

CHAPTER 1**Localized Chemical Bonding**

Localized chemical bonding may be defined as bonding in which the electrons are shared by two and only two nuclei. Such bonding is the essential feature associated with the structure of organic molecules.¹ Chapter 2 will discuss *delocalized bonding*, in which electrons are shared by more than two nuclei.

1.A. COVALENT BONDING²

Wave mechanics is based on the fundamental principle that electrons behave as waves (e.g., they can be diffracted). Consequently, a wave equation can be written for electrons, in the same sense that light waves, sound waves, and so on 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:

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

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 Ψ 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. The equation is similar, but more complicated, for systems containing more than one electron.

The Schrödinger equation is a differential equation, so solutions to it are themselves equations; however, the solutions are not differential equations but simple equations for which graphs can be drawn. Such graphs are essentially three-dimensional (3D) pictures

¹ See Hoffmann, R.; Schleyer, P.v.R.; Schaefer III, H.F. *Angew. Chem. Int. Ed.* **2008**, *47*, 7164.

² This treatment of orbitals is simplified by necessity. For more detailed treatments of orbital theory, as applied to organic chemistry, see Matthews, P.S.C. *Quantum Chemistry of Atoms and Molecules*, Cambridge University Press, Cambridge, **1986**; Clark, T. *A Handbook of Computational Chemistry*, Wiley, NY, **1985**; Albright, T.A.; Burdett, J.K.; Whangbo, M. *Orbital Interactions in Chemistry*, Wiley, NY, **1985**; MacWeeny, R.M. *Coulson's Valence*, Oxford University Press, Oxford, **1980**; Murrell, J.N.; Kettle, S.F.A.; Tedder, J.M. *The Chemical Bond*, Wiley, NY, **1978**; Dewar, M.J.S.; Dougherty, R.C. *The PMO Theory of Organic Chemistry*, Plenum, NY, **1975**; Zimmerman, H.E. *Quantum Mechanics for Organic Chemists*, Academic Press, NY, **1975**; Borden, W.T. *Modern Molecular Orbital Theory for Organic Chemists*, Prentice-Hall, Englewood Cliffs, NJ, **1975**.

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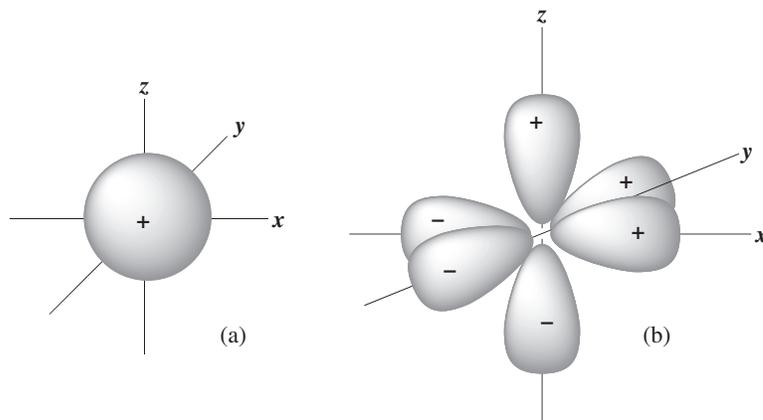


FIGURE 1.1. (a) The 1s orbital. (b) The three degenerate 2p orbitals.

that show the electron density, and these pictures are representations of *orbitals*, which are electron clouds. Most students are familiar with the shapes of the *s* and *p* atomic orbitals (Figure 1.1).³ Note that each *p* orbital has a *node*: a region in space where the probability of finding the electron is extremely small.⁴ Also note that in Figure 1.1 some lobes of the orbitals are labeled (+) and others (−). These signs do not refer to positive or negative charges, since both lobes of an electron cloud must be negatively charged, but rather refer to the signs of the wave function Ψ . When a node separates two parts of an orbital, a point of zero electron density, Ψ , 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,⁵ a precise picture of the shape of the orbitals available to each electron (especially for the important ground state) would become available, as well as 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 an electron cloud effectively surrounds the nuclei of two or more atoms, rather than just one atom. In other words, the electrons are shared by more than one

³ The argument has been proposed that hybrid atomic orbitals should not be taught in a chemistry curriculum. See Grushow, A. *J. Chem. Educ.* **2011**, *88*, 860.

⁴ 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, R.E. *J. Chem. Educ.* **1968**, *45*, 558. See also, Ellison, F.O.; Hollingsworth, C.A. *J. Chem. Educ.* **1976**, *53*, 767; McKelvey, D.R. *J. Chem. Educ.* **1983**, *60*, 112; Nelson, P.G. *J. Chem. Educ.* **1990**, *67*, 643. For a general review of relativistic effects on chemical structures, see Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

⁵ See Roothaan, C.C.J.; Weiss, A.W. *Rev. Mod. Phys.* **1960**, *32*, 194; Kolos, W.; Roothaan, C.C.J. *Rev. Mod. Phys.* **1960**, *32*, 219. See Clark, R.G.; Stewart, E.T. *Q. Rev. Chem. Soc.* **1970**, *24*, 95.

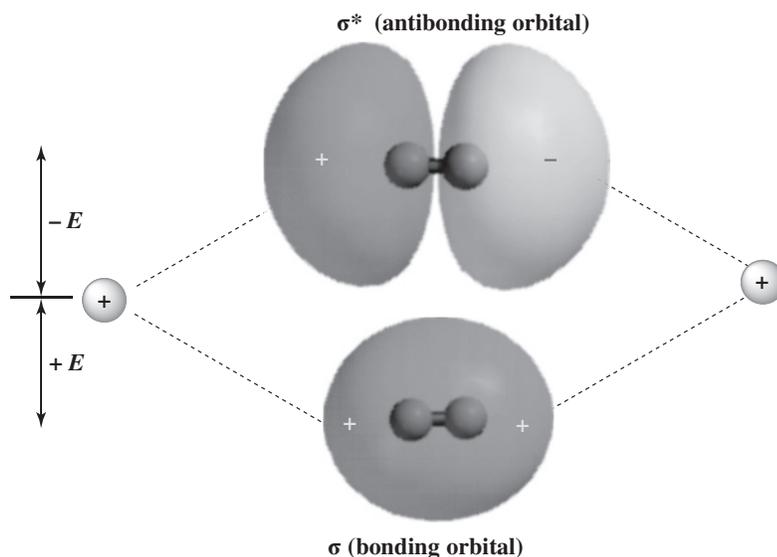


FIGURE 1.2. Overlap of two 1s orbitals gives rise to a σ orbital and a σ^* orbital.

atom rather than being localized on a single atom. In localized bonding for a single covalent bond, 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 will reside in the new *molecular bonding orbital*, which is lower in energy. Remember that *any orbital can hold only two electrons*. The higher energy antibonding orbital remains empty in the ground state.

The strength of a bond is determined by the amount of electron density that resides between the two nuclei. The greater the overlap of the orbitals, the stronger the bond, but total overlap is prevented by repulsion between the nuclei. Determining the electron density at the carbon atom, although difficult, is important for the stability of a molecule. One method to determine this parameter is quantum theory using the atomic charges and volumes of carbon atoms,⁶ as these are good descriptors of electron depletion and are indicative of the stability and reactivity of a molecule.

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. When the centers of electron density are on the axis common to the two nuclei, the molecular orbitals formed by the overlap of two atomic orbitals are called σ (*sigma*) orbitals, and the bonds are called σ bonds. The corresponding antibonding orbitals are designated σ^* . Sigma orbitals may be formed by the overlap of any of the atomic orbitals (*s*, *p*, *d*, or *f*), whether the same or different, not only by the overlap of two *s* orbitals. However, the two lobes that overlap must have the same sign: a positive *s* orbital can form a bond only by

⁶ Kržan, A.; Mavri, J. *J. Org. Chem.* **2011**, *76*, 1891.

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overlapping with another positive s orbital or with a positive lobe of a p , d , or f orbital. Any σ molecular orbital may be represented as approximately ellipsoidal in shape.

Orbitals are frequently designated by their symmetry properties. The σ orbital of hydrogen is often written ψ_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 σ^* orbital is *ungerade* (designated ψ_u). An *ungerade* orbital changes sign when inverted through its center of symmetry.

