CHAPTER 1

CHEMICAL BONDING

S**tructure*** is the key to everything in chemistry. The properties of a substance depend on the atoms it contains and the way the atoms are connected. What is less obvious, but very powerful, is the idea that someone who is trained in chemistry can look at a structural formula of a substance and tell you a lot about its properties. This chapter begins your training toward understanding the relationship between structure and properties in organic compounds. It reviews some fundamental principles of molecular structure and chemical **bonding.** By applying these principles you will learn to recognize the structural patterns that are more stable than others and develop skills in communicating chemical information by way of structural formulas that will be used throughout your study of organic chemistry.

1.1 ATOMS, ELECTRONS, AND ORBITALS

Before discussing bonding principles, let's first review some fundamental relationships between atoms and electrons. Each element is characterized by a unique **atomic number Z,** which is equal to the number of protons in its nucleus. A neutral atom has equal numbers of protons, which are positively charged, and electrons, which are negatively charged.

Electrons were believed to be particles from the time of their discovery in 1897 until 1924, when the French physicist Louis de Broglie suggested that they have wave-like properties as well. Two years later Erwin Schrödinger took the next step and calculated the energy of an electron in a hydrogen atom by using equations that treated the electron as if it were a wave. Instead of a single energy, Schrödinger obtained a series of **energy levels,** each of which corresponded to a different mathematical description of the electron wave. These mathematical descriptions are called **wave functions** and are symbolized by the Greek letter ψ (psi).

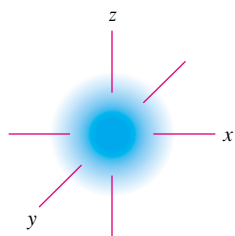*A glossary of important terms may be found immediately before the index at the back of the book.

FIGURE 1.1 Probability distribution (ψ^2) for an electron in a 1s orbital.

According to the Heisenberg uncertainty principle, we can't tell exactly where an electron is, but we can tell where it is most likely to be. The probability of finding an electron at a particular spot relative to an atom's nucleus is given by the square of the wave function (ψ^2) at that point. Figure 1.1 illustrates the probability of finding an electron at various points in the lowest energy (most stable) state of a hydrogen atom. The darker the color in a region, the higher the probability. The probability of finding an electron at a particular point is greatest near the nucleus, and decreases with increasing distance from the nucleus but never becomes zero. We commonly describe Figure 1.1 as an "electron cloud" to call attention to the spread-out nature of the electron probability. Be careful, though. The "electron cloud" of a hydrogen atom, although drawn as a collection of many dots, represents only one electron.

Wave functions are also called **orbitals.** For convenience, chemists use the term "orbital" in several different ways. A drawing such as Figure 1.1 is often said to represent an orbital. We will see other kinds of drawings in this chapter, use the word "orbital" to describe them too, and accept some imprecision in language as the price to be paid for simplicity of expression.

Orbitals are described by specifying their size, shape, and directional properties. Spherically symmetrical ones such as shown in Figure 1.1 are called *s orbitals*. The letter *s* is preceded by the **principal quantum number** n (n = 1, 2, 3, etc.) which specifies the **shell** and is related to the energy of the orbital. An electron in a 1s orbital is likely to be found closer to the nucleus, is lower in energy, and is more strongly held than an electron in a 2s orbital.

Regions of a single orbital may be separated by **nodal surfaces** where the probability of finding an electron is zero. A 1s orbital has no nodes; a 2s orbital has one. A 1s and a 2s orbital are shown in cross section in Figure 1.2. The 2s wave function changes sign on passing through the nodal surface as indicated by the plus ($+$) and minus ($-$) signs in Figure 1.2. *Do not confuse these signs with electric charges—they have nothing to do with electron or nuclear charge.* Also, be aware that our "orbital" drawings are really representations of ψ^2 (which must be a positive number), whereas $+$ and $-$ refer to the sign of the wave function (ψ) itself. These customs may seem confusing at first but turn out not to complicate things in practice. Indeed, most of the time we won't
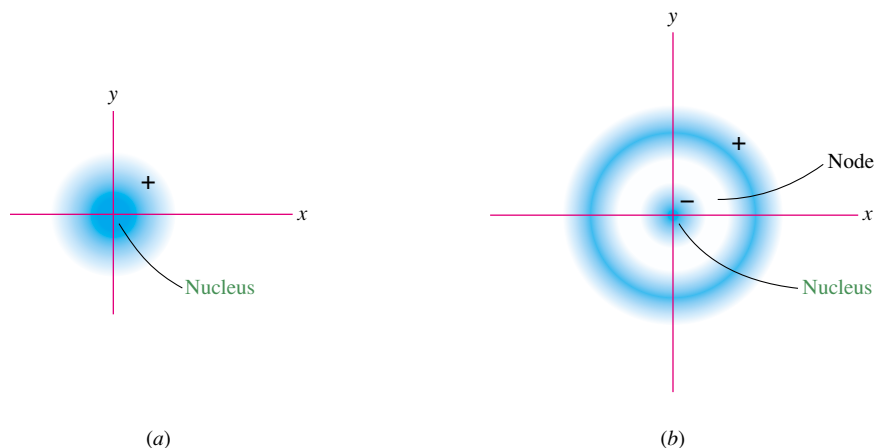

(a)

(b)

FIGURE 1.2 Cross sections of (a) a 1s orbital and (b) a 2s orbital. The wave function has the same sign over the entire 1s orbital. It is arbitrarily shown as +, but could just as well have been designated as −. The 2s orbital has a spherical node where the wave function changes sign.

even include $+$ and $-$ signs of wave functions in our drawings but only when they are necessary for understanding a particular concept.

Instead of probability distributions, it is more common to represent orbitals by their **boundary surfaces,** as shown in Figure 1.3 for the $1s$ and $2s$ orbitals. The boundary surface encloses the region where the probability of finding an electron is high—on the order of 90–95%. Like the probability distribution plot from which it is derived, a picture of a boundary surface is usually described as a drawing of an orbital.

A hydrogen atom ($Z = 1$) has one electron; a helium atom ($Z = 2$) has two. The single electron of hydrogen occupies a $1s$ orbital, as do the two electrons of helium. The respective electron configurations are described as:

<p align="center">Hydrogen: $1s^1$ Helium: $1s^2$</p>

In addition to being negatively charged, electrons possess the property of **spin.** The **spin quantum number** of an electron can have a value of either $+\frac{1}{2}$ or $-\frac{1}{2}$. According to the **Pauli exclusion principle,** two electrons may occupy the same orbital only when they have opposite, or "paired," spins. For this reason, no orbital can contain more than two electrons. Since two electrons fill the $1s$ orbital, the third electron in lithium ($Z = 3$) must occupy an orbital of higher energy. After $1s$, the next higher energy orbital is $2s$. The third electron in lithium therefore occupies the $2s$ orbital, and the electron configuration of lithium is

<p align="center">Lithium: $1s^2 2s^1$</p>

The **period** (or **row**) of the periodic table in which an element appears corresponds to the principal quantum number of the highest numbered occupied orbital ($n = 1$ in the case of hydrogen and helium). Hydrogen and helium are first-row elements; lithium ($n = 2$) is a second-row element.

With beryllium ($Z = 4$), the $2s$ level becomes filled, and the next orbitals to be occupied in it and the remaining second-row elements are the $2p_x$, $2p_y$, and $2p_z$ orbitals. These orbitals, portrayed in Figure 1.4, have a boundary surface that is usually described as "dumbbell-shaped." Each orbital consists of two "lobes," that is, slightly flattened spheres that touch each other along a nodal plane passing through the nucleus. The $2p_x$, $2p_y$, and $2p_z$ orbitals are equal in energy and mutually perpendicular.

The electron configurations of the first 12 elements, hydrogen through magnesium, are given in Table 1.1. In filling the $2p$ orbitals, notice that each is singly occupied before any one is doubly occupied. This is a general principle for orbitals of equal energy known

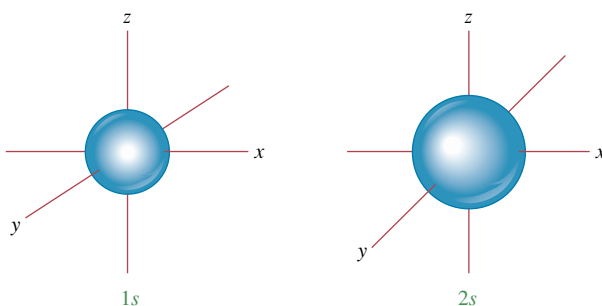> A complete periodic table of the elements is presented on the inside back cover.

FIGURE 1.3   Boundary surfaces of a $1s$ orbital and a $2s$ orbital. The boundary surfaces enclose the volume where there is a 90–95% probability of finding an electron.
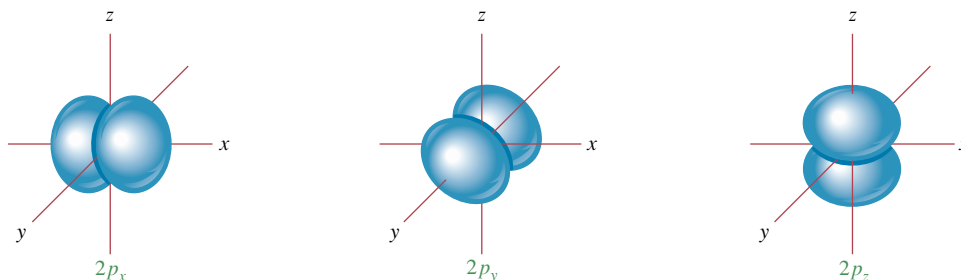
FIGURE 1.4   Boundary surfaces of the 2p orbitals. The wave function changes sign at the nucleus. The *yz*-plane is a nodal surface for the $2p_x$ orbital. The probability of finding a $2p_x$ electron in the *yz*-plane is zero. Analogously, the *xz*-plane is a nodal surface for the $2p_y$ orbital, and the *xy*-plane is a nodal surface for the $2p_z$ orbital.

as **Hund's rule.** *Of particular importance in Table 1.1 are hydrogen, carbon, nitrogen, and oxygen.* Countless organic compounds contain nitrogen, oxygen, or both in addition to carbon, the essential element of organic chemistry. Most of them also contain hydrogen.

It is often convenient to speak of the **valence electrons** of an atom. These are the outermost electrons, the ones most likely to be involved in chemical bonding and reactions. For second-row elements these are the 2s and 2p electrons. Because four orbitals ($2s$, $2p_x$, $2p_y$, $2p_z$) are involved, the maximum number of electrons in the **valence shell** of any second-row element is 8. Neon, with all its 2s and 2p orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table.

PROBLEM 1.1   How many valence electrons does carbon have?

Once the 2s and 2p orbitals are filled, the next level is the 3s, followed by the $3p_x$, $3p_y$, and $3p_z$ orbitals. Electrons in these orbitals are farther from the nucleus than those in the 2s and 2p orbitals and are of higher energy.

TABLE 1.1	Electron Configurations of the First Twelve Elements of the Periodic Table						
		Number of electrons in indicated orbital					
Element	**Atomic number Z**	**1s**	**2s**	**2px**	**2py**	**2pz**	**3s**
Hydrogen	1	1					
Helium	2	2					
Lithium	3	2	1				
Beryllium	4	2	2				
Boron	5	2	2	1			
Carbon	6	2	2	1	1		
Nitrogen	7	2	2	1	1	1	
Oxygen	8	2	2	2	1	1	
Fluorine	9	2	2	2	2	1	
Neon	10	2	2	2	2	2	
Sodium	11	2	2	2	2	2	1
Magnesium	12	2	2	2	2	2	2

> **PROBLEM 1.2**   Referring to the periodic table as needed, write electron configurations for all the elements in the third period.
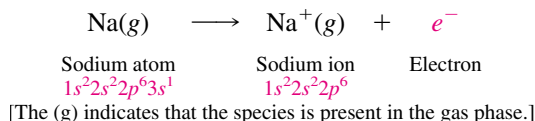>
> **SAMPLE SOLUTION**   The third period begins with sodium and ends with argon. The atomic number Z of sodium is 11, and so a sodium atom has 11 electrons. The maximum number of electrons in the 1s, 2s, and 2p orbitals is ten, and so the eleventh electron of sodium occupies a 3s orbital. The electron configuration of sodium is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$.

Neon, in the second period, and argon, in the third, possess eight electrons in their valence shell; they are said to have a complete **octet** of electrons. Helium, neon, and argon belong to the class of elements known as **noble gases** or **rare gases.** The noble gases are characterized by an extremely stable "closed-shell" electron configuration and are very unreactive.
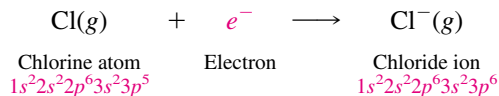
1.2   IONIC BONDS

Atoms combine with one another to give **compounds** having properties different from the atoms they contain. The attractive force between atoms in a compound is a **chemical bond.** One type of chemical bond, called an **ionic bond,** is the force of attraction between oppositely charged species (**ions**) (Figure 1.5). Ions that are positively charged are referred to as **cations;** those that are negatively charged are **anions.**

Whether an element is the source of the cation or anion in an ionic bond depends on several factors, for which the periodic table can serve as a guide. In forming ionic compounds, elements at the left of the periodic table typically lose electrons, forming a cation that has the same electron configuration as the nearest noble gas. Loss of an electron from sodium, for example, gives the species Na^+, which has the same electron configuration as neon.

FIGURE 1.5   An ionic bond is the force of electrostatic attraction between oppositely charged ions, illustrated in this case by Na^+ (red) and Cl^- (green). In solid sodium chloride, each sodium ion is surrounded by six chloride ions and vice versa in a crystal lattice.

$$Na(g) \longrightarrow Na^+(g) + e^-$$

Sodium atom	Sodium ion	Electron
$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6$	

[The (g) indicates that the species is present in the gas phase.]

A large amount of energy, called the **ionization energy,** must be added to any atom in order to dislodge one of its electrons. The ionization energy of sodium, for example, is 496 kJ/mol (119 kcal/mol). Processes that absorb energy are said to be **endothermic.** Compared with other elements, sodium and its relatives in group IA have relatively low ionization energies. In general, ionization energy increases across a row in the periodic table.

Elements at the right of the periodic table tend to gain electrons to reach the electron configuration of the next higher noble gas. Adding an electron to chlorine, for example, gives the anion Cl^-, which has the same closed-shell electron configuration as the noble gas argon.

$$Cl(g) + e^- \longrightarrow Cl^-(g)$$

Chlorine atom	Electron	Chloride ion
$1s^2 2s^2 2p^6 3s^2 3p^5$		$1s^2 2s^2 2p^6 3s^2 3p^6$

Energy is released when a chlorine atom captures an electron. Energy-releasing reactions are described as **exothermic,** and the energy change for an exothermic process has a negative sign. The energy change for addition of an electron to an atom is referred to as its **electron affinity** and is -349 kJ/mol (-83.4 kcal/mol) for chlorine.

The SI (*Système International d'Unites*) unit of energy is the *joule* (J). An older unit is the *calorie* (cal). Most organic chemists still express energy changes in units of kilocalories per mole (1 kcal/mol = 4.184 kJ/mol).

In-chapter problems that contain multiple parts are accompanied by a sample solution to part (a). Answers to the other parts of the problem are found in Appendix 2, and detailed solutions are presented in the Study Guide.
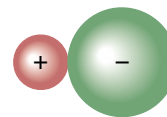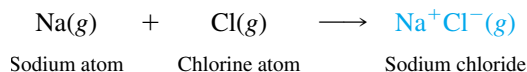
PROBLEM 1.3 Which of the following ions possess a noble gas electron configuration?

(a) K^+

(b) He^+

(c) H^-

(d) O^-

(e) F^-

(f) Ca^{2+}

SAMPLE SOLUTION (a) Potassium has atomic number 19, and so a potassium atom has 19 electrons. The ion K^+, therefore, has 18 electrons, the same as the noble gas argon. The electron configurations of K^+ and Ar are the same: $1s^2 2s^2 2p^6 3s^2 3p^6$.

Transfer of an electron from a sodium atom to a chlorine atom yields a sodium cation and a chloride anion, both of which have a noble gas electron configuration:

$$\text{Na}(g) \quad + \quad \text{Cl}(g) \quad \longrightarrow \quad \text{Na}^+\text{Cl}^-(g)$$

Sodium atom   Chlorine atom   Sodium chloride

> Ionic bonding was proposed by the German physicist Walter Kossel in 1916, in order to explain the ability of substances such as sodium chloride to conduct an electric current.

Were we to simply add the ionization energy of sodium (496 kJ/mol) and the electron affinity of chlorine (-349 kJ/mol), we would conclude that the overall process is endothermic with $\Delta H° = +147$ kJ/mol. The energy liberated by adding an electron to chlorine is insufficient to override the energy required to remove an electron from sodium. This analysis, however, fails to consider the force of attraction between the oppositely charged ions Na^+ and Cl^-, which exceeds 500 kJ/mol and is more than sufficient to make the overall process exothermic. Attractive forces between oppositely charged particles are termed **electrostatic,** or **coulombic, attractions** and are what we mean by an **ionic bond** between two atoms.

PROBLEM 1.4 What is the electron configuration of C^+? Of C^-? Does either one of these ions have a noble gas (closed-shell) electron configuration?

Ionic bonds are very common in *inorganic* compounds, but rare in *organic* ones. The ionization energy of carbon is too large and the electron affinity too small for carbon to realistically form a C^{4+} or C^{4-} ion. What kinds of bonds, then, link carbon to other elements in millions of organic compounds? Instead of losing or gaining electrons, carbon *shares* electrons with other elements (including other carbon atoms) to give what are called covalent bonds.

1.3   COVALENT BONDS

The **covalent,** or **shared electron pair,** model of chemical bonding was first suggested by G. N. Lewis of the University of California in 1916. Lewis proposed that a *sharing* of two electrons by two hydrogen atoms permits each one to have a stable closed-shell electron configuration analogous to helium.

