

# PART ONE

This book contains 19 chapters. Chapters 10 to 19, which make up Part 2, are directly concerned with organic reactions and their mechanisms. Chapters 1 to 9 may be thought of as an introduction to Part 2. The first five chapters deal with the structure of organic compounds. In these chapters are discussed the kinds of bonding important in organic chemistry, the three-dimensional structure of organic molecules, and the structure of species in which the valence of carbon is less than 4. Chapters 6 to 9 are concerned with other topics that help to form a background to Part 2: acids and bases, photochemistry, the relationship between structure and reactivity, and a general discussion of mechanisms and the means by which they are determined.

# 1

## LOCALIZED CHEMICAL BONDING

*Localized chemical bonding* may be defined as bonding in which the electrons are shared by two and only two nuclei. In Chapter 2 we shall consider *delocalized bonding*, in which electrons are shared by more than two nuclei.

### Covalent Bonding<sup>1</sup>

Wave mechanics is based on the fundamental principle that electrons behave as waves (e.g., they can be diffracted) and that consequently a wave equation can be written for them, in the same sense that light waves, sound waves, etc. can be described by wave equations. The equation that serves as a mathematical model for electrons is known as the *Schrödinger equation*, which for a one-electron system is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

where  $m$  is the mass of the electron,  $E$  is its total energy,  $V$  is its potential energy, and  $h$  is Planck's constant. In physical terms, the function  $\psi$  expresses the square root of the probability of finding the electron at any position defined by the coordinates  $x$ ,  $y$ , and  $z$ , where the origin is at the nucleus. For systems containing more than one electron the equation is similar but more complicated.

The Schrödinger equation is a differential equation, which means that solutions of it are themselves equations. The solutions, however, are not differential equations, but simple equations for which graphs can be drawn. Such graphs, which are three-dimensional pictures that show the electron density, are called *orbitals* or electron clouds. Most students are familiar with the shapes of the  $s$  and  $p$  atomic orbitals (Figure 1.1). Note that each  $p$  orbital has a *node*—a region in space where the probability of finding the electron is extremely small.<sup>2</sup> Also note that in Figure 1.1 some lobes of the orbitals are labeled + and others -.

<sup>1</sup>The treatment of orbitals given here is necessarily simplified. For much fuller treatments of orbital theory as applied to organic chemistry, see Matthews *Quantum Chemistry of Atoms and Molecules*; Cambridge University Press: Cambridge, 1986; Clark *A Handbook of Computational Chemistry*; Wiley: New York, 1985; Albright; Burdett; Whangbo *Orbital Interactions in Chemistry*; Wiley: New York, 1985; McWeeny *Coulson's Valence*; Oxford University Press: Oxford, 1980; Murrell; Kettle; Tedder, *The Chemical Bond*; Wiley: New York, 1978; Dewar; Dougherty *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975; Zimmerman *Quantum Mechanics for Organic Chemists*; Academic Press: New York, 1975; Borden *Modern Molecular Orbital Theory for Organic Chemists*; Prentice-Hall: Englewood Cliffs, NJ, 1975; Dewar *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; Liberles *Introduction to Molecular Orbital Theory*; Holt, Rinehart, and Winston: New York, 1966.

<sup>2</sup>When wave-mechanical calculations are made according to the Schrödinger equation, the probability of finding the electron in a node is zero, but this treatment ignores relativistic considerations. When such considerations are applied, Dirac has shown that nodes do have a very small electron density: Powell *J. Chem. Educ.* **1968**, *45*, 558. See also Ellison and Hollingsworth *J. Chem. Educ.* **1976**, *53*, 767; McKelvey *J. Chem. Educ.* **1983**, *60*, 112; Nelson, *J. Chem. Educ.* **1990**, *67*, 643. For a review of relativistic effects on chemical structures in general, see Pyykkö *Chem. Rev.* **1988**, *88*, 563-594.

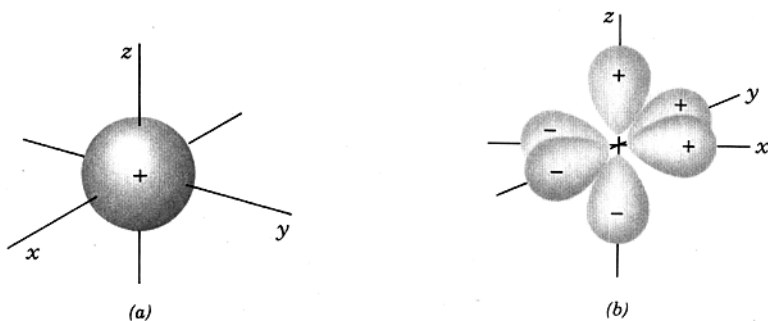


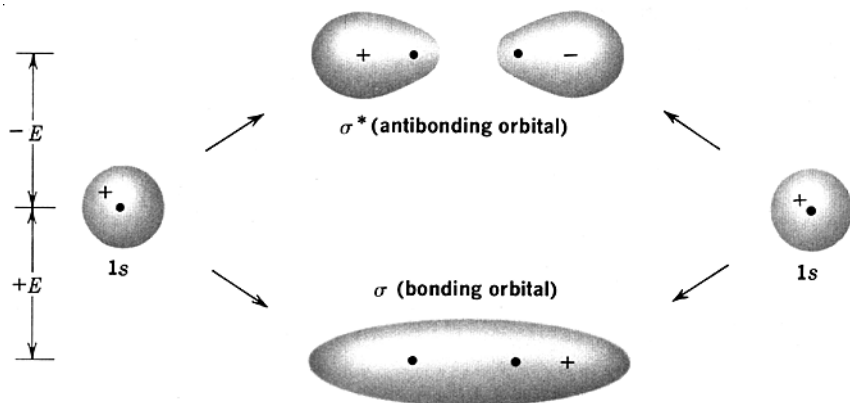
FIGURE 1.1 (a) the 1s orbital. (b) The three 2p orbitals.

These signs do not refer to positive or negative *charges*, since both lobes of an electron cloud must be negatively charged. They are the signs of the wave function  $\psi$ . When two parts of an orbital are separated by a node,  $\psi$  always has opposite signs on the two sides of the node. According to the Pauli exclusion principle, no more than two electrons can be present in any orbital, and they must have opposite spins.

Unfortunately, the Schrödinger equation can be solved exactly only for one-electron systems such as the hydrogen atom. If it could be solved exactly for molecules containing two or more electrons,<sup>3</sup> we would have a precise picture of the shape of the orbitals available to each electron (especially for the important ground state) and the energy for each orbital. Since exact solutions are not available, drastic approximations must be made. There are two chief general methods of approximation: the *molecular-orbital* method and the *valence-bond* method.

In the molecular-orbital method, bonding is considered to arise from the overlap of atomic orbitals. When any number of atomic orbitals overlap, they combine to form an equal number of new orbitals, called *molecular orbitals*. Molecular orbitals differ from atomic orbitals in that they are clouds that surround the nuclei of two or more atoms, rather than just one atom. In localized bonding the number of atomic orbitals that overlap is two (each containing one electron), so that two molecular orbitals are generated. One of these, called a *bonding orbital*, has a lower energy than the original atomic orbitals (otherwise a bond would not form), and the other, called an *antibonding orbital*, has a higher energy. Orbitals of lower energy fill first. Since the two original atomic orbitals each held one electron, both of these electrons can now go into the new molecular *bonding* orbital, since any orbital can hold two electrons. The antibonding orbital remains empty in the ground state. The greater the overlap, the stronger the bond, although total overlap is prevented by repulsion between the nuclei. Figure 1.2 shows the bonding and antibonding orbitals that arise by the overlap of two 1s electrons. Note that since the antibonding orbital has a node between the nuclei, there is practically no electron density in that area, so that this orbital cannot be expected to bond very well. Molecular orbitals formed by the overlap of two atomic orbitals when the centers of electron density are on the axis common to the two nuclei are called  $\sigma$  (*sigma*) orbitals, and the bonds are called  $\sigma$  bonds. Corresponding antibonding orbitals are designated  $\sigma^*$ . Sigma orbitals are formed not only by the overlap of two *s* orbitals, but also by the

<sup>3</sup>For a number of simple systems containing two or more electrons, such as the  $H_2$  molecule or the He atom, approximate solutions are available that are so accurate that for practical purposes they are as good as exact solutions. See, for example, Roothaan; Weiss *Rev. Mod. Phys.* **1960**, *32*, 194; Kolos; Roothaan *Rev. Mod. Phys.* **1960**, *32*, 219. For a review, see Clark; Stewart *Q. Rev., Chem. Soc.* **1970**, *24*, 95-118.



**FIGURE 1.2** Overlap of two 1s orbitals gives rise to a  $\sigma$  and a  $\sigma^*$  orbital.

overlap of any of the kinds of atomic orbital ( $s$ ,  $p$ ,  $d$ , or  $f$ ) whether the same or different, but the two lobes that overlap must have the same sign: a positive  $s$  orbital can form a bond only by overlapping with another positive  $s$  orbital or with a positive lobe of a  $p$ ,  $d$ , or  $f$  orbital. Any  $\sigma$  orbital, no matter what kind of atomic orbitals it has arisen from, may be represented as approximately ellipsoidal in shape.

Orbitals are frequently designated by their symmetry properties. The  $\sigma$  orbital of hydrogen is often written  $\Psi_g$ . The  $g$  stands for *gerade*. A gerade orbital is one in which the sign on the orbital does not change when it is inverted through its center of symmetry. The  $\sigma^*$  orbital is *ungerade* (designated  $\Psi_u$ ). An ungerade orbital changes sign when inverted through its center of symmetry.

In molecular-orbital calculations, a wave function is formulated that is a linear combination of the atomic orbitals that have overlapped (this method is often called the *linear combination of atomic orbitals*, or LCAO). Addition of the atomic orbitals gives the bonding molecular orbital:

$$\Psi = c_A\psi_A + c_B\psi_B \quad (1)$$

The functions  $\psi_A$  and  $\psi_B$  are the functions for the atomic orbitals of atoms A and B, respectively, and  $c_A$  and  $c_B$  represent weighting factors. Subtraction is also a linear combination:

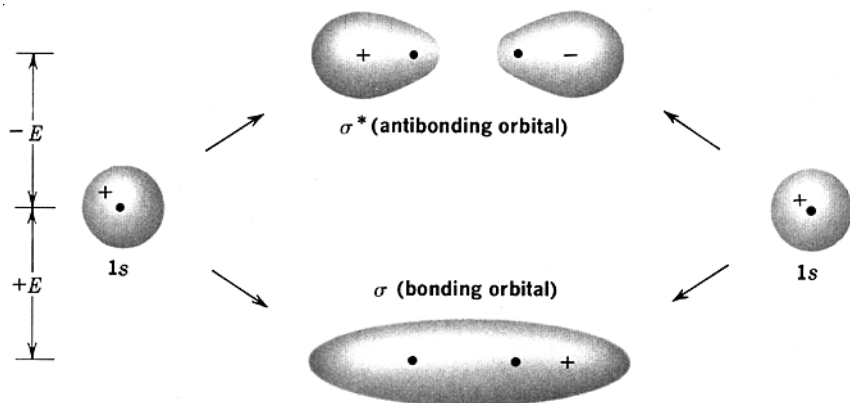
$$\Psi = c_A\psi_A - c_B\psi_B \quad (2)$$

This gives rise to the antibonding molecular orbital.