In molecular-orbital calculations, the *linear combination of atomic orbitals* (known as LCAO) generates a wave function from a linear combination of overlapped atomic orbitals. Addition of the atomic orbitals gives the bonding molecular orbital:

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

The functions ψ_A and ψ_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:

$$\Psi = c_A \psi_A - c_B \psi_B \quad (1-2)$$

This gives rise to the antibonding molecular orbital.

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

$$\Psi = c_1 \psi_1 + c_2 \psi_2 + \dots \quad (1-3)$$

This resembles Eq. (1-1), but here each ψ 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:⁷



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. It is noted that orbital functions can indeed be reconstructed from measured data using several different approaches. However, the results are often less accurate than those achieved with purely theoretical methods.⁸

⁷ In this book, a pair of electrons in a bond is represented by a straight line.

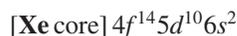
⁸ Schwarz, W.H.E. *Angew. Chem. Int. Ed.* **2006**, *45*, 1508. For the ball-in-box model, see Pierrefixe, S.C.A.H.; Guerra, C.F.; Bickelhaupt, F.M. *Chem. Eur. J.* **2008**, *14*, 819; Pierrefixe, S.C.A.H.; Bickelhaupt, F.M. *J. Phys. Chem. A.* **2008**, *112*, 12816.

1.B. MULTIPLE VALENCE

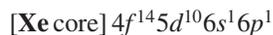
A univalent atom has only one orbital available for bonding. But atoms with a valence of 2 or more must form bonds by using at least two orbitals. An oxygen atom has two half-filled orbitals, giving it a valence of 2. It forms single bonds by the overlap of these with the orbitals of two other atoms. According to the principle of maximum overlap, the other two nuclei should form an angle of 90° with the oxygen nucleus, since the two available orbitals on oxygen are p orbitals, which are perpendicular. If this is correct, nitrogen, which has three mutually perpendicular p orbitals, would also have bond angles of 90° when it forms three single bonds. However, these are not the observed bond angles. The bond angles are $104^\circ 27'$ in water and $106^\circ 46'$ in ammonia.⁹ For alcohols and ethers the angles are even larger (Sec. 1.K). A discussion of this difference in bond angles will be deferred to Section 1.K, 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.

1.C. 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. This bonding can be explained 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.

The new molecular orbitals are a mixture of the two original orbitals, so they are called *hybrid orbitals*.¹⁰ Each orbital is a merger of an s orbital and a p orbital and is called an sp orbital. *Note that only lobes of the same sign can overlap.* The sp orbitals, each of which consists of a large lobe and a very small one, arise only in the bonding process and do not represent a possible structure for the free atom. An example is the mercury atom, which forms its two bonds by overlapping each of the large lobes shown in Figure 1.3 with an orbital from an external atom. The orbital of this external atom may be any of the atomic orbitals previously considered (s , p , d , or f), or it may be another hybrid orbital. In any of

⁹ Bent, H.A. *Chem. Rev.* **1961**, *61*, 275, see p. 277.

¹⁰ See Alabugin, I.V.; Bresch, S.; Gomes, G.d.P. *J. Phys. Org. Chem.* **2015**, *28*, 147.

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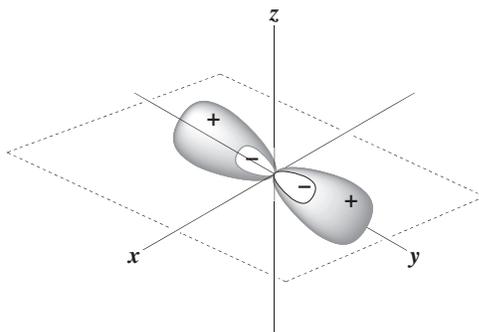
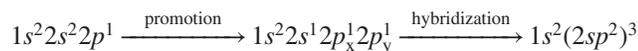


FIGURE 1.3. The two sp orbitals formed by mercury.

these cases, the molecular orbital that arises is called a σ orbital since it fits the previous definition of a σ orbital.

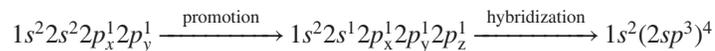
In general, equivalent orbitals lie as far away from each other as possible because of mutual repulsion, so two sp orbitals form an angle of 180° . In other words, an atom that forms only two σ bonds uses two sp orbitals. HgCl_2 , for example, should be a linear molecule, and it is. This kind of hybridization 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. Compare HgCl_2 with water (OH_2). It is known that the shape of HgCl_2 is linear, but water is angular. This fact suggests that the hybrid orbitals utilized by oxygen in water are different from those used by mercury in HgCl_2 .

Many other kinds of hybridization are possible. Consider boron, which has the electronic configuration $1s^2 2s^2 2p^1$ yet has a valence of 3. Boron has only three valence electrons available to form bonds, hence the valence of 3. Any hybridization model must take this into account. As before, imagine promotion of an electron 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 . The key is to understand that an atom forms two σ bonds for sp hybridization and three σ bonds for sp^2 hybridization. The sp^2 hybrid orbitals just noted 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 BF_3 , a planar molecule with angles of 120° .

Another type of hybrid orbital is possible, formed by atoms that can form four σ bonds. Carbon is an important atom that can form four single bonds (four σ bonds). Imagine promotion of an electron and hybridization that leads to:



There are four equivalent molecular orbitals connected to a central locus, each called sp^3 , and mutual electron repulsion leads to a shape in which *the orbitals point to the corners of a regular tetrahedron* (Figure 1.4). A typical molecule is methane, CH_4 , and assuming

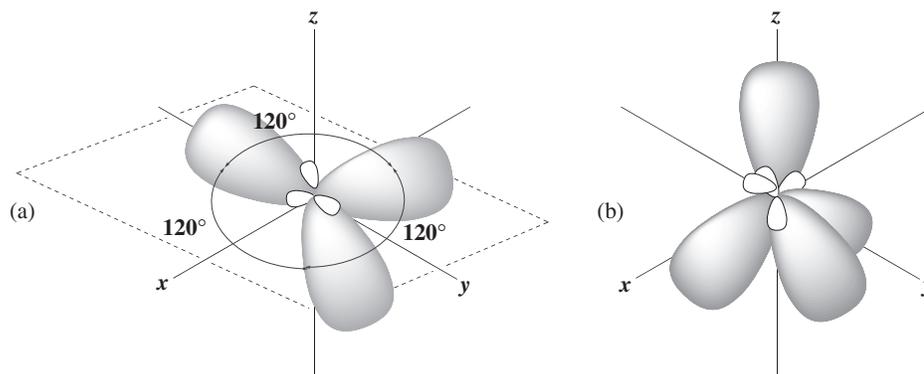


FIGURE 1.4. (a) The three sp^2 and (b) the four sp^3 orbitals.

that carbon forms four bonds with sp^3 hybrid orbitals, the bond angles of methane would thus be expected to be $109^\circ 28'$. Indeed, those are the angles of a regular tetrahedron. *In reality, electrons are not “promoted” in atomic orbitals but atomic orbitals are different from molecular orbitals, such as those found in methane.* The model of promoting an electron is a mathematical device to describe molecular orbitals using the atomic orbitals. With the realization that electrons are not really “promoted”, it is important to remember that the hybridization model is just that, a *model*, so the VSEPR (valence shell electron pair repulsion) model¹¹ can be used to show electron distribution, and molecules will form the strongest bonds possible using available orbitals.

The hybrid orbitals discussed in this section stem from only one possible approximate solution of the Schrödinger equation. The s and the three p atomic orbitals used to form sp^3 orbitals, for example, can be combined in other equally valid ways. As will be seen in Section 1.E, the four C–H bonds of methane do not always behave as if they are equivalent. Bickelhaupt⁸ has proposed an alternative approach to the bonding in carbon, which suggests that the maximum coordination number of carbon cannot exceed four because it is too small to allow more than four substituents to approach and form the appropriate bonds.