> Gilbert Newton Lewis (born Weymouth, Massachusetts, 1875; died Berkeley, California, 1946) has been called the greatest American chemist. The January 1984 issue of the *Journal of Chemical Education* contains five articles describing Lewis' life and contributions to chemistry.

$$\text{H·} \qquad \text{·H} \qquad\qquad \text{H:H}$$

Two hydrogen atoms,   Hydrogen molecule:
each with a single   covalent bonding by way of
electron   a shared electron pair

Structural formulas of this type in which electrons are represented as dots are called **Lewis structures.**

The amount of energy required to dissociate a hydrogen molecule H_2 to two separate hydrogen atoms is called its **bond dissociation energy** (or **bond energy**). For H_2 it is quite large, being equal to 435 kJ/mol (104 kcal/mol). The main contributor to the strength of the covalent bond in H_2 is the increased binding force exerted on its two electrons. Each electron in H_2 "feels" the attractive force of two nuclei, rather than one as it would in an isolated hydrogen atom.
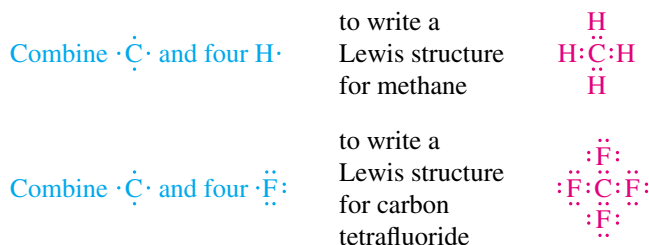
Covalent bonding in F_2 gives each fluorine 8 electrons in its valence shell and a stable electron configuration equivalent to that of the noble gas neon:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}\cdot \qquad \cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \qquad\qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$$

Two fluorine atoms, each
with seven electrons in
its valence shell

Fluorine molecule:
covalent bonding by way of
a shared electron pair

PROBLEM 1.5 Hydrogen is bonded to fluorine in hydrogen fluoride by a covalent bond. Write a Lewis formula for hydrogen fluoride.

The Lewis model limits second-row elements (Li, Be, B, C, N, O, F, Ne) to a total of 8 electrons (shared plus unshared) in their valence shells. Hydrogen is limited to 2. Most of the elements that we'll encounter in this text obey the **octet rule:** *in forming compounds they gain, lose, or share electrons to give a stable electron configuration characterized by eight valence electrons.* When the octet rule is satisfied for carbon, nitrogen, oxygen, and fluorine, they have an electron configuration analogous to the noble gas neon.

Now let's apply the Lewis model to the organic compounds methane and carbon tetrafluoride.

Combine $\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot$ and four $H\cdot$

to write a
Lewis structure
for methane

$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H \\ H \end{array}$$

Combine $\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot$ and four $\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:$

to write a
Lewis structure
for carbon
tetrafluoride

$$\begin{array}{c} :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \\ :\overset{\cdot\cdot}{F}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:\overset{\cdot\cdot}{F}: \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}: \end{array}$$

Carbon has 8 electrons in its valence shell in both methane and carbon tetrafluoride. By forming covalent bonds to four other atoms, carbon achieves a stable electron configuration analogous to neon. Each covalent bond in methane and carbon tetrafluoride is quite strong—comparable to the bond between hydrogens in H_2 in bond dissociation energy.
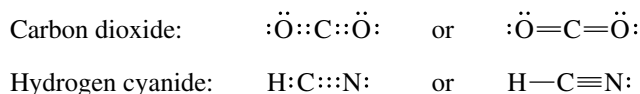
PROBLEM 1.6 Given the information that it has a carbon–carbon bond, write a satisfactory Lewis structure for C_2H_6 (ethane).

Representing a 2-electron covalent bond by a dash (—), the Lewis structures for hydrogen fluoride, fluorine, methane, and carbon tetrafluoride become:
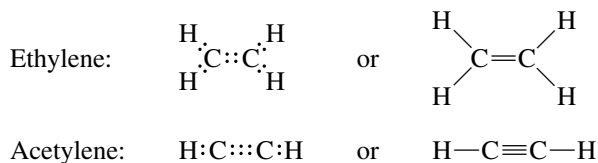
$$H\text{—}\ddot{\underset{\cdot\cdot}{F}}\text{:} \qquad \text{:}\ddot{\underset{\cdot\cdot}{F}}\text{—}\ddot{\underset{\cdot\cdot}{F}}\text{:} \qquad H\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{—}H \qquad \text{:}\ddot{\underset{\cdot\cdot}{F}}\text{—}\overset{\displaystyle :\ddot{F}:}{\underset{\displaystyle :\ddot{F}:}{C}}\text{—}\ddot{\underset{\cdot\cdot}{F}}\text{:}$$

| Hydrogen fluoride | Fluorine | Methane | Carbon tetrafluoride |
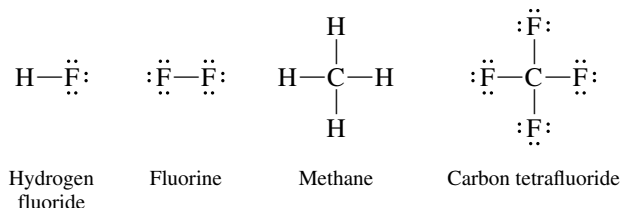
1.4   DOUBLE BONDS AND TRIPLE BONDS

Lewis's concept of shared electron pair bonds allows for 4-electron **double bonds** and 6-electron **triple bonds.** Carbon dioxide (CO_2) has two carbon–oxygen double bonds, and the octet rule is satisfied for both carbon and oxygen. Similarly, the most stable Lewis structure for hydrogen cyanide (HCN) has a carbon–nitrogen triple bond.

Carbon dioxide: $\text{:}\ddot{O}\text{::}C\text{::}\ddot{O}\text{:}$ or $\text{:}\ddot{O}\text{=}C\text{=}\ddot{O}\text{:}$

Hydrogen cyanide: $H\text{:}C\text{:::}N\text{:}$ or $H\text{—}C\text{≡}N\text{:}$

Multiple bonds are very common in organic chemistry. Ethylene (C_2H_4) contains a carbon–carbon double bond in its most stable Lewis structure, and each carbon has a completed octet. The most stable Lewis structure for acetylene (C_2H_2) contains a carbon–carbon triple bond. Here again, the octet rule is satisfied.

Ethylene: $\overset{\displaystyle H}{\underset{\displaystyle H}{\cdot}}C\text{::}C\overset{\displaystyle H}{\underset{\displaystyle H}{\cdot}}$ or $\underset{\displaystyle H}{\overset{\displaystyle H}{}}C\text{=}C\underset{\displaystyle H}{\overset{\displaystyle H}{}}$

Acetylene: $H\text{:}C\text{:::}C\text{:}H$ or $H\text{—}C\text{≡}C\text{—}H$

PROBLEM 1.7 Write the most stable Lewis structure for each of the following compounds:
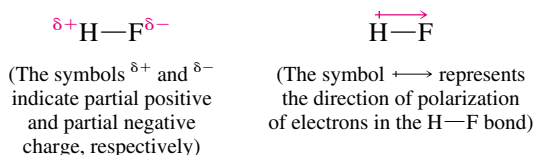
(a) Formaldehyde, CH_2O. Both hydrogens are bonded to carbon. (A solution of formaldehyde in water is sometimes used to preserve biological specimens.)

(b) Tetrafluoroethylene, C_2F_4. (The starting material for the preparation of Teflon.)

(c) Acrylonitrile, C_3H_3N. The atoms are connected in the order CCCN, and all hydrogens are bonded to carbon. (The starting material for the preparation of acrylic fibers such as Orlon and Acrilan.)

SAMPLE SOLUTION (a) Each hydrogen contributes 1 valence electron, carbon contributes 4, and oxygen 6 for a total of 12 valence electrons. We are told that both hydrogens are bonded to carbon. Since carbon forms four bonds in its stable compounds, join carbon and oxygen by a double bond. The partial structure so generated accounts for 8 of the 12 electrons. Add the remaining four electrons to oxygen as unshared pairs to complete the structure of formaldehyde.

$$\underset{\displaystyle H\qquad H}{\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}} \qquad\qquad \underset{\displaystyle H\qquad H}{\overset{\displaystyle :O:}{\underset{\displaystyle \|}{C}}}$$

| Partial structure showing covalent bonds | Complete Lewis structure of formaldehyde |
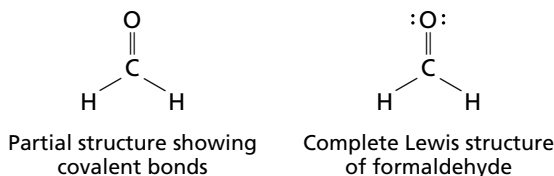
1.5 POLAR COVALENT BONDS AND ELECTRONEGATIVITY

Electrons in covalent bonds are not necessarily shared equally by the two atoms that they connect. If one atom has a greater tendency to attract electrons toward itself than the other, we say the electron distribution is *polarized,* and the bond is referred to as a **polar covalent bond.** Hydrogen fluoride, for example, has a polar covalent bond. Because fluorine attracts electrons more strongly than hydrogen, the electrons in the H—F bond are pulled toward fluorine, giving it a partial negative charge, and away from hydrogen giving it a partial positive charge. This polarization of electron density is represented in various ways.

$$^{\delta+}H—F^{\delta-} \qquad \overset{\longrightarrow}{H—F}$$

(The symbols $^{\delta+}$ and $^{\delta-}$
indicate partial positive
and partial negative
charge, respectively)

(The symbol $\longrightarrow$ represents
the direction of polarization
of electrons in the H—F bond)

The tendency of an atom to draw the electrons in a covalent bond toward itself is referred to as its **electronegativity.** An **electronegative** element attracts electrons; an **electropositive** one donates them. Electronegativity increases across a row in the periodic table. The most electronegative of the second-row elements is fluorine; the most electropositive is lithium. Electronegativity decreases in going down a column. Fluorine is more electronegative than chlorine. The most commonly cited electronegativity scale was devised by Linus Pauling and is presented in Table 1.2.

> **PROBLEM 1.8** Examples of carbon-containing compounds include methane (CH_4), chloromethane (CH_3Cl), and methyllithium (CH_3Li). In which one does carbon bear the greatest partial positive charge? The greatest partial negative charge?

Centers of positive and negative charge that are separated from each other constitute a **dipole.** The **dipole moment μ** of a molecule is equal to the charge e (either the positive or the negative charge, since they must be equal) multiplied by the distance between the centers of charge:

$$\mu = e \times d$$

TABLE 1.2	Selected Values from the Pauling Electronegativity Scale						
	Group number						
Period	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
1	H 2.1						
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0					Br 2.8
5							I 2.5

Linus Pauling (1901–1994) was born in Portland, Oregon and was educated at Oregon State University and at the California Institute of Technology, where he earned a Ph.D. in chemistry in 1925. In addition to research in bonding theory, Pauling studied the structure of proteins and was awarded the Nobel Prize in chemistry for that work in 1954. Pauling won a second Nobel Prize (the Peace Prize) for his efforts to limit the testing of nuclear weapons. He was one of only four scientists to have won two Nobel Prizes. The first double winner was a woman. Can you name her?

Because the charge on an electron is 4.80×10^{-10} electrostatic units (esu) and the distances within a molecule typically fall in the 10^{-8} cm range, molecular dipole moments are on the order of 10^{-18} esu·cm. In order to simplify the reporting of dipole moments this value of 10^{-18} esu·cm is defined as a **debye, D.** Thus the experimentally determined dipole moment of hydrogen fluoride, 1.7×10^{-18} esu·cm is stated as 1.7 D.

Table 1.3 lists the dipole moments of various bond types. For H—F, H—Cl, H—Br, and H—I these "bond dipoles" are really molecular dipole moments. A **polar** molecule has a dipole moment, a **nonpolar** one does not. Thus, all of the hydrogen halides are polar molecules. In order to be polar, a molecule must have polar bonds, but can't have a shape that causes all the individual bond dipoles to cancel. We will have more to say about this in Section 1.11 after we have developed a feeling for the three-dimensional shapes of molecules.

The bond dipoles in Table 1.3 depend on the difference in electronegativity of the bonded atoms and on the bond distance. The polarity of a C—H bond is relatively low; substantially less than a C—O bond, for example. Don't lose sight of an even more important difference between a C—H bond and a C—O bond, and that is the *direction* of the dipole moment. In a C—H bond the electrons are drawn away from H, toward C. In a C—O bond, electrons are drawn from C toward O. As we'll see in later chapters, the kinds of reactions that a substance undergoes can often be related to the size and direction of key bond dipoles.

1.6   FORMAL CHARGE

Lewis structures frequently contain atoms that bear a positive or negative charge. If the molecule as a whole is neutral, the sum of its positive charges must equal the sum of its negative charges. An example is nitric acid, HNO_3:
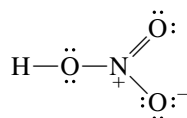
As written, the structural formula for nitric acid depicts different bonding patterns for its three oxygens. One oxygen is doubly bonded to nitrogen, another is singly bonded

Bond*	Dipole moment, D	Bond*	Dipole moment, D
H—F	1.7	C—F	1.4
H—Cl	1.1	C—O	0.7
H—Br	0.8	C—N	0.4
H—I	0.4	C=O	2.4
H—C	0.3	C=N	1.4
H—N	1.3	C≡N	3.6
H—O	1.5		

TABLE 1.3   Selected Bond Dipole Moments

*The direction of the dipole moment is toward the more electronegative atom. In the listed examples hydrogen and carbon are the positive ends of the dipoles. Carbon is the negative end of the dipole associated with the C—H bond.

to both nitrogen and hydrogen, and the third has a single bond to nitrogen and a negative charge. Nitrogen is positively charged. The positive and negative charges are called **formal charges,** and the Lewis structure of nitric acid would be incomplete were they to be omitted.

We calculate formal charges by counting the number of electrons "owned" by each atom in a Lewis structure and comparing this **electron count** with that of a neutral atom. Figure 1.6 illustrates how electrons are counted for each atom in nitric acid. Counting electrons for the purpose of computing the formal charge differs from counting electrons to see if the octet rule is satisfied. A second-row element has a filled valence shell if the sum of all the electrons, shared and unshared, is 8. Electrons that connect two atoms by a covalent bond count toward filling the valence shell of both atoms. When calculating the formal charge, however, only half the number of electrons in covalent bonds can be considered to be "owned" by an atom.

To illustrate, let's start with the hydrogen of nitric acid. As shown in Figure 1.6, hydrogen is associated with only two electrons—those in its covalent bond to oxygen. It shares those two electrons with oxygen, and so we say that the electron count of each hydrogen is $\frac{1}{2}(2) = 1$. Since this is the same as the number of electrons in a neutral hydrogen atom, the hydrogen in nitric acid has no formal charge.

Moving now to nitrogen, we see that it has four covalent bonds (two single bonds + one double bond), and so its electron count is $\frac{1}{2}(8) = 4$. A neutral nitrogen has five electrons in its valence shell. The electron count for nitrogen in nitric acid is 1 less than that of a neutral nitrogen atom, so its formal charge is $+1$.

Electrons in covalent bonds are counted as if they are shared equally by the atoms they connect, but unshared electrons belong to a single atom. Thus, the oxygen which is doubly bonded to nitrogen has an electron count of 6 (four electrons as two unshared pairs + two electrons from the double bond). Since this is the same as a neutral oxygen atom, its formal charge is 0. Similarly, the OH oxygen has two bonds plus two unshared electron pairs, giving it an electron count of 6 and no formal charge.

The oxygen highlighted in yellow in Figure 1.6 owns three unshared pairs (six electrons) and shares two electrons with nitrogen to give it an electron count of 7. This is 1 more than the number of electrons in the valence shell of an oxygen atom, and so its formal charge is -1.

The method described for calculating formal charge has been one of reasoning through a series of logical steps. It can be reduced to the following equation:

$$\text{Formal charge} = \frac{\text{group number in}}{\text{periodic table}} - \text{number of bonds} - \text{number of unshared electrons}$$

The number of valence electrons in an atom of a main-group element such as nitrogen is equal to its group number. In the case of nitrogen this is 5.

It will always be true that a covalently bonded hydrogen has no formal charge (formal charge = 0).

It will always be true that a nitrogen with four covalent bonds has a formal charge of $+1$. (A nitrogen with four covalent bonds cannot have unshared pairs, because of the octet rule.)

It will always be true that an oxygen with two covalent bonds and two unshared pairs has no formal charge.

It will always be true that an oxygen with one covalent bond and three unshared pairs has a formal charge of -1.

Electron count (O) $= \frac{1}{2}(4) + 4 = 6$

Electron count (H) $= \frac{1}{2}(2) = 1$

Electron count (N) $= \frac{1}{2}(8) = 4$

Electron count (O) $= \frac{1}{2}(4) + 4 = 6$
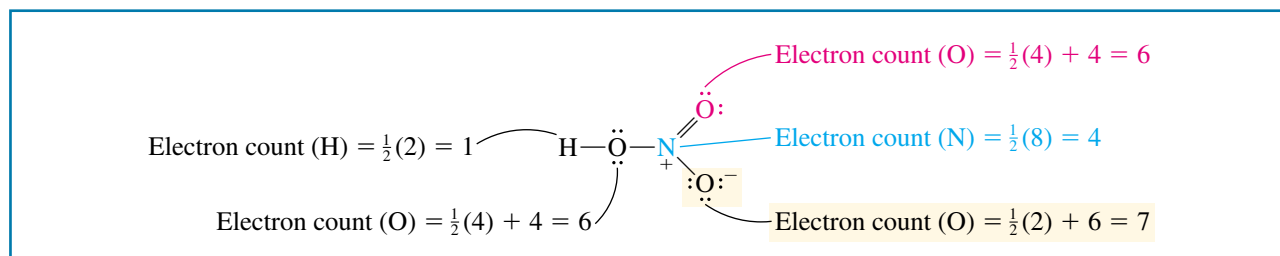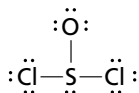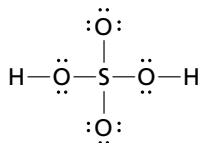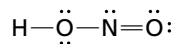
Electron count (O) $= \frac{1}{2}(2) + 6 = 7$

FIGURE 1.6 Counting electrons in nitric acid. The electron count of each atom is equal to half the number of electrons it shares in covalent bonds plus the number of electrons in its own unshared pairs.

PROBLEM 1.9 Like nitric acid, each of the following inorganic compounds will be frequently encountered in this text. Calculate the formal charge on each of the atoms in the Lewis structures given.

$$:\!\ddot{O}\!: \qquad\qquad :\!\ddot{O}\!:$$
$$:\!\ddot{C}l\!-\!\overset{|}{S}\!-\!\ddot{C}l\!: \qquad H\!-\!\ddot{O}\!-\!\overset{|}{S}\!-\!\ddot{O}\!-\!H \qquad H\!-\!\ddot{O}\!-\!\ddot{N}\!=\!\ddot{O}\!:$$
$$\qquad\qquad\qquad\qquad\qquad :\!\ddot{O}\!:$$

(a) Thionyl chloride   (b) Sulfuric acid   (c) Nitrous acid

SAMPLE SOLUTION (a) The formal charge is the difference between the number of valence electrons in the neutral atom and the electron count in the Lewis structure. (The number of valence electrons is the same as the group number in the periodic table for the main-group elements.)

