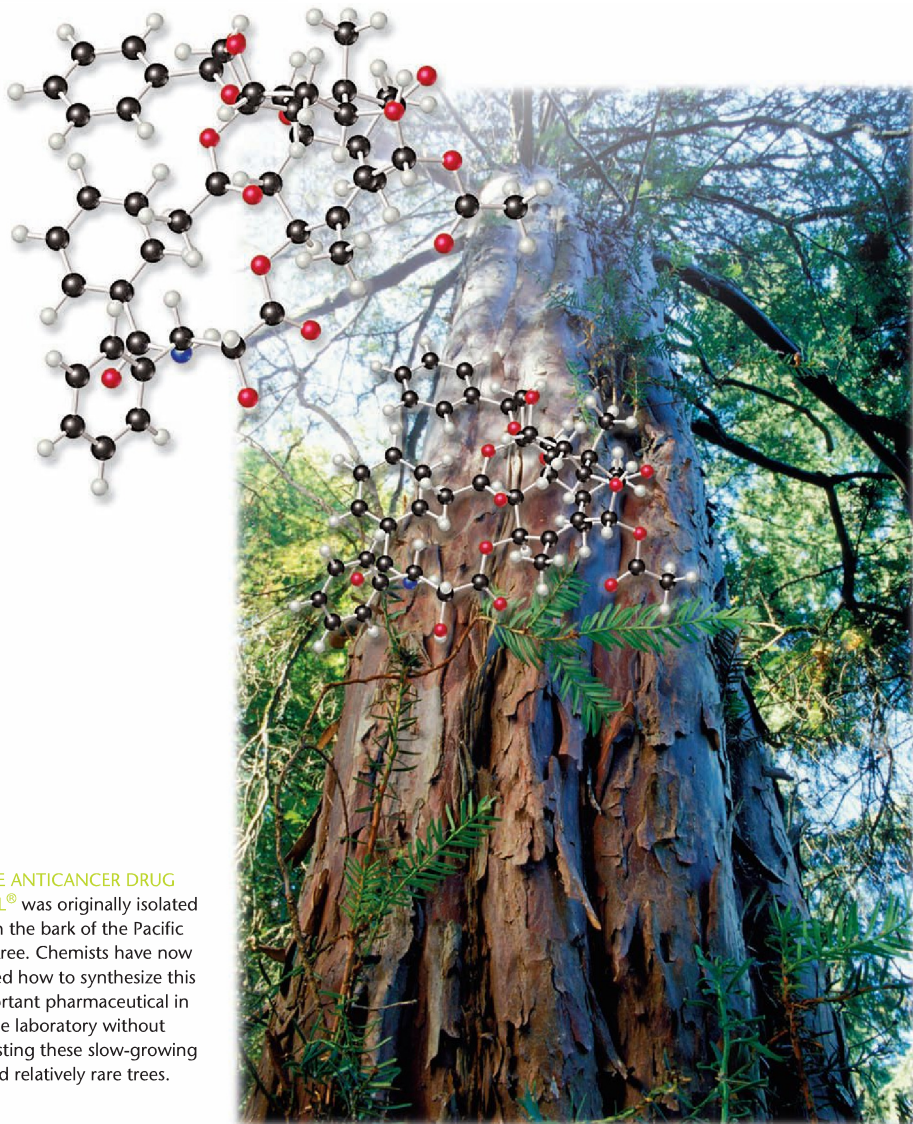


MOLECULAR GEOMETRY
AND BONDING THEORIES

THE ANTICANCER DRUG
TAXOL[®] was originally isolated from the bark of the Pacific yew tree. Chemists have now learned how to synthesize this important pharmaceutical in the laboratory without harvesting these slow-growing and relatively rare trees.

WHAT'S AHEAD

9.1 Molecular Shapes

We begin by discussing how *molecular geometries* are described and by examining some common geometries exhibited by molecules.

9.2 The VSEPR Model

We next consider how molecular geometries can be predicted using a simple model (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 type of bonds in a molecule and the geometry of the molecule, we can determine whether the molecule is *polar* or *nonpolar*.

9.4 Covalent Bonding and Orbital Overlap

We recognize that 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 different atoms. The covalent bond between the atoms arises when these orbitals overlap in space.

9.5 Hybrid Orbitals

To account for molecular shape, we consider how the orbitals of one atom mix with one another, or *hybridize*, to create *hybrid orbitals* suitable for bonding within molecules.

9.6 Multiple Bonds

We consider that overlapping atomic orbitals that underlie covalent bonding in a molecule can overlap in multiple ways, based on geometry, to produce *sigma* (σ) and *pi* (π) bonds between atoms. Single bonds generally consist of one sigma bond between the bonded atoms; multiple bonds involve one sigma and one or more pi bonds.

9.7 Molecular Orbitals

We evaluate a more sophisticated treatment of bonding that uses *molecular orbital theory*, which introduces the concepts of *bonding and antibonding molecular orbitals* arising from atomic orbitals.

9.8 Second-Row Diatomic Molecules

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

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.

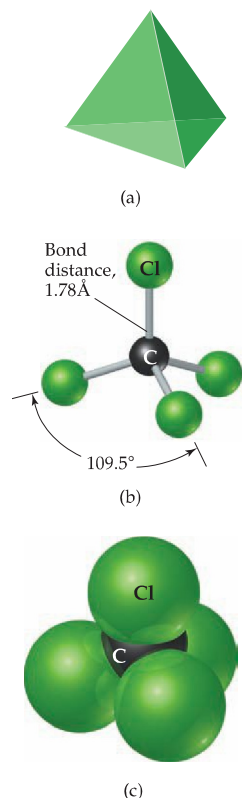
Molecules have shapes and sizes that are defined by the

angles and distances between the nuclei of their component atoms. Indeed, chemists often refer to molecular *architecture* when describing the distinctive shapes and sizes of molecules.

The shape and size of a molecule of a particular 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 shape and size are seen in biochemical reactions and in substances produced by living species. For example, the chapter-opening photograph shows a Pacific yew tree, a species that grows along the Pacific coast of the northwestern United States and Canada. In 1967 two chemists isolated from the

bark of the Pacific yew small amounts of a molecule that was found to be among the most effective treatments for breast and ovarian cancer. This molecule, now known as the pharmaceutical Taxol[®], has a complex molecular architecture that leads to its powerful therapeutic effectiveness. Even a small modification to the shape and size of the molecule decreases its effectiveness and can lead to the formation of a substance toxic to humans. Chemists now know how to synthesize the drug in the laboratory, which has made it more available and has saved the slow-growing Pacific yew tree from possible extinction. Before the drug was synthesized, six trees had to be harvested to provide the Taxol[®] necessary to treat one cancer patient.

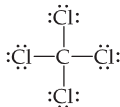
Our first goal in this chapter is to learn the relationship between two-dimensional Lewis structures and three-dimensional molecular shapes. Armed with this knowledge, we can then examine more closely the nature of covalent bonds. The lines that are used to depict bonds in Lewis structures provide important clues about the orbitals that molecules use in bonding. By examining these orbitals, we can gain a greater understanding of the behavior of molecules. You will find that the material in this chapter will help you in later discussions of the physical and chemical properties of substances.



▲ Figure 9.1 Tetrahedral geometry. (a) A tetrahedron is an object with four faces and four vertices. Each face is an equilateral triangle. (b) The geometry of the CCl_4 molecule. Each C—Cl bond in the molecule points toward a vertex of a tetrahedron. All of the C—Cl bonds are the same length, and all of the Cl—C—Cl bond angles are the same. This type of drawing of CCl_4 is called a ball-and-stick model. (c) A representation of CCl_4 , called a space-filling model. It shows the relative sizes of the atoms, but the geometry is somewhat harder to see.

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 between atoms. For example, the Lewis structure of CCl_4 tells us only that four Cl atoms are bonded to a central C atom:

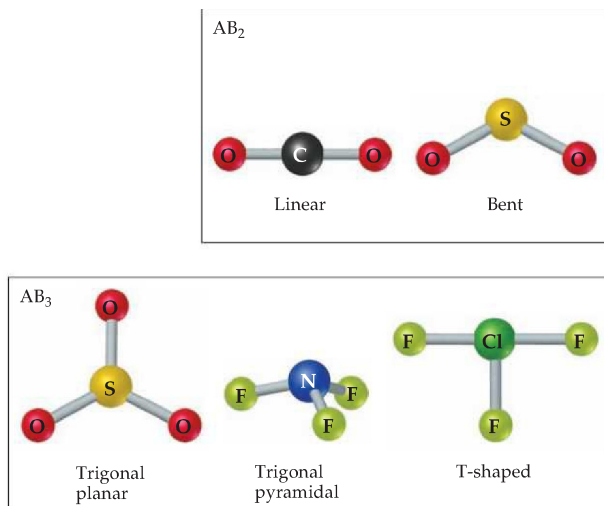


The Lewis structure is drawn with the atoms all in the same plane. As shown in Figure 9.1 \blacktriangleleft , however, the actual three-dimensional arrangement of the atoms shows the Cl atoms at the corners of a *tetrahedron*, a geometric object with four corners and four faces, each of which is an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

The overall 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), accurately define the shape and size of the molecule. In CCl_4 the bond angles are defined as the angles between the C—Cl bonds. You should be able to see that there are six Cl—C—Cl angles in CCl_4 , and they all have the same value— 109.5° , which is characteristic of a tetrahedron. In addition, all four C—Cl bonds are the same length (1.78 \AA). 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 \AA .

In our discussion of the shapes of molecules, we will begin 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 conform to 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 possible shapes of AB_n molecules depend on the value of n . We observe only a few general shapes for a given value of n . Those commonly found for AB_2 and AB_3 molecules are shown in Figure 9.2 \blacktriangleright . Therefore, an AB_2 molecule must be either linear (bond angle = 180°) or bent (bond angle $\neq 180^\circ$). For example, CO_2 is linear, and SO_2 is bent. For AB_3 molecules, the two most common



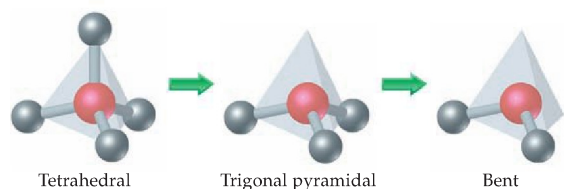
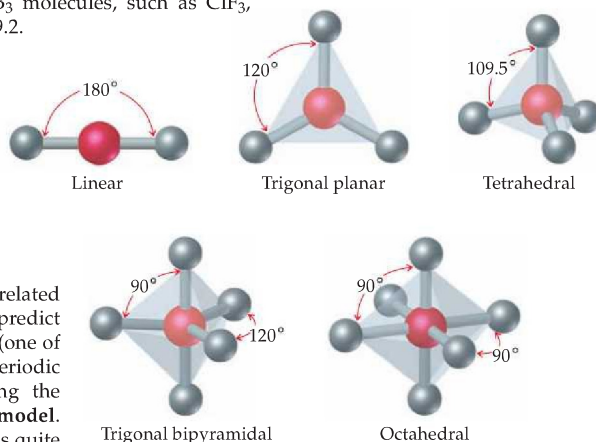
◀ **Figure 9.2 Shapes of AB_2 and AB_3 molecules.** Top: AB_2 molecules can be either linear or bent. Bottom: Three possible shapes for AB_3 molecules.

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). For example, SO_3 is trigonal planar, and NF_3 is trigonal pyramidal. Some AB_3 molecules, such as ClF_3 , exhibit the more unusual *T shape* shown in Figure 9.2.

The shape of any particular AB_n molecule can usually be derived from one of the five basic geometric structures shown in Figure 9.3▶. Starting with a tetrahedron, for example, we can remove atoms successively from the corners as shown in Figure 9.4▼. When an atom is removed from one corner of the tetrahedron, the remaining fragment has a trigonal-pyramidal geometry, such as that found for NF_3 . When two atoms are removed, a bent geometry results.

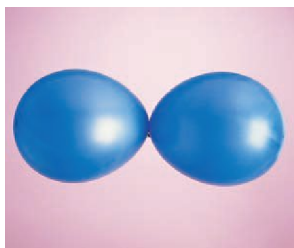
Why do so many AB_n molecules have shapes related to the basic shapes in Figure 9.3, and can we predict these shapes? When A is a representative element (one of the elements from the *s* block or *p* block of the periodic table), we can answer these questions by using the **valence-shell electron-pair 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.

▼ **Figure 9.3 Shapes of AB_n molecules.** For molecules whose formula is of the general form AB_n , there are five fundamental shapes.



◀ **Figure 9.4 Derivatives from the AB_n geometries.**

Additional molecular shapes can be obtained by removing corner atoms from the basic shapes shown in Figure 9.3. Here we begin with a tetrahedron and successively remove corners, producing first a trigonal-pyramidal geometry and then a bent geometry, each having ideal bond angles of 109.5° . Molecular shape is meaningful only when there are at least three atoms. If there are only two, they must be arranged next to each other, and no special name is given to describe the molecule.



(a) Two balloons adopt a linear arrangement.



(b) Three balloons adopt a trigonal-planar arrangement.



(c) Four balloons adopt a tetrahedral arrangement.

▲ **Figure 9.5 A balloon analogy for electron domains.** Balloons tied together at their ends naturally adopt their lowest-energy arrangement.

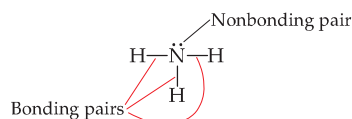
GIVE IT SOME THOUGHT

One of the common shapes for AB_4 molecules is *square planar*: All five atoms lie in the same plane, the B atoms lie at the corners of a square, and the A atom is at the center of the square. Which of the shapes in Figure 9.3 could lead to a square-planar geometry upon the removal of one or more atoms?

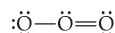
9.2 THE VSEPR MODEL

Imagine tying two identical balloons together at their ends. As shown in Figure 9.5(a), the 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 as shown in Figure 9.5(b). If we add a fourth balloon, they adopt a tetrahedral shape [Figure 9.5(c)]. We see that an optimum geometry exists for each number of balloons.

In some ways the electrons in molecules behave like the balloons shown in Figure 9.5. 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 will most likely be found. We will refer to such a region as an **electron domain**. Likewise, a **nonbonding pair** (or **lone pair**) of electrons defines an electron domain that is located principally on one atom. For example, the Lewis structure of NH_3 has four electron domains around the central nitrogen atom (three bonding pairs and one nonbonding pair):



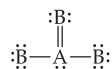
Each multiple bond in a molecule also constitutes a single electron domain. Thus, the following resonance structure for O_3 has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):



In general, each nonbonding pair, single bond, or multiple bond produces an electron domain around the central atom.

GIVE IT SOME THOUGHT

An AB_3 molecule has the resonance structure



Does this Lewis 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

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

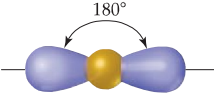
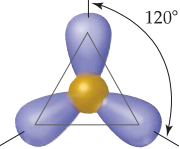
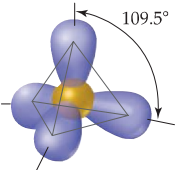
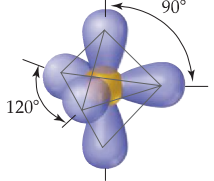
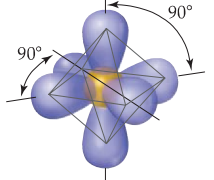
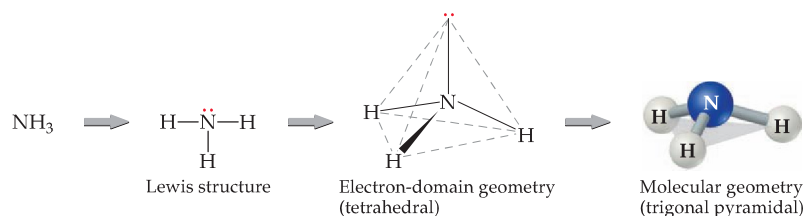
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

Figure 9.5, two electron domains are arranged *linearly*, three domains are arranged in a *trigonal-planar* fashion, and four are arranged *tetrahedrally*. These arrangements, together with those for five electron domains (*trigonal bipyramidal*) and six electron domains (*octahedral*), 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 A atom.*

The arrangement of electron domains about the central atom of an AB_n molecule or ion is called its **electron-domain geometry**. In contrast, the **molecular geometry** is the arrangement of *only the atoms* in a molecule or ion—any nonbonding pairs are not part of the description of the molecular geometry. In the VSEPR model, we predict the electron-domain geometry. From knowing how many domains are due to nonbonding pairs, we can then predict the molecular geometry of a molecule or ion from its electron-domain geometry.



▲ **Figure 9.6 The molecular geometry of NH_3 .** The geometry is predicted by first drawing the Lewis structure, then using the VSEPR model to determine the electron-domain geometry, and finally focusing on the atoms themselves to describe the molecular geometry.