In the valence-bond method, a wave equation is written for each of various possible electronic structures that a molecule may have (each of these is called a *canonical form*), and the total  $\Psi$  is obtained by summation of as many of these as seem plausible, each with its weighting factor:

$$\Psi = c_1\psi_1 + c_2\psi_2 + \dots \quad (3)$$

This resembles Eq. (1), but here each  $\psi$  represents a wave equation for an imaginary canonical form and each  $c$  is the amount contributed to the total picture by that form. For



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This resembles Eq. (1), but here each  $\psi$  represents a wave equation for an imaginary canonical form and each  $c$  is the amount contributed to the total picture by that form. For

example, a wave function can be written for each of the following canonical forms of the hydrogen molecule:<sup>4</sup>



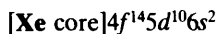
Values for  $c$  in each method are obtained by solving the equation for various values of each  $c$  and choosing the solution of lowest energy. In practice, both methods give similar solutions for molecules that contain only localized electrons, and these are in agreement with the Lewis structures long familiar to the organic chemist. Delocalized systems are considered in Chapter 2.

## Multiple Valence

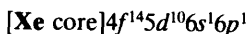
A univalent atom has only one orbital available for bonding. But atoms with a valence of 2 or more must form bonds by using at least two orbitals. An oxygen atom has two half-filled orbitals, giving it a valence of 2. It forms single bonds by the overlap of these with the orbitals of two other atoms. According to the principle of maximum overlap, the other two nuclei should form an angle of  $90^\circ$  with the oxygen nucleus, since the two available orbitals on oxygen are  $p$  orbitals, which are perpendicular. Similarly, we should expect that nitrogen, which has three mutually perpendicular  $p$  orbitals, would have bond angles of  $90^\circ$  when it forms three single bonds. However, these are not the observed bond angles. The bond angles are,<sup>5</sup> in water,  $104^\circ 27'$ , and in ammonia,  $106^\circ 46'$ . For alcohols and ethers the angles are even larger (see p. 22). A discussion of this will be deferred to p. 22, but it is important to note that covalent compounds do have definite bond angles. Although the atoms are continuously vibrating, the mean position is the same for each molecule of a given compound.

## Hybridization

Consider the case of mercury. Its electronic structure is



Although it has no half-filled orbitals, it has a valence of 2 and forms two covalent bonds. We can explain this by imagining that one of the  $6s$  electrons is promoted to a vacant  $6p$  orbital to give the excited configuration



In this state the atom has two half-filled orbitals, but they are not equivalent. If bonding were to occur by the overlap of these orbitals with the orbitals of external atoms, the two bonds would not be equivalent. The bond formed from the  $6p$  orbital would be more stable than the one formed from the  $6s$  orbital, since a larger amount of overlap is possible with the former. A more stable situation is achieved when, in the course of bond formation, the  $6s$  and  $6p$  orbitals combine to form two new orbitals that *are* equivalent; these are shown in Figure 1.3.

Since these new orbitals are a mixture of the two original orbitals, they are called *hybrid orbitals*. Each is called an  $sp$  orbital, since a merger of an  $s$  and a  $p$  orbital was required to

<sup>4</sup>In this book a pair of electrons, whether in a bond or unshared, is represented by a straight line.

<sup>5</sup>Bent *Chem. Rev.* **1961**, *61*, 275-311, p. 277.

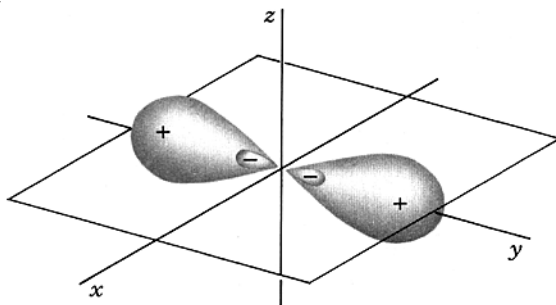
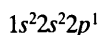


FIGURE 1.3 The two  $sp$  orbitals formed by mercury.

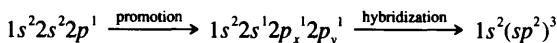
form it. The  $sp$  orbitals, each of which consists of a large lobe and a very small one, are atomic orbitals, although they arise only in the bonding process and do not represent a possible structure for the free atom. A mercury atom forms its two bonds by overlapping each of the large lobes shown in Figure 1.3 with an orbital from an external atom. This external orbital may be any of the atomic orbitals previously considered ( $s$ ,  $p$ ,  $d$ , or  $f$ ) or it may be another hybrid orbital, although only lobes of the same sign can overlap. In any of these cases the molecular orbital that arises is called a  $\sigma$  orbital since it fits our previous definition of a  $\sigma$  orbital.

In general, because of mutual repulsion, equivalent orbitals lie as far away from each other as possible, so the two  $sp$  orbitals form an angle of  $180^\circ$ . This means that  $\text{HgCl}_2$ , for example, should be a linear molecule (in contrast to  $\text{H}_2\text{O}$ ), and it is. This kind of hybridization is called *digonal hybridization*. An  $sp$  hybrid orbital forms a stronger covalent bond than either an  $s$  or a  $p$  orbital because it extends out in space in the direction of the other atom's orbital farther than the  $s$  or the  $p$  and permits greater overlap. Although it would require energy to promote a  $6s$  electron to the  $6p$  state, the extra bond energy more than makes up the difference.

Many other kinds of hybridization are possible. Consider boron, which has the electronic configuration

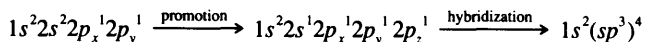


yet has a valence of 3. Once again we may imagine promotion and hybridization:



In this case there are three equivalent hybrid orbitals, each called  $sp^2$  (*trigonal hybridization*). This method of designating hybrid orbitals is perhaps unfortunate since nonhybrid orbitals are designated by single letters, but it must be kept in mind that *each* of the three orbitals is called  $sp^2$ . These orbitals are shown in Figure 1.4. The three axes are all in one plane and point to the corners of an equilateral triangle. This accords with the known structure of  $\text{BF}_3$ , a planar molecule with angles of  $120^\circ$ .

The case of carbon (in forming four single bonds) may be represented as



There are four equivalent orbitals, each called  $sp^3$ , which point to the corners of a regular tetrahedron (Figure 1.4). The bond angles of methane would thus be expected to be  $109^\circ 28'$ , which is the angle for a regular tetrahedron.

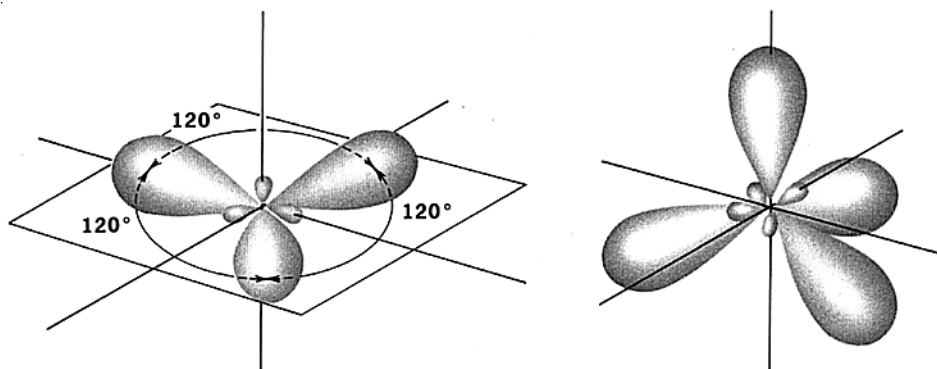


FIGURE 1.4 The three  $sp^2$  and the four  $sp^3$  orbitals.

Although the hybrid orbitals discussed in this section satisfactorily account for most of the physical and chemical properties of the molecules involved, it is necessary to point out that the  $sp^3$  orbitals, for example, stem from only one possible approximate solution of the Schrödinger equation. The  $s$  and the three  $p$  atomic orbitals can also be combined in many other equally valid ways. As we shall see on p. 12, the four C—H bonds of methane do not always behave as if they are equivalent.

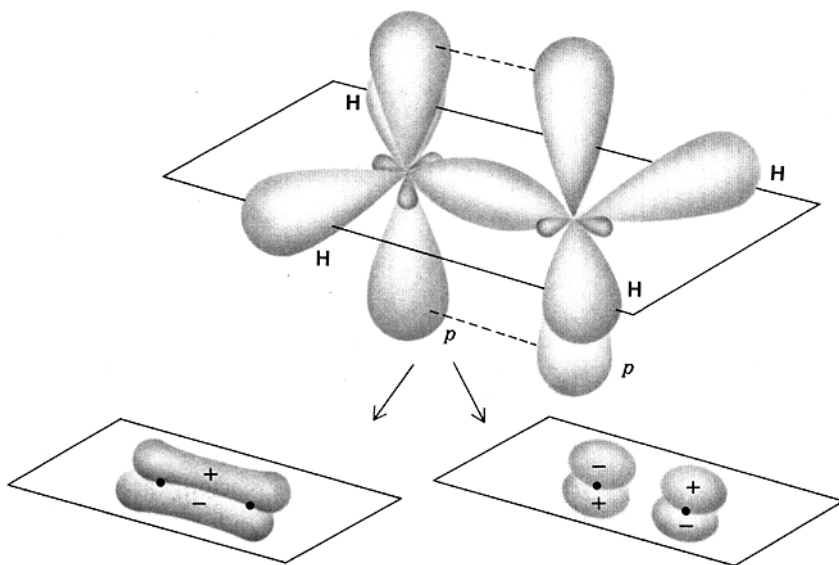
### Multiple Bonds

If we consider the ethylene molecule in terms of the molecular-orbital concepts discussed so far, we have each carbon using  $sp^2$  orbitals to form bonds with the three atoms to which it is connected. These  $sp^2$  orbitals arise from hybridization of the  $2s^1$ ,  $2p_x^1$ , and  $2p_y^1$  electrons of the promoted state shown on p. 7. We may consider that any carbon atom that is bonded to only three different atoms uses  $sp^2$  orbitals for this bonding. Each carbon of ethylene is thus bonded by three  $\sigma$  bonds: one to each hydrogen and one to the other carbon. Each carbon therefore has another electron in the  $2p_z$  orbital that is perpendicular to the plane of the  $sp^2$  orbitals. The two parallel  $2p_z$  orbitals can overlap sideways to generate two new orbitals, a bonding and an antibonding orbital (Figure 1.5). Of course, in the ground state, both electrons go into the bonding orbital and the antibonding orbital remains vacant. Molecular orbitals formed by the overlap of atomic orbitals whose axes are parallel are called  $\pi$  orbitals if they are bonding and  $\pi^*$  if they are antibonding.

