9

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 atorvastatin, better known as Lipitor®. In the body, Lipitor inhibits the action of a key enzyme, called *HMG-CoA reductase* (we will discuss enzymes in Section 14.7). HMG-CoA reductase is a large complex biomolecule that is critical in the biochemical sequence that synthesizes cholesterol in the liver, and inhibition of its action leads to reduced cholesterol production. The molecules of Lipitor have two properties that lead to their pharmaceutical effectiveness: First, the molecule has the correct overall *shape* to fit perfectly in an important cavity in the HMG-CoA reductase enzyme, thus blocking that site from the molecules involved in cholesterol synthesis. Second, the molecule has the right atoms and arrangements of electrons to form strong interactions within the cavity, assuring that the Lipitor molecule will "stick" where it should. Thus, the drug action of Lipitor is largely a consequence of the shape and size of the molecule as well as the charge distributions within it. Even a small modification to molecular shape or size alters the drug's effectiveness.

▶ **THE DRUG SHOWN HERE IS ATORVASTATIN,** better known by its trade name Lipitor®. It is a member of a class of pharmaceuticals called *statins*, which lower blood cholesterol levels, thereby reducing the risk of heart attacks and strokes. Lipitor was first synthesized in 1985 by Bruce Roth of Warner-Lambert/Parke Davis (now part of Pfizer) and was approved for use in 1996. It is the best-selling drug in pharmaceutical history, with sales of more than $125 billion from 1997 to 2011. It became available as a generic drug in 2011.

WHAT'S AHEAD

9.1 MOLECULAR SHAPES We begin by discussing *molecular shapes* and examining some shapes commonly encountered in molecules.

9.2 THE VSEPR MODEL We see how molecular geometries can be predicted using the *valence-shell electron-pair repulsion*, or *VSEPR*, model, which is based on Lewis structures and the repulsions between regions of high electron density.

9.3 MOLECULAR SHAPE AND MOLECULAR POLARITY Once we know the geometry of a molecule and the types of bonds it contains, we can determine whether the molecule is *polar* or *nonpolar*.

9.4 COVALENT BONDING AND ORBITAL OVERLAP We explore how electrons are shared between atoms in a covalent bond. In *valence-bond theory*, the bonding electrons are visualized as originating in atomic orbitals on two atoms. A covalent bond is formed when these orbitals overlap.

9.5 HYBRID ORBITALS To account for molecular shape, we examine 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 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.

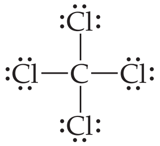
9.7 Molecular Orbitals We examine a more sophisticated treatment of bonding called *molecular orbital theory*, which introduces the concepts of *bonding* and *antibonding molecular orbitals*.

9.8 Period 2 Diatomic Molecules We extend the concepts of molecular orbital theory to construct *energy-level diagrams* for second-row diatomic molecules.

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



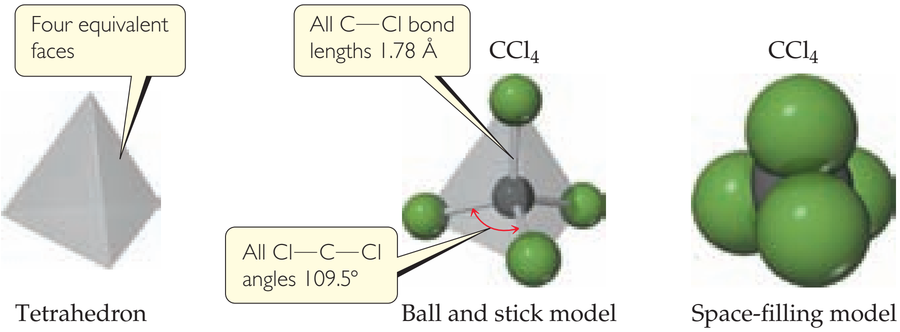
$$\begin{array}{ccccc} & & :\overset{..}{\underset{}{\text{Cl}}}: & & \\ & & | & & \\ :\overset{..}{\underset{..}{\text{Cl}}} & - & \text{C} & - & \overset{..}{\underset{..}{\text{Cl}}}: \\ & & | & & \\ & & :\underset{..}{\text{Cl}}: & & \end{array}$$

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

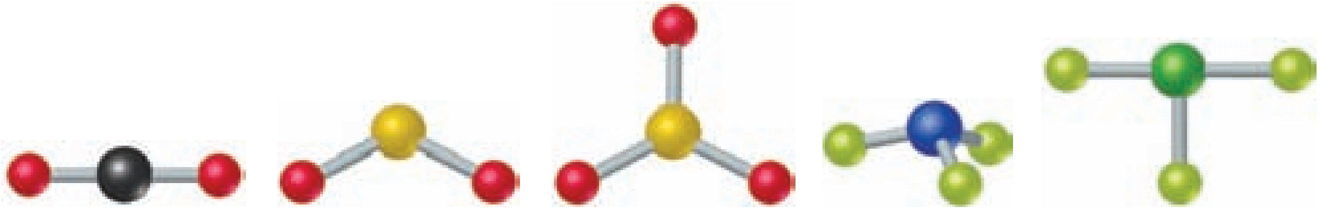
The shape of a molecule is determined by its **bond angles**, the angles made by the lines joining the nuclei of the atoms in the molecule. The bond angles of a molecule, together with the bond lengths (Section 8.8), define the shape and size of the molecule. In Figure 9.1, you should be able to see that there are six Cl—C—Cl bond angles in CCl_4, all of which have the same value. That bond angle, 109.5°, is characteristic of a tetrahedron. In addition, all four C—Cl bonds are of 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.

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.**

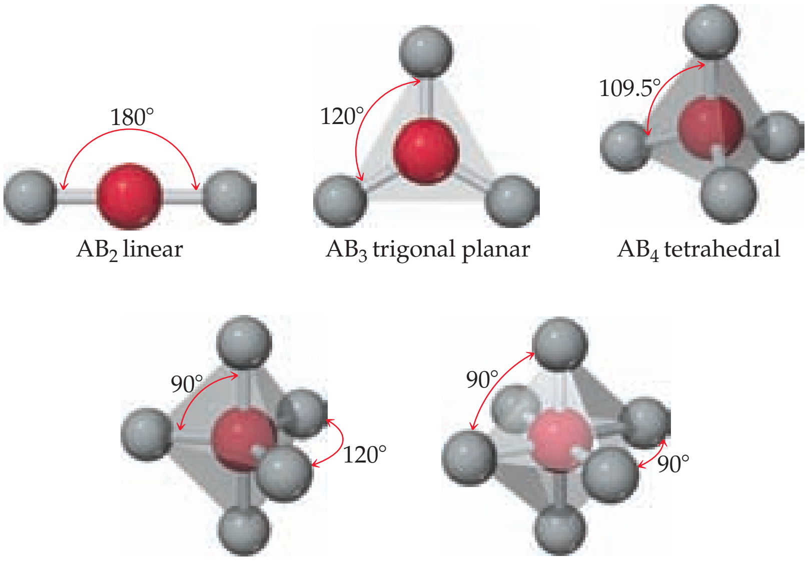
We begin our discussion of molecular shapes with molecules (and ions) that, like CCl_4, have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula AB_n in which the central atom A is bonded to n B atoms. Both CO_2 and H_2O are AB_2 molecules, for 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 called *trigonal planar*. If the A atom lies above the plane of the B atoms, the shape is called *trigonal pyramidal* (a pyramid with an equilateral triangle as its base). Some AB_3 molecules, such as ClF_3, are *T-shaped*, a relatively unusual shape shown in Figure 9.2. The atoms lie in one plane with two B—A—B angles of about 90°, and a third angle close to 180°.

Quite remarkably, the shapes of most AB_n molecules can be derived from just five basic geometric arrangements, shown in ▼ Figure 9.3. All of these are highly

GO FIGURE

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



AB_2 linear

AB_3 trigonal planar

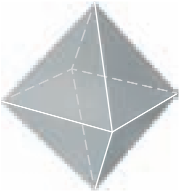
AB_4 tetrahedral

AB_5 trigonal bipyramidal

AB_6 octahedral

▲ Figure 9.3 **Shapes allowing maximum distances between B atoms in AB_n molecules.**

symmetric arrangements of the n B atoms around the central A atom. We have already seen the first three shapes: linear, trigonal planar, and tetrahedral. The trigonal bipyramid shape for AB_5 can be thought of as a trigonal planar AB_3 arrangement with two additional atoms, one above and one below the equilateral triangle. The octahedral shape for AB_6 has all six B atoms at the same distance from atom A with 90° B—A—B angles between all neighboring B atoms. Its symmetric shape (and its name) is derived from the *octahedron*, with eight faces, all of which are equilateral triangles.



Octahedron

You may have noticed that some of the shapes we have already discussed are *not* among the five shapes in Figure 9.3. For example, in Figure 9.2, neither the bent shape of the SO_2 molecule nor the trigonal pyramidal shape of the NF_3 molecule is among the shapes in Figure 9.3. However, as we soon will see, we can derive additional shapes, such as bent and trigonal pyramidal, by starting with one of our five basic arrangements. Starting with a tetrahedron, for example, we can remove atoms successively from the vertices, as shown in ▼ Figure 9.4. When an atom is removed from one vertex of a tetrahedron, the remaining AB_3 fragment has a trigonal-pyramidal geometry. When a second atom is removed, the remaining AB_2 fragment has a bent geometry.

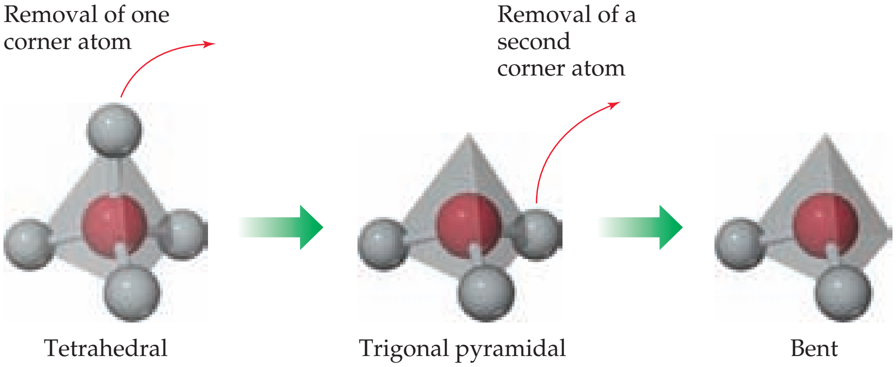
Why do most AB_n molecules have shapes related to those shown in Figure 9.3? Can we predict these shapes? When A is a representative element (one from the *s* block or *p* block of the periodic table), we can answer these questions by using the **valence-shell electron-pair repulsion (VSEPR) model**.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

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?

GO FIGURE

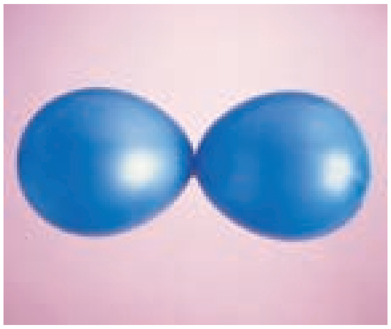
In going from the tetrahedral shape to the bent shape, does it matter which two of the atoms we choose to remove?



▲ Figure 9.4 **Derivatives of the tetrahedral molecular shape.**

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.



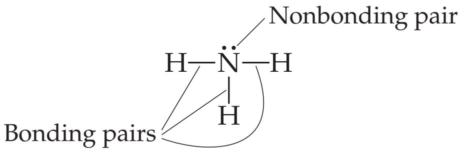
Two balloons
linear orientation

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, which was also discussed in Section 8.3, defines an electron domain that is located principally on one atom. For example, the Lewis structure of NH_3 has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):



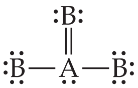
Each multiple bond in a molecule also constitutes a single electron domain. Thus, the following resonance structure for O_3 has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):

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

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



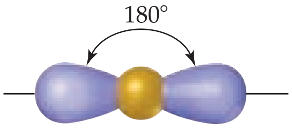
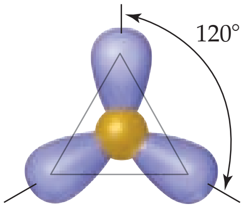
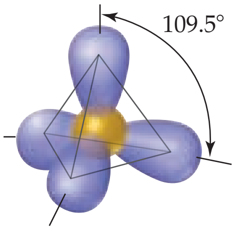
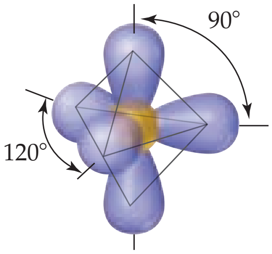
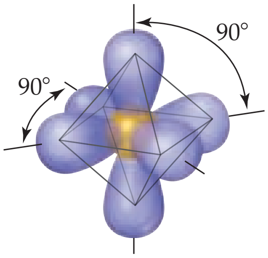
$$:\ddot{\underset{\cdot\cdot}{B}}-\underset{\cdot\cdot}{\overset{\overset{:B:}{\|}}{A}}-\ddot{\underset{\cdot\cdot}{B}}:$$

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, 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

Table 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

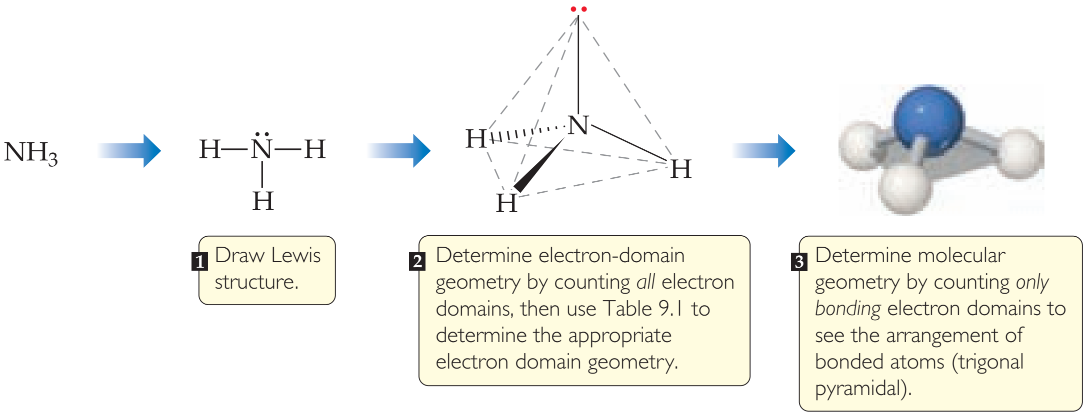
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

the 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 that *the molecular geometry involves only electron domains due to bonds* even though the nonbonding pairs contribute to the electron-domain geometry.

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 (Section 8.5), and count the number of electron domains around the central atom. Each nonbonding electron



▲ **Figure 9.6** **Determining the molecular geometry of NH_3.**

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*.

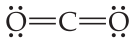
▲ **Figure 9.6** shows how these steps are applied to predict the geometry of the NH_3 molecule. The three bonds and one nonbonding pair in the Lewis structure tell us we have four electron domains. Thus, from Table 9.1, the electron-domain geometry of NH_3 is tetrahedral. We know from the Lewis structure that one electron domain is due to a nonbonding pair, which occupies one of the four vertices of the tetrahedron. In determining the molecular geometry, we consider only the three N—H bond domains, which leads to a trigonal pyramidal geometry. The situation is just like the middle drawing in Figure 9.4 in which removing one atom from a tetrahedral molecule results in a trigonal pyramidal molecule. Notice that the tetrahedral arrangement of the four electron domains leads us to predict the trigonal-pyramidal molecular geometry.

Because the trigonal-pyramidal molecular geometry is based on a tetrahedral electron-domain geometry, the *ideal bond angles* are 109.5°. 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?

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:

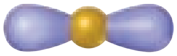
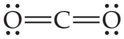
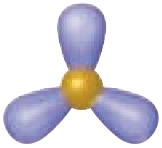
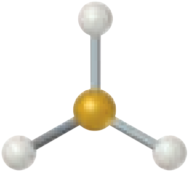
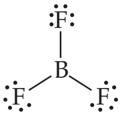
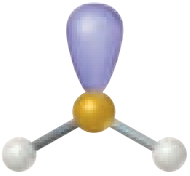
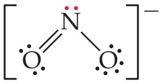
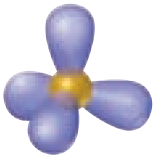
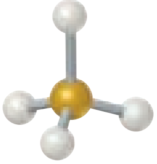
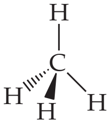
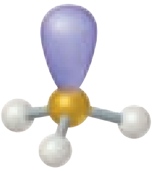
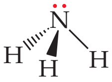
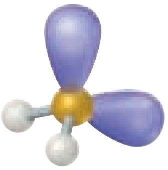
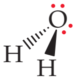


$$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$$

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	 $\ddot{O}=C=\ddot{O}$
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**) $SnCl_3^-$.

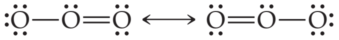
SOLUTION

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. (Notice that for O_3, the A and B atoms are all oxygen atoms.)

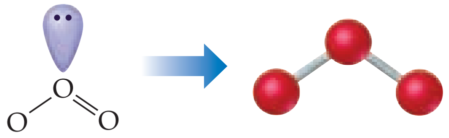
Plan To predict the molecular geometries, we draw their Lewis structures and count electron domains around the central atom to get the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

Solve

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

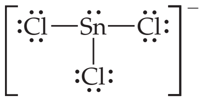


Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double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

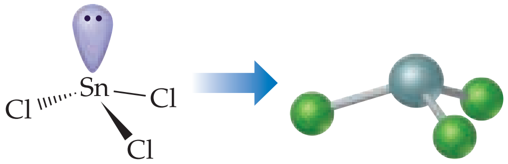


Comment As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(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 a tetrahedral electron-domain geometry (Table 9.1) with one vertex occupied by a nonbonding pair of electrons. A tetrahedral electron-domain geometry with three bonding and one nonbonding domains leads to a trigonal-pyramidal molecular geometry (Table 9.2).



Practice Exercise 1

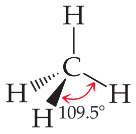
Consider the following AB_3 molecules and ions: PCl_3, SO_3, $AlCl_3$, SO_3^{2-}, and CH_3^+. How many of these molecules and ions do you predict to have a trigonal-planar molecular geometry?
(a) 1 **(b)** 2 **(c)** 3 **(d)** 4 **(e)** 5

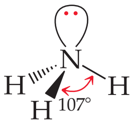
Practice Exercise 2

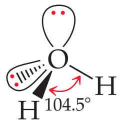
Predict the electron-domain and molecular geometries for **(a)** $SeCl_2$, **(b)** CO_3^{2-}.

Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

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

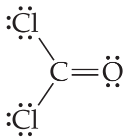




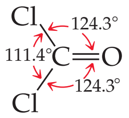


Notice that the bond angles decrease as the number of nonbonding electron pairs increases. A bonding pair of electrons is attracted by both nuclei of the bonded atoms, but a nonbonding pair is attracted primarily by only one nucleus. Because a nonbonding pair experiences less nuclear attraction, its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

Because multiple bonds contain a higher electronic-charge density than single bonds, multiple bonds also represent enlarged electron domains. Consider the Lewis structure of *phosgene*, Cl_2CO:



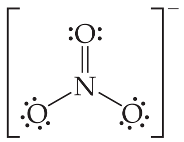
Because three electron domains surround the central atom, we might expect a trigonal-planar geometry with 120° bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the Cl—C—Cl bond angle to 111.4°:



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

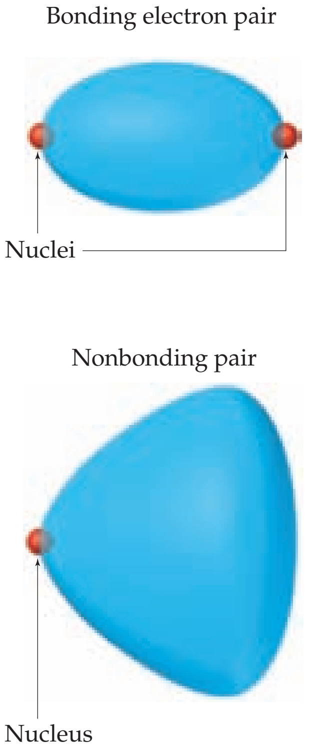
One resonance structure of the nitrate ion is



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?