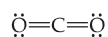
When all the electron domains in a molecule arise from bonds, the molecular geometry is identical to the electron-domain geometry. When, however, one or more of the domains involve nonbonding pairs of electrons, we must remember to ignore those domains when predicting molecular shape. Consider the NH_3 molecule, which has four electron domains around the nitrogen atom (Figure 9.6 ▲). We know from Table 9.1 that the repulsions among four electron domains are minimized when the domains point toward the vertices of a tetrahedron, so the electron-domain geometry of NH_3 is tetrahedral. We know from the Lewis structure of NH_3 that one of the electron domains is due to a nonbonding pair of electrons, which will occupy one of the four vertices of the tetrahedron. Hence the molecular geometry of NH_3 is trigonal pyramidal, as shown in Figure 9.6. Notice that the tetrahedral arrangement of the four electron domains leads us to predict the trigonal-pyramidal molecular 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, and count the total number of electron domains around the central atom. Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as an 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. Because the trigonal-pyramidal molecular geometry is based on tetrahedral electron-domain geometry, the *ideal bond angles* are 109.5° . As we will soon see, bond angles deviate from the ideal angles when the surrounding atoms and electron domains are not identical.

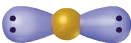

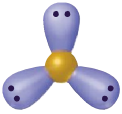
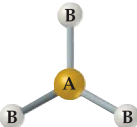

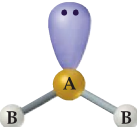
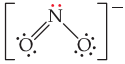

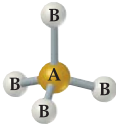

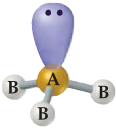

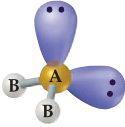

Let's apply these steps to determine the shape of the CO_2 molecule. We first draw its Lewis structure, which reveals two electron domains (two double bonds) around the central carbon:



Two electron domains will arrange themselves to give 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 $\text{O}-\text{C}-\text{O}$ 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 commonly occurring shapes found for molecules or ions that obey the octet rule.

TABLE 9.2 Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains around the Central Atom

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

SAMPLE EXERCISE 9.1 Using the VSEPR Model

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

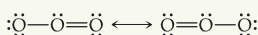
SOLUTION

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

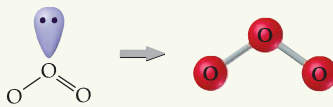
Plan: To predict the molecular geometries of these species, we first draw their Lewis structures and then count the number of electron domains around the central atom. The number of electron domains gives the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the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

Solve:

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

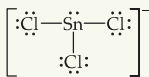


Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double 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 molecule has a bent shape with an ideal bond angle of 120° (Table 9.2).



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 the $SnCl_3^-$ ion is

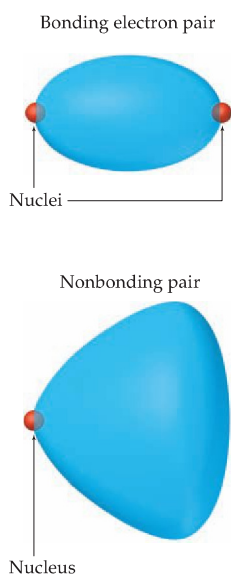


The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair. Therefore, the Sn atom has four electron domains around it. The resulting electron-domain geometry is tetrahedral (Table 9.1) with one of the corners occupied by a nonbonding pair of electrons. The molecular geometry is therefore trigonal pyramidal (Table 9.2), like that of NH_3 .

**PRACTICE EXERCISE**

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

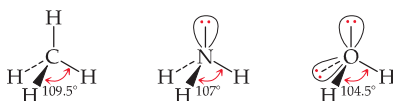
Answers: (a) tetrahedral, bent; (b) trigonal planar, trigonal planar



▲ **Figure 9.7** Relative “sizes” of bonding and nonbonding electron domains.

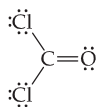
The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

We can refine the VSEPR model to predict and explain slight distortions of molecules 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 tetrahedral electron-domain geometries, 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. By contrast, 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, as shown in Figure 9.7. Nonbonding pairs of electrons, therefore, take up more space than bonding pairs. As a result, the electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress the bond angles. Using the analogy in Figure 9.5, we can envision the domains for nonbonding electron pairs as represented by balloons that are slightly larger and slightly fatter than those for bonding pairs.

Because multiple bonds contain a higher electronic-charge density than single bonds, multiple bonds also represent larger electron domains (“fatter balloons”). Consider the Lewis structure of phosgene, $COCl_2$:



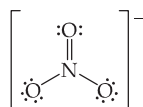
Because three electron domains surround the central carbon atom, we might expect a trigonal-planar geometry with 120° bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the Cl—C—Cl bond angle from the ideal angle of 120° to an actual angle of 111.4°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



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 of the resonance structures of the nitrate ion, NO_3^- , is



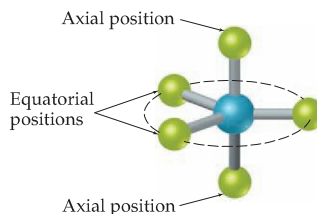
The bond angles in this ion are exactly 120° . Is this observation consistent with the above discussion of the effect of multiple bonds on bond angles?

Molecules with Expanded Valence Shells

So far, our discussion of the VSEPR model has considered molecules with no more than an octet of electrons around the central atom. Recall, however, that when the central atom of a molecule is from the third period of the periodic table and beyond, that atom may have more than four electron pairs around it. ∞ (Section 8.7) Molecules with five or six electron domains around the central atom display a variety of molecular geometries based on the *trigonal-bipyramidal* (five electron domains) or the *octahedral* (six electron domains) electron-domain geometries, as shown in Table 9.3 \blacktriangledown .

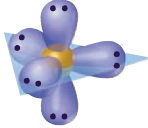
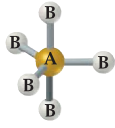
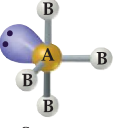
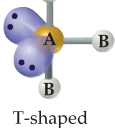
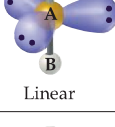
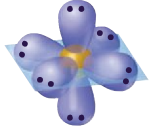

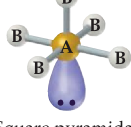
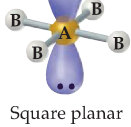
The most stable electron-domain geometry for five electron domains is the trigonal bipyramid (two trigonal pyramids sharing a base). Unlike the arrangements we have seen to this point, the electron domains in a trigonal bipyramid can point toward two geometrically distinct types of positions. Two of the five domains point toward *axial positions*, and the remaining three domains point toward *equatorial positions* (Figure 9.8 \blacktriangleright). 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, one or more of which originates from a nonbonding pair. Will the electron domains from the nonbonding pairs occupy axial or equatorial positions? To answer this question, we must determine which location minimizes the repulsions between the electron domains. Repulsions between domains are 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 two axial domains). By contrast, an axial domain is situated 90° from *three* other domains (the three 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, they always occupy the equatorial positions in a trigonal bipyramid.



▲ Figure 9.8 Trigonal-bipyramidal geometry. Five electron domains arrange themselves around a central atom as a trigonal bipyramid. The three *equatorial* electron domains define an equilateral triangle. The two *axial* domains lie above and below the plane of the triangle. If a molecule has nonbonding electron domains, they will occupy the equatorial positions.

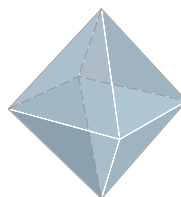
TABLE 9.3 ■ Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains around the Central Atom

Total 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

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*. As shown in Figure 9.9, an octahedron is a polyhedron with eight faces and six vertices, each of which is an equilateral triangle. If an atom has six electron domains around it, that atom can be visualized as being at the center of the octahedron with the electron domains pointing toward the six vertices. All the bond angles in an octahedron 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.



▲ **Figure 9.9** An octahedron. The octahedron is an object with eight faces and six vertices. Each face is an equilateral triangle.

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 atom from the p block of the periodic table.

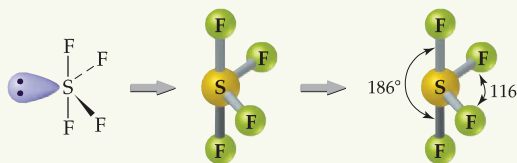
Plan: We can predict their structures by first drawing Lewis structures and then using the VSEPR model to determine the electron-domain geometry and molecular geometry.

Solve:

(a) The Lewis structure for SF_4 is



The sulfur has five electron domains around it: four from the $\text{S}-\text{F}$ 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:

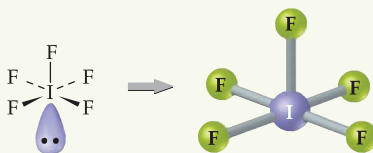


Comment: The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial $\text{S}-\text{F}$ bonds are slightly bent back away from the nonbonding domain, suggesting that the bonding domains are “pushed” by the nonbonding domain, which is larger and has 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 from a nonbonding pair. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair. The resulting molecular geometry is therefore *square pyramidal* (Table 9.3):



Comment: Because the domain for the nonbonding pair is larger than the other domains, the four F atoms in the base of the pyramid are tipped up slightly toward the F atom on top. Experimentally, we find that the angle between the base and top F atoms is 82° , smaller than the ideal 90° angle of an octahedron.

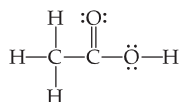
PRACTICE EXERCISE

Predict the electron-domain geometry and molecular geometry of (a) ClF_3 , (b) ICl_4^- .

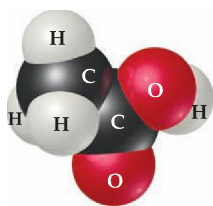
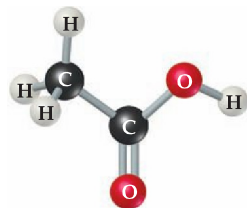
Answers: (a) trigonal bipyramidal, T-shaped; (b) octahedral, square planar

Shapes of Larger Molecules

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



Acetic acid has three interior atoms: the left C atom, the central C atom, and the right-most O atom. We can use the VSEPR model to predict the geometry about each of these atoms individually:



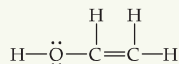
▲ **Figure 9.10** Ball-and-stick (top) and space-filling (bottom) representations of acetic acid, CH_3COOH .

	$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C} \\ \\ \text{H} \end{array} $	$ \begin{array}{c} \text{:O:} \\ // \\ \text{C} \end{array} $	$ \begin{array}{c} \ddot{\text{O}}-\text{H} \end{array} $
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

The leftmost C has four electron domains (all from bonding pairs), and so the geometry around that atom is tetrahedral. The central C has three electron domains (counting the double bond as one domain). Thus, the geometry around that atom is trigonal planar. The O atom has four electron domains (two from bonding pairs and two from nonbonding pairs), so its electron-domain geometry is tetrahedral, and the molecular geometry around O is bent. The bond angles about the central C atom and the O atom are expected to deviate slightly from the ideal values of 120° and 109.5° because of the spatial demands of multiple bonds and nonbonding electron pairs. The structure of the acetic acid molecule is shown in Figure 9.10 ◀.

■ 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 called *vinyl alcohol*:



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

SOLUTION

Analyze: We are given a molecular structure and asked to determine two bond angles in the structure.

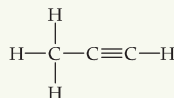
Plan: To predict a particular bond angle, we consider the middle atom of the angle and determine the number of electron domains surrounding that atom. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple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

Solve: For the $\text{H}-\text{O}-\text{C}$ bond angle, the middle O atom has four electron domains (two bonding and two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5° . The $\text{H}-\text{O}-\text{C}$ angle will be 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 must examine the leftmost C atom, which is the central atom for this angle. 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, however, the O—C—C bond angle should be slightly greater than 120° .

PRACTICE EXERCISE

Predict the H—C—H and C—C—C bond angles in the following molecule, called *propyne*:



Answers: 109.5° , 180°

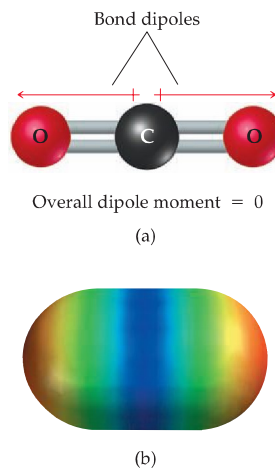
9.3 MOLECULAR SHAPE AND MOLECULAR POLARITY

We now have a sense of the shapes that molecules adopt and why they do so. We will spend the rest of this chapter looking more closely at the ways in which electrons are shared to form the bonds between atoms in molecules. We will begin by returning to a topic that we first discussed in Section 8.4, namely *bond polarity* and *dipole moments*.

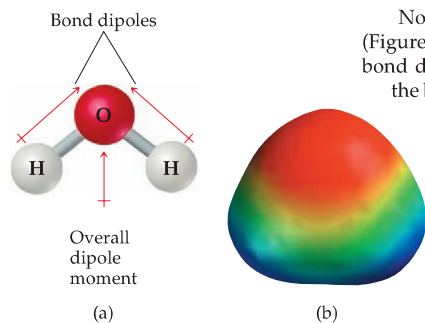
Recall that bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond: As the difference in electronegativity between the two atoms increases, so does the bond polarity. ∞ (Section 8.4) We saw that the dipole moment of a diatomic molecule is a quantitative measure of the amount of charge separation in the molecule. The charge separation in molecules has a significant effect on physical and chemical properties. We will see in Chapter 11, for example, how molecular polarity affects boiling points, melting points, and other physical properties.

For a molecule that consists 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 can consider the **bond dipole**, which is the dipole moment that is due only to the two atoms in that bond. Consider the linear CO_2 molecule, for example. As shown in Figure 9.11(a), 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 electron density of the CO_2 molecule, shown in Figure 9.11(b), clearly shows that the bonds are polar: On the oxygen atoms, regions of high electron density (red) are at the ends of the molecule. On the carbon atom, regions of low electron density (blue) are in the center. But what can we say about the *overall* dipole moment of the CO_2 molecule?

Bond dipoles and dipole moments are *vector* quantities; that is, they have both a magnitude and a direction. The *overall* 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 these vectors. The two bond dipoles in CO_2 , although equal in magnitude, are exactly opposite in direction. Adding them together 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 overall dipole moment of CO_2 is zero, even though the individual bonds are polar. Thus, the geometry of the molecule dictates that the overall dipole moment be zero, making CO_2 a *nonpolar* molecule.



▲ Figure 9.11 CO_2 , a nonpolar molecule. (a) The overall dipole moment of a molecule is the sum of its bond dipoles. In CO_2 the bond dipoles are equal in magnitude, but exactly oppose each other. The overall dipole moment is zero, therefore, making the molecule nonpolar. (b) The electron-density model shows that the regions of higher electron density (red) are at the ends of the molecule while the region of lower electron density (blue) is at the center.



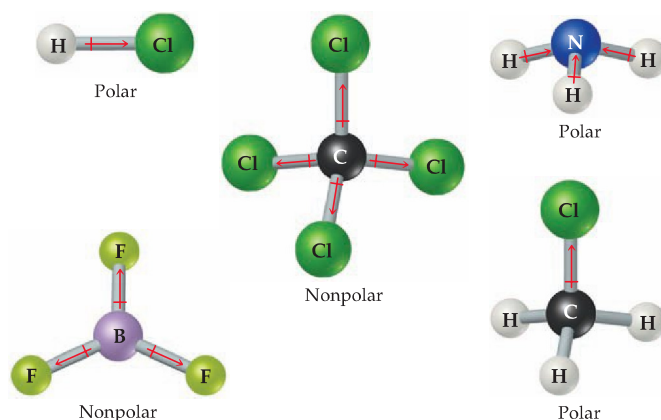
▲ **Figure 9.12** The dipole moment of a bent molecule. (a) In H₂O the bond dipoles are equal in magnitude, but do not exactly oppose each other. The molecule has a nonzero dipole moment overall, making the molecule polar. (b) The electron-density shows that one end of the molecule has more electron density (the oxygen end) while the other end has less electron density (the hydrogens).

Now let's consider H₂O, which is a bent molecule with two polar bonds (Figure 9.12 ◀). Again, the two bonds in the molecule 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 each other. Hence, the H₂O molecule has an overall nonzero dipole moment ($\mu = 1.85$ D). Because H₂O has a nonzero dipole moment, it is a *polar* molecule. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge, as shown by the electron-density model in Figure 9.12(b).

GIVE IT SOME THOUGHT

The molecule O=C=S has a Lewis structure analogous to that of CO₂ and is a linear molecule. Will it necessarily have a zero dipole moment like that of CO₂?

Figure 9.13 ▼ shows examples of polar and nonpolar molecules, all of which have polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms (BF₃ and CCl₄) are nonpolar. For AB_{*n*} molecules in which all the B atoms are the same, certain symmetrical shapes—linear (AB₂), trigonal planar (AB₃), tetrahedral and square planar (AB₄), trigonal bipyramidal (AB₅), and octahedral (AB₆)—must lead to nonpolar molecules even though the individual bonds might be polar.



► **Figure 9.13** Molecules containing polar bonds. Two of these molecules have a zero dipole moment because their bond dipoles cancel one another, while the other molecules are polar.

SAMPLE EXERCISE 9.4 | Polarity of Molecules

Predict whether the following molecules are polar or nonpolar: (a) BrCl, (b) SO₂, (c) SF₆.

SOLUTION

Analyze: We are given the molecular formulas of several substances and asked to predict whether the molecules are polar.