In this picture of ethylene, the two orbitals that make up the double bond are not equivalent.<sup>6</sup> The  $\sigma$  orbital is ellipsoidal and symmetrical about the C—C axis. The  $\pi$  orbital is in the shape of two ellipsoids, one above the plane and one below. The plane itself represents a node for the  $\pi$  orbital. In order for the  $p$  orbitals to maintain maximum overlap, they must be parallel. This means that free rotation is not possible about the double bond, since the two  $p$  orbitals would have to reduce their overlap to allow one H—C—H plane to rotate with respect to the other. The six atoms of a double bond are therefore in a plane

<sup>6</sup>The double bond can also be pictured as consisting of two equivalent orbitals, where the centers of electron density point away from the C—C axis. This is the *bent-bond* or *banana-bond* picture. Support for this view is found in Pauling *Theoretical Organic Chemistry, The Kekulé Symposium*; Butterworth: London, 1959, pp. 2-5; Palke *J. Am. Chem. Soc.* **1986**, *108*, 6543. However, most of the literature of organic chemistry is written in terms of the  $\sigma$ - $\pi$  picture, and in this book we will use it.



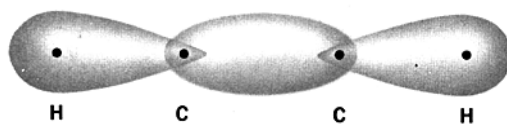


**FIGURE 1.5** Overlapping  $p$  orbitals form a  $\pi$  and a  $\pi^*$  orbital. The  $\sigma$  orbitals are shown in the upper figure. They are still there in the states represented by the diagrams below, but have been removed from the picture for clarity.

with angles that should be about  $120^\circ$ . Double bonds are shorter than the corresponding single bonds because maximum stability is obtained when the  $p$  orbitals overlap as much as possible. Double bonds between carbon and oxygen or nitrogen are similarly represented: they consist of one  $\sigma$  and one  $\pi$  orbital.

In triple-bond compounds, carbon is connected to only two other atoms and hence uses  $sp$  hybridization, which means that the four atoms are in a straight line (Figure 1.6).<sup>7</sup> Each carbon has two  $p$  orbitals remaining, with one electron in each. These orbitals are perpendicular to each other and to the C—C axis. They overlap in the manner shown in Figure 1.7 to form two  $\pi$  orbitals. A triple bond is thus composed of one  $\sigma$  and two  $\pi$  orbitals. Triple bonds between carbon and nitrogen can be represented in a similar manner.

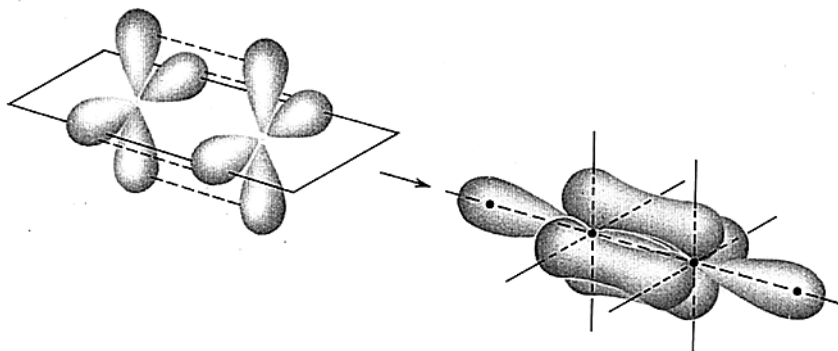
Double and triple bonds are important only for the first-row elements carbon, nitrogen, and oxygen.<sup>8</sup> For second-row elements multiple bonds are rare and compounds containing



**FIGURE 1.6** The  $\sigma$  electrons of acetylene.

<sup>7</sup>For reviews of triple bonds, see Simonetta; Gavezzotti, in Patai *The Chemistry of the Carbon-Carbon Triple Bond*; Wiley: New York, 1978, pp. 1-56; Dale, in *Vicine Acetylenes*; Marcel Dekker: New York, 1969, pp. 3-96.

<sup>8</sup>This statement applies to the representative elements. Multiple bonding is also important for some transition elements. For a review of metal-metal multiple bonds, see Cotton *J. Chem. Educ.* **1983**, *60*, 713-720.



**FIGURE 1.7** Overlap of  $p$  orbitals in a triple bond. For clarity, the  $\sigma$  orbitals have been removed from the drawing on the left, though they are shown on the right.

them are generally less stable<sup>9</sup> because these elements tend to form weaker  $\pi$  bonds than do the first-row elements.<sup>10</sup> The only ones of any importance at all are  $\text{C}=\text{S}$  bonds, and  $\text{C}=\text{S}$  compounds are generally much less stable than the corresponding  $\text{C}=\text{O}$  compounds (however, see  $p\pi-d\pi$  bonding, p. 38). Stable compounds with  $\text{Si}=\text{C}$  and  $\text{Si}=\text{Si}$  bonds are rare, but examples have been reported,<sup>11</sup> including a pair of *cis* and *trans*  $\text{Si}=\text{Si}$  isomers.<sup>12</sup>

## Photoelectron Spectroscopy

Although the four bonds of methane are equivalent according to most physical and chemical methods of detection (for example, neither the nmr nor the ir spectrum of methane contains peaks that can be attributed to different kinds of  $\text{C}-\text{H}$  bonds), there is one physical technique that shows that the eight valence electrons of methane can be differentiated. In this tech-

<sup>9</sup>For a review of double bonds between carbon and elements other than C, N, S, or O, see Jutzi *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 232-245 [*Angew. Chem.* **87**, 269-283]. For reviews of multiple bonds involving silicon and germanium, see Barrau; Escudié; Satgé *Chem. Rev.* **1990**, *90*, 283-319 (Ge only); Raabe; Michl, in Patai and Rappoport *The Chemistry of Organic Silicon Compounds*, part 2, Wiley: New York, 1989, pp. 1015-1142; *Chem. Rev.* **1985**, *85*, 419-509 (Si only); Wiberg *J. Organomet. Chem.* **1984**, *273*, 141-177 (Si only); Gusev; Nametkin *Chem. Rev.* **1979**, *79*, 529-577 (Si only). For reviews of  $\text{C}=\text{P}$  and  $\text{C}=\text{As}$  bonds, see Regitz *Chem. Rev.* **1990**, *90*, 191-213; Appel; Knoll *Adv. Inorg. Chem.* **1989**, *33*, 259-361; Markovski; Romanenko *Tetrahedron* **1989**, *45*, 6019-6090; Regitz; Binger *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1484-1508 [*Angew. Chem.* **100**, 1541-1565]; Appel; Knoll; Ruppert *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 731-744 [*Angew. Chem.* **93**, 771-784]. For reviews of other second-row double bonds, see West *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1201-1211 [*Angew. Chem.* **99**, 1231-1241] ( $\text{Si}=\text{Si}$  bonds); Brook; Baines *Adv. Organometal. Chem.* **1986**, *25*, 1-44 ( $\text{Si}=\text{C}$  bonds); Kutney; Turnbull *Chem. Rev.* **1982**, *82*, 333-357 ( $\text{S}=\text{S}$  bonds). For reviews of multiple bonds between heavier elements, see Cowley; Norman *Prog. Inorg. Chem.* **1986**, *34*, 1-63; Cowley *Polyhedron* **1984**, *3*, 389-432; *Acc. Chem. Res.* **1984**, *17*, 386-392. For a theoretical study of multiple bonds to silicon, see Gordon *Mol. Struct. Energ.* **1986**, *1*, 101-148.

<sup>10</sup>For discussions, see Schmidt; Truong; Gordon *J. Am. Chem. Soc.* **1987**, *109*, 5217; Schleyer; Kost *J. Am. Chem. Soc.* **1988**, *110*, 2105.

<sup>11</sup>For  $\text{Si}=\text{C}$  bonds, see Brook; Nyburg; Abdesaken; Gutekunst; Gutekunst; Kallury; Poon; Chang; Wong-Ng *J. Am. Chem. Soc.* **1982**, *104*, 5667; Schaefer *Acc. Chem. Res.* **1982**, *15*, 283; Wiberg; Wagner; Riede; Müller *Organometallics* **1987**, *6*, 32. For  $\text{Si}=\text{Si}$  bonds, see West; Fink; Michl *Science* **1981**, *214*, 1343; Boudjouk; Han; Anderson *J. Am. Chem. Soc.* **1982**, *104*, 4992; Zilm; Grant; Michl; Fink; West *Organometallics* **1983**, *2*, 193; Fink; DeYoung; West; Michl *J. Am. Chem. Soc.* **1983**, *105*, 1070; Fink; Michalczuk; Haller; West; Michl *Organometallics* **1984**, *3*, 793; West *Pure Appl. Chem.* **1984**, *56*, 163-173; Masamune; Eriyama; Kawase *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 584 [*Angew. Chem.* **99**, 601]; Shepherd; Campana; West *Heteroat. Chem.* **1990**, *1*, 1. For an  $\text{Si}=\text{N}$  bond, see Wiberg; Schurz; Reber; Müller *J. Chem. Soc., Chem. Commun.* **1986**, 591.

<sup>12</sup>Michalczuk; West; Michl *J. Am. Chem. Soc.* **1984**, *106*, 821. *Organometallics* **1985**, *4*, 826.

nique, called *photoelectron spectroscopy*,<sup>13</sup> a molecule or free atom is bombarded with vacuum uv radiation, causing an electron to be ejected. The energy of the ejected electron can be measured, and the difference between the energy of the radiation used and that of the ejected electron is the *ionization potential* of that electron. A molecule that contains several electrons of differing energies can lose any one of them as long as its ionization potential is less than the energy of the radiation used (a single molecule loses only one electron; the loss of two electrons by any individual molecule almost never occurs). A photoelectron spectrum therefore consists of a series of bands, each corresponding to an orbital of a different energy. The spectrum gives a direct experimental picture of all the orbitals present, in order of their energies, provided that radiation of sufficiently high energy is used.<sup>14</sup> Broad bands usually correspond to strongly bonding electrons and narrow bands to weakly bonding or nonbonding electrons. A typical spectrum is that of N<sub>2</sub>, shown in Figure 1.8.<sup>15</sup> The N<sub>2</sub> molecule has the electronic structure shown in Figure 1.9. The two 2s orbitals of the nitrogen atoms combine to give the two orbitals marked 1 (bonding) and 2 (antibonding), while the six 2p orbitals combine to give six orbitals, three of which (marked 3, 4, and 5) are bonding. The three antibonding orbitals (not indicated in Figure 1.9) are unoccupied. Electrons ejected from orbital 1 are not found in Figure 1.8 because the ionization potential of these electrons is greater than the energy of the light used (they can be seen when higher-energy light is used). The broad band in Figure 1.8 (the individual peaks within this band are caused by different vibrational levels; see Chapter 7) corresponds to the four electrons in the degenerate orbitals 3 and 4. The triple bond of N<sub>2</sub> is therefore composed of these two orbitals and orbital 1. The bands corresponding to orbitals 2 and 5 are narrow; hence these orbitals contribute little to the bonding and may be regarded as the two unshared pairs of  $\bar{N}\equiv\bar{N}$ . Note that this result is contrary to that expected from a