1.D. MULTIPLE BONDS

If ethene ($H_2C=CH_2$); the old name is ethylene) is examined in terms of the molecular-orbital concepts discussed so far, each carbon has three σ bonds (see Figure 1.5), one to each of the three atoms. Therefore, sp^2 orbitals are used to form those three bonds. These sp^2 orbitals arise from hybridization of the $2s^1$, $2p_x^1$, and $2p_y^1$ electrons after promotion of electrons (Sec. 1.C). In general, any carbon atom that is bonded to only three different atoms uses sp^2 orbitals for this bonding. The three σ bonds of ethene are identified as one to each of two hydrogen atoms 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, one on each of the two adjacent carbon atoms, can overlap sideways to generate a bonding and an antibonding orbital (Figure 1.5). In the ground state, both electrons go into the bonding orbital and the antibonding orbital remains vacant. In other words, a new bond

¹¹ Smith, M.B. *Organic Chemistry. An Acid–Base Approach*, 2nd ed., CRC Press, Boca Raton, FL, 2016, pp. 66–67.

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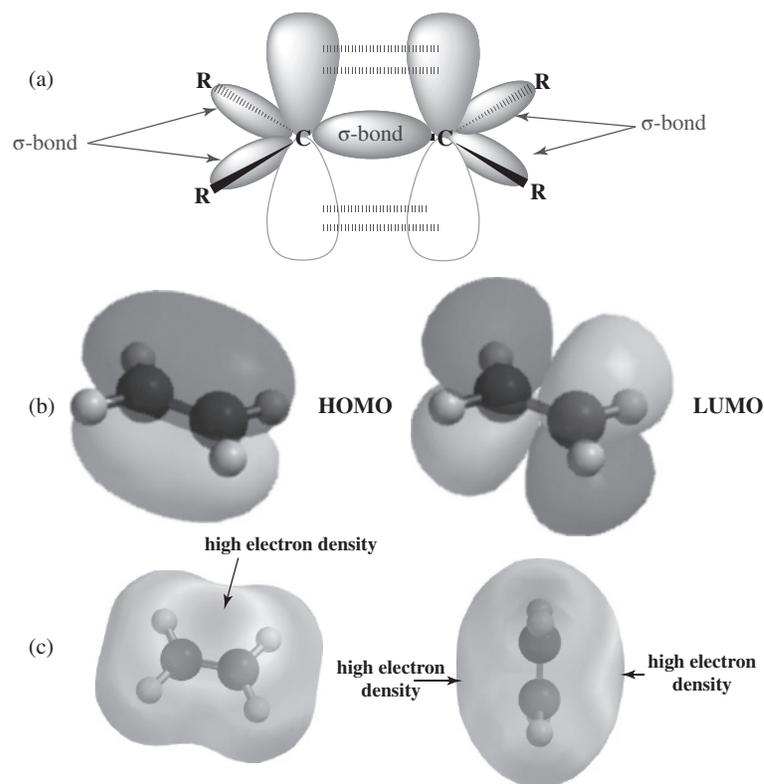


FIGURE 1.5. Overlapping p orbitals form a π orbital and a π^* orbital. The σ orbitals are shown in (a). The π orbitals are shown in (b) as the HOMO (on the left) and the LUMO (on the right). In (c) the electron potential map of ethene shows the concentration of electron density above and below the plane of the atoms, consistent with a π bond.

is formed, but it is formed by sideways overlap of adjacent p orbitals rather than direct overlap of σ orbitals. Molecular orbitals formed by the overlap of atomic orbitals whose axes are parallel are called π orbitals if they are bonding and π^* if they are antibonding.

In this picture of ethene, there are two bonds connecting the adjacent carbon atoms, but the two orbitals that make up the double bond are not equivalent.¹² In other words, the two bonds are different one from the other. The σ orbital is ellipsoidal and symmetrical about the C–C axis, the familiar σ bond. The π orbital is in the shape of two ellipsoids, one above the plane and one below, and forms the second bond, a π bond. The plane itself represents a node for the π orbital. In order for the p orbitals to maintain maximum overlap, they must be parallel. Since both a σ bond and the π bond connect the two carbon atoms, free rotation is not possible about the double bond. In other words, overlap of the two p orbitals does not allow one H–C–H plane to rotate with respect to the other; i.e., *the π bond would have to disappear*. With two sp^2 hybrid carbon atoms in ethene, the six atoms associated with the double bond ($H_2C=CH_2$) are in a plane with angles that should be $\sim 120^\circ$. Double bonds are shorter than the corresponding single bonds because maximum stability is obtained when

¹² For an alternative representation, see Pauling, L. *Theoretical Organic Chemistry, The Kekulé Symposium*; Butterworth: London, 1959, pp. 2–5; Palke, W.E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.



FIGURE 1.6. The σ electrons of ethyne.

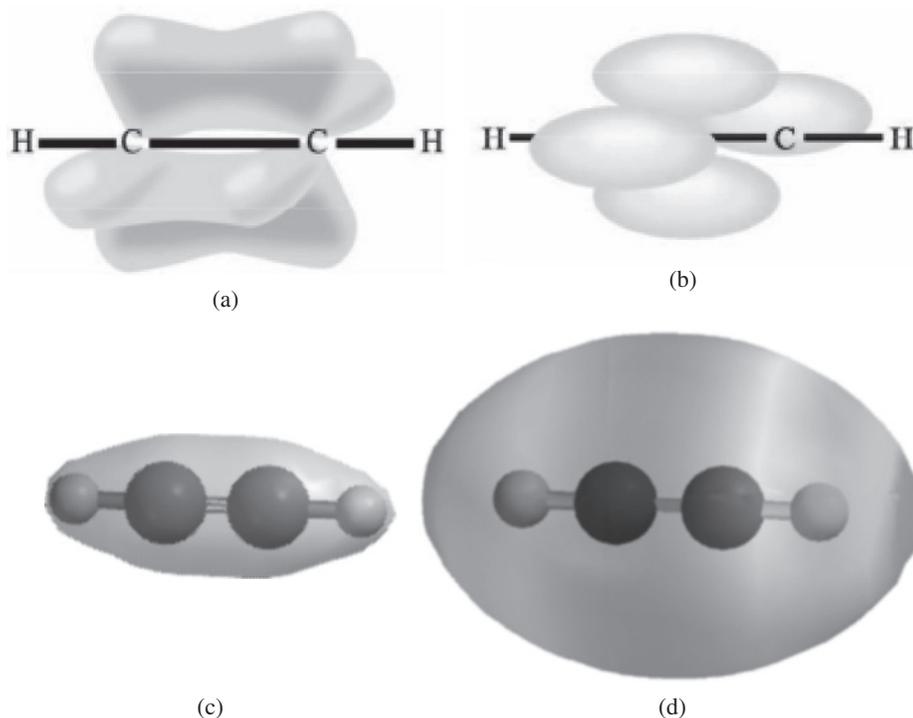


FIGURE 1.7. (a) The overlap of mutually perpendicular π orbitals. (b) Two orthogonal π bonds. (c) The electron density map of ethyne. Note the concentration of electron density along a line between the nuclei of each atom, consistent with overlap of σ orbitals in a triple bond. (d) Electron potential map of ethyne showing the concentration of electron density between the carbon atoms, consistent with two orthogonal π bonds.

the p orbitals overlap as much as possible (Sec. 1.J). Double bonds between carbon and oxygen ($C=O$) or carbon and nitrogen ($C=N$) similarly consist of one σ orbital and one π orbital.

When carbon is connected to another carbon atom by a triple bond, as in ethyne ($HC\equiv CH$; the common name is acetylene), each carbon is connected to only two other atoms by a σ bond and hence uses sp hybridization. This fact requires that the four atoms of acetylene (2H and 2C) are in a straight line (Figure 1.6).¹³ Each carbon has two p orbitals remaining, with one electron in each. These orbitals are perpendicular to each other and also to the C–C axis. The mutually perpendicular p orbitals overlap in the manner shown in Figure 1.7a to form two orthogonal π orbitals, as shown in Figure 1.7b. A triple bond is

¹³ See Simonetta, M.; Gavezzotti, A., in Patai, S. *The Chemistry of the Carbon–Carbon Triple Bond*, Wiley, NY, 1978, pp. 1–56; Dale, J., in Viehe, H.G. *Acetylenes*, Marcel Dekker, NY, 1969, pp. 3–96.

