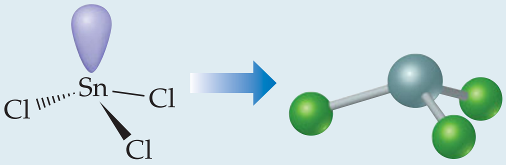


Comment As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(b) The Lewis structure for $SnCl_3^-$ is



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



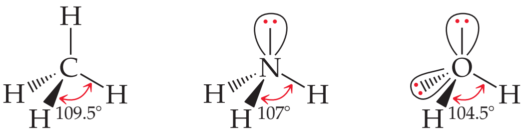
PRACTICE EXERCISE

Predict the electron-domain and molecular geometries for **(a)** $SeCl_2$, **(b)** CO_3^{2-}.

Answers: **(a)** tetrahedral, bent; **(b)** trigonal planar, trigonal planar

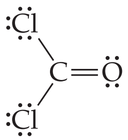
Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

We can refine the VSEPR model to explain slight distortions from the ideal geometries summarized in Table 9.2. For example, consider methane (CH_4), ammonia (NH_3), and water (H_2O). All three have a tetrahedral electron-domain geometry, but their bond angles differ slightly:

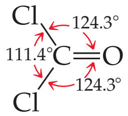


Notice that the bond angles decrease as the number of nonbonding electron pairs increases. A bonding pair of electrons is attracted by both nuclei of the bonded atoms, but a nonbonding pair is attracted primarily by only one nucleus. Because a nonbonding pair experiences less nuclear attraction, its 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. 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:



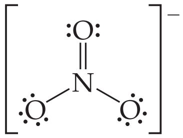
Because three electron domains surround the central atom, we might expect a trigonal-planar geometry with 120° bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the Cl—C—Cl bond angle to 111.4°:



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

GIVE IT SOME THOUGHT

One resonance structure of the nitrate ion is



The bond angles in this ion are 120°. Is this observation consistent with the preceding discussion of the effect of multiple bonds on bond angles?

Molecules with Expanded Valence Shells

Atoms from period 3 and beyond may be surrounded by more than four electron pairs. (Section 8.7) 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 bipyramid (two trigonal pyramids sharing a base). Unlike the other arrangements we have seen, the electron domains in a trigonal bipyramid 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° angle with any equatorial domain. Each equatorial domain makes a 120° angle with either of the other two equatorial domains and a 90° angle with either axial domain.

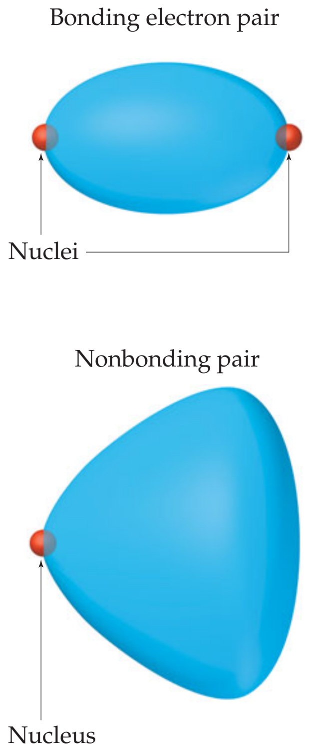
Suppose a molecule has five electron domains, and there are one or more nonbonding pairs. Will the domains from the nonbonding pairs occupy axial or equatorial positions? To answer this question, we must determine which location minimizes repulsion between domains. Repulsion between two domains is much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

GIVE IT SOME THOUGHT

It might seem that a square-planar geometry of four electron domains around a central atom would be more favorable than a tetrahedron. Can you rationalize why the tetrahedron is preferred, based on angles between electron domains?

GO FIGURE

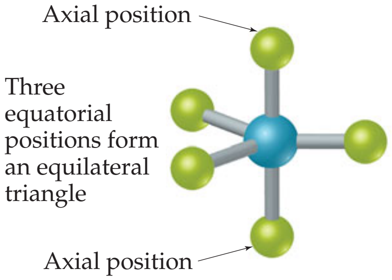
Why is the volume occupied by the nonbonding electron pair domain larger than the volume occupied by the bonding domain?



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

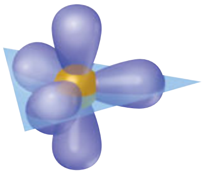
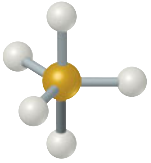
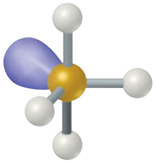
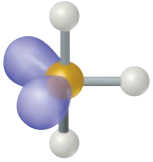
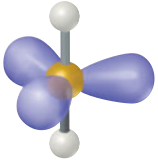
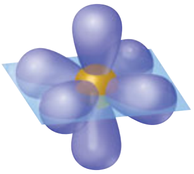
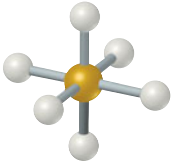
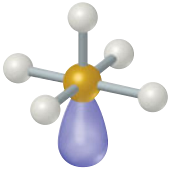
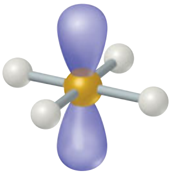
GO FIGURE

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	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

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°, 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**) SF_4, (**b**) IF_5.

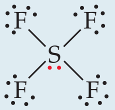
SOLUTION

Analyze The molecules are of the AB_n type with a central *p*-block atom.

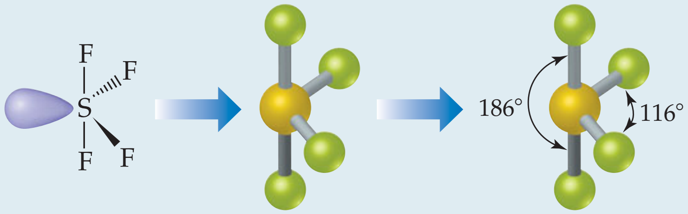
Plan We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.

Solve

(**a**) The Lewis structure for SF_4 is

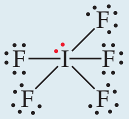


The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions,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

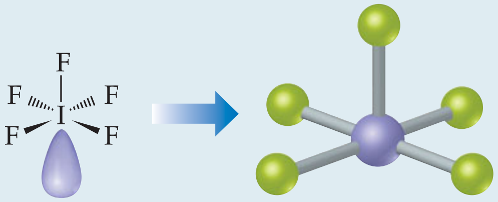


Comment The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are "pushed" by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

(**b**) The Lewis structure of 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. Experimentally, we find that the angle between the base atoms and top F atom is 82°, smaller than the ideal 90° angle of an octahedron.

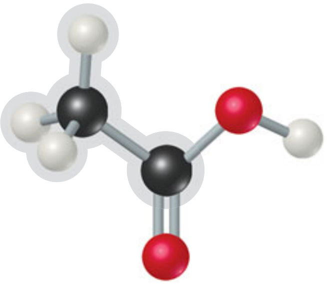
PRACTICE EXERCISE

Predict the electron-domain and molecular geometries of (**a**) BrF_3, (**b**) ICl_4^-.

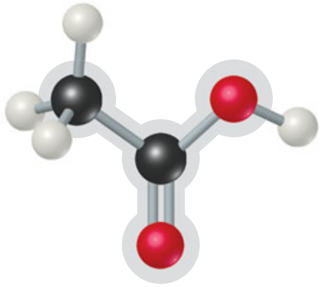
Answers: (**a**) trigonal bipyramidal, T-shaped; (**b**) octahedral, square planar

GO FIGURE

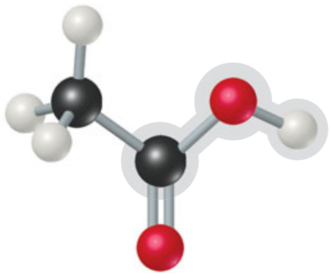
Although the electron-domain geometry around the right O is tetrahedral, the C—O—H bond is slightly less than 109.5°. Explain.



Electron-domain geometry tetrahedral, molecular geometry tetrahedral



Electron-domain geometry trigonal planar, molecular geometry trigonal planar

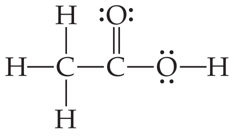


Electron-domain geometry tetrahedral, molecular geometry bent

▲ **FIGURE 9.9** **Acetic acid, CH_3COOH.**

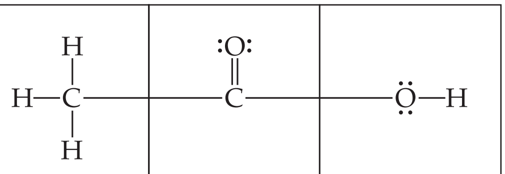
Shapes of Larger Molecules

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



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{:O:}{\overset{\|}{C}}{-}\ddot{\underset{..}{O}}{-}H}$$

we can use the VSEPR model to predict the geometry about each atom:



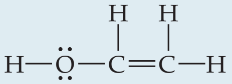
	H—C(H)(H)—	—C(=O:)—	—Ö—H
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

The left C has four electron domains (all bonding), and 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° and 109.5° because of the spatial demands of multiple bonds and nonbonding electron pairs.

The structure 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*:



$$\mathrm{H{-}\ddot{\underset{..}{O}}{-}\underset{}{\overset{H}{C}}{=}\overset{H}{C}{-}H}$$

Predict the approximate values for the H—O—C and O—C—C bond angles in vinyl alcohol.

SOLUTION

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

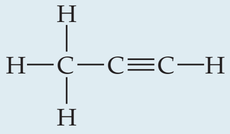
Plan To predict a bond angle, we determine the number of electron domains surrounding the middle atom in the bond. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

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, and 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

Predict the $H-C-H$ and $C-C-C$ bond angles in *propyne*:



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-C\equiv C-H$$

Answers: 109.5°, 180°

9.3 MOLECULAR SHAPE AND MOLECULAR POLARITY

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. ∞ (Section 8.4) 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 CO_2 molecule, for example. As shown in ▶ **FIGURE 9.10**, each $C{=}O$ bond is polar, and because the $C{=}O$ 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 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 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 CO_2 a *nonpolar* molecule.

Now consider H_2O, a bent molecule with two polar bonds (▶ **FIGURE 9.11**). 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 H_2O molecule has an overall nonzero dipole moment ($\mu = 1.85$ 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 the electron-density model.

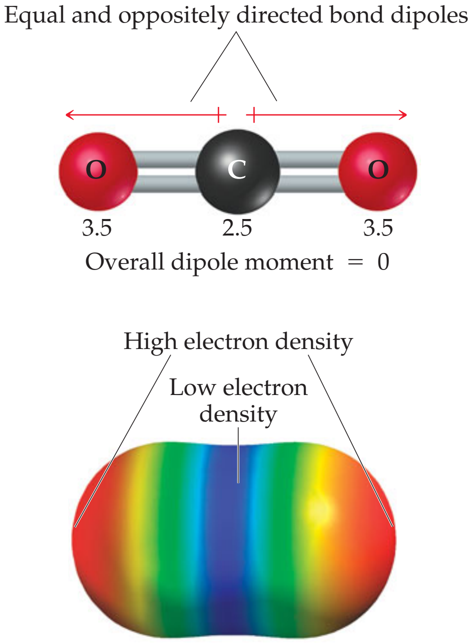
GIVE IT SOME THOUGHT

The molecule $O{=}C{=}S$ is linear and has a Lewis structure analogous to that of CO_2. Would you expect this molecule to have a dipole moment?

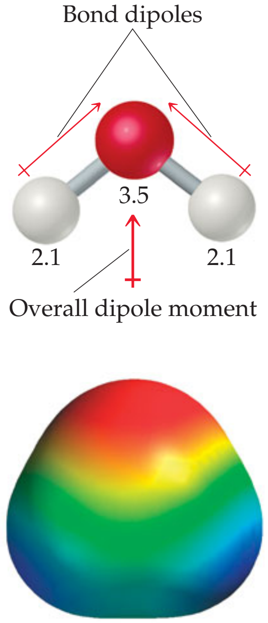
▶ **FIGURE 9.12** shows some polar and nonpolar molecules, all with polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms (BF_3 and CCl_4) are nonpolar. For AB_n molecules in which all the B atoms are the same, certain symmetrical shapes—linear (AB_2), trigonal planar (AB_3), tetrahedral and square planar (AB_4), trigonal bipyramidal (AB_5), and octahedral (AB_6)—must lead to nonpolar molecules even though the individual bonds might be polar.

GO FIGURE

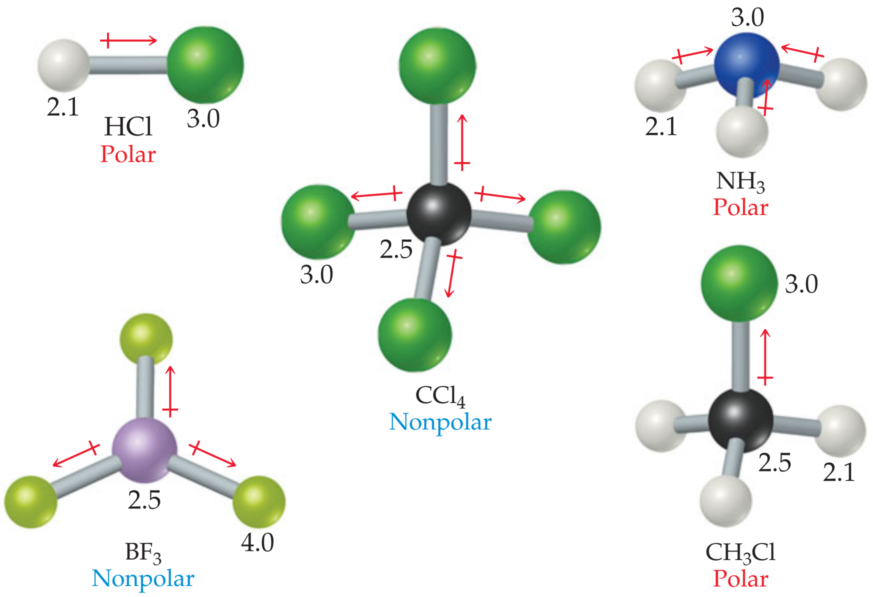
Explain how the directions of the red bond dipole arrows relate to the electron density picture.