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.**

Molecules with Expanded Valence Shells

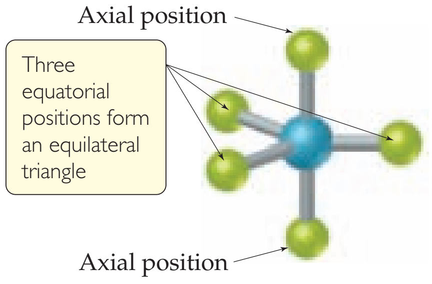
Atoms from period 3 and beyond may be surrounded by more than four electron pairs. (Section 8.7) Molecules with five or six electron domains around the central atom have molecular geometries based on either a *trigonal-bipyramidal* (five domains) or *octahedral* (six domains) electron-domain geometry (▶ 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.

GO FIGURE

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



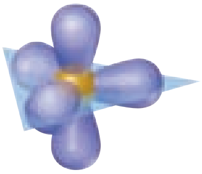
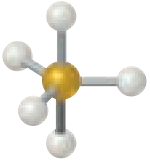
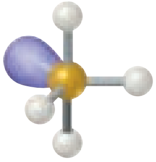
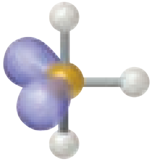
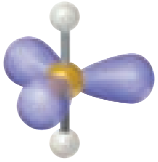
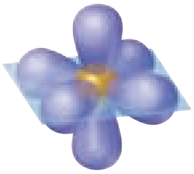
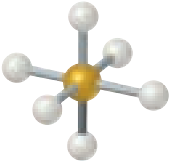
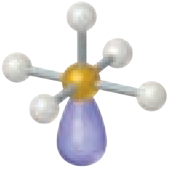
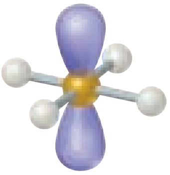
▲ **Figure 9.8 In a trigonal-bipyramidal geometry, there are two types of positions for the outer atoms.**

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?

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

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

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.

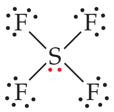
SOLUTION

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

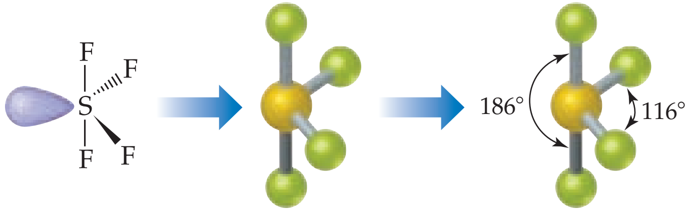
Plan We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.

Solve

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

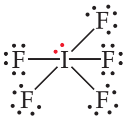


The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions,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

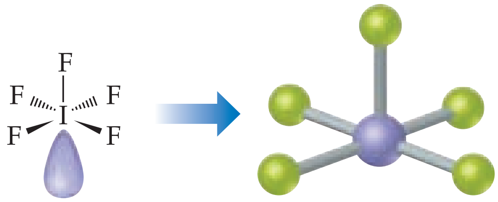


Comment The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are "pushed" by 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 the top F atom is 82°, smaller than the ideal 90° angle of an octahedron.

Practice Exercise 1

A certain AB_4 molecule has a square-planar molecular geometry. Which of the following statements about the molecule is or are true?:

(i) The molecule has four electron domains about the central atom A.
(ii) The B—A—B angles between neighboring B atoms is 90°.
(iii) The molecule has two nonbonding pairs of electrons on atom A.

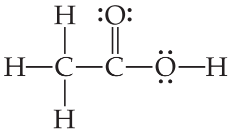
(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

Practice Exercise 2

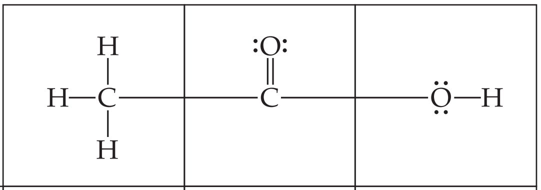
Predict the electron-domain and molecular geometries of (**a**) BrF_3, (**b**) SF_5^+.

Shapes of Larger Molecules

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



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



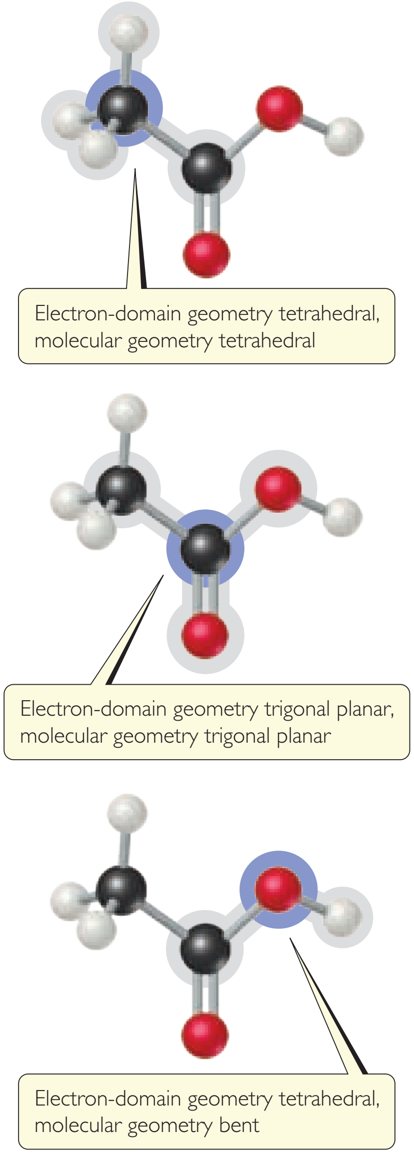
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

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

Our analysis of the acetic acid molecule is shown in ▶ Figure 9.9.

GO FIGURE

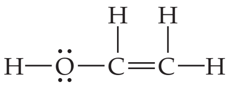
In the actual structure of acetic acid, which bond angle is expected to be the smallest?



▲ **Figure 9.9 The electron-domain and molecular geometries around the three central atoms of acetic acid, CH_3COOH.**

SAMPLE EXERCISE 9.3 Predicting Bond Angles

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



Predict the approximate values for the 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.

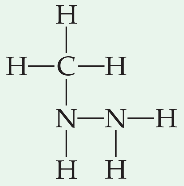
Plan To predict a bond angle, we determine the number of electron domains surrounding the middle atom in the bond. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

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 1

The atoms of the compound methylhydrazine, CH_6N_2, which is used as a rocket propellant, are connected as follows (note that lone pairs are not shown):

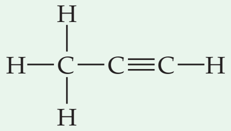


$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & H & & \\ & & | & & & & \\ & & N & - & N & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

What do you predict for the ideal values of the C—N—N and H—N—H angles, respectively?
(a) 109.5° and 109.5° **(b)** 109.5° and 120° **(c)** 120° and 109.5° **(d)** 120° and 120°
(e) None of the above

Practice Exercise 2

Predict the H—C—H and C—C—C bond angles in *propyne*:



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & C\equiv C & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

9.3 | Molecular Shape and Molecular Polarity

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

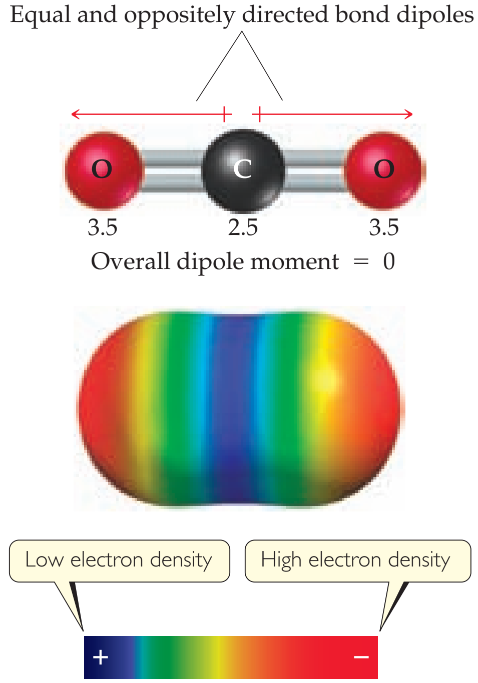
For a molecule consisting of more than two atoms, *the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule*. For each bond in the molecule, we consider the **bond dipole**, which is the dipole moment due only to the two atoms in that bond. Consider the 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 let's 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.

GO FIGURE

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

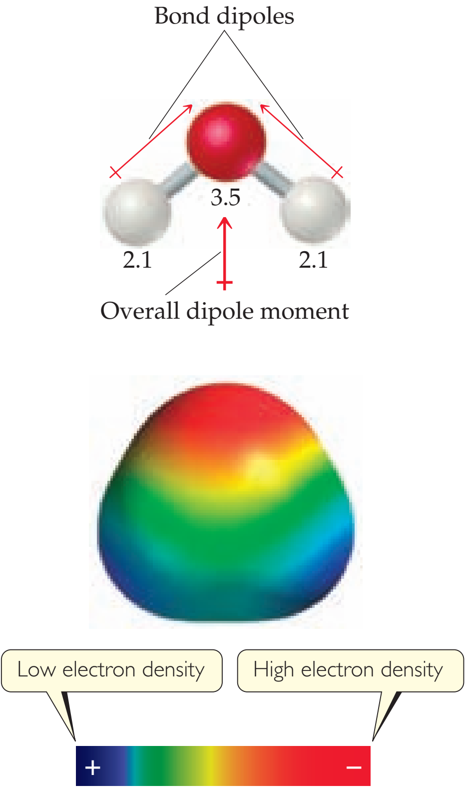


▲ **Figure 9.10** **CO_2, a nonpolar molecule.** The numbers are electronegativity values for these two atoms.

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 be nonpolar?

Figure 9.12 shows some examples of polar and nonpolar molecules, all with polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms (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.



▲ **Figure 9.11** **H_2O, a polar molecule.** 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.

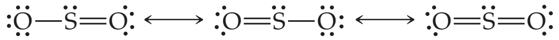
Solve

(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:

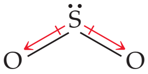
$Br—Cl$

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:

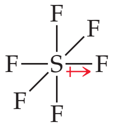


For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:



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:



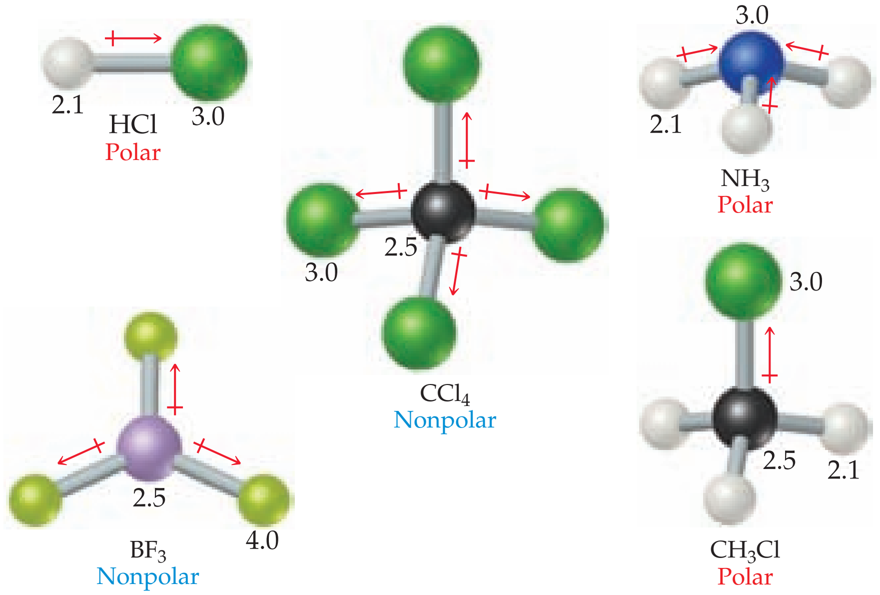
Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that $\mu = 0$.

Practice Exercise 1

Consider an AB_3 molecule in which A and B differ in electronegativity. You are told that the molecule has an overall dipole moment of zero. Which of the following could be the molecular geometry of the molecule? **(a)** Trigonal pyramidal **(b)** Trigonal planar **(c)** T-shaped **(d)** Tetrahedral **(e)** More than one of the above

Practice Exercise 2

Determine whether the following molecules are polar or nonpolar: **(a)** SF_4, **(b)** $SiCl_4$.



▲ **Figure 9.12** **Polar and nonpolar molecules containing polar bonds.** The numbers are electronegativity values.

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.

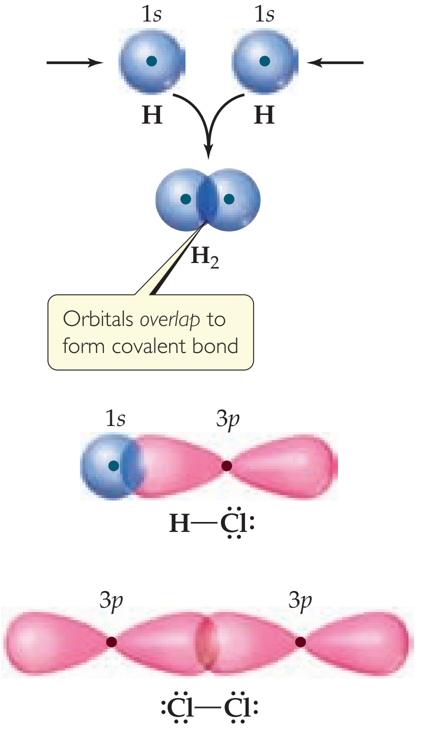
In Lewis theory, covalent bonding occurs when atoms share electrons because the sharing concentrates electron density between the nuclei. In valence-bond theory, we visualize the buildup of electron density between two nuclei as occurring when a valence atomic orbital of one atom shares space, or *overlaps*,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

◀ **Figure 9.13** shows three examples of how valence-bond theory describes the coming together of two atoms to form a molecule. In the example of the formation of H_2, each hydrogen 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.

The idea of orbital overlap producing a covalent bond applies equally well to other molecules. In HCl, for example, chlorine has the electron configuration $[\mathrm{Ne}]3s^2 3p^5$. 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 the covalent bond that holds HCl together (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.

GO FIGURE

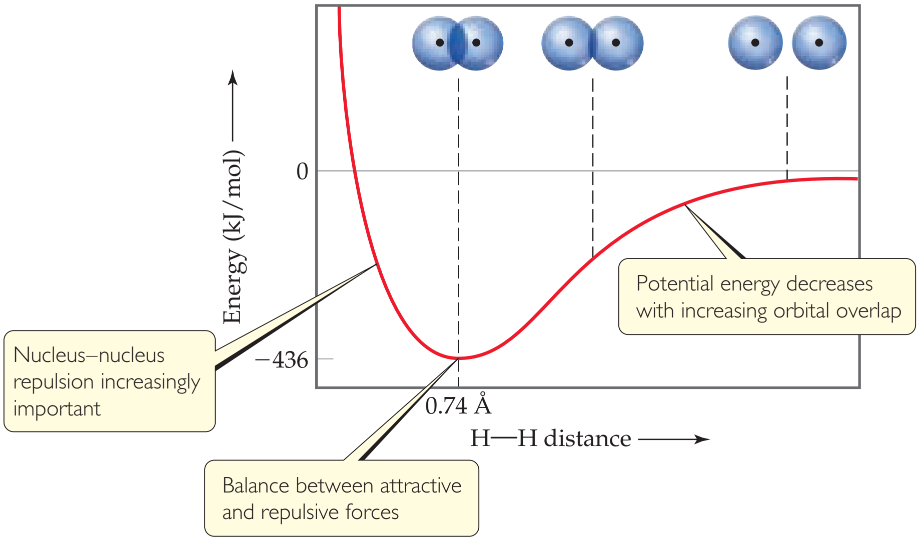
How does the notion of overlap explain why the bond in HCl is longer than the bond in H_2?



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

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.**

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 the energy increases sharply when the distance between the two hydrogen nuclei is less than 0.74 Å. The increase in potential energy of the system, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance at the minimum of the potential-energy curve (in this example, at 0.74 Å) corresponds to the bond length of the molecule. The potential energy at this minimum corresponds to the bond strength. Thus, the observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron–electron and nucleus–nucleus).

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, we would like to understand how to account for the tetrahedral arrangement of C—H bonds in methane in terms of the 2*s* and 2*p* orbitals of the central carbon atom, which are not directed toward the apices of a tetrahedron. How can we reconcile the notion that covalent bonds are formed from overlap of atomic orbitals with the molecular geometries that come from the VSEPR model?

To begin with, we recall that atomic orbitals are mathematical functions that come from the quantum mechanical model for atomic structure. ∞ (Section 6.5) To explain molecular geometries, we often assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called **hybrid orbitals**. The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called **hybridization**. The total number of atomic orbitals on an atom remains constant, so the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

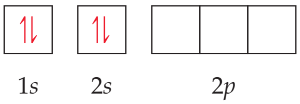
As we examine the common types of hybridization, notice the connection between the type of hybridization and some of the molecular geometries predicted by the VSEPR model: linear, bent, trigonal planar, and tetrahedral.

sp Hybrid Orbitals

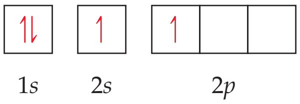
To illustrate the process of hybridization, consider the BeF_2 molecule, which has the Lewis structure

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 ($1s^2 2s^2 2p^5$) indicates an unpaired electron in a $2p$ orbital. This electron can be paired with an unpaired Be electron to form a polar covalent bond. Which orbitals on the Be atom, however, overlap with those on the F atoms to form the Be—F bonds?

The orbital diagram for a ground-state Be atom is

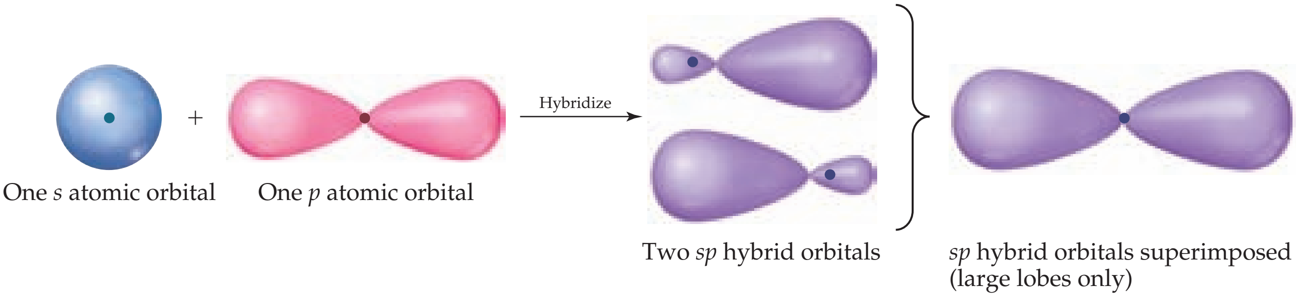


Because it has no unpaired electrons, the Be atom in its ground state cannot bond with the fluorine atoms. The Be atom could form two bonds, however, by envisioning that we "promote" one of the $2s$ electrons to a $2p$ orbital:



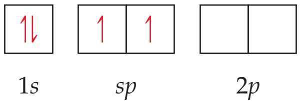
The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with F atoms. The two bonds would not be identical, however, because a Be $2s$ orbital would be used to form one of the bonds and a $2p$ orbital would be used to form the other. Therefore, although the promotion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

We can solve this dilemma by "mixing" the $2s$ orbital with one $2p$ 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 are shown in 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.**

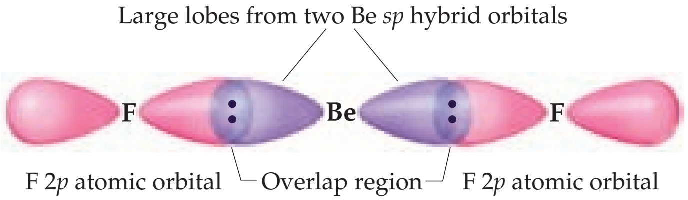
For the Be atom of BeF_2, we write the orbital diagram for the formation of two *sp* hybrid orbitals as



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 directions, BeF_2 has two identical bonds and a linear geometry. We have used one of the 2*p* orbitals in making the hybrids; 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.