	Valence electrons of neutral atom	Electron count	Formal charge
Sulfur:	6	$\frac{1}{2}(6) + 2 = 5$	+1
Oxygen:	6	$\frac{1}{2}(2) + 6 = 7$	−1
Chlorine:	7	$\frac{1}{2}(2) + 6 = 7$	0

The formal charges are shown in the Lewis structure of thionyl chloride as

$$\qquad\quad :\!\ddot{O}\!:^-$$
$$:\!\ddot{C}l\!-\!\overset{|}{\overset{+}{S}}\!-\!\ddot{C}l\!:$$
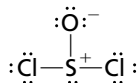
So far we've only considered neutral molecules—those in which the sums of the positive and negative formal charges were equal. With ions, of course, these sums will not be equal. Ammonium cation and borohydride anion, for example, are ions with net charges of +1 and −1, respectively. Nitrogen has a formal charge of +1 in ammonium ion, and boron has a formal charge of −1 in borohydride. None of the hydrogens in the Lewis structures shown for these ions bears a formal charge.

$$\begin{array}{ccc} H & & H \\ | & & | \\ H\!-\!\overset{+}{N}\!-\!H & \qquad & H\!-\!\overset{-}{B}\!-\!H \\ | & & | \\ H & & H \end{array}$$
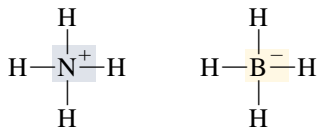
Ammonium ion   Borohydride ion

PROBLEM 1.10 Verify that the formal charges on nitrogen in ammonium ion and boron in borohydride ion are as shown.

Formal charges are based on Lewis structures in which electrons are considered to be shared equally between covalently bonded atoms. Actually, polarization of N—H bonds in ammonium ion and of B—H bonds in borohydride leads to some transfer of positive and negative charge, respectively, to the hydrogens.

PROBLEM 1.11 Use $\delta+$ and $\delta-$ notation to show the dispersal of charge to the hydrogens in NH_4^+ and BH_4^-.

Determining formal charges on individual atoms of Lewis structures is an important element in good "electron bookkeeping." So much of organic chemistry can be made more understandable by keeping track of electrons that it is worth taking some time at the beginning to become proficient at the seemingly simple task of counting electrons.

1.7   STRUCTURAL FORMULAS OF ORGANIC MOLECULES

Table 1.4 outlines a systematic procedure for writing Lewis structures. Notice that the process depends on knowing not only the molecular formula, but also the order in which the atoms are attached to one another. This order of attachment is called the **constitution,** or **connectivity,** of the molecule and is determined by experiment. Only rarely is it possible to deduce the constitution of a molecule from its molecular formula.

Organic chemists have devised a number of shortcuts to speed the writing of structural formulas. Sometimes we leave out unshared electron pairs, but only when we are sure enough in our ability to count electrons to know when they are present and when they're not. We've already mentioned representing covalent bonds by dashes. In **condensed structural formulas** we leave out some, many, or all of the covalent bonds and use subscripts to indicate the number of identical groups attached to a particular atom. These successive levels of simplification are illustrated as shown for isopropyl alcohol ("rubbing alcohol").

$$
\begin{array}{c}
\overset{\displaystyle \text{H}\quad\text{H}\quad\text{H}}{\underset{\displaystyle \text{H}\quad:\!\ddot{\text{O}}:\,\text{H}}{\text{H}\!-\!\text{C}\!-\!\text{C}\!-\!\text{C}\!-\!\text{H}}}\\
\underset{\displaystyle \text{H}}{|}
\end{array}
\qquad\text{written as}\qquad
\underset{\displaystyle \text{OH}}{\overset{\displaystyle \text{CH}_3\text{CHCH}_3}{|}}
\qquad
\begin{array}{l}\text{or condensed even further to}\\ (\text{CH}_3)_2\text{CHOH}\end{array}
$$
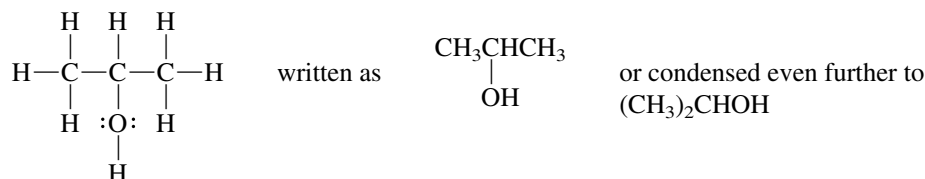
PROBLEM 1.12 Expand the following condensed formulas so as to show all the bonds and unshared electron pairs.

(a) $HOCH_2CH_2NH_2$ (d) CH_3CHCl_2

(b) $(CH_3)_3CH$ (e) $CH_3NHCH_2CH_3$
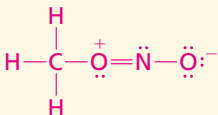
(c) $ClCH_2CH_2Cl$ (f) $(CH_3)_2CHCH{=}O$
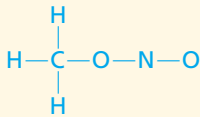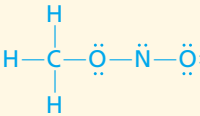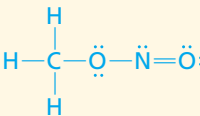
SAMPLE SOLUTION (a) The molecule contains two carbon atoms, which are bonded to each other. Both carbons bear two hydrogens. One carbon bears the group HO—; the other is attached to —NH_2.

$$
\underset{\displaystyle \text{H}\quad\text{H}}{\overset{\displaystyle \text{H}\quad\text{H}\quad\text{H}}{\text{H}\!-\!\text{O}\!-\!\text{C}\!-\!\text{C}\!-\!\text{N}\!-\!\text{H}}}
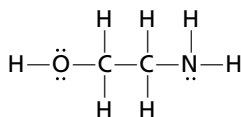$$
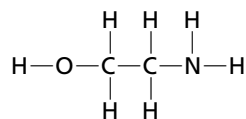
When writing the constitution of a molecule, it is not necessary to concern yourself with the spatial orientation of the atoms. There are many other correct ways to represent the constitution shown. What is important is to show the sequence OCCN (or its equivalent NCCO) and to have the correct number of hydrogens present on each atom.

In order to locate unshared electron pairs, first count the total number of valence electrons brought to the molecule by its component atoms. Each hydrogen contributes 1, each carbon 4, nitrogen 5, and oxygen 6, for a total of 26. There are ten bonds shown, accounting for 20 electrons; therefore 6 electrons must be contained in unshared pairs. Add pairs of electrons to oxygen and nitrogen so that their octets are complete, two unshared pairs to oxygen and one to nitrogen.


TABLE 1.4	How to Write Lewis Structures

Step	Illustration
1. The molecular formula and the connectivity are determined experimentally and are included among the information given in the statement of the problem.	Methyl nitrite has the molecular formula CH_3NO_2. All hydrogens are bonded to carbon, and the order of atomic connections is CONO.
2. Count the number of valence electrons available. For a neutral molecule this is equal to the sum of the valence electrons of the constituent atoms.	Each hydrogen contributes 1 valence electron, carbon contributes 4, nitrogen contributes 5, and each oxygen contributes 6 for a total of 24 in CH_3NO_2.
3. Connect bonded atoms by a shared electron pair bond (:) represented by a dash (—).	For methyl nitrite we write the partial structure $$\begin{array}{c} H \\ | \\ H-C-O-N-O \\ | \\ H \end{array}$$
4. Count the number of electrons in shared electron pair bonds (twice the number of bonds), and subtract this from the total number of electrons to give the number of electrons to be added to complete the structure.	The partial structure in step 3 contains 6 bonds equivalent to 12 electrons. Since CH_3NO_2 contains 24 electrons, 12 more electrons need to be added.
5. Add electrons in pairs so that as many atoms as possible have 8 electrons. (Hydrogen is limited to 2 electrons.) When the number of electrons is insufficient to provide an octet for all atoms, assign electrons to atoms in order of decreasing electronegativity.	With 4 bonds, carbon already has 8 electrons. The remaining 12 electrons are added as indicated. Both oxygens have 8 electrons, but nitrogen (less electronegative than oxygen) has only 6. $$\begin{array}{c} H \\ | \\ H-C-\ddot{O}-\ddot{N}-\ddot{O}: \\ | \\ H \end{array}$$
6. If one or more atoms have fewer than 8 electrons, use unshared pairs on an adjacent atom to form a double (or triple) bond to complete the octet.	An electron pair on the terminal oxygen is shared with nitrogen to give a double bond. $$\begin{array}{c} H \\ | \\ H-C-\ddot{O}-\ddot{N}=\ddot{O}: \\ | \\ H \end{array}$$ The structure shown is the best (most stable) Lewis structure for methyl nitrite. All atoms except hydrogen have 8 electrons (shared + unshared) in their valence shell.
7. Calculate formal charges.	None of the atoms in the Lewis structure shown in step 6 possesses a formal charge. An alternative Lewis structure for methyl nitrite, $$\begin{array}{c} H \\ | \\ H-C-\overset{+}{\ddot{O}}=\ddot{N}-\ddot{O}:^{-} \\ | \\ H \end{array}$$ although it satisfies the octet rule, is less stable than the one shown in step 6 because it has a separation of positive charge from negative charge.

$$H-\overset{\overset{\displaystyle H \quad H \quad H}{\displaystyle | \quad\;\; | \quad\;\; |}}{\underset{\underset{\displaystyle H \quad H}{\displaystyle | \quad\;\; |}}{\ddot{O}-C-C-N}}-H$$
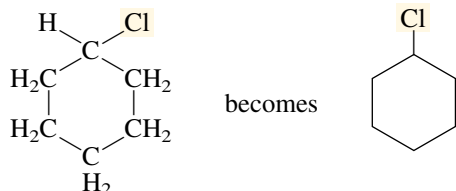
As you practice, you will begin to remember patterns of electron distribution. A neutral oxygen with two bonds has two unshared electron pairs. A neutral nitrogen with three bonds has one unshared pair.
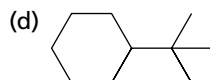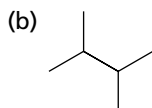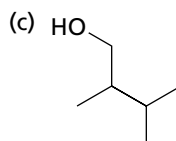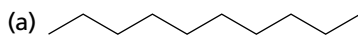
With practice, writing structural formulas for organic molecules soon becomes routine and can be simplified even more. For example, a chain of carbon atoms can be represented by drawing all of the C—C bonds while omitting individual carbons. The resulting structural drawings can be simplified still more by stripping away the hydrogens.

$CH_3CH_2CH_2CH_3$ becomes   [structure]   simplified to   [bond-line structure]
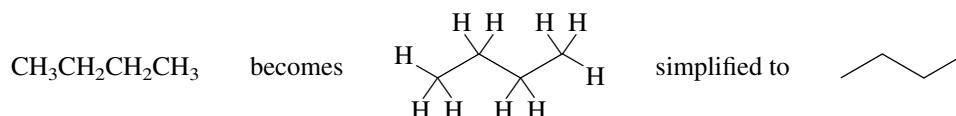
In these simplified representations, called **bond-line formulas** or **carbon skeleton diagrams,** the only atoms specifically written in are those that are neither carbon nor hydrogen bound to carbon. Hydrogens bound to these *heteroatoms* are shown, however.

$CH_3CH_2CH_2CH_2OH$ becomes   [bond-line structure with OH]

[ring structure]   becomes   [cyclohexane with Cl]

PROBLEM 1.13   Expand the following bond-line representations to show all the atoms including carbon and hydrogen.

(a) [zigzag chain structure]

(c) [HO branched structure]

(b) [branched structure]

(d) [cyclohexane with branched group]

SAMPLE SOLUTION   (a) There is a carbon at each bend in the chain and at the ends of the chain. Each of the ten carbon atoms bears the appropriate number of hydrogen substituents so that it has four bonds.

[bond-line structure] $\equiv$ [expanded structure with 10 carbons and hydrogens]
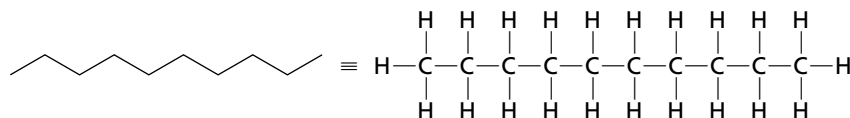
Alternatively, the structure could be written as $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ or in condensed form as $CH_3(CH_2)_8CH_3$.

1.8   CONSTITUTIONAL ISOMERS

In the introduction we noted that both Berzelius and Wöhler were fascinated by the fact that two different compounds with different properties, ammonium cyanate and urea, possessed exactly the same molecular formula, CH_4N_2O. Berzelius had studied examples of similar phenomena earlier and invented the word **isomer** to describe *different compounds that have the same molecular formula.*

We can illustrate isomerism by referring to two different compounds, *nitromethane* and *methyl nitrite,* both of which have the molecular formula CH_3NO_2. Nitromethane,

Nitromethane   Methyl nitrite
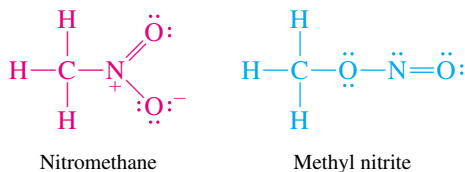
used to power race cars, is a liquid with a boiling point of 101°C. Methyl nitrite is a gas boiling at −12°C, which when inhaled causes dilation of blood vessels. Isomers that differ in the order in which their atoms are bonded are often referred to as **structural isomers.** A more modern term is **constitutional isomer.** As noted in the previous section, the order of atomic connections that defines a molecule is termed its *constitution,* and we say that two compounds are *constitutional isomers* if they have the same molecular formula but differ in the order in which their atoms are connected.

PROBLEM 1.14 There are many more isomers of CH_3NO_2 other than nitromethane and methyl nitrite. Some, such as *carbamic acid,* an intermediate in the commercial preparation of urea for use as a fertilizer, are too unstable to isolate. Given the information that the nitrogen and both oxygens of carbamic acid are bonded to carbon and that one of the carbon–oxygen bonds is a double bond, write a Lewis structure for carbamic acid.

PROBLEM 1.15 Write structural formulas for all the constitutionally isomeric compounds having the given molecular formula.

(a) C_2H_6O (c) $C_4H_{10}O$

(b) C_3H_8O

**SAMPLE SOLUTION**   (a) Begin by considering the ways in which two carbons and one oxygen may be bonded. There are two possibilities: C—C—O and C—O—C. Add the six hydrogens so that each carbon has four bonds and each oxygen two. There are two constitutional isomers: ethyl alcohol and dimethyl ether.

Ethyl alcohol   Dimethyl ether
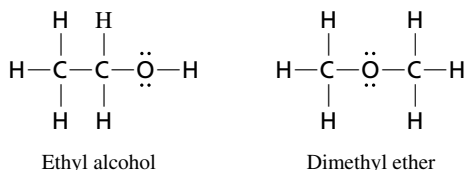
In Chapter 3 another type of isomerism, called **stereoisomerism,** will be introduced. Stereoisomers have the same constitution but differ in the arrangement of atoms in space.
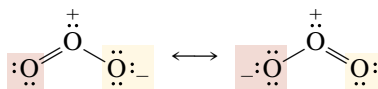
1.9   RESONANCE

When writing a Lewis structure, we restrict a molecule's electrons to certain well-defined locations, either linking two atoms by a covalent bond or as unshared electrons on a single atom. Sometimes more than one Lewis structure can be written for a molecule, especially those that contain multiple bonds. An example often cited in introductory chemistry courses is ozone (O_3). Ozone occurs naturally in large quantities in the upper atmosphere, where it screens the surface of the earth from much of the sun's ultraviolet rays. Were it not for this ozone layer, most forms of surface life on earth would be damaged or even destroyed by the rays of the sun. The following Lewis structure for ozone satisfies the octet rule; all three oxygens have 8 electrons in their valence shell.
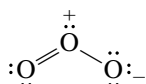
This Lewis structure, however, doesn't accurately portray the bonding in ozone, because the two terminal oxygens are bonded differently to the central oxygen. The central oxygen is depicted as doubly bonded to one and singly bonded to the other. Since it is generally true that double bonds are shorter than single bonds, we would expect ozone to exhibit two different O—O bond lengths, one of them characteristic of the O—O single bond distance (147 pm in hydrogen peroxide, H—O—O—H) and the other one characteristic of the O=O double bond distance (121 pm in O_2). Such is not the case. Both bond distances in ozone are exactly the same (128 pm)—somewhat shorter than the single bond distance and somewhat longer than the double bond distance. The structure of ozone requires that *the central oxygen must be identically bonded to both terminal oxygens.*

In order to deal with circumstances such as the bonding in ozone, the notion of **resonance** between Lewis structures was developed. According to the resonance concept, when more than one Lewis structure may be written for a molecule, a single structure is not sufficient to describe it. Rather, the true structure has an electron distribution that is a "hybrid" of all the possible Lewis structures that can be written for the molecule. In the case of ozone, two equivalent Lewis structures may be written. We use a double-headed arrow to represent resonance between these two Lewis structures.

It is important to remember that the double-headed resonance arrow does not indicate a *process* in which the two Lewis structures interconvert. Ozone, for example, has a *single* structure; it does not oscillate back and forth between two Lewis structures, rather its true structure is not adequately represented by any single Lewis structure.

Resonance attempts to correct a fundamental defect in Lewis formulas. Lewis formulas show electrons as being **localized;** they either are shared between two atoms in a covalent bond or are unshared electrons belonging to a single atom. In reality, electrons distribute themselves in the way that leads to their most stable arrangement. This sometimes means that a pair of electrons is **delocalized,** or shared by several nuclei. What we try to show by the resonance description of ozone is the delocalization of the lone-pair electrons of one oxygen and the electrons in the double bond over the three atoms of the molecule. Organic chemists often use curved arrows to show this electron

Bond distances in organic compounds are usually 1 to 2Å (1Å = 10^{-10}m). Since the angstrom (Å) is not an SI unit, we will express bond distances in picometers (1 pm = 10^{-12}m). Thus, 128 pm =1.28 Å.

delocalization. Alternatively, an average of two Lewis structures is sometimes drawn using a dashed line to represent a "partial" bond. In the dashed-line notation the central oxygen is linked to the other two by bonds that are halfway between a single bond and a double bond, and the terminal oxygens each bear one half of a unit negative charge.
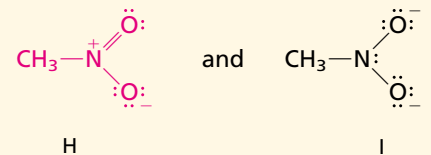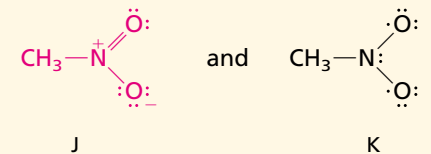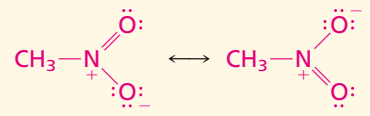

Curved arrow notation   Dashed-line notation
Electron delocalization in ozone
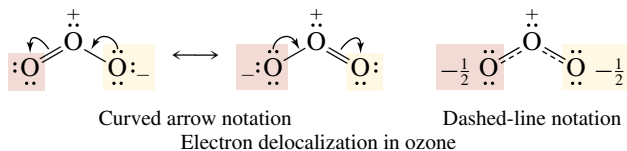
    The rules to be followed when writing resonance structures are summarized in Table 1.5.