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thus composed of one σ orbital and two π orbitals. The electron density map of ethyne in shown in Figure 1.7c and shows a concentration of electron density along a line between the nuclei of each atom, consistent with overlap of σ orbitals in a triple bond. In Figure 1.7d the concentration of electron density is shown to be surrounding the space between the carbon atoms, consistent with two orthogonal π bonds. Triple bonds between carbon and nitrogen can be represented in a similar manner, $C\equiv N$.

For most organic molecules, double and triple bonds typically involve the first-row elements carbon, nitrogen, and oxygen.¹⁴ Second-row elements tend to form weaker π bonds than do the first-row elements,¹⁵ so multiple bonds are less common and compounds containing them are generally less stable.¹⁶ Compounds with $C=S$ bonds are known, for example, and $C=S$ compounds are generally much less stable than the corresponding $C=O$ compounds (however, see $p\pi-d\pi$ bonding in Sec. 2.H). Stable compounds with $Si=C$ and $Si=Si$ bonds are rare, but examples have been reported,¹⁷ including a pair of *cis* and *trans* $Si=Si$ isomers.¹⁸

There is at least one report of a so-called two-electron, four-center C—C bond for the dimer of tetracyanoethylene.¹⁹ While such multi-center bonding is not formally an example of the multiple bonding described in this section, it constitutes a different type of bonding when compared to the simple C—C bonds described earlier.

1.E. PHOTOELECTRON SPECTROSCOPY

Based on the hybridization model, methane is expected to have four equivalent σ bonds. Indeed, the four bonds of methane are equivalent according to most physical and chemical methods of detection. The *nuclear magnetic resonance* (NMR) and the *infrared* (IR) spectra of methane show *no* peaks that can be attributed to different kinds of C—H bonds. However, there is one physical technique that shows that the eight valence electrons of methane can be differentiated. In this technique, called *photoelectron spectroscopy* (PES),²⁰ a molecule or a free atom is bombarded with vacuum *ultraviolet* (UV) radiation, causing an electron to

¹⁴ For a review of metal–metal multiple bonds, see Cotton, F.A. *J. Chem. Educ.* **1983**, *60*, 713.

¹⁵ For discussions, see Schmidt, M.W.; Truong, P.N.; Gordon, M.S. *J. Am. Chem. Soc.* **1987**, *109*, 5217; Schleyer, P.v.R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

¹⁶ For double bonds between carbon and elements other than C, N, S, or O, see Jutzi, P. *Angew. Chem. Int. Ed.* **1975**, *14*, 232; Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419 (Si only); Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141 (Si only); Gordon, M.S. *Mol. Struct. Energ.* **1986**, *1*, 101. For reviews of $C=P$ and $C\equiv P$ bonds, see Regitz, M. *Chem. Rev.* **1990**, *90*, 191; Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259; Markovski, L.N.; Romanenko, V.D. *Tetrahedron* **1989**, *45*, 6019.

¹⁷ For $Si=C$ bonds, see Fink, M.J.; DeYoung, D.J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070; Fink, M.J.; Michalczyk, M.J.; Haller, K.J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793; West, R. *Pure Appl. Chem.* **1984**, *56*, 163; Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem. Int. Ed.* **1987**, *26*, 584; Shepherd, B.D.; Campana, C.F.; West, R. *Heteroat. Chem.* **1990**, *1*, 1.

¹⁸ Michalczyk, M.J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821, *Organometallics* **1985**, *4*, 826.

¹⁹ Miller, J.S.; Novoa, J.J. *Acc. Chem. Res.* **2007**, *40*, 189.

²⁰ See Ballard, R.E. *Photoelectron Spectroscopy and Molecular Orbital Theory*, Wiley, NY, **1978**; Rabalais, J.W. *Principles of Ultraviolet Photoelectron Spectroscopy*, Wiley, NY, **1977**; Baker, A.D.; Betteridge, D. *Photoelectron Spectroscopy*, Pergamon, Elmsford, NY, **1972**; Turner, D.W.; Baker, A.D.; Baker, C.; Brundle, C.R. *High Resolution Molecular Photoelectron Spectroscopy*, Wiley, NY, **1970**. For reviews, see Westwood, N.P.C. *Chem. Soc. Rev.* **1989**, *18*, 317; Baker, C.; Brundle, C.R.; Thompson, M. *Chem. Soc. Rev.* **1972**, *1*, 355; Bock, H.; Ramsey, B.G. *Angew. Chem. Int. Ed.* **1973**, *12*, 734; Turner, D.W. *Adv. Phys. Org. Chem.* **1966**, *4*, 31. For the IUPAC descriptive classification of various electron spectroscopy techniques, see Porter, H.Q.; Turner, D.W. *Pure Appl. Chem.* **1987**, *59*, 1343.

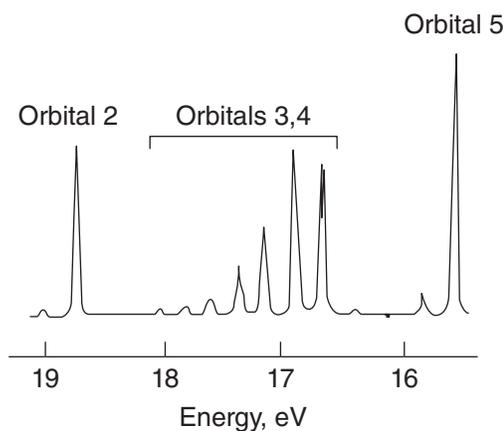


FIGURE 1.8. Photoelectron spectrum of N₂.²² [Reprinted with permission from Brundle, C.R.; Robin M.B. in Nachod, F.C.; Zuckerman, J.J. *Determination of Organic Structures by Physical Methods, Vol. 1*, Academic Press, NY, 1971, p. 18. Copyright © 1971, with permission of C. Richard Brundle, 2012.]

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. Since electrons reside in orbitals, a photoelectron spectrum consists of a series of bands, *each corresponding to an orbital of a different energy*. The spectrum gives a direct experimental picture of all orbitals that are present, and they are ejected in ascending order of their energies, provided that radiation of sufficiently high energy is used.²¹ Broad bands usually correspond to strongly bonding electrons and narrow bands to weakly bonding or nonbonding electrons.

Using photoelectron spectroscopy, it is possible to probe the validity of the hybridization model for bonding. Dinitrogen, N₂, is a typical diatomic molecule and the photoelectron spectrum is shown in Figure 1.8.²² The N₂ molecule has the electronic structure shown in Figure 1.9 using the VSPER model. In this model, 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 shown 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 corresponds to the four electrons in the degenerate orbitals 3 and 4. The individual peaks within this band are caused by different vibrational levels (see Chapter 7). The triple bond of N₂ 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 $\ddot{N}\equiv\ddot{N}$. Note that this

²¹ 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.

²² From Brundle, C.R.; Robin, M.B., in Nachod, F.C.; Zuckerman, J.J. *Determination of Organic Structures by Physical Methods, Vol. 3*, Academic Press, NY, 1971, p. 18.

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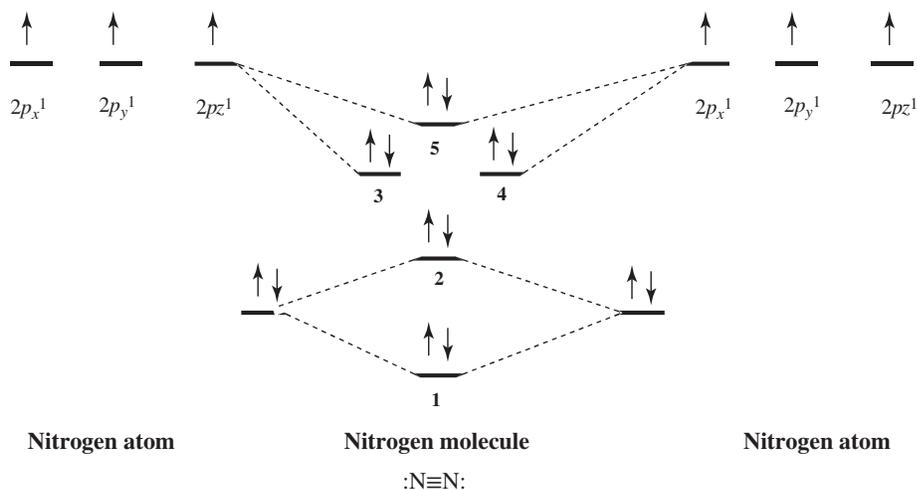


FIGURE 1.9. Electronic structure of N_2 (inner-shell electrons omitted).