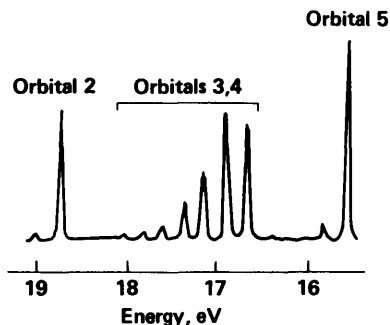


FIGURE 1.8 Photoelectron spectrum of N<sub>2</sub>.<sup>15</sup>

<sup>13</sup>Only the briefest description of this subject is given here. For monographs, see Ballard *Photoelectron Spectroscopy and Molecular Orbital Theory*; Wiley: New York, 1978; Rabalais, *Principles of Ultraviolet Photoelectron Spectroscopy*; Wiley: New York, 1977; Baker; Betteridge *Photoelectron Spectroscopy*; Pergamon: Elmsford, NY, 1972; Turner; Baker; Baker; Brundle *High Resolution Molecular Photoelectron Spectroscopy*; Wiley: New York, 1970. For reviews, see Westwood *Chem. Soc. Rev.* **1969**, *18*, 317-345; Carlson *Annu. Rev. Phys. Chem.* **1975**, *26*, 211-233; Baker; Brundle; Thompson *Chem. Soc. Rev.* **1972**, *1*, 355-380; Bock; Mollère *J. Chem. Educ.* **1974**, *51*, 506-514; Bock; Ramsey *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 734-752 [*Angew. Chem.* **85**, 773-792]; Turner *Adv. Phys. Org. Chem.* **1966**, *4*, 31-71. For the IUPAC descriptive classification of the electron spectroscopies, see Porter; Turner *Pure Appl. Chem.* **1987**, *59*, 1343-1406.

<sup>14</sup>The correlation is not perfect, but the limitations do not seriously detract from the usefulness of the method. The technique is not limited to vacuum uv radiation. Higher energy radiation can also be used.

<sup>15</sup>From Brundle; Robin, in Nachod; Zuckerman *Determination of Organic Structures by Physical Methods*, Vol. 3; Academic Press: New York, 1971, p. 18.

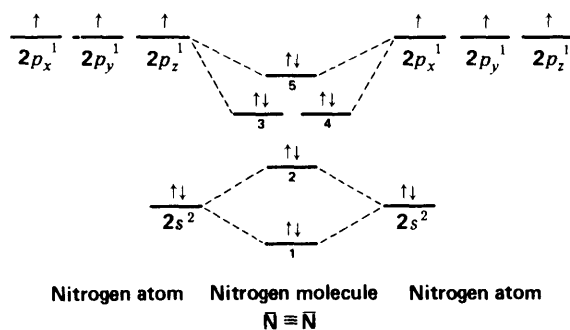


FIGURE 1.9 Electronic structure of  $\text{N}_2$  (inner-shell electrons omitted).<sup>15</sup>

naive consideration of orbital overlaps, where it would be expected that the two unshared pairs would be those of orbitals 1 and 2, resulting from the overlap of the filled  $2s$  orbitals, and that the triple bond would be composed of orbitals 3, 4, and 5, resulting from overlap of the  $p$  orbitals. This example is one illustration of the value of photoelectron spectroscopy.

The photoelectron spectrum of methane<sup>16</sup> shows two bands,<sup>17</sup> at about 23 and 14 eV, and not the single band we would expect from the equivalency of the four C—H bonds. The reason is that ordinary  $sp^3$  hybridization is not adequate to explain phenomena involving ionized molecules (such as the  $\text{CH}_4^+$  radical ion, which is left behind when an electron is ejected from methane). For these phenomena it is necessary to use other combinations of atomic orbitals (see p. 8). The band at 23 eV comes from two electrons in a low-energy level (called the  $a_1$  level), which can be regarded as arising from a combination of the  $2s$  orbital of carbon with an appropriate combination of hydrogen  $1s$  orbitals. The band at 14 eV comes from six electrons in a triply degenerate level (the  $t_2$  level), arising from a combination of the three  $2p$  orbitals of carbon with other combinations of  $1s$  hydrogen orbitals. As was mentioned above, most physical and chemical processes cannot distinguish these levels, but photoelectron spectroscopy can.

## Electronic Structures of Molecules

For each molecule, ion, or free radical that has only localized electrons, it is possible to draw an electronic formula, called a *Lewis structure*, that shows the location of these electrons. Only the valence electrons are shown. Valence electrons may be found in covalent bonds connecting two atoms or they may be unshared.<sup>18</sup> The student must be able to draw these structures correctly, since the position of electrons changes in the course of a reaction, and it is necessary to know where the electrons are initially before one can follow where they are going. To this end, the following rules operate:

1. The total number of valence electrons in the molecule (or ion or free radical) must be the sum of all outer-shell electrons "contributed" to the molecule by each atom plus the

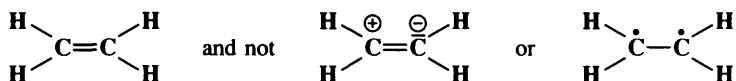
<sup>16</sup>Brundle; Robin; Basch *J. Chem. Phys.* **1970**, *53*, 2196; Baker; Betteridge; Kemp; Kirby *J. Mol. Struct.* **1971**, *8*, 75; Potts; Price *Proc. R. Soc. London, Ser A* **1972**, *326*, 165.

<sup>17</sup>A third band, at 290 eV, caused by the  $1s$  electrons of carbon, can also be found if radiation of sufficiently high energy is used.

<sup>18</sup>It has been argued that although the Lewis picture of two electrons making up a covalent bond may work well for organic compounds, it cannot be successfully applied to the majority of inorganic compounds: Jørgensen *Top. Curr. Chem.* **1964**, *124*, 1-31.

negative charge or minus the positive charge, for the case of ions. Thus, for  $\text{H}_2\text{SO}_4$ , there are 2 (one for each hydrogen) + 6 (for the sulfur) + 24 (6 for each oxygen) = 32; while for  $\text{SO}_4^{2-}$ , the number is also 32, since each atom "contributes" 6 plus 2 for the negative charge.

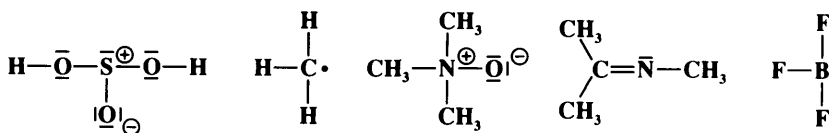
2. Once the number of valence electrons has been ascertained, it is necessary to determine which of them are found in covalent bonds and which are unshared. Unshared electrons (either a single electron or a pair) form part of the outer shell of just one atom, but electrons in a covalent bond are part of the outer shell of both atoms of the bond. *First-row atoms* (B, C, N, O, F) can have a maximum of eight valence electrons, and usually have this number, although some cases are known where a first-row atom has only six or seven. Where there is a choice between a structure that has six or seven electrons around a first-row atom and one in which all such atoms have an octet, it is the latter that generally has the lower energy and that consequently exists. For example, ethylene is



There are a few exceptions. In the case of the molecule  $\text{O}_2$ , the structure  $|\ddot{\text{O}}-\ddot{\text{O}}|$  has a lower energy than  $|\text{O}=\text{O}|$ . Although first-row atoms are limited to 8 valence electrons, this is not so for second-row atoms, which can accommodate 10 or even 12 because they can use their empty *d* orbitals for this purpose.<sup>19</sup> For example,  $\text{PCl}_5$  and  $\text{SF}_6$  are stable compounds. In  $\text{SF}_6$ , one *s* and one *p* electron from the ground state  $3s^23p^4$  of the sulfur are promoted to empty *d* orbitals, and the six orbitals hybridize to give six  $sp^3d^2$  orbitals, which point to the corners of a regular octahedron.

3. It is customary to show the formal charge on each atom. For this purpose an atom is considered to "own" all unshared electrons, but only *one-half of the electrons in covalent bonds*. The sum of electrons that thus "belong" to an atom is compared with the number "contributed" by the atom. An excess belonging to the atom results in a negative charge, and a deficiency results in a positive charge. The total of the formal charges on all atoms equals the charge on the whole molecule or ion. It should be noted that the counting procedure is not the same for determining formal charge as for determining the number of valence electrons. For both purposes an atom "owns" all unshared electrons, but for outer-shell purposes it "owns" both the electrons of the covalent bond, while for formal-charge purposes it "owns" only one-half of these electrons.

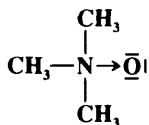
Examples of electronic structures are (as mentioned in footnote 4, in this book an electron pair, whether unshared or in a bond, is represented by a straight line):



A coordinate-covalent bond, represented by an arrow, is one in which both electrons come from the same atom; i.e., the bond can be regarded as being formed by the overlap

<sup>19</sup>For a review concerning sulfur compounds with a valence shell larger than eight, see Salmond *Q. Rev., Chem. Soc.* **1968**, 22, 235-275.

of an orbital containing two electrons with an empty one. Thus trimethylamine oxide would be represented



For a coordinate-covalent bond the rule concerning formal charge is amended, so that both electrons count for the donor and neither for the recipient. Thus the nitrogen and oxygen atoms of trimethylamine oxide bear no formal charges. However, it is apparent that the electronic picture is exactly the same as the picture of trimethylamine oxide given just above, and we have our choice of drawing an arrowhead or a charge separation. Some compounds, e.g., amine oxides, must be drawn one way or the other. It seems simpler to use charge separation, since this spares us from having to consider as a "different" method of bonding a way that is really the same as ordinary covalent bonding once the bond has formed.

### Electronegativity

The electron cloud that bonds two atoms is not symmetrical (with respect to the plane that is the perpendicular bisector of the bond) except when the two atoms are the same and have the same substituents. The cloud is necessarily distorted toward one side of the bond or the other, depending on which atom (nucleus plus electrons) maintains the greater attraction for the cloud. This attraction is called *electronegativity*;<sup>20</sup> it is greatest for atoms in the upper-right corner of the periodic table and lowest for atoms in the lower-left corner. Thus a bond between fluorine and chlorine is distorted so that there is a higher probability of finding the electrons near the fluorine than near the chlorine. This gives the fluorine a partial negative charge and the chlorine a partial positive charge.