Plan: If the molecule contains only two atoms, it will be polar if the atoms differ in electronegativity. If the molecule contains three or more atoms, its polarity depends on both its molecular geometry and the polarity of its bonds. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry. We then use the relative electronegativities of the atoms in each bond to determine the direction of the bond dipoles. Finally, we see if the bond dipoles cancel each other to give a nonpolar molecule or reinforce each other to give a polar one.

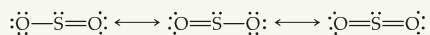
Solve:

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

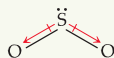


The actual dipole moment of BrCl, as determined by experimental measurement, is $\mu = 0.57$ D.

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



For each of these, the VSEPR model predicts a bent 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. The six S—F bonds are arranged octahedrally around the central sulfur:



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

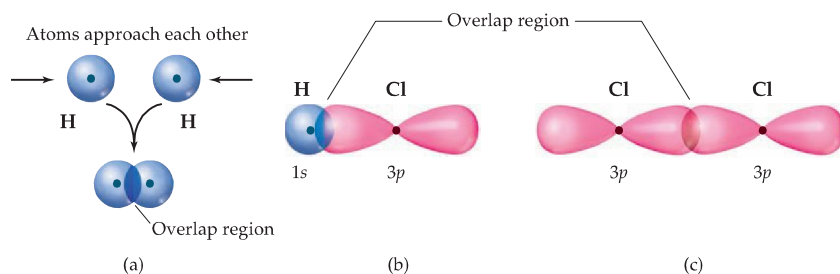
PRACTICE EXERCISE

Determine whether the following molecules are polar or nonpolar: (a) NF_3 , (b) BCl_3 .
Answers: (a) polar because polar bonds are arranged in a trigonal-pyramidal geometry, (b) nonpolar because polar bonds are arranged in a trigonal-planar geometry

9.4 COVALENT BONDING AND ORBITAL OVERLAP

The VSEPR model provides a simple means for predicting the shapes of molecules. However, it 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 the geometries of molecules? 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**. By extending this approach to include the ways in which atomic orbitals can mix with one another, we obtain a picture that corresponds nicely to the VSEPR model.

In the Lewis theory, covalent bonding occurs when atoms share electrons, which concentrates electron density between the nuclei. In the 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 that of another atom. The overlap of orbitals allows two electrons of opposite spin to share the common space between the nuclei, forming a covalent bond.



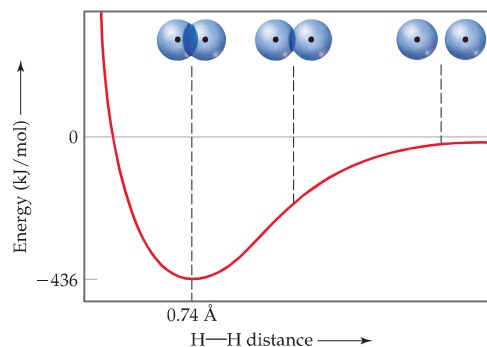
▲ **Figure 9.14 The overlap of orbitals to form covalent bonds.** (a) The bond in H_2 results from the overlap of two $1s$ orbitals from two H atoms. (b) The bond in HCl results from the overlap of a $1s$ orbital of H and one of the lobes of a $3p$ orbital of Cl. (c) The bond in Cl_2 results from the overlap of two $3p$ orbitals from two Cl atoms.

The coming together of two H atoms to form H_2 is depicted in Figure 9.14(a)▲. Each atom has a single electron in a $1s$ orbital. As the orbitals overlap, electron density is concentrated between the nuclei. Because the electrons in the overlap region are simultaneously attracted to both nuclei, they hold the atoms together, forming a covalent bond.

The idea of orbital overlap producing a covalent bond applies equally well to other molecules. In HCl, for example, chlorine has the electron configuration $[\text{Ne}]3s^23p^5$. All the valence orbitals of chlorine are full except one $3p$ orbital, which contains a single electron. This electron pairs with the single electron of H to form a covalent bond. Figure 9.14(b) shows the overlap of the $3p$ orbital of Cl with the $1s$ orbital of H. Likewise, we can explain the covalent bond in the Cl_2 molecule in terms of the overlap of the $3p$ orbital of one atom with the $3p$ orbital of another, as shown in Figure 9.14(c).

There is always an optimum distance between the two bonded nuclei in any covalent bond. Figure 9.15▼ shows how the potential energy of the system changes as two H atoms come together to form an H_2 molecule. At infinite distance, the atoms do not “feel” each other and so the energy approaches zero. As the distance between the atoms decreases, the overlap between their $1s$ orbitals increases. Because of the 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 energy on the curve. However, the curve also shows that as the atoms come very close together, the energy increases sharply. This increase, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance, or bond length, is the distance that corresponds to the minimum of the potential-energy curve. The potential energy at this minimum corresponds to the bond strength. Thus, the observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron–electron and nucleus–nucleus).

► **Figure 9.15 Formation of the H_2 molecule.** Plot of the change in potential energy as two hydrogen atoms come together to form the H_2 molecule. The minimum in the energy, at 0.74 \AA , represents the equilibrium bond distance. The energy at that point, -436 kJ/mol , corresponds to the energy change for formation of the H—H bond.



GIVE IT SOME THOUGHT

If you could put pressure on the hydrogen molecule so that its bond length decreased, would its bond strength increase or decrease? (Refer to Figure 9.15).

9.5 HYBRID ORBITALS

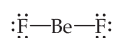
The VSEPR model, simple as it is, does a surprisingly good job at predicting molecular shape, despite the fact that it has no obvious relationship to the filling and shapes of atomic orbitals. For example, based on the shapes and orientations of the $2s$ and $2p$ orbitals on a carbon atom, it is not obvious why a CH_4 molecule should have a tetrahedral geometry. How can we reconcile the notion that covalent bonds are formed from the overlap of atomic orbitals with the molecular geometries that come from the VSEPR model?

To explain geometries, we 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 called **hybridization**. The total number of atomic orbitals on an atom remains constant, however, and so the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

Let's examine the common types of hybridization. As we do so, notice the connection between the type of hybridization and the five basic electron-domain geometries predicted by the VSEPR model: linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral.

sp Hybrid Orbitals

To illustrate the process of hybridization, consider the BeF_2 molecule, which is generated when solid BeF_2 is heated to high temperatures. The Lewis structure of BeF_2 is

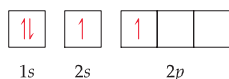


The VSEPR model correctly predicts that BeF_2 is linear with two identical Be—F bonds. How can we use valence-bond theory to describe the bonding? The electron configuration of F ($1s^2 2s^2 2p^5$) indicates there is an unpaired electron in a $2p$ orbital. This $2p$ electron can be paired with an unpaired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

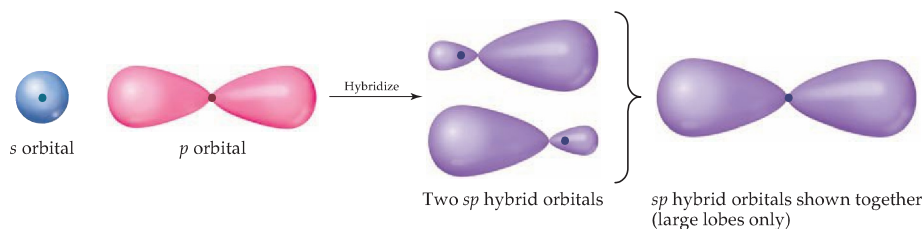
The orbital diagram for a ground-state Be atom is



Because it has no unpaired electrons, the Be atom in its ground state is incapable of forming bonds with the fluorine atoms. The Be atom could form two bonds, however, by “promoting” one of the $2s$ electrons to a $2p$ orbital:



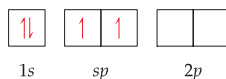
The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with the F atoms. The two bonds would not be identical, however, because a Be $2s$ orbital would be used to form one of the bonds and a $2p$ orbital would be used for the other. Therefore, although the promotion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



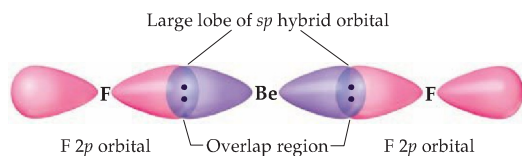
▲ **Figure 9.16 Formation of sp hybrid orbitals.** One s orbital and one p orbital can hybridize to form two equivalent sp hybrid orbitals. The two hybrid orbitals have their large lobes pointing in opposite directions, 180° apart.

We can solve this dilemma by “mixing” the $2s$ orbital with one of the $2p$ orbitals to generate two new orbitals, as shown in Figure 9.16▲. Like p orbitals, each of the new orbitals 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 are hybrid orbitals. Because we have hybridized one s and one p orbital, we call each hybrid an sp hybrid orbital. *According to the valence-bond model, a linear arrangement of electron domains implies sp hybridization.*

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



The electrons in the sp hybrid orbitals can form two-electron bonds with the two fluorine atoms (Figure 9.17◀). Because the sp hybrid orbitals are equivalent but point in opposite directions, BeF_2 has two identical bonds and a linear geometry. The remaining two $2p$ orbitals remain unhybridized.



▲ **Figure 9.17 Formation of two equivalent Be—F bonds in BeF_2 .** Each sp hybrid orbital on Be overlaps with a $2p$ orbital on F to form a bond. The two bonds are equivalent to each other and form an angle of 180° .

GIVE IT SOME THOUGHT

Suppose that the two unhybridized $2p$ orbitals on Be were used to make the Be—F bonds in BeF_2 . Would the two bonds be equivalent to each other? What would be the expected F—Be—F bond angle?

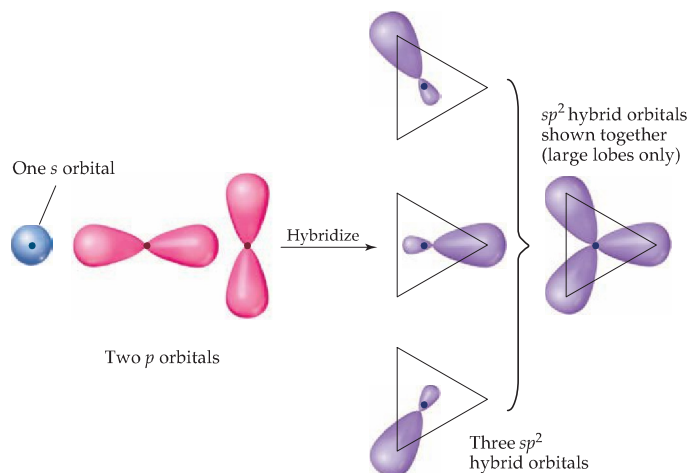
sp^2 and sp^3 Hybrid Orbitals

Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each of these hybrid orbitals is equivalent to the others but points in a different direction. Thus, mixing one $2s$ and one $2p$ orbital yields two equivalent sp hybrid orbitals that point in opposite directions (Figure 9.16). Other combinations of atomic orbitals can be hybridized to obtain different geometries. In BF_3 , for example, mixing the $2s$ and two of the $2p$ orbitals yields three equivalent sp^2 (pronounced “ s - p -two”) hybrid orbitals (Figure 9.18▶).

The three sp^2 hybrid orbitals lie in the same plane, 120° apart from one another (Figure 9.18). They are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal-planar geometry of BF_3 . Notice that an unfilled $2p$ orbital remains unhybridized. This unhybridized orbital will be important when we discuss double bonds in Section 9.6.

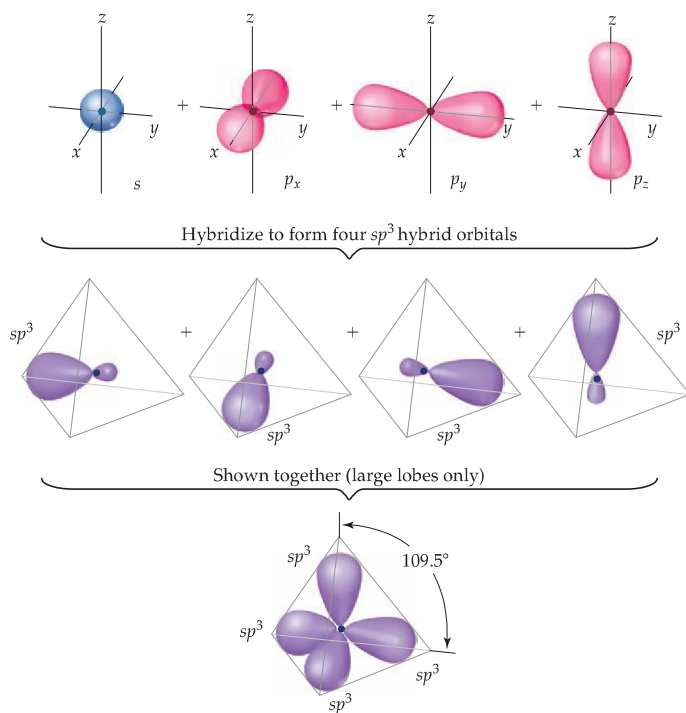
GIVE IT SOME THOUGHT

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

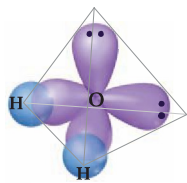


◀ **Figure 9.18 Formation of sp^2 hybrid orbitals.** One s orbital and two p orbitals can hybridize to form three equivalent sp^2 hybrid orbitals. The large lobes of the hybrid orbitals point toward the corners of an equilateral triangle.

An s orbital can also mix with all three p 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 $2s$ and all three $2p$ atomic orbitals of carbon to create four equivalent sp^3 (pronounced “ s - p -three”) hybrid orbitals. Each sp^3 hybrid orbital has a large lobe that points toward a vertex of a tetrahedron, as shown in Figure 9.19 ▼.



◀ **Figure 9.19 Formation of sp^3 hybrid orbitals.** One s orbital and three p orbitals can hybridize to form four equivalent sp^3 hybrid orbitals. The large lobes of the hybrid orbitals point toward the corners of a tetrahedron.



▲ **Figure 9.20 Valence-bond description of H₂O.** The bonding in a water molecule can be envisioned as sp^3 hybridization of the orbitals on O. Two of the four hybrid orbitals overlap with $1s$ orbitals of H to form covalent bonds. The other two hybrid orbitals are occupied by nonbonding pairs of electrons.

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 CH₄ as the overlap of four equivalent sp^3 hybrid orbitals on C with the $1s$ orbitals of the four H atoms to form four equivalent bonds.

The idea of hybridization is used in a similar way to describe the bonding in molecules containing nonbonding pairs of electrons. In H₂O, for example, the electron-domain geometry around the central O atom is approximately tetrahedral. Thus, the four electron pairs can be envisioned as occupying sp^3 hybrid orbitals. Two of the hybrid orbitals contain nonbonding pairs of electrons, while the other two are used to form bonds with hydrogen atoms, as shown in Figure 9.20 ◀.

Hybridization Involving d Orbitals

With the exception of H and He, all atoms have one s and three p orbitals in their valence shell. Because the number of hybrid orbitals must be equal to the number of atomic orbitals that mix to form the hybrids, this fact would seem to limit the maximum number of hybrid orbitals to four. How, then, can we apply the concept of hybridization to molecules where the central atom has more than an octet of electrons around it, such as PF₅ and SF₆? To do so we turn to the unfilled d orbitals with the same value of the principal quantum number, n . Mixing one s orbital, three p orbitals, and one d orbital leads to five sp^3d hybrid orbitals. These hybrid orbitals are directed toward the vertices of a trigonal bipyramid.

Similarly, mixing one s orbital, three p orbitals, and two d orbitals gives six sp^3d^2 hybrid orbitals that are directed toward the vertices of an octahedron. The use of d orbitals in constructing hybrid orbitals nicely corresponds to the notion of an expanded valence shell. ∞ (Section 8.7) Keep in mind, however, that only atoms in the third period and beyond (atoms beyond Ne) possess vacant d orbitals that can be used to form hybrid orbitals of this type. The geometric arrangements characteristic of hybrid orbitals are summarized in Table 9.4 ▶.

Hybrid Orbital Summary

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

The following steps allow us to predict the hybrid orbitals used by an atom in bonding:

1. Draw the *Lewis structure* for the molecule or ion.
2. Determine the electron-domain geometry using the *VSEPR model*.
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 9.21 ▼, which shows how the hybridization employed by N in NH₃ is determined.

▼ **Figure 9.21 Bonding in NH₃.** The hybrid orbitals used by N in the NH₃ molecule are predicted by first drawing the Lewis structure, then using the VSEPR model to determine the electron-domain geometry, and then specifying the hybrid orbitals that correspond to that geometry. This is essentially the same procedure as that used to determine molecular structure (Figure 9.6), except we focus on the orbitals used to make bonds and to hold nonbonding pairs.