▲ **FIGURE 9.10** **CO_2, a nonpolar molecule.** The numbers are electronegativity values for these two atoms.



▲ **FIGURE 9.11** **H_2O, a polar molecule.** The numbers are electronegativity values.



▶ FIGURE 9.12 Polar and nonpolar molecules containing polar bonds. The numbers are electronegativity values.

SAMPLE EXERCISE 9.4 Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (**a**) BrCl, (**b**) SO_2, (**c**) 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.

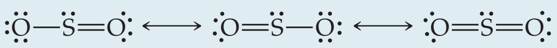
Solve

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

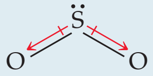
$$\overset{+\!\!\longrightarrow}{\mathrm{Br}-\mathrm{Cl}}$$

The measured dipole moment of BrCl is $\mu = 0.57$ D.

(**b**) Because oxygen is more electronegative than sulfur, SO_2 has polar bonds. Three resonance forms can be written:

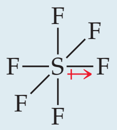


For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:



Experimentally, the dipole moment of SO_2 is $\mu = 1.63$ 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

Determine whether the following molecules are polar or nonpolar: (**a**) NF_3, (**b**) BCl_3.

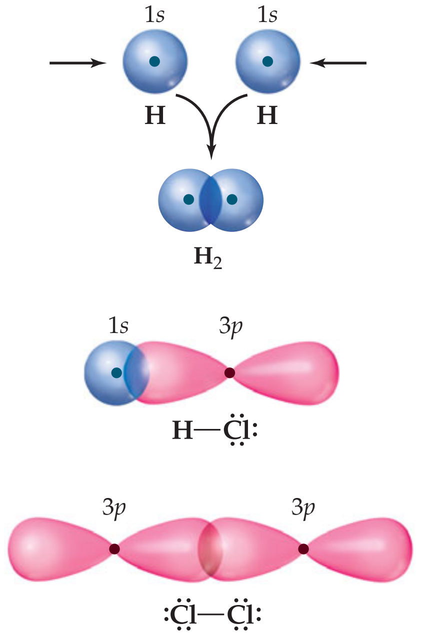
Answers: (**a**) polar because polar bonds are arranged in a trigonal-pyramidal geometry, (**b**) nonpolar because polar bonds are arranged in a trigonal-planar geometry

9.4 COVALENT BONDING AND ORBITAL OVERLAP

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 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.

The coming together of two H atoms to form H_2 is depicted in ▶ **FIGURE 9.13**. Each atom has a single electron in a 1*s* 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.



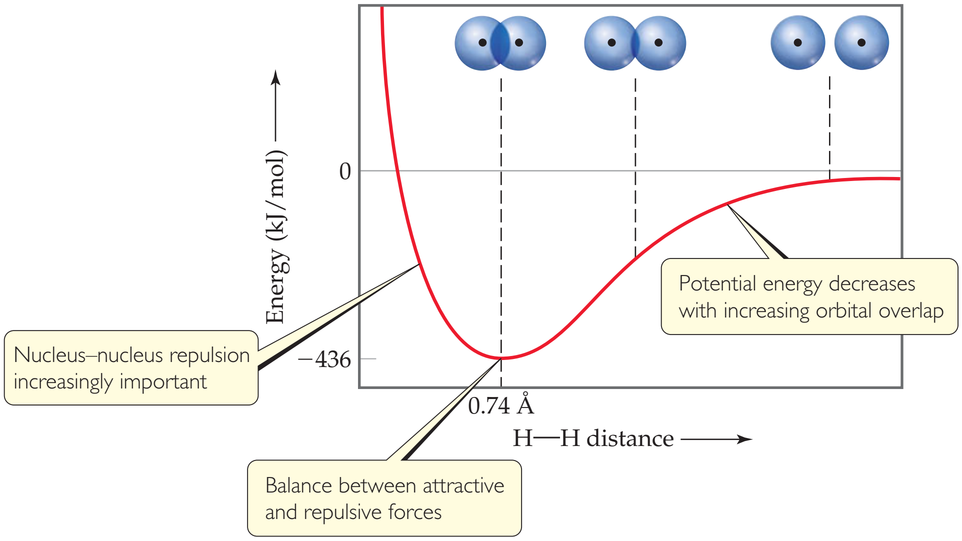
▲ **FIGURE 9.13 Covalent bonds in H_2, HCl, and Cl_2 result from overlap of atomic orbitals.**

The idea of orbital overlap producing a covalent bond applies equally well to other molecules. In HCl, for example, chlorine has the electron configuration $[Ne]3s^2 3p^5$. All the valence orbitals of chlorine are full except one 3*p* orbital, which contains a single electron. This 3*p* electron pairs with the single 1*s* electron of H to form a covalent bond (Figure 9.13). Because the other two chlorine 3*p* orbitals are already filled with a pair of electrons, they do not participate in the bonding to hydrogen. Likewise, we can explain the covalent bond in Cl_2 in terms of the overlap of the singly occupied 3*p* orbital of one Cl atom with the singly occupied 3*p* orbital of another.

There is always an optimum distance between the two nuclei in any covalent bond. ▶ **FIGURE 9.14** shows how the potential energy of a system consisting of two H atoms changes as the atoms come together to form an 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 1*s* orbitals increases. Because of the resultant 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 the potential energy of the two-atom system. However, Figure 9.14 also shows that as the atoms come closer together than 0.74 Å, the energy increases sharply. This increase, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance, or bond length, is the distance that corresponds to the minimum of the potential-energy curve. 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).

GO FIGURE

On the left part of the curve the potential energy rises above zero. What causes this to happen?



▲ **FIGURE 9.14** **Formation of the H_2 molecule as atomic orbitals overlap.**

9.5 HYBRID ORBITALS

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, based on the shapes and orientations of the 2*s* and 2*p* orbitals on a carbon atom, it is not obvious why a CH_4 molecule should have a tetrahedral geometry. 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. ∞ (Section 6.5) To explain molecular geometries, we can 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 certain of the molecular geometries predicted by the VSEPR model: linear, bent, trigonal planar, and tetrahedral.

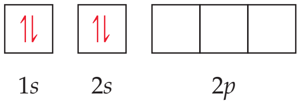
sp Hybrid Orbitals

To illustrate the process of hybridization, consider the BeF_2 molecule, which has the Lewis structure

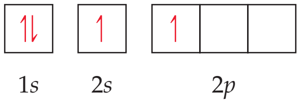
$$:\ddot{\underset{\cdot\cdot}{F}}—Be—\ddot{\underset{\cdot\cdot}{F}}:$$

The VSEPR model correctly predicts that BeF_2 is linear with two identical Be—F bonds. How can we use valence-bond theory to describe the bonding? The electron configuration of F ($1s^22s^22p^5$) indicates an unpaired electron in a 2*p* 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

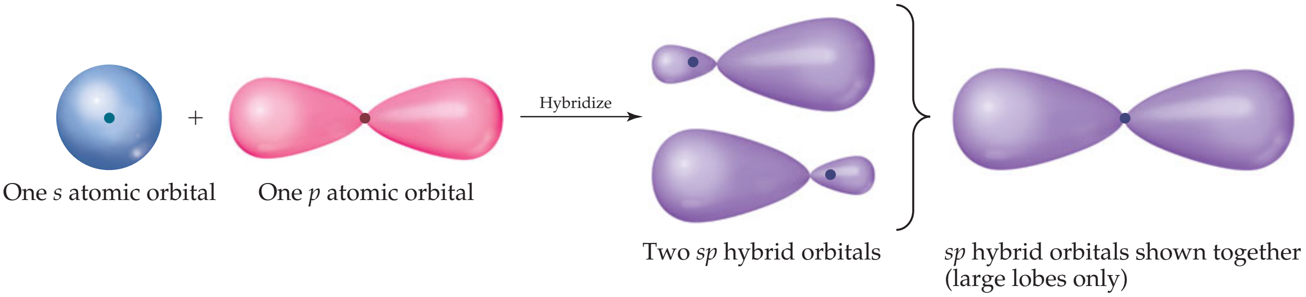


Because it has no unpaired electrons, the Be atom in its ground state cannot bond with the fluorine atoms. The Be atom could form two bonds, however, by "promoting" one of the 2*s* electrons to a 2*p* orbital:



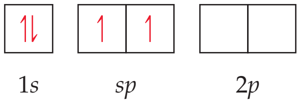
The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with F atoms. The two bonds would not be identical, however, because a Be 2*s* orbital would be used to form one of the bonds and a 2*p* orbital would be used to form the other. Therefore, although the promotion of an electron allows two Be—F bonds to form, we still have not explained the structure of BeF_2.

We can solve this dilemma by "mixing" the 2*s* orbital with one 2*p* orbital to generate two new orbitals, as shown in ▼ **FIGURE 9.15**. 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 we color-code purple in Figure 9.15, 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.*



▲ **FIGURE 9.15** **Formation of *sp* hybrid orbitals.**

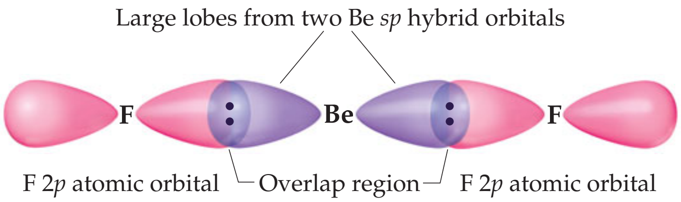
For the Be atom of BeF_2, we write the orbital diagram for the formation of two *sp* hybrid orbitals as



The electrons in the *sp* hybrid orbitals can form bonds with the two fluorine atoms (▼ **FIGURE 9.16**). Because the *sp* hybrid orbitals are equivalent but point in opposite

GO FIGURE

Why is it reasonable to take account of only the large lobes of the Be hybrid orbitals in considering the bonding to F?



◀ **FIGURE 9.16** **Formation of two equivalent Be—F bonds in BeF_2.**

directions, BeF_2 has two identical bonds and a linear geometry. The remaining two 2*p* 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 9.16 to keep the illustration simpler.

GIVE IT SOME THOUGHT

What is the orientation of the two unhybridized *p* orbitals on Be with respect to the two Be—F bonds?

sp^2 and sp^3 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 2*s* and one 2*p* atomic orbital yields two equivalent *sp* hybrid orbitals that point in opposite directions (Figure 9.15). Other combinations of atomic orbitals can be hybridized to obtain different geometries. In BF_3, for example, mixing the 2*s* and two of the 2*p* atomic orbitals yields three equivalent sp^2 (pronounced "*s*-*p*-two") hybrid orbitals (▼ **FIGURE 9.17**).

The three sp^2 hybrid orbitals lie in the same plane, 120° 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 BF_3. Notice that an unfilled 2*p* atomic orbital remains unhybridized. This unhybridized orbital will be important when we discuss double bonds in Section 9.6.

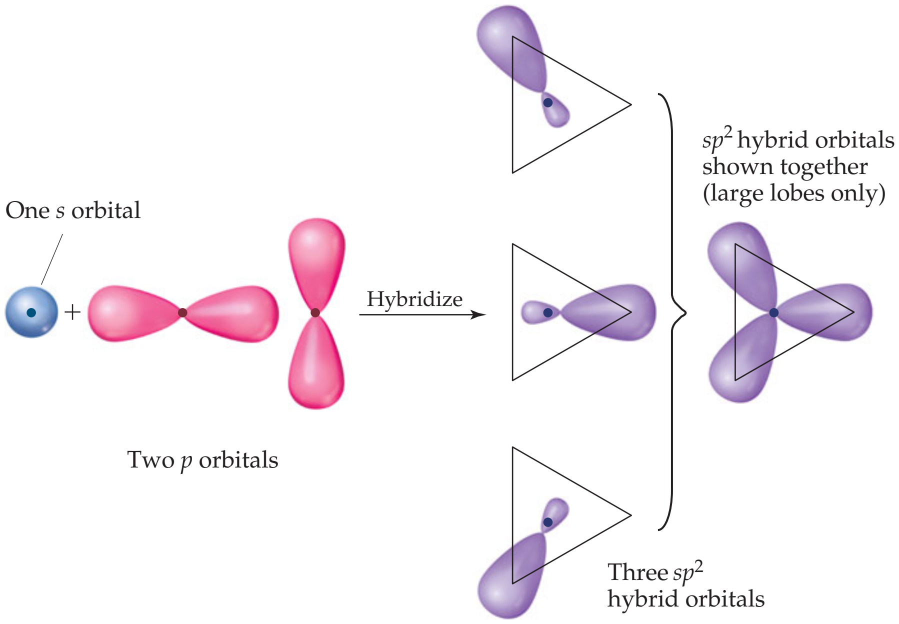
GIVE IT SOME THOUGHT

In an sp^2 hybridized atom, what is the orientation of the unhybridized *p* atomic orbital relative to the three sp^2 hybrid orbitals?