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.**

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

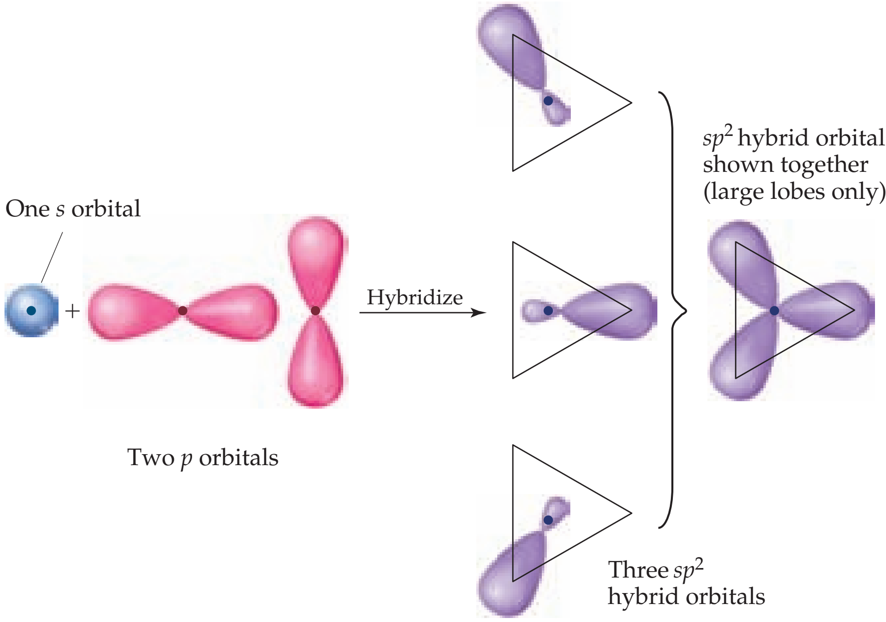
Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each hybrid orbital is equivalent to the others but points in a different direction. Thus, mixing one 2*s* and one 2*p* atomic orbital yields two equivalent *sp* hybrid orbitals that point in opposite directions (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; it is oriented perpendicular to the plane defined by the three sp^2 hybrid orbitals, with one lobe above and one below the plane. This unhybridized orbital will be important when we discuss double bonds in Section 9.6.

An *s* atomic orbital can 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 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

GO FIGURE

What is the angle formed between the large lobes of the three sp^2 hybrid orbitals?



▲ **Figure 9.17** **Formation of sp^2 hybrid orbitals.**

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.

Give It Some Thought

In an sp^2 hybridized atom, we saw that there was one unhybridized 2*p* orbital. How many unhybridized 2*p* orbitals remain on an atom that has sp^3 hybrid orbitals?

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.

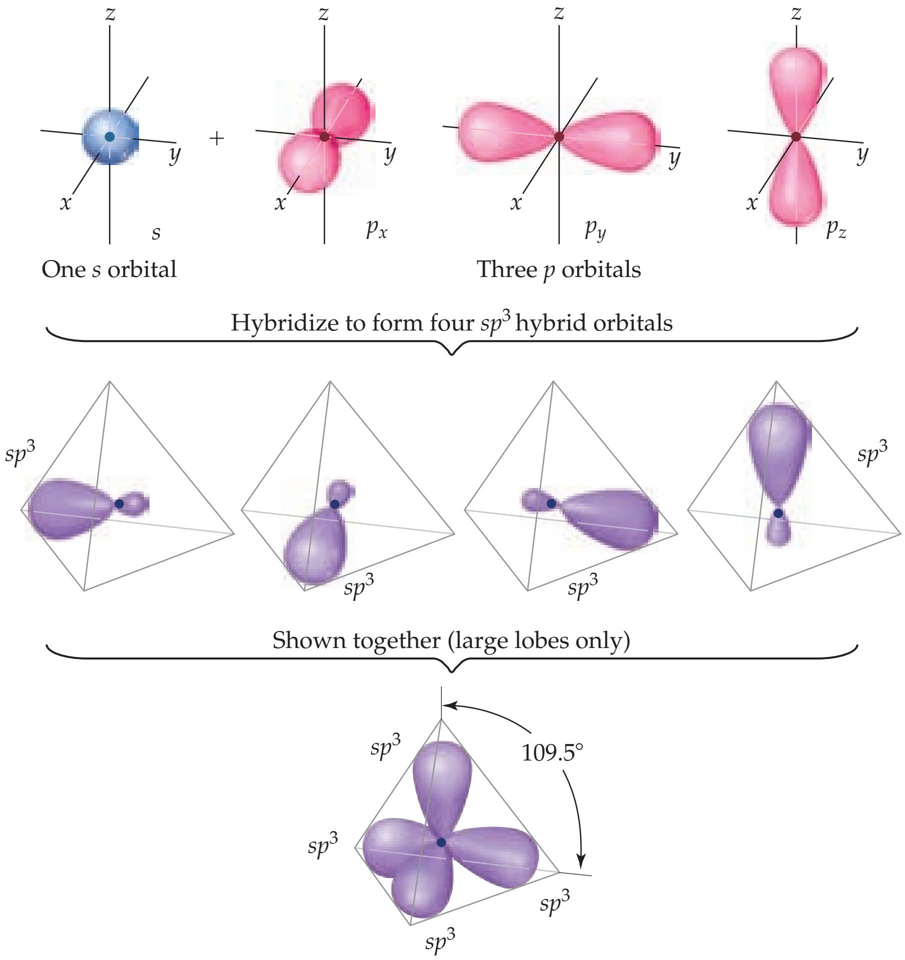
Hypervalent Molecules

So far our discussion of hybridization has extended only to period 2 elements, specifically carbon, nitrogen, and oxygen. The elements of period 3 and beyond introduce a new consideration because in many of their compounds these elements are **hypervalent**—they have more than an octet of electrons around the central atom. ∞ (Section 8.7) We saw in Section 9.2 that the VSEPR model works well to predict the geometries of hypervalent molecules such as PCl_5, SF_6, or BrF_5. But can we extend the use of hybrid orbitals to describe the bonding in these molecules? In short, the answer to this question is that it is best *not* to use hybrid orbitals for hypervalent molecules, as we now briefly discuss.

The valence-bond model we developed for period 2 elements works well for compounds of period 3 elements so long as we have no more than an octet of electrons in

GO FIGURE

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



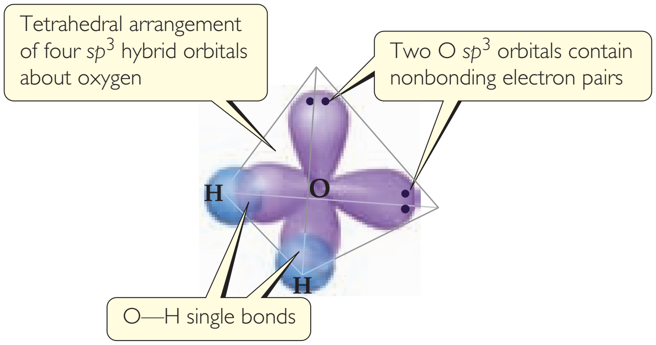
▲ Figure 9.18 **Formation of sp^3 hybrid orbitals.**

the valence-shell orbitals. Thus, for example, it is appropriate to discuss the bonding in PF_3 or H_2Se in terms of hybridized *s* and *p* orbitals on the central atom.

For compounds with more than an octet, we could imagine increasing the number of hybrid orbitals formed by including valence-shell *d* orbitals. For example, for SF_6 we could envision mixing in two sulfur 3*d* orbitals in addition to the 3*s* and three 3*p* orbitals to make a total of six hybrid orbitals. However, the sulfur 3*d* orbitals are substantially higher in energy than the 3*s* and 3*p* orbitals, so the amount of energy needed to form the six hybrid orbitals is greater than the amount returned by forming bonds with the six fluorine atoms. Theoretical calculations suggest that the sulfur 3*d* orbitals do not participate to a significant degree in the bonding between sulfur and the six fluorine atoms, and that it would not be valid to describe the bonding in SF_6 in terms of six hybrid orbitals. The more detailed bonding model needed to discuss the bonding in SF_6 and other hypervalent molecules requires a treatment beyond the scope of a general chemistry text. Fortunately, the VSEPR model, which explains the geometrical properties of such molecules in terms of electrostatic repulsions, does a good job of predicting their geometries.

GO FIGURE

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



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

This discussion reminds us that models in science are not reality but rather are our attempts to describe aspects of reality that we have been able to measure, such as bond distances, bond energies, molecular geometries, and so on. A model may work well up to a certain point but not beyond it, as is the case for hybrid orbitals. The hybrid orbital model for period 2 elements has proven very useful and is an essential part of any modern discussion of bonding and molecular geometry in organic chemistry. When it comes to molecules such as SF_6, however, we encounter the limitations of the model.

Hybrid Orbital Summary

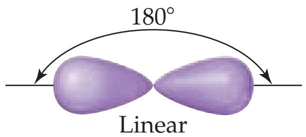
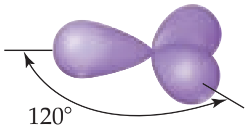
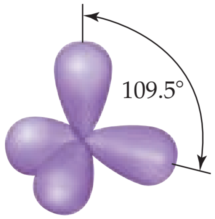
Overall, hybrid orbitals provide a convenient model for using valence-bond theory to describe covalent bonds in molecules that have an octet or less of electrons around the central atom and in which the molecular geometry conforms to the electron-domain geometry predicted by the VSEPR model. While the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

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**).

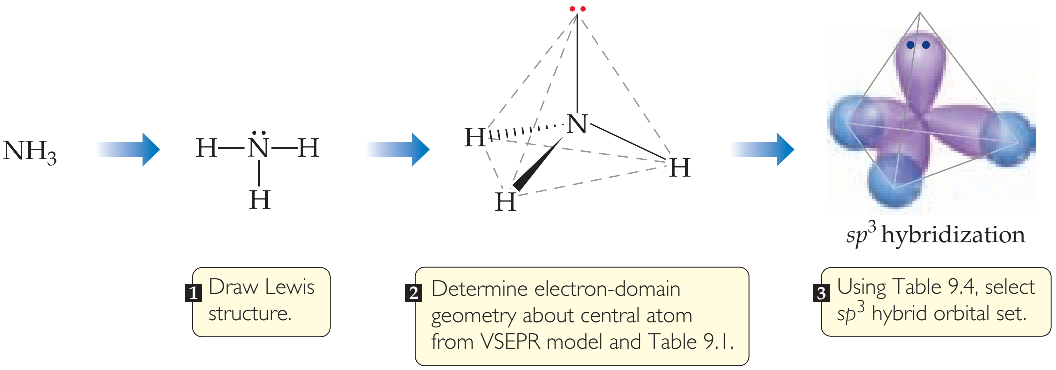
These steps are illustrated in ▶ **Figure 9.20**, which shows how the hybridization at N in NH_3 is determined.

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^+

GO FIGURE

How would we modify the figure if we were looking at PH_3 rather than NH_3?



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 to hold nonbonding electron pairs.

SAMPLE EXERCISE 9.5 Describing the Hybridization of a Central Atom

Describe 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 1

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

(a) CO_2 **(b)** H_2S **(c)** O_3 **(d)** CO_3^{2-}
(e) More than one of the above

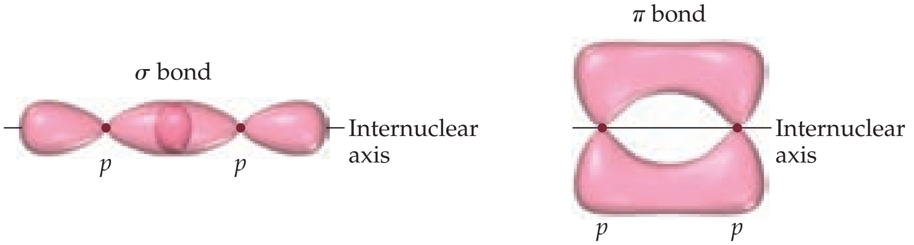
Practice Exercise 2

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

9.6 | Multiple Bonds

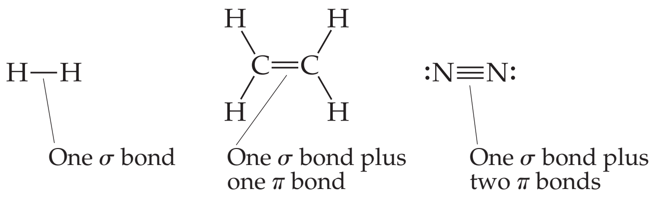
In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the *internuclear axis*). The line joining the two nuclei passes through the middle of the overlap region, forming a type of covalent bond called a **sigma** (σ) **bond**. The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

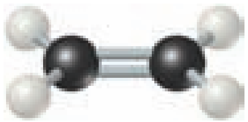
To describe multiple bonding, we must consider a second kind of bond, this one the result of overlap between two *p* orbitals oriented perpendicularly to the internuclear axis (Figure 9.21). The sideways overlap of *p* orbitals produces what is called a **pi** (π) **bond**. A π bond is one in which the overlap regions lie above and below the internuclear axis. Unlike 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.



▲ **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.

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:





▲ **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. Note that this unhybridized 2*p* orbital is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals.

Let's go through the steps of building the bonds in the ethylene molecule. Each sp^2 hybrid orbital on a carbon atom contains one electron. ▶ **Figure 9.23** shows how we can first envision forming the C—C σ bond by the overlap of two sp^2 hybrid orbitals, one on each carbon atom. Two electrons are used in forming the C—C σ bond. Next, the C—H σ bonds are formed by overlap of the remaining sp^2 hybrid orbitals on the C atoms with the 1*s* orbitals on each H atom. We use eight more electrons to form these four C—H bonds. Thus, 10 of the 12 valence electrons in the C_2H_4 molecule are used to form five σ bonds.

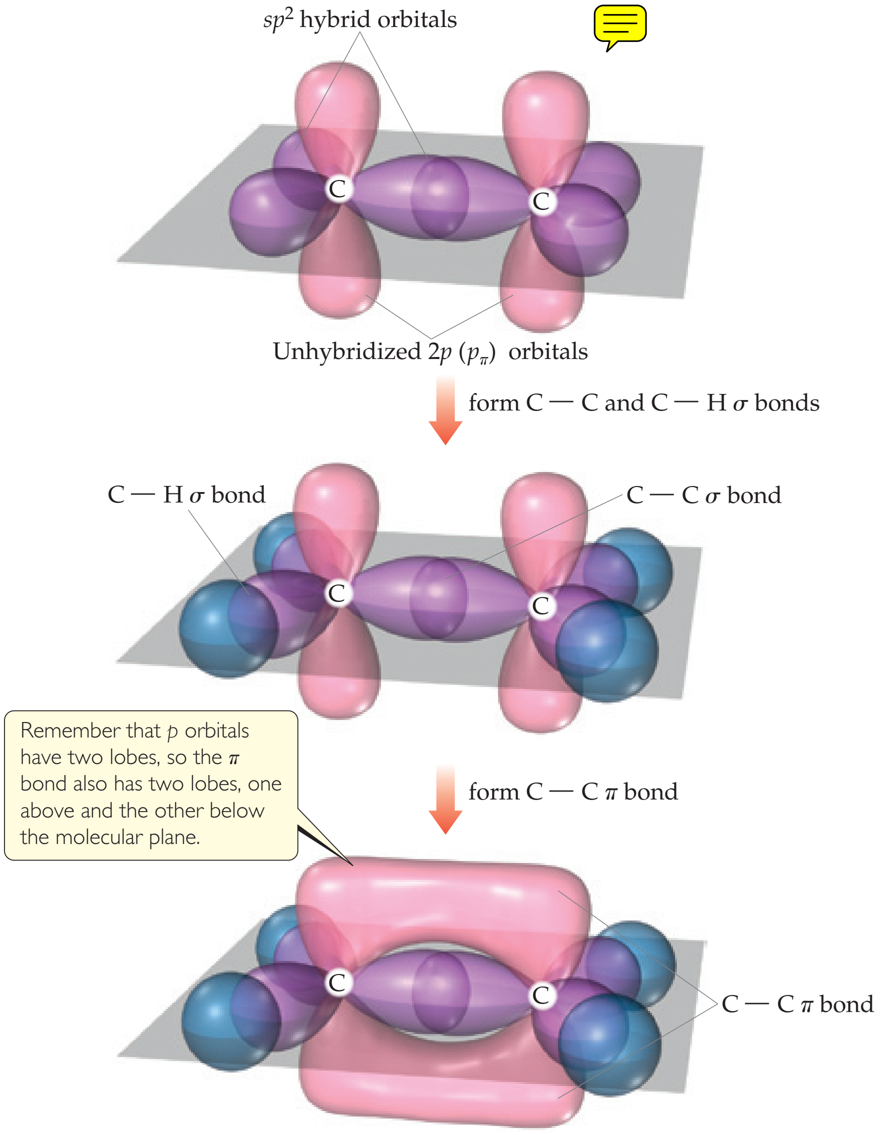
The remaining two valence electrons reside in the unhybridized 2*p* orbitals, one electron on each carbon. These two orbitals can overlap sideways with each other, as shown in Figure 9.23. The resultant electron density is concentrated above and below the C—C bond axis: It is a π bond (Figure 9.21). Thus, the C=C double bond in ethylene consists of one σ bond and one π bond.

We often refer to the unhybridized 2*p* atomic orbital of an sp^2 hybridized atom as a **p_π ("pee-pie") orbital** (because it is a *p* orbital that can be involved in forming a π bond). Thus, the two-electron π bond in ethylene is formed from the overlap of two p_π orbitals, one on each C atom and each holding one electron. Remember that the formation of the π bond involves the "sideways" overlap of the p_π orbitals as compared to the more direct "head on" overlap used in making the C—C and C—H σ bonds. As a result, 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 p_π orbitals on each C atom that make up the π bond can

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 π bond also has two lobes, one above and the other below the molecular plane.

▲ **Figure 9.23** **The orbital structure of ethylene, C_2H_4.**

achieve a good overlap only when the two CH_2 fragments 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

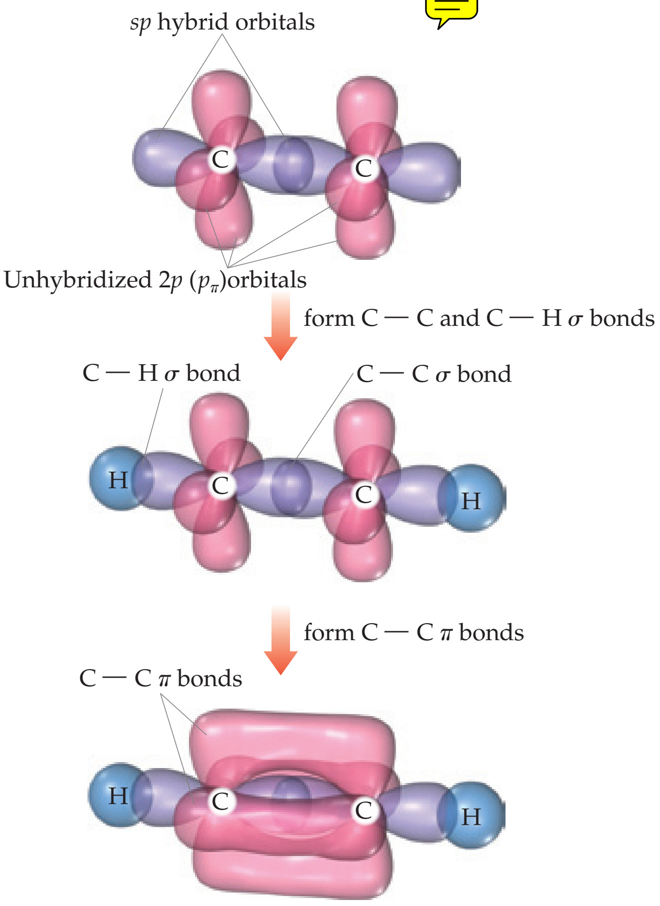
The molecule called *diazine* has the formula N_2H_2 and the Lewis structure

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

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)?

GO FIGURE

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



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

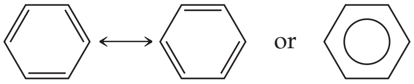
Triple bonds can also be explained using hybrid orbitals. Acetylene (C_2H_2), for example, is a linear molecule containing a triple bond: H—C≡C—H. The linear geometry suggests that each carbon atom uses *sp* hybrid orbitals to form σ bonds with the other carbon and one hydrogen. Each carbon atom thus has two unhybridized 2*p* orbitals at right angles to each other and to the axis of the *sp* hybrid set (◀ **Figure 9.24**). Thus, there are *two* p_π orbitals remaining on an *sp*-hybridized carbon atom. These p_π 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.