A number of attempts have been made to set up quantitative tables of electronegativity that indicate the direction and extent of electron-cloud distortion for a bond between any pair of atoms. The most popular of these scales, devised by Pauling, is based on bond energies (see p. 23) of diatomic molecules. The reasoning here is that if in a molecule A—B the electron distribution were symmetrical, the bond energy would be the mean of the energies of A—A and B—B, since in these cases the cloud must be undistorted. If the actual bond energy of A—B is higher than this (and it usually is), it is the result of the partial charges, since the charges attract each other and make a stronger bond, which requires more energy to break. It is necessary to assign a value to one element arbitrarily ( $F = 4.0$ ). Then the electronegativity of another is obtained from the difference between the actual energy of A—B and the mean of A—A and B—B (this difference is called  $\Delta$ ) by the formula

$$x_A - x_B = \sqrt{\frac{\Delta}{23.06}}$$

where  $x_A$  and  $x_B$  are the electronegativities of the known and unknown atoms and 23.06 is an arbitrary constant. Part of the scale derived from this treatment is shown in Table 1.1.

<sup>20</sup>For a collection of articles on this topic, see Sen; Jørgensen *Electronegativity* (Vol. 6 of *Structure and Bonding*); Springer: New York, 1987. For a review, see Batsanov *Russ. Chem. Rev.* **1968**, *37*, 332-351.

**TABLE 1.1** Electronegativities of some atoms on the Pauling<sup>21</sup> and Sanderson<sup>25</sup> scales

| Element | Pauling | Sanderson | Element | Pauling | Sanderson |
|---------|---------|-----------|---------|---------|-----------|
| F       | 4.0     | 4.000     | H       | 2.1     | 2.592     |
| O       | 3.5     | 3.654     | P       | 2.1     | 2.515     |
| Cl      | 3.0     | 3.475     | B       | 2.0     | 2.275     |
| N       | 3.0     | 3.194     | Si      | 1.8     | 2.138     |
| Br      | 2.8     | 3.219     | Mg      | 1.2     | 1.318     |
| S       | 2.5     | 2.957     | Na      | 0.9     | 0.835     |
| I       | 2.5     | 2.778     | Cs      | 0.7     | 0.220     |
| C       | 2.5     | 2.746     |         |         |           |

Other treatments<sup>22</sup> have led to scales that are based on different principles, e.g., the average of the ionization potential and the electron affinity,<sup>23</sup> the average one-electron energy of valence-shell electrons in ground-state free atoms,<sup>24</sup> or the "compactness" of an atom's electron cloud.<sup>25</sup> In some of these treatments electronegativities can be calculated for different valence states, for different hybridizations (e.g., *sp* carbon atoms are more electronegative than *sp*<sup>2</sup>, which are still more electronegative than *sp*<sup>3</sup>),<sup>26</sup> and even differently for primary, secondary, and tertiary carbon atoms. Also, electronegativities can be calculated for groups rather than atoms (Table 1.2).<sup>27</sup>

Electronegativity information can be obtained from nmr spectra. In the absence of a magnetically anisotropic group<sup>28</sup> the chemical shift of a <sup>1</sup>H or a <sup>13</sup>C nucleus is approximately proportional to the electron density around it and hence to the electronegativity of the atom or group to which it is attached. The greater the electronegativity of the atom or group, the lower the electron density around the proton and the further downfield the chemical shift. An example of the use of this correlation is found in the variation of chemical shift of the *ring* protons in the series toluene, ethylbenzene, isopropylbenzene, *t*-butylbenzene (there is a magnetically anisotropic group here, but its effect should be constant throughout the

**TABLE 1.2** Some group electronegativities relative to H = 2.176<sup>27</sup>

|                                     |       |                                   |       |
|-------------------------------------|-------|-----------------------------------|-------|
| <b>CH<sub>3</sub></b>               | 2.472 | <b>CCl<sub>3</sub></b>            | 2.666 |
| <b>CH<sub>3</sub>CH<sub>2</sub></b> | 2.482 | <b>C<sub>6</sub>H<sub>5</sub></b> | 2.717 |
| <b>CH<sub>2</sub>Cl</b>             | 2.538 | <b>CF<sub>3</sub></b>             | 2.985 |
| <b>CBr<sub>3</sub></b>              | 2.561 | <b>CN</b>                         | 3.208 |
| <b>CHCl<sub>2</sub></b>             | 2.602 | <b>NO<sub>2</sub></b>             | 3.421 |

<sup>21</sup>Taken from Pauling *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, p. 93, except for the value for Na, which is from Ref. 25.

<sup>22</sup>For several sets of electronegativity values, see Huheey *Inorganic Chemistry*, 3rd ed., Harper and Row: New York, 1983, pp. 146-148; Mullay, in Sen and Jørgensen, Ref. 20, p. 9.

<sup>23</sup>Mulliken *J. Chem. Phys.* **1934**, *2*, 782; Iczkowski; Margrave *J. Am. Chem. Soc.* **1961**, *83*, 3547; Hinze; Jaffé *J. Am. Chem. Soc.* **1962**, *84*, 540.

<sup>24</sup>Allen *J. Am. Chem. Soc.* **1989**, *111*, 9003.

<sup>25</sup>See Sanderson *J. Am. Chem. Soc.* **1983**, *105*, 2259; *J. Chem. Educ.* **1988**, *65*, 112, 223.

<sup>26</sup>Walsh *Discuss. Faraday Soc.* **1947**, *2*, 18; Bergmann; Hinze, in Sen; Jørgensen, Ref. 20, pp. 146-190.

<sup>27</sup>Inamoto; Masuda *Chem. Lett.* **1982**, 1003. For a review of group electronegativities, see Wells *Prog. Phys. Org. Chem.* **1968**, *6*, 111-145. See also Bratsch *J. Chem. Educ.* **1988**, *65*, 223; Mullay *J. Am. Chem. Soc.* **1985**, *107*, 7271; Zefirov; Kirpichenok; Izmailov; Trofimov *Dokl. Chem.* **1987**, *296*, 440; Boyd; Edgecombe *J. Am. Chem. Soc.* **1988**, *110*, 4182.

<sup>28</sup>A magnetically anisotropic group is one that is not equally magnetized along all three axes. The most common such groups are benzene rings (see p. 41) and triple bonds.

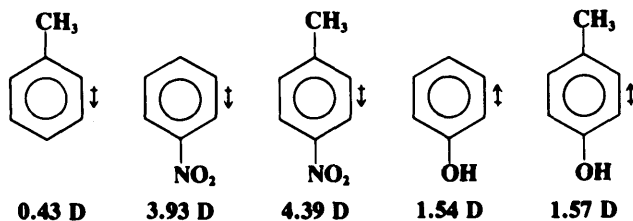
series). It is found that the electron density surrounding the ring protons decreases<sup>29</sup> in the order given.<sup>30</sup> However, this type of correlation is by no means perfect, since all the measurements are being made in a powerful field, which itself may affect the electron density distribution. Coupling constants between the two protons of a system  $\text{—CH—CH—X}$  have also been found to depend on the electronegativity of X.<sup>31</sup>

When the difference in electronegativities is great, the orbital may be so far over to one side that it barely covers the other nucleus. This is an *ionic bond*, which is seen to arise naturally out of the previous discussion, leaving us with basically only one type of bond in organic molecules. Most bonds can be considered intermediate between ionic and covalent. We speak of percent ionic character of a bond, which indicates the extent of electron-cloud distortion. There is a continuous gradation from ionic to covalent bonds.

## Dipole Moment

The *dipole moment* is a property of the molecule that results from charge separations like those discussed above. However, it is not possible to measure the dipole moment of an individual bond within a molecule; we can measure only the total moment of the molecule, which is the vectorial sum of the individual bond moments.<sup>32</sup> These individual moments are roughly the same from molecule to molecule,<sup>33</sup> but this constancy is by no means universal. Thus, from the dipole moments of toluene and nitrobenzene (Figure 1.10)<sup>34</sup> we should expect the moment of *p*-nitrotoluene to be about 4.36 D. The actual value 4.39 D is reasonable. However, the moment of *p*-cresol (1.57 D) is quite far from the predicted value of 1.11 D. In some cases, molecules may have substantial individual bond moments but no total moments at all because the individual moments are canceled out by the overall symmetry of the molecule. Some examples are  $\text{CCl}_4$ , *trans*-1,2-dibromoethene, and *p*-dinitrobenzene.

Because of the small difference between the electronegativities of carbon and hydrogen, alkanes have very small dipole moments, so small that they are difficult to measure. For



**FIGURE 1.10** Some dipole moments, in debye units, measured in benzene. The arrow points to the negative part of the molecule.<sup>34</sup>

<sup>29</sup>This order is opposite to that expected from the field effect (p. 17). It is an example of the Baker–Nathan order (p. 68).

<sup>30</sup>Moodie; Connor; Stewart *Can. J. Chem.* **1960**, *38*, 626.

<sup>31</sup>Williamson *J. Am. Chem. Soc.* **1963**, *85*, 516; Laszlo; Schleyer *J. Am. Chem. Soc.* **1963**, *85*, 2709; Niwa *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2192.

<sup>32</sup>For methods of determining dipole moments and discussions of their applications, see Exner *Dipole Moments in Organic Chemistry*; Georg Thieme Publishers: Stuttgart, 1975. For tables of dipole moments, see McClellan *Tables of Experimental Dipole Moments*, Vol. 1; W.H. Freeman: San Francisco, 1963; Vol. 2, Raha Enterprises: El Cerrito, CA, 1974.

<sup>33</sup>For example, see Koudelka; Exner *Collect. Czech. Chem. Commun.* **1985**, *50*, 188, 200.

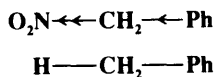
<sup>34</sup>The values for toluene, nitrobenzene, and *p*-nitrotoluene are from McClellan, Ref. 32. The values for phenol and *p*-cresol were determined by Goode; Ibbitson *J. Chem. Soc.* **1960**, 4265.





more important than inductive effects.<sup>40</sup> In most cases the two types of effect are considered together; in this book we will not attempt to separate them but will use the name *field effect* to refer to their combined action.<sup>41</sup>

Functional groups can be classified as electron-withdrawing ( $-I$ ) or electron-donating ( $+I$ ) groups relative to hydrogen. This means, for example, that  $\text{NO}_2$ , a  $-I$  group, will draw electrons to itself more than a hydrogen atom would if it occupied the same position in the molecule.



Thus, in  $\alpha$ -nitrotoluene, the electrons in the  $\text{N—C}$  bond are farther away from the carbon atom than the electrons in the  $\text{H—C}$  bond of toluene. Similarly, the electrons of the  $\text{C—Ph}$  bond are farther away from the ring in  $\alpha$ -nitrotoluene than they are in toluene. Field effects are always comparison effects. We compare the  $-I$  or  $+I$  effect of one group with another (usually hydrogen). It is commonly said that, compared with hydrogen, the  $\text{NO}_2$  group is electron-withdrawing and the  $\text{O}^-$  group electron-donating or electron-releasing. However, there is no actual donation or withdrawal of electrons, though these terms are convenient to use; there is merely a difference in the position of electrons due to the difference in electronegativity between  $\text{H}$  and  $\text{NO}_2$  or between  $\text{H}$  and  $\text{O}^-$ .