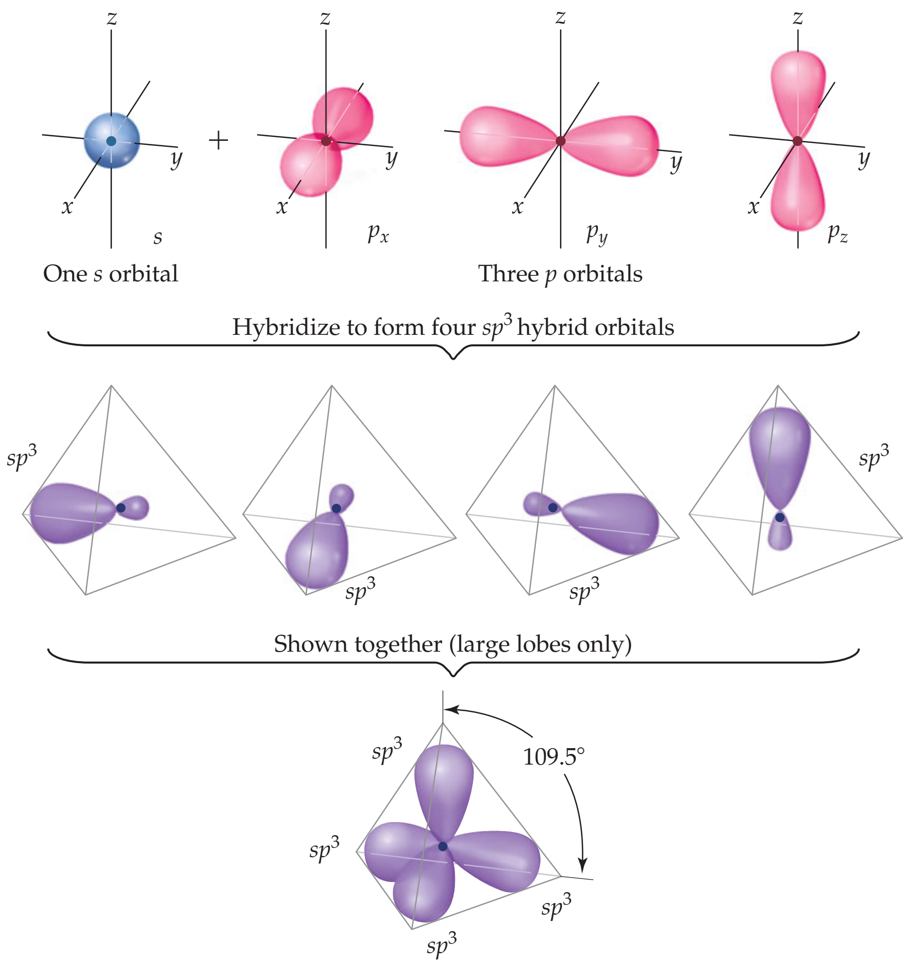
An *s* atomic orbital can also mix with all three *p* atomic orbitals in the same subshell. For example, the carbon atom in CH_4 forms four equivalent bonds with the four

GO FIGURE.

How many atomic orbitals contribute to form the three sp^2 hybrid orbitals?



▶ **FIGURE 9.17** **Formation of sp^2 hybrid orbitals.**



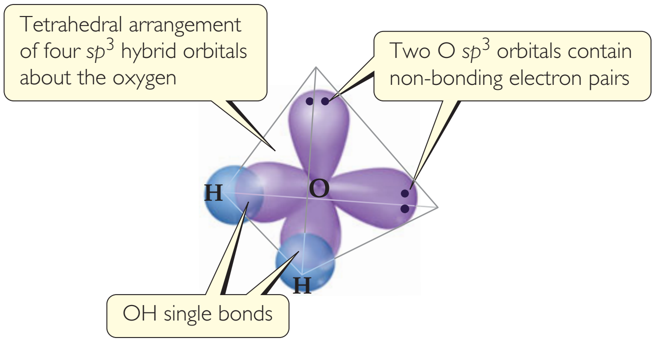
◀ **FIGURE 9.18 Formation of sp^3 hybrid orbitals.**

hydrogen atoms. We envision this process as resulting from the mixing of the 2*s* and all three 2*p* 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 9.18**). 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 CH_4 as the overlap of four equivalent sp^3 hybrid orbitals on C with the 1*s* 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 H_2O, for example, the electron-domain geometry around the central O atom is approximately tetrahedral (▶ **FIGURE 9.19**). 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.

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 have more than an octet of electrons in the valence shell, as we saw in Section 9.2. How do we analyze the bonding in compounds such as PCl_5, SF_6, or BrF_5? The use of only *s* and *p* orbitals on the central atom limits us to four hybrid orbitals, yet in these compounds the central atom is involved in bonding to five or six other atoms.

For such elements, the number of hybrid orbitals formed could be increased by including valence-shell *d* orbitals. For example, to explain the bonding in SF_6 we could include two sulfur 3*d* orbitals



▲ **FIGURE 9.19 Hybrid orbital description of H_2O.**

in addition to the *3s* and three *3p* orbitals. These six atomic orbitals could make six hybrid orbitals, but there is more involved in hybridization than simply finding a set of orbitals that point in the right directions; we must also consider orbital energies. The sulfur *3d* orbitals lie substantially higher in energy than the *3s* and *3p* orbitals. 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 seem to show that the sulfur *3d* orbitals do not participate to a significant degree in the bonding between sulfur and the six fluorine atoms.

The valence-bond model we have 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 PF_3 or H_2Se in terms of hybrid *s* and *p* orbitals on the central atom. However, the model turns out not to be appropriate when there is more than an octet of electrons about the central atom. How then do we account for the bonding in SF_6 and other compounds of the main group elements in which the central atom has more than an octet of valence electrons? To address that question from the viewpoint of bonding theory requires a treatment beyond the scope of a general chemistry text. Fortunately, the VSEPR model, although it does not explain the bonding in such molecules, can accurately predict their geometries.

This discussion points up the important fact 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 with the idea of 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 substances such as SF_6, however, we encounter the limitations of the model.

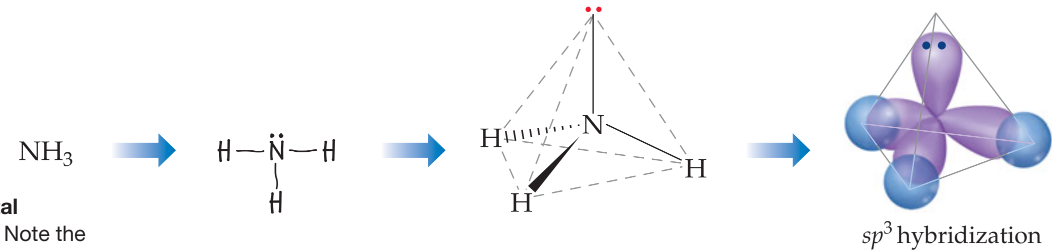
Hybrid Orbital Summary

Overall, hybrid orbitals provide a convenient model for using valence-bond theory to describe covalent bonds in molecules in which the molecular geometry conforms to the electron-domain geometry predicted by the VSEPR model. The picture of hybrid orbitals has limited predictive value. When we know the electron-domain geometry, however, we can employ hybridization to describe the atomic orbitals used by the central atom in bonding.

The following steps allow us 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**).

These steps are illustrated in ▼ **FIGURE 9.20**, which shows how the hybridization at N in NH_3 is determined.



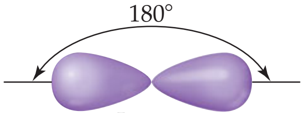
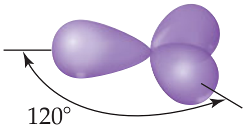
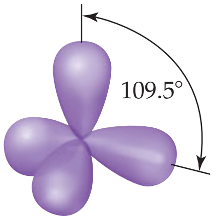
1. Draw Lewis structure

2. Determine electron-domain geometry about central atom from VSEPR model and Table 9.1

3. Using Table 9.4, select sp^3 hybrid orbital set

▶ **FIGURE 9.20 Hybrid orbital description of bonding in NH_3.** Note the comparison with Figure 9.6. Here we focus on the hybrid orbitals used to make bonds and hold nonbonding electron pairs.

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

SAMPLE EXERCISE 9.5 Hybridization

Indicate the orbital hybridization around the central atom in 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

$$\left[\mathrm{H}{:}\underset{\cdot\cdot}{\ddot{\mathrm{N}}}{:}\mathrm{H}\right]^-$$

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.

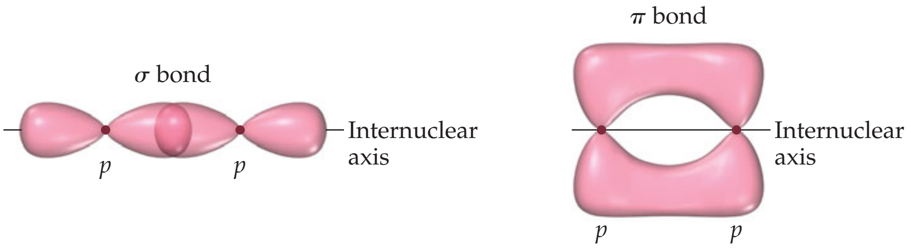
PRACTICE EXERCISE

Predict the electron-domain geometry and hybridization of the central atom in SO_3^{2-}.

Answer: tetrahedral, sp^3

9.6 MULTIPLE BONDS

In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the *internuclear axis*). In other words, the line joining the two nuclei passes through the middle of the overlap region. These bonds are called **sigma** (σ) **bonds**. The overlap of two *s* orbitals in H_2, the overlap of an *s* and a *p*

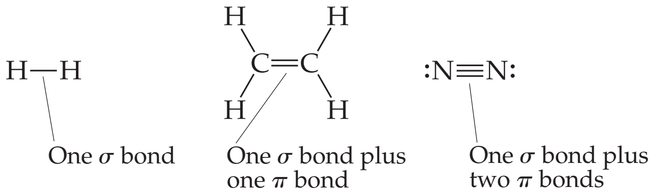


▶ **FIGURE 9.21 Comparison of σ and π bonds.** Note that the two regions of overlap in the π bond, above and below the internuclear axis, constitute a *single* π bond.

orbital in HCl, the overlap of two *p* orbitals in Cl_2 (all shown in Figure 9.13), and the overlap of a *p* orbital and an *sp* hybrid orbital in BeF_2 (Figure 9.16) are all σ bonds.

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 9.21**). This sideways overlap of *p* orbitals produces a **pi (π) bond**. A π bond is one in which the overlap regions lie above and below the internuclear axis. Unlike in a σ bond, in a π bond the electron density is not concentrated on the internuclear axis. Although it is not evident in Figure 9.21, the sideways orientation of *p* orbitals in a π bond makes for weaker overlap. As a result, π bonds are generally weaker than σ bonds.

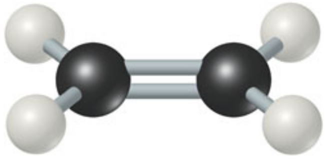
In almost all cases, single bonds are σ bonds. A double bond consists of one σ bond and one π bond, and a triple bond consists of one σ bond and two π bonds:



One σ bond

One σ bond plus one π bond

One σ bond plus two π bonds



▲ **FIGURE 9.22 Trigonal-planar molecular geometry of ethylene.** The double bond is made up of one C—C σ bond and one C—C π bond.

To see how these ideas are used, consider ethylene (C_2H_4), which has a C=C double bond. As illustrated by the ball-and-stick model of ◀ **FIGURE 9.22**, the three bond angles about each carbon are all approximately 120°, suggesting that each carbon atom uses sp^2 hybrid orbitals (Figure 9.17) to form σ 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 2*p* orbital, which is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals.

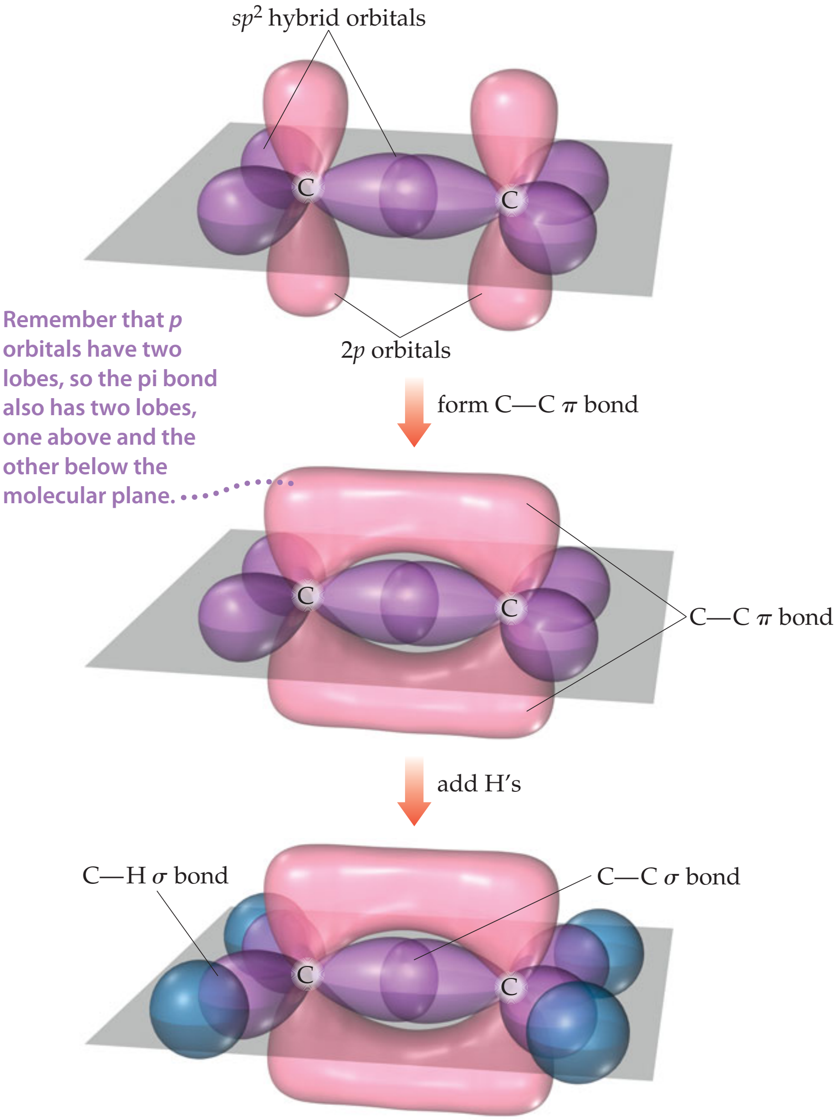
Each sp^2 hybrid orbital on a carbon atom contains one electron. ▶ **FIGURE 9.23** shows how the C—H σ bonds are formed by overlap of sp^2 hybrid orbitals on C with the 1*s* orbitals on each H atom. We use eight electrons to form these four C—H bonds. The C—C σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Thus, ten of the 12 valence electrons in the C_2H_4 molecule are used to form five σ bonds.

The remaining two valence electrons reside in the unhybridized 2*p* orbitals, one electron on each carbon. These two orbitals can overlap sideways with each other, as shown in Figure 9.23. The resultant electron density is concentrated above and below the C—C bond axis, which means this is a π bond (Figure 9.21). Thus, the C=C double bond in ethylene consists of one σ bond and one π bond. You should note one point about the carbon *p* orbitals that form the π bond. It appears from Figure 9.21 that the *p* orbitals on the two carbons don't overlap sufficiently to form a π bond. The problem is that we can't show the true extent of overlap in the drawing without obscuring other aspects of the figure. Although π bonding of the *p* orbitals does occur, as pointed out earlier, π bonds are generally weaker than σ bonds.