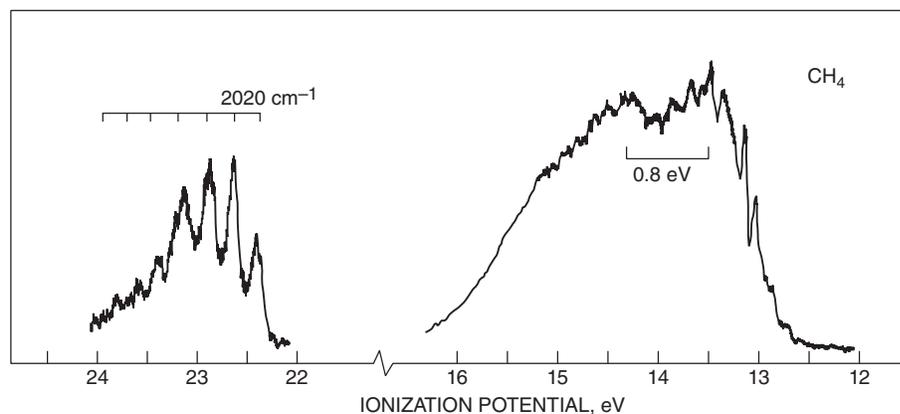


FIGURE 1.10. Photoelectron spectroscopy scan of methane.²³ [Reprinted with permission from Brundle, C.R.; Robin, M.B. *Journal of Chemical Physics* **1970**, *53*, 2196. Copyright © 1970, American Institute of Physics.]

result is contrary to that expected from a 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 methane²³ in Figure 1.10 shows two bands,²⁴ at ~ 23 and 14 eV, and not the single band expected from the equivalency of the four C–H bonds. Indeed, Figure 1.10 suggests that carbon uses two available orbitals to form four bonds and

²³ Brundle, C.R.; Robin, M.B.; Basch, H. *J. Chem. Phys.* **1970**, *53*, 2196; Baker, A.D.; Betteridge, D.; Kemp, N.R.; Kirby, R.E. *J. Mol. Struct.* **1971**, *8*, 75; Potts, A.W.; Price, W.C. *Proc. R. Soc. London, Ser A* **1972**, *326*, 165.

²⁴ 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.

the electrons in the bonds are distributed between carbon and the four atoms involved in the bonds. Remember that the hybridization model predicts four identical σ bonds made by overlap of four identical hybrid orbitals. 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 mentioned above, most physical and chemical processes cannot distinguish these levels, but photoelectron spectroscopy can. This spectrum suggests that the traditional sp^3 hybridization model does not explain phenomena involving ionized molecules (e.g., the 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 (Sec. 1.C). Since methane is known to form a tetrahedral array of atoms about carbon, a different bonding model assumes that the four σ bonds are formed by the best overlap of s and p orbitals of carbon with the orbital of each of the four atoms approaching at the angles of a regular tetrahedron. Such tetrahedral approach of the atoms allows the $2s$ and all three $2p$ orbitals of carbon for overlap. Overlap with the available orbitals of the carbon atom will form the best bonds possible. The overlap of an atom with the $2s$ orbitals and all three $2p$ orbitals is consistent with the sp^3 hybrid description. Such a model is not real, of course, since an elemental carbon atom does not form bonds with four individual atoms to form a molecule in this manner. However, this model is an alternative to the hybridization model used for methane. The photoelectron spectra of many other organic molecules are known as well,²⁵ including monocyclic alkenes, in which bands <10 eV are due to π -orbital ionization and those >10 eV originate from ionization of σ orbitals only.²⁶

1.F. 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*, which 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.²⁷ Drawing these structures correctly is essential, 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:

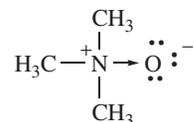
1. The total number of valence electrons in the molecule (or ion or free radical) must be the sum of all outer-shell electrons “contributed” to the molecule by each atom plus the negative charge or minus the positive charge, for the case of ions. Thus, for H_2SO_4 , there are 2 (one for each hydrogen) +6 (for the sulfur) +24 (6 for each oxygen) = 32; while for SO_4^{2-} , the number is also 32, since each atom “contributes” 6 plus 2 for the negative charge.

²⁵ Robinson, J.W. *Practical Handbook of Spectroscopy*, CRC Press, Boca Raton, FL **1991**, p. 178.

²⁶ Novak, I.; Potts, A.W. *Tetrahedron* **1997**, *53*, 14713.

²⁷ 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, C.K. *Top. Curr. Chem.* **1984**, *124*, 1.

being formed by the overlap of an orbital containing two electrons with an empty orbital. Thus trimethylamine *N*-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 *N*-oxide bear no formal charges. However, it is apparent that the electronic picture is exactly the same as the picture of trimethylamine *N*-oxide given just above, and there is a choice of drawing an arrowhead or a charge separation. Some compounds, for example, amine *N*-oxides, must be drawn one way or the other. It is usually simpler to use charge separation. It is noted that the electronic descriptions of molecules, especially complex molecules, is much more complicated, in large part due to the ultra-fast dynamics that characterize such molecules. One method has been developed, called attosecond electron dynamics,²⁹ and may allow the investigation and understanding of complex ultrafast dynamics in large molecular systems.

1.G. ELECTRONEGATIVITY

When two atoms are the same and have the same substituents, the electron cloud that bonds the two atoms is symmetrical (with respect to the plane that is the perpendicular bisector of the bond), but when two atoms are not the same, the electron cloud that bonds those two atoms is not symmetrical. In other words, a symmetrical electron cloud typically occurs when there is a bond between two identical atoms, and an unsymmetrical electron cloud occurs when there are two different atoms. When there are two different atoms, and one is more electronegative (the tendency of an atom to acquire electrons) than the other, the electron cloud is necessarily distorted toward the atom (nucleus plus electrons) that maintains the greater attraction for the cloud. This attraction is called *electronegativity*;³⁰ and 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 carbon (C–F) shows distortion of the electron cloud associated with the bond toward the atom with the greater electronegativity. In other words, there is a higher probability of finding the electrons near the fluorine than near the carbon. Such a bond is said to be *polarized*, and the C–F bond is an example of a polarized covalent bond. The polarization gives the fluorine a partial negative charge (shown by the symbol δ^-) and the carbon a partial positive charge (shown by the symbol δ^+). This distortion of electron density is called an *induced dipole*.

A number of attempts have been made to set up quantitative tables of electronegativity that will 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 (Sec. 1.L) of diatomic molecules. It is rationalized that if the electron distribution

²⁹ Nisoli, M.; Decleva, P.; Calegari, F.; Palacios, A.; Martín, F. *Chem. Rev.* **2017**, *117*, 10760.

³⁰ For a collection of articles on this topic, see Sen, K.D.; Jørgensen, C.K. *Electronegativity* (Vol. 6 of *Structure and Bonding*); Springer, NY, **1987**. For a review, see Batsanov, S.S. *Russ. Chem. Rev.* **1968**, *37*, 332.

TABLE 1.1 Some group electronegativities relative to H = 2.176³¹

CH ₃	2.472	CCl ₃	2.666
CH ₃ CH ₂	2.482	C ₆ H ₅	2.717
CH ₂ Cl	2.538	CF ₃	2.985
CBr ₃	2.561	C≡N	3.208
CHCl ₂	2.602	NO ₂	3.421

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were symmetrical in a molecule A–B, 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 (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 Δ) 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. The electronegativities of several atoms have been calculated using the Pauling scale³² and the Sanderson scale.³³ Using the Pauling scale, $F = 4.0$, $O = 3.5$, Cl and $N = 3.0$, $Br = 2.8$, S, I , and $C = 2.5$, and H and $P = 2.1$.