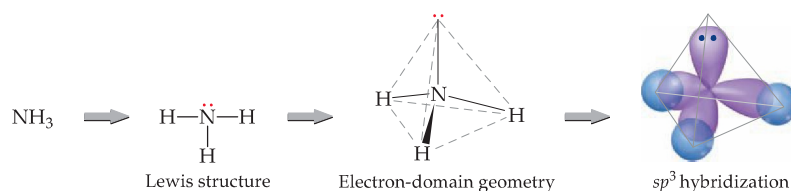
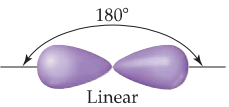
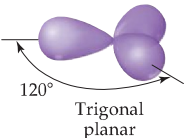
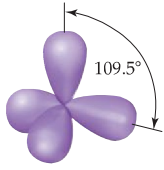
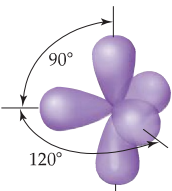
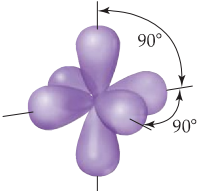


TABLE 9.4 ■ Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s, p	Two sp	 Linear	$\text{BeF}_2, \text{HgCl}_2$
s, p, p	Three sp^2	 Trigonal planar	BF_3, SO_3
s, p, p, p	Four sp^3	 Tetrahedral	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$
s, p, p, p, d	Five sp^3d	 Trigonal bipyramidal	$\text{PF}_5, \text{SF}_4, \text{BrF}_3$
s, p, p, p, d, d	Six sp^3d^2	 Octahedral	$\text{SF}_6, \text{ClF}_5, \text{XeF}_4, \text{PF}_6^-$

SAMPLE EXERCISE 9.5 Hybridization

Indicate the hybridization of orbitals employed by the central atom in (a) NH_2^- , (b) SF_4 (see Sample Exercise 9.2).

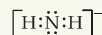
SOLUTION

Analyze: We are given two chemical formulas—one for a polyatomic anion and one for a molecular compound—and asked to describe the type of hybrid orbitals surrounding the central atom in each case.

Plan: To determine the hybrid orbitals used by an atom in bonding, we must know the electron-domain geometry around the atom. Thus, we first 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:

(a) The Lewis structure of NH_2^- is



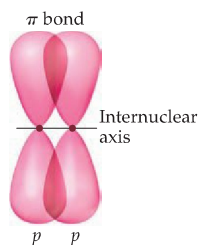
Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp^3 (Table 9.4). Two of the sp^3 hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with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

(b) The Lewis structure and electron-domain geometry of SF_4 are shown in Sample Exercise 9.2. The S atom has five electron domains around it, giving rise to a trigonal-bipyramidal electron-domain geometry. With an expanded octet of ten electrons, a d orbital on the sulfur must be used. The trigonal-bipyramidal electron-domain geometry corresponds to sp^3d hybridization (Table 9.4). One of the hybrid orbitals that points in an equatorial direction contains a nonbonding pair of electrons; the other four are used to form the S—F bonds.

PRACTICE EXERCISE

Predict the electron-domain geometry and the hybridization of the central atom in (a) SO_3^{2-} (b) SF_6 .

Answers: (a) tetrahedral, sp^3 ; (b) octahedral, sp^3d^2



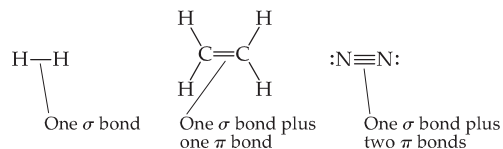
▲ **Figure 9.22 The π bond.** When two p orbitals overlap in a sideways fashion, the result is a π bond. Note that the two regions of overlap constitute a single π bond.

9.6 MULTIPLE BONDS

In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the *internuclear axis*). In other words, the line joining the two nuclei passes through the middle of the overlap region. These bonds are called **sigma (σ) bonds**. The overlap of two s orbitals as in H_2 [Figure 9.14(a)], the overlap of an s and a p orbital as in HCl [Figure 9.14(b)], the overlap between two p orbitals as in Cl_2 [Figure 9.14(c)], and the overlap of a p orbital with an sp hybrid orbital as in BeF_2 (Figure 9.17) are all examples of σ bonds.

To describe multiple bonding, we must consider a second kind of bond that results from the overlap between two p orbitals oriented perpendicularly to the internuclear axis (Figure 9.22 ◀). This sideways overlap of p orbitals produces a **pi (π) bond**. A π bond is a covalent bond in which the overlap regions lie above and below the internuclear axis. Unlike in a σ bond, in a π bond there is no probability of finding the electron on the internuclear axis. Because the p orbitals in a π bond overlap sideways rather than directly facing each other, the total overlap in a π bond tends to be less than that in a σ bond. Consequently, π bonds are generally weaker than σ bonds.

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

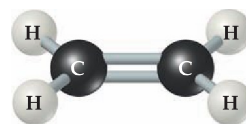


To see how these ideas are used, consider ethylene (C_2H_4), which possesses a $C=C$ double bond. The bond angles in ethylene are all approximately 120° (Figure 9.23), suggesting that each carbon atom uses sp^2 hybrid orbitals (Figure 9.18) to form σ bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after sp^2 hybridization one electron in each of the carbon atoms remains in the *unhybridized* $2p$ orbital. The unhybridized $2p$ orbital is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals.

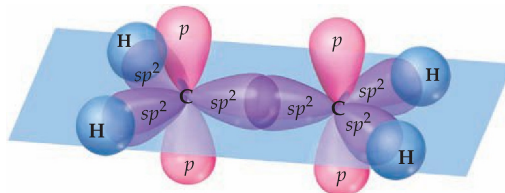
Each sp^2 hybrid orbital on a carbon atom contains one electron. Figure 9.24 shows how the four $C-H$ σ bonds are formed by overlap of sp^2 hybrid orbitals on C with the $1s$ orbitals on each H atom. We use eight electrons to form these four electron-pair bonds. The $C-C$ σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Thus ten of the 12 valence electrons in the C_2H_4 molecule are used to form five σ bonds.

The remaining two valence electrons reside in the unhybridized $2p$ orbitals, one electron on each carbon atom. These two $2p$ orbitals can overlap with each other in a side-ways fashion, as shown in Figure 9.25. The resultant electron density is concentrated above and below the $C-C$ bond axis, which means this is a π bond (Figure 9.22). Thus, the $C=C$ double bond in ethylene consists of one σ bond and one π bond.

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 \AA) is much shorter than in compounds with $C-C$ single bonds (1.54 \AA), 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 $2p$ orbitals that make up the π bond can achieve a good overlap only when the two CH_2 fragments lie in the same plane. If the π bond were absent, there would be no reason for the two CH_2 fragments of ethylene to lie in the same plane. Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.



▲ **Figure 9.23 The molecular geometry of ethylene.** Ethylene, C_2H_4 , has one $C-C$ σ bond and one $C-C$ π bond.



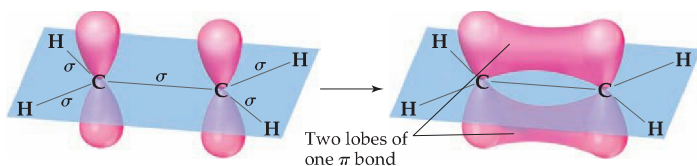
▲ **Figure 9.24 Hybridization in ethylene.** The σ bonding framework is formed from sp^2 hybrid orbitals on the carbon atoms. The unhybridized $2p$ orbitals on the C atoms are used to make a π bond.

GIVE IT SOME THOUGHT

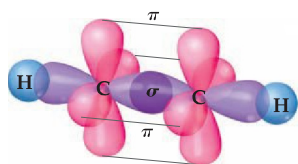
The molecule called *diazine* has the formula N_2H_2 and the Lewis structure



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



▲ **Figure 9.25 The π bond in ethylene.** The unhybridized $2p$ orbitals on each C atom overlap to form a π bond. The electron density in the π bond is above and below the bond axis, whereas in the σ bonds the electron density lies directly along the bond axes. As noted in Figure 9.22, the two lobes constitute one π bond.



▲ **Figure 9.26** Formation of two π bonds. In acetylene, C_2H_2 , the overlap of two sets of unhybridized carbon $2p$ orbitals leads to the formation of two π bonds.

Triple bonds can also be explained using hybrid orbitals. Acetylene (C_2H_2), for example, is a linear molecule containing a triple bond: $H-C\equiv C-H$. The linear geometry suggests that each carbon atom uses sp hybrid orbitals to form σ bonds with the other carbon and one hydrogen. Each carbon atom thus has two remaining unhybridized $2p$ orbitals at right angles to each other and to the axis of the sp hybrid set (Figure 9.26 ◀). These p orbitals overlap to form a pair of π bonds. Thus, the triple bond in acetylene consists of one σ bond and two π bonds.

Although it is possible to make π bonds from d orbitals, the only π bonds we will consider are those formed by the overlap of p orbitals. These π bonds can form only if unhybridized p orbitals are present on the bonded atoms. Therefore, only atoms having sp or sp^2 hybridization can be involved in such π bonding. Further, double and triple bonds (and hence π bonds) are more common in molecules made up of small atoms from the second period, especially C, N, and O. Larger atoms, such as S, P, and Si, form π bonds less readily.

■ 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 appropriate hybridized and unhybridized orbitals.

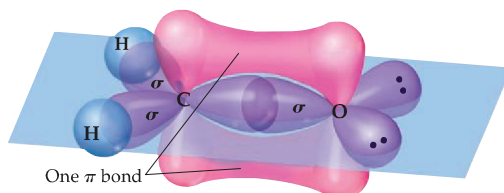
SOLUTION

Analyze: We are asked to describe the bonding in formaldehyde in terms of orbital overlaps.

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

Solve: The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about 120° . This geometry implies sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C—H and one C—O σ bonds to C. There remains an unhybridized $2p$ orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

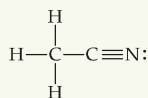
The O atom also has three electron domains around it, and so we will assume that it has sp^2 hybridization as well. One of these hybrids participates in the C—O σ bond, while the other two hybrids hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized $2p$ orbital that is perpendicular to the plane of the molecule. The unhybridized $2p$ orbitals on the C and O atoms overlap to form a C—O π bond, as illustrated in Figure 9.27 ▼.



▲ **Figure 9.27** Formation of σ and π bonds in formaldehyde, H_2CO .

PRACTICE EXERCISE

Consider the acetonitrile molecule:



(a) Predict the bond angles around each carbon atom; (b) describe the hybridization at each of the carbon atoms; (c) determine the total number of σ and π bonds in the molecule.

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

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: \leftrightarrow (Section 8.6)



To describe the bonding in benzene using hybrid orbitals, we first choose a hybridization scheme consistent with the geometry of the molecule. Because each carbon is surrounded by three atoms at 120° angles, the appropriate hybrid set is sp^2 . Six localized C—C σ bonds and six localized C—H σ bonds are formed from the sp^2 hybrid orbitals, as shown in Figure 9.28(a). This leaves a $2p$ orbital on each carbon that is oriented perpendicularly to the plane of the molecule. The situation is very much like that in ethylene, except we now have six carbon $2p$ orbitals arranged in a ring [Figure 9.28(b)]. Each of the unhybridized $2p$ orbitals is occupied by one electron, leaving a total of six electrons to be accounted for by π bonding.

We could envision using the unhybridized $2p$ orbitals of benzene to form three localized π bonds. As shown in Figure 9.29(a) and (b), there are two equivalent ways to make these localized bonds, and each corresponds to one of the resonance structures of the molecule. A representation that reflects *both* resonance structures has the

Figure 9.28 The σ and π bond networks in benzene, C_6H_6 . (a) The C—C and C—H σ bonds all lie in the plane of the molecule and are formed by using carbon sp^2 hybrid orbitals. (b) Each carbon atom has an unhybridized $2p$ orbital that lies perpendicular to the molecular plane. These six $2p$ orbitals form the π orbitals of benzene.

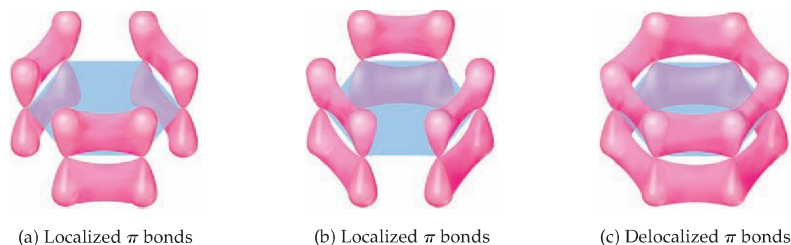
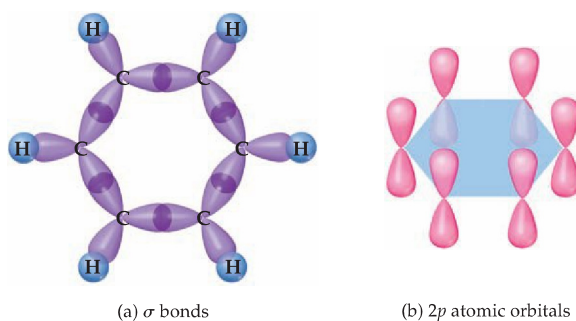


Figure 9.29 Delocalized π bonds. The six $2p$ orbitals of benzene, shown in Figure 9.28(b), can be used to make C—C π bonds. (a, b) Two equivalent ways to make localized π bonds. These π bonds correspond to the two resonance structures for benzene. (c) A representation of the smearing out, or delocalization, of the three C—C π bonds among the six C atoms.

six π electrons “smeared out” among all six carbon atoms, as shown in Figure 9.29(c). Notice how this figure corresponds to the “circle-in-a-hexagon” drawing we often use to represent benzene. This model leads to the description of each carbon-carbon bond as having identical bond lengths that are between the length of a C—C single bond (1.54 Å) and the length of a C=C double bond (1.34 Å), consistent with the observed bond lengths in benzene (1.40 Å).

Because we cannot describe the π bonds in benzene as individual electron-pair bonds between neighboring atoms, we say that the π bonds are **delocalized** among the six carbon atoms. Delocalization of the electrons in its π bonds gives benzene a special stability, as we will discuss in Section 25.3. Delocalization of π bonds is also responsible for the color of many organic molecules. A final important point to remember about delocalized π bonds is the constraint they place upon the geometry of a molecule. For optimal overlap of the unhybridized p orbitals, all of the atoms involved in the delocalized π bonding network should lie in the same plane. This location 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

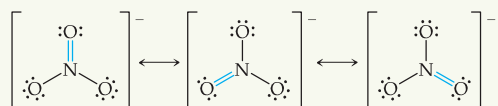
Describe the bonding in the nitrate ion, NO_3^- . Does this ion have delocalized π bonds?

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 in describing the bonding in NO_3^- is to construct appropriate Lewis structures. If there are multiple resonance structures that involve the placement of the double bonds in different locations, that suggests that the π component of the double bonds is delocalized.

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



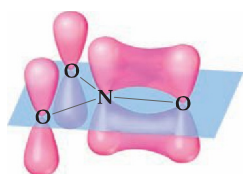
In each of these structures the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. The sp^2 hybrid orbitals are used to construct the three N—O σ bonds that are present in each of the resonance structures.

The unhybridized $2p$ orbital on the N atom can be used to make π bonds. For any one of the three resonance structures shown, we might imagine a single localized N—O π bond formed by the overlap of the unhybridized $2p$ orbital on N and a $2p$ orbital on one of the O atoms, as shown in Figure 9.30(a). Because each resonance structure contributes equally to the observed structure of NO_3^- , however, we represent the π bonding as spread out, or delocalized, over the three N—O bonds, as shown in Figure 9.30(b).

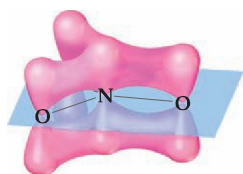
PRACTICE EXERCISE

Which of the following molecules or ions will exhibit delocalized bonding: SO_3 , SO_3^{2-} , H_2CO , O_3 , NH_4^+ ?

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



(a) N—O π bond in one of the resonance structures of NO_3^- .



(b) Delocalization of the π bonds in the NO_3^- ion.

▲ **Figure 9.30** Localized and delocalized π bonds in NO_3^- .

In recent years scientists have begun to understand the complex 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 9.31 ▽). The human retina contains about 3 million cones and 100 million rods. 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*. Rhodopsin consists of a protein, called *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.

Double bonds between atoms are stronger than single bonds between the same atoms (Table 8.4). For example, a C=C double bond is stronger (614 kJ/mol) than a C—C single bond (348 kJ/mol), though not twice as strong. Our recent discussions now allow us to appreciate another aspect of double bonds: the stiffness or rigidity that they introduce into molecules.

Imagine taking the —CH₂ group of the ethylene molecule and rotating it relative to the other —CH₂ group as shown in

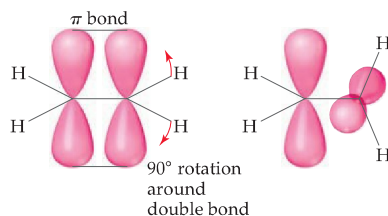


▲ **Figure 9.31 Inside the eye.** A color-enhanced scanning electron micrograph of the rods (yellow) and cones (blue) in the retina of the human eye.