Table 1.3 lists a number of the most common  $-I$  and  $+I$  groups.<sup>42</sup> It can be seen that compared with hydrogen, most groups are electron-withdrawing. The only electron-donating groups are groups with a formal negative charge (but not even all these), atoms of low

**TABLE 1.3** Field effects of various groups relative to hydrogen

*The groups are listed approximately in order of decreasing strength for both  $-I$  and  $+I$  groups*

| $+I$                  | $-I$                   |  |
|-----------------------|------------------------|--|
| $\text{O}^-$          | $\text{NR}_3^+$        | $\text{COOH}$ $\text{OR}$              |
| $\text{COO}^-$        | $\text{SR}_2^+$        | $\text{F}$ $\text{COR}$                |
| $\text{CR}_3$         | $\text{NH}_3^+$        | $\text{Cl}$ $\text{SH}$                |
| $\text{CHR}_2$        | $\text{NO}_2$          | $\text{Br}$ $\text{SR}$                |
| $\text{CH}_2\text{R}$ | $\text{SO}_2\text{R}$  | $\text{I}$ $\text{OH}$                 |
| $\text{CH}_3$         | $\text{CN}$            | $\text{OAr}$ $\text{C}\equiv\text{Cr}$ |
| $\text{D}$            | $\text{SO}_2\text{Ar}$ | $\text{COOR}$ $\text{Ar}$              |
|                       |                        | $\text{CH}=\text{CR}_2$                |

<sup>40</sup>For example, see Dewar; Grisdale *J. Am. Chem. Soc.* **1962**, *84*, 3548; Stock *J. Chem. Educ.* **1972**, *49*, 400; Golden; Stock *J. Am. Chem. Soc.* **1972**, *94*, 3080; Liotta; Fisher; Greene; Joyner *J. Am. Chem. Soc.* **1972**, *94*, 4891; Wilcox; Leung *J. Am. Chem. Soc.* **1968**, *90*, 336; Butler *J. Chem. Soc. B* **1970**, 867; Adcock; Bettess; Rizvi *Aust. J. Chem.* **1970**, *23*, 1921; Rees; Ridd; Ricci *J. Chem. Soc., Perkin Trans. 2*, **1976**, 294; Topsom *Prog. Phys. Org. Chem.* **1976**, *12*, 1-20; *J. Am. Chem. Soc.* **1981**, *103*, 39; Grob; Kaiser; Schweizer *Helv. Chim. Acta* **1977**, *60*, 391; Reynolds *J. Chem. Soc., Perkin Trans. 2*, **1980**, 985; *Prog. Phys. Org. Chem.* **1983**, *14*, 165-203; Adcock; Butt; Kok; Marriott; Topsom *J. Org. Chem.* **1985**, *50*, 2551; Schneider; Becker *J. Phys. Org. Chem.* **1989**, *2*, 214; Bowden; Ghadir *J. Chem. Soc., Perkin Trans. 2* **1990**, 1333. Inductive effects may be important in certain systems. See, for example, Exner; Fiedler *Collect. Czech. Chem. Commun.* **1980**, *45*, 1251; Li; Schuster *J. Org. Chem.* **1987**, *52*, 3975.

<sup>41</sup>There has been some question as to whether it is even meaningful to maintain the distinction between the two types of effect: see Grob *Helv. Chim. Acta* **1985**, *68*, 882; Lenoir; Frank *Chem. Ber.* **1985**, *118*, 753; Sacher *Tetrahedron Lett.* **1986**, *27*, 4683.

<sup>42</sup>See also Ceppi; Eckhardt; Grob *Tetrahedron Lett.* **1973**, 3627.

electronegativity, such as Si,<sup>43</sup> Mg, etc., and perhaps alkyl groups. Alkyl groups<sup>44</sup> were formerly regarded as electron-donating, but many examples of behavior have been found that can be interpreted only by the conclusion that alkyl groups are electron-withdrawing compared with hydrogen.<sup>45</sup> In accord with this is the value of 2.472 for the group electronegativity of CH<sub>3</sub> (Table 1.2) compared with 2.176 for H. We shall see that when an alkyl group is attached to an unsaturated or trivalent carbon (or other atom), its behavior is best explained by assuming it is +I (see, for example, pp. 168, 176, 270, 511), but when it is connected to a saturated atom, the results are not as clear, and alkyl groups seem to be +I in some cases and -I in others<sup>46</sup> (see also p. 271). Similarly, it is clear that the field-effect order of alkyl groups attached to unsaturated systems is tertiary > secondary > primary > CH<sub>3</sub>, but this order is not always maintained when the groups are attached to saturated systems. Deuterium is electron-donating with respect to hydrogen.<sup>47</sup> Other things being equal, atoms with *sp* bonding generally have a greater electron-withdrawing power than those with *sp*<sup>2</sup> bonding, which in turn have more electron-withdrawing power than those with *sp*<sup>3</sup> bonding.<sup>48</sup> This accounts for the fact that aryl, vinylic, and alkynyl groups are -I. Field effects always decrease with increasing distance, and in most cases (except when a very powerful +I or -I group is involved), cause very little difference in a bond four bonds away or more. There is evidence that field effects can be affected by the solvent.<sup>49</sup>

For discussions of field effects on acid and base strength and on reactivity, see Chapters 8 and 9, respectively.

## Bond Distances<sup>50</sup>

The distances between atoms in a molecule are characteristic properties of the molecule and can give us information if we compare the same bond in different molecules. The chief methods of determining bond distances and angles are x-ray diffraction (only for solids), electron diffraction (only for gases), and spectroscopic methods, especially microwave spectroscopy. The distance between the atoms of a bond is not constant, since the molecule is always vibrating; the measurements obtained are therefore average values, so that different methods give different results.<sup>51</sup> However, this must be taken into account only when fine distinctions are made.

Measurements vary in accuracy, but indications are that similar bonds have fairly constant lengths from one molecule to the next, though exceptions are known.<sup>52</sup> The variation is generally less than 1%. Table 1.4 shows distances for single bonds between two *sp*<sup>3</sup> carbons.

<sup>43</sup>For a review of field and other effects of silicon-containing groups, see Bassindale; Taylor, in Patai and Rappoport, *Ref. 9*, pp. 893-963.

<sup>44</sup>For a review of the field effects of alkyl groups, see Levitt; Widing *Prog. Phys. Org. Chem.* **1976**, *12*, 119-157.

<sup>45</sup>See Sebastian *J. Chem. Educ.* **1971**, *48*, 97.

<sup>46</sup>See, for example, Schleyer; Woodworth *J. Am. Chem. Soc.* **1968**, *90*, 6528; Wahl; Peterson *J. Am. Chem. Soc.* **1970**, *92*, 7238. The situation may be even more complicated. See, for example, Minot; Eisenstein; Hiberty; Anh *Bull. Soc. Chim. Fr.* **1980**, *11*-119.

<sup>47</sup>Streitwieser; Klein *J. Am. Chem. Soc.* **1963**, *85*, 2759.

<sup>48</sup>*Bent Chem. Rev.* **1961**, *61*, 275-311, p. 281.

<sup>49</sup>See Laurence; Berthelot; Lucon; Helbert; Morris; Gal *J. Chem. Soc., Perkin Trans. 2* **1984**, 705.

<sup>50</sup>For tables of bond distances and angles, see Allen; Kennard; Watson; Brammer; Orpen; Taylor *J. Chem. Soc., Perkin Trans. 2* **1987**, S1-S19; Tables of Interatomic Distances and Configurations in Molecules and Ions *Chem. Soc. Spec. Publ.* No. 11, 1958; Interatomic Distances Supplement *Chem. Soc. Spec. Publ.* No. 18, 1965; Harmony; Laurie; Kuczkowski; Schwendeman; Ramsay; Lovas; Lafferty; Maki *J. Phys. Chem. Ref. Data* **1979**, *8*, 619-721. For a review of molecular shapes and energies for many small organic molecules, radicals, and cations calculated by molecular orbital methods, see Lathan; Curtiss; Hehre; Lisle; Pople *Prog. Phys. Org. Chem.* **1974**, *11*, 175-261. For a discussion of substituent effects on bond distances, see Topsom *Prog. Phys. Org. Chem.* **1987**, *16*, 85-124.

<sup>51</sup>Burkert; Allinger *Molecular Mechanics*; ACS Monograph 177, American Chemical Society: Washington, 1982, pp. 6-9; Whiffen *Chem. Br.* **1971**, *7*, 57-61; Stals *Rev. Pure Appl. Chem.* **1970**, *20*, 1-22, pp. 2-5.

<sup>52</sup>Schleyer; Bremer *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1226 [*Angew. Chem.* *101*, 1264].

**TABLE 1.4** Bond lengths between  $sp^3$  carbons in some compounds

| C—C bond in                                    | Bond length, Å  | C—C bond in   | Bond length, Å |
|--|-----------------|---|----------------|
| Diamond <sup>53</sup>                          | 1.544           | Cyclohexane <sup>57</sup>                           | 1.540 ± 0.015  |
| C <sub>2</sub> H <sub>6</sub> <sup>54</sup>    | 1.5324 ± 0.0011 | <i>t</i> -Butyl chloride <sup>58</sup>              | 1.532          |
| C <sub>2</sub> H <sub>5</sub> Cl <sup>55</sup> | 1.5495 ± 0.0005 | <i>n</i> -Butane to <i>n</i> -heptane <sup>59</sup> | 1.531–1.534    |
| C <sub>3</sub> H <sub>8</sub> <sup>56</sup>    | 1.532 ± 0.003   | Isobutane <sup>60</sup>                             | 1.535 ± 0.001  |

However, an analysis of C—OR bond distances in more than 2000 ethers and carboxylic esters (all with  $sp^3$  carbon) shows that this distance increases with increasing electron withdrawal in the R group and as the C changes from primary to secondary to tertiary.<sup>61</sup> For these compounds, mean bond lengths of the various types ranged from 1.418 to 1.475 Å.

Bond distances for some important bond types are given in Table 1.5.<sup>62</sup> As can be seen in this table, carbon bonds are shortened by increasing  $s$  character. This is most often explained by the fact that, as the percentage of  $s$  character in a hybrid orbital increases, the orbital becomes more like an  $s$  orbital and hence is held more tightly by the nucleus than an orbital with less  $s$  character. However, other explanations have also been offered (see p. 31), and the matter is not completely settled.

Indications are that a C—D bond is slightly shorter than a corresponding C—H bond. Thus, electron-diffraction measurements of C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>D<sub>6</sub> showed a C—H bond distance of  $1.1122 \pm 0.0012$  Å and a C—D distance of  $1.1071 \pm 0.0012$  Å.<sup>54</sup>

## Bond Angles

It might be expected that the bond angles of  $sp^3$  carbon would always be the tetrahedral angle  $109^\circ 28'$ , but this is so only where the four groups are identical, as in methane, neopentane, or carbon tetrachloride. In most cases the angles deviate a little from the pure tetrahedral value. For example, the C—C—Br angle in 2-bromopropane is  $114.2^\circ$ .<sup>70</sup> Similarly, slight variations are generally found from the ideal values of  $120^\circ$  and  $180^\circ$  for  $sp^2$  and  $sp$  carbon, respectively. These deviations occur because of slightly different hybridizations, that is, a carbon bonded to four other atoms hybridizes one  $s$  and three  $p$  orbitals, but the four hybrid orbitals thus formed are generally not exactly equivalent, nor does each contain exactly 25%  $s$  and 75%  $p$  character. Because the four atoms have (in the most general case) different electronegativities, each makes its own demand for electrons from the carbon atom.<sup>71</sup> The carbon atom supplies more  $p$  character when it is bonded to more electronegative atoms, so that in chloromethane, for example, the bond to chlorine has somewhat more

<sup>53</sup>Lonsdale *Phil. Trans. R. Soc. London* **1947**, A240, 219.