Although we cannot experimentally observe a π bond directly (all we can observe are the positions of the atoms), the structure of ethylene provides strong support for its presence. First, the C—C bond length in ethylene (1.34 Å) is much shorter than in compounds with C—C single bonds (1.54 Å), 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 2*p* orbitals that make up the π bond can achieve a good overlap only when the two CH_2

GO FIGURE

Why is it important that the sp^2 hybrid orbitals of the two carbon atoms lie in the same plane?



Remember that p orbitals have two lobes, so the pi bond also has two lobes, one above and the other below the molecular plane.

◀ **FIGURE 9.23 The orbital structure of ethylene.**

fragments lie in the same plane. If the π bond were absent, there would be no reason for the two CH_2 fragments to lie in the same plane. Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.

GIVE IT SOME THOUGHT

The molecule called *diazine* has the formula N_2H_2 and the Lewis structure

$$\mathrm{H{-}\ddot{N}{=}\ddot{N}{-}H}$$

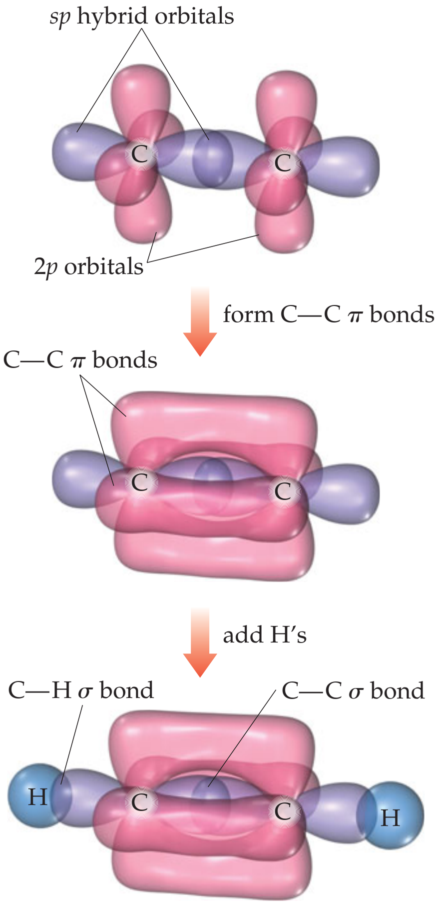
Do you expect diazine to be a linear molecule (all four atoms on the same line)? If not, do you expect the molecule to be planar (all four atoms in the same plane)?

Triple bonds can also be explained using hybrid orbitals. Acetylene (C_2H_2), for example, is a linear molecule containing a triple bond: $\mathrm{H{-}C{\equiv}C{-}H}$. The linear geometry suggests that each carbon atom uses sp hybrid orbitals to form σ bonds with the other carbon and one hydrogen. Each carbon atom thus has two unhybridized 2*p* orbitals at right angles to each other and to the axis of the *sp* hybrid set (◀ **FIGURE 9.24**). These *p* orbitals overlap to form a pair of π bonds. Thus, the triple bond in acetylene consists of one σ bond and two π bonds.

Although it is possible to make π bonds from *d* orbitals, the only π bonds we will consider are those formed by the overlap of *p* orbitals. These π bonds can form only if unhybridized *p* orbitals are present on the bonded atoms. Therefore, only atoms having *sp* or sp^2 hybridization can form π bonds. Further, double and triple bonds (and hence π 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 π bonds less readily.

GO FIGURE

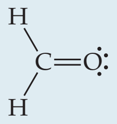
Based on the models of bonding in ethylene and acetylene, which molecule should have the higher carbon–carbon bond energy?



▲ **FIGURE 9.24 Formation of two π bonds in acetylene, C_2H_2.**

SAMPLE EXERCISE 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



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

SOLUTION

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

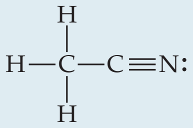
Plan Single bonds are σ bonds, and double bonds consist of one σ bond and one π bond. The ways in which these bonds form can be deduced from the molecular geometry, which we predict using the VSEPR model.

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^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C—H and one C—O σ bonds to C. There remains an unhybridized 2*p* orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

The O atom also has three electron domains around it, and so we assume it has sp^2 hybridization as well. One of these hybrid orbitals participates in the C—O σ bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized 2*p* orbital that is perpendicular to the plane of the molecule. These two orbitals overlap to form a C—O π bond (▼ **FIGURE 9.25**).

PRACTICE EXERCISE

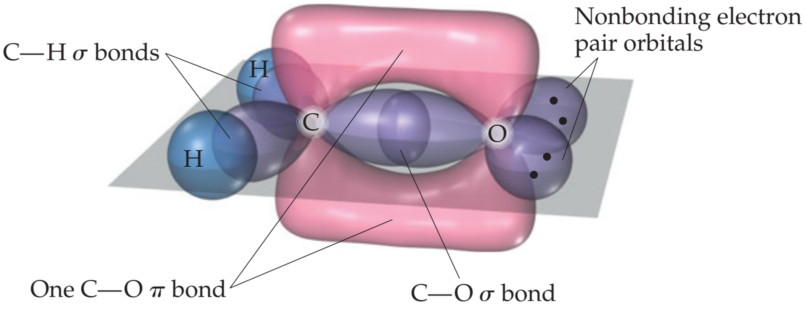
(**a**) Predict the bond angles around each carbon atom in acetonitrile:



$$\mathrm{H_3C{-}C{\equiv}N{:}}$$

(**b**) Describe the hybridization at each carbon atom, and (**c**) determine the number of σ and π bonds in the molecule.

Answers: (**a**) approximately 109° around the left C and 180° around the right C; (**b**) sp^3, *sp*; (**c**) five σ bonds and two π bonds

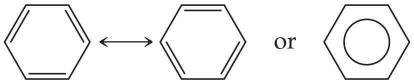


▶ **FIGURE 9.25 Formation of σ and π bonds in formaldehyde, H_2CO.**

Resonance Structures, Delocalization, and π Bonding

In the molecules we have discussed thus far in this section, the bonding electrons are *localized*. By this we mean that the σ and π 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 π bonds.

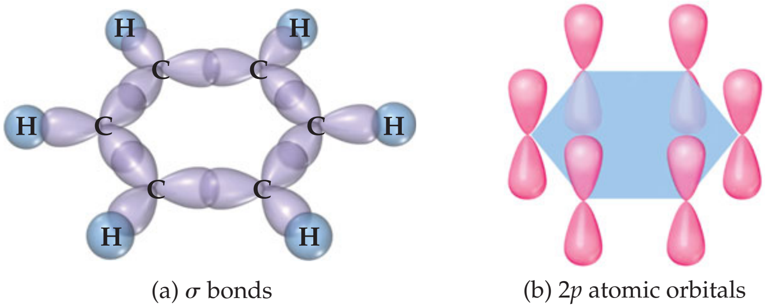
One molecule that cannot be described with localized π bonds is benzene (C_6H_6), which has two resonance structures: (Section 8.6)



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° angles, the appropriate hybrid set is sp^2. Six localized C—C σ bonds and six localized C—H σ bonds are formed from the sp^2 hybrid orbitals, as shown in ▼ **FIGURE 9.26**(a). This leaves on each carbon a $2p$ orbital oriented perpendicular to the plane of the molecule. The situation is very much like that in ethylene except we now have six carbon $2p$ orbitals arranged in a ring [Figure 9.26(b)]. Each unhybridized $2p$ orbital is occupied by one electron, leaving six electrons to be accounted for by π bonding.

GO FIGURE

What are the two kinds of σ bonds found in benzene?

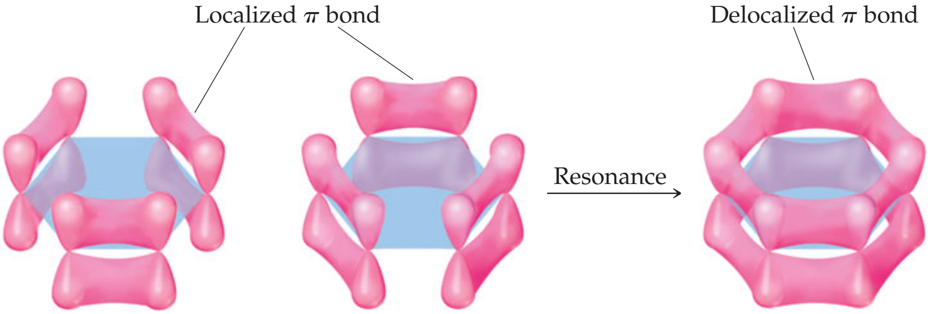


(a) σ bonds

(b) $2p$ atomic orbitals

◀ **FIGURE 9.26 σ and π bond networks in benzene, C_6H_6.** (a) The σ bond framework. (b) The π bonds are formed from overlap of the unhybridized $2p$ orbitals on the six carbon atoms.

We could envision using the unhybridized $2p$ orbitals to form three localized π bonds. As shown in ▼ **FIGURE 9.27**, 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 π electrons "smeared out" among all six carbon atoms, as shown on the right in Figure 9.27. Notice how this combined representation corresponds to the circle-in-a-hexagon drawing we often use to represent benzene. 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 (1.54 Å) and that of a C═C double bond (1.34 Å). This prediction is consistent with the observed carbon–carbon bond length in benzene (1.40 Å).



◀ **FIGURE 9.27 Delocalized π bonds in benzene.**

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

If you take a course in organic chemistry, you will see many examples of how electron delocalization influences the properties of organic molecules.

SAMPLE EXERCISE 9.7 Delocalized Bonding

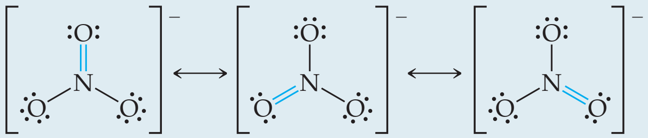
Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

SOLUTION

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

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

Solve In Section 8.6 we saw that NO_3^- has three resonance structures:



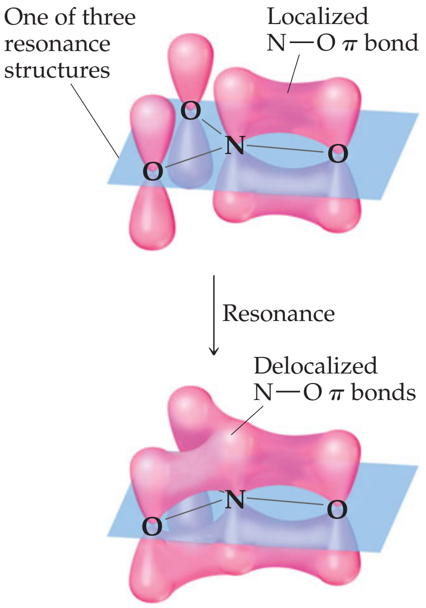
In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. The sp^2 hybrid orbitals are used to construct the three N—O σ bonds present in each resonance structure.

The unhybridized 2*p* orbital on the N atom can be used to make π bonds. For any one of the three resonance structures shown, we might imagine a single localized N—O π bond formed by the overlap of the unhybridized 2*p* orbital on N and a 2*p* orbital on one of the O atoms, as shown in ◀ **FIGURE 9.28**. Because each resonance structure contributes equally to the observed structure of NO_3^-, however, we represent the π bonding as delocalized over the three N—O bonds, as shown in the figure.

PRACTICE EXERCISE

Which of these species have delocalized bonding: SO_3, SO_3^{2-}, H_2CO, O_3, NH_4^+?

Answer: SO_3 and O_3, as indicated by the presence of two or more resonance structures involving π bonding for each of these molecules



▲ **FIGURE 9.28 Localized and delocalized π bonds in NO_3^-.**

General Conclusions

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

1. Every pair of bonded atoms shares one or more pairs of electrons. The lines we draw in Lewis structures represent two electrons each. In every bond at least one pair of electrons is localized in the space between the atoms in a σ bond. The appropriate set of hybrid orbitals used to form the σ 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.
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contribution to the bonding between any other two atoms.
3. When atoms share more than one pair of electrons, one pair is used to form a σ bond; the additional pairs form π bonds. The centers of charge density in a π bond lie above and below the internuclear axis.

4. Molecules with two or more resonance structures can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two atoms are said to be "delocalized."

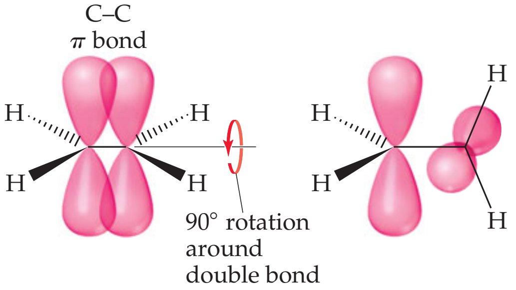
CHEMISTRY AND LIFE

THE CHEMISTRY OF VISION

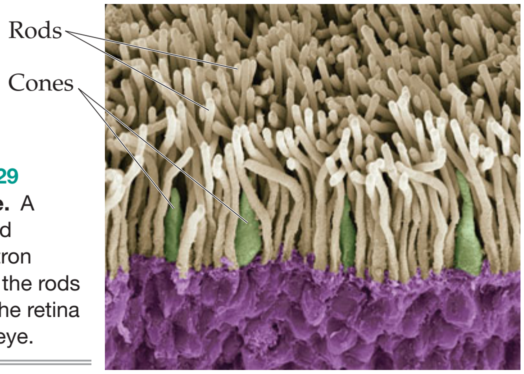
Vision begins when light is focused by the lens of the eye onto the retina, the layer of cells lining the interior of the eyeball. The retina contains *photoreceptor* cells called rods and cones (▼ **FIGURE 9.29**). The rods are sensitive to dim light and are used in night vision. The cones are sensitive 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.* Structural changes around a double bond in the retinal portion of the molecule trigger a series of chemical reactions that result in vision.

We know that a double bond between two atoms is stronger than a single bond between the same atom, but our recent discussions allow us to appreciate another aspect of double bonds: the rigidity they introduce into molecules.