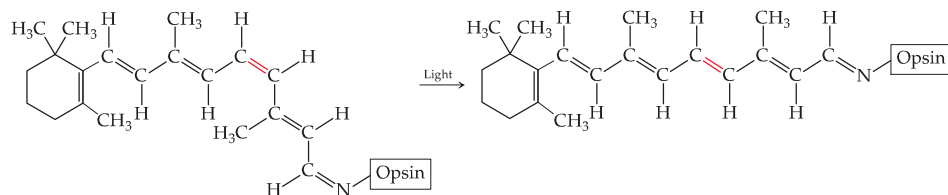
Figure 9.32 ▽. This rotation destroys the overlap of *p* orbitals, breaking the π bond, a process that requires considerable energy. Thus, the presence of a double bond restricts the rotation of the bonds in a molecule. In contrast, molecules can rotate almost freely around the bond axis in single (σ) bonds because this motion has no effect on the orbital overlap for a σ bond. This rotation allows molecules with single bonds to twist and fold almost as if their atoms were attached by hinges.

Our vision depends on the rigidity of double bonds in retinal. In its normal form, retinal is held rigid by its double bonds, as shown on the left in Figure 9.33 ▽. Light entering the eye is absorbed by rhodopsin, and the energy is used to break the π -bond portion of the indicated double bond. The molecule then rotates around this bond, changing its geometry. The retinal then separates from the opsin, triggering the reactions that produce a nerve impulse that the brain interprets as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus, only five photons of light are necessary to stimulate the eye.

The retinal slowly reverts to its original form and reattaches to the opsin. The slowness of this process helps explain why intense bright light causes temporary blindness. The light causes all the retinal to separate from opsin, leaving no further molecules to absorb light.
Related Exercises: 9.99 and 9.100



▲ **Figure 9.32 Rotation about the carbon-carbon double bond in ethylene.** The overlap of the *p* orbitals that form the π bond is lost in the rotation. For this reason, rotation about double bonds requires the absorption of energy.



▲ **Figure 9.33 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.

General Conclusions

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

1. Every pair of bonded atoms shares one or more pairs of electrons. The lines we draw in Lewis structures represent two electrons each. In every bond at least one pair of electrons is localized in the space between the atoms in a σ bond. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule. The correlation between the set of hybrid orbitals and the geometry about an atom is given in Table 9.4.
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contribution to the bonding between any other two atoms.
3. When atoms share more than one pair of electrons, one pair is used to form a σ bond; the additional pairs form π bonds. The centers of charge density in a π bond lie above and below the internuclear axis.
4. Molecules with two or more resonance structures can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two atoms are delocalized.

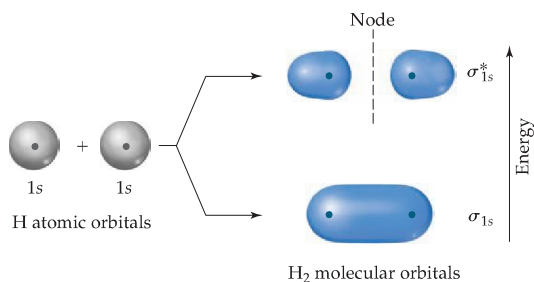
9.7 MOLECULAR ORBITALS

Valence-bond theory and hybrid orbitals allow us to move in a straightforward way from Lewis structures to rationalizing the observed geometries of molecules in terms of atomic orbitals. For example, we can use this theory to understand why methane has the formula CH_4 , how the carbon and hydrogen atomic orbitals are used to form electron-pair bonds, and why the arrangement of the C—H bonds about the central carbon is tetrahedral. This model, however, does not explain all aspects of bonding. It is not successful, for example, in describing the excited states of molecules, which we must understand to explain how molecules absorb light, giving them color.

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

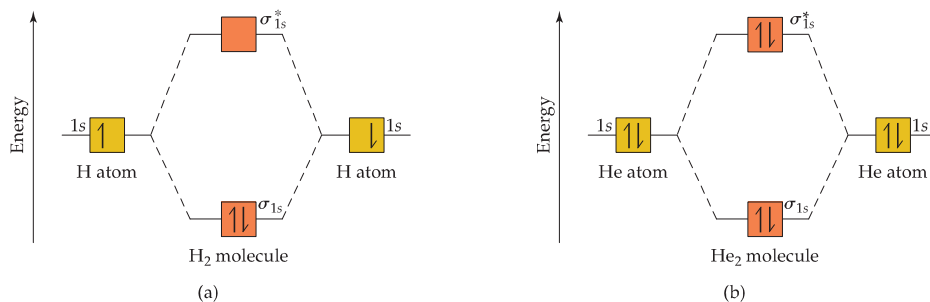
Molecular orbitals have many of the same characteristics as atomic orbitals. For example, an MO can hold a maximum of two electrons (with opposite spins), it has a definite energy, and we can visualize its electron-density distribution by using a contour representation, as we did when we discussed atomic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

▼ **Figure 9.34 The molecular orbitals of H_2 .** The combination of two H $1s$ atomic orbitals forms two molecular orbitals (MOs) of H_2 . In the bonding MO, σ_{1s} , the atomic orbitals combine constructively, leading to a buildup of electron density between the nuclei. In the antibonding MO, σ_{1s}^* , the orbitals combine destructively in the bonding region. Note that the σ_{1s}^* MO has a node between the two nuclei.



The Hydrogen Molecule

To appreciate the approach taken in MO theory, we will begin with the simplest molecule: the hydrogen molecule, H_2 . We will use the two $1s$ atomic orbitals (one on each H atom) to “build” molecular orbitals for the H_2 molecule. *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 (Figure 9.34 ◀). One of the molecular orbitals lies lower in energy from the two atomic orbitals from which it was made; the other molecular orbital lies higher in energy.



▲ **Figure 9.35 Energy-level diagrams for H₂ and He₂.** (a) The two electrons in the H₂ molecule occupy the σ_{1s} bonding MO. (b) In the (hypothetical) He₂ molecule, both the σ_{1s} bonding MO and the σ_{1s}^* antibonding MO are occupied by two electrons.

The lower-energy MO of H₂ concentrates electron density between the two hydrogen nuclei and is called the **bonding molecular orbital**. This sausage-shaped MO results from summing the two atomic orbitals so that the atomic orbital wave functions combine in the region between the two nuclei. Because an electron in this MO is attracted to both nuclei, the electron is more stable (it has lower energy) than it is in the 1s atomic orbital of an isolated hydrogen atom. Further, because this bonding MO concentrates electron density between the nuclei, it holds the atoms together in a covalent bond.

The higher-energy MO in Figure 9.34 has very little electron density between the nuclei and is called the **antibonding molecular orbital**. 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 nuclei. Thus, this MO excludes electrons from the very region in which a bond must be formed. An electron in this MO is repelled from the bonding region and is therefore less stable (it has higher energy) than it is in the 1s atomic orbital of a hydrogen atom.

The electron density in both the bonding MO and the antibonding MO of H₂ is centered about the internuclear axis. MOs of this type are called **sigma (σ) molecular orbitals** (by analogy to the σ bonds that were defined in Section 9.6). The bonding sigma MO of H₂ is labeled σ_{1s} ; the subscript indicates that the MO is formed from two 1s orbitals. The antibonding sigma MO of H₂ is labeled σ_{1s}^* (read “sigma-star-one-s”); the asterisk denotes that the MO is antibonding.

The interaction between two 1s atomic orbitals and the molecular orbitals that result can be represented by an **energy-level diagram** (also called a **molecular orbital diagram**), such as those in Figure 9.35 ▲. Such diagrams show the interacting atomic orbitals in the left and right columns and the MOs in the middle column. Note that the bonding molecular orbital, σ_{1s} , is lower in energy than the atomic 1s orbitals, whereas the antibonding orbital, σ_{1s}^* , is higher in energy than the 1s orbitals. Like atomic orbitals, each MO can accommodate two electrons with their spins paired (Pauli exclusion principle). ∞ (Section 6.7) The molecular orbital diagram of the H₂ molecule is shown in Figure 9.35(a). Each H atom brings one electron to the molecule, so there are two electrons in H₂. These two electrons occupy the lower-energy bonding (σ_{1s}) MO, and their spins are paired. Electrons occupying a bonding molecular orbital are called *bonding electrons*. Because the σ_{1s} MO is lower in energy than the isolated 1s atomic orbitals, the H₂ molecule is more stable than the two separate H atoms. By analogy with atomic electron configurations, the electron configurations for molecules can also be written with superscripts to indicate electron occupancy. The electron configuration for H₂, then, is σ_{1s}^2 .

In contrast, the hypothetical He₂ molecule requires four electrons to fill its molecular orbitals, as in Figure 9.35(b). Because only two electrons can be put in the σ_{1s} MO, the other two electrons must be placed in the σ_{1s}^* MO. The electron configuration of He₂ is $\sigma_{1s}^2 \sigma_{1s}^{*2}$. The energy decrease from the two electrons in the bonding MO is offset by the energy increase from the two electrons in the antibonding MO.* Hence, He₂ 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:

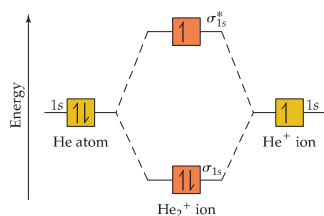
$$\text{Bond order} = \frac{1}{2} (\text{no. of bonding electrons} - \text{no. of antibonding electrons})$$

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

Because H₂ has two bonding electrons and zero antibonding electrons [Figure 9.35(a)], it has a bond order of 1. Because He₂ has two bonding and two antibonding electrons [Figure 9.35(b)], it has a bond order of 0. A bond order of 0 means that no bond exists.

GIVE IT SOME THOUGHT

Suppose light is used to excite one of the electrons in the H₂ molecule 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?



▲ Figure 9.36 Energy-level diagram for the He₂⁺ ion.

SAMPLE EXERCISE 9.8 | Bond Order

What is the bond order of the He₂⁺ 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 He₂⁺ ion and use it to predict whether the ion is stable.

Plan: To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the 1s orbital, and the 1s orbitals combine to give an MO diagram like that for H₂ or He₂ (Figure 9.35). 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 He₂⁺ ion is shown in Figure 9.36. This ion has three electrons. Two are placed in the bonding orbital, the third in the antibonding orbital. Thus, the bond order is

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

Because the bond order is greater than 0, we predict the He₂⁺ ion to be stable relative to the separated He and He⁺. Formation of He₂⁺ in the gas phase has been demonstrated in laboratory experiments.

PRACTICE EXERCISE

Determine the bond order of the H₂⁻ ion.

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

*In fact, antibonding MOs are slightly more unfavorable than bonding MOs are 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 and no bond is formed.

9.8 SECOND-ROW DIATOMIC MOLECULES

Just as we treated the bonding in H_2 by using molecular orbital theory, we can consider the MO description of other diatomic molecules. Initially we will restrict our discussion to *homonuclear* diatomic molecules (those composed of two identical atoms) of elements in the second row of the periodic table. As we will see, the procedure for determining the distribution of electrons in these molecules closely follows the one we used for H_2 .

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

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

Molecular Orbitals for Li_2 and Be_2

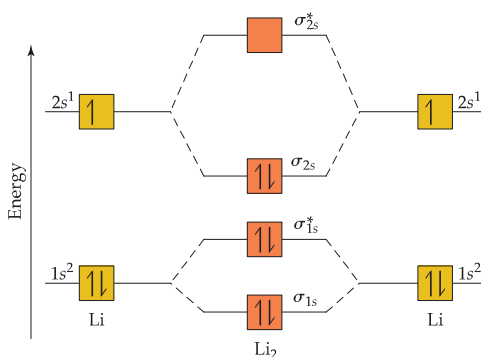
Lithium, the first element of the second period, has a $1s^2 2s^1$ electron configuration. When lithium metal is heated above its boiling point ($1342^\circ C$), Li_2 molecules are found in the vapor phase. The Lewis structure for Li_2 indicates a $Li-Li$ single bond. We will now use MOs to describe the bonding in Li_2 .

Because the $1s$ and $2s$ orbitals of Li are so different in energy, we may assume that the $1s$ orbital on one Li atom interacts only with the $1s$ orbital on the other atom (rule 2). Likewise, the $2s$ orbitals interact only with each other. The resulting energy-level diagram is shown in Figure 9.37. Notice that combining four atomic orbitals produces four MOs (rule 1).

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

Each Li atom has three electrons, so six electrons must be placed in the MOs of Li_2 . As shown in Figure 9.37, 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 equals $\frac{1}{2}(4 - 2) = 1$. 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 $1s$ orbitals contribute almost nothing to the bonding. The single bond in Li_2 is due essentially to the interaction of the valence $2s$ orbitals on the Li atoms. This example



▲ Figure 9.37 Energy-level diagram for the Li_2 molecule.

illustrates the general rule that *core electrons usually do not contribute significantly to bonding in molecule formation*. The rule is equivalent to using only the valence electrons when drawing Lewis structures. Thus, we need not consider further the $1s$ orbitals while discussing the other second-row diatomic molecules.

The MO description of Be_2 follows readily from the energy-level diagram for Li_2 . Each Be atom has four electrons ($1s^2 2s^2$), so we must place eight electrons in molecular orbitals. Thus, we completely fill the σ_{1s} , σ_{1s}^* , σ_{2s} , and σ_{2s}^* MOs. We have an equal number of bonding and antibonding electrons, so the bond order equals 0. Consistent with this analysis, Be_2 does not exist.

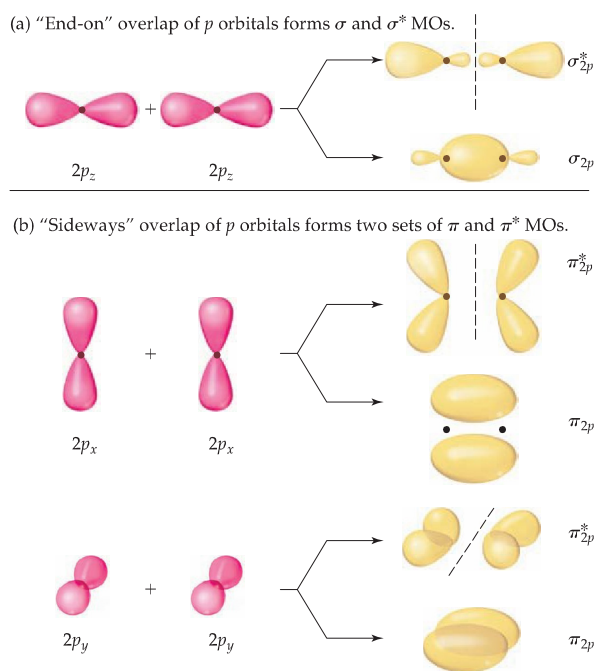
GIVE IT SOME THOUGHT

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

Molecular Orbitals from $2p$ Atomic Orbitals

Before we can consider the remaining second-row molecules, we must look at the MOs that result from combining $2p$ atomic orbitals. The interactions between p orbitals are shown in Figure 9.38, where we have arbitrarily chosen the internuclear axis to be the z -axis. The $2p_z$ orbitals face each other in a “head-to-head” fashion. Just as we did for the s orbitals, we can combine the $2p_z$ 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; it is an antibonding molecular orbital. In each of these MOs the electron density lies along the line through the nuclei, 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 a line connecting the nuclei. MOs of this type are called **pi (π) molecular orbitals**, by analogy to π bonds we saw in Section 9.6. 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. The π_{2p}^* orbitals are mutually 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 the Figure 9.38. The $2p_z$ orbitals on two atoms point directly at each other. Hence, the overlap of two $2p_z$ orbitals is greater than that for 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.



◀ **Figure 9.38** Contour representations of the molecular orbitals formed by $2p$ orbitals. Each time we combine two atomic orbitals, we obtain two MOs: one bonding and one antibonding.

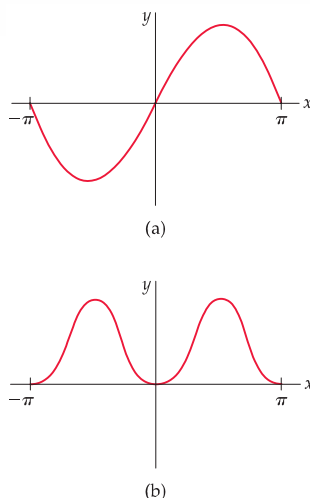
A Closer Look

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 obtaining two characteristics of the electrons—namely, 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 itself does not have a direct physical meaning. (Section 6.5) The contour representations of atomic and molecular orbitals that we have presented thus far are based on the square of the wave function, ψ^2 (the *probability density*), which gives the probability of finding the electron at a given point in space.