Resonance Structures, Delocalization, and π Bonding

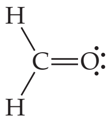
In the molecules we have discussed thus far in this section, the bonding electrons are *localized*. By this we mean that the σ and π electrons are associated totally with the two atoms that form the bond. In many molecules, however, we cannot adequately describe the bonding as being entirely localized. 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)



SAMPLE EXERCISE 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



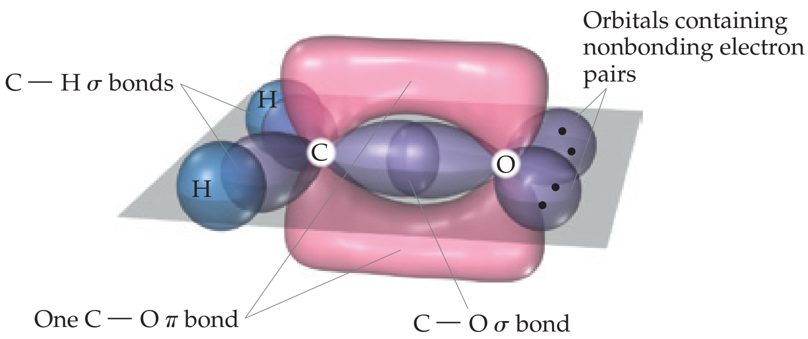
Describe how the bonds in formaldehyde are formed in terms of overlaps of hybrid and unhybridized orbitals.

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



▲ **Figure 9.25** **Formation of σ and π bonds in formaldehyde, H_2CO.**

(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 (a p_π 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 a p_π orbital that is perpendicular to the plane of the molecule. The two p_π orbitals overlap to form a C—O π bond (▲ Figure 9.25).

Practice Exercise 1

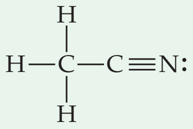
We have just arrived at a bonding description for the formaldehyde molecule. Which of the following statements about the molecule is or are true?

(i) Two of the electrons in the molecule are used to make the π bond in the molecule.
(ii) Six of the electrons in the molecule are used to make the σ bonds in the molecule.
(iii) The C—O bond length in formaldehyde should be shorter than that in methanol, H_3COH.

(a) Only one of the statements is true.
(b) Statements (i) and (ii) are true.
(c) Statements (i) and (iii) are true.
(d) Statements (ii) and (iii) are true.
(e) All three statements are true.

Practice Exercise 2

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



$$\begin{array}{c} \text{H} \\ | \\ \text{H—C—C}\equiv\text{N:} \\ | \\ \text{H} \end{array}$$

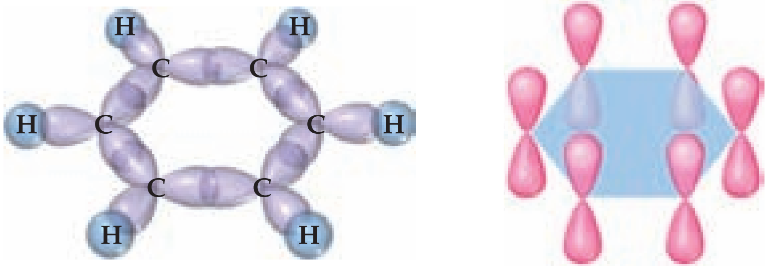
(b) Describe the hybridization at each carbon atom, and (**c**) determine the number of σ and π bonds in the molecule.

Benzene has a total of 30 valence electrons. To describe the bonding in benzene using hybrid orbitals, we first choose a hybridization scheme consistent with the geometry of the molecule. Because each carbon is surrounded by three atoms at 120° 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**). Thus, 24 of the valence electrons are used to form the σ bonds in the molecule.

Because the hybridization at each C atom is sp^2, there is one p_π orbital on each C atom, each oriented perpendicular to the plane of the molecule. The situation is very much like that in ethylene except we now have six p_π orbitals arranged in a ring

GO FIGURE

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

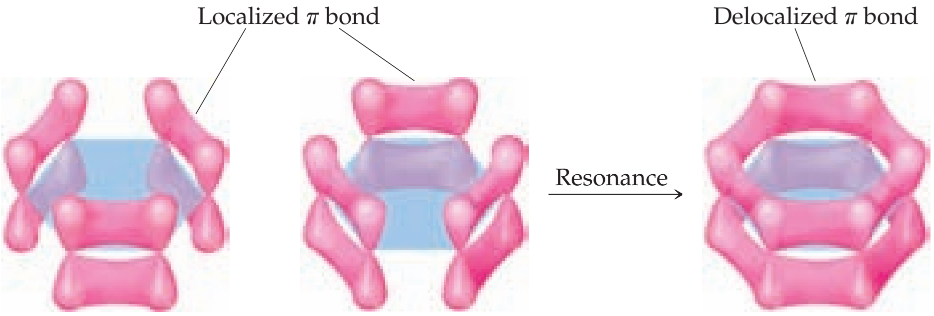


(a) σ bonds **(b)** p_π orbitals

▲ **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 2*p* orbitals on the six carbon atoms.

[Figure 9.26(b)]. The remaining six valence electrons occupy these six p_π orbitals, one per orbital.

We could envision using the p_π 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 smeared 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 benzene has a six-electron π system **delocalized** among the six carbon atoms. Delocalization of the electrons in its π bonds gives benzene a special stability. Electron delocalization in 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 p_π 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

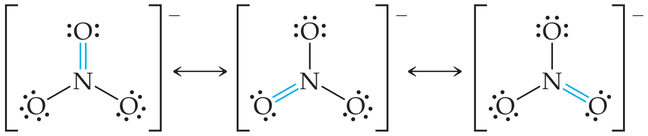
Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

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.

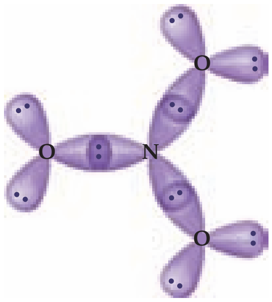
Plan Our first step is to draw Lewis structures. Multiple resonance structures involving the placement of the double bonds in different locations would suggest that the π component of the double bonds is delocalized.

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



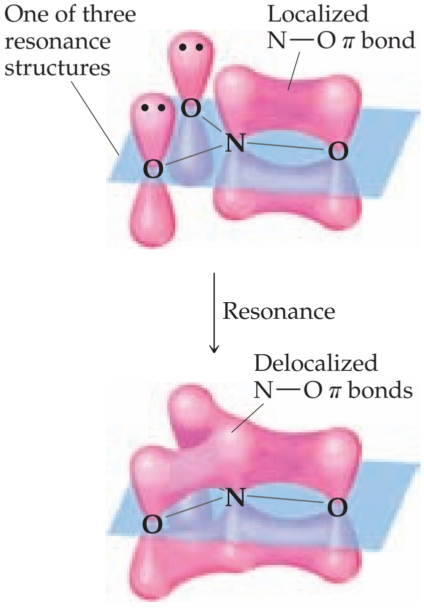
In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. It is helpful when considering delocalized π bonding to consider atoms with lone pairs that are bonded to the central atom to be sp^2 hybridized as well. Thus, we can envision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

The NO_3^- ion has 24 valence electrons. We can first use the sp^2 hybrid orbitals on the four atoms to construct the three N—O σ bonds. That uses all of the sp^2 hybrids on the N atom and one sp^2 hybrid on each O atom. Each of the two remaining sp^2 hybrids on each O atom is used to hold a nonbonding pair of electrons. Thus, for any of the resonance structures, we have the following arrangement in the plane of the ion:



Notice that we have accounted for a total of 18 electrons—six in the three N—O σ bonds, and 12 as nonbonding pairs on the O atoms. The remaining six electrons will reside in the π system of the ion.

The four p_π orbitals—one on each of the four atoms — are used to build the π system. 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 p_π orbital on N and a p_π orbital on one of the O atoms. The remaining two O atoms have nonbonding pairs in their p_π orbitals. Thus, for each of the resonance structures, we have the situation 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. We see that the NO_3^- ion has a six-electron π system delocalized among the four atoms in the ion.



▲ **Figure 9.28 Localized and delocalized representations of the six-electron π system in NO_3^-.**

Practice Exercise 1

How many electrons are in the π system of the ozone molecule, O_3?
(a) 2 **(b)** 4 **(c)** 6 **(d)** 14 **(e)** 18

Practice Exercise 2

Which of these species have delocalized bonding: SO_2, SO_3, SO_3^{2-}, H_2CO, NH_4^+?

General Conclusions about σ and π Bonding

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

1. Every pair of bonded atoms shares one or more pairs of electrons. Each bond line we draw in a Lewis structures represents two shared electrons. In every σ bond at least one pair of electrons is localized in the space between the atoms. 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. Because the electrons in σ bonds are localized in the region between two bonded atoms, they do not make a significant contribution to the bonding between any other two atoms.
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 can have π systems that extend over more than two bonded atoms. Electrons in extended π systems are said to be "delocalized." We can determine the number of electrons in the π system of a molecule using the procedures we discussed in this section.

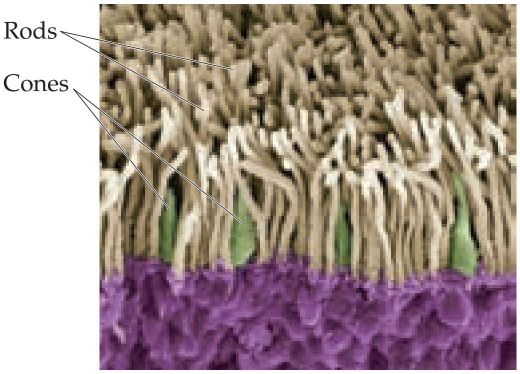
Chemistry and Life

The Chemistry of Vision

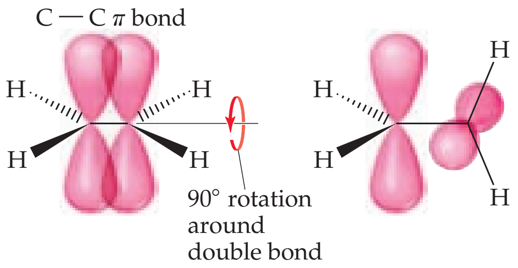
Vision begins when light is focused by the lens of the eye onto the retina, the layer of cells lining the interior of the eyeball. The retina contains *photoreceptor* cells called rods and cones (▼ Figure 9.29). The rods are sensitive to dim light and are used in night vision. The cones are sensitive 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 those same two atoms (Table 8.4). We are now in a position to appreciate another aspect of double bonds: They introduce rigidity into molecules.

Consider the C—C double bond in ethylene. Imagine rotating one —CH_2 group in ethylene relative to the other —CH_2 group, as pictured in ▶ Figure 9.30. This rotation destroys the overlap of the p_π 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. Rotation allows molecules with single bonds to twist and fold almost as if their atoms were attached by hinges.



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

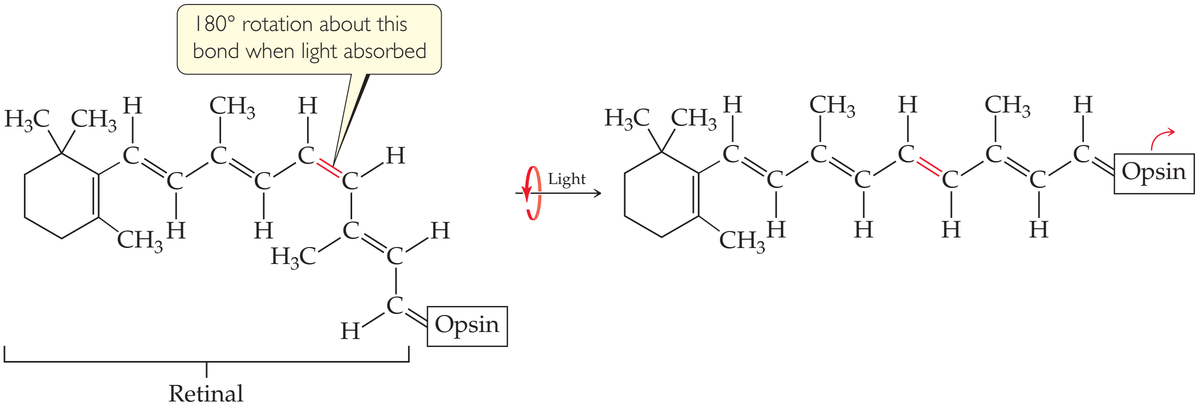


▲ Figure 9.30 **Rotation about the carbon–carbon double bond in ethylene breaks the π bond.**

Our vision depends on the rigidity of double bonds in retinal. In its normal form, retinal is held rigid by its double bonds. Light entering the eye is absorbed by rhodopsin, and it is the energy of that light which is used to break the π-bond portion of the double bond shown in red in ▶ Figure 9.31. Breaking the double bond allows rotation around the bond axis, changing the geometry of the retinal molecule. The retinal then separates from the opsin, triggering the reactions that produce a nerve impulse that the brain interprets as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus, only five photons of light are necessary to stimulate the eye.

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: 9.112, 9.116



▲ **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

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

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

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

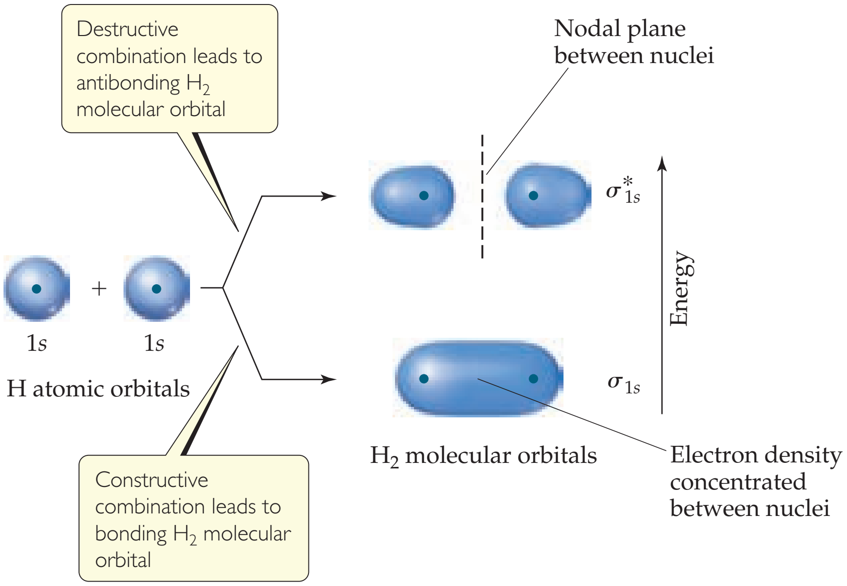
Molecular Orbitals of the Hydrogen Molecule

We begin our study of MO theory with the hydrogen molecule, H_2. We will use the two $1s$ atomic orbitals (one on each H atom) to construct molecular orbitals for H_2. *Whenever two atomic orbitals overlap, two molecular orbitals form.* Thus, the overlap of the $1s$ orbitals of two hydrogen atoms to form H_2 produces two MOs. The first MO, which is shown at the bottom right of **Figure 9.32**, is formed by adding the wave functions for the two $1s$ orbitals. We refer to this as *constructive combination*. The energy of the resulting MO is lower in energy than the two atomic orbitals from which it was made. It is called the **bonding molecular orbital**.

The second MO is formed by what is called *destructive combination:* combining the two atomic orbitals in a way that causes the electron density to be canceled in the central region where the two overlap. The process is discussed more fully in the "Closer Look" box later in the chapter. The energy of the resulting MO, referred to as the **antibonding molecular orbital**, is higher than the energy of the atomic orbitals. The antibonding MO of H_2 is shown at the top right in Figure 9.32.

GO FIGURE

What is the value of the σ^*_{1s} MO wave function at the nodal plane?



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

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 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, an antibonding MO excludes electrons from the very region in which a bond must be formed. Antibonding orbitals invariably have a *plane* in the region between the nuclei where the electron density is zero. This plane is called a **nodal plane** of the MO. (The nodal plane is shown as a dashed line in Figure 9.32 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.

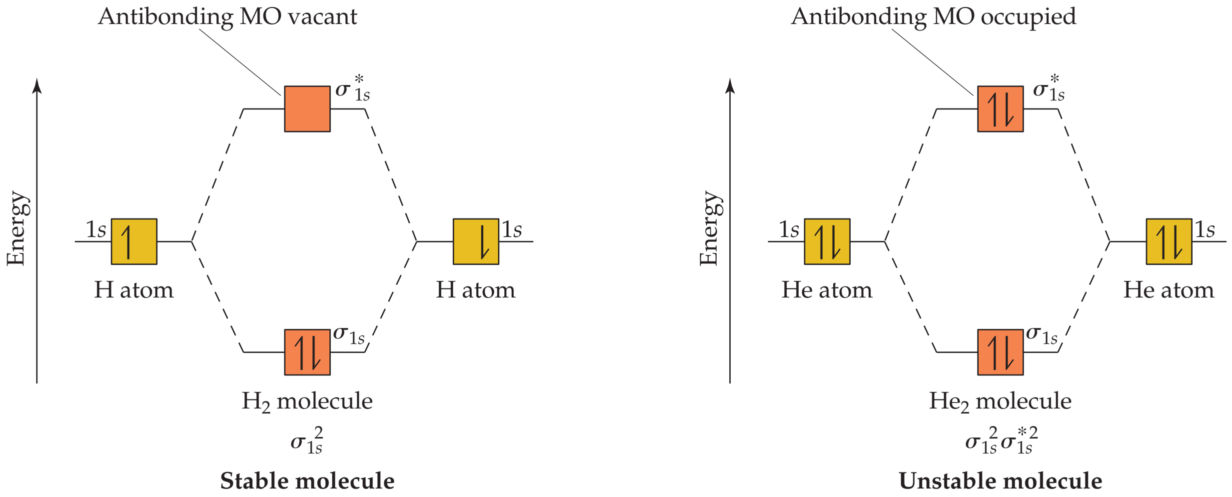
Notice from Figure 9.32 that the electron density in both the bonding MO and the antibonding MO of H_2 is centered about the internuclear axis. MOs of this type are called **sigma (σ) molecular orbitals** (by analogy to σ bonds). The bonding sigma MO of H_2 is labeled σ_{1s}; the subscript indicates 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 has one electron, so there are two electrons in H_2. These two electrons occupy the lower-energy bonding

GO FIGURE

What would happen to the energy of the σ_{1s} MO if the H atoms in H_2 were pulled apart to a distance twice as long as its normal bond length?



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

(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 H 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_{1s}^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 σ^*_{1s} MO. The electron configuration of He_2 is thus $\sigma_{1s}^2\sigma_{1s}^{*2}$. The energy decrease realized in going from He atomic orbitals to the He bonding MO is offset by the energy increase realized in going from the atomic orbitals to the He antibonding MO.* 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:

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

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

Let's now consider the bond order in H_2 and He_2, referring to Figure 9.33. H_2 has two bonding electrons and zero antibonding electrons, so it has a bond order of 1.

---

*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.

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 σ^*_{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.

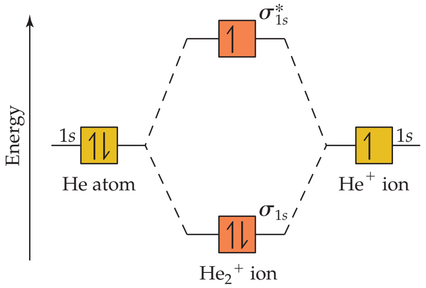
Solve The energy-level diagram for the He_2^+ ion is shown in ◀ Figure 9.34. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

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

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.

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**

Practice Exercise 1

How many of the following molecules and ions have a bond order of $\frac{1}{2}$: H_2, H_2^+, H_2^-, and He_2^{2+}?
(a) 0 **(b)** 1 **(c)** 2 **(d)** 3 **(e)** 4

Practice Exercise 2

What are the electron configuration and the bond order of the H_2^- ion?

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

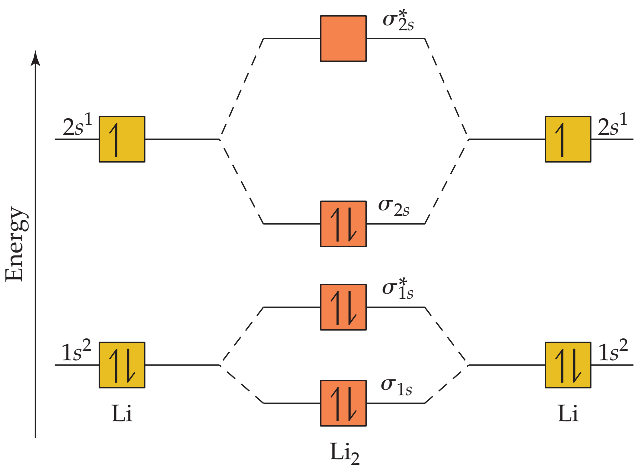
Lithium has the electron configuration $1s^22s^1$. When lithium metal is heated above its boiling point (1342 °C), Li_2 molecules are found in the vapor phase. The Lewis structure for Li_2 indicates a Li—Li single bond. We will now use MOs to describe the bonding in Li_2.