Other treatments³⁴ have led to scales that are based on different principles, for example, the average of the ionization potential and the electron affinity,³⁵ the average one-electron energy of valence-shell electrons in ground-state free atoms,³⁶ or the “compactness” of an atom’s electron cloud.²⁸ 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^2 , which are still more electronegative than sp^3),³⁷ and even differently for primary, secondary, and tertiary carbon atoms. Also, electronegativity values can be calculated for groups rather than atoms (Table 1.1).³⁸ A new descriptor Q has been described

³¹ A magnetically anisotropic group is one that is not equally magnetized along all three axes. The most common such groups are benzene rings (Sec. 2.I) and triple bonds.

³² Taken from Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960, p. 93, except for the value for Na, which is from Sanderson, R.T. *J. Am. Chem. Soc.* **1983**, *105*, 2259; *J. Chem. Educ.* **1988**, *65*, 112, 223.

³³ See Sanderson, R.T. *J. Am. Chem. Soc.* **1983**, *105*, 2259; *J. Chem. Educ.* **1988**, *65*, 112, 223.

³⁴ See Huheey, J.E. *Inorganic Chemistry*, 3rd ed., Harper and Row, NY, **1983**, pp. 146–148; Mullay, J., in Sen, K.D.; Jørgensen, C.K. *Electronegativity* (Vol. 6 of *Structure and Bonding*), Springer, NY, **1987**, p. 9.

³⁵ Hinze, J.; Jaffé, H.H. *J. Am. Chem. Soc.* **1962**, *84*, 540; Rienstra-Kiracofe, J.C.; Tschumper, G.S.; Schaefer III, H.F.; Nandi, S.; Ellison, G.B. *Chem. Rev.* **2002**, *102*, 231.

³⁶ Allen, L.C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

³⁷ Walsh, A.D. *Discuss. Faraday Soc.* **1947**, *2*, 18; Bergmann, D.; Hinze, J., in Sen, K.D.; Jørgensen, C.K. *Electronegativity* (Vol. 6 of *Structure and Bonding*), Springer, NY, **1987**, pp. 146–190.

³⁸ Inamoto, N.; Masuda, S. *Chem. Lett.* **1982**, 1003. See also, Bratsch, S.G. *J. Chem. Educ.* **1988**, *65*, 223; Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271; Zefirov, N.S.; Kirpichenok, M.A.; Izmailov, F.F.; Trofimov, M.I. *Dokl. Chem.* **1987**, *296*, 440; Boyd, R.J.; Edgcombe, K.E. *J. Am. Chem. Soc.* **1988**, *110*, 4182.

that when plotted versus the bond energy, separates nicely a wide variety of bonding types, covalent, polar and increasingly ionic, metallogenic, electrostatic, charge-shift bonds, and dispersion interactions.³⁹

Electronegativity information can be obtained from NMR spectra. In the absence of a magnetically anisotropic group,³¹ the chemical shift of a ^1H or a ^{13}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 (relative to tetramethylsilane, TMS, as zero ppm). 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, *tert*-butylbenzene (there is a magnetically anisotropic group here, but its effect should be constant throughout the series). The electron density surrounding the ring protons decreases⁴⁰ in the order given.⁴¹ However, this type of correlation is by no means perfect, since all the measurements are made in a powerful field, which itself may affect the electron density distribution. Coupling constants between the two protons of a system $-\text{CH}-\text{CH}-\text{X}$ have also been found to depend on the electronegativity of X.⁴²

When the difference in electronegativity between two atoms is great, the electron density in an orbital may be effectively localized on only one nucleus. Such a bond is called an *ionic bond*, which arises naturally out of the previous discussion. It is possible to view polarized covalent bonds as intermediate between ionic and covalent. With this view, the extent of electron-cloud distortion is expressed as the percent ionic character of a bond. In this model, there is a continuous gradation from ionic to covalent bonds.

1.H. DIPOLE MOMENT

The *dipole moment* is a property of a 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. Only the total moment of the molecule may be measured, and it is the vectorial sum of the individual bond moments.⁴³ These individual moments are roughly the same from molecule to molecule,⁴⁴ but this constancy is by no means universal. Thus, from the dipole moments of toluene and nitrobenzene (Figure 1.11)⁴⁵ the moment of *p*-nitrotoluene is predicted to be ~ 4.36 D. The actual value of 4.39 D is reasonable. However, the moment of *p*-cresol (1.57 D) is different from the predicted value of 1.11 D. In

³⁹ Rahm, M.; Hoffmann, R. *J. Am. Chem. Soc.* **2016**, *138*, 3731.

⁴⁰ This order is opposite to that expected from the field effect (Sec. 1.I). It is an example of the *Baker-Nathan order* (Sec. 2.M).

⁴¹ Moodie, R.B.; Connor, T.M.; Stewart, R. *Can. J. Chem.* **1960**, *38*, 626.

⁴² Williamson, K.L. *J. Am. Chem. Soc.* **1963**, *85*, 516; Laszlo, P.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1963**, *85*, 2709; Niwa, J. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2192.

⁴³ See Exner, O. *Dipole Moments in Organic Chemistry*, Georg Thieme Publishers, Stuttgart, **1975**; McClellan, A.L. *Tables of Experimental Dipole Moments*, Vol. 1, W.H. Freeman, San Francisco, **1963**, Vol. 2, Rahara Enterprises, El Cerrito, CA, **1974**.

⁴⁴ For example, see Koudelka, J.; Exner, O. *Collect. Czech. Chem. Commun.* **1985**, *50*, 188, 200.

⁴⁵ The values for toluene, nitrobenzene, and *p*-nitrotoluene are from MacClellan, A.L. *Tables of Experimental Dipole Moments*, Vol. 1, W.H. Freeman, San Francisco, **1963**; Vol. 2, Rahara Enterprises, El Cerrito, CA, **1974**. The values for phenol and *p*-cresol were determined by Goode, E.V.; Ibbitson, D.A. *J. Chem. Soc.* **1960**, 4265.

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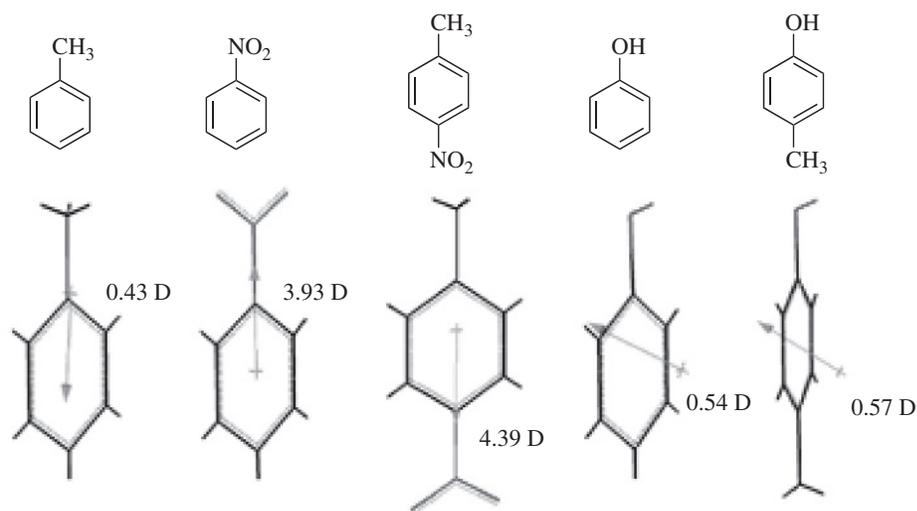


FIGURE 1.11. Some dipole moments, in Debye units, measured in benzene. In each 3D model, the arrow indicates the direction of the dipole moment for the molecule, pointing to the negative pole.⁴⁷

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 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 example, the dipole moment of isobutane is 0.132 D ⁴⁶ and that of propane is 0.085 D .⁴⁷ Of course, methane and ethane, because of their symmetry, have no dipole moments.⁴⁸ It is known that simple alkanes with more highly branched carbon skeletons are more stable than their straight-chain isomers.⁴⁹ Few organic molecules have dipole moments $>7 \text{ D}$. The most polar compound that has been reported is 5,6-diaminobenzene-1,2,3,4-tetracarbonitrile, which has a measured dipole moment of 14.1 D .⁵⁰

1.1. INDUCTIVE AND FIELD EFFECTS

The C–C bond in ethane has no polarity because it connects two equivalent atoms with identical electronegativities. The presence of a more electronegative atom attached to one of the carbon atoms will lead to bond polarization however, in what is known as an *induced*

⁴⁶ Lide Jr., D.R.; Mann, D.E. *J. Chem. Phys.* **1958**, *29*, 914.