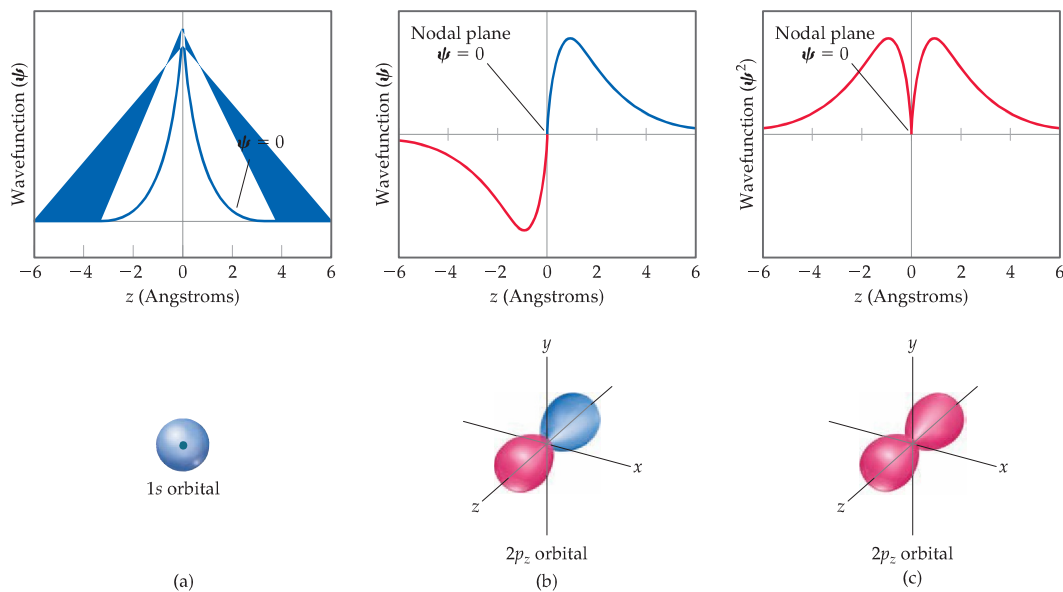
Because probability densities are squares of functions, their values must be nonnegative (zero or positive) at all points in space. However, the functions themselves can have negative values. Consider, for example, the simple sine function, plotted in Figure 9.39. From the drawing on the top, you can see that the sine function has negative values for x between 0 and $-\pi$, and positive values 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 look the same on each side of the origin. Both of the peaks are positive because squaring a negative number produces a positive number—we lose the phase information of the function upon squaring it.

The wave functions for the atomic orbitals are much more complicated than the simple sine function, but like the sine function they can have phases. Consider, for example, the representations of the 1s orbital in Figure 9.40a. The 1s orbital is plotted a bit differently than we saw in Chapter 6. The origin



◀ **Figure 9.39** Phases in the sine function. (a) A full cycle of a sine wave ($y = \sin x$) has two equivalent halves that are opposite in sign (phase). The origin is a node. (b) Squaring the sine function ($y = \sin^2 x$) produces two equivalent positive peaks. The origin is still a node.

▼ **Figure 9.40** Phases in s and p atomic orbital wavefunctions. (a) The wave function for a 1s orbital is plotted on top, with its contour representation below. The 1s orbital has no nodes. (b) The wave function for a $2p$ orbital is plotted on top, with its contour representation below. The $2p$ orbital has a node, and the phase of the wave function changes on either side of the node. In the contour picture, this change of phase is represented by two colors for the two lobes of the orbital. (c) The square of the wave function gives the probability density for the $2p$ orbital. The square of the wave function is plotted on top, with the contour representation below. The contour representation has only one color to denote that the phase information has been lost by squaring the wave function.



1s orbital

(a)

$2p_z$ orbital

(b)

$2p_z$ orbital

(c)

is the point where the nucleus is, and the wave function for the $1s$ orbital extends from the origin in space. The plot shows the value of the wave function, 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. Thus, it has only one phase. Notice also that the wave function never goes to zero. It therefore has no nodes, as we saw in Chapter 6.

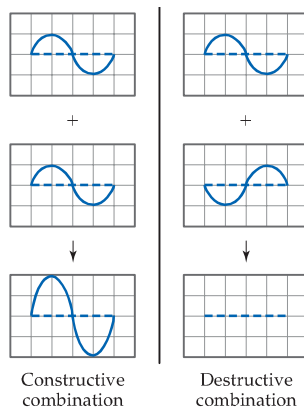
In Figure 9.40b we see a similar set of representations for the $2p_z$ orbital. Now the wave function changes sign upon crossing through $z = 0$. Notice that the two halves of the wave have the same shape except that one has positive values and the other negative values; the wave function changes phase upon crossing 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 9.40b gives a typical representation used by chemists of the wave function for a p_z orbital.* The two different colors for the lobes indicate the different signs or phases of the orbital. Like the sine function, the origin is a node.

What happens if we square the $2p_z$ wave function? Figure 9.40c shows that when we square the wave function of the $2p_z$ orbital, we get two peaks that look the same on each side of the origin. Both of the peaks are positive because squaring a negative number produces a positive number—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_x orbital, we get the probability density for the orbital, which is given as a contour representation in Figure 9.40c. For this function, both lobes have the same phase and therefore the same color. We use this representation throughout most of this book.

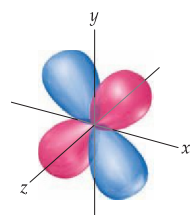
The lobes of the wave functions for the d orbitals also have different phases. For example, the wave function for a d_{xy} orbital has four lobes that alternate in phase, as shown in Figure 9.41. The wave functions for the other d orbitals likewise have lobes of alternating phase.

Why do we need to consider the additional complexity that is introduced by considering the sign or phase of the wave function? While it is true that the phase of the wave function 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 together that are of the same phase, they add

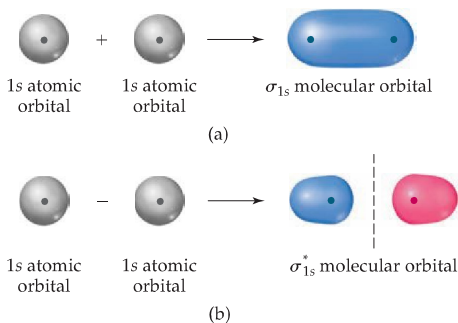
constructively, resulting in increased amplitude as shown in the accompanying figure. On the other hand, if you add two sine functions together that are of the opposite phase, they add *destructively* and cancel each other.



The idea of constructive and destructive interactions of wave functions is key to understanding the origin of bonding and antibonding molecular orbitals that arise from combining or overlapping of atomic orbitals. For example, the wave function of the σ_{1s} MO of H_2 is generated by adding the wave function for the $1s$ orbital on one atom to the wave function for the $1s$ orbital on the other atom, with both orbitals having the same phase. We can say that the atomic wave functions overlap *constructively* in this case, to increase the electron density between the two atoms (Figure 9.42a). The wave function of the σ_{1s}^* MO of H_2 is generated by adding the wave function for a $1s$ orbital on one atom to the wave function for a $1s$ orbital on the other atom, but with the two orbitals having opposite phases. This amounts to subtracting $1s$ orbital from the other. The atomic orbital wave functions overlap *destructively* in this case, to create a region of zero electron density between the two atoms—a node. Chemists generally sketch the wave functions by simply drawing the contour representations of the $1s$ orbitals in different colors to denote the two phases (Figure 9.42b).



◀ **Figure 9.41 Phases in d orbitals.** The wave function for the d_{xy} orbital has lobes of alternating sign.



▲ **Figure 9.42 Molecular orbitals from atomic orbital wave functions.** (a) The mixing of two $1s$ orbitals that are of the same phase produces a σ_{1s} MO. (b) The mixing of two $1s$ orbitals that are opposite in phase produces a σ_{1s}^* MO.

*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.

Notice how this wave function has similarities to both the sine function and to a p orbital—in each of these cases we have two parts of the function of opposite phase separated by a node. When we square the wave function of the σ_{1s}^* MO, we get the probability density representation given in Figure 9.34—notice that we once again lose the phase information when we look at the probability density.

Our brief discussion has given you only an introduction to the mathematical subtleties of atomic and molecular orbitals. Chemists use the wave functions of atomic and molecular orbitals to understand many aspects of chemical bonding and spectroscopy. You will probably see orbitals drawn in color to show phases if you take a course in organic chemistry. *Related Exercises: 9.89, 9.103, 9.105*

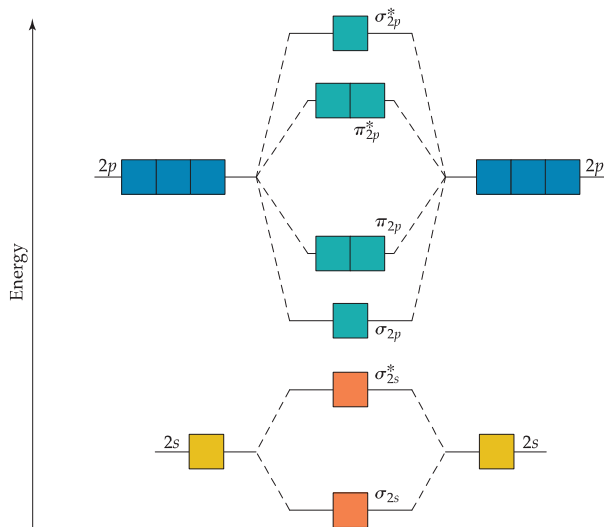
Electron Configurations for B_2 Through Ne_2

So far, we have independently considered the MOs that result from s orbitals (Figure 9.34) and from p orbitals (Figure 9.38). We can combine these results to construct an energy-level diagram (Figure 9.43) for homonuclear diatomic molecules of the elements boron through neon, all of which have valence $2s$ and $2p$ atomic orbitals. The following features of the diagram are notable:

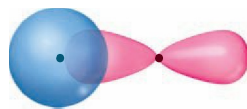
1. The $2s$ atomic orbitals are lower in energy than the $2p$ atomic orbitals. ∞ (Section 6.7) Consequently, both of the molecular orbitals that result from the $2s$ orbitals, the bonding σ_{2s} and antibonding σ_{2s}^* , are lower in energy than the lowest-energy MO derived from the $2p$ atomic orbitals.
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}^* molecular orbitals are *doubly degenerate*; that is, there are two degenerate MOs of each type.

Before we can add electrons to the energy-level diagram in Figure 9.43, we must consider one more effect. We have constructed the diagram assuming there is no interaction between the $2s$ orbital on one atom and the $2p$ orbitals on the other. In fact, such interactions can and do take place. Figure 9.44 shows the overlap of a $2s$ orbital on one of the atoms with a $2p_z$ orbital on the other. These interactions affect the energies of the σ_{2s} and σ_{2p} molecular orbitals in such a way that these MOs move further apart in energy, the σ_{2s} falling and the σ_{2p} rising in energy (Figure 9.45). These $2s$ – $2p$ interactions are 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 second-row diatomic molecules B_2 through Ne_2 . For example, a boron atom has three valence electrons. (Remember that we are ignoring the inner-shell $1s$ electrons.) Thus, for B_2 we must place six electrons in MOs. Four of these electrons fully occupy the σ_{2s} and σ_{2s}^* MOs, leading to no net bonding. The last two electrons are put in the π_{2p} bonding MOs; one electron is put in one π_{2p} MO and the other electron is put 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 the second row, two more electrons must be placed in the diagram. For example, on moving to C_2 , we have two more electrons than in B_2 , and these electrons are placed in the

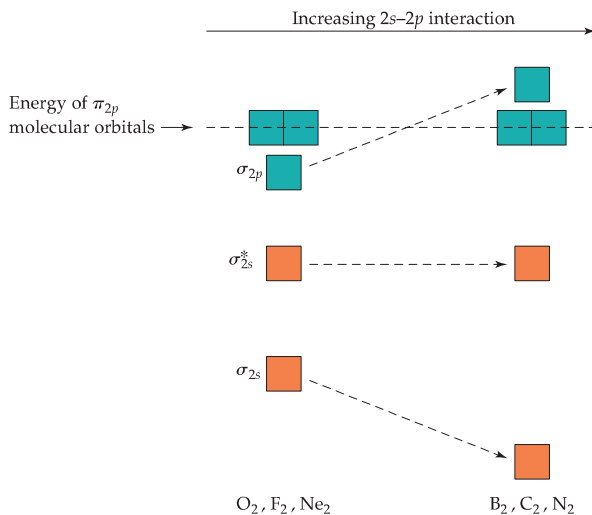


▲ **Figure 9.43 Energy-level diagram for MOs of second-row homonuclear diatomic molecules.** The diagram assumes no interaction between the $2s$ atomic orbital on one atom and the $2p$ atomic orbitals on the other atom, and experiment shows that it fits only for O_2 , F_2 , and Ne_2 .



▲ **Figure 9.44 Interaction of $2s$ and $2p$ atomic orbitals.** The $2s$ orbital on one atom of a diatomic molecule can overlap with the $2p_z$ orbital on the other atom. These $2s$ – $2p$ interactions can alter the energetic ordering of the MOs of the molecule.

► **Figure 9.45 The effect of 2s–2p interactions.** When the 2s and 2p orbitals interact, the σ_{2s} MO falls in energy and the σ_{2p} MO rises in energy. For O_2 , F_2 , and Ne_2 , the interaction is small, and the σ_{2p} MO remains below the π_{2p} MOs, as in Figure 9.43. For B_2 , C_2 , and N_2 , the 2s–2p interaction is great enough that the σ_{2p} MO rises above the π_{2p} MOs, as shown on the right.



π_{2p} MOs, completely filling them. The electron configurations and bond orders for the diatomic molecules B_2 through Ne_2 are given in Figure 9.46 ▼.

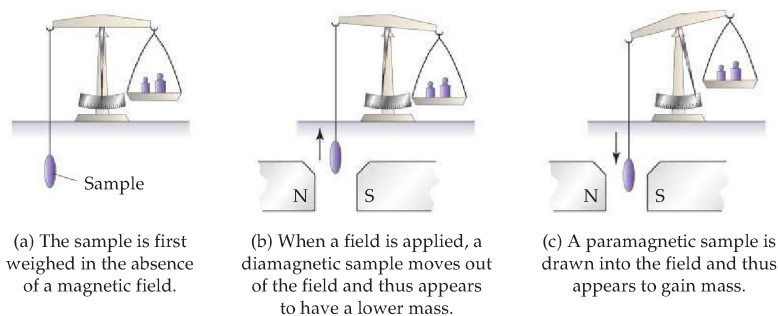
Electron Configurations and Molecular Properties

The way a substance behaves in a magnetic field provides an important insight into the arrangements of its electrons. Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons in a species, the stronger the force of attraction will be. This type of magnetic behavior is called **paramagnetism**.

Substances with no unpaired electrons are weakly repelled from a magnetic field. This property is called **diamagnetism**. Diamagnetism is a much weaker effect than paramagnetism. A straightforward method for measuring the

	Large 2s–2p interaction			Small 2s–2p interaction		
	B_2	C_2	N_2	O_2	F_2	Ne_2
σ_{2p}^*						
π_{2p}^*						
σ_{2p}						
π_{2p}						
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 9.46 The second-row diatomic molecules.** Molecular orbital electron configurations and some experimental data for several second-row diatomic molecules.



(a) The sample is first weighed in the absence of a magnetic field. (b) When a field is applied, a diamagnetic sample moves out of the field and thus appears to have a lower mass. (c) A paramagnetic sample is drawn into the field and thus appears to gain mass.

▲ **Figure 9.47 Determining the magnetic properties of a sample.** The response of a sample to a magnetic field indicates whether it is diamagnetic or paramagnetic. Paramagnetism is a much stronger effect than diamagnetism.

magnetic properties of a substance, illustrated in Figure 9.47 ▲, involves weighing the substance in the presence and absence of a magnetic field. If the substance is paramagnetic, it will appear to weigh more in the magnetic field; if it is diamagnetic, it will appear to weigh less. The magnetic behaviors observed for the diatomic molecules of the second-row elements agree with the electron configurations shown in Figure 9.46.

GIVE IT SOME THOUGHT

Figure 9.46 indicates that the C_2 molecule is diamagnetic. Would that be expected if the σ_{2p} MO were lower in energy than the π_{2p} MOs?

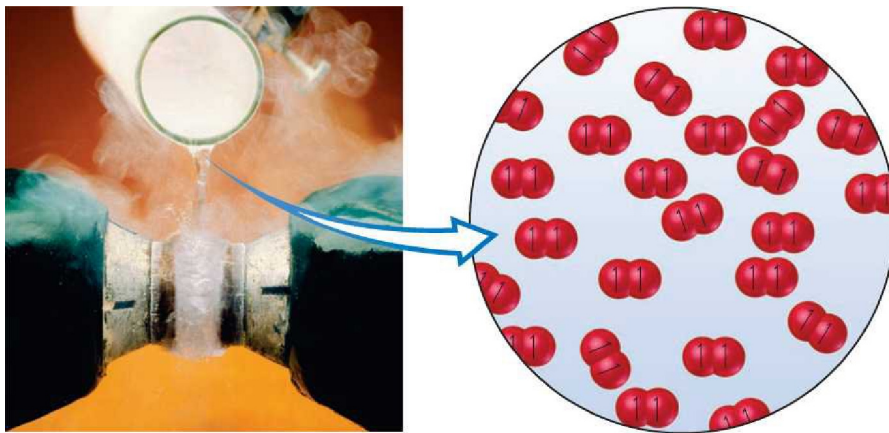
The electron configurations can also be related to the bond distances and bond enthalpies of the molecules. $\infty\infty$ (Section 8.8) As bond orders increase, bond distances decrease and bond enthalpies increase. N_2 , for example, whose bond order is 3, has a short bond distance and a large bond 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 the nuclear charges and the extent of orbital overlap.

Bonding in the dioxygen molecule, O_2 , is especially interesting. Its Lewis structure shows a double bond and complete pairing of electrons:



The short O—O bond distance (1.21 Å) and the relatively high bond enthalpy (495 kJ/mol) are in agreement with the presence of a double bond. However, the molecule contains two unpaired electrons. The paramagnetism of O_2 is demonstrated in Figure 9.48 ▼. Although the Lewis structure fails to account for the paramagnetism of O_2 , molecular orbital theory correctly predicts that two unpaired electrons are in the π_{2p}^* orbital of the molecule (Figure 9.46). The MO description also correctly indicates a bond order of 2.