TABLE 1.5	Introduction to the Rules of Resonance*
Rule	**Illustration**
1. Atomic positions (connectivity) must be the same in all resonance structures; only the electron positions may vary among the various contributing structures.	The structural formulas represent different compounds, not different resonance forms of the same compound. A is a Lewis structure for *nitromethane;* B is *methyl nitrite.*
2. Lewis structures in which second-row elements own or share more than 8 valence electrons are especially unstable and make no contribution to the true structure. (The octet rule may be exceeded for elements beyond the second row.)	Structural formula C, has 10 electrons around nitrogen. It is not a permissible Lewis structure for nitromethane and so cannot be a valid resonance form.
3. When two or more structures satisfy the octet rule, the most stable one is the one with the smallest separation of oppositely charged atoms.	The two Lewis structures D and E of methyl nitrite satisfy the octet rule: Structure D has no separation of charge and is more stable than E, which does. The true structure of methyl nitrite is more like D than E.

(Continued)

| TABLE 1.5	Introduction to the Rules of Resonance* *(Continued)*

Rule	Illustration
4. Among structural formulas in which the octet rule is satisfied for all atoms and one or more of these atoms bears a formal charge, the most stable resonance form is the one in which negative charge resides on the most electronegative atom (or positive charge on the most electropositive one).	The most stable Lewis structure for cyanate ion is F because the negative charge is on its oxygen. $$:N{\equiv}C{-}\ddot{\underset{..}{O}}{:}^{-} \longleftrightarrow {}^{-}:\underset{..}{N}{=}C{=}\underset{..}{O}{:}$$ F G In G the negative charge is on nitrogen. Oxygen is more electronegative than nitrogen and can better support a negative charge.
5. Each contributing Lewis structure must have the same number of electrons and the same *net* charge, although the formal charges of individual atoms may vary among the various Lewis structures.	The Lewis structures $$CH_3{-}\overset{+}{N}\big\langle\substack{\ddot{O}:\\ :\ddot{O}:^{-}} \quad \text{and} \quad CH_3{-}\overset{..}{N}\big\langle\substack{:\ddot{O}:^{-}\\ \ddot{O}:^{-}}$$ H I are *not* resonance forms of one another. Structure H has 24 valence electrons and a net charge of 0; I has 26 valence electrons and a net charge of -2.
6. Each contributing Lewis structure must have the same number of *unpaired* electrons.	Structural formula J is a Lewis structure of nitromethane; K is not, even though it has the same atomic positions and the same number of electrons. $$CH_3{-}\overset{+}{N}\big\langle\substack{\ddot{O}:\\ :\ddot{O}:^{-}} \quad \text{and} \quad CH_3{-}N\big\langle\substack{\cdot\ddot{O}:\\ :\ddot{O}:}$$ J K Structure K has 2 unpaired electrons. Structure J has all its electrons paired and is a more stable structure.
7. Electron delocalization stabilizes a molecule. A molecule in which electrons are delocalized is more stable than implied by any of the individual Lewis structures that may be written for it. The degree of stabilization is greatest when the contributing Lewis structures are of equal stability.	Nitromethane is stabilized by electron delocalization more than methyl nitrite is. *The two most stable resonance forms of nitromethane are equivalent to each other.* $$CH_3{-}N\big\langle\substack{\ddot{O}:\\ \underset{+}{\,}:\ddot{O}:^{-}} \longleftrightarrow CH_3{-}N\big\langle\substack{:\ddot{O}:^{-}\\ \underset{+}{\,}\ddot{O}:}$$ *The two most stable resonance forms of methyl nitrite are not equivalent.* $$CH_3{-}\ddot{\underset{..}{O}}{-}\overset{..}{N}{=}\ddot{\underset{..}{O}}{:} \longleftrightarrow CH_3{-}\overset{+}{\underset{..}{O}}{=}\overset{..}{N}{-}\ddot{\underset{..}{O}}{:}^{-}$$

*These are the most important rules to be concerned with at present. Additional aspects of electron delocalization, as well as additional rules for its depiction by way of resonance structures, will be developed as needed in subsequent chapters.

PROBLEM 1.16 Electron delocalization can be important in ions as well as in neutral molecules. Using curved arrows, show how an equally stable resonance structure can be generated for each of the following anions:

(a)

(c)

(b)

(d)

SAMPLE SOLUTION (a) When using curved arrows to represent the reorganization of electrons, begin at a site of high electron density, preferably an atom that is negatively charged. Move electron pairs until a proper Lewis structure results. For nitrate ion, this can be accomplished in two ways:
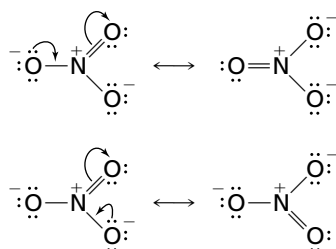
Three equally stable Lewis structures are possible for nitrate ion. The negative charge in nitrate is shared equally by all three oxygens.

It is good chemical practice to represent molecules by their most stable Lewis structure. The ability to write alternative resonance forms and to compare their relative stabilities, however, can provide insight into both molecular structure and chemical behavior. This will become particularly apparent in the last two thirds of this text, where the resonance concept will be used regularly.

1.10 THE SHAPES OF SOME SIMPLE MOLECULES

So far our concern has emphasized "electron bookkeeping." We now turn our attention to the shapes of molecules.

Methane, for example, is described as a tetrahedral molecule because its four hydrogens occupy the corners of a tetrahedron with carbon at its center as the various methane models in Figure 1.7 illustrate. We often show three-dimensionality in structural formulas by using a solid wedge (▬◤) to depict a bond projecting from the paper toward the reader and a dashed wedge (⑈⑈⑈⑈) to depict one receding from the paper. A simple line (—) represents a bond that lies in the plane of the paper (Figure 1.8).

The tetrahedral geometry of methane is often explained in terms of the **valence shell electron-pair repulsion (VSEPR) model.** The VSEPR model rests on the idea that an electron pair, either a bonded pair or an unshared pair, associated with a particular atom will be as far away from the atom's other electron pairs as possible. Thus, a tetrahedral geometry permits the four bonds of methane to be maximally separated and is characterized by H—C—H angles of 109.5°, a value referred to as the **tetrahedral angle.**

Although reservations have been expressed concerning VSEPR as an *explanation* for molecular geometries, it remains a useful *tool* for predicting the shapes of organic compounds.

LEARNING BY MODELING

As early as the nineteenth century many chemists built scale models in order to better understand molecular structure. We can gain a clearer idea about the features that affect structure and reactivity when we examine the three-dimensional shape of a molecule. Several types of molecular models are shown for methane in Figure 1.7. Probably the most familiar are ball-and-stick models (Figure 1.7*b*), which direct approximately equal attention to the atoms and the bonds that connect them. Framework models (Figure 1.7*a*) and space-filling models (Figure 1.7*c*) represent opposite extremes. Framework models emphasize the pattern of bonds of a molecule while ignoring the sizes of the atoms. Space-filling models emphasize the volume occupied by individual atoms at the cost of a clear depiction of the bonds; they are most useful in cases in which one wishes to examine the overall molecular shape and to assess how closely two nonbonded atoms approach each other.

The earliest ball-and-stick models were exactly that: wooden balls in which holes were drilled to accommodate dowels that connected the atoms. Plastic versions, including relatively inexpensive student sets, became available in the 1960s and proved to be a valuable learning aid. Precisely scaled stainless steel framework and plastic space-filling models, although relatively expensive, were standard equipment in most research laboratories.

Computer graphics-based representations are rapidly replacing classical molecular models. Indeed, the term "molecular modeling" as now used in organic chemistry implies computer generation of models. The methane models shown in Figure 1.7 were all drawn on a personal computer using software that possesses the feature of displaying and printing the same molecule in framework, ball-and-stick, and space-filling formats. In addition to permitting models to be constructed rapidly, even the simplest software allows the model to be turned and viewed from a variety of perspectives.

More sophisticated programs not only draw molecular models, but also incorporate computational tools that provide useful insights into the electron distribution. Figure 1.7*d* illustrates this higher level approach to molecular modeling by using colors to display the electric charge distribution within the boundaries defined by the space-filling model. Figures such as 1.7*d* are called *electrostatic potential maps.* They show the transition from regions of highest to lowest electron density according to the colors of the rainbow. The most electron-rich regions are red; the most electron-poor are blue. For methane, the overall shape of the electrostatic potential map is similar to the volume occupied by the space-filling model. The most electron-rich regions are closer to carbon and the most electron-poor regions closer to the hydrogen atoms.
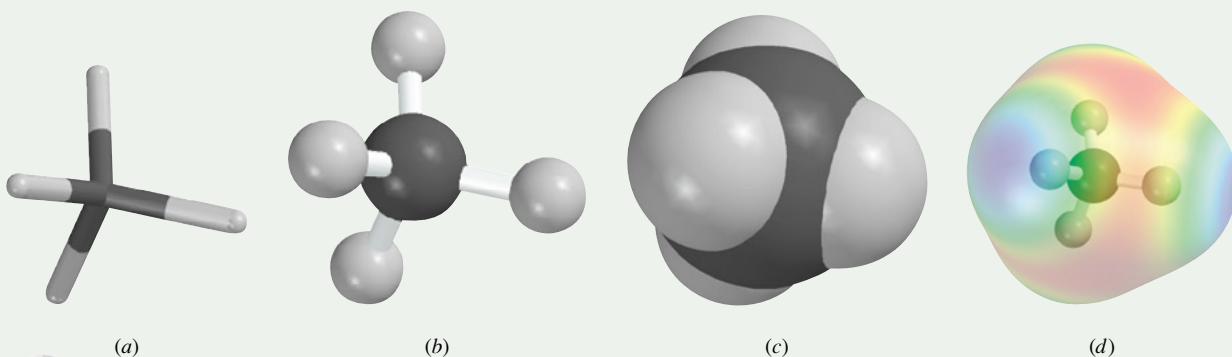
—*Cont.*

(*a*) (*b*) (*c*) (*d*)

FIGURE 1.7 (*a*) A framework (tube) molecular model of methane (CH_4). A framework model shows the bonds connecting the atoms of a molecule, but not the atoms themselves. (*b*) A ball-and-stick (ball-and-spoke) model of methane. (*c*) A space-filling model of methane. (*d*) An electrostatic potential map superimposed on a ball-and-stick model of methane. The electrostatic potential map corresponds to the space-filling model, but with an added feature. The colors identify regions according to their electric charge, with red being the most negative and blue the most positive.

Organic chemistry is a very visual science and computer modeling is making it even more so. Accompanying this text is a CD-ROM entitled *Learning By Modeling.* As its name implies, it is a learning tool, designed to help you better understand molecular structure and properties, and contains two major components:

- *SpartanBuild* software that you can use to build molecular models of various types include tube, ball-and-spoke, and space-filling. This text includes a number of modeling exercises for you to do, but don't limit yourself to them. You can learn a lot by simply experimenting with *SpartanBuild* to see what you can make.

- *SpartanView* software with which you can browse through an archive of already-prepared models on the *Learning By Modeling* CD. These models include many of the same substances that appear in this text. *SpartanView* is the tool you will use to view electrostatic potential maps as well as animations of many organic chemical transformations.

All of the models, those you make yourself and those already provided on *Learning By Modeling,* can be viewed in different formats and rotated in three dimensions.

Immediately preceding the Glossary at the back of this text is a tutorial showing you how to use *SpartanBuild* and *SpartanView,* and describing some additional features.

As you go through this text, you will see two different modeling icons. The *SpartanBuild* icon alerts you to a model-building opportunity, the *SpartanView* icon indicates that the *Learning By Modeling* CD includes a related model or animation.

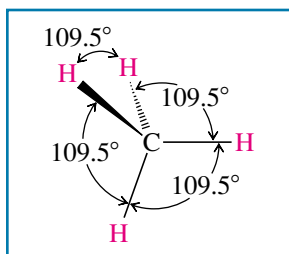*SpartanBuild* icon   *SpartanView* icon

FIGURE 1.8 A wedge-and-dash drawing of the structure of methane. A solid wedge projects from the plane of the paper toward you; a dashed wedge projects away from you. A bond represented by a line drawn in the customary way lies in the plane of the paper.

Water, ammonia, and methane share the common feature of an approximately tetrahedral arrangement of four electron pairs. Because we describe the shape of a molecule according to the positions of its atoms rather than the disposition of its electron pairs, however, water is said to be *bent,* and ammonia is *trigonal pyramidal* (Figure 1.9). The H—O—H angle in water (105°) and the H—N—H angle in ammonia (107°) are slightly less than the tetrahedral angle.

Boron trifluoride (BF_3; Figure 1.10) is a *trigonal planar* molecule. There are 6 electrons, 2 for each B—F bond, associated with the valence shell of boron. These three bonded pairs are farthest apart when they are coplanar, with F—B—F bond angles of 120°.

PROBLEM 1.17   The salt sodium borohydride, $NaBH_4$, has an ionic bond between Na^+ and the anion BH_4^-. What are the H—B—H angles in the borohydride anion?

Multiple bonds are treated as a single unit in the VSEPR model. Formaldehyde (Figure 1.11) is a trigonal planar molecule in which the electrons of the double bond and those of the two single bonds are maximally separated. A linear arrangement of atoms in carbon dioxide (Figure 1.12) allows the electrons in one double bond to be as far away as possible from the electrons in the other double bond.

PROBLEM 1.18   Specify the shape of the following:

(a) H—C≡N: (Hydrogen cyanide)

(b) H_4N^+ (Ammonium ion)

(c) $:\ddot{N}=\overset{+}{N}=\ddot{N}:^-$ (Azide ion)

(d) CO_3^{2-} (Carbonate ion)

SAMPLE SOLUTION   (a) The structure shown accounts for all the electrons in hydrogen cyanide. There are no unshared electron pairs associated with carbon, and so the structure is determined by maximizing the separation between its single bond to hydrogen and the triple bond to nitrogen. Hydrogen cyanide is a *linear* molecule.

(*a*) Water (H_2O) has a bent structure.
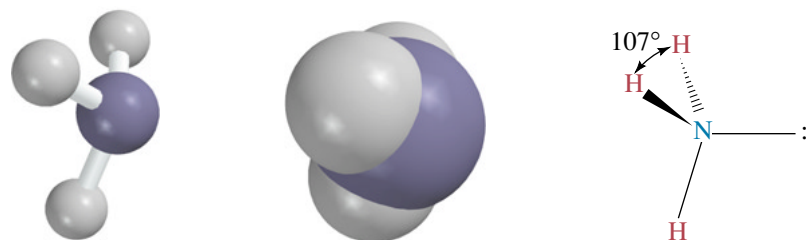
(*b*) Ammonia (NH_3) has a trigonal pyramidal structure.

FIGURE 1.9 Ball-and-spoke and space-filling models and wedge-and-dash drawings of (*a*) water and (*b*) ammonia. The shape of a molecule is described in terms of its atoms. An approximately tetrahedral arrangement of electron pairs translates into a bent geometry for water and a trigonal pyramidal geometry for ammonia.
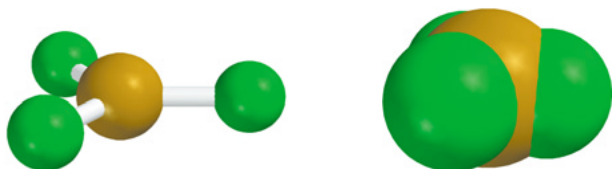
FIGURE 1.10 Representations of the trigonal planar geometry of boron trifluoride (BF_3). There are 6 electrons in the valence shell of boron, a pair for each covalent bond to fluorine. The three pairs of electrons are farthest apart when the F—B—F angle is 120°.
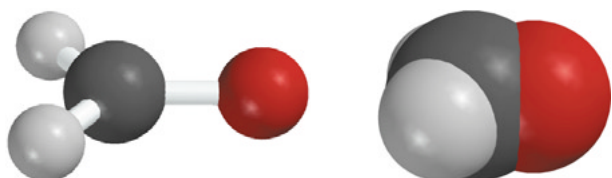
FIGURE 1.11 Models of formaldehyde ($H_2C{=}O$) showing the trigonal planar geometry of the bonds to carbon. Many molecular models, including those shown here, show only the connections between the atoms without differentiating among single bonds, double bonds, and triple bonds.

FIGURE   1.12
Ball-and-spoke and space-
filling models showing the
linear geometry of carbon
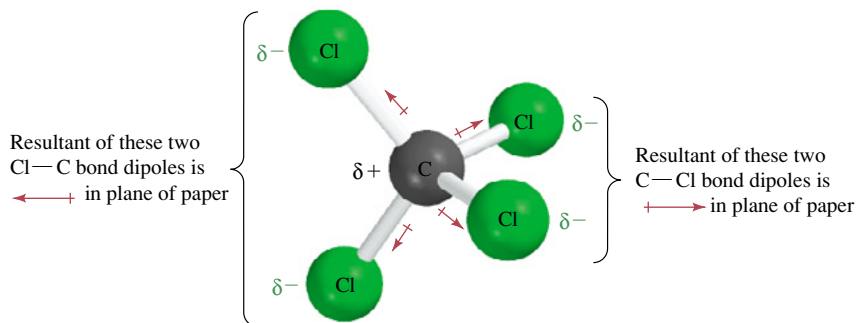dioxide (O=C=O).
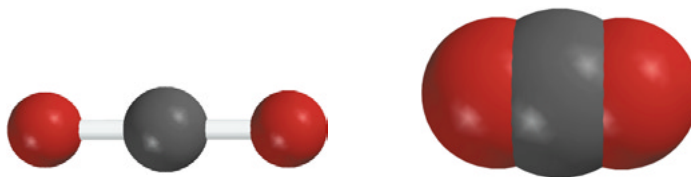
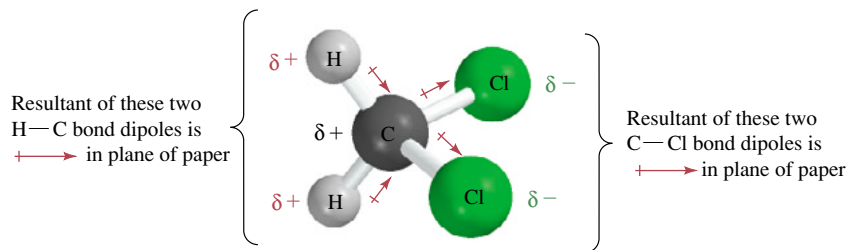## 1.11   MOLECULAR DIPOLE MOMENTS

We can combine our knowledge of molecular geometry with a feel for the polarity of
chemical bonds to predict whether a molecule has a dipole moment or not. The molec-
ular dipole moment is the resultant of all of the individual bond dipole moments of a
substance. Some molecules, such as carbon dioxide, have polar bonds, but lack a dipole
moment because their shape (see Figure 1.12) causes the individual C=O bond dipoles
to cancel.

$$:\ddot{O}=C=\ddot{O}:\qquad \text{Dipole moment} = 0 \text{ D}$$

Carbon dioxide
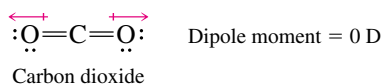
Carbon tetrachloride, with four polar C—Cl bonds and a tetrahedral shape, has no net
dipole moment, because the resultant of the four bond dipoles, as shown in Figure 1.13,
is zero. Dichloromethane, on the other hand, has a dipole moment of 1.62 D. The C—H
bond dipoles reinforce the C—Cl bond dipoles.