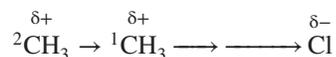
⁴⁷ Muentzer, J.S.; Laurie, V.W. *J. Chem. Phys.* **1966**, *45*, 855.

⁴⁸ Actually, symmetrical tetrahedral molecules like methane do have extremely small dipole moments, caused by centrifugal distortion effects; these moments are so small that they can be ignored for all practical purposes. For CH_4 μ is $\sim 5.4 \times 10^{-6} \text{ D}$: Ozier, I. *Phys. Rev. Lett.* **1971**, *27*, 1329; Rosenberg, A.; Ozier, I.; Kudian, A.K. *J. Chem. Phys.* **1972**, *57*, 568.

⁴⁹ McKee, W.C.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **2013**, *135*, 13008.

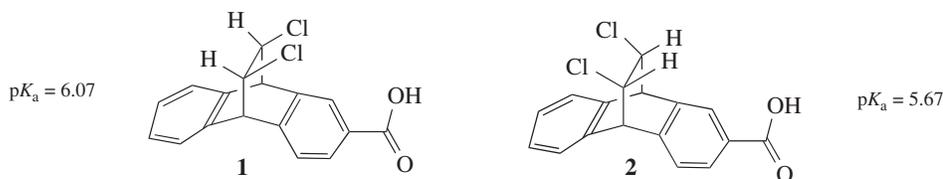
⁵⁰ Wudarczyk, J.; Papamokos, G.; Margaritis, V.; Schollmeyer, D.; Hinkel, F.; Baumgarten, M.; Floudas, G.; Millen, K. *Angew. Chem. Int. Ed.* **2016**, *55*, 3220.

dipole (Sec. 1.G). The C—C bond in chloroethane, for example, is polarized by the presence of the electronegative chlorine atom.



This polarization is actually the sum of two effects. In the first of these, the C-1 atom is deprived of some of its electron density by the greater electronegativity of Cl, and this effect is partially compensated by drawing the C—C electrons closer to itself. The result is a polarization of the C—C bond and a slightly positive charge on the C-2 atom: an induced dipole. This polarization of one bond caused by the polarization of an adjacent bond is known as an *inductive effect*. The effect is greatest for adjacent bonds but may also be felt farther away; thus the polarization of the C—C bond causes a (slight) polarization of the three methyl C—H bonds. As a practical matter, the effect is negligible if the polarizing group is more than three bonds away.

The other effect operates not through bonds, but directly through space or solvent molecules, and is called a *field effect*.⁵¹ It is often very difficult to separate the two kinds of effect, but a number of cases have been reported, generally by taking advantage of the fact that the field effect depends on the geometry of the molecule but the inductive effect depends only on the nature of the bonds. For example, in isomers **1** and **2**⁵² the inductive effect of the chlorine atoms on the position of the electrons in the COOH group (and hence on the acidity, see Chapter 8) should be the same since the same bonds intervene. The field effect is different, however, because the chlorine atoms are closer in space to the COOH in **1** than they are in **2**. Thus, a comparison of the acidity of **1** and **2** should reveal whether a field effect is truly operating. The evidence obtained from such experiments is overwhelming that field effects are much more important than inductive effects.⁵³ In most cases, the two types of effect are considered together; in this book, they will not be separated but will use the name *field effect* to refer to their combined action.⁵⁴ Note that the field effect for **1** may be viewed as internal hydrogen bonding (Sec. 3.A).



Functional groups can be classified as electron-withdrawing ($-I$) or electron-donating ($+I$) groups relative to hydrogen. This means, for example, that NO_2 , a $-I$ group, will draw

⁵¹ Roberts, J.D.; Moreland, Jr., W.T. *J. Am. Chem. Soc.* **1953**, *75*, 2167.

⁵² See Grubbs, E.J.; Fitzgerald, R.; Phillips, R.E.; Petty, R. *Tetrahedron* **1971**, *27*, 935.

⁵³ See Schneider, H.; Becker, N. *J. Phys. Org. Chem.* **1989**, *2*, 214; Bowden, K.; Ghadir, K.D.F. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1333. Also see Exner, O.; Fiedler, P. *Collect. Czech. Chem. Commun.* **1980**, *45*, 1251; Li, Y.; Schuster, G.B. *J. Org. Chem.* **1987**, *52*, 3975.

⁵⁴ There has been some question as to whether it is even meaningful to maintain the distinction between the two types of effect: see Grob, C.A. *Helv. Chim. Acta* **1985**, *68*, 882; Lenoir, D.; Frank, R.M. *Chem. Ber.* **1985**, *118*, 753; Sacher, E. *Tetrahedron Lett.* **1986**, *27*, 4683.

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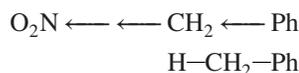
TABLE 1.2⁵⁵ Field effects of various groups relative to hydrogen^a

+I		-I	
O ⁻	NR ₃ ⁺	COOH	OR
COO ⁻	SR ₂ ⁺	F	COR
CR ₃	NH ₃ ⁺	Cl	SH
CHR ₂	NO ₂	Br	SR
CH ₂ R	SO ₂ R	I	OH
CH ₃	CN	OAr	C=CR
D	SO ₂ Ar	COOR	Ar
			C=CR

^aThe groups are listed approximately in order of decreasing strength for both -I and +I groups.

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electrons to itself more than a hydrogen atom would if it occupied the same position in the molecule.



Thus, in α -nitrotoluene, the electrons in the N-C bond are farther away from the carbon atom than the electrons in the H-C bond of toluene. Similarly, the electrons of the C-Ph bond are farther away from the ring in α -nitrotoluene than they are in toluene. Field effects are always comparison effects. For example, we compare the -I or +I effect of one group with another (usually hydrogen). Therefore, it may be said that, compared with hydrogen, the NO₂ group is electron withdrawing and the O⁻ group is electron donating or electron releasing. However, there is no actual donation or withdrawal of electrons but rather electron distortion or electron redistribution. While “withdrawing” and “releasing” terms are convenient to use, the terms merely represent a difference in the position of electrons due to the difference in electronegativity between H and NO₂ or between H and O⁻.

Table 1.2 lists a number of the most common -I and +I groups.⁵⁶ It can be seen that, compared with hydrogen, most groups are electron withdrawing. The only electron-donating groups are those with a formal negative charge (but not even all of these) and atoms of low electronegativity (Si,⁵⁷ Mg, etc., and perhaps alkyl groups). Alkyl groups⁵⁵ 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.⁵⁸ In accord with this is the value of 2.472 for the group electronegativity of CH₃ (Table 1.1) compared with 2.176 for H. 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 (e.g., Secs. 5.A.ii, 5.B.i, 8.E, and 11.B.i), but when an alkyl group is connected to a

⁵⁵ See Levitt, L.S.; Widing, H.F. *Prog. Phys. Org. Chem.* **1976**, 12, 119. See Tandon, R.; Tobias, A. Nigst, T.A.; Zipse, H. *Eur. J. Org. Chem.* **2013**, 5423.

⁵⁶ See also, Ceppi, E.; Eckhardt, W.; Grob, C.A. *Tetrahedron Lett.* **1973**, 3627.

⁵⁷ For a review of field and other effects of silicon-containing groups, see Bassindale, A.R.; Taylor, P.G., in Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds*, pt. 2, Wiley, NY, **1989**, pp. 893-963.

⁵⁸ See Sebastian, J.F. *J. Chem. Educ.* **1971**, 48, 97.

saturated atom, the results are not as clear, and alkyl groups seem to be $+I$ in some cases and $-I$ in others⁵⁹ (see also, Sec. 8.F). When connected to a positive carbon, alkyl groups are clearly electron releasing.