▶ **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). 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, the energy of the σ^*_{1s} antibonding MO is much lower than the energy of σ_{2s} bonding MO.

GO FIGURE

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



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

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. Therefore, we completely fill the σ_{1s}, σ^*_{1s}, σ_{2s}, and σ^*_{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

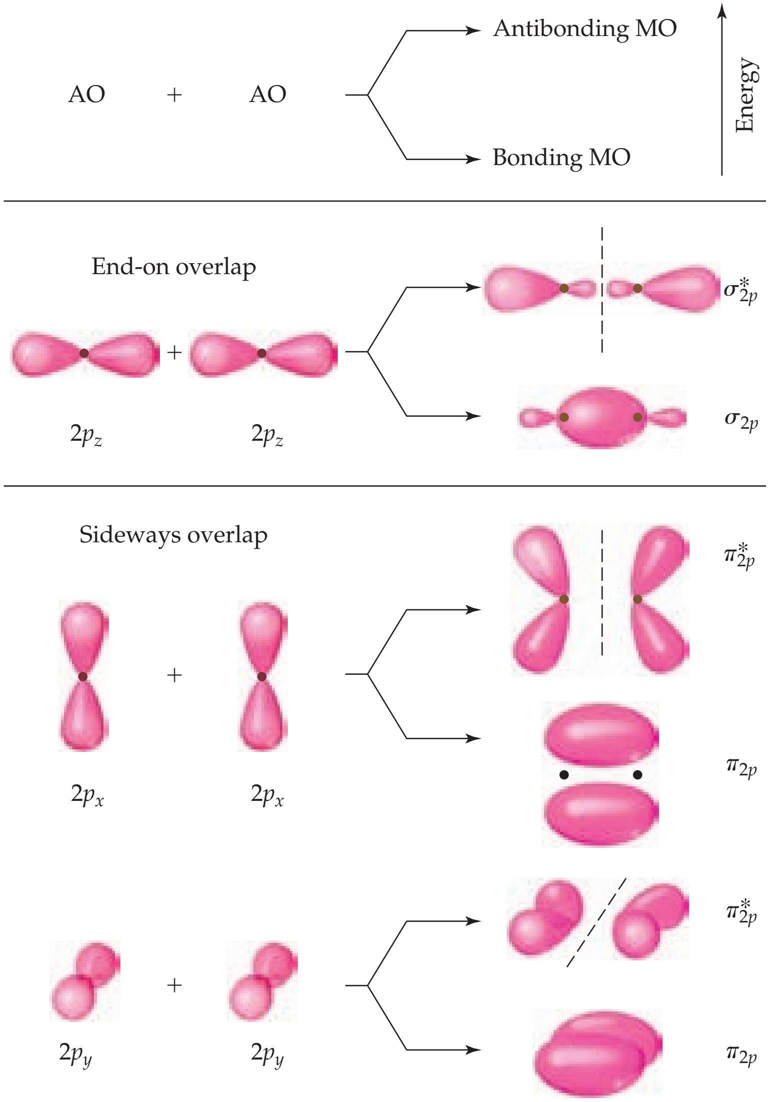
Would you expect Be_2^+ to be a stable ion?

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

GO FIGURE

In which MO is the overlap of atomic orbitals greater, a σ_{2p} or a π_{2p}?



▲ **Figure 9.36** **Contour representations of the molecular orbitals formed by 2*p* orbitals.**

molecular orbital. In both MOs, the electron density lies along the internuclear axis, so they are σ molecular orbitals: σ_{2p} and σ^*_{2p}.

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

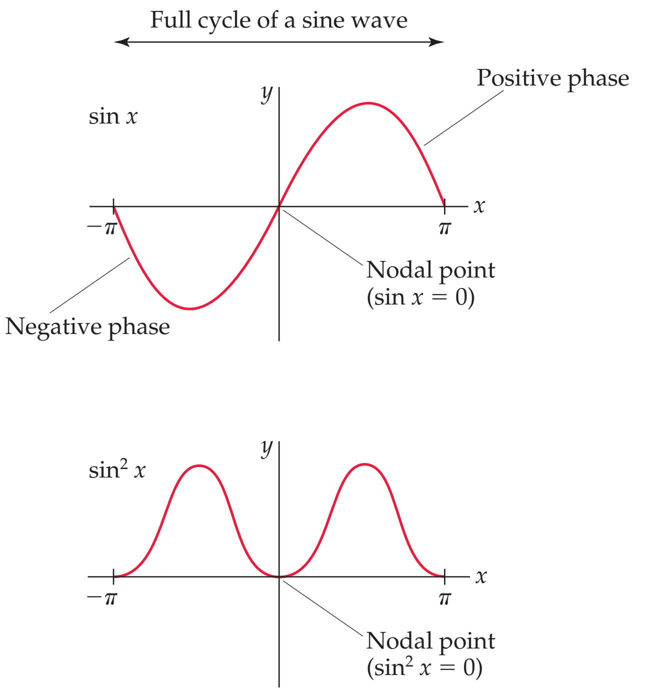
The $2p_z$ orbitals on two atoms point directly at each other. Hence, the overlap of two $2p_z$ orbitals is greater than that of two $2p_x$ or $2p_y$ orbitals. From rule 3 we therefore expect the σ_{2p} MO to be lower in energy (more stable) than the π_{2p} MOs. Similarly, the σ^*_{2p} MO should be higher in energy (less stable) than the π^*_{2p} MOs.

A Closer Look

Phases in Atomic and Molecular Orbitals

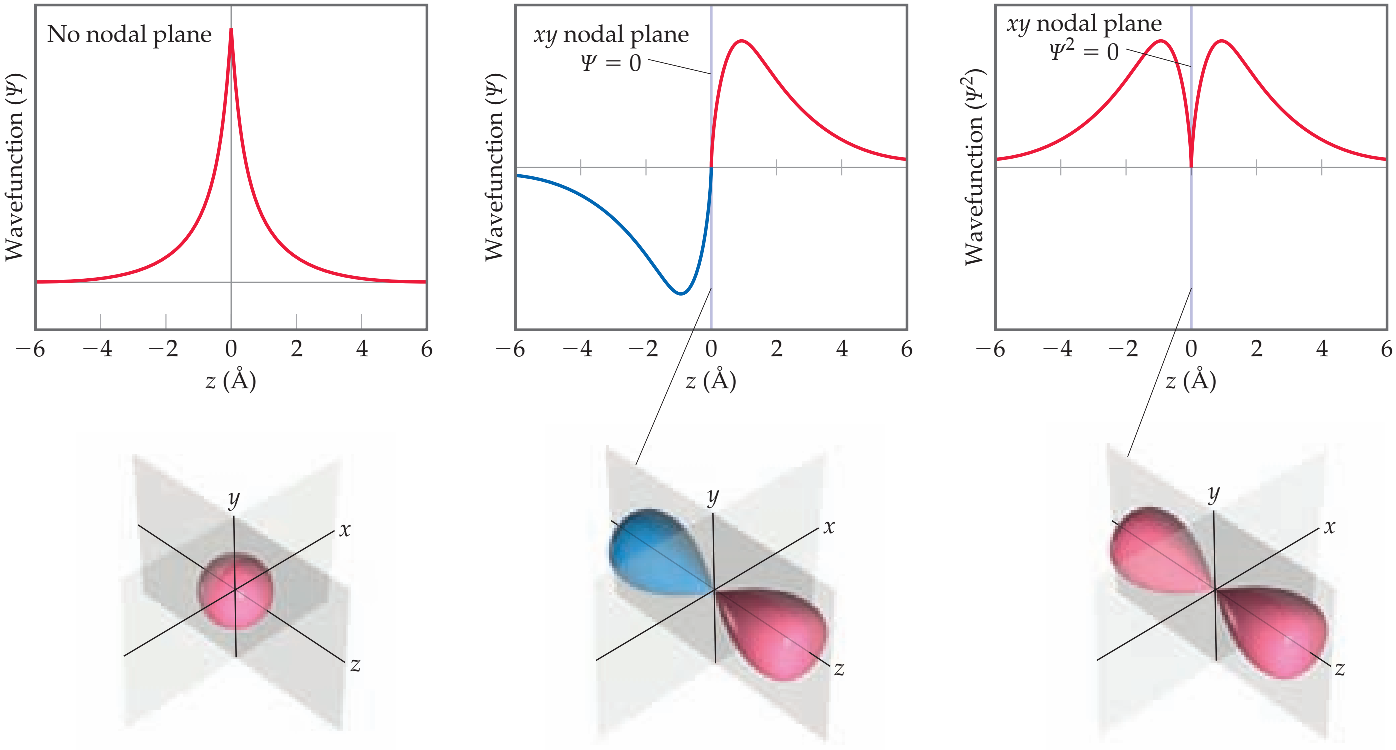
Our discussion of atomic orbitals in Chapter 6 and molecular orbitals in this chapter highlights some of the most important applications of quantum mechanics in chemistry. In the quantum mechanical treatment of electrons in atoms and molecules, we are mainly interested in determining two characteristics 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. The situation is like that of 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 $1s$ 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 the $1s$ 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 $1s$ orbital. Notice that the value of the $1s$ wave function is always a positive number (we show positive values in red in Figure 9.38). 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 6.22.



$1s$ orbital

$2p_z$ orbital

$(2p_z)^2$ orbital

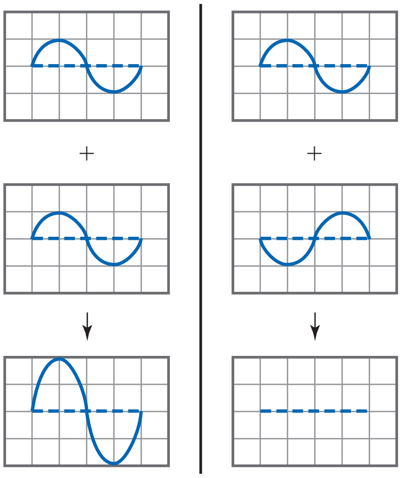
▲ **Figure 9.38 Phases in wave functions of *s* and *p* atomic orbitals.** Red shading means a positive value for the wave function and blue shading means a negative value.

In the graph for the $2p_z$ orbital in Figure 9.38, the wave function changes sign when it passes through $z = 0$. Notice that the two halves of the wave have the same shape except that one has positive (red) values and the other negative (blue) values. Analogously to the sine function, the wave function changes phase when it passes through the origin. Mathematically the $2p_z$ wave function is equal to zero whenever $z = 0$. This corresponds to any point on the *xy* plane, so we say that the *xy* plane is a *nodal plane* of the $2p_z$ orbital. The wave function for a *p* orbital is much like a sine function because it has two equal parts that have opposite phases. Figure 9.38 gives a typical representation used by chemists of the wave function for a p_z orbital.* The red and blue lobes indicate the different phases of the orbital. (Note: The colors do *not* represent charge, as they did in the plots in Figures 9.10 and 9.11.) As with the sine function, the origin is a node.

The third graph in Figure 9.38 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.

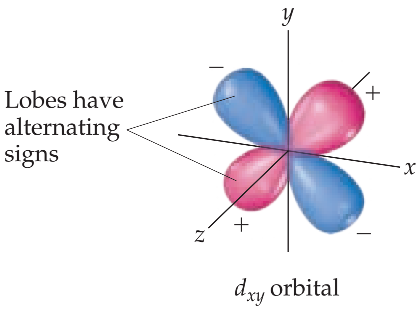
The lobes of the wave functions for the *d* orbitals also have different phases. For example, the wave function for a d_{xy} orbital has four lobes, with the phase of each lobe opposite the phase of its nearest neighbors (▶ **Figure 9.39**). The wave functions for the other *d* orbitals likewise have 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:



Constructive combination

Destructive combination



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

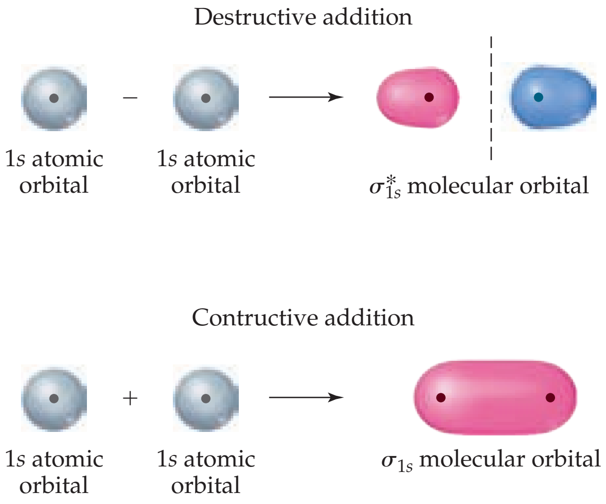
but if you add two sine functions having opposite phases, they add *destructively* and cancel each other.

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 $\sigma^{\star}_{1s}$ 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 red and blue shading to denote positive and negative phases in the H atomic orbitals. However, chemists may alternatively draw contour representations in different colors, or with one phase shaded and one unshaded, to denote the two phases.

When we square the wave function of the $\sigma^{\star}_{1s}$ 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.

The wave functions of atomic and molecular orbitals are used by chemists to understand many aspects of chemical bonding, spectroscopy, and reactivity. If you take a course in organic chemistry, you will probably see orbitals drawn to show the phases as in this box.

Related Exercises: 9.107, 9.119, 9.121



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

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*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 6.23.

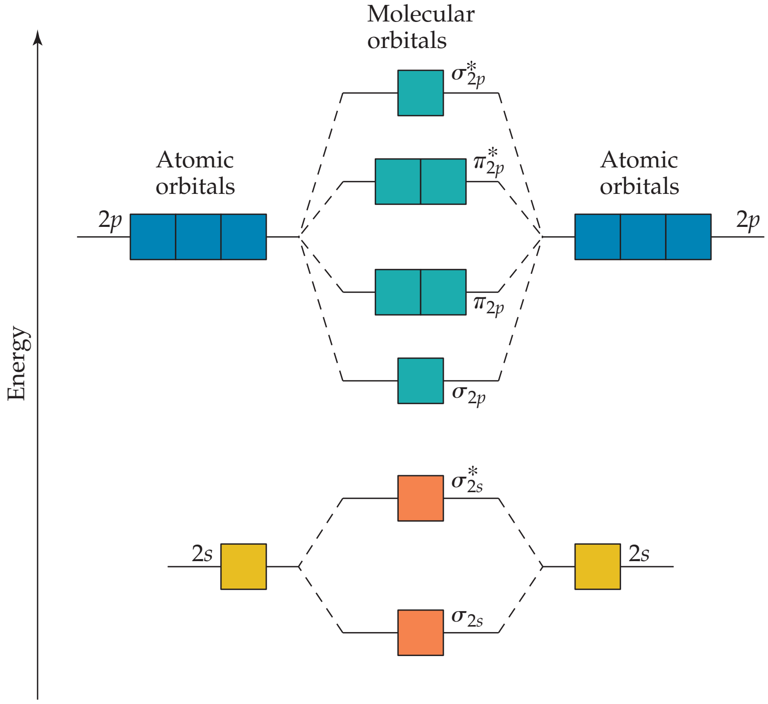
Electron Configurations for B_2 through Ne_2

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.

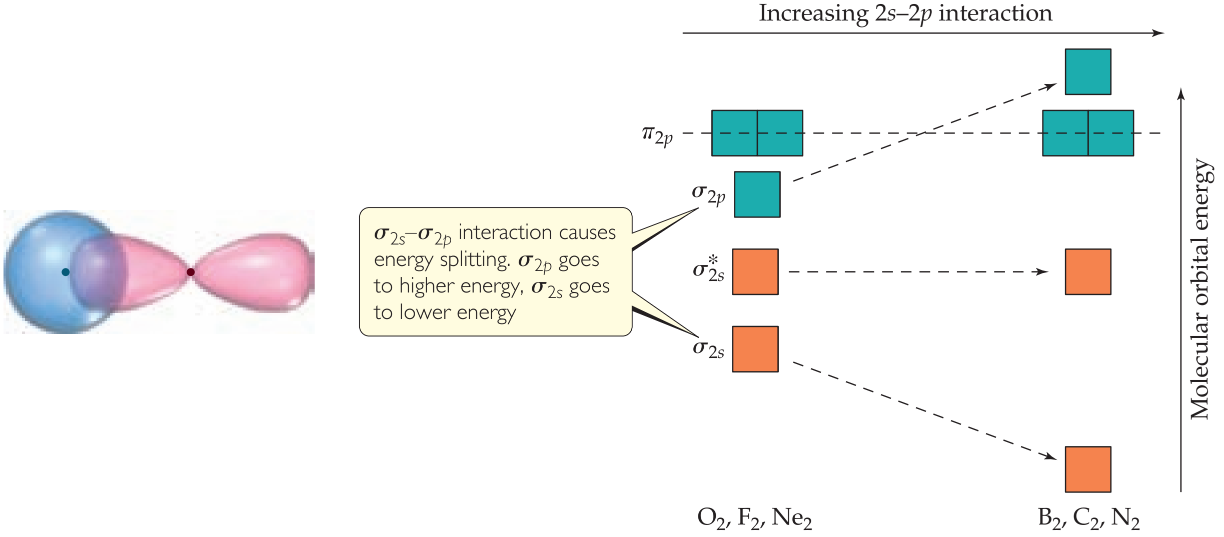
Given the energy ordering of the molecular orbitals, it is a simple matter to determine the electron configurations for the diatomic molecules B_2 through Ne_2. For example, a boron atom has three valence electrons. (Remember that we are ignoring the core 1*s* electrons.) Thus, for B_2 we must place 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



▲ **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.**

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.

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?

	Large 2s–2p interaction				**Small 2s–2p interaction**		
	B_2	**C_2**	**N_2**		**O_2**	**F_2**	**Ne_2**
σ^*_{2p}	☐	☐	☐	σ^*_{2p}	☐	☐	↑↓
π^*_{2p}	☐ ☐	☐ ☐	☐ ☐	π^*_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓
σ_{2p}	☐	☐	↑↓	π_{2p}	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
π_{2p}	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	σ_{2p}	↑↓	↑↓	↑↓
σ^*_{2s}	↑↓	↑↓	↑↓	σ^*_{2s}	↑↓	↑↓	↑↓
σ_{2s}	↑↓	↑↓	↑↓	σ_{2s}	↑↓	↑↓	↑↓
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.**

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?

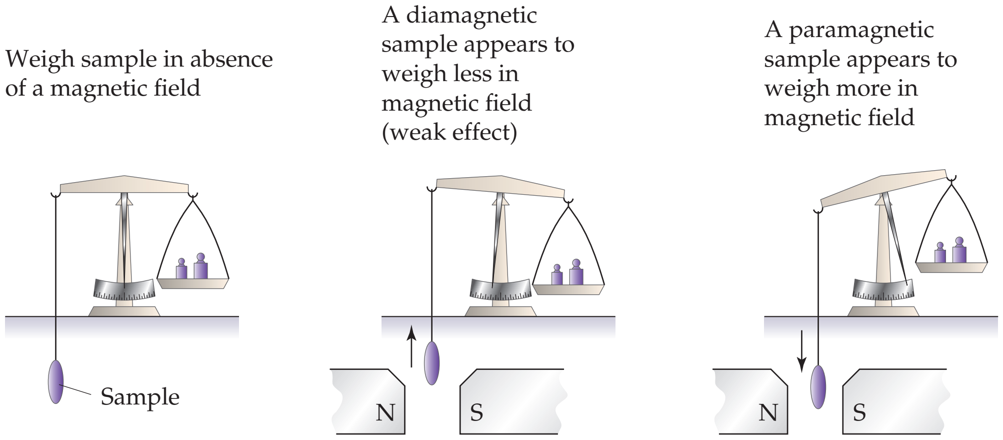
Electron configurations in molecules can also be related to bond distances and bond enthalpies. (Section 8.8) As bond order increases, bond distances decrease and bond enthalpies increase. N_2, for example, whose bond order is 3, has a short bond distance and a large bond enthalpy. The N_2 molecule does not react readily with other substances to form nitrogen compounds. The 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:

$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$$

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 the molecule contains two unpaired electrons and should therefore be paramagnetic, a detail not discernible in the Lewis structure. The paramagnetism of O_2 is demonstrated in **Figure 9.45**, which confirms the prediction from MO theory. The MO description also correctly predicts a bond order of 2 as did the Lewis structure.