Resultant of these two
Cl—C bond dipoles is
⟵+ in plane of paper

Resultant of these two
C—Cl bond dipoles is
+⟶ in plane of paper

(*a*)   There is a mutual cancellation of individual bond dipoles in carbon tetrachloride.
It has no dipole moment.

Resultant of these two
H—C bond dipoles is
+⟶ in plane of paper

Resultant of these two
C—Cl bond dipoles is
+⟶ in plane of paper

FIGURE 1.13 Contri-
bution of individual bond
dipole moments to the mo-
lecular dipole moments of (*a*)
carbon tetrachloride (CCl₄)
and (*b*) dichloromethane
(CH₂Cl₂).

(*b*)   The H—C bond dipoles reinforce the C—Cl bond moment in dichloromethane.
The molecule has a dipole moment of 1.62 D.

PROBLEM 1.19 Which of the following compounds would you expect to have a dipole moment? If the molecule has a dipole moment, specify its direction.

(a) BF_3

(b) H_2O

(c) CH_4

(d) CH_3Cl

(e) CH_2O

(f) HCN

SAMPLE SOLUTION (a) Boron trifluoride is planar with 120° bond angles. Although each boron–fluorine bond is polar, their combined effects cancel and the molecule has no dipole moment.

$$\mu = 0 \text{ D}$$
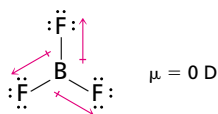
1.12 ELECTRON WAVES AND CHEMICAL BONDS

Lewis proposed his shared electron-pair model of bonding in 1916, almost a decade before de Broglie's theory of wave–particle duality. De Broglie's radically different view of an electron, and Schrödinger's success in using wave equations to calculate the energy of an electron in a hydrogen *atom,* encouraged the belief that bonding in *molecules* could be explained on the basis of interactions between electron waves. This thinking produced two widely used theories of chemical bonding: one is called the **valence bond model,** the other the **molecular orbital model.**

Before we describe these theories, let's first think about bonding between two hydrogen atoms in the most fundamental terms. We'll begin with two hydrogen atoms that are far apart and see what happens as the distance between them decreases. The forces involved are electron–electron $(- -)$ repulsions, nucleus–nucleus $(+ +)$ repulsions, and electron–nucleus $(- +)$ attractions. All of these forces increase as the distance between the two hydrogens decreases. Because the electrons are so mobile, however, they can choreograph their motions so as to minimize their mutual repulsion while maximizing their attractive forces with the protons. Thus, as shown in Figure 1.14, there is a net, albeit weak, attractive force between the two hydrogens even when the atoms are far apart. This interaction becomes stronger as the two atoms approach each other— the electron of each hydrogen increasingly feels the attractive force of two protons rather than one, the total energy decreases, and the system becomes more stable. A potential energy minimum is reached when the separation between the nuclei reaches 74 pm, which corresponds to the H—H bond length in H_2. At distances shorter than this, the nucleus–nucleus and electron–electron repulsions dominate, and the system becomes less stable.

The valence bond and molecular orbital theories differ in how they use the orbitals of two hydrogen atoms to describe the orbital that contains the electron pair in H_2. Both theories assume that electron waves behave much like more familiar waves, such as sound and light waves. One property of waves that is important here is called "interference" in physics. *Constructive interference* occurs when two waves combine so as to reinforce each other ("in phase"); *destructive interference* occurs when they oppose each other ("out of phase") (Figure 1.15). In the valence bond model constructive interference between two electron waves is seen as the basis for the shared electron-pair bond. In the molecular orbital model, the wave functions of molecules are derived by combining wave functions of atoms.

All of the forces in chemistry, except for nuclear chemistry, are electrical. Opposite charges attract; like charges repel. This simple fact can take you a long way.

FIGURE 1.14 Plot of potential energy versus distance for two hydrogen atoms. At long distances, there is a weak attractive force. As the distance decreases, the potential energy decreases, and the system becomes more stable because each electron now feels the attractive force of two protons rather than one. The optimum distance of separation (74 pm) corresponds to the normal bond distance of an H_2 molecule. At shorter distances, nucleus–nucleus and electron–electron repulsions are greater than electron–nucleus attractions, and the system becomes less stable.
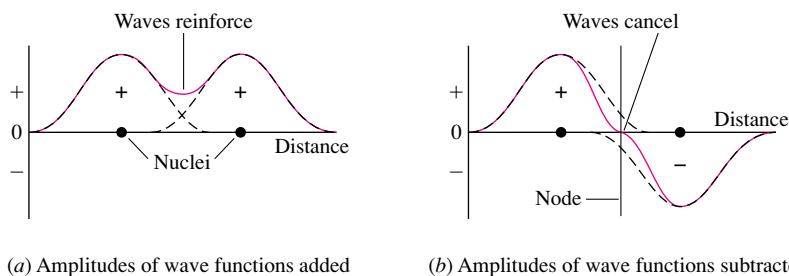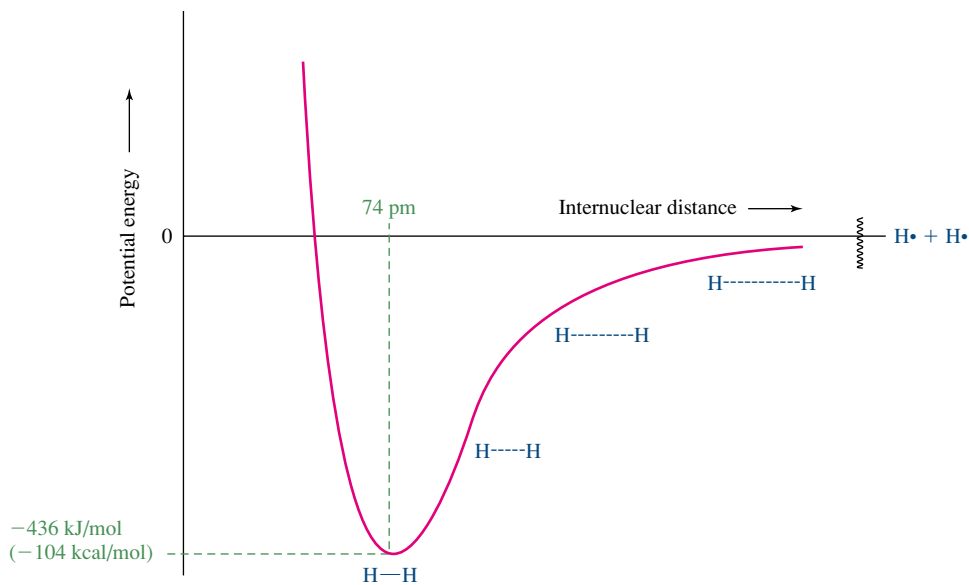

(a) Amplitudes of wave functions added   (b) Amplitudes of wave functions subtracted

FIGURE 1.15 Interference between waves. (a) Constructive interference occurs when two waves combine in phase with each other. The amplitude of the resulting wave at each point is the sum of the amplitudes of the original waves. (b) Destructive interference in the case of two phases out of phase with each other causes a mutual cancellation.

1.13   BONDING IN H_2: THE VALENCE BOND MODEL

The characteristic feature of valence bond theory is that it describes a covalent bond between two atoms in terms of an in-phase overlap of a half-filled orbital of one atom with a half-filled orbital of the other, illustrated for the case of H_2 in Figure 1.16. Two hydrogen atoms, each containing an electron in a $1s$ orbital, combine so that their orbitals overlap to give a new orbital associated with both of them. In-phase orbital overlap (constructive interference) increases the probability of finding an electron in the region of overlap.

Figure 1.17 uses electrostatic potential maps to show the buildup of electron density in the region between the atoms as two hydrogen atoms approach each other closely enough for their orbitals to overlap.

Were we to slice through the H_2 molecule perpendicular to the internuclear axis, its cross section would appear as a circle. We describe the electron distribution in such a bond as having rotational symmetry and refer to it as a **sigma (σ) bond.**
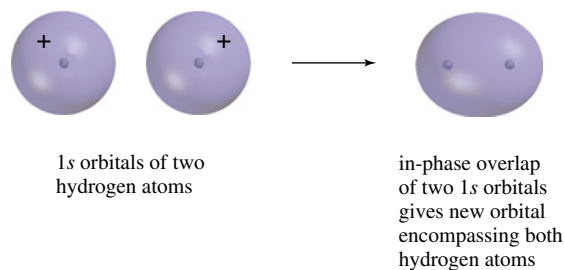
1s orbitals of two
hydrogen atoms

in-phase overlap
of two 1s orbitals
gives new orbital
encompassing both
hydrogen atoms

FIGURE 1.16   Valence bond picture of bonding in H_2. Overlap of half-filled 1s orbitals of two hydrogen atoms gives a new orbital encompassing both atoms. This new orbital contains the two original electrons. The electron density (electron probability) is highest in the region between the two atoms. The black dots correspond to the nuclei, and the + signs to the signs of the wave functions. When the wave functions are of the same sign, constructive interference leads to an increase in the probability of finding an electron in the region where the two orbitals overlap.
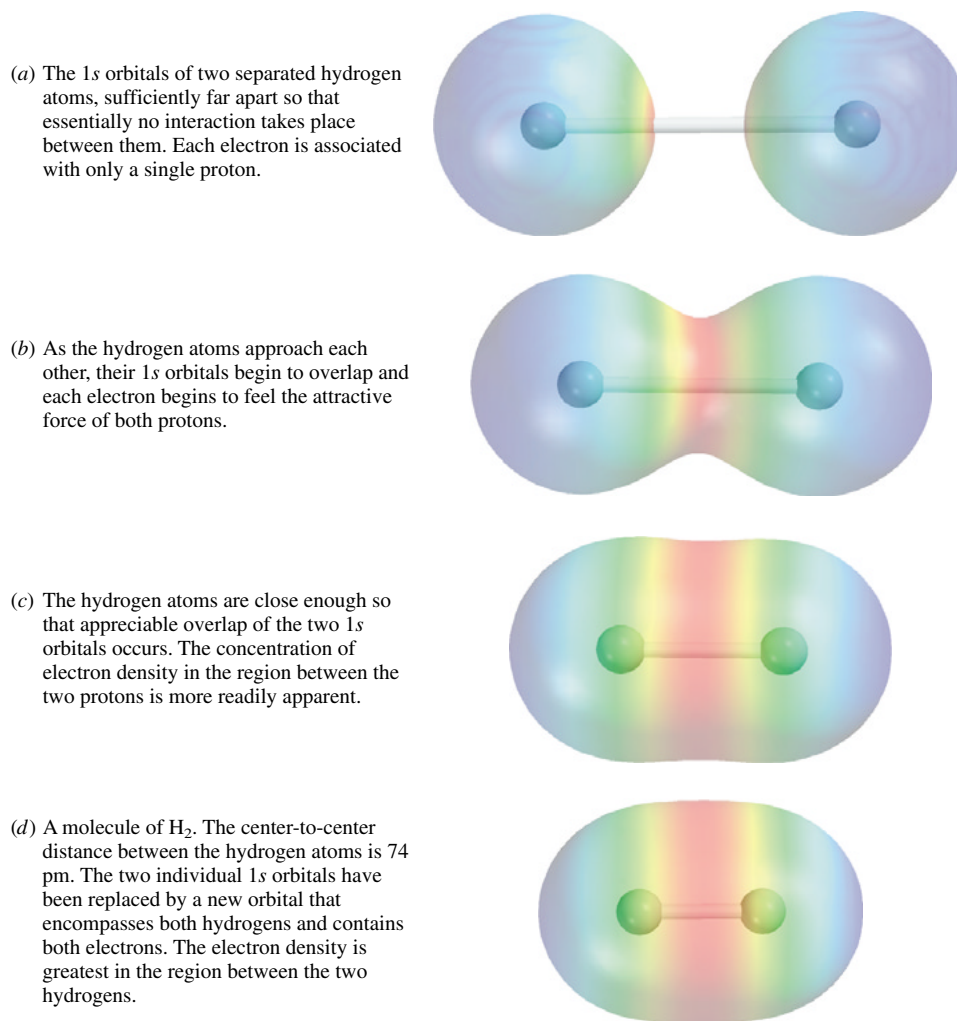
(*a*) The 1s orbitals of two separated hydrogen atoms, sufficiently far apart so that essentially no interaction takes place between them. Each electron is associated with only a single proton.

(*b*) As the hydrogen atoms approach each other, their 1s orbitals begin to overlap and each electron begins to feel the attractive force of both protons.

(*c*) The hydrogen atoms are close enough so that appreciable overlap of the two 1s orbitals occurs. The concentration of electron density in the region between the two protons is more readily apparent.

FIGURE 1.17   Valence bond picture of bonding in H_2. The drawings illustrate how the 1s orbitals of two hydrogen atoms overlap to give the orbital that contains both electrons of a hydrogen molecule. The colors of the rainbow, red through violet, are used to depict highest to lowest electrostatic potential, respectively.

(*d*) A molecule of H_2. The center-to-center distance between the hydrogen atoms is 74 pm. The two individual 1s orbitals have been replaced by a new orbital that encompasses both hydrogens and contains both electrons. The electron density is greatest in the region between the two hydrogens.

We will use the valence bond approach extensively in our discussion of organic molecules and expand on it later in this chapter. First though, let's introduce the molecular orbital method to see how it uses the $1s$ orbitals of two hydrogen atoms to generate the orbitals of an H_2 molecule.

1.14   BONDING IN H_2: THE MOLECULAR ORBITAL MODEL

The molecular orbital approach to chemical bonding is based on the notion that, as electrons in atoms occupy *atomic orbitals,* electrons in molecules occupy *molecular orbitals.* Just as the first task in writing the electron configuration of an atom is to identify the atomic orbitals that are available to it, so too must we first describe the orbitals available to a molecule. In the molecular orbital method this is accomplished by representing molecular orbitals as combinations of atomic orbitals, the *linear combination of atomic orbitals-molecular orbital* (LCAO-MO) method.

Take H_2 for example. Two molecular orbitals (MOs) are generated by combining the $1s$ atomic orbitals (AOs) of two hydrogen atoms. In one combination, the two wave functions are added; in the other they are subtracted. The two new orbitals that are produced are portrayed in Figure 1.18. The additive combination generates a **bonding orbital;** the subtractive combination generates an **antibonding orbital.** Both the bonding and antibonding orbitals have rotational symmetry around the line connecting the two atoms; they have σ symmetry. The two are differentiated by calling the bonding orbital σ and the antibonding orbital σ* ("sigma star"). The bonding orbital is characterized by a region of high electron probability between the two atoms, and the antibonding orbital has a nodal surface between them.

A molecular orbital diagram for H_2 is shown in Figure 1.19. The customary format shows the starting AOs at the left and right sides and the MOs in the middle. It must always be true that *the number of MOs is the same as the number of AOs that combine to produce them.* Thus, when the $1s$ AOs of two hydrogen atoms combine, two MOs result. The bonding MO (σ) is lower in energy and the antibonding MO (σ*) higher in energy than either of the original $1s$ orbitals.

(*a*) Add the $1s$ wave functions of two hydrogen atoms to generate a bonding molecular orbital (σ) of H_2. There is a high probability of finding both electrons in the region between the two nuclei.
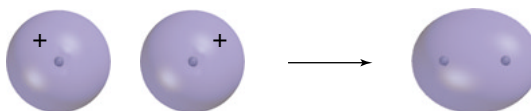
(*b*) Subtract the $1s$ wave function of one hydrogen atom from the other to generate an antibonding molecular orbital (σ*) of H_2. There is a nodal surface where there is a zero probability of finding the electrons in the region between the two nuclei.
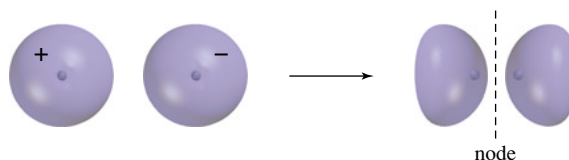

node

FIGURE 1.18 Generation of σ and σ* molecular orbitals of H_2 by combining $1s$ orbitals of two hydrogen atoms.
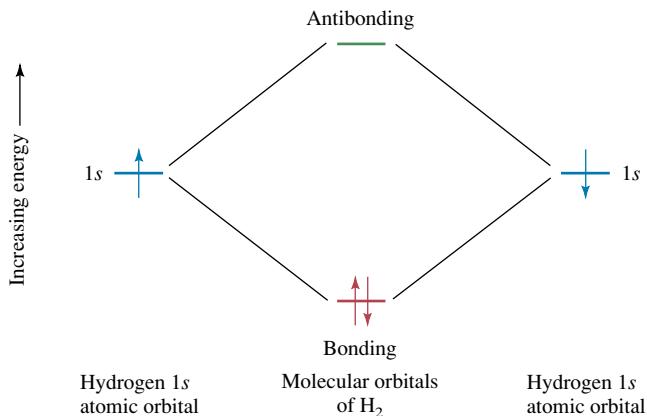
FIGURE 1.19 Two molecular orbitals are generated by combining two hydrogen $1s$ orbitals. One molecular orbital is a bonding molecular orbital and is lower in energy than either of the atomic orbitals that combine to produce it. The other molecular orbital is antibonding and is of higher energy than either atomic orbital. Each arrow indicates one electron; the electron spins are opposite in sign. The bonding orbital contains both electrons of H_2.