Imagine rotating one —CH_2 group in ethylene relative to the other —CH_2 group, as in ▶ **FIGURE 9.30**. This rotation destroys the overlap of p orbitals, breaking the π bond, a process that requires considerable energy. Thus, the presence of a double bond restricts bond rotation in a molecule. In contrast, molecules can rotate almost freely around the bond axis in single (σ) bonds because this motion has no effect on the orbital overlap for a σ bond. This rotation allows molecules with single bonds to twist and fold almost as if their atoms were attached by hinges.



▲ **FIGURE 9.30 Rotation about the carbon–carbon double bond in ethylene breaks the π bond.**

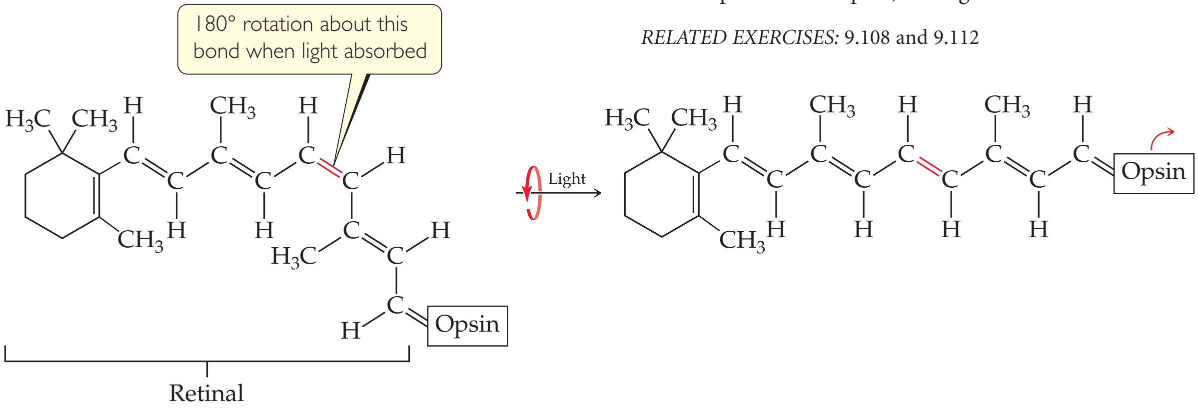


▶ **FIGURE 9.29**
Inside the eye. A color-enhanced scanning electron micrograph of the rods and cones in the retina of the human eye.

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 the energy is used to break the π-bond portion of the double bond shown in red in ▼ **FIGURE 9.31**. The molecule then rotates around this bond, changing its geometry. 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.

The retinal slowly reverts to its original form and reattaches to the opsin. The slowness of this process helps explain why intense bright light causes temporary blindness. The light causes all the retinal to separate from opsin, leaving no molecules to absorb light.

RELATED EXERCISES: 9.108 and 9.112



▲ **FIGURE 9.31 The rhodopsin molecule, the chemical basis of vision.** When rhodopsin absorbs visible light, the π component of the double bond shown in red breaks, allowing rotation that produces a change in molecular geometry before the π bond re-forms.

GIVE IT SOME THOUGHT

When two atoms are bonded by a triple bond, what is the hybridization of the orbitals that make up the σ-bond component of the bond?

9.7 MOLECULAR ORBITALS

Valence-bond theory and hybrid orbitals allow us to move in a straightforward way from Lewis structures to rationalizing the observed geometries of molecules in terms of atomic orbitals. The valence-bond model, however, 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 called **molecular orbitals (MO)**.

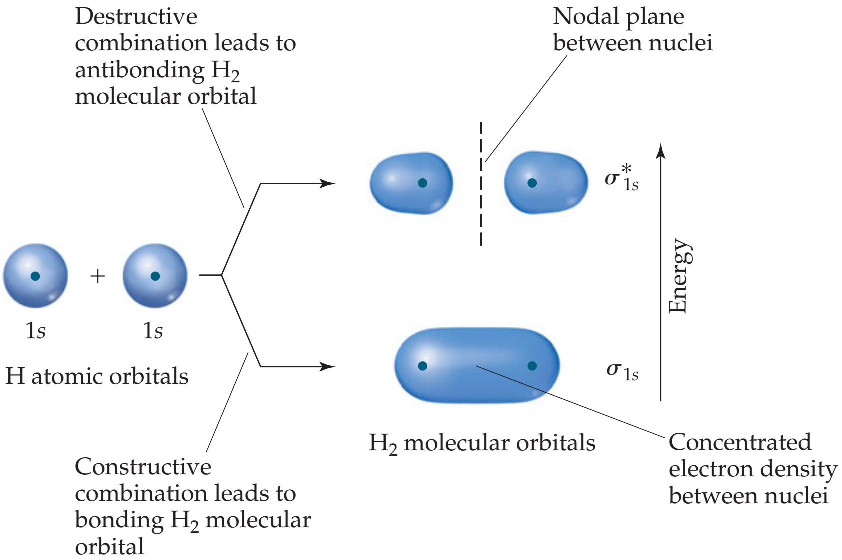
Molecular orbitals have many of the same characteristics as atomic orbitals. For example, an MO can hold a maximum of two electrons (with opposite spins), it has a definite energy, and we can visualize its electron-density distribution by using a contour representation, as we did with atomic orbitals.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

The Hydrogen Molecule

We begin our study of MO theory with the hydrogen molecule, H_2. *Whenever two atomic orbitals overlap, two molecular orbitals form*. Thus, the overlap of the 1*s* orbitals of two hydrogen atoms to form H_2 produces two MOs (▼ **FIGURE 9.32**). One MO is formed by adding the wave functions for the two 1*s* orbitals. We refer to this as *constructive combination*. The energy of the resulting MO is lower than the energy of the two atomic orbitals from which it was made. It is called the **bonding molecular orbital**.

The other MO is formed by combining the two atomic orbitals in a way that causes the electron density to be more or less canceled in the central region where the two overlap. We refer to this as *destructive combination*. The process is discussed more fully in the "Closer Look" box later in the chapter; we don't need to concern ourselves with it to understand molecular orbital bond formation. The energy of the resulting MO, referred to as the **antibonding molecular orbital**, is higher than the energy of the atomic orbitals.

As illustrated in Figure 9.32, in the bonding MO electron density is concentrated in the region between the two nuclei. This sausage-shaped MO results from summing the



► **FIGURE 9.32** **The two molecular orbitals of H_2, one a bonding MO and one an antibonding MO.**

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 1*s* 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, this MO excludes electrons from the very region in which a bond must be formed. Antibonding orbitals invariably have a nodal plane in the region between the nuclei, where the electron density is zero. (The nodal plane is shown as a dashed line in Figure 9.32 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 1*s* atomic orbital of a hydrogen atom.

Notice from Figure 9.32 that the electron density in both the bonding MO and the antibonding MO of H_2 is centered about the internuclear axis. MOs of this type are called **sigma ($\boldsymbol{\sigma}$) molecular orbitals** (by analogy to σ bonds). The bonding sigma MO of H_2 is labeled σ_{1s}; the subscript indicates that the MO is formed from two 1*s* orbitals. The antibonding sigma MO of H_2 is labeled σ^{*}_{1s} (read "sigma-star-one-*s*"); the asterisk denotes that the MO is antibonding.

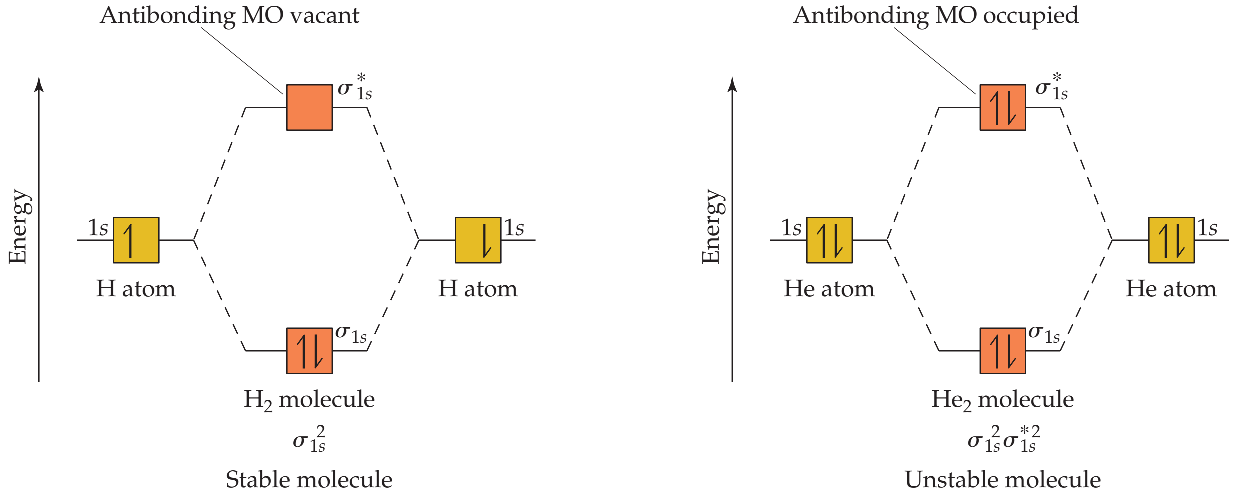
The relative energies of two 1*s* atomic orbitals and the molecular orbitals formed from them are represented by an **energy-level diagram** (also called a **molecular orbital diagram**). Such diagrams show the interacting atomic orbitals on the left and right and the MOs in the middle, as shown in ▼ **FIGURE 9.33**. Like atomic orbitals, each MO can accommodate two electrons with their spins paired (Pauli exclusion principle). (Section 6.7)

As the MO diagram for H_2 in Figure 9.33 shows, each H atom brings one electron to the molecule, so there are two electrons in H_2. These two electrons occupy the lower-energy bonding (σ_{1s}) MO, and their spins are paired. Electrons occupying a bonding molecular orbital are called *bonding electrons*. Because the σ_{1s} MO is lower in energy than the 1*s* atomic orbitals, the H_2 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_2, then, is σ^{2}_{1s}.

GO FIGURE

By referring to Figure 9.32, determine which molecular orbital in He_2 has a node between the nuclei.



▲ **FIGURE 9.33** **Energy-level diagrams and electron configurations for H_2 and He_2.**

Figure 9.33 also shows the energy-level diagram for the hypothetical He_2 molecule, which requires four electrons to fill its molecular orbitals. Because only two electrons can go in the σ_{1s} MO, the other two electrons must go in the $\sigma^{\star}_{1s}$ MO. The electron configuration of He_2 is thus $\sigma_{1s}{}^{2}\sigma^{\star}_{1s}{}^{2}$. 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.† Hence, He_2 is an unstable molecule. Molecular orbital theory correctly predicts that hydrogen forms diatomic molecules but helium does not.

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:

$$\text{Bond order} = \tfrac{1}{2}\,(\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \qquad [9.1]$$

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.

Because, as Figure 9.33 shows, H_2 has two bonding electrons and zero antibonding electrons, it has a bond order of 1. Because He_2 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.

GIVE IT SOME THOUGHT

Suppose one electron in H_2 is excited from the σ_{1s} MO to the $\sigma^{\star}_{1s}$ MO. Would you expect the H atoms to remain bonded to each other, or would the molecule fall apart?

SAMPLE EXERCISE 9.8 Bond Order

What is the bond order of the $He_2{}^{+}$ ion? Would you expect this ion to be stable relative to the separated He atom and He^{+} ion?

SOLUTION

Analyze We will determine the bond order for the $He_2{}^{+}$ 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 1*s* orbital, and the 1*s* orbitals combine to give an MO diagram like that for H_2 or He_2 (Figure 9.33). 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 $He_2{}^{+}$ ion is shown in ◀ **FIGURE 9.34**. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

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

Because the bond order is greater than 0, we predict the $He_2{}^{+}$ ion to be stable relative to the separated He and He^{+}. Formation of $He_2{}^{+}$ in the gas phase has been demonstrated in laboratory experiments.

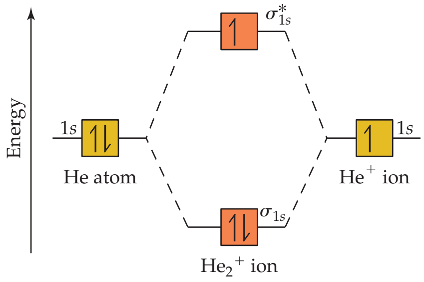
PRACTICE EXERCISE

Determine the bond order of the $H_2{}^{-}$ ion.

Answer: $\frac{1}{2}$

GO FIGURE

Which electrons in this diagram contribute to the stability of the $He_2{}^{+}$ ion?



▲ **FIGURE 9.34 Energy-level diagram for the $He_2{}^{+}$ ion.**

---

†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.

9.8 PERIOD 2 DIATOMIC MOLECULES

In considering the MO description of diatomic molecules other than 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 2*s* and 2*p* 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). ∞ (Section 6.7)
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). ∞ (Section 6.8)

Molecular Orbitals for Li_2 and Be_2

Lithium has the electron configuration $1s^22s^1$. When lithium metal is heated above its boiling point (1342 °C), Li_2 molecules are found in the vapor phase. The Lewis structure for Li_2 indicates a Li—Li single bond. We will now use MOs to describe the bonding in Li_2.

▶ **FIGURE 9.35** shows that the Li 1*s* and 2*s* atomic orbitals have substantially different energy levels. From this, we can assume that the 1*s* orbital on one Li atom interacts only with the 1*s* orbital on the other atom (rule 2), just as Figure 9.35 indicates. Likewise, the 2*s* orbitals interact only with each other. Notice that combining four atomic orbitals produces four MOs (rule 1).

The Li 1*s* orbitals combine to form σ_{1s} and σ^*_{1s} bonding and antibonding MOs, as they did for H_2. The 2*s* orbitals interact with one another in exactly the same way, producing bonding (σ_{2s}) and antibonding (σ^*_{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 2*s* orbitals extend farther from the nucleus than the 1*s* orbitals do, the 2*s* orbitals overlap more effectively. As a result, the energy difference between the σ_{2s} and σ^*_{2s} orbitals is greater than the energy difference between the σ_{1s} and σ^*_{1s} orbitals. The 1*s* orbitals of Li are so much lower in energy than the 2*s* orbitals, however, that the energy of the σ^*_{1s} antibonding MO is much lower than the energy of σ_{2s} bonding MO.