Going from O_2 to F_2 , we add two more 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 9.48 Paramagnetism of O_2 .** Liquid O_2 being poured between the poles of a magnet. Because each O_2 molecule contains two unpaired electrons, O_2 is paramagnetic. It is therefore attracted into the magnetic field and “sticks” between the magnetic poles.

■ SAMPLE EXERCISE 9.9 | Molecular Orbitals of a Second-Row Diatomic Ion

Predict the following properties of O_2^+ : (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 the data in Figure 9.46 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 9.46). Therefore, O_2^+ has just 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

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

(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, respectively. The experimental bond enthalpy and bond length of the ion are 625 kJ/mol and 1.123 Å, respectively.

■ PRACTICE EXERCISE

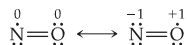
Predict the magnetic properties and bond orders of (a) the peroxide ion, O_2^{2-} ; (b) the acetylide ion, C_2^{2-} .

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

Heteronuclear Diatomic Molecules

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

The NO molecule controls several important human physiological functions. Our bodies use it, for example, to relax muscles, to kill foreign cells, and to 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 “signalling” 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:

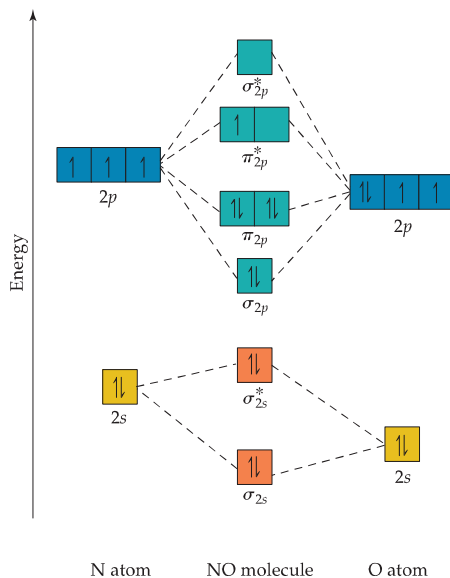


Both structures indicate the presence of a double bond, but when compared with the molecules in Figure 9.46, the experimental bond length of NO (1.15 Å) suggests a bond order greater than two. How do we treat NO using the MO model?

If the atoms in a heteronuclear diatomic molecule do not differ too greatly in their electronegativities, the description of their MOs will resemble those for homonuclear diatomics, with one important modification: The atomic energies of the more electronegative atom will be lower in energy than those of the less electronegative element. The MO diagram for NO is shown in Figure 9.49. You can see that the $2s$ and $2p$ atomic orbitals of oxygen are slightly lower than those of nitrogen because oxygen is more electronegative than nitrogen. We see that the MO energy-level diagram 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 change in the MOs when we consider heteronuclear molecules. The MOs that result are still a mix of the atomic orbitals from both atoms, but in general *an MO will have 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.

We complete the MO diagram for NO by filling the MOs in Figure 9.49 with the 11 valence electrons. We see that there are eight bonding and three antibonding electrons, giving 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 are more heavily weighted toward the N atom. Thus, the Lewis structure that places the unpaired electron on nitrogen (the one preferred on the basis of formal charge) is a more accurate description of the true electron distribution in the molecule.



▲ Figure 9.49 The MO energy-level diagram for NO.

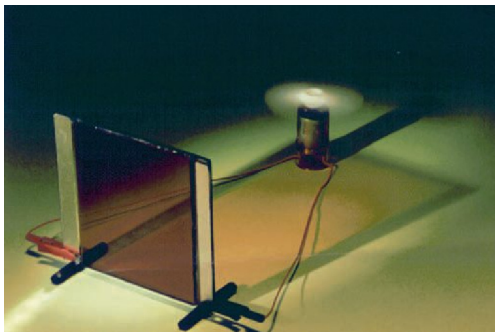
Chemistry Put to Work

ORBITALS AND ENERGY

If you were asked to identify the major technological challenge for the twenty-first century, you might say “energy.” The development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. Currently, the majority of the world, in one way or another, relies on exothermic combustion reactions of oil, coal, or natural gas to provide heat and ultimately power. Oil, coal, and natural gas are examples of “fossil fuels”—carbon-containing compounds that are the long-term decomposition products of ancient plants and animals. Fossil fuels are not renewable in the several-hundred-year timeframe in which we need them. But every day our planet receives plenty of energy from the Sun to easily power the world for millions of years. Whereas the combustion of fossil fuels results in release of CO_2 into the atmosphere, solar energy represents a renewable energy source that is potentially less harmful to the environment. One way to utilize solar energy is to convert it into electrical energy using photovoltaic solar cells. The problem with this alternative is that the current efficiency of solar cell devices is low; only about 10–15% of sunlight is converted into useful energy. Furthermore, the cost of manufacturing solar cells is relatively high.

How does solar energy conversion work? Fundamentally, we need to be able to use photons from the Sun to excite electrons in molecules and materials to different energy levels. The brilliant colors around you—those of your clothes, the photographs in this book, the foods you eat—are due to the selective absorption of light by chemicals. Light excites electrons in molecules. In a molecular orbital picture, we can envision light exciting an electron from a filled molecular orbital to an empty one at higher energy. Because the MOs have definite energies, only light of the proper wavelengths can excite electrons. The situation is analogous to that of atomic line spectra. ∞ (Section 6.3) If the appropriate wavelength for exciting electrons is in the visible portion of the electromagnetic spectrum, the substance will appear colored: Certain wavelengths of white light are absorbed; others are not. A green leaf appears green because only green light is reflected by the leaf; other wavelengths of visible light are absorbed by the leaf.

In using molecular orbital theory to discuss the absorptions of light by molecules, we can focus on two MOs in particular. 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 π_{2p} MO and the LUMO is the π_{2p}^* MO (Figure 9.46). 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



▲ **Figure 9.50 Light into electricity.** The light from a flashlight, to the left of the photograph frame, is sufficient to excite electrons from one energy level to another in this simple solar cell, producing electricity that powers the small fan. To capture more light, a red ruthenium-containing complex is added to the colorless TiO_2 paste between the glass plates.

needed to excite an electron 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 any visible light and is therefore colorless.

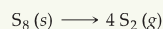
The magnitude of the energy gap between filled and empty electronic states is critical for solar energy conversion. Ideally, we would like to have a substance that absorbs as many solar photons as possible and then convert the energy of those photons into a useful form of energy such as electricity. Titanium dioxide, for example, 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 output. Scientists are working to make solar cells in which TiO_2 is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light. That way, the molecules can absorb more of the solar spectrum. The molecule’s HOMO must also be higher in energy than the TiO_2 ’s HOMO so that the excited electrons can flow from the molecules into the TiO_2 , thereby generating electricity when the device is illuminated with light and connected to an external circuit.

Figure 9.50 ▲ shows a simple solar cell made from ruthenium-containing molecules, which appear red, mixed with TiO_2 in a paste, sandwiched between two glass plates. Light that shines from a flashlight to the left of the device generates enough current to run the small fan that is connected to it with wires.

Related Exercises: 9.93, 9.104

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

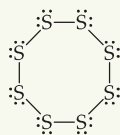
Elemental sulfur is a yellow solid that consists of S_8 molecules. The structure of the S_8 molecule is a puckered, eight-membered ring (Figure 7.34). Heating elemental sulfur to high temperatures produces gaseous S_2 molecules:



(a) With respect to electronic structure, which element in the second row of the periodic table is most similar to 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 . Is the molecule expected to be diamagnetic or paramagnetic? (d) Use average bond enthalpies (Table 8.4) to estimate the enthalpy change for the reaction just described. 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 we would expect a tetrahedral electron-domain geometry corresponding to sp^3 hybridization. ∞ (Sections 9.2, 9.5) Because of the nonbonding pairs, we would expect the S—S—S angles to be somewhat less than 109° , 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 (like a stop sign), 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 entirely analogous to those of O_2 , although the MOs for S_2 are constructed from the 3s and 3p atomic orbitals of sulfur. Further, S_2 has the same number of valence electrons as O_2 . Thus, by analogy to our discussion of O_2 , we would 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 . ∞ (Section 9.8) (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 course of 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:

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

Because $\Delta H_{\text{rxn}} > 0$, 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 REVIEW

SUMMARY AND KEY TERMS

Introduction and Section 9.1 The three-dimensional shapes and sizes of molecules are determined by their **bond angles** and bond lengths. Molecules with a central atom A surrounded by n atoms B, denoted AB_n , adopt a number of different geometric shapes, depending on the value of n and on the particular atoms involved. In the

overwhelming majority of cases, these geometries are related to five basic shapes (linear, trigonal pyramidal, tetrahedral, trigonal bipyramidal, and octahedral).

Section 9.2 The **valence-shell electron-pair repulsion (VSEPR) model** rationalizes molecular geometries based

on the repulsions between **electron domains**, which are regions about a central atom in which electrons are likely to be found. **Bonding pairs** of electrons, which are those involved in making bonds, and **nonbonding pairs** of electrons, also called lone pairs, both create electron domains around an atom. According to the VSEPR model, electron domains orient themselves to minimize electrostatic repulsions; that is, they remain as far apart as possible. Electron domains from nonbonding pairs exert slightly greater repulsions than those from bonding pairs, which leads to certain preferred positions for nonbonding pairs and to the departure of bond angles from idealized values. Electron domains from multiple bonds exert slightly greater repulsions than those from single bonds. The arrangement of electron domains around a central atom is called the **electron-domain geometry**; the arrangement of atoms is called the **molecular geometry**.

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

Section 9.4 Valence-bond theory is an extension of Lewis's notion of electron-pair bonds. In valence-bond theory, covalent bonds are formed when atomic orbitals on neighboring atoms **overlap** one another. The overlap region is a favorable one for the two electrons because of their attraction to two nuclei. The greater the overlap between two orbitals, the stronger will be the bond that is formed.

Section 9.5 To extend the ideas of valence-bond theory to polyatomic molecules, we must envision mixing s , p , and sometimes d orbitals to form **hybrid orbitals**. The process of **hybridization** leads to hybrid atomic orbitals that have a large lobe directed to overlap with orbitals on another atom to make a bond. Hybrid orbitals can also accommodate nonbonding pairs. A particular mode of hybridization can be associated with each of the five common electron-domain geometries (linear = sp ; trigonal planar = sp^2 ; tetrahedral = sp^3 ; trigonal bipyramidal = sp^3d ; and octahedral = sp^3d^2).

Section 9.6 Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called **sigma (σ) bonds**. Bonds can also be formed from the sideways overlap of p orbitals. Such a bond is called a **pi (π) bond**. A double bond, such as that in C_2H_4 , consists of one σ bond and one π bond; a triple bond, such as that in C_2H_2 , consists of one σ and two π bonds. The formation of a π bond requires that molecules adopt a specific orientation; the two CH_2 groups in C_2H_4 , for example, must lie in the same plane. As a result, the presence of π bonds introduces rigidity into molecules.

In molecules that have multiple bonds and more than one resonance structure, such as C_6H_6 , the π bonds are **delocalized**; that is, the π bonds are spread among several atoms.

Section 9.7 Molecular orbital theory is another model used to describe the bonding in molecules. In this model the electrons exist in allowed energy states called **molecular orbitals (MOs)**. These orbitals can be spread among 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. The combination of two atomic orbitals leads to the formation of two MOs, one at lower energy, and one at higher energy relative to the energy of the atomic orbitals. The lower-energy MO concentrates charge density in the region between the nuclei and is called a **bonding molecular orbital**. The higher-energy MO excludes electrons from the region between the nuclei and is called an **antibonding molecular orbital**. Occupation of bonding MOs favors bond formation, whereas occupation of antibonding MOs is unfavorable. The bonding and antibonding MOs formed by the combination of s orbitals are **sigma (σ) molecular orbitals**; like σ bonds, they lie on the internuclear axis.

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

Section 9.8 Electrons in core orbitals do not contribute to the bonding between atoms, so a molecular orbital description usually needs to consider only electrons in the outermost electron subshells. In order to describe the MOs of second-row 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 pairs of degenerate (same energy) bonding and 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. This ordering is reversed in B_2 , C_2 , and N_2 because of interaction between the $2s$ and $2p$ atomic orbitals of different atoms.

The molecular orbital description of second-row 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**, an attraction of a molecule by a magnetic field due to unpaired electrons. Those molecules in which all the electrons are paired exhibit **diamagnetism**, a weak repulsion from a magnetic field.

KEY SKILLS

- Be able to describe the three-dimensional shapes of molecules using the VSEPR model.
- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments.
- Be able to identify the hybridization state of atoms in molecules.
- Be able to sketch how orbitals overlap to form sigma (σ) and pi (π) bonds.
- Be able to explain the concept of bonding and antibonding orbitals.
- Be able to 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.
- Understand the relationships among bond order, bond strength, and bond length.

KEY EQUATIONS

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

VISUALIZING CONCEPTS

- 9.1 A certain AB_4 molecule has a “seesaw” shape:

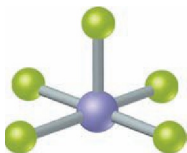


From which of the fundamental geometries shown in Figure 9.3 could you remove one or more atoms to create a molecule having this seesaw shape? [Section 9.1]

- 9.2 (a) If the three balloons shown on the right 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, what happens to the angle between the red and green balloons? (c) What aspect of the VSEPR model is illustrated by part (b)? [Section 9.2]



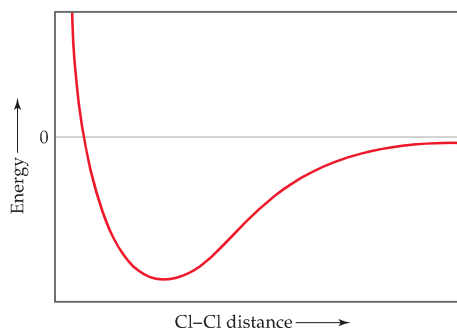
- 9.3 An AB_5 molecule adopts the geometry shown below. (a) What is the name of this geometry? (b) Do you think there are any nonbonding electron pairs on atom A? Why or why not? (c) Suppose the atoms B are halogen atoms. Can you determine uniquely to which group in the periodic table atom A belongs? [Section 9.2]



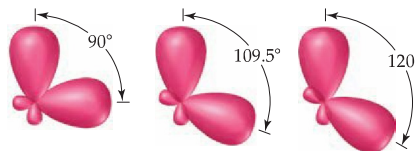
- 9.4 The molecule shown here is *difluoromethane* (CH_2F_2), which is used as a refrigerant called R-32. (a) Based on the structure, how many electron domains surround the C atom in this molecule? (b) Would the molecule have a nonzero dipole moment? (c) If the molecule is polar, in what direction will the overall dipole moment vector point in the molecule? [Sections 9.2 and 9.3]



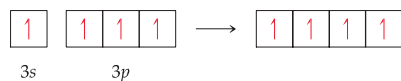
- 9.5 The plot below shows the potential energy of two Cl atoms as a function of the distance between them. (a) To what does an energy of zero correspond in this diagram? (b) According to the valence-bond model, why does the energy decrease as the Cl atoms move from a large separation to a smaller one? (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]



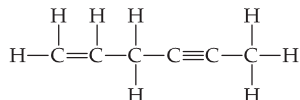
- 9.6 Shown below are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type or types of hybridization that could lead to hybrid orbitals at the specified angle. [Section 9.5]



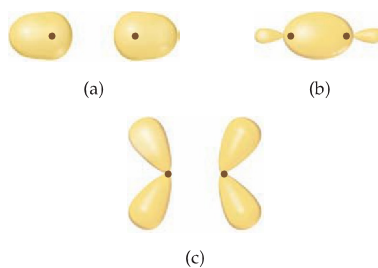
- 9.7 The orbital diagram below presents the final step in the formation of hybrid orbitals by a silicon atom. What type of hybrid orbitals is produced in this hybridization? [Section 9.5]



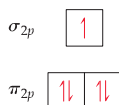
- 9.8 Consider the hydrocarbon drawn below. (a) What is the hybridization at each carbon atom in the molecule? (b) How many σ bonds are there in the molecule? (c) How many π bonds? [Section 9.6]



- 9.9 For each of the following contour representations of molecular orbitals, identify (i) the atomic orbitals (s or p) used to construct the MO, (ii) the type of MO (σ or π), and (iii) whether the MO is bonding or antibonding. [Sections 9.7 and 9.8]



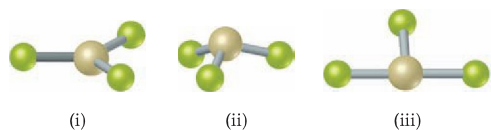
- 9.10 The diagram below shows the highest occupied MOs of a neutral molecule CX, where element X is in the same row of the periodic table as C. (a) Based on the number of electrons, can you determine the identity of X? (b) Would the molecule be diamagnetic or paramagnetic? (c) Consider the π_{2p} MOs 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]



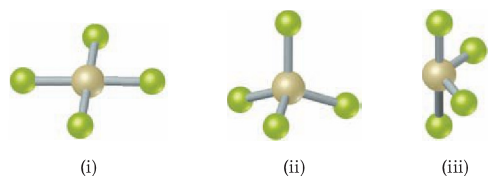
EXERCISES

Molecular Shapes; the VSEPR Model

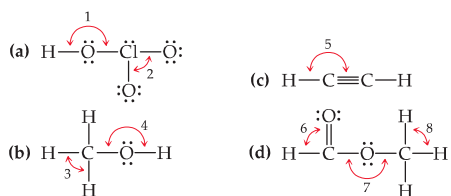
- 9.11 An AB_2 molecule is described as linear, and the A—B bond length is known. (a) Does this information completely describe the geometry of the molecule? (b) Can you tell how many nonbonding pairs of electrons are around the A atom from this information?
- 9.12 (a) Methane (CH_4) and the perchlorate 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?
- 9.13 (a) What is meant by the term *electron domain*? (b) Explain in what way electron domains behave like the balloons in Figure 9.5. Why do they do so?
- 9.14 (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*?
- 9.15 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 ?
- 9.16 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.
- 9.17 What is the difference between the electron-domain geometry and the molecular geometry of a molecule? Use the water molecule as an example in your discussion.
- 9.18 An AB_3 molecule is described as having a trigonal-bipyramidal electron-domain geometry. How many nonbonding domains are on atom A? Explain.
- 9.19 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.
- 9.20 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.
- 9.21 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^- .
- 9.22 Draw the Lewis structure for each of the following molecules or ions, and predict their electron-domain and molecular geometries: (a) PF_3 , (b) CH_3^+ , (c) BrF_3 , (d) ClO_4^- , (e) XeF_2 , (f) BrO_2^- .
- 9.23 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.