When assigning electrons to MOs, the same rules apply as for writing electron configurations of atoms. Electrons fill the MOs in order of increasing orbital energy, and the maximum number of electrons in any orbital is 2. The 2 electrons of H_2 occupy the bonding orbital, have opposite spins, and both are held more strongly than they would be in separated hydrogen atoms. There are no electrons in the antibonding orbital.

For a molecule as simple as H_2, it is hard to see much difference between the valence bond and molecular orbital methods. The most important differences appear in molecules with more than two atoms—a very common situation indeed. In those cases, the valence bond method continues to view a molecule as a collection of bonds between connected atoms. The molecular orbital method, however, leads to a picture in which the same electron can be associated with many, or even all, of the atoms in a molecule.

In the remaining sections of this chapter we will use a modification of valence bond theory to describe CH and CC bonds in some fundamental types of organic compounds.

1.15 BONDING IN METHANE AND ORBITAL HYBRIDIZATION

A vexing puzzle in the early days of valence bond theory concerned the bonding in methane (CH_4). Since covalent bonding requires the overlap of half-filled orbitals of the connected atoms, carbon with an electron configuration of $1s^2 2s^2 2p_x^1 2p_y^1$ has only two half-filled orbitals (Figure 1.20a), so how can it have bonds to four hydrogens?
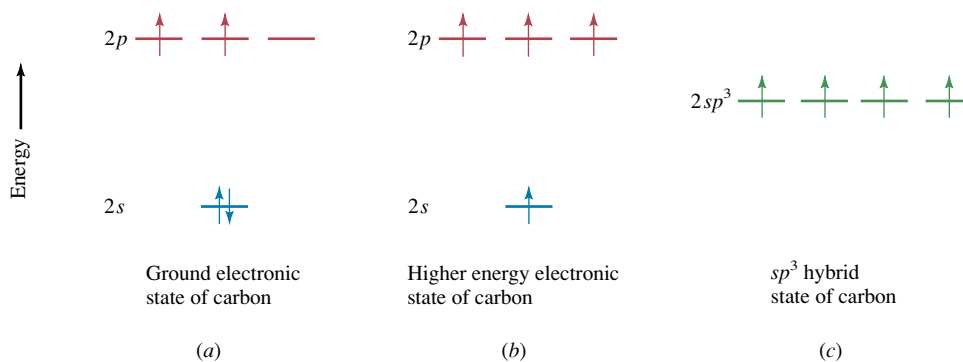

FIGURE 1.20 (a) Electron configuration of carbon in its most stable state. (b) An electron is "promoted" from the $2s$ orbital to the vacant $2p$ orbital. (c) The $2s$ orbital and the three $2p$ orbitals are combined to give a set of four equal-energy sp^3-hybridized orbitals, each of which contains one electron.

In the 1930s Linus Pauling offered an ingenious solution to the puzzle. He began with a simple idea: "promoting" one of the $2s$ electrons to the empty $2p_z$ orbital gives four half-filled orbitals and allows for four C—H bonds (Figure 1.20b). The electron configuration that results ($1s^22s^12p_x{}^12p_y{}^12p_z{}^1$), however, is inconsistent with the fact that all of these bonds are equivalent and directed toward the corners of a tetrahedron. The second part of Pauling's idea was novel: mix together (**hybridize)** the four valence orbitals of carbon ($2s$, $2p_x$, $2p_y$, and $2p_z$) to give four half-filled orbitals of equal energy (Figure 1.20c). The four new orbitals in Pauling's scheme are called sp^3 **hybrid orbitals** because they come from one s orbital and three p orbitals.

Figure 1.21 depicts some of the spatial aspects of orbital hybridization. Each sp^3 hybrid orbital has two lobes of unequal size, making the electron density greater on one side of the nucleus than the other. In a bond to hydrogen, it is the larger lobe of a carbon sp^3 orbital that overlaps with a hydrogen $1s$ orbital. The orbital overlaps corresponding to the four C—H bonds of methane are portrayed in Figure 1.22. Orbital overlap along the internuclear axis generates a bond with rotational symmetry—in this case a C($2sp^3$)—H($1s$) σ bond. *A tetrahedral arrangement of four σ bonds is characteristic of sp^3-hybridized carbon.*

The peculiar shape of sp^3 hybrid orbitals turn out to have an important consequence. Since most of the electron density in an sp^3 hybrid orbital lies to one side of a carbon atom, overlap with a half-filled $1s$ orbital of hydrogen, for example, on that side produces a stronger bond than would result otherwise. If the electron probabilities were equal on both sides of the nucleus, as it would be in a p orbital, half of the time the electron would be remote from the region between the bonded atoms, and the bond would be weaker. Thus, not only does Pauling's orbital hybridization proposal account for carbon forming four bonds rather than two, these bonds are also stronger than they would be otherwise.

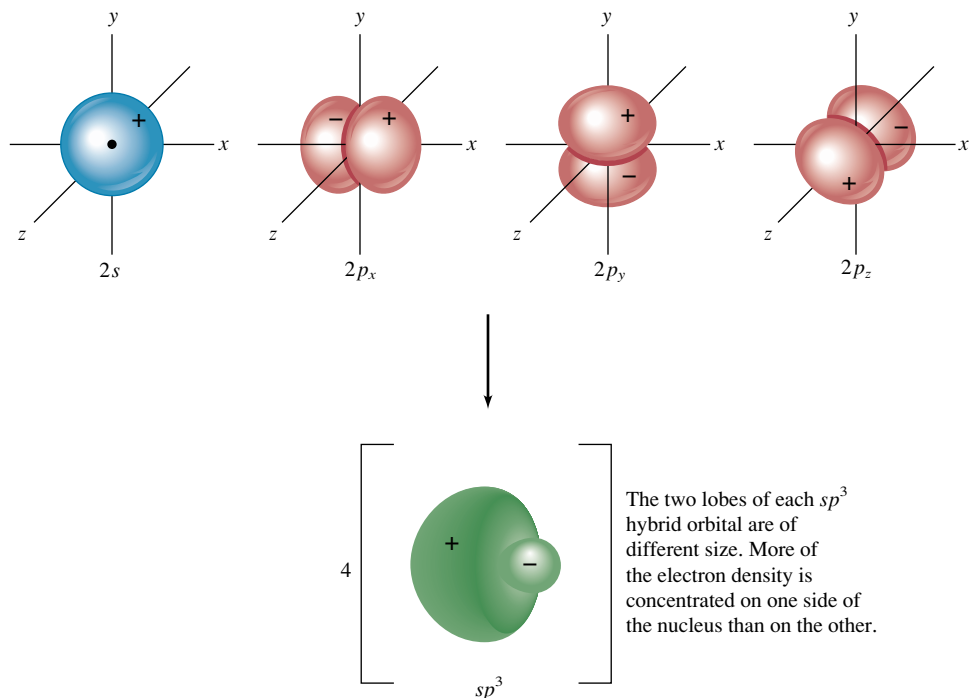Combine one $2s$ and three $2p$ orbitals to give four equivalent sp^3 hybrid orbitals:

FIGURE 1.21 Representation of orbital mixing in sp^3 hybridization. Mixing of one s orbital with three p orbitals generates four sp^3 hybrid orbitals. Each sp^3 hybrid orbital has 25% s character and 75% p character. The four sp^3 hybrid orbitals have their major lobes directed toward the corners of a tetrahedron, which has the carbon atom at its center.
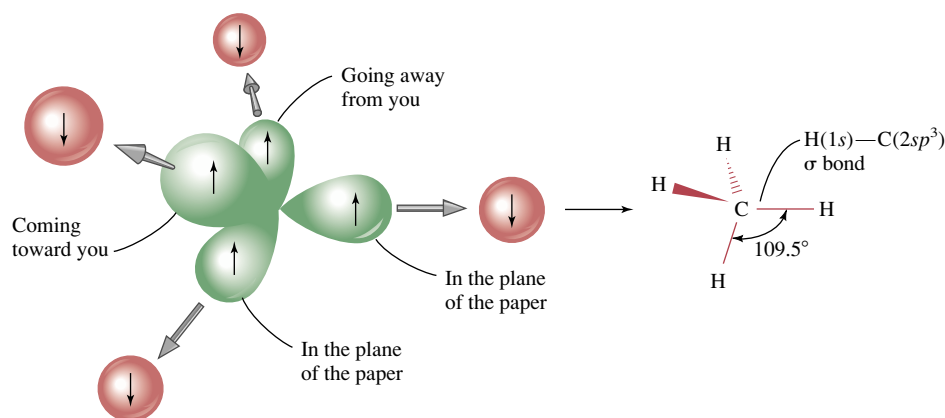
The two lobes of each sp^3 hybrid orbital are of different size. More of the electron density is concentrated on one side of the nucleus than on the other.

FIGURE 1.22 The sp^3 hybrid orbitals are arranged in a tetrahedral fashion around carbon. Each orbital contains one electron and can form a bond with a hydrogen atom to give a tetrahedral methane molecule. (*Note:* Only the major lobe of each sp^3 orbital is shown. As indicated in Figure 1.21, each orbital contains a smaller back lobe, which has been omitted for the sake of clarity.)

PROBLEM 1.20 Construct an orbital diagram like that of Figure 1.20 for nitrogen in ammonia, assuming sp^3 hybridization. In what kind of orbital is the unshared pair? What orbital overlaps are involved in the N—H bonds?

1.16 sp^3 HYBRIDIZATION AND BONDING IN ETHANE

The orbital hybridization model of covalent bonding is readily extended to carbon–carbon bonds. As Figure 1.23 illustrates, ethane is described in terms of a carbon–carbon σ bond joining two CH_3 (**methyl**) groups. Each methyl group consists of an sp^3-hybridized carbon attached to three hydrogens by sp^3–$1s$ σ bonds. Overlap of the remaining half-filled orbital of one carbon with that of the other generates a σ bond between them. Here is a third kind of σ bond, one that has as its basis the overlap of two sp^3-hybridized orbitals. *In general, you can expect that carbon will be sp^3-hybridized when it is directly bonded to four atoms.*

> The C—H and C—C bond distances in ethane are 111 and 153 pm, respectively, and the bond angles are close to tetrahedral.

PROBLEM 1.21 Describe the bonding in methylsilane (H_3CSiH_3), assuming that it is analogous to that of ethane. What is the principal quantum number of the orbitals of silicon that are hybridized?

The orbital hybridization model of bonding is not limited to compounds in which all the bonds are single, but can be adapted to compounds with double and triple bonds, as described in the following two sections.
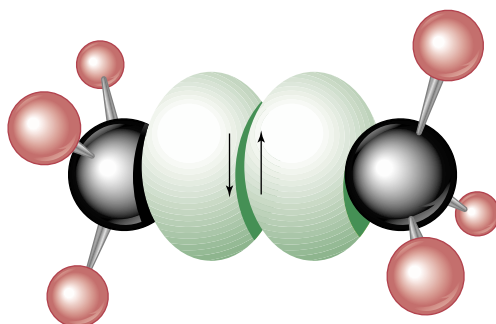

FIGURE 1.23 Orbital overlap description of the sp^3–sp^3 σ bond between the two carbon atoms of ethane.

1.17   *sp²* HYBRIDIZATION AND BONDING IN ETHYLENE

Ethylene is a planar molecule, as the structural representations of Figure 1.24 indicate. Because sp^3 hybridization is associated with a tetrahedral geometry at carbon, it is not appropriate for ethylene, which has a trigonal planar geometry at both of its carbons. The hybridization scheme is determined by the number of atoms to which the carbon is directly attached. In ethane, four atoms are attached to carbon by σ bonds, and so four equivalent sp^3 hybrid orbitals are required. In ethylene, three atoms are attached to each carbon, so three equivalent hybrid orbitals are required. As shown in Figure 1.25, these three orbitals are generated by mixing the carbon 2s orbital with two of the 2p orbitals and are called **sp^2 hybrid orbitals.** One of the 2p orbitals is left unhybridized.

FIGURE 1.24 (*a*) All the atoms of ethylene lie in the same plane. All the bond angles are close to 120°, and the carbon–carbon bond distance is significantly shorter than that of ethane. (*b*) A space-filling model of ethylene.
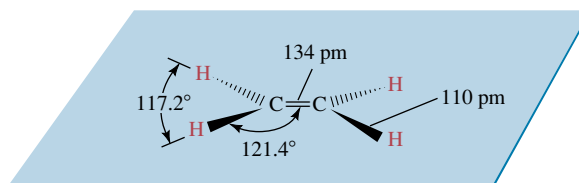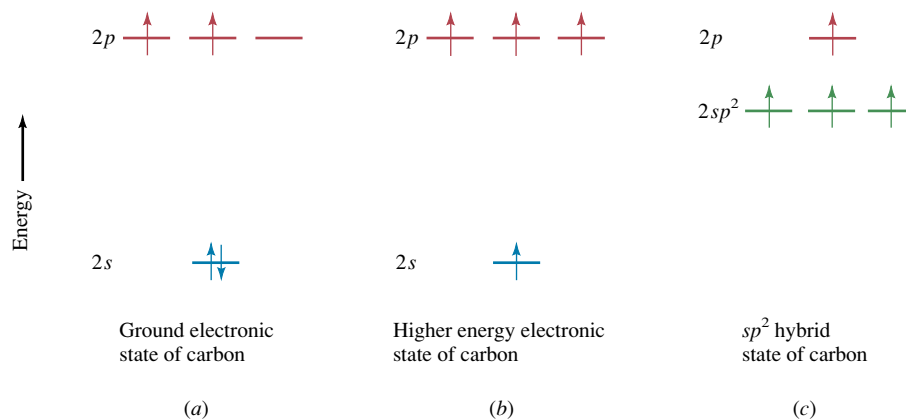
(*a*)
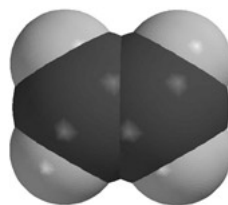
(*b*)

FIGURE 1.25 (*a*) Electron configuration of carbon in its most stable state. (*b*) An electron is "promoted" from the 2s orbital to the vacant 2p orbital. (*c*) The 2s orbital and two of the three 2p orbitals are combined to give a set of three equal-energy sp^2-hybridized orbitals. One of the 2p orbitals remains unchanged.

Figure 1.26 illustrates the mixing of orbitals in sp^2 hybridization. The three sp^2 orbitals are of equal energy; each has one-third *s* character and two-thirds *p* character. Their axes are coplanar, and each has a shape much like that of an sp^3 orbital.

Each carbon of ethylene uses two of its sp^2 hybrid orbitals to form σ bonds to two hydrogen atoms, as illustrated in the first part of Figure 1.27. The remaining sp^2 orbitals, one on each carbon, overlap along the internuclear axis to give a σ bond connecting the two carbons.

As Figure 1.27 shows, each carbon atom still has, at this point, an unhybridized $2p$ orbital available for bonding. These two half-filled $2p$ orbitals have their axes perpendicular to the framework of σ bonds of the molecule and overlap in a side-by-side manner to give what is called a **pi (π) bond.** According to this analysis, the carbon–carbon double bond of ethylene is viewed as a combination of a σ bond plus a π bond. The additional increment of bonding makes a carbon–carbon double bond both stronger and shorter than a carbon–carbon single bond.

Electrons in a π bond are called **π electrons.** The probability of finding a π electron is highest in the region above and below the plane of the molecule. The plane of the molecule corresponds to a nodal plane, where the probability of finding a π electron is zero.

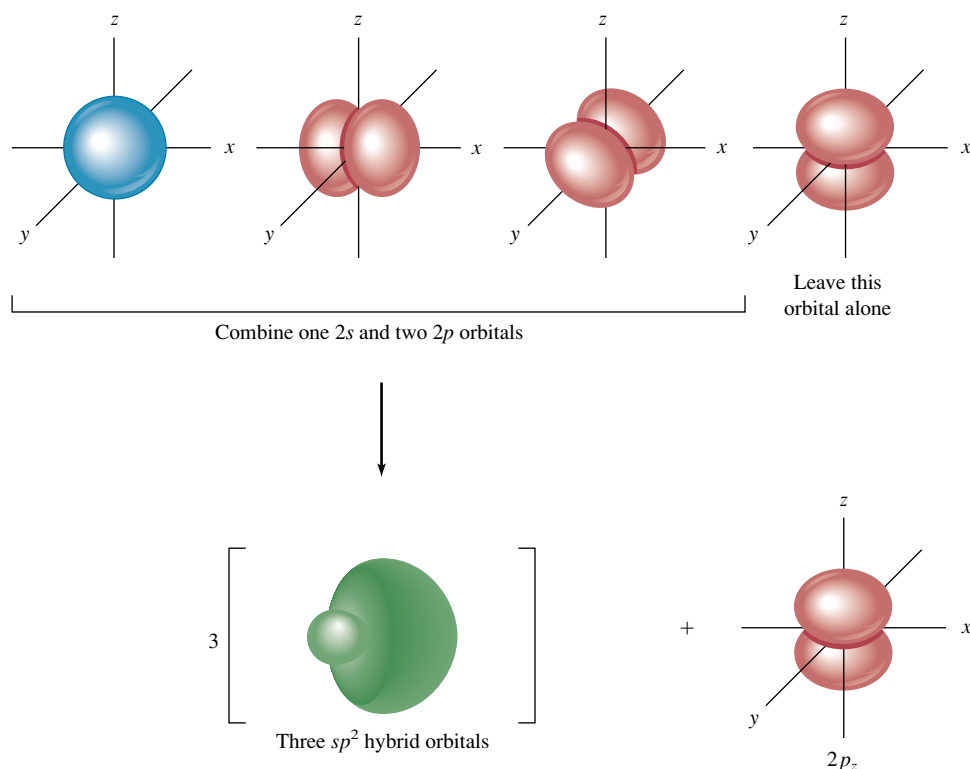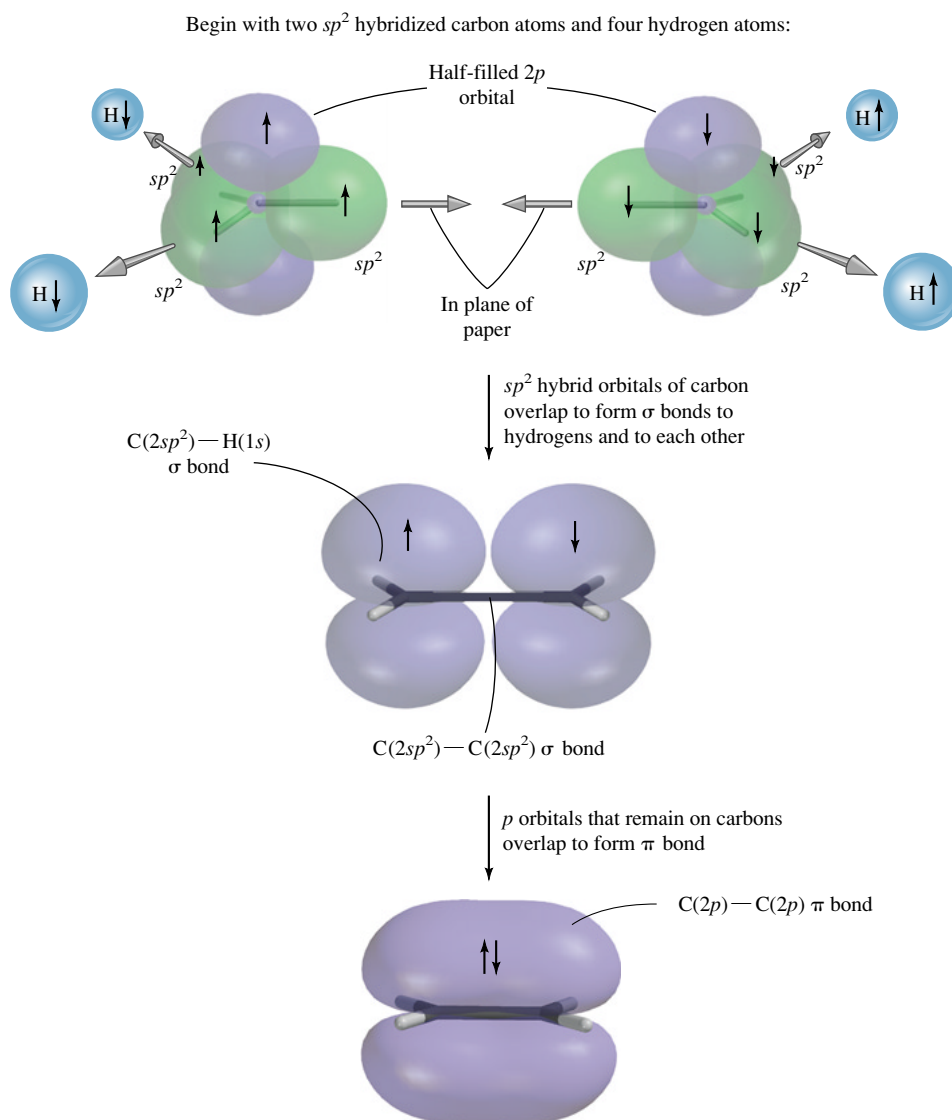*In general, you can expect that carbon will be sp^2-hybridized when it is directly bonded to three atoms.*

One measure of the strength of a bond is its *bond dissociation energy.* This topic will be introduced in Section 4.17 and applied to ethylene in Section 5.2.