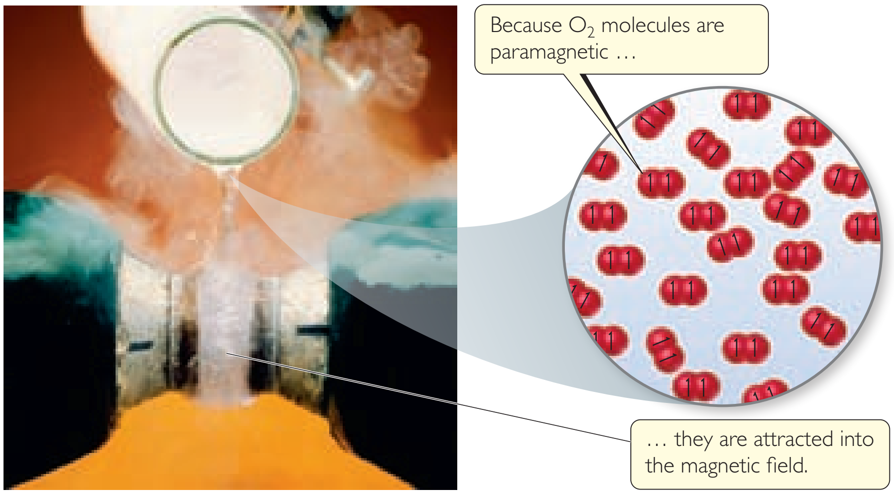
Going from O_2 to F_2, we add two electrons, completely filling the π^*_{2p} MOs. Thus, F_2 is expected to be diamagnetic and have an F—F single bond, in accord with its Lewis structure. Finally, the addition of two more electrons to make Ne_2 fills all the bonding and antibonding MOs. Therefore, the bond order of Ne_2 is zero, and the molecule is not expected to exist.



▲ **Figure 9.44** **Determining the magnetic properties of a sample.**

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.** When liquid oxygen is poured through a magnet, it "sticks" to the poles.

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 π_{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 1

Place the following molecular ions in order from smallest to largest bond order: C_2^{2+}, N_2^-, O_2^-, and F_2^-.

(a) $C_2^{2+} < N_2^- < O_2^- < F_2^-$ **(b)** $F_2^- < O_2^- < N_2^- < C_2^{2+}$
(c) $O_2^- < C_2^{2+} < F_2^- < N_2^-$ **(d)** $C_2^{2+} < F_2^- < O_2^- < N_2^-$
(e) $F_2^- < C_2^{2+} < O_2^- < N_2^-$

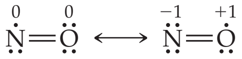
Practice Exercise 2

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

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:



$$\overset{0}{\mathrm{N}}=\overset{0}{\mathrm{O}} \longleftrightarrow \overset{-1}{\mathrm{N}}=\overset{+1}{\mathrm{O}}$$

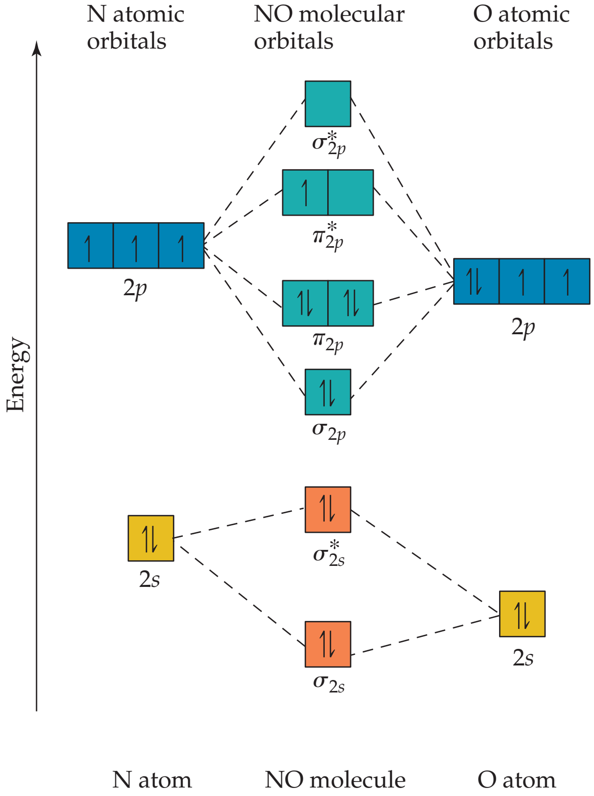
Both structures indicate the presence of a double bond, but when compared with the molecules in Figure 9.43, the experimental bond length of NO (1.15 Å) suggests a bond order greater than 2. How do we treat NO using the MO model?

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 $2s$ and $2p$ 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 $2s$ and $2p$ orbitals on the two atoms interact, the same types of MOs are produced.

There is one other important difference in the MOs of heteronuclear molecules. The MOs are still a mix of atomic orbitals from both atoms, but in general *an MO in a heteronuclear diatomic molecule has a greater contribution from the atomic orbital to which it is closer in energy*. In the case of NO, for example, the σ_{2s} bonding MO is closer in energy to the O $2s$ atomic orbital than to the N $2s$ 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 σ^*_{2s} antibonding MO is weighted more heavily toward the N atom because that MO is closest in energy to the N $2s$ 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.**

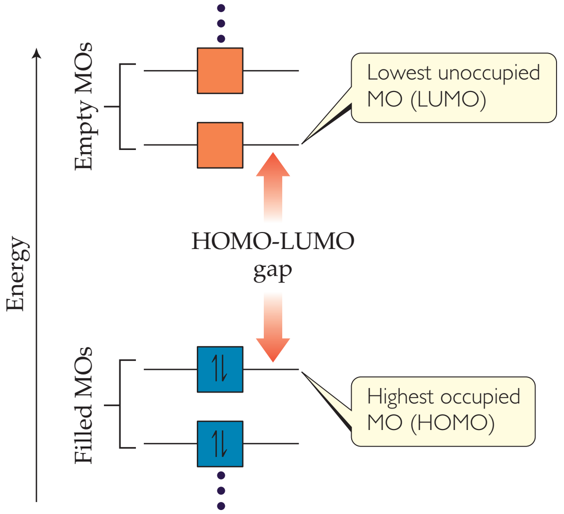
Chemistry Put to Work

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. One of the most remarkable sources of clean energy is the Sun, which receives plenty of energy daily to power the world for millions of years. Our challenge is to capture enough of this energy in a form that allows us to use it as needed. *Photovoltaic solar cells* convert the light from the Sun into usable electricity, and the development of more efficient solar cells is one way to address Earth's future energy needs.

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

In discussing light absorption by molecules, we can focus on the two MOs shown in ▶ **Figure 9.47**. 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).



▲ **Figure 9.47 Definitions of the highest occupied and lowest unoccupied molecular orbitals.** The energy difference between these is the HOMO-LUMO gap.

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—molecules that can absorb more of the solar spectrum. If the HOMO of these molecules is higher in energy than the HOMO of TiO_2, the excited electrons will flow from the molecules into the TiO_2, thereby generating electricity when the device is illuminated with light and connected to an external circuit.

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

Related Exercises: 9.109, 9.120, Design an Experiment

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 π^*_{2p} MOs, which have a greater contribution from the N atom. (We could have placed this electron in either the left or right π^*_{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 7.27). Heating elemental sulfur to high temperatures produces gaseous S_2 molecules:

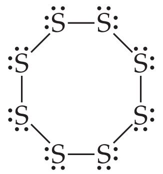
$$S_8(s) \longrightarrow 4\,S_2(g)$$

(**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 $[Ne]3s^23p^4$ electron configuration. It is expected to be most similar electronically to oxygen (electron configuration, $[He]2s^22p^4$), which is immediately above it in the periodic table.

(b) The Lewis structure of S_8 is



There is a single bond between each pair of S atoms and two nonbonding electron pairs on each S atom. Thus, we see four electron domains around each S atom and expect a tetrahedral electron-domain geometry corresponding to sp^3 hybridization. Because of the nonbonding pairs, we expect the S—S—S angles to be somewhat less than 109.5°, 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 π^*_{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:

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

Recall that $D(X{-}Y)$ represents the X—Y bond enthalpy. Because $\Delta H_{rxn} > 0$, 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

MOLECULAR SHAPES (INTRODUCTION AND SECTION 9.1)

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

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

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

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

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

HYBRID ORBITALS (SECTION 9.5) To extend the ideas of valence-bond theory to polyatomic molecules, we must envision mixing *s* and *p* orbitals to form **hybrid orbitals**. The process of **hybridization** leads to hybrid atomic orbitals that have a large lobe directed to overlap with orbitals on another atom to make a bond. Hybrid orbitals can also accommodate nonbonding pairs. A particular mode of hybridization can be associated with each of three common electron-domain geometries (linear = *sp*; trigonal planar = sp^2; tetrahedral = sp^3). The bonding in **hypervalent** molecules—those with more than an octet of electrons—are not as readily discussed in terms of hybrid orbitals.

MULTIPLE BONDS (SECTION 9.6) Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called **sigma (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; each carbon atom has an unhybridized **p_π orbital**, and these are the orbitals that overlap to form π bonds. 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.

MOLECULAR ORBITALS (SECTION 9.7) **Molecular orbital theory** is another model used to describe the bonding in molecules. In this model the electrons exist in allowed energy states called **molecular orbitals (MOs)**. An MO can extend over all the atoms of a molecule. Like an atomic orbital, a molecular orbital has a definite energy and can hold two electrons of opposite spin. We can build molecular orbitals by combining atomic orbitals on different atomic centers. In the simplest case, the combination of two atomic orbitals leads to the formation of two MOs, one at lower energy and one at higher energy relative to the energy of the atomic orbitals. The lower-energy MO concentrates charge density in the region between the nuclei and is called a **bonding molecular orbital**. The higher-energy MO excludes electrons from the region between the nuclei and is called an **antibonding molecular orbital**. Antibonding MOs exclude electron density from the region between the nuclei and have a **nodal plane**—a place at which the electron density is zero—between the nuclei. Occupation of bonding MOs favors bond formation, whereas occupation of antibonding MOs is unfavorable. The bonding and antibonding MOs formed by the combination of *s* orbitals are **sigma (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 is put into the MOs, we can calculate the **bond order** of a bond, which is half the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A bond order of 1 corresponds to a single bond, and so forth. Bond orders can be fractional numbers.

MOLECULAR ORBITALS OF PERIOD 2 DIATOMIC MOLECULES (SECTION 9.8) Electrons in core orbitals do not contribute to the bonding between atoms, so a molecular orbital description usually needs to consider only electrons in the outermost electron subshells. To describe the MOs of period 2 homonuclear diatomic molecules, we need to consider the MOs that can form by the combination of *p* orbitals. The *p* orbitals that point directly at one another can form 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. The molecular orbitals of heteronuclear diatomic molecules are often closely related to those of homonuclear diatomic molecules.

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

- Predict the three-dimensional shapes of molecules using the VSEPR model. (Section 9.2)
- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments. (Section 9.3)
- Explain the role of orbital overlap in the formation of covalent bonds. (Section 9.4)
- Determine the hybridization atoms in molecules based on observed molecular structures. (Section 9.5)
- Sketch how orbitals overlap to form sigma (σ) and pi (π) bonds. (Section 9.6)
- Explain the existence of delocalized π bonds in molecules such as benzene. (Section 9.6)

- Count the number of electrons in a delocalized π system. (Section 9.6)
- Explain the concept of bonding and antibonding molecular orbitals and draw examples of σ and π MOs. (Section 9.7)
- Draw molecular orbital energy-level diagrams and place electrons into them to obtain the bond orders and electron configurations of diatomic molecules using molecular orbital theory. (Sections 9.7 and 9.8)
- Correlate bond order, bond strength (bond enthalpy), bond length, and magnetic properties with molecular orbital descriptions of molecules. (Section 9.8)

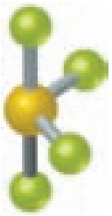
Key Equations

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

Exercises

Visualizing Concepts

9.1 A certain AB_4 molecule has a "seesaw" shape:



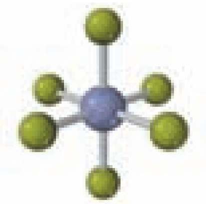
From which of the fundamental geometries shown in Figure 9.3 could you remove one or more atoms to create a molecule having this seesaw shape? [Section 9.1]

9.2 (**a**) If these three balloons are all the same size, what angle is formed between the red one and the green one? (**b**) If additional air is added to the blue balloon so that it gets larger, will the angle between the red and green balloons increase, decrease, or stay the same? (**c**) Which of the following aspects of the VSEPR model is illustrated by part (b): (i) The electron-domain geometry for four electron domains is tetrahedral. (ii) The electron domains for nonbonding pairs are larger than those for bonding pairs. (iii) The hybridization that corresponds to a trigonal planar electron-domain geometry is sp^2? [Section 9.2]

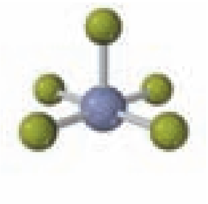
9.3 For each molecule (a)–(f), indicate how many different electron-domain geometries are consistent with the molecular geometry shown. [Section 9.2]

(a)

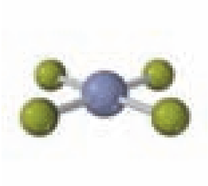
(b)



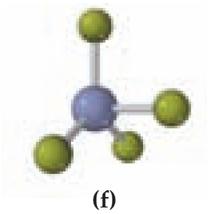
(c)



(d)



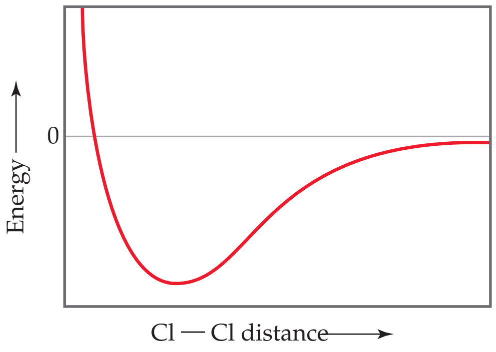
(e)



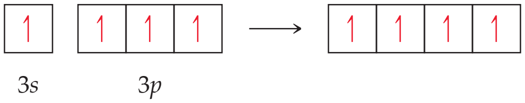
(f)

9.4 The molecule shown here is *difluoromethane* (CH_2F_2), which is used as a refrigerant called R-32. (**a**) Based on the structure, how many electron domains surround the C atom in this molecule? (**b**) Would the molecule have a nonzero dipole moment? (**c**) If the molecule is polar, which of the following describes the direction of the overall dipole moment vector in the molecule: (i) from the carbon atom toward a fluorine atom, (ii) from the carbon atom to a point midway between the fluorine atoms, (iii) from the carbon atom to a point midway between the hydrogen atoms, or (iv) From the carbon atom toward a hydrogen atom? [Sections 9.2 and 9.3]

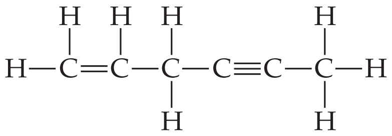
9.5 The following plot shows the potential energy of two Cl atoms as a function of the distance between them. (**a**) To what does an energy of zero correspond in this diagram? (**b**) According to the valence-bond model, why does the energy decrease as the Cl atoms move from a large separation to a smaller one? (**c**) What is the significance of the Cl—Cl distance at the minimum point in the plot? (**d**) Why does the energy rise at Cl—Cl distances less than that at the minimum point in the plot? (**e**) How can you estimate the bond strength of the Cl—Cl bond from the plot? [Section 9.4]



9.6 The orbital diagram that follows presents the final step in the formation of hybrid orbitals by a silicon atom. (**a**) Which of the following best describes what took place before the step pictured in the diagram: (i) Two 3*p* electrons became unpaired, (ii) An electron was promoted from the 2*p* orbital to the 3*s* orbital, or (iii) An electron was promoted from the 3*s* orbital to the 3*p* orbital? (**b**) What type of hybrid orbital is produced in this hybridization? [Section 9.5]

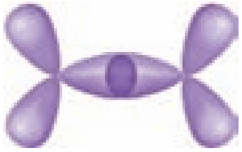


9.7 In the hydrocarbon

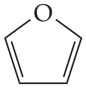

$H_2C{=}CH{-}CH_2{-}C{\equiv}C{-}CH_3$

(**a**) What is the hybridization at each carbon atom in the molecule? (**b**) How many σ bonds are there in the molecule? (**c**) How many π bonds? (**d**) Identify all the 120° bond angles in the molecule. [Section 9.6]

9.8 The drawing below shows the overlap of two hybrid orbitals to form a bond in a hydrocarbon. (**a**) Which of the following types of bonds is being formed: (i) C—C σ, (ii) C—C π, or (iii) C—H σ? (**b**) Which of the following could be the identity of the hydrocarbon: (i) CH_4, (ii) C_2H_6, (iii) C_2H_4, or (iv) C_2H_2? [Section 9.6]

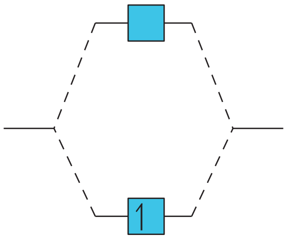


9.9 The molecule shown below is called *furan*. It is represented in typical shorthand way for organic molecules, with hydrogen atoms not shown.



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

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



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

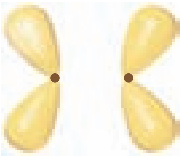
H_2, He_2, H_2^+, He_2^+, or H_2^-?

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

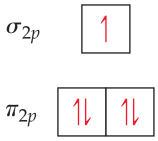
9.11 For each of these contour representations of molecular orbitals, identify (**a**) the atomic orbitals (*s* or *p*) used to construct the MO (**b**) the type of MO (σ or π), (**c**) whether the MO is bonding or antibonding, and (**d**) the locations of nodal planes. [Sections 9.7 and 9.8]


(i)


(ii)


(iii)

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



Molecular Shapes; the VSEPR Model (sections 9.1 and 9.2)

9.13 An AB_2 molecule is described as linear, and the A—B bond length is known. (**a**) Does this information completely describe the geometry of the molecule? (**b**) Can you tell how many nonbonding pairs of electrons are around the A atom from this information?

9.14 (**a**) Methane (CH_4) and the perchlorate ion (ClO_4^-) are both described as tetrahedral. What does this indicate about their bond angles? (**b**) The NH_3 molecule is trigonal pyramidal, while BF_3 is trigonal planar. Which of these molecules is flat?

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

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

9.17 (**a**) How does one determine the number of electron domains in a molecule or ion? (**b**) What is the difference between a *bonding electron domain* and a *nonbonding electron domain*?

9.18 Would you expect the nonbonding electron-pair domain in NH_3 to be greater or less in size than for the corresponding one in PH_3?

9.19 In which of these molecules or ions does the presence of nonbonding electron pairs produce an effect on molecular shape? (**a**) SiH_4, (**b**) PF_3, (**c**) HBr, (**d**) HCN, (**e**) SO_2.

9.20 In which of the following molecules can you confidently predict the bond angles about the central atom, and for which would you be a bit uncertain? Explain in each case. (**a**) H_2S, (**b**) BCl_3, (**c**) CH_3I, (**d**) CBr_4, (**e**) $TeBr_4$.

9.21 How many nonbonding electron pairs are there in each of the following molecules: (**a**) $(CH_3)_2S$, (**b**) HCN, (**c**) H_2C_2, (**d**) CH_3F?

9.22 Describe the characteristic electron-domain geometry of each of the following numbers of electron domains about a central atom: (**a**) 3, (**b**) 4, (**c**) 5, (**d**) 6.

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

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

9.25 Give the electron-domain and molecular geometries for the following molecules and ions: (**a**) HCN, (**b**) SO_3^{2-}, (**c**) SF_4, (**d**) PF_6^-, (**e**) NH_3Cl^+, (**f**) N_3^-.

9.26 Draw the Lewis structure for each of the following molecules or ions, and predict their electron-domain and molecular geometries: (**a**) AsF_3, (**b**) CH_3^+, (**c**) BrF_3, (**d**) ClO_3^-, (**e**) XeF_2, (**f**) BrO_2^-.