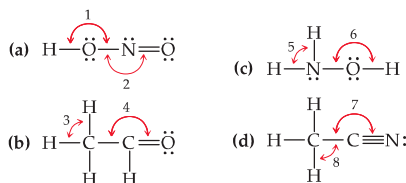
- 9.24 The figure that follows contains ball-and-stick drawings of three possible shapes of an AF_4 molecule. (a) For each shape, give the electron-domain geometry on which the molecular geometry is based. (b) For each shape, how many nonbonding electron domains are there on atom A? (c) Which of the 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).



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



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



- 9.27 Predict the trend in the F(axial)—A—F(equatorial) bond angle in the following AF_n molecules: PF_5 , SF_4 , and ClF_3 .

- 9.28 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.

- 9.29 (a) Explain why BrF_4^- is square planar, whereas BF_4^- is tetrahedral. (b) Water, H_2O , is a bent molecule. Predict the shape of the molecular ion formed from the water molecule if you were able to remove four electrons to make $(H_2O)^{4+}$.

- 9.30 (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 and not bent.

Polarity of Polyatomic Molecules

- 9.31 (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?

- 9.32 (a) The PH_3 molecule is polar. How does this offer experimental proof that the molecule cannot be planar? (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?

- 9.33 (a) Consider the AF_3 molecules in Exercise 9.23. Which of these will have a nonzero dipole moment? Explain. (b) Which of the AF_4 molecules in Exercise 9.24 will have a zero dipole moment?

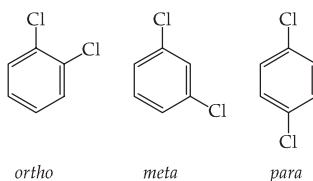
- 9.34 (a) What conditions must be met if a molecule with polar bonds is nonpolar? (b) What geometries will give nonpolar molecules for AB_2 , AB_3 , and AB_4 geometries?

- 9.35 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 .

- 9.36 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 .

- 9.37 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?

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



- Which of these would have a nonzero dipole moment? Explain.

Orbital Overlap; Hybrid Orbitals

- 9.39 (a) What is meant by the term *orbital overlap*? (b) Describe what a chemical bond is in terms of electron density between two atoms.
- 9.40 Draw sketches illustrating the overlap between the following orbitals on two atoms: (a) the $2s$ orbital on each atom, (b) the $2p_z$ orbital on each atom (assume both atoms are on the z -axis), (c) the $2s$ orbital on one atom and the $2p_z$ orbital on the other atom.
- 9.41 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 $1s$ atomic orbital.
- 9.42 How would you expect the extent of overlap of atomic orbitals to vary in the series IF , ICl , IBr , and I_2 ?
- 9.43 Fill 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	octahedral		no
		sp^2	yes
	trigonal bipyramidal		no
XeF_2			

Multiple Bonds

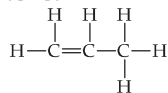
- 9.49 (a) Draw a picture showing how two p orbitals on two different atoms can be combined to make a sigma bond. (b) Sketch a π bond that is constructed from p orbitals. (c) Which is generally stronger, a σ bond or a π bond? Explain. (d) Can two s orbitals make a π bond? Explain.
- 9.50 (a) If the valence 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? Explain.
- 9.51 (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? (e) Suppose that silicon could form molecules that are precisely the analogs of ethane, ethylene, and acetylene. How would you describe the bonding about Si in terms of hybrid

9.44 Why are there no sp^4 or sp^5 hybrid orbitals?

- 9.45 (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 there any valence atomic orbitals of B that are left unhybridized? If so, how are they oriented relative to the hybrid orbitals?
- 9.46 (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 the hybrid orbitals constructed in part (a). (d) Would the hybridization scheme in part (a) be appropriate for SF_4 ? Explain.
- 9.47 Indicate the hybridization of the central atom in (a) BCl_3 , (b) AlCl_4^- , (c) CS_2 , (d) KrF_2 , (e) PF_6^- .
- 9.48 What is the hybridization of the central atom in (a) SiCl_4 , (b) HCN , (c) SO_3 , (d) ICl_2^- , (e) BrF_4^- ?

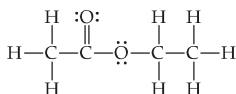
orbitals? Does it make a difference that Si lies in the row below C in the periodic table? Explain.

- 9.52 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 a stronger N—N bond?
- 9.53 Propylene, C_3H_6 , is a gas that is used to form the important polymer called polypropylene. Its Lewis structure is



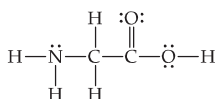
(a) What is the total number of valence electrons in the propylene molecule? (b) How many valence electrons are used to make σ bonds in the molecule? (c) How many valence electrons are used to make π bonds in the molecule? (d) How many valence electrons remain in nonbonding pairs in the molecule? (e)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

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



- (a) What is the hybridization at each of the carbon atoms of the molecule? (b) What is the total number of valence electrons in 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 non-bonding pairs in the molecule?

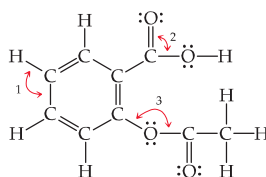
- 9.55 Consider the Lewis structure for glycine, the simplest amino acid:



- (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?

- 9.56 The compound with the following Lewis structure is acetylsalicylic acid, better known as aspirin:



- (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?

- 9.57 (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?

- 9.58 (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? Explain.

Molecular Orbitals

- 9.59 (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?

- 9.60 (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.

- 9.61 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) Draw 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? Explain.

- 9.62 (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? Explain.

- 9.63 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?

- 9.64 (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) Why are the π_{2p} MOs lower in energy than the π_{2p}^* MOs?

- 9.65 (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.

- 9.66 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.

- 9.67 (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^- ?

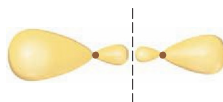
- 9.68 (a) What does the term *paramagnetism* mean? (b) How can one determine experimentally whether a substance is paramagnetic? (c) Which of the following ions would you expect to be paramagnetic: O_2^+ , N_2^{2-} , Li_2^+ , O_2^{2-} ? For those ions that are paramagnetic, determine the number of unpaired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

- 9.69 Using Figures 9.37 and 9.45 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.
- 9.70 If we assume that the energy-level diagrams for homonuclear diatomic molecules shown in Figure 9.42 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^+ .
- 9.71 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?
- 9.72 (a) The nitric oxide molecule, NO , readily loses one electron to form the NO^+ ion. Why is this consistent with the electronic structure of NO ? (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)?
- [9.73] 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 below 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? Explain.



- [9.74] 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 below. 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?



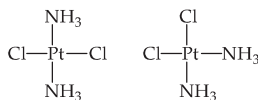
ADDITIONAL EXERCISES

- 9.75 (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?
- 9.76 The molecules SiF_4 , SF_4 , and XeF_4 have molecular formulas of the type AF_4 , but the molecules have different molecular geometries. Predict the shape of each molecule, and explain why the shapes differ.
- [9.77] 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.
- 9.78 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?
- 9.79 From their Lewis structures, determine the number of σ and π bonds in each of the following molecules or ions: (a) CO_2 ; (b) thiocyanate ion, NCS^- ; (c) formaldehyde, H_2CO ; (d) formic acid, $HCOOH$, which has one H and two O atoms attached to C.
- 9.80 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 each carbon atom associated with that short bond? (e) What are the approximate bond angles around each carbon atom in the molecule?

- 9.81 The PF_3 molecule has a dipole moment of 1.03 D, but BF_3 has a dipole moment of zero. How can you explain the difference?

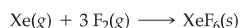
- 9.82 There are two compounds of the formula $Pt(NH_3)_2Cl_2$:



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*?

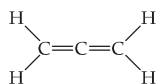
[9.83] The O—H bond lengths in the water molecule (H_2O) are 0.96 \AA , and the H—O—H angle is 104.5° . The dipole moment of the water molecule is 1.85 D . (a) In what directions do the bond dipoles of the O—H bonds point? In what direction does the dipole moment vector of the water molecule point? (b) 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?

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



(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) Suggest a hybridization scheme for the Xe atom in XeF_6 . (e) 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 .

[9.85] The Lewis structure for allene is

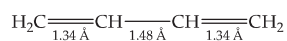


Make a sketch of the structure of this molecule that is analogous to Figure 9.27. In addition, answer the following three questions: (a) Is the molecule planar? (b) Does it have a nonzero dipole moment? (c) Would the bonding in allene be described as delocalized? Explain.

[9.86] The azide ion, N_3^- , is linear with two N—N bonds of equal length, 1.16 \AA . (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 only 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^- ?

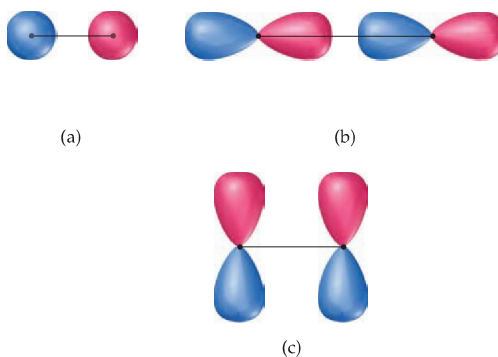
[9.87] In ozone, O_3 , the two oxygen atoms on the ends of the molecule are equivalent to one another. (a) What is the best choice of hybridization scheme for the atoms of ozone? (b) For one of the resonance forms of ozone, which of the orbitals are used to make bonds and which are used to hold nonbonding 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?

9.88 Butadiene, C_4H_6 , is a planar molecule that has the following carbon—carbon bond lengths:



(a) Predict the bond angles around each of the carbon atoms, and sketch the molecule. (b) Compare the bond lengths to the average bond lengths listed in Table 8.5. Can you explain any differences?

[9.89] The sketches below 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 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.



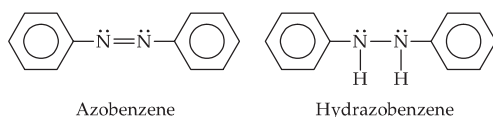
[9.90] The cyclopentadienide ion has the formula C_5H_5^- . The ion consists of a regular pentagon of C atoms, each bonded to two C neighbors, with a hydrogen atom bonded to each C atom. All the atoms lie in the same plane. (a) Draw a Lewis structure for the ion. According to your structure, do all five C atoms have the same hybridization? Explain. (b) Chemists generally view this ion as having sp^2 hybridization at each C atom. Is that view consistent with your answer to part (a)? (c) Your Lewis structure should show one nonbonding pair of electrons. Under the assumption of part (b), in what type of orbital must this nonbonding pair reside? (d) Are there resonance structures equivalent to the Lewis structure you drew in part (a)? If so, how many? (e) The ion is often drawn as a pentagon enclosing a circle. Is this representation consistent with your answer to part (d)? Explain. (f) Both benzene and the cyclopentadienide ion are often described as systems containing six π electrons. What do you think is meant by this description?

9.91 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? Explain.

9.92 Figure 9.47 shows how the magnetic properties of a compound can be measured experimentally. When such measurements are made, the sample is generally covered by an atmosphere of pure nitrogen gas rather than air. Why do you suppose this is done?

9.93 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, $\text{C}_{12}\text{H}_{10}\text{N}_2$.

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.)

- [9.94] (a) Using only the valence atomic orbitals of a hydrogen atom and a fluorine atom, 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) Do you think the MO diagram shown in Figure 9.49 could be used to describe the MOs of the HF molecule? Why or

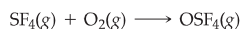
why not? (d) It turns out that the difference in energies between the valence atomic orbitals of H and F are sufficiently different that we can neglect the interaction of the 1s orbital of hydrogen with the 2s orbital of fluorine. The 1s orbital of hydrogen will mix only with one 2p orbital of fluorine. Draw pictures showing the proper orientation of all three 2p orbitals on F interacting with a 1s orbital on H. Which of the 2p orbitals can actually make a bond with a 1s orbital, assuming that the atoms lie on the z-axis? (e) 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.) (f) Look at the Lewis structure for HF. Where are the nonbonding electrons?

- [9.95] 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 9.49 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 9.49? If not, what modification needs to be made to the diagram? How does this modification relate to Figure 9.45? (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?

INTEGRATIVE EXERCISES

- 9.96 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?

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

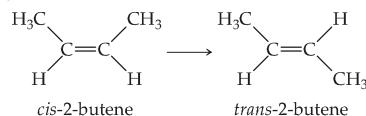


The O atom and the four F atoms in OSF_4 are bonded to a central S atom. (a) Balance the equation. (b) Write a Lewis structure of OSF_4 in which the formal charges of all atoms are zero. (c) Use average bond enthalpies (Table 8.4) to estimate the enthalpy of the reaction. Is it endothermic or exothermic? (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.

- [9.98] 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 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 $PBrCl_4$.

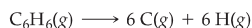
- [9.99] The molecule 2-butene, C_4H_8 , can undergo a geometric change called *cis-trans isomerization*:



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 9.32, 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.

- 9.100 (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).
- 9.101 Use average bond enthalpies (Table 8.4) to estimate ΔH for the atomization of benzene, C_6H_6 :



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?

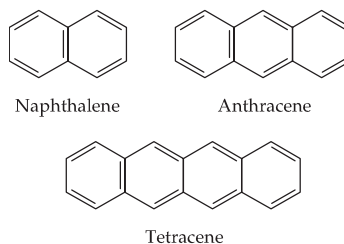
- 9.102 For both atoms and molecules, ionization energies (Section 7.4) are related to the energies of orbitals: The lower the energy of the orbital, the greater the ionization energy. The first ionization energy of a molecule is therefore a measure of the energy of the highest occupied molecular orbital (HOMO). See the "Chemistry Put to Work" box on Orbitals and Energy. The first ionization energies of several diatomic molecules are given in electron-volts in the following table:

Molecule	I_1 (eV)
H_2	15.4
N_2	15.6
O_2	12.1
F_2	15.7

(a) Convert these ionization energies to kJ/mol. (b) On the same plot, graph I_1 for the H, N, O, and F atoms (Figure 7.11) and I_1 for the molecules listed. (c) Do the ionization energies of the molecules follow the same periodic trends as the ionization energies of the atoms? (d) Use molecular orbital energy-level diagrams to explain the trends in the ionization energies of the molecules.

- 9.103 Many compounds of the transition-metal elements contain direct bonds between metal atoms. We will assume that the z -axis is defined as the metal-metal bond axis. (a) Which of the $3d$ orbitals (Figure 6.24) 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 $3d$ orbital from part (a) is important. (e) What is the bond order in Sc_2 ?
- 9.104 The organic molecules shown below are derivatives of benzene in which additional six-membered rings are "fused" at the edges of the hexagons. The compounds are shown in the usual abbreviated method for organic molecules. (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 compounds it is? (c) Naphthalene, which is 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 below 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.



- 9.105 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.
- 9.106 You can think of the bonding in the Cl_2 molecule in several ways. For example, you can picture the Cl-Cl bond containing two electrons that each come from the $3p$ orbitals of a Cl atom that are pointing in the appropriate direction. However, you can also think about hybrid orbitals. (a) Draw the Lewis structure of the Cl_2 molecule. (b) What is the hybridization of each Cl atom? (c) What kind of orbital overlap, in this view, makes the Cl-Cl bond? (d) Imagine if you could measure the positions of the lone pairs of electrons in Cl_2 . How would you distinguish between the atomic orbital and hybrid orbital models of bonding using that knowledge? (e) You can also treat Cl_2 using molecular orbital theory to obtain an energy level diagram similar to that for F_2 . Design an experiment that could tell you if the MO picture of Cl_2 is the best one, assuming you could easily measure bond lengths, bond energies, and the light absorption properties for any ionized species.