Combine one 2*s* and two 2*p* orbitals

Leave this orbital alone

$$3 \left[\text{Three } sp^2 \text{ hybrid orbitals} \right] + \quad 2p_z$$

FIGURE 1.26 Representation of orbital mixing in sp^2 hybridization. Mixing of one *s* orbital with two *p* orbitals generates three sp^2 hybrid orbitals. Each sp^2 hybrid orbital has one-third *s* character and two-thirds *p* character. The axes of the three sp^2 hybrid orbitals are coplanar. One $2p$ orbital remains unhybridized, and its axis is perpendicular to the plane defined by the axes of the sp^2 orbitals.

FIGURE 1.27 The carbon–carbon double bond in ethylene has a σ component and a π component. The σ component arises from overlap of sp^2-hybridized orbitals along the internuclear axis. The π component results from a side-by-side overlap of $2p$ orbitals.

Begin with two sp^2 hybridized carbon atoms and four hydrogen atoms:

Half-filled $2p$ orbital

H

H

sp^2

sp^2

sp^2

sp^2

sp^2

sp^2

H

H

In plane of paper

sp^2 hybrid orbitals of carbon overlap to form σ bonds to hydrogens and to each other

$C(2sp^2)$—$H(1s)$ σ bond

$C(2sp^2)$—$C(2sp^2)$ σ bond

p orbitals that remain on carbons overlap to form π bond

$C(2p)$—$C(2p)$ π bond

1.18 *sp* HYBRIDIZATION AND BONDING IN ACETYLENE

One more hybridization scheme is important in organic chemistry. It is called **sp hybridization** and applies when carbon is directly bonded to two atoms, as it is in acetylene. The structure of acetylene is shown in Figure 1.28 along with its bond distances and bond angles.

> Another name for acetylene is *ethyne*.

Since each carbon in acetylene is bonded to two other atoms, the orbital hybridization model requires each carbon to have two equivalent orbitals available for the formation of σ bonds as outlined in Figures 1.29 and 1.30. According to this model the carbon $2s$ orbital and one of the $2p$ orbitals combine to generate a pair of two equivalent sp hybrid orbitals. Each sp hybrid orbital has 50% s character and 50% p character. These two sp orbitals share a common axis, but their major lobes are oriented at an angle of 180° to each other. Two of the original $2p$ orbitals remain unhybridized. Their axes are perpendicular to each other and to the common axis of the pair of sp hybrid orbitals.

180° 180°

H — C ≡ C — H

106 120 106
pm   pm   pm

(*a*)

(*b*)

2*p*   2*p*   2*p*

                                        2*sp*

2*s*   2*s*

Ground electronic   Higher energy electronic   *sp* hybrid
state of carbon   state of carbon   state of carbon

(*a*)   (*b*)   (*c*)

FIGURE 1.29 (*a*) Electron configuration of carbon in its most stable state. (*b*) An electron is "promoted" from the 2*s* orbital to the vacant 2*p* orbital. (*c*) The 2*s* orbital and one of the three 2*p* orbitals are combined to give a set of two equal-energy *sp*-hybridized orbitals. Two of the 2*p* orbitals remain unchanged.

2*s*   2*p_x*   2*p_z*   2*p_y*

Combine one 2*s* and one 2*p* orbital   Leave these two orbitals alone

2   2*p_z*   2*p_y*

Two 2*sp* hybrid orbitals   Unhybridized *p* orbitals

FIGURE 1.30 Representation of orbital mixing in *sp* hybridization. Mixing of the 2*s* orbital with one of the *p* orbitals generates two *sp* hybrid orbitals. Each *sp* hybrid orbital has 50% *s* character and 50% *p* character. The axes of the two *sp* hybrid orbitals are colinear. Two 2*p* orbitals remain unhybridized, and their axes are perpendicular to each other and to the long axis of the molecule.

As portrayed in Figure 1.31, the two carbons of acetylene are connected to each other by a 2*sp*–2*sp* σ bond, and each is attached to a hydrogen substituent by a 2*sp*–1*s* σ bond. The unhybridized 2*p* orbitals on one carbon overlap with their counterparts on the other to form two π bonds. The carbon–carbon triple bond in acetylene is viewed as a multiple bond of the σ + π + π type.

In general, you can expect that carbon will be sp-hybridized when it is directly bonded to two atoms.

FIGURE 1.31 A description of bonding in acetylene based on *sp* hybridization of carbon. The carbon–carbon triple bond is viewed as consisting of one σ bond and two π bonds.
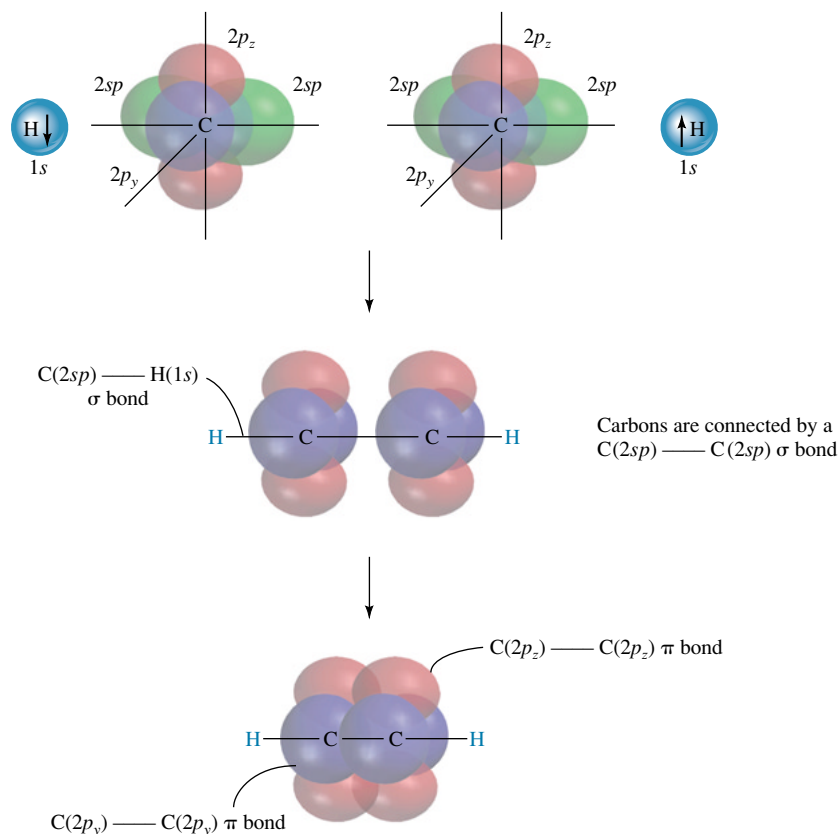
PROBLEM 1.22 Give the hybridization state of each carbon in the following compounds:

(a) Carbon dioxide (O=C=O)

(b) Formaldehyde (H_2C=O)

(c) Ketene (H_2C=C=O)

(d) Propene (CH_3CH=CH_2)

(e) Acetone [(CH_3)$_2$C=O]

(f) Acrylonitrile (CH_2=CHC≡N)

SAMPLE SOLUTION (a) Carbon in CO_2 is directly bonded to two other atoms. It is *sp*-hybridized.

1.19   WHICH THEORY OF CHEMICAL BONDING IS BEST?

We have introduced three approaches to chemical bonding in this chapter:

1. The Lewis model
2. The orbital hybridization model (which is a type of valence bond model)
3. The molecular orbital model

Which one should you learn?

Generally speaking, the three models offer complementary information. Organic chemists use all three, emphasizing whichever one best suits a particular feature of structure or reactivity. Until recently, the Lewis and orbital hybridization models were used far more than the molecular orbital model. But that is changing.

The Lewis rules are relatively straightforward, easiest to master, and the most familiar. You will find that your ability to write Lewis formulas increases rapidly with experience. *Get as much practice as you can early in the course. Success in organic chemistry depends on writing correct Lewis structures.*

Orbital hybridization descriptions, since they too are based on the shared electron-pair bond, enhance the information content of Lewis formulas by distinguishing among various types of atoms, electrons, and bonds. As you become more familiar with a variety of structural types, you will find that the term "sp^3-hybridized carbon" triggers a group of associations in your mind that are different from those of some other term, such as "sp^2-hybridized carbon," for example.

Molecular orbital theory can provide insights into structure and reactivity that the Lewis and orbital hybridization models can't. It is the least intuitive of the three methods, however, and requires the most training, background, and chemical knowledge to apply. We have *discussed* molecular orbital theory so far only in the context of the bonding in H_2. We have *used* the results of molecular orbital theory, however, several times without acknowledging it until now. The electrostatic potential map of methane that opened this chapter and was repeated as Figure 1.7*d* was obtained by a molecular orbital calculation. Four molecular orbital calculations provided the drawings that illustrated how electron density builds up between the atoms in the valence bond (!) treatment of H_2 (see Figure 1.17). Molecular orbital theory is well suited to quantitative applications and is becoming increasingly available for routine use via software that runs on personal computers. You will see the results of molecular orbital theory often in this text, but the theory itself will be developed only at an introductory level.

1.20   SUMMARY

The first half of this chapter reviews the Lewis model of chemical bonding and the procedures for writing structural formulas of chemical compounds, especially organic ones. The second half discusses bonding in terms of the wave nature of electrons and concludes with its application to compounds that contain carbon–carbon single bonds, double bonds, and triple bonds.

Section 1.1   A review of some fundamental knowledge about atoms and electrons leads to a discussion of **wave functions, orbitals,** and the **electron configurations** of atoms. Neutral atoms have as many electrons as the number of protons in the nucleus. These electrons occupy orbitals in order of increasing energy, with no more than two electrons in any one orbital. The most frequently encountered atomic orbitals in this text are *s* orbitals (spherically symmetrical) and *p* orbitals ("dumbbell"-shaped).
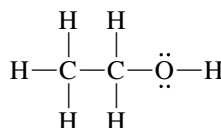
Boundary surface of an *s* orbital   Boundary surface of a *p* orbital
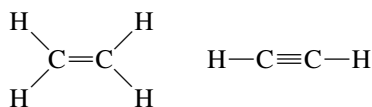with carbon at its center   with carbon at its center

Section 1.2   An **ionic bond** is the force of electrostatic attraction between two oppositely charged ions. Atoms at the upper right of the periodic table, especially fluorine and oxygen, tend to gain electrons to form anions. Elements toward the left of the periodic table, especially metals such as sodium, tend to lose electrons to form cations. Ionic bonds in which carbon is the cation or anion are rare.

Section 1.3   The most common kind of bonding involving carbon is **covalent bonding.** A covalent bond is the sharing of a pair of electrons between two atoms. **Lewis structures** are written on the basis of the **octet rule,** which limits second-row elements to no more than 8 electrons in their valence shells. In most of its compounds, carbon has four bonds.

$$
\begin{array}{ccc}
& \text{H} \quad \text{H} & \\
& | \quad\quad | & \\
\text{H}-&\text{C}-\text{C}-\ddot{\text{O}}-&\text{H} \\
& | \quad\quad | \quad\; \ddot{} & \\
& \text{H} \quad \text{H} &
\end{array}
$$

Each carbon has four bonds in ethyl alcohol;
oxygen and each carbon are surrounded by eight electrons.

Section 1.4   Many organic compounds have **double** or **triple bonds** to carbon. Four electrons are involved in a double bond; six in a triple bond.

$$
\begin{array}{cc}
\text{H} \qquad\quad \text{H} & \\
\;\;\diagdown \qquad \diagup & \\
\quad \text{C}=\text{C} & \qquad \text{H}-\text{C}\equiv\text{C}-\text{H} \\
\;\;\diagup \qquad \diagdown & \\
\text{H} \qquad\quad \text{H} &
\end{array}
$$

Ethylene has a carbon carbon double bond;
acetylene has a carbon carbon triple bond.

Section 1.5   When two atoms that differ in **electronegativity** are covalently bonded, the electrons in the bond are drawn toward the more electronegative element.

$$
{}^{\delta+}\text{C}-\text{F}\,{}^{\delta-}
$$
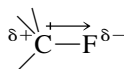
The electrons in a carbon fluorine bond are
drawn away from carbon, toward fluorine.

Section 1.6   Counting electrons and assessing charge distribution in molecules is essential to understanding how structure affects properties. A particular atom in a Lewis structure may be neutral, positively charged, or negatively charged. The **formal charge** of an atom in the Lewis structure of a molecule can be calculated by comparing its electron count with that of the neutral atom itself.

Formal charge = (number of electrons in neutral atom)
$\qquad\qquad$ − (number of electrons in unshared pairs)
$\qquad\qquad$ − $\frac{1}{2}$ (number of electrons in covalent bonds)

Section 1.7   Table 1.4 in this section sets forth the procedure to be followed in writing Lewis structures for organic molecules. It begins with experimentally

determined information: the **molecular formula** and the **constitution** (order in which the atoms are connected).
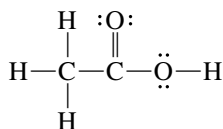

The Lewis structure of acetic acid

Section 1.8 Different compounds that have the same molecular formula are called **isomers.** If they are different because their atoms are connected in a different order, they are called **constitutional isomers.**
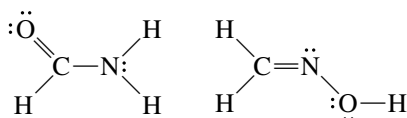
Formamide (*left*) and formaldoxime (*right*) are constitutional isomers; both have the same molecular formula (CH_3NO), but the atoms are connected in a different order.

Section 1.9 Many molecules can be represented by two or more Lewis structures that differ only in the placement of electrons. In such cases the electrons are delocalized, and the real electron distribution is a composite of the contributing Lewis structures, each of which is called a **resonance** form. The rules for resonance are summarized in Table 1.5.
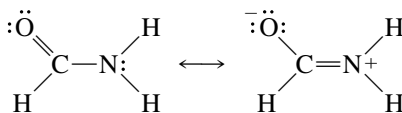
Two Lewis structures (resonance forms) of formamide; the atoms are connected in the same order, but the arrangment of the electrons is different.

Section 1.10 The shapes of molecules can often be predicted on the basis of **valence shell electron-pair repulsions.** A tetrahedral arrangement gives the maximum separation of four electron pairs (*left*); a trigonal planar arrangement is best for three electron pairs (*center*), and a linear arrangement for two electron pairs (*right*).

Section 1.11   Knowing the shape of a molecule and the polarity of its various bonds allows the presence or absence of a **molecular dipole moment** and its direction to be predicted.
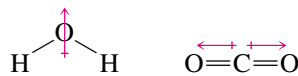
Both water and carbon dioxide have polar bonds,
but water is a polar molecule and carbon dioxide is not.

Section 1.12   Both modern theories of bonding, **valence bond** and **molecular orbital theory,** are based on the wave nature of an electron. Constructive interference between the electron wave of one atom and that of another gives a region between the two atoms in which the probability of sharing an electron is high—a bond.

Section 1.13   In valence bond theory a covalent bond is described in terms of in-phase overlap of a half-filled orbital of one atom with a half-filled orbital of another.
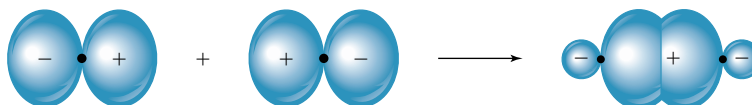
Overlap of two *p* orbitals along internuclear axis
gives a σ bond.

Section 1.14   In molecular orbital theory, molecular wave functions (MOs) are approximated by combining the wave functions of the molecule's atoms (AOs). The number of MOs must equal the number of AOs in the molecule's atoms.

Section 1.15   Bonding in methane is most often described by an **orbital hybridization** model, which is a modified form of valence bond theory. Four equivalent sp^3 hybrid orbitals of carbon are generated by mixing the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals. The C—H σ bonds are formed by overlap of each half-filled **sp^3 hybrid** orbital with a half-filled hydrogen $1s$ orbital.
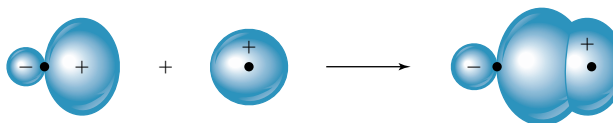

Overlap of an sp^3-hybridized orbital of carbon with
the $2s$ orbital of hydrogen to give a C—H σ bond.