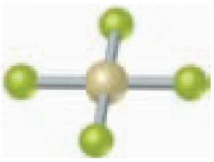
9.27 The figure that follows shows ball-and-stick drawings of three possible shapes of an AF_3 molecule. (**a**) For each shape, give the electron-domain geometry on which the molecular geometry is based. (**b**) For each shape, how many nonbonding electron domains are there on atom A? (**c**) Which of the following elements will lead to an AF_3 molecule with the shape in (ii): Li, B, N, Al, P, Cl? (**d**) Name an element A that is expected to lead to the AF_3 structure shown in (iii). Explain your reasoning.

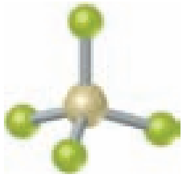

(i)

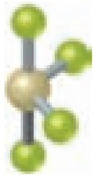

(ii)


(iii)

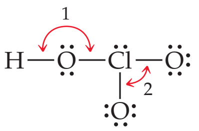
9.28 The figure that follows contains ball-and-stick drawings of three possible shapes of an AF_4 molecule. (**a**) For each shape, give the electron-domain geometry on which the molecular geometry is based. (**b**) For each shape, how many nonbonding electron domains are there on atom A? (**c**) Which of the following elements will lead to an AF_4 molecule with the shape in (iii): Be, C, S, Se, Si, Xe? (**d**) Name an element A that is expected to lead to the AF_4 structure shown in (i).

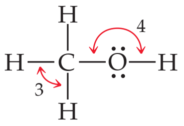

(i)

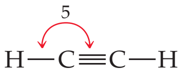

(ii)

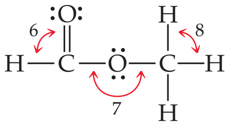

(iii)

9.29 Give the approximate values for the indicated bond angles in the following molecules:

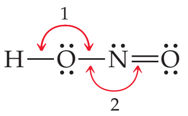
(**a**)


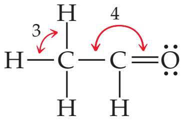
(**b**)


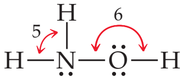
(**c**)


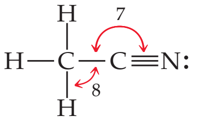
(**d**)


9.30 Give approximate values for the indicated bond angles in the following molecules:

(**a**)


(**b**)


(**c**)


(**d**)


9.31 The three species NH_2^-, NH_3, and NH_4^+ have H—N—H bond angles of 105°, 107°, and 109°, respectively. Explain this variation in bond angles.

9.32 In which of the following AF_n molecules or ions is there more than one F—A—F bond angle: SiF_4, PF_5, SF_4, AsF_3?

9.33 (**a**) Explain why BrF_4^- is square planar, whereas BF_4^- is tetrahedral. (**b**) How would you expect the H—X—H bond angle to vary in the series H_2O, H_2S, H_2Se? Explain. (*Hint:* The size of an electron pair domain depends in part on the electronegativity of the central atom.)

9.34 (**a**) Explain why the following ions have different bond angles: ClO_2^- and NO_2^-. Predict the bond angle in each case. (**b**) Explain why the XeF_2 molecule is linear.

Shapes and Polarity of Polyatomic Molecules (section 9.3)

9.35 What is the distinction between a bond dipole and a molecular dipole moment?

9.36 Consider a molecule with formula AX_3. Supposing the A—X bond is polar, how would you expect the dipole moment of the AX_3 molecule to change as the X—A—X bond angle increases from 100° to 120°?

9.37 (**a**) Does SCl_2 have a dipole moment? If so, in which direction does the net dipole point? (**b**) Does $BeCl_2$ have a dipole moment? If so, in which direction does the net dipole point?

9.38 (**a**) The PH_3 molecule is polar. Does this offer experimental proof that the molecule cannot be planar? Explain. (**b**) It turns out that ozone, O_3, has a small dipole moment. How is this possible, given that all the atoms are the same?

9.39 (**a**) What conditions must be met if a molecule with polar bonds is nonpolar? (**b**) What geometries will signify nonpolar molecules for AB_2, AB_3, and AB_4 geometries?

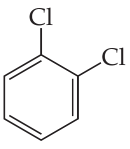
9.40 (**a**) Consider the AF_3 molecules in Exercise 9.27. Which of these will have a nonzero dipole moment? (**b**) Which of the AF_4 molecules in Exercise 9.30 will have a zero dipole moment?

9.41 Predict whether each of the following molecules is polar or nonpolar: (**a**) IF, (**b**) CS_2, (**c**) SO_3, (**d**) PCl_3, (**e**) SF_6, (**f**) IF_5.

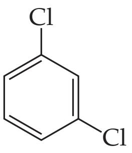
9.42 Predict whether each of the following molecules is polar or nonpolar: (**a**) CCl_4, (**b**) NH_3, (**c**) SF_4, (**d**) XeF_4, (**e**) CH_3Br, (**f**) GaH_3.

9.43 Dichloroethylene ($C_2H_2Cl_2$) has three forms (isomers), each of which is a different substance. (**a**) Draw Lewis structures of the three isomers, all of which have a carbon–carbon double bond. (**b**) Which of these isomers has a zero dipole moment? (**c**) How many isomeric forms can chloroethylene, C_2H_3Cl, have? Would they be expected to have dipole moments?

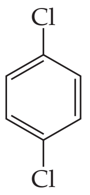
9.44 Dichlorobenzene, $C_6H_4Cl_2$, exists in three forms (isomers) called *ortho, meta,* and *para*:



ortho



meta



para

Which of these has a nonzero dipole moment?

Orbital Overlap; Hybrid Orbitals (sections 9.4 and 9.5)

9.45 (**a**) What is meant by the term *orbital overlap*? (**b**) Describe what a chemical bond is in terms of electron density between two atoms.

9.46 Draw sketches illustrating the overlap between the following orbitals on two atoms: (**a**) the 2*s* orbital on each atom, (**b**) the $2p_z$ orbital on each atom (assume both atoms are on the *z*-axis), (**c**) the 2*s* orbital on one atom and the $2p_z$ orbital on the other atom.

9.47 Consider the bonding in an MgH_2 molecule. (**a**) Draw a Lewis structure for the molecule, and predict its molecular geometry. (**b**) What hybridization scheme is used in MgH_2? (**c**) Sketch one of the two-electron bonds between an Mg hybrid orbital and an H 1*s* atomic orbital.

9.48 How would you expect the extent of overlap of the bonding atomic orbitals to vary in the series IF, ICl, IBr, and I_2? Explain your answer.

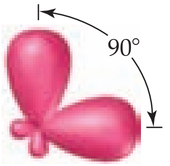
9.49 (**a**) Starting with the orbital diagram of a boron atom, describe the steps needed to construct hybrid orbitals appropriate to describe the bonding in BF_3. (**b**) What is the name given to the hybrid orbitals constructed in (a)? (**c**) Sketch the large lobes of the hybrid orbitals constructed in part (a). (**d**) Are any valence atomic orbitals of B left unhybridized? If so, how are they oriented relative to the hybrid orbitals?

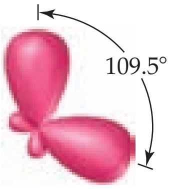
9.50 (**a**) Starting with the orbital diagram of a sulfur atom, describe the steps needed to construct hybrid orbitals appropriate to describe the bonding in SF_2. (**b**) What is the name given to the hybrid orbitals constructed in (a)? (**c**) Sketch the large lobes of these hybrid orbitals. (**d**) Would the hybridization scheme in part (a) be appropriate for SF_4? Explain.

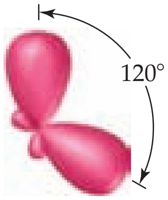
9.51 Indicate the hybridization of the central atom in (**a**) BCl_3, (**b**) $AlCl_4^-$, (**c**) CS_2, (**d**) GeH_4.

9.52 What is the hybridization of the central atom in (**a**) $SiCl_4$, (**b**) HCN, (**c**) SO_3, (**d**) $TeCl_2$.

9.53 Shown here are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type of hybridization, if any, that could lead to hybrid orbitals at the specified angle.







9.54 (**a**) Which geometry and central atom hybridization would you expect in the series BH_4^-, CH_4, NH_4^+? (**b**) What would you expect for the magnitude and direction of the bond dipoles in this series? (**c**) Write the formulas for the analogous species of the elements of period 3; would you expect them to have the same hybridization at the central atom?

Multiple Bonds (section 9.6)

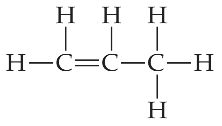
9.55 (**a**) Draw a picture showing how two *p* orbitals on two different atoms can be combined to make a σ bond. (**b**) Sketch a π bond that is constructed from *p* orbitals. (**c**) Which is generally stronger, a σ bond or a π bond? Explain. (**d**) Can two *s* orbitals combine to form a π bond? Explain.

9.56 (**a**) If the valence atomic orbitals of an atom are *sp* hybridized, how many unhybridized *p* orbitals remain in the valence shell? How many π bonds can the atom form? (**b**) Imagine that you could hold two atoms that are bonded together, twist them, and not change the bond length. Would it be easier to twist (rotate) around a single σ bond or around a double (σ plus π) bond, or would they be the same?

9.57 (**a**) Draw Lewis structures for ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2). (**b**) What is the hybridization of the carbon atoms in each molecule? (**c**) Predict which molecules, if any, are planar. (**d**) How many σ and π bonds are there in each molecule?

9.58 The nitrogen atoms in N_2 participate in multiple bonding, whereas those in hydrazine, N_2H_4, do not. (**a**) Draw Lewis structures for both molecules. (**b**) What is the hybridization of the nitrogen atoms in each molecule? (**c**) Which molecule has the stronger N—N bond?

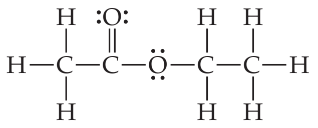
9.59 Propylene, C_3H_6, is a gas that is used to form the important polymer called polypropylene. Its Lewis structure is



$$\begin{array}{ccccccccc} & & \text{H} & & \text{H} & & \text{H} & & \\ & & | & & | & & | & & \\ \text{H} & - & \text{C} & = & \text{C} & - & \text{C} & - & \text{H} \\ & & & & & & | & & \\ & & & & & & \text{H} & & \end{array}$$

(**a**) What is the total number of valence electrons in the propylene molecule? (**b**) How many valence electrons are used to make σ bonds in the molecule? (**c**) How many valence electrons are used to make π bonds in the molecule? (**d**) How many valence electrons remain in nonbonding pairs in the molecule? (**e**) What is the hybridization at each carbon atom in the molecule?

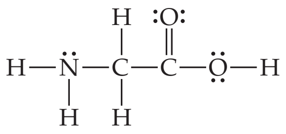
9.60 Ethyl acetate, $C_4H_8O_2$, is a fragrant substance used both as a solvent and as an aroma enhancer. Its Lewis structure is



$$\begin{array}{ccccccccccccc} & & \text{H} & & :\text{O}: & & & & \text{H} & & \text{H} & & \\ & & | & & \| & & & & | & & | & & \\ \text{H} & - & \text{C} & - & \text{C} & - & \ddot{\underset{\cdot\cdot}{\text{O}}} & - & \text{C} & - & \text{C} & - & \text{H} \\ & & | & & & & & & | & & | & & \\ & & \text{H} & & & & & & \text{H} & & \text{H} & & \end{array}$$

(**a**) What is the hybridization at each of the carbon atoms of the molecule? (**b**) What is the total number of valence electrons in ethyl acetate? (**c**) How many of the valence electrons are used to make σ bonds in the molecule? (**d**) How many valence electrons are used to make π bonds? (**e**) How many valence electrons remain in nonbonding pairs in the molecule?

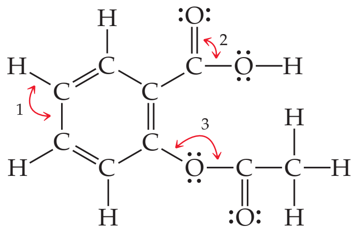
9.61 Consider the Lewis structure for glycine, the simplest amino acid:



$$\begin{array}{ccccccccccc} & & & & \text{H} & & :\text{O}: & & & & \\ & & & & | & & \| & & & & \\ \text{H} & - & \ddot{\text{N}} & - & \text{C} & - & \text{C} & - & \ddot{\underset{\cdot\cdot}{\text{O}}} & - & \text{H} \\ & & | & & | & & & & & & \\ & & \text{H} & & \text{H} & & & & & & \end{array}$$

(**a**) What are the approximate bond angles about each of the two carbon atoms, and what are the hybridizations of the orbitals on each of them? (**b**) What are the hybridizations of the orbitals on the two oxygens and the nitrogen atom, and what are the approximate bond angles at the nitrogen? (**c**) What is the total number of σ bonds in the entire molecule, and what is the total number of π bonds?

9.62 Acetylsalicylic acid, better known as aspirin, has the Lewis structure



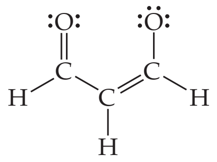
(**a**) What are the approximate values of the bond angles labeled 1, 2, and 3? (**b**) What hybrid orbitals are used about the central atom of each of these angles? (**c**) How many σ bonds are in the molecule?

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

9.64 (**a**) Write a single Lewis structure for SO_3, and determine the hybridization at the S atom. (**b**) Are there other equivalent Lewis structures for the molecule? (**c**) Would you expect SO_3 to exhibit delocalized π bonding?

9.65 In the formate ion, HCO_2^-, the carbon atom is the central atom with the other three atoms attached to it. (**a**) Draw a Lewis structure for the formate ion. (**b**) What hybridization is exhibited by the C atom? (**c**) Are there multiple equivalent resonance structures for the ion? (**d**) Which of the atoms in the ion have p_π orbitals? (**e**) How many electrons are in the π system of the ion?

9.66 Consider the Lewis structure shown below.

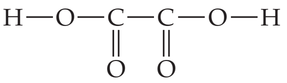


(**a**) Does the Lewis structure depict a neutral molecule or an ion? If it is an ion, what is the charge on the ion? (**b**) What hybridization is exhibited by each of the carbon atoms? (**c**) Are there multiple equivalent resonance structures for the species? (**d**) Which of the atoms in the species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

9.67 Predict the molecular geometry of each of the following molecules:

(**a**) $H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$

(**b**)



$$\begin{array}{ccccccccccc} \text{H} & - & \text{O} & - & \text{C} & - & \text{C} & - & \text{O} & - & \text{H} \\ & & & & \| & & \| & & & & \\ & & & & \text{O} & & \text{O} & & & & \end{array}$$

(**c**) $H{-}N{=}N{-}H$

9.68 What hybridization do you expect for the atom indicated in red in each of the following species?

(**a**) $CH_3CO_2^-$; (**b**) PH_4^+; (**c**) AlF_3; (**d**) $H_2C{=}CH{-}CH_2^+$

Molecular Orbitals and Period 2 Diatomic Molecules (sections 9.7 and 9.8)

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

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

9.71 Consider the H_2^+ ion. (**a**) Sketch the molecular orbitals of the ion and draw its energy-level diagram. (**b**) How many electrons are there in the H_2^+ ion? (**c**) Write the electron configuration of the ion in terms of its MOs. (**d**) What is the bond order in H_2^+? (**e**) Suppose that the ion is excited by light so that an electron moves from a lower-energy to a higher-energy MO. Would you expect the excited-state H_2^+ ion to be stable or to fall apart? (**f**) Which of the following statements about part (e) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

9.72 (**a**) Sketch the molecular orbitals of the H_2^- ion and draw its energy-level diagram. (**b**) Write the electron configuration of the ion in terms of its MOs. (**c**) Calculate the bond order in H_2^-. (**d**) Suppose that the ion is excited by light, so that an electron moves from a lower-energy to a higher-energy molecular orbital. Would you expect the excited-state H_2^- ion to be stable? (**e**) Which of the following statements about part (d) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

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

9.74 (**a**) What is the probability of finding an electron on the internuclear axis if the electron occupies a π molecular orbital? (**b**) For a homonuclear diatomic molecule, what similarities and differences are there between the π_{2p} MO made from the $2p_x$ atomic orbitals and the π_{2p} MO made from the $2p_y$ atomic orbitals? (**c**) How do the π_{2p}^* MOs formed from the $2p_x$ and $2p_y$ atomic orbitals differ from the π_{2p} MOs in terms of energies and electron distributions?

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

9.76 Explain the following: (**a**) The *peroxide* ion, O_2^{2-}, has a longer bond length than the *superoxide* ion, O_2^-. (**b**) The magnetic properties of B_2 are consistent with the π_{2p} MOs being lower in energy than the σ_{2p} MO. (**c**) The O_2^{2+} ion has a stronger O—O bond than O_2 itself.

9.77 (**a**) What does the term *diamagnetism* mean? (**b**) How does a diamagnetic substance respond to a magnetic field? (**c**) Which of the following ions would you expect to be diamagnetic: N_2^{2-}, O_2^{2-}, Be_2^{2+}, C_2^-?

9.78 (**a**) What does the term *paramagnetism* mean? (**b**) How can one determine experimentally whether a substance is paramagnetic? (**c**) Which of the following ions would you expect to be paramagnetic: O_2^+, N_2^{2-}, Li_2^+, O_2^{2-}? For those ions that are paramagnetic, determine the number of unpaired electrons.

9.79 Using Figures 9.35 and 9.43 as guides, draw the molecular orbital electron configuration for (**a**) B_2^+, (**b**) Li_2^+, (**c**) N_2^+, (**d**) Ne_2^{2+}. In each case indicate whether the addition of an electron to the ion would increase or decrease the bond order of the species.

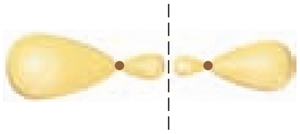
9.80 If we assume that the energy-level diagrams for homonuclear diatomic molecules shown in Figure 9.43 can be applied to heteronuclear diatomic molecules and ions, predict the bond order and magnetic behavior of (**a**) CO^+, (**b**) NO^-, (**c**) OF^+, (**d**) NeF^+.

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

9.82 (**a**) The nitric oxide molecule, NO, readily loses one electron to form the NO^+ ion. Which of the following is the best explanation of why this happens: (i) Oxygen is more electronegative than nitrogen, (ii) The highest energy electron in NO lies in a π_{2p}^* molecular orbital, or (iii) The π_{2p}^* MO in NO is completely filled. (**b**) Predict the order of the N—O bond strengths in NO, NO^+, and NO^-, and describe the magnetic properties of each. (**c**) With what neutral homonuclear diatomic molecules are the NO^+ and NO^- ions isoelectronic (same number of electrons)?

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

[9.84] The iodine bromide molecule, IBr, is an *interhalogen compound*. Assume that the molecular orbitals of IBr are analogous to the homonuclear diatomic molecule F_2. (**a**) Which valence atomic orbitals of I and of Br are used to construct the MOs of IBr? (**b**) What is the bond order of the IBr molecule? (**c**) One of the valence MOs of IBr is sketched here. Why are the atomic orbital contributions to this MO different in size? (**d**) What is the label for the MO? (**e**) For the IBr molecule, how many electrons occupy the MO?



Additional Exercises

9.85 (**a**) What is the physical basis for the VSEPR model? (**b**) When applying the VSEPR model, we count a double or triple bond as a single electron domain. Why is this justified?

9.86 An AB_3 molecule is described as having a trigonal-bipyramidal electron-domain geometry. (**a**) How many nonbonding domains are on atom A? (**b**) Based on the information given, which of the following is the molecular geometry of the molecule: (i) trigonal planar, (ii) trigonal pyramidal, (iii) T-shaped, or (iv) tetrahedral?

9.87 Consider the following XF_4 ions: PF_4^-, BrF_4^-, ClF_4^+, and AlF_4^-. (**a**) Which of the ions have more than an octet of electrons around the central atom? (**b**) For which of the ions will the electron-domain and molecular geometries be the same? (**c**) Which of the ions will have an octahedral electron-domain geometry? (**d**) Which of the ions will exhibit a see-saw molecular geometry?

9.88 Consider the molecule PF_4Cl. (**a**) Draw a Lewis structure for the molecule, and predict its electron-domain geometry. (**b**) Which would you expect to take up more space, a P—F bond or a P—Cl bond? Explain. (**c**) Predict the molecular geometry of PF_4Cl. How did your answer for part (b) influence your answer here in part (c)? (**d**) Would you expect the molecule to distort from its ideal electron-domain geometry? If so, how would it distort?