<sup>54</sup>Bartell; Higginbotham *J. Chem. Phys.* **1965**, 42, 851.

<sup>55</sup>Wagner; Dailey *J. Chem. Phys.* **1957**, 26, 1588.

<sup>56</sup>Iijima *Bull. Chem. Soc. Jpn.* **1972**, 45, 1291.

<sup>57</sup>Tables of Interatomic Distances, Ref. 50.

<sup>58</sup>Momany; Bonham; Druelinger *J. Am. Chem. Soc.* **1963**, 85, 3075; also see Lide; Jen *J. Chem. Phys.* **1963**, 38, 1504.

<sup>59</sup>Bonham; Bartell; Kohl *J. Am. Chem. Soc.* **1959**, 81, 4765.

<sup>60</sup>Hilderbrandt; Wieser *J. Mol. Struct.* **1973**, 15, 27.

<sup>61</sup>Allen; Kirby *J. Am. Chem. Soc.* **1984**, 106, 6197; Jones; Kirby *J. Am. Chem. Soc.* **1984**, 106, 6207.

<sup>62</sup>Except where noted, values are from Allen et al., Ref. 50. In this source, values are given to three significant figures.

<sup>63</sup>Costain; Stoicheff *J. Chem. Phys.* **1959**, 30, 777.

<sup>64</sup>For a full discussion of alkyne bond distances, see Simonetta; Gavezzotti, Ref. 7.

**TABLE 1.5** Bond distances  
*The values given are average lengths and do not necessarily apply exactly to the compounds mentioned<sup>62</sup>*

| Bond type                                       | Length, Å          | Typical compounds              |                    |                    |
|---|--------------------|--------------------------------|--------------------|--------------------|
| <b>C—C</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>3</sup> — <i>sp</i> <sup>3</sup> | 1.53               |                                |                    |                    |
| <i>sp</i> <sup>3</sup> — <i>sp</i> <sup>2</sup> | 1.51               | Acetaldehyde, toluene, propene |                    |                    |
| <i>sp</i> <sup>3</sup> — <i>sp</i>              | 1.47               | Acetonitrile, propyne          |                    |                    |
| <i>sp</i> <sup>2</sup> — <i>sp</i> <sup>2</sup> | 1.48               | Butadiene, glyoxal, biphenyl   |                    |                    |
| <i>sp</i> <sup>2</sup> — <i>sp</i>              | 1.43               | Acrylonitrile, vinylacetylene  |                    |                    |
| <i>sp</i> — <i>sp</i>                           | 1.38               | Cyanoacetylene, butadiyne      |                    |                    |
| <b>C=C</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>2</sup> — <i>sp</i> <sup>2</sup> | 1.32               | Ethylene                       |                    |                    |
| <i>sp</i> <sup>2</sup> — <i>sp</i>              | 1.31               | Ketene, allenes                |                    |                    |
| <i>sp</i> — <i>sp</i> <sup>63</sup>             | 1.28               | Butatriene, carbon suboxide    |                    |                    |
| <b>C≡C<sup>64</sup></b>                         |                    |                                |                    |                    |
| <i>sp</i> — <i>sp</i>                           | 1.18               | Acetylene                      |                    |                    |
| <b>C—H<sup>65</sup></b>                         |                    |                                |                    |                    |
| <i>sp</i> <sup>3</sup> —H                       | 1.09               | Methane                        |                    |                    |
| <i>sp</i> <sup>2</sup> —H                       | 1.08               | Benzene, ethylene              |                    |                    |
| <i>sp</i> —H <sup>66</sup>                      | 1.08               | HCN, acetylene                 |                    |                    |
| <b>C—O</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>3</sup> —O                       | 1.43               | Dimethyl ether, ethanol        |                    |                    |
| <i>sp</i> <sup>2</sup> —O                       | 1.34               | Formic acid                    |                    |                    |
| <b>C=O</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>2</sup> —O                       | 1.21               | Formaldehyde, formic acid      |                    |                    |
| <i>sp</i> —O <sup>57</sup>                      | 1.16               | CO <sub>2</sub>                |                    |                    |
| <b>C—N</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>3</sup> —N                       | 1.47               | Methylamine                    |                    |                    |
| <i>sp</i> <sup>2</sup> —N                       | 1.38               | Formamide                      |                    |                    |
| <b>C=N</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>2</sup> —N                       | 1.28               | Oximes, imines                 |                    |                    |
| <b>C≡N</b>                                      |                    |                                |                    |                    |
| <i>sp</i> —N                                    | 1.14               | HCN                            |                    |                    |
| <b>C—S</b>                                      |                    |                                |                    |                    |
| <i>sp</i> <sup>3</sup> —S                       | 1.82               | Methanethiol                   |                    |                    |
| <i>sp</i> <sup>2</sup> —S                       | 1.75               | Diphenyl sulfide               |                    |                    |
| <i>sp</i> —S                                    | 1.68               | CH <sub>3</sub> SCN            |                    |                    |
| <b>C=S</b>                                      |                    |                                |                    |                    |
| <i>sp</i> —S                                    | 1.67               | CS <sub>2</sub>                |                    |                    |
| <b>C—halogen<sup>67</sup></b>                   | <b>F</b>           | <b>Cl</b>                      | <b>Br</b>          | <b>I</b>           |
| <i>sp</i> <sup>3</sup> —halogen                 | 1.40               | 1.79                           | 1.97               | 2.16               |
| <i>sp</i> <sup>2</sup> —halogen                 | 1.34               | 1.73                           | 1.88               | 2.10               |
| <i>sp</i> —halogen                              | 1.27 <sup>68</sup> | 1.63                           | 1.79 <sup>69</sup> | 1.99 <sup>69</sup> |

<sup>65</sup>For an accurate method of C—H bond distance determination, see Henry *Acc. Chem. Res.* **1987**, *20*, 429-435.

<sup>66</sup>Bartell; Roth; Hollowell; Kuchitsu; Young *J. Chem. Phys.* **1965**, *42*, 2683.

<sup>67</sup>For reviews of carbon-halogen bonds, see Trotter, in Patai *The Chemistry of the Carbon-Halogen Bond*, pt. 1: Wiley: New York, 1973, pp. 49-62; Mikhailov *Russ. Chem. Rev.* **1971**, *40*, 983-997.

<sup>68</sup>Lide, *Tetrahedron* **1962**, *17*, 125.

<sup>69</sup>Rajput; Chandra *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1854.

<sup>70</sup>Schwendeman; Tobiasson *J. Chem. Phys.* **1965**, *43*, 201.

<sup>71</sup>For a review of this concept, see Bingel; Lüttke *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 899-910 [*Angew. Chem.* **93**, 944-956].

than 75%  $p$  character, which of course requires that the other three bonds have somewhat less, since there are only three  $p$  orbitals (and one  $s$ ) to be divided among the four hybrid orbitals.<sup>72</sup> Of course, in strained molecules, the bond angles may be greatly distorted from the ideal values (see p. 150).

For oxygen and nitrogen, angles of  $90^\circ$  are predicted from  $p^2$  bonding. However, as we have seen (p. 6), the angles of water and ammonia are much larger than this, as are the angles of other oxygen and nitrogen compounds (Table 1.6); in fact, they are much closer to the tetrahedral angle of  $109^\circ 28'$  than to  $90^\circ$ . These facts have led to the suggestion that in these compounds oxygen and nitrogen use  $sp^3$  bonding, i.e., instead of forming bonds by the overlap of two (or three)  $p$  orbitals with  $1s$  orbitals of the hydrogen atoms, they hybridize their  $2s$  and  $2p$  orbitals to form four  $sp^3$  orbitals and then use only two (or three) of these for bonding with hydrogen, the others remaining occupied by unshared pairs (also called *lone pairs*). If this description is valid, and it is generally accepted by most chemists today,<sup>78</sup> it becomes necessary to explain why the angles of these two compounds are in fact not  $109^\circ 28'$  but a few degrees smaller. One explanation that has been offered is that the unshared pair actually has a greater steric requirement than a pair in a bond, since there is no second nucleus to draw away some of the electron density and the bonds are thus crowded together. However, most evidence is that unshared pairs have smaller steric requirements than bonds<sup>79</sup> and the explanation most commonly accepted is that the hybridization is not pure  $sp^3$ . As we have seen above, an atom supplies more  $p$  character when it is bonded to more elec-

**TABLE 1.6** Oxygen, sulfur, and nitrogen bond angles in some compounds

| Angle | Value                   | Compound              | Ref. |
|-------|-------------------------|-----------------------|------|
| H—O—H | $104^\circ 27'$         | Water                 | 5    |
| C—O—H | $107\text{--}109^\circ$ | Methanol              | 57   |
| C—O—C | $111^\circ 43'$         | Dimethyl ether        | 73   |
| C—O—C | $124 \pm 5^\circ$       | Diphenyl ether        | 74   |
| H—S—H | $92.1^\circ$            | <b>H<sub>2</sub>S</b> | 74   |
| C—S—H | $99.4^\circ$            | Methanethiol          | 74   |
| C—S—C | $99.1^\circ$            | Dimethyl sulfide      | 75   |
| H—N—H | $106^\circ 46'$         | Ammonia               | 5    |
| H—N—H | $106^\circ$             | Methylamine           | 76   |
| C—N—H | $112^\circ$             | Methylamine           | 76   |
| C—N—C | $108.7^\circ$           | Trimethylamine        | 77   |

<sup>72</sup>This assumption has been challenged: see Pomerantz; Liebman *Tetrahedron Lett.* **1975**, 2385.

<sup>73</sup>Blukis; Kasai; Myers *J. Chem. Phys.* **1963**, 38, 2753.

<sup>74</sup>Abrahams *Q. Rev., Chem. Soc.* **1956**, 10, 407-436.

<sup>75</sup>Iijima; Tsuchiya; Kimura *Bull. Chem. Soc. Jpn.* **1977**, 50, 2564.

<sup>76</sup>Lide *J. Chem. Phys.* **1957**, 27, 343.

<sup>77</sup>Lide; Mann *J. Chem. Phys.* **1958**, 28, 572.

<sup>78</sup>An older theory holds that the bonding is indeed  $p^2$ , and that the increased angles come from repulsion of the hydrogen or carbon atoms. See Laing, *J. Chem. Educ.* **1987**, 64, 124.