Section 1.16   The carbon–carbon bond in ethane (CH_3CH_3) is a σ bond generated by overlap of an sp^3 orbital of one carbon with an sp^3 orbital of the other.
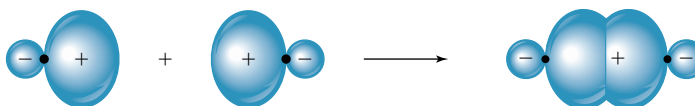

Overlap of an sp^3-hybridized orbital of each
of two carbon atoms to give a C—C σ bond.

Section 1.17   Carbon is **sp^2-hybridized** in ethylene, and the double bond is considered to have a σ component and a π component. The sp^2 hybridization state of carbon is derived by mixing the $2s$ and two of the three $2p$ orbitals. Three equivalent sp^2 orbitals result, and the axes of these orbitals are coplanar. Overlap of an sp^2 orbital of one carbon with an sp^2 orbital of another produces a σ bond between them. Each carbon still has one unhybridized p orbital available for bonding, and "side-by-side" overlap of the p orbitals of adjacent carbons gives a π bond between them.
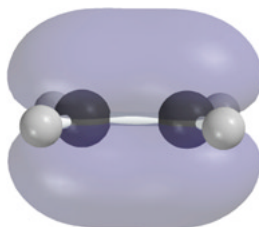
The π bond in ethylene generated by
overlap of p orbitals of adjacent carbons

Section 1.18   Carbon is **sp-hybridized** in acetylene, and the triple bond is of the $\sigma + \pi + \pi$ type. The $2s$ orbital and one of the $2p$ orbitals combine to give two equivalent sp orbitals that have their axes in a straight line. A σ bond between the two carbons is supplemented by two π bonds formed by overlap of the remaining half-filled p orbitals.
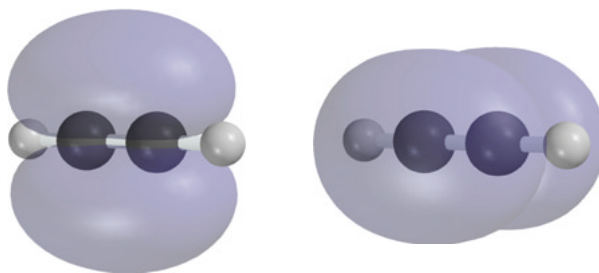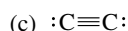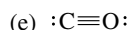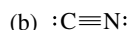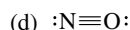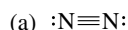
The triple bond of acetylene has a σ bond component and two π bonds;
the two π bonds are shown here and are perpendicular to each other.

Section 1.19   Lewis structures, orbital hybridization, and molecular orbital descriptions of bonding are all used in organic chemistry. Lewis structures are used the most, MO descriptions the least. All will be used in this text.
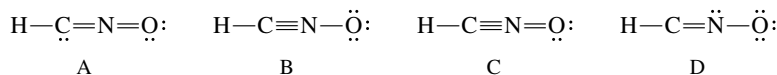
PROBLEMS

1.23   Each of the following species will be encountered at some point in this text. They all have the same number of electrons binding the same number of atoms and the same arrangement of bonds; they are *isoelectronic*. Specify which atoms, if any, bear a formal charge in the Lewis structure given and the net charge for each species.
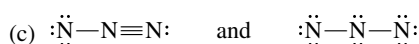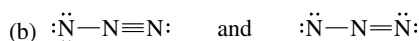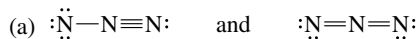
(a) :N≡N: (d) :N≡O:

(b) :C≡N: (e) :C≡O:

(c) :C≡C:

1.24 You will meet all the following isoelectronic species in this text. Repeat the previous problem for these three structures.

(a) $:\ddot{O}=C=\ddot{O}:$ (b) $:\ddot{N}=N=\ddot{N}:$ (c) $:\ddot{O}=N=\underset{..}{O}:$

1.25 All the following compounds are characterized by ionic bonding between a group I metal cation and a tetrahedral anion. Write an appropriate Lewis structure for each anion, remembering to specify formal charges where they exist.

(a) $NaBF_4$ (c) K_2SO_4

(b) $LiAlH_4$ (d) Na_3PO_4

1.26 Determine the formal charge at all the atoms in each of the following species and the net charge on the species as a whole.

(a) $H—\overset{..}{O}—H$ (d) $H—\underset{|}{\overset{|}{C}}—H$
$\quad\quad\underset{|}{}$ $\quad\quad H$
$\quad\quad H$

(b) $H—\overset{..}{C}—H$ (e) $H—\overset{..}{C}—H$
$\quad\quad\underset{|}{}$
$\quad\quad H$

(c) $H—\overset{.}{C}—H$
$\quad\quad\underset{|}{}$
$\quad\quad H$

1.27 What is the formal charge of oxygen in each of the following Lewis structures?

(a) $CH_3\overset{..}{\underset{..}{O}}:$ (b) $(CH_3)_2\overset{..}{O}:$ (c) $(CH_3)_3O:$

1.28 Write a Lewis structure for each of the following organic molecules:

(a) C_2H_5Cl (ethyl chloride: sprayed from aerosol cans onto skin to relieve pain)

(b) C_2H_3Cl [vinyl chloride: starting material for the preparation of poly(vinyl chloride), or PVC, plastics]

(c) $C_2HBrClF_3$(halothane: a nonflammable inhalation anesthetic; all three fluorines are bonded to the same carbon)

(d) $C_2Cl_2F_4$(Freon 114: formerly used as a refrigerant and as an aerosol propellant; each carbon bears one chlorine)

1.29 Write a structural formula for the CH_3NO isomer characterized by the structural unit indicated. None of the atoms in the final structure should have a formal charge.

(a) $C—N=O$ (c) $O—C=N$

(b) $C=N—O$ (d) $O=C—N$

1.30 Consider structural formulas A, B, and C:

$$H_2\overset{..}{C}—N≡N: \quad\quad H_2C=N=\ddot{N}: \quad\quad H_2C—\ddot{N}=\ddot{N}:$$

$$\quad A \quad\quad\quad\quad\quad B \quad\quad\quad\quad\quad C$$

(a) Are A, B, and C constitutional isomers, or are they resonance forms?

(b) Which structures have a negatively charged carbon?

(c) Which structures have a positively charged carbon?

(d) Which structures have a positively charged nitrogen?

(e) Which structures have a negatively charged nitrogen?

(f) What is the net charge on each structure?

(g) Which is a more stable structure, A or B? Why?

(h) Which is a more stable structure, B or C? Why?
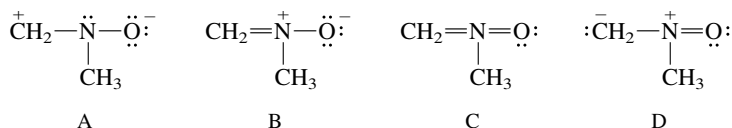
(i) What is the CNN geometry in each structure according to VSEPR?

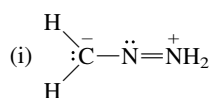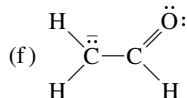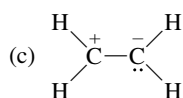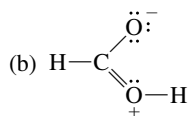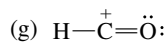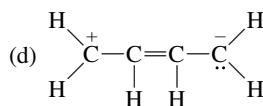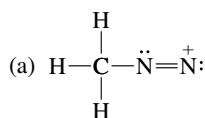**1.31** Consider structural formulas A, B, C, and D:

$$H-\underset{..}{\overset{}{C}}=N=\overset{..}{\underset{..}{O}}: \qquad H-C\equiv N-\overset{..}{\underset{..}{O}}: \qquad H-C\equiv N=\overset{..}{\underset{..}{O}}: \qquad H-C=\overset{..}{N}-\overset{..}{\underset{..}{O}}:$$

$$\qquad A \qquad\qquad\qquad B \qquad\qquad\qquad C \qquad\qquad\qquad D$$

(a) Which structures contain a positively charged carbon?

(b) Which structures contain a positively charged nitrogen?

(c) Which structures contain a positively charged oxygen?

(d) Which structures contain a negatively charged carbon?

(e) Which structures contain a negatively charged nitrogen?

(f) Which structures contain a negatively charged oxygen?

(g) Which structures are electrically neutral (contain equal numbers of positive and negative charges)? Are any of them cations? Anions?

(h) Which structure is the most stable?

(i) Which structure is the least stable?

1.32 In each of the following pairs, determine whether the two represent resonance forms of a single species or depict different substances. If two structures are not resonance forms, explain why.

(a) $:\overset{..}{N}-N\equiv N:$ and $:N=N=N:$

(b) $:\overset{..}{N}-N\equiv N:$ and $:\overset{..}{N}-N=\overset{..}{N}:$

(c) $:\overset{..}{N}-N\equiv N:$ and $:\overset{..}{N}-\overset{..}{N}-\overset{..}{N}:$

1.33 Among the following four structures, one is *not* a permissible resonance form. Identify the wrong structure. Why is it incorrect?

$$\overset{+}{C}H_2-\overset{..}{N}-\overset{..}{\underset{..}{O}}: \qquad CH_2=\overset{+}{N}-\overset{..}{\underset{..}{O}}: \qquad CH_2=N=O: \qquad :\overset{-}{C}H_2-\overset{+}{N}=O:$$
$$\underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$

$$\qquad A \qquad\qquad\qquad B \qquad\qquad\qquad C \qquad\qquad\qquad D$$

1.34 Keeping the same atomic connections and moving only electrons, write a more stable Lewis structure for each of the following. Be sure to specify formal charges, if any, in the new structure.

(a) $H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{..}{N}=\overset{+}{N}:$

(b) $H-C\overset{\overset{\overset{..}{O}:^-}{\diagup}}{\diagdown}{\overset{..}{\underset{+}{O}}-H}$

(c) $\overset{H}{\underset{H}{\diagdown}}\overset{+}{C}-\overset{-}{\underset{..}{C}}\overset{\diagup H}{\diagdown H}$

(d) $\overset{H}{\diagdown}\overset{+}{C}-C=C-\overset{-}{\underset{..}{C}}\overset{\diagup H}{\diagdown H}$ (H H below)

(e) $\overset{H}{\diagdown}\overset{+}{C}-C=C-\overset{..}{\underset{..}{O}}:^-$

(f) $\overset{H}{\diagdown}\overset{..}{C}-C\overset{\overset{..}{O}:}{\diagdown H}$

(g) $H-\overset{+}{C}=\overset{..}{O}:$

(h) $\overset{H}{\diagdown}\overset{+}{C}-\overset{..}{O}H$

(i) $:\overset{-}{C}-\overset{..}{N}=\overset{+}{N}H_2$
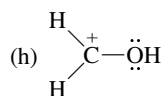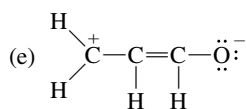
1.35 (a) Write a Lewis structure for sulfur dioxide in which the octet rule is satisfied for all three atoms. Show all electron pairs and include any formal charges. The atoms are connected in the order OSO.

(b) The octet rule may be violated for elements beyond the second period of the periodic table. Write a Lewis structure for sulfur dioxide in which each oxygen is connected to sulfur by a double bond. Show all electron pairs and formal charges.

1.36 Write structural formulas for all the constitutionally isomeric compounds having the given molecular formula.

(a) C_4H_{10} (d) C_4H_9Br

(b) C_5H_{12} (e) C_3H_9N

(c) $C_2H_4Cl_2$
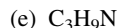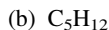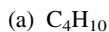
1.37 Write structural formulas for all the constitutional isomers of

(a) C_3H_8 (b) C_3H_6 (c) C_3H_4
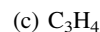
1.38 Write structural formulas for all the constitutional isomers of molecular formula C_3H_6O that contain

(a) Only single bonds   (b) One double bond

1.39 For each of the following molecules that contain polar covalent bonds, indicate the positive and negative ends of the dipole, using the symbol $\leftrightarrow$. Refer to Table 1.2 as needed.

(a) HCl   (c) HI   (e) HOCl

(b) ICl   (d) H_2O

1.40 The compounds FCl and ICl have dipole moments μ that are similar in magnitude (0.9 and 0.7 D, respectively) but opposite in direction. In one compound, chlorine is the positive end of the dipole; in the other it is the negative end. Specify the direction of the dipole moment in each compound, and explain your reasoning.

1.41 Which compound in each of the following pairs would you expect to have the greater dipole moment μ? Why?
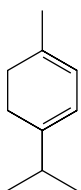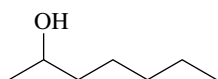
(a) NaCl or HCl   (e) $CHCl_3$ or CCl_3F

(b) HF or HCl   (f) CH_3NH_2 or CH_3OH

(c) HF or BF_3 (g) CH_3NH_2 or CH_3NO_2
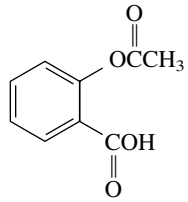
(d) $(CH_3)_3CH$ or $(CH_3)_3CCl$
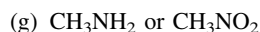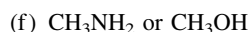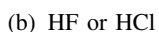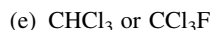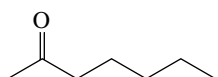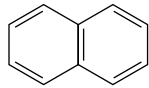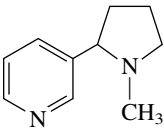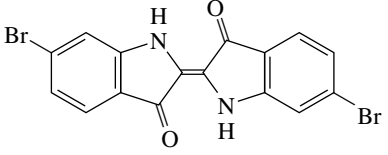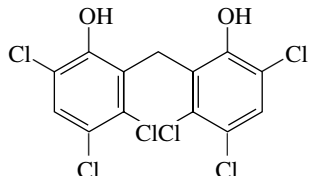
1.42 Apply the VSEPR method to deduce the geometry around carbon in each of the following species:

(a) $:\overset{-}{C}H_3$ (b) $\overset{+}{C}H_3$ (c) $:CH_2$
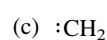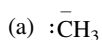
1.43 Expand the following structural representations so as to more clearly show all the atoms and any unshared electron pairs.

(a)   A component of high-octane gasoline

(b)   Occurs in bay and verbena oil
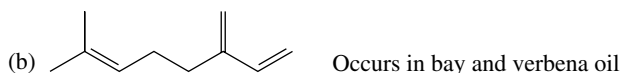
(c) Pleasant-smelling substance
found in marjoram oil

OH

(d) Present in oil of cloves

O

(e) Found in Roquefort cheese

(f) Benzene: parent compound of a large
family of organic substances

(g) Naphthalene: sometimes used as a
moth repellent

O
‖
OCCH₃

(h) Aspirin

COH
‖
O

(i) Nicotine: a toxic substance
present in tobacco

(j) Tyrian purple: a purple
dye extracted from a
species of Mediterranean
sea snail

OH   OH

(k) Hexachlorophene:
an antiseptic

1.44 Molecular formulas of organic compounds are customarily presented in the fashion $C_2H_5BrO_2$. The number of carbon and hydrogen atoms are presented first, followed by the other atoms in alphabetical order. Give the molecular formulas corresponding to each of the compounds in the preceding problem. Are any of them isomers?

1.45 Select the compounds in Problem 1.43 in which all the carbons are

(a) sp^3-hybridized   (b) sp^2-hybridized

Do any of the compounds in Problem 1.43 contain an sp-hybridized carbon?

1.46 Account for all the electrons in each of the following species, assuming sp^3 hybridization of the second-row element in each case. Which electrons are found in sp^3-hybridized orbitals? Which are found in σ bonds?

(a) Ammonia (NH_3)

(b) Water (H_2O)

(c) Hydrogen fluoride (HF)

(d) Ammonium ion ($NH_4{}^+$)

(e) Borohydride anion ($BH_4{}^-$)

(f) Amide anion ($:\!\ddot{N}H_2$)

(g) Methyl anion ($:\!\bar{C}H_3$)

1.47 Imagine describing the bonding in ammonia as arising by overlap of the half-filled *unhybridized* $2p_x$, $2p_y$, and $2p_z$ orbitals of nitrogen with the half-filled $1s$ orbitals of three hydrogen atoms.

(a) What kind of orbital would the unshared pair occupy?

(b) What would you expect the bond angles to be?

1.48 Of the orbital overlaps shown in the illustration, one is bonding, one is antibonding, and the third is nonbonding (neither bonding nor antibonding). Which orbital overlap corresponds to which interaction? Why?

(*a*)   (*b*)   (*c*)
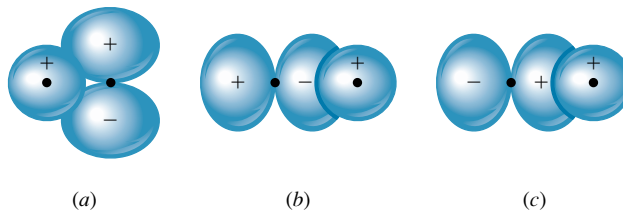
1.49 Practice working with your *Learning By Modeling* software. Construct molecular models of ethane, ethylene, and acetylene, and compare them with respect to their geometry, bond angles, and C—H and C—C bond distances.

1.50 How many different structures (isomers) can you make that have the formula (a) CH_2Cl_2; (b) $Cl_2C{=}CH_2$; and (c) $ClCH{=}CHCl$?

1.51 Examine the molecular models of H_2, HF, CH_4, CH_3F, and CF_4. Find the calculated dipole moment of each compound, and examine their electrostatic potential maps.

1.52 Examine the electrostatic potential map of ethylene. Where is the most negative region? What kinds of electrons are most responsible for the high electron density in this region? Are they electrons in σ bonds or in the π bond?

1.53 (a) Find the models of I—Br and Cl—F, and compare their calculated dipole moments. Which is more important, the difference in electronegativity between the bonded halogens or the length of the bond between them? [Remember that the dipole moment depends on both charge and distance ($\mu = e \times d$).]

(b) Compare the electrostatic potential maps of IBr and ClF. How do they correspond to the information provided by the dipole moment calculations?

1.54 Compare the dipole moments of cyanogen bromide ($BrC{\equiv}N$) and cyanogen chloride ($ClC{\equiv}N$). Which is larger? Why? What does this tell you about the electronegativity of the CN group?

1.55 Problem 1.8 concerned the charge distribution in methane (CH_4), chloromethane (CH_3Cl), and methyllithium (CH_3Li). Inspect molecular models of each of these compounds, and compare them with respect to how charge is distributed among the various atoms (carbon, hydrogen, chlorine, and lithium). Compare their electrostatic potential maps.