[9.89] The vertices of a tetrahedron correspond to four alternating corners of a cube. By using analytical geometry, demonstrate that the angle made by connecting two of the vertices to a point at the center of the cube is 109.5°, the characteristic angle for tetrahedral molecules.

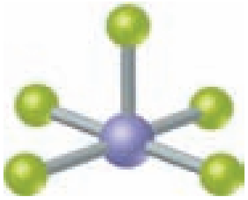
9.90 Fill in the blank spaces in the following chart. If the molecule column is blank, find an example that fulfills the conditions of the rest of the row.

Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO_2			
		sp^3	Yes
		sp^3	No
	Trigonal planar		No
SF_4		sp^2	
	Octahedral		No
		sp^2	Yes
	Trigonal bipyramidal		No
XeF_2			

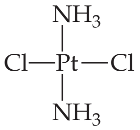
9.91 From their Lewis structures, determine the number of σ and π bonds in each of the following molecules or ions: (**a**) CO_2; (**b**) cyanogen, $(CN)_2$; (**c**) formaldehyde, H_2CO; (**d**) formic acid, HCOOH, which has one H and two O atoms attached to C.

9.92 The lactic acid molecule, $CH_3CH(OH)COOH$, gives sour milk its unpleasant, sour taste. (**a**) Draw the Lewis structure for the molecule, assuming that carbon always forms four bonds in its stable compounds. (**b**) How many π and how many σ bonds are in the molecule? (**c**) Which CO bond is shortest in the molecule? (**d**) What is the hybridization of atomic orbitals around the carbon atom associated with that short bond? (**e**) What are the approximate bond angles around each carbon atom in the molecule?

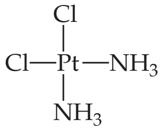
9.93 An AB_5 molecule adopts the geometry shown here. (**a**) What is the name of this geometry? (**b**) Do you think there are any nonbonding electron pairs on atom A? (**c**) Suppose the atoms B are halogen atoms. Of which group in the periodic table is atom A a member: (i) Group 5A, (ii) Group 6A, (iii) Group 7A, (iv) Group 8A, or (v) More information is needed?



9.94 There are two compounds of the formula $Pt(NH_3)_2Cl_2$:



$$Cl-\overset{\displaystyle NH_3}{\underset{\displaystyle NH_3}{Pt}}-Cl$$



$$Cl-\overset{\displaystyle Cl}{\underset{\displaystyle NH_3}{Pt}}-NH_3$$

The compound on the right, *cisplatin,* is used in cancer therapy. The compound on the left, *transplatin,* is ineffective for cancer therapy. Both compounds have a square-planar geometry. (**a**) Which compound has a nonzero dipole moment? (**b**) The reason cisplatin is a good anticancer drug is that it binds tightly to DNA. Cancer cells are rapidly dividing, producing a lot of DNA. Consequently, cisplatin kills cancer cells at a faster rate than normal cells. However, since normal cells also are making DNA, cisplatin also attacks healthy cells, which leads to unpleasant side effects. The way both molecules bind to DNA involves the Cl^- ions leaving the Pt ion, to be replaced by two nitrogens in DNA. Draw a picture in which a long vertical line represents a piece of DNA. Draw the $Pt(NH_3)_2$ fragments of cisplatin and transplatin with the proper shape. Also draw them attaching to your DNA line. Can you explain from your drawing why the shape of the cisplatin causes it to bind to DNA more effectively than transplatin?

[9.95] The O—H bond lengths in the water molecule (H_2O) are 0.96 Å, and the H—O—H angle is 104.5°. The dipole moment of the water molecule is 1.85 D. (**a**) In what directions do the bond dipoles of the O—H bonds point? In what direction does the dipole moment vector of the water molecule point? (**b**) Calculate the magnitude of the bond dipole of the O—H bonds. (*Note:* You will need to use vector addition to do this.) (**c**) Compare your answer from part (b) to the dipole moments of the hydrogen halides (Table 8.3). Is your answer in accord with the relative electronegativity of oxygen?

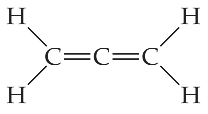
9.96 The reaction of three molecules of fluorine gas with a Xe atom produces the substance xenon hexafluoride, XeF_6:

$$Xe(g) + 3\,F_2(g) \longrightarrow XeF_6(s)$$

(**a**) Draw a Lewis structure for XeF_6. (**b**) If you try to use the VSEPR model to predict the molecular geometry of XeF_6, you run into a problem. What is it? (**c**) What could you do to resolve the difficulty in part (b)? (**d**) The molecule IF_7 has a pentagonal-bipyramidal structure (five equatorial fluorine atoms at the vertices of a regular pentagon and two axial fluorine atoms). Based on the structure of IF_7, suggest a structure for XeF_6.

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

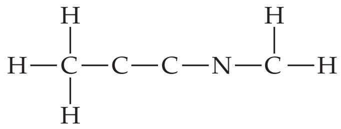
[9.98] The Lewis structure for allene is



$$\overset{H}{\underset{H}{}}\!\!>C=C=C<\!\!\overset{H}{\underset{H}{}}$$

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

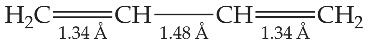
9.99 Consider the molecule C_4H_5N, which has the connectivity shown below. (**a**) After the Lewis structure for the molecule is completed, how many σ and how many π bonds are there in this molecule? (**b**) How many atoms in the molecule exhibit (i) *sp* hybridization, (ii) sp^2 hybridization, and (iii) sp^3 hybridization?



[9.100] The azide ion, N_3^-, is linear with two N—N bonds of equal length, 1.16 Å. (**a**) Draw a Lewis structure for the azide ion. (**b**) With reference to Table 8.5, is the observed N—N bond length consistent with your Lewis structure? (**c**) What hybridization scheme would you expect at each of the nitrogen atoms in N_3^-? (**d**) Show which hybridized and unhybridized orbitals are involved in the formation of σ and π bonds in N_3^-. (**e**) It is often observed that σ bonds that involve an *sp* hybrid orbital are shorter than those that involve only sp^2 or sp^3 hybrid orbitals. Can you propose a reason for this? Is this observation applicable to the observed bond lengths in N_3^-?

[9.101] In ozone, O_3, the two oxygen atoms on the ends of the molecule are equivalent to one another. (**a**) What is the best choice of hybridization scheme for the atoms of ozone? (**b**) For one of the resonance forms of ozone, which of the orbitals are used to make bonds and which are used to hold nonbonding pairs of electrons? (**c**) Which of the orbitals can be used to delocalize the π electrons? (**d**) How many electrons are delocalized in the π system of ozone?

9.102 Butadiene, C_4H_6, is a planar molecule that has the following carbon–carbon bond lengths:



$$H_2C \underset{1.34\ \text{Å}}{=\!=\!=} CH \underset{1.48\ \text{Å}}{-\!-\!-} CH \underset{1.34\ \text{Å}}{=\!=\!=} CH_2$$

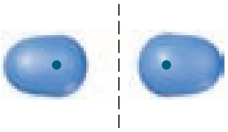
(**a**) Predict the bond angles around each of the carbon atoms and sketch the molecule.

(**b**) Compare the bond lengths to the average bond lengths listed in Table 8.5. Can you explain any differences?

9.103 (**a**) The structure of *borazine*, $B_3N_3H_6$, is a six-membered ring of alternating B and N atoms. There is one H atom bonded to each B and to each N atom. The molecule is planar. (**a**) Write a Lewis structure for borazine in which the formal charges on every atom is zero. (**b**) Write a Lewis structure for borazine in which the octet rule is satisfied for every atom. (**c**) What are the formal charges on the atoms in the Lewis structure from part (b)? Given the electronegativities of B and N, do the formal charges seem favorable or unfavorable? (**d**) Do either of the Lewis structures in parts (a) and (b) have multiple resonance structures? (**e**) What are the hybridizations at the B and N atoms in the Lewis structures from parts (a) and (b)? Would you expect the molecule to be planar for both Lewis structures? (**f**) The six B—N bonds in the borazine molecule are all identical in length at 1.44 Å. Typical values for the bond lengths of B—N single and double bonds are 1.51 Å and 1.31 Å, respectively. Does the value of the B—N bond length seem to favor one Lewis structure over the other? (**g**) How many electrons are in the π system of borazine?

9.104 Suppose that silicon could form molecules that are precisely the analogs of ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2). How would you describe the bonding about Si in terms of hydrid orbitals? Silicon does not readily form some of the analogous compounds containing π bonds. Why might this be the case?

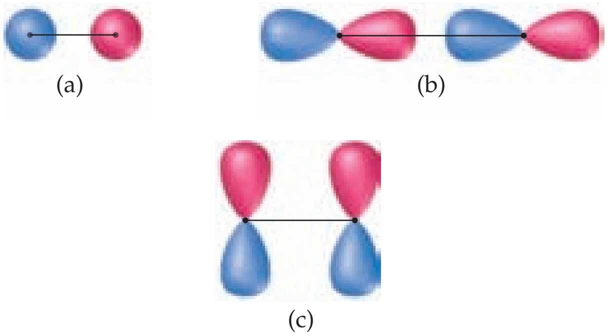
9.105 One of the molecular orbitals of the H_2^- ion is sketched below:



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

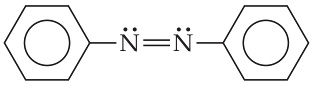
9.106 Place the following molecules and ions in order from smallest to largest bond order: H_2^+, B_2, N_2^+, F_2^+, and Ne_2.

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

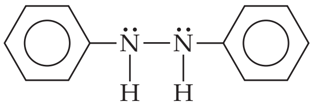


9.108 Write the electron configuration for the first excited state for N_2; that is, the state with the highest-energy electron moved to the next available energy level. (**a**) Is the nitrogen in its first excited state diamagnetic or paramagnetic? (**b**) Is the N—N bond strength in the first excited state stronger or weaker compared to that in the ground state?

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



Azobenzene



Hydrazobenzene

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

[9.110] (**a**) Using only the valence atomic orbitals of a hydrogen atom and a fluorine atom, and following the model of Figure 9.46, how many MOs would you expect for the HF molecule? (**b**) How many of the MOs from part (a) would be occupied by electrons? (**c**) It turns out that the difference in energies between the valence atomic orbitals of H and F are sufficiently different that we can neglect the interaction of the 1*s* orbital of hydrogen with the 2*s* orbital of fluorine. The 1*s* orbital of hydrogen will mix only with one 2*p* orbital of fluorine. Draw pictures showing the proper orientation of all three 2*p* orbitals on F interacting with a 1*s* orbital on H. Which of the 2*p* orbitals can actually make a bond with a 1*s* orbital, assuming that the atoms lie on the *z*-axis? (**d**) In the most accepted picture of HF, all the other atomic orbitals on fluorine move over at the same energy into the molecular orbital energy-level diagram for HF. These are called "nonbonding orbitals." Sketch the energy-level diagram for HF using this information and calculate the bond order. (Nonbonding electrons do not contribute to bond order.) (**e**) Look at the Lewis structure for HF. Where are the nonbonding electrons?

[9.111] Carbon monoxide, CO, is isoelectronic to N_2. (**a**) Draw a Lewis structure for CO that satisfies the octet rule. (**b**) Assume that the diagram in Figure 9.46 can be used to describe the MOs of CO. What is the predicted bond order for CO? Is this answer in accord with the Lewis structure you drew in part (a)? (**c**) Experimentally, it is found that the highest-energy electrons in CO reside in a σ-type MO. Is that observation consistent with Figure 9.46? If not, what modification needs to be made to the diagram? How does this modification relate to Figure 9.43? (**d**) Would you expect the π_{2p} MOs of CO to have equal atomic orbital contributions from the C and O atoms? If not, which atom would have the greater contribution?

9.112 The energy-level diagram in Figure 9.36 shows that the sideways overlap of a pair of *p* orbitals produces two molecular orbitals, one bonding and one antibonding. In ethylene there is a pair of electrons in the bonding p orbital between the two carbons. Absorption of a photon of the appropriate wavelength can result in promotion of one of the bonding electrons from the π_{2p} to the π^*_{2p} molecular orbital. (**a**) What would you expect this electronic transition to do to the carbon–carbon bond order in ethylene? (**b**) How does this relate to the fact that absorption of a photon of appropriate wavelength can cause ready rotation about the carbon–carbon bond, as described in the "Chemistry and Life" box and shown in Figure 9.30?

Integrative Exercises

9.113 A compound composed of 2.1% H, 29.8% N, and 68.1% O has a molar mass of approximately 50 g/mol. (**a**) What is the molecular formula of the compound? (**b**) What is its Lewis structure if H is bonded to O? (**c**) What is the geometry of the molecule? (**d**) What is the hybridization of the orbitals around the N atom? (**e**) How many σ and how many π bonds are there in the molecule?

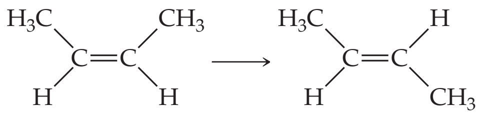
9.114 Sulfur tetrafluoride (SF_4) reacts slowly with O_2 to form sulfur tetrafluoride monoxide (OSF_4) according to the following unbalanced reaction:

$$SF_4(g) + O_2(g) \longrightarrow OSF_4(g)$$

The O atom and the four F atoms in OSF_4 are bonded to a central S atom. (**a**) Balance the equation. (**b**) Write a Lewis structure of OSF_4 in which the formal charges of all atoms are zero. (**c**) Use average bond enthalpies (Table 8.4) to estimate the enthalpy of the reaction. Is it endothermic or exothermic? (**d**) Determine the electron-domain geometry of OSF_4, and write two possible molecular geometries for the molecule based on this electron-domain geometry. (**e**) Which of the molecular geometries in part (d) is more likely to be observed for the molecule? Explain.

[9.115] The phosphorus trihalides (PX_3) show the following variation in the bond angle X—P—X: PF_3, 96.3°; PCl_3, 100.3°; PBr_3, 101.0°; PI_3, 102.0°. The trend is generally attributed to the change in the electronegativity of the halogen. (**a**) Assuming that all electron domains are the same size, what value of the X—P—X angle is predicted by the VSEPR model? (**b**) What is the general trend in the X—P—X angle as the halide electronegativity increases? (**c**) Using the VSEPR model, explain the observed trend in X—P—X angle as the electronegativity of X changes. (**d**) Based on your answer to part (c), predict the structure of $PBrCl_4$.

[9.116] The molecule 2-butene, C_4H_8, can undergo a geometric change called *cis-trans isomerization*:



cis-2-butene *trans*-2-butene

As discussed in the "Chemistry and Life" box on the chemistry of vision, such transformations can be induced by light and are the key to human vision. (**a**) What is the hybridization at the two central carbon atoms of 2-butene? (**b**) The isomerization occurs by rotation about the central C—C bond. With reference to Figure 9.30, explain why the π bond between the two central carbon atoms is destroyed halfway through the rotation from *cis*- to *trans*-2-butene. (**c**) Based on average bond enthalpies (Table 8.4), how much energy per molecule must be supplied to break the C—C π bond? (**d**) What is the longest wavelength of light that will provide photons of sufficient energy to break the C—C π bond and cause the isomerization? (**e**) Is the wavelength in your answer to part (d) in the visible portion of the electromagnetic spectrum? Comment on the importance of this result for human vision.

9.117 (**a**) Compare the bond enthalpies (Table 8.4) of the carbon–carbon single, double, and triple bonds to deduce an average π-bond contribution to the enthalpy. What fraction of a single bond does this quantity represent? (**b**) Make a similar comparison of nitrogen–nitrogen bonds. What do you observe? (**c**) Write Lewis structures of N_2H_4, N_2H_2, and N_2, and determine the hybridization around nitrogen in each case. (**d**) Propose a reason for the large difference in your observations of parts (a) and (b).

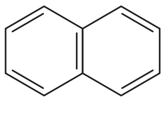
9.118 Use average bond enthalpies (Table 8.4) to estimate ΔH for the atomization of benzene, C_6H_6:

$$C_6H_6(g) \longrightarrow 6\,C(g) + 6\,H(g)$$

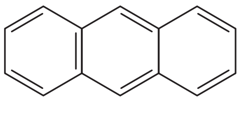
Compare the value to that obtained by using ΔH_f° data given in Appendix C and Hess's law. To what do you attribute the large discrepancy in the two values?

[9.119] Many compounds of the transition-metal elements contain direct bonds between metal atoms. We will assume that the *z*-axis is defined as the metal–metal bond axis. (**a**) Which of the 3*d* orbitals (Figure 6.23) can be used to make a σ bond between metal atoms? (**b**) Sketch the σ_{3d} bonding and σ^*_{3d} antibonding MOs. (**c**) With reference to the "Closer Look" box on the phases of orbitals, explain why a node is generated in the σ^*_{3d} MO. (**d**) Sketch the energy-level diagram for the Sc_2 molecule, assuming that only the 3*d* orbital from part (a) is important. (**e**) What is the bond order in Sc_2?

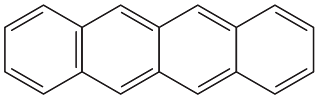
[9.120] The organic molecules shown here are derivatives of benzene in which six-membered rings are "fused" at the edges of the hexagons.



Naphthalene



Anthracene



Tetracene

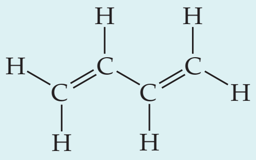
(**a**) Determine the empirical formula of benzene and of these three compounds. (**b**) Suppose you are given a sample of one of the compounds. Could combustion analysis be used to determine unambiguously which of the three it is? (**c**) Naphthalene, the active ingredient in mothballs, is a white solid. Write a balanced equation for the combustion of naphthalene to $CO_2(g)$ and $H_2O(g)$. (**d**) Using the Lewis structure for naphthalene and the average bond enthalpies in Table 8.4, estimate the heat of combustion of naphthalene in kJ/mol. (**e**) Would you expect naphthalene, anthracene, and tetracene to have multiple resonance structures? If so, draw the additional resonance structures for naphthalene. (**f**) Benzene, naphthalene, and anthracene are colorless, but tetracene is orange. What does this imply about the relative HOMO–LUMO energy gaps in these molecules? See the "Chemistry Put to Work" box on orbitals and energy.

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

9.122 Methyl isocyanate, CH_3NCO, was made infamous in 1984 when an accidental leakage of this compound from a storage tank in Bhopal, India, resulted in the deaths of about 3,800 people and severe and lasting injury to many thousands more. (**a**) Draw a Lewis structure for methyl isocyanate. (**b**) Draw a ball-and-stick model of the structure, including estimates of all the bond angles in the compound. (**c**) Predict all the bond distances in the molecule. (**d**) Do you predict that the molecule will have a dipole moment? Explain.

Design an Experiment

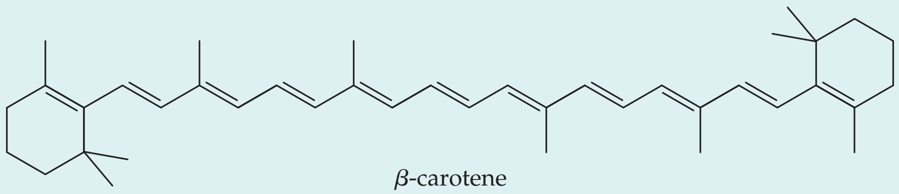
In this chapter we have seen a number of new concepts, including the delocalization of π systems of molecules and the molecular orbital description of molecular bonding. A connection between these concepts is provided by the field of *organic dyes*, molecules with delocalized π systems that have color. The color is due to the excitation of an electron from the *highest occupied molecular orbital* (HOMO) to the *lowest unoccupied molecular orbital* (LUMO). It is hypothesized that the energy gap between the HOMO and the LUMO depends on the length of the π system. Imagine that you are given samples of the following substances to test this hypothesis:



or, in shorthand notation for organic molecules

butadiene

hexatriene



β-carotene

β-carotene is the substance chiefly responsible for the bright orange color of carrots. It is also an important nutrient for the body's production of retinal (see the "Chemistry and Life" box in Section 9.6). (**a**) What experiments could you design to determine the amount of energy needed to excite an electron from the HOMO to the LUMO in each of these molecules? (**b**) How might you graph your data to determine whether a relationship exists between the length of the π system and the excitation energy? (**c**) What additional molecules might you want to procure to further test the ideas developed here? (**d**) How could you design an experiment to determine whether the delocalized π systems and not some other molecular features, such as molecular length or the presence of π bonds, are important in making the excitations occur in the visible portion of the spectrum? (*Hint*: You might want to test some additional molecules not shown here.)