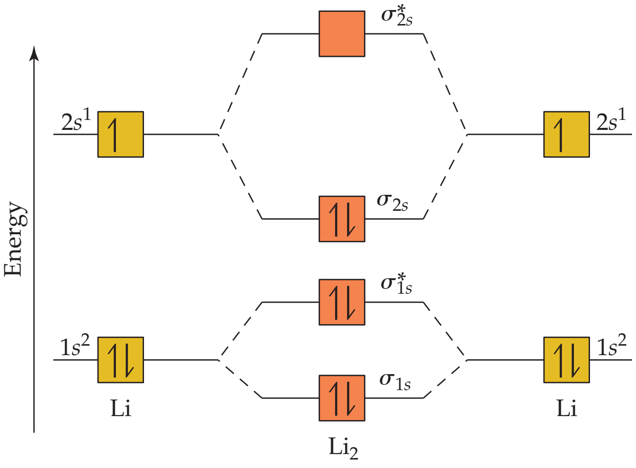
Each Li atom has three electrons, so six electrons must be placed in Li_2 MOs. As shown in Figure 9.35, these electrons occupy the σ_{1s}, σ^*_{1s}, and σ_{2s} MOs, each with two electrons. There are four electrons in bonding orbitals and two in antibonding orbitals, so the bond order is $\frac{1}{2}(4 - 2) = 1$. The molecule has a single bond, in agreement with its Lewis structure.

Because both the σ_{1s} and σ^*_{1s} MOs of Li_2 are completely filled, the 1*s* orbitals contribute almost nothing to the bonding. The single bond in Li_2 is due essentially to the interaction of the valence 2*s* 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 1*s* orbitals while discussing the other period 2 diatomic molecules.

The MO description of Be_2 follows readily from the energy-level diagram for Li_2. Each Be atom has four electrons ($1s^22s^2$), so we must place eight electrons in molecular orbitals. Thus, we completely fill the

GO FIGURE

Why do the 1*s* orbitals of the Li atoms not contribute to the bonding in Li_2?



▲ **FIGURE 9.35 Energy-level diagram for the Li_2 molecule.**

σ_{1s}, $\sigma^{\star}_{1s}$, σ_{2s}, and $\sigma^{\star}_{2s}$ MOs. With equal numbers of bonding and antibonding electrons, the bond order is zero; thus, Be_2 does not exist.

GIVE IT SOME THOUGHT

Would you expect Be_2^+ to be a stable ion?

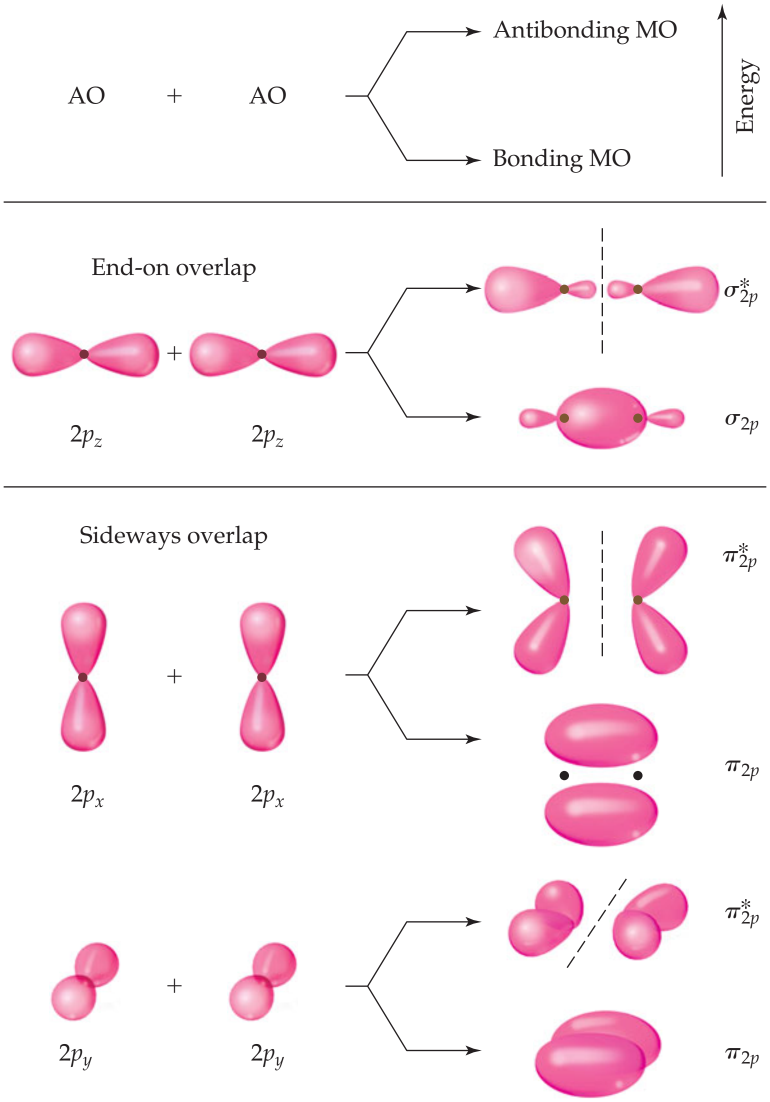
Molecular Orbitals from 2*p* Atomic Orbitals

Before we can consider the remaining period 2 diatomic molecules, we must look at the MOs that result from combining 2*p* atomic orbitals. The interactions between *p* orbitals are shown in ▼ **FIGURE 9.36**, 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 σ molecular orbitals: σ_{2p} and $\sigma^{\star}_{2p}$.

The other 2*p* orbitals overlap sideways and thus concentrate electron density above and below the internuclear axis. MOs of this type are called **pi (π) molecular orbitals** by

GO FIGURE

In what types of MOs do we find nodal planes?



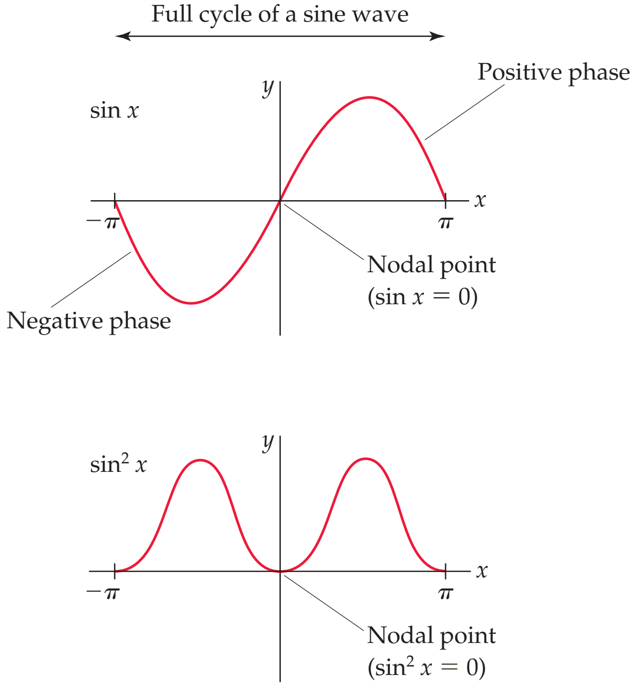
▶ **FIGURE 9.36** **Contour representations of the molecular orbitals formed by 2*p* orbitals.**

A CLOSER LOOK

PHASES IN ATOMIC AND MOLECULAR ORBITALS

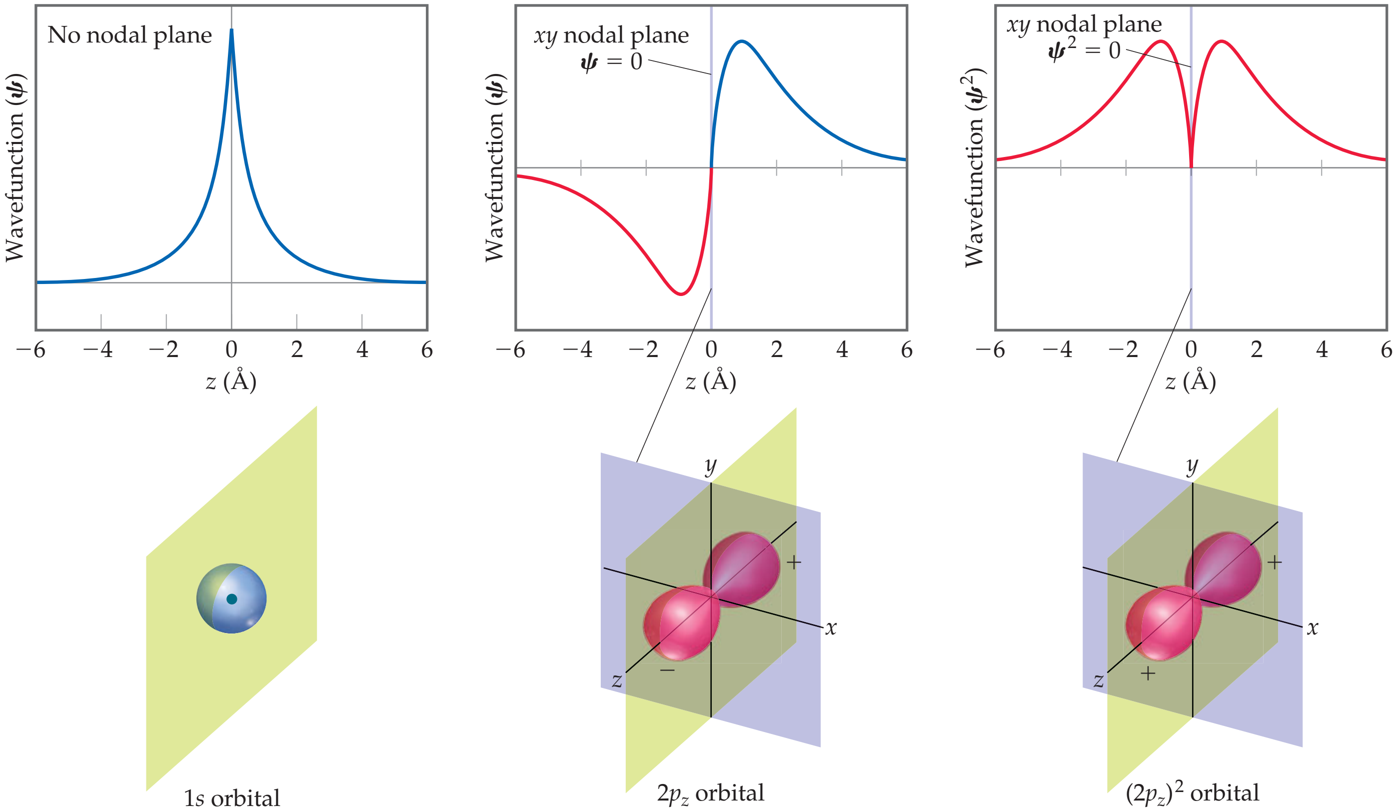
Our discussion of atomic orbitals in Chapter 6 and molecular orbitals in this chapter highlights some of the most important applications of quantum mechanics in chemistry. In the quantum mechanical treatment of electrons in atoms and molecules, we are mainly interested in determining two characteristics 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, ψ, but that ψ does not have a direct physical meaning. ∞ (Section 6.5) The contour representations of atomic and molecular orbitals we have presented thus far are based on ψ^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. Consider, for example, the sine function plotted in ▶ **FIGURE 9.37**. 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*.



▲ **FIGURE 9.37 Graphs for a sine function and the same function squared.**

Like the sine function, the more complicated wave functions for atomic orbitals can also have phases. Consider, for example, the representations of the 1*s* orbital in ▼ **FIGURE 9.38**. 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



▲ **FIGURE 9.38 Phases in wave functions of *s* and *p* atomic orbitals.**

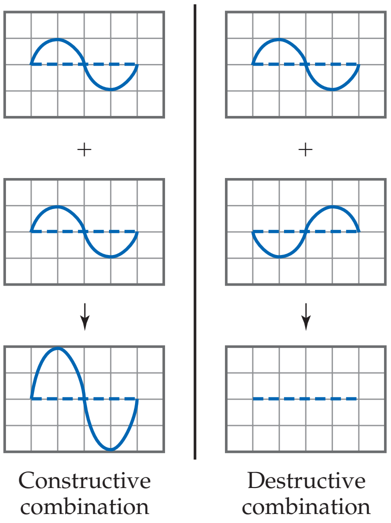
the 1*s* orbital extends from the origin out into space. The plot shows the value of ψ for a slice taken along the z-axis. Below the plot is a contour representation of the 1*s* orbital. Notice that the value of the 1*s* wave function is always a positive number. Thus, it has only one phase. Notice also 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.

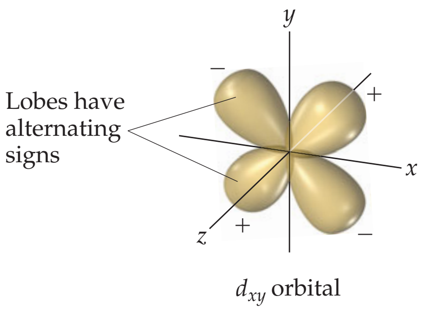
In the Figure 9.38 graph for the $2p_z$ orbital, the wave function changes sign when it passes through $z = 0$. Notice that the two halves of the wave have the same shape except that one has positive values and the other negative values. Analogously to the sine function, the wave function changes phase 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 9.38 gives a typical representation used by chemists of the wave function for a p_z orbital.* The plus and minus signs indicate the phases of the orbital. As with the sine function, the origin is a node.