<sup>79</sup>See, for example, Pumphrey; Robinson *Chem. Ind. (London)* **1963**, 1903; Allinger; Carpenter; Karkowski *Tetrahedron Lett.* **1964**, 3345; Eliel; Knoeber *J. Am. Chem. Soc.* **1966**, 88, 5347; **1968**, 90, 3444; Jones; Katritzky; Richards; Wyatt; Bishop; Sutton *J. Chem. Soc. B* **1970**, 127; Blackburne; Katritzky; Takeuchi *J. Am. Chem. Soc.* **1974**, 96, 682; *Acc. Chem. Res.* **1975**, 8, 300-306; Aaron; Ferguson *J. Am. Chem. Soc.* **1976**, 98, 7013; Anet; Yavari *J. Am. Chem. Soc.* **1977**, 99, 2794; Vierhapper; Eliel *J. Org. Chem.* **1979**, 44, 1081; Gust; Fagan *J. Org. Chem.* **1980**, 45, 2511. For other views, see Lambert; Featherman *Chem. Rev.* **1975**, 75, 611-626; Crowley; Morris; Robinson *Tetrahedron Lett.* **1976**, 3575; Breuker; Kos; van der Plas; van Veldhuizen *J. Org. Chem.* **1982**, 47, 963.

tronegative atoms. An unshared pair may be considered to be an "atom" of the lowest possible electronegativity, since there is no attracting power at all. Consequently, the unshared pairs have more *s* and the bonds more *p* character than pure  $sp^3$  orbitals, making the bonds somewhat more like  $p^2$  bonds and reducing the angle. As seen in Table 1.6, oxygen, nitrogen, and sulfur angles generally increase with decreasing electronegativity of the substituents. Note that the explanation given above cannot explain why some of these angles are *greater* than the tetrahedral angle.

### Bond Energies<sup>80</sup>

There are two kinds of bond energy. The energy necessary to cleave a bond to give the constituent radicals is called the *dissociation energy* *D*. For example, *D* for  $\text{H}_2\text{O} \rightarrow \text{HO} + \text{H}$  is 118 kcal/mol (494 kJ/mol). However, this is not taken as the energy of the O—H bond in water, since *D* for  $\text{H—O} \rightarrow \text{H} + \text{O}$  is 100 kcal/mol (418 kJ/mol). The average of these two values, 109 kcal/mol (456 kJ/mol), is taken as the *bond energy* *E*. In diatomic molecules, of course,  $D = E$ .

*D* values may be easy or difficult to measure, but there is no question as to what they mean. With *E* values the matter is not so simple. For methane, the total energy of conversion from  $\text{CH}_4$  to  $\text{C} + 4\text{H}$  (at 0 K) is 393 kcal/mol (1644 kJ/mol).<sup>81</sup> Consequently, *E* for the C—H bond in methane is 98 kcal/mol (411 kJ/mol) at 0 K. The more usual practice, though, is not to measure the heat of atomization (i.e., the energy necessary to convert a compound to its atoms) directly but to calculate it from the heat of combustion. Such a calculation is shown in Figure 1.11.

Heats of combustion are very accurately known for hydrocarbons.<sup>82</sup> For methane the value at 25°C is 212.8 kcal/mol (890.4 kJ/mol), which leads to a heat of atomization of 398.0 kcal/mol (1665 kJ/mol) or a value of *E* for the C—H bond at 25°C of 99.5 kcal/mol

|   | kcal         | kJ        |
|---|--------------|-----------|
| $\text{C}_2\text{H}_6(\text{gas}) + 3\frac{1}{2}\text{O}_2(\text{gas}) = 2\text{CO}_2(\text{gas}) + 3\text{H}_2\text{O}(\text{liq.})$ | + 372.9      | + 1560    |
| $2\text{CO}_2(\text{gas}) = 2\text{C}(\text{graphite}) + 2\text{O}_2(\text{gas})$   | - 188.2      | - 787     |
| $3\text{H}_2\text{O}(\text{liq.}) = 3\text{H}_2(\text{gas}) + 1\frac{1}{2}\text{O}_2(\text{gas})$                                     | - 204.9      | - 857     |
| $3\text{H}_2(\text{gas}) = 6\text{H}(\text{gas})$   | - 312.5      | - 1308    |
| $2\text{C}(\text{graphite}) = 2\text{C}(\text{gas})$  | - 343.4      | - 1437    |
|   |              |           |
| $\text{C}_2\text{H}_6(\text{gas}) = 6\text{H}(\text{gas}) + 2\text{C}(\text{gas})$  | - 676.1 kcal | - 2829 kJ |

FIGURE 1.11 Calculation of the heat of atomization of ethane at 25°C.

<sup>80</sup>For reviews including methods of determination, see Wayner; Griller *Adv. Free Radical Chem. (Greenwich, Conn.)* **1990**, *1*, 159-192; Kerr; *Chem. Rev.* **1966**, *66*, 465-500; Benson *J. Chem. Educ.* **1965**, *42*, 520-518; Wiberg, in Nachod; Zuckerman *Determination of Organic Structures by Physical Methods*, Vol. 3; Academic Press: New York, 1971, pp. 207-245.

<sup>81</sup>For the four steps, *D* values are 101 to 102, 88, 124, and 80 kcal/mol (423-427, 368, 519, and 335 kJ/mol), respectively, though the middle values are much less reliable than the other two: Knox; Palmer *Chem. Rev.* **1961**, *61*, 247-255; Brewer; Kester *J. Chem. Phys.* **1964**, *40*, 812; Linevsky *J. Chem. Phys.* **1967**, *47*, 3485.

<sup>82</sup>For values of heats of combustion of large numbers of organic compounds: hydrocarbons and others, see Cox; Pilcher, *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970; Domalski *J. Phys. Chem. Ref. Data* **1972**, *1*, 221-277. For large numbers of heats-of-formation values (from which heats of combustion are easily calculated) see Stull; Westrum; Sinke *The Chemical Thermodynamics of Organic Compounds*, Wiley: New York, 1969.

(416 kJ/mol). This method is fine for molecules like methane in which all the bonds are equivalent, but for more complicated molecules assumptions must be made. Thus for ethane, the heat of atomization at 25°C is 676.1 kcal/mol or 2829 kJ/mol (Figure 1.11), and we must decide how much of this energy is due to the C—C bond and how much to the six C—H bonds. Any assumption must be artificial, since there is no way of actually obtaining this information, and indeed the question has no real meaning. If we make the assumption that  $E$  for each of the C—H bonds is the same as  $E$  for the C—H bond in methane (99.5 kcal/mol or 416 kJ/mol), then  $6 \times 99.5$  (or 416) = 597.0 (or 2498), leaving 79.1 kcal/mol (331 kJ/mol) for the C—C bond. However, a similar calculation for propane gives a value of 80.3 (or 336) for the C—C bond, and for isobutane, the value is 81.6 (or 341). A consideration of heats of atomization of isomers also illustrates the difficulty.  $E$  values for the C—C bonds in pentane, isopentane, and neopentane, calculated from heats of atomization in the same way, are (at 25°C) 81.1, 81.8, and 82.4 kcal/mol (339, 342, 345 kJ/mol), respectively, even though all of them have twelve C—H bonds and four C—C bonds.

These differences have been attributed to various factors caused by the introduction of new structural features. Thus isopentane has a tertiary carbon whose C—H bond does not have exactly the same amount of  $s$  character as the C—H bond in pentane, which for that matter contains secondary carbons not possessed by methane. It is known that  $D$  values, which *can* be measured, are not the same for primary, secondary, and tertiary C—H bonds (see Table 5.3). There is also the steric factor. Hence it is certainly not correct to use the value of 99.5 kcal/mol (416 kJ/mol) from methane as the  $E$  value for all C—H bonds. Several empirical equations have been devised that account for these factors; the total energy can be computed<sup>83</sup> if the proper set of parameters (one for each structural feature) is inserted. Of course these parameters are originally calculated from the known total energies of some molecules which contain the structural feature.

Table 1.7 gives  $E$  values for various bonds. The values given are averaged over a large series of compounds. The literature contains charts that take account of hybridization (thus an  $sp^3$  C—H bond does not have the same energy as an  $sp^2$  C—H bond).<sup>87</sup>

Certain generalizations can be derived from the data in Table 1.7.

**TABLE 1.7** Bond energy  $E$  values at 25°C for some important bond types<sup>84</sup>  
*E* values are arranged within each group in order of decreasing strength. The values are averaged over a large series of compounds.

| Bond              | kcal/mol | kJ/mol  | Bond              | kcal/mol | kJ/mole |
|-------------------|----------|---------|-------------------|----------|---------|
| O—H               | 110–111  | 460–464 | C—S <sup>86</sup> | 61       | 255     |
| C—H               | 96–99    | 400–415 | C—I               | 52       | 220     |
| N—H               | 93       | 390     | C≡C               | 199–200  | 835     |
| S—H               | 82       | 340     | C=C               | 146–151  | 610–630 |
| C—F               | ...      | ...     | C—C               | 83–85    | 345–355 |
| C—H               | 96–99    | 400–415 | C≡N               | 204      | 854     |
| C—O               | 85–91    | 355–380 | C=O               | 173–81   | 724–757 |
| C—C               | 83–85    | 345–355 | C=N <sup>85</sup> | 143      | 598     |
| C—Cl              | 79       | 330     |                   |          |         |
| C—N <sup>85</sup> | 69–75    | 290–315 |                   |          |         |
| C—Br              | 66       | 275     |                   |          |         |

<sup>83</sup>For a review, see Cox; Pilcher, Ref. 82, pp. 531–597. See also Gasteiger; Jacob; Strauss *Tetrahedron* **1979**, 35, 139.

<sup>84</sup>These values, except where noted, are from Lovering; Laidler *Can. J. Chem.* **1960**, 38, 2367; Levi; Balandin *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1960**, 149.

<sup>85</sup>Bedford; Edmondson; Mortimer *J. Chem. Soc.* **1962**, 2927.

<sup>86</sup>Grelbig; Pötter; Seppelt *Chem. Ber.* **1987**, 120, 815.

<sup>87</sup>Ref. 83; Cox *Tetrahedron* **1962**, 18, 1337.



1. There is a correlation of bond strengths with bond distances. A comparison of Tables 1.5 and 1.7 shows that, in general, *shorter bonds are stronger bonds*. Since we have already seen that increasing *s* character shortens bonds (p. 20), it follows that bond strengths increase with increasing *s* character.

2. Bonds become weaker as we move down the periodic table. Compare C—O and C—S or the four carbon–halogen bonds. This is a consequence of the first generalization, since bond distances must increase as we go down the periodic table because the number of inner electrons increases.

3. Double bonds are both shorter and stronger than the corresponding single bonds, but not twice as strong, because  $\pi$  overlap is less than  $\sigma$  overlap. This means that a  $\sigma$  bond is stronger than a  $\pi$  bond. The difference in energy between a single bond, say C—C, and the corresponding double bond is the amount of energy necessary to cause rotation around the double bond.<sup>88</sup>

<sup>88</sup>For a discussion of the different magnitudes of the bond energies of the two bonds of the double bond, see Miller *J. Chem. Educ.* **1978**, *55*, 778.