The third graph in Figure 9.38 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 9.38. This is what we saw in the earlier presentation of *p* orbitals. (Section 6.6) 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 9.39**). The wave functions for the 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:





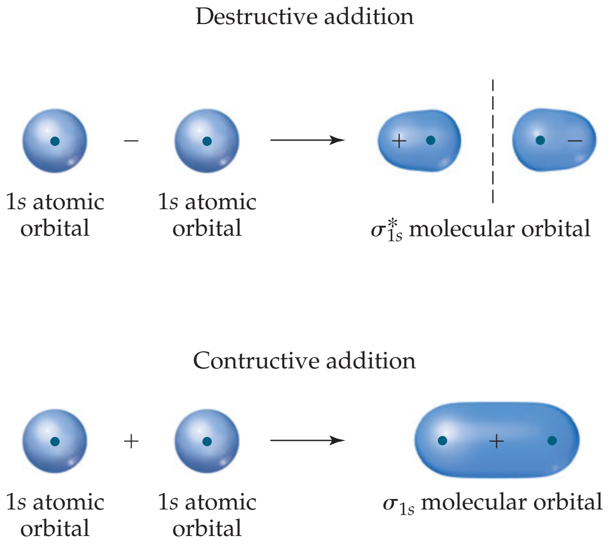
▲ **FIGURE 9.39 Phases in *d* orbitals.**

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 σ_{1s} MO of H_2 is generated by adding the wave function for the 1*s* orbital on one atom to the wave function for the 1*s* 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 9.40**). The wave function of the σ^*_{1s} MO of H_2 is generated by subtracting the wave function for a 1*s* orbital on one atom from the wave function for a 1*s* 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 9.32. In Figure 9.40 we use plus and minus signs to denote positive and negative phases in the H atomic orbitals. However, chemists may alternatively draw contour representations in different colors to denote the two phases.

When we square the wave function of the σ^*_{1s} MO, we get the electron density representation which we saw earlier, in Figure 9.32. Notice once again that we lose the phase information when we look at the electron density.

RELATED EXERCISES: 9.103, 9.115, 9.117



▲ **FIGURE 9.40 Molecular orbitals from atomic orbital wave functions.**

---

*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 6.22.

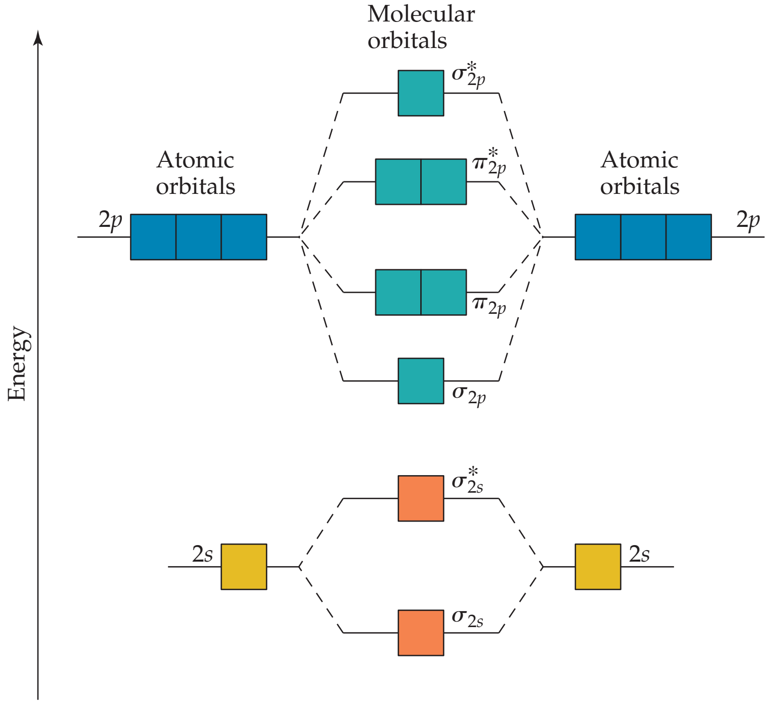
analogy to π bonds. We get one π bonding MO by combining the $2p_x$ atomic orbitals and another from the $2p_y$ atomic orbitals. These two π_{2p} molecular orbitals have the same energy; in other words, they are degenerate. Likewise, we get two degenerate π^*_{2p} antibonding MOs that are perpendicular to each other like the $2p$ orbitals from which they were made. These π^*_{2p} orbitals have four lobes, pointing away from the two nuclei, as shown in Figure 9.36. The $2p_z$ orbitals on two atoms point directly at each other. Hence, the overlap of two $2p_z$ orbitals is greater than that of two $2p_x$ or $2p_y$ orbitals. From rule 3 we therefore expect the σ_{2p} MO to be lower in energy (more stable) than the π_{2p} MOs. Similarly, the σ^*_{2p} MO should be higher in energy (less stable) than the π^*_{2p} MOs.

Electron Configurations for B_2 through Ne_2

We can combine our analyses of MOs formed from *s* orbitals (Figure 9.32) and from *p* orbitals (Figure 9.36) to construct an energy-level diagram (▼ **FIGURE 9.41**) for homonuclear diatomic molecules of the elements boron through neon, all of which have valence 2*s* and 2*p* atomic orbitals. The following features of the diagram are notable:

1. The 2*s* atomic orbitals are substantially lower in energy than the 2*p* atomic orbitals. ∞ (Section 6.7) Consequently, both MOs formed from the 2*s* orbitals are lower in energy than the lowest-energy MO derived from the 2*p* atomic orbitals.
2. 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 σ_{2p} MO is lower in energy than the π_{2p} MOs, and the antibonding σ^*_{2p} MO is higher in energy than the π^*_{2p} MOs.
3. Both the π_{2p} and π^*_{2p} MOs are *doubly degenerate*; that is, there are two degenerate MOs of each type.

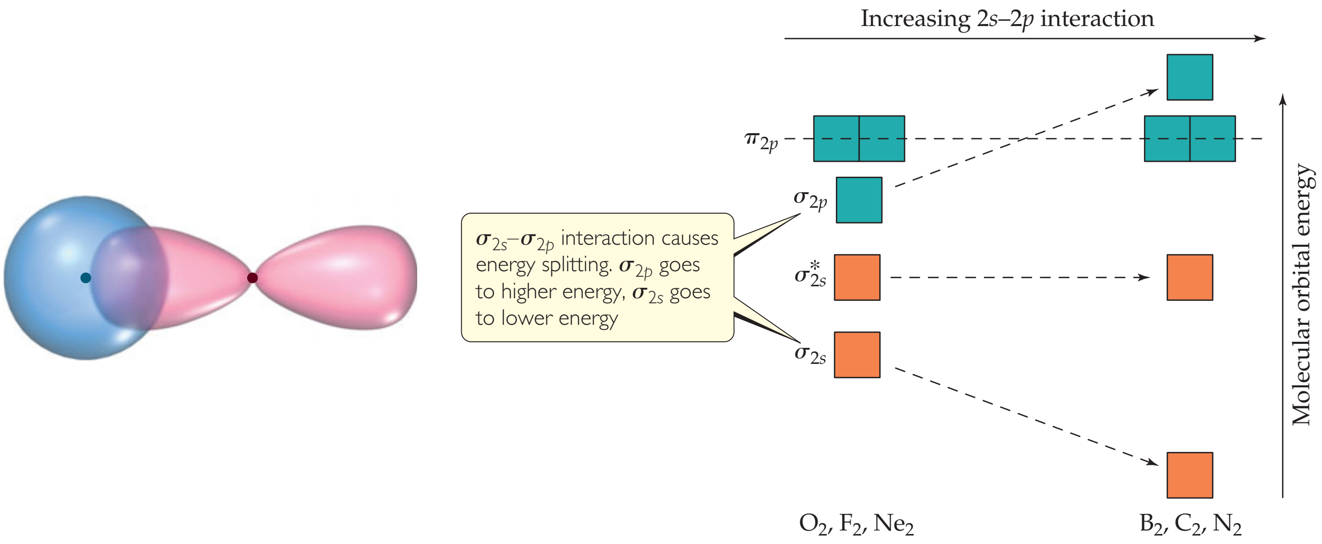
Before we can add electrons to Figure 9.41, we must consider one more effect. We have constructed the diagram assuming no interaction between the 2*s* orbital on one atom and the 2*p* orbitals on the other. In fact, such interactions can and do take place. ► **FIGURE 9.42** shows the overlap of a 2*s* orbital on one of the atoms with a 2*p* orbital on the other. These interactions increase the energy difference between the σ_{2s} and σ_{2p} MOs, with the σ_{2s} energy decreasing and the σ_{2p} energy increasing (Figure 9.42). These 2*s*–2*p* interactions can be strong enough that the energetic ordering of the MOs can be altered: For B_2, C_2, and N_2, the σ_{2p} MO is above the π_{2p} MOs in energy. For O_2, F_2, and Ne_2, the σ_{2p} MO is below the π_{2p} MOs .



◄ **FIGURE 9.41 Energy-level diagram for MOs of period 2 homonuclear diatomic molecules.** The diagram assumes no interaction between the 2*s* atomic orbital on one atom and the 2*p* 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?



σ_{2s}–σ_{2p} interaction causes energy splitting. σ_{2p} goes to higher energy, σ_{2s} goes to lower energy

▲ **FIGURE 9.42 The effect of interactions between 2*s* and 2*p* atomic orbitals.**

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 1*s* electrons.) Thus, for B_2 we must place six electrons in MOs. Four of them fill the σ_{2s} and σ^*_{2s} MOs, leading to no net bonding. The fifth electron goes in one π_{2p} MO, and the sixth goes in the other π_{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 diagram of Figure 9.41. For example, on moving to C_2, we have two more electrons than in B_2, and these electrons are placed in the π_{2p} MOs, completely filling them. The electron configurations and bond orders for B_2 through Ne_2 are given in ▶ **FIGURE 9.43**.

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 9.44**). 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 9.43.

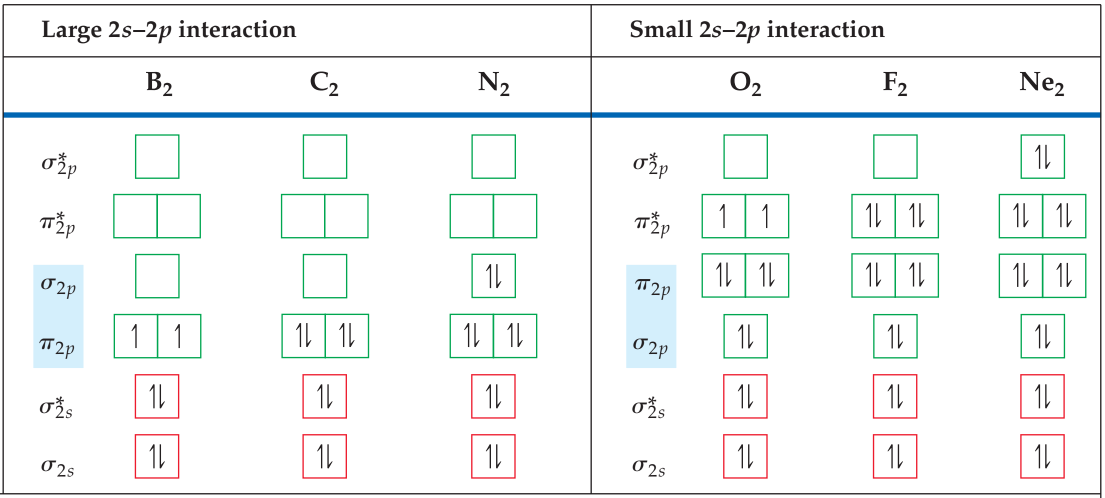
GIVE IT SOME THOUGHT

Figure 9.43 indicates that C_2 is diamagnetic. Would that be expected if the σ_{2p} MO were lower in energy than the π_{2p} MOs?

Electron configurations in molecules can also be related to bond distances and bond enthalpies. ∞ (Section 8.8) As bond order increases, bond distances decrease

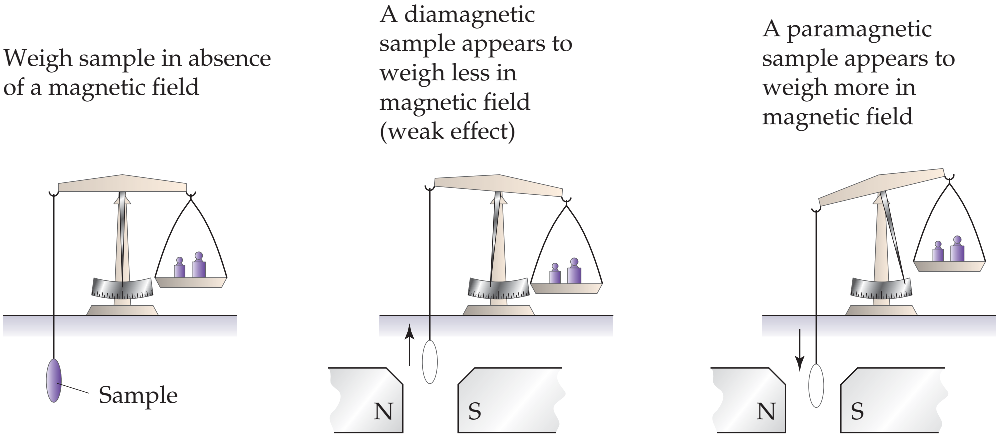
GO FIGURE

What difference in electron configuration accounts for most of the difference between the bond enthalpy of N_2 and that of F_2?



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

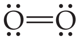
▲ **FIGURE 9.43 Molecular orbital electron configurations and some experimental data for period 2 diatomic molecules.**



◀ **FIGURE 9.44 Determining the magnetic properties of a sample.**

and bond enthalpies increase. N_2, for example, whose bond order is 3, has a short bond distance and a large bond enthalpy. The N_2 molecule does not react readily with other substances to form nitrogen compounds. The relatively 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_2 provides an interesting test case for molecular orbital theory. The Lewis structure for this molecule shows a double bond and complete pairing of electrons:



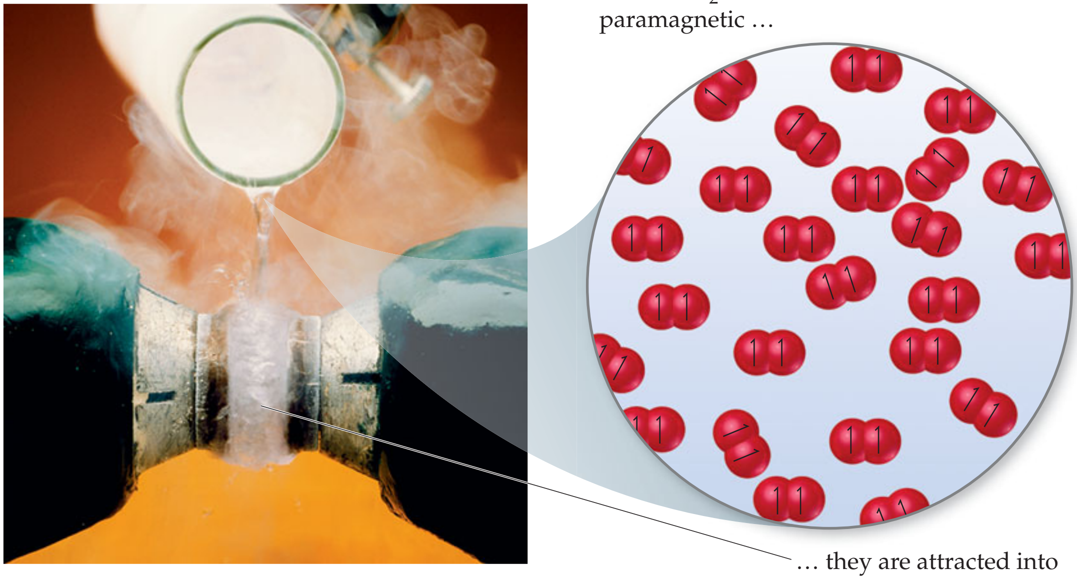
$$\ddot{\underset{..}{O}}=\ddot{\underset{..}{O}}$$

The short O—O bond distance (1.21 Å) and relatively high bond enthalpy (495 kJ/mol) are in agreement with the presence of a double bond. However, Figure 9.43 tells us that

GO FIGURE

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

Because O_2 molecules are paramagnetic …



… they are attracted into the magnetic field.

▲ **FIGURE 9.45** **Paramagnetism of O_2.**

the molecule contains two unpaired electrons, a detail not discernible in the Lewis structure. Unpaired electrons mean paramagnetism, and the paramagnetism of O_2 is demonstrated in ▲ **FIGURE 9.45**. The Lewis structure fails to account for this paramagnetism, but molecular orbital theory correctly predicts two unpaired electrons in the $\pi^{\star}_{2p}$ orbital. The MO description also correctly indicates a bond order of 2.

Going from O_2 to F_2, we add two electrons, completely filling the $\pi^{\star}_{2p}$ MOs. Thus, F_2 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_2 fills all the bonding and antibonding MOs. Therefore, the bond order of Ne_2 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_2^+ 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_2^+.

Plan We will use the MO description of O_2^+ to determine the desired properties. We must first determine the number of electrons in O_2^+ 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 9.43 to estimate the bond enthalpy and bond length.

Solve

(a) The O_2^+ ion has 11 valence electrons, one fewer than O_2. The electron removed from O_2 to form O_2^+ is one of the two unpaired $\pi^{\star}_{2p}$ electrons (see Figure 9.43). Therefore, O_2^+ has one unpaired electron.

(b) The molecule has eight bonding electrons (the same as O_2) and three antibonding electrons (one fewer than O_2). Thus, its bond order is

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

(c) The bond order of O_2^+ is between that for O_2 (bond order 2) and N_2 (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O_2 and N_2, approximately 700 kJ/mol and 1.15 Å. (The experimentally measured values are 625 kJ/mol and 1.123 Å.)

PRACTICE EXERCISE

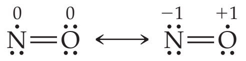
Predict the magnetic properties and bond orders of **(a)** the peroxide ion, O_2^{2-}; **(b)** the acetylide ion, C_2^{2-}.

Answers: **(a)** diamagnetic, 1; **(b)** diamagnetic, 3

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—and we conclude this section with a fascinating heteronuclear diatomic molecule—nitric oxide, NO.

The NO molecule controls several important human physiological functions. Our bodies use it, for example, 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 NO as a "signaling" molecule in the cardiovascular system. NO also functions as a neurotransmitter and is implicated in many other biological pathways. That NO plays such an important role in human metabolism was unsuspected before 1987 because NO has an odd number of electrons and is highly reactive. The 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:



$$\overset{0}{\underset{\cdot\cdot}{\dot{N}}}=\overset{0}{\underset{\cdot\cdot}{\ddot{O}}} \longleftrightarrow \overset{-1}{\underset{\cdot\cdot}{\ddot{N}}}=\overset{+1}{\underset{\cdot\cdot}{\dot{O}}}$$

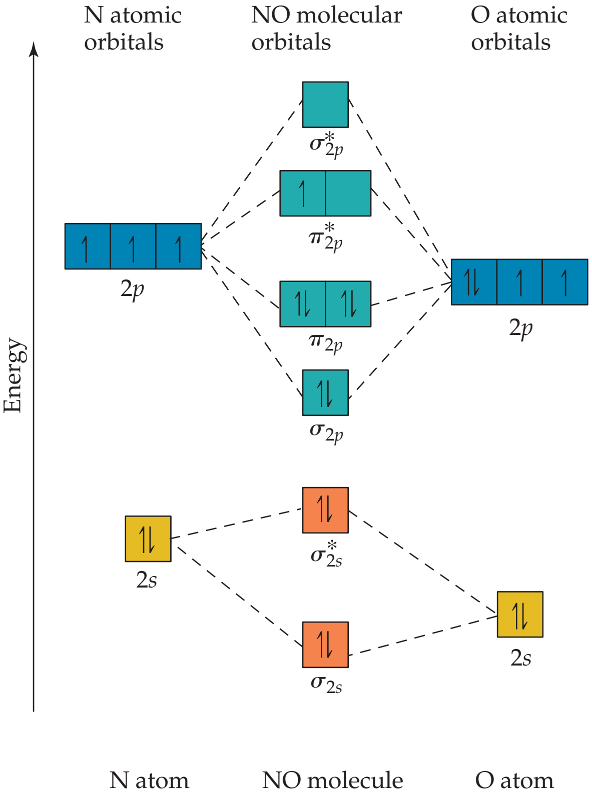
Both structures indicate the presence of a double bond, but when compared with the molecules in Figure 9.43, the experimental bond length of NO (1.15 Å) suggests a bond order greater than 2. How do we treat NO using the MO model?

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 9.46**, you see that the 2*s* and 2*p* atomic orbitals of oxygen are slightly lower 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 2*s* and 2*p* 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 σ_{2s} bonding MO is closer in energy to the O 2*s* atomic orbital than to the N 2*s* atomic orbital. As a result, the σ_{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 $\sigma_{2s}^{\star}$ antibonding MO is weighted more heavily toward the N atom because that MO is closest in energy to the N 2*s* atomic orbital.

GO FIGURE

How many valence-shell electrons are there in NO?



▲ **FIGURE 9.46 The energy-level diagram for atomic and molecular orbitals in NO.**

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. Currently, the majority of the world, in one way or another, relies on exothermic combustion reactions of oil, coal, or natural gas to provide heat and power. These are all *fossil fuels*—carbon-containing compounds that are the long-term decomposition products of ancient plants and animals.

Fossil fuels are not renewable in the several-hundred-year timeframe in which we need them, but every day our planet receives plenty of energy from the Sun to easily power the world for millions of years. Whereas combustion of fossil fuels releases CO_2 into the atmosphere, solar energy represents a renewable energy source that is potentially less harmful to the environment. One way to utilize solar energy is to convert it into electrical energy via photovoltaic solar cells. The problem with this alternative is that the current efficiency of solar-cell devices is low; only about 10–15% of sunlight is converted into useful energy. Furthermore, the cost of manufacturing solar cells is relatively high.

How does solar energy conversion work? Fundamentally, we need to be able to use photons from the Sun 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 light by chemicals. Light excites electrons in molecules. In a molecular orbital picture, we can envision light exciting an electron from a filled molecular orbital to an empty one at higher energy. Because the MOs have definite energies, only light of the proper wavelengths can excite electrons. The situation is analogous to that of atomic line spectra. ∞ (Section 6.3) If the appropriate wavelength for exciting electrons is in the visible portion of the electromagnetic spectrum, the substance appears colored: Certain wavelengths of white light are absorbed; others are not. A green leaf appears green because green light is most strongly reflected by the leaf while other wavelengths of visible light are absorbed.

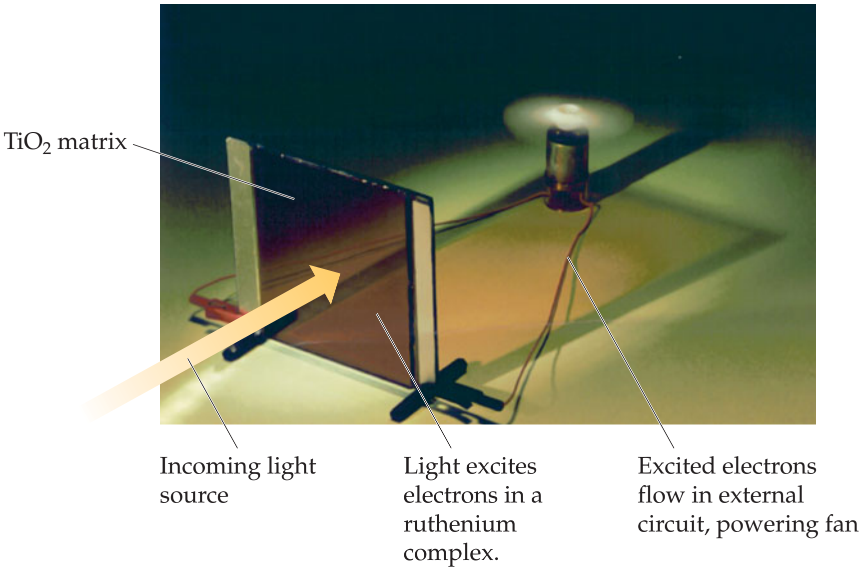
In discussing light absorption by molecules, we can focus on two MOs. The *highest occupied molecular orbital* (HOMO) is the MO of highest energy that has electrons in it. The *lowest unoccupied molecular orbital* (LUMO) is the MO of lowest energy that does not have electrons in it. In N_2, for example, the HOMO is the σ_{2p} MO and the LUMO is the π^{*}_{2p} MO (Figure 9.43).

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_2 corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. ∞ (Figure 6.4) As a result, N_2 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_2 is white and absorbs only a small amount of the Sun's radiant energy. Scientists are working to make solar cells in which TiO_2 is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light. That way, the molecules can absorb more of the solar spectrum. The molecule's HOMO must also be higher in energy than the TiO_2's HOMO so that the excited electrons can flow from the molecules into the TiO_2, thereby generating electricity when the device is illuminated with light and connected to an external circuit.

▼ **FIGURE 9.47** shows a solar cell made from ruthenium-containing molecules, which appear red, mixed with TiO_2 in a paste that is sandwiched between two glass plates. Incoming light excites electrons on the ruthenium-containing molecules from occupied MOs to empty MOs. The electrons are then transferred into the TiO_2 and move through the external circuit, generating enough current to run the small fan.

RELATED EXERCISES: 9.105, 9.116



▲ **FIGURE 9.47** **Light into electricity.**

We complete the MO diagram for NO by filling the MOs in Figure 9.46 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 $\pi^{\star}_{2p}$ MOs, which are more heavily weighted toward the N atom. (We could have placed this electron in either the left or right $\pi^{\star}_{2p}$ 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.

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:

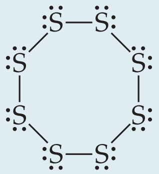
$$S_8(s) \longrightarrow 4\ S_2(g)$$

(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 8.4) to estimate the enthalpy change for this reaction. Is the reaction exothermic or endothermic?

SOLUTION

(a) Sulfur is a group 6A element with an $[\mathrm{Ne}]3s^2 3p^4$ electron configuration. It is expected to be most similar electronically to oxygen (electron configuration, $[\mathrm{He}]2s^2 2p^4$), 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°, the tetrahedral angle. Experimentally, the S—S—S angle in S_8 is 108°, in good agreement with this prediction. Interestingly, if S_8 were a planar ring, it would have S—S—S angles of 135°. Instead, the S_8 ring puckers 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 3*s* and 3*p* 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 $\pi^{\star}_{3p}$ 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 8.12 and the average bond enthalpies in Table 8.4:

$$\Delta H_{\mathrm{rxn}} = 8\,D(\mathrm{S{-}S}) - 4\,D(\mathrm{S{=}S}) = 8(266\ \mathrm{kJ}) - 4(418\ \mathrm{kJ}) = +456\ \mathrm{kJ}$$

Recall that $D(\mathrm{X{-}Y})$ represents the X—Y bond enthalpy. Because $\Delta H_{\mathrm{rxn}} > 0$, the reaction is endothermic. (Section 5.4) The very positive value of ΔH_{rxn} suggests that high temperatures are required to cause the reaction to occur.

CHAPTER SUMMARY AND KEY TERMS

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).

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**.

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, assure that the bond dipoles cancel, producing a nonpolar molecule, which is one whose 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).

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 low energy, or greater stability, for the two electrons because of their simultaneous attraction to two nuclei. The greater the overlap between two orbitals, the stronger will be the bond that is formed.

SECTION 9.5 To extend the ideas of valence-bond theory to polyatomic molecules, we must envision mixing *s, p,* and sometimes *d* 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).

SECTION 9.6 Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called **sigma (σ) bonds**. Bonds can also be formed from the sideways overlap of *p* orbitals. Such a bond is called a **pi (π) bond**. A double bond, such as that in C_2H_4, consists of one σ bond and one π bond; a triple bond, such as that in C_2H_2, consists of one σ and two π bonds. The formation of a π 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 π bonds introduces rigidity into molecules. In molecules that have multiple bonds and more than one resonance structure, such as C_6H_6, the π bonds are **delocalized**; that is, the π bonds are spread among several atoms.

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 think of molecular orbitals as built up 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**. 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 (σ) 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 are 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.

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. In order 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 σ bonding and σ^* antibonding MOs. The *p* orbitals that are oriented perpendicular to the internuclear axis combine to form **pi (π) molecular orbitals**. In diatomic molecules the π molecular orbitals occur as a pair of degenerate (same energy) bonding MOs and a pair of degenerate antibonding MOs. The σ_{2p} bonding MO is expected to be lower in energy than the π_{2p} bonding MOs because of larger orbital overlap of the *p* orbitals directed along the internuclear axis. However, this ordering is reversed in B_2, C_2, and N_2 because of interaction between the 2*s* and 2*p* 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 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.