It is clear that the field-effect order of alkyl groups attached to unsaturated systems is tertiary > secondary > primary > CH₃, but this order is not always maintained when the groups are attached to saturated systems. Deuterium is electron donating with respect to hydrogen.⁶⁰ Other things being equal, atoms with sp bonding generally have a greater electron-withdrawing power than those with sp^2 bonding, which in turn have more electron-withdrawing power than those with sp^3 bonding.⁶¹ This observation 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.⁶²

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

1.J. BOND DISTANCES⁶³

The distances between atoms in a molecule are characteristic properties of the molecule and can give information if compared with 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.⁶⁴ 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. While exceptions are known,⁶⁵ the variation is generally less than 1%. Table 1.3 shows distances for single bonds between two sp^3 carbons. However, an analysis of C—OR bond distances in >2000 ethers and carboxylic esters

⁵⁹ See Wahl Jr., G.H.; Peterson Jr., M.R. *J. Am. Chem. Soc.* **1970**, *92*, 7238; Minot, C.; Eisenstein, O.; Hiberty, P.C.; Anh, N.T. *Bull. Soc. Chim. Fr.* **1980**, II-119.

⁶⁰ Streitwieser Jr., A.; Klein, H.S. *J. Am. Chem. Soc.* **1963**, *85*, 2759.

⁶¹ Bent, H.A. *Chem. Rev.* **1961**, *61*, 275, p. 281.

⁶² See Laurence, C.; Berthelot, M.; Lucon, M.; Helbert, M.; Morris, D.G.; Gal, J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 705.

⁶³ For tables of bond distances and angles, see Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19 (follows p. 1914); 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, M.D.; Laurie, V.W.; Kuczynski, R.L.; Schwendeman, R.H.; Ramsay, D.A.; Lovas, F.J.; Lafferty, W.J.; Maki, A.G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–721. See Lathan, W.A.; Curtiss, L.A.; Hehre, W.J.; Lisle, J.B.; Pople, J.A. *Prog. Phys. Org. Chem.* **1974**, *11*, 175; Topsom, R.D. *Prog. Phys. Org. Chem.* **1987**, *16*, 85.

⁶⁴ Burkert, U.; Allinger, N.L. *Molecular Mechanics*, ACS Monograph 177, American Chemical Society, Washington, **1982**, pp. 6–9; Whiffen, D.H. *Chem. Ber.* **1971**, *7*, 57–61; Stals, J. *Rev. Pure Appl. Chem.* **1970**, *20*, 1 (pp. 2–5).

⁶⁵ Schleyer, P.v.R.; Bremer, M. *Angew. Chem. Int. Ed.* **1989**, *28*, 1226.

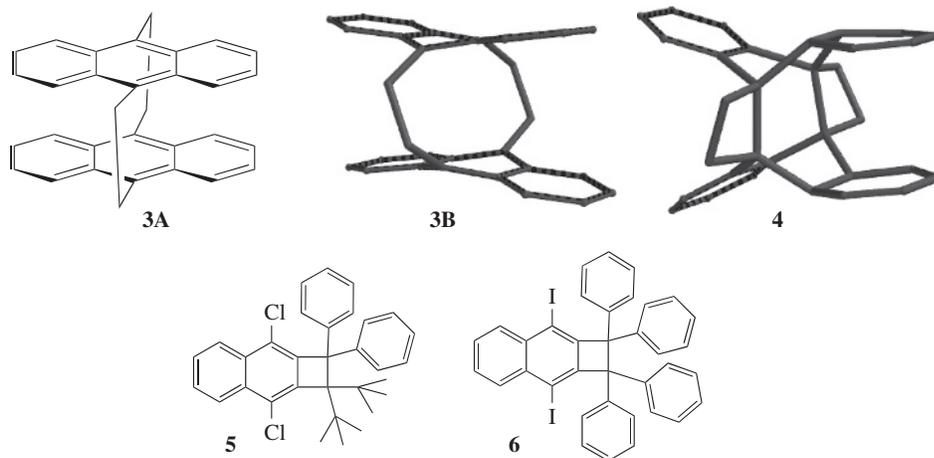
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TABLE 1.3 Bond lengths between sp^3 carbons in some compounds

C—C Bond in	Reference	Bond Length (Å)
Diamond	66	1.544
C_2H_6	67	1.5324 ± 0.0011
C_2H_5Cl	68	1.5495 ± 0.0005
C_3H_8	69	1.532 ± 0.003
Cyclohexane	70	1.540 ± 0.015
<i>tert</i> -Butyl chloride	71	1.532
<i>n</i> -Butane to <i>n</i> -heptane	72	1.531–1.534
Isobutane	73	1.535 ± 0.001

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(all with sp^3 carbons) shows that this distance increases with increasing electron withdrawal in the R group and as the C changes from primary to secondary to tertiary.⁷⁴ For these compounds, mean bond lengths of the various types ranged from 1.418 to 1.475 Å. Certain substituents can also influence bond length. The presence of a silyl substituent β to a C—O (ester) linkage can lengthen the C—O, thereby weakening it.⁷⁵ This is believed to result from $\sigma-\sigma^*$ interactions in which the C—Si σ bonding orbital acts as the donor and the C—O σ^* orbitals acts as the receptor.



⁶⁶ Lonsdale, K. *Phil. Trans. R. Soc. London* **1947**, A240, 219.

⁶⁷ Bartell, L.S.; Higginbotham, H.K. *J. Chem. Phys.* **1965**, 42, 851.

⁶⁸ Wagner, R.S.; Dailey, B.P. *J. Chem. Phys.* **1957**, 26, 1588.

⁶⁹ Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, 45, 1291.

⁷⁰ For tables of interatomic distances, see ref. 63.

⁷¹ Momany, F.A.; Bonham, R.A.; Druelinger, M.L. *J. Am. Chem. Soc.* **1963**, 85, 3075. Also see, Lide Jr., D.R.; Jen, M. *J. Chem. Phys.* **1963**, 38, 1504.

⁷² Bonham, R.A.; Bartell, L.S.; Kohl, D.A. *J. Am. Chem. Soc.* **1959**, 81, 4765.

⁷³ Hilderbrandt, R.L.; Wieser, J.D. *J. Mol. Struct.* **1973**, 15, 27.

⁷⁴ Allen, F.H.; Kirby, A.J. *J. Am. Chem. Soc.* **1984**, 106, 6197; Jones, P.G.; Kirby, A.J. *J. Am. Chem. Soc.* **1984**, 106, 6207.

⁷⁵ White, J.M.; Robertson, G.B. *J. Org. Chem.* **1992**, 57, 4638.

Bond distances for some important bond types are given in Table 1.4.⁷⁶ Although a typical C–C single bond has a bond length of ~ 1.54 Å, certain molecules are known that have significantly longer bond lengths.⁷⁷ Calculations have been done for unstable molecules

TABLE 1.4⁷⁶ Bond distances^a

Bond Type	Length, Å	Typical Compounds
C–C		
sp^3 – sp^3	1.53	
sp^3 – sp^2	1.51	Acetaldehyde, toluene, propene
sp^3 – sp	1.47	Acetonitrile, propyne
sp^2 – sp^2	1.48	Butadiene, glyoxal, biphenyl
sp^2 – sp	1.43	Acrylonitrile, vinylacetylene
sp – sp	1.38	Cyanoacetylene, butadiyne
C=C		
sp^2 – sp^2	1.32	Ethylene
sp^2 – sp	1.31	Ketene, allenes
sp – sp ⁷⁸	1.28	Butatriene, carbon suboxide
C≡C ⁷⁹		
sp – sp	1.18	Ethyne
C–H ⁸⁰		
sp^3 –H	1.09	Methane
sp^2 –H	1.08	Benzene, ethene
sp –H ⁸¹	1.08	HCN, ethyne
C–O		
sp^3 –O	1.43	Dimethyl ether, ethanol
sp^2 –O	1.34	Formic acid
C=O		
sp^2 –O	1.21	Formaldehyde, formic acid
sp –O ⁷¹	1.16	CO ₂
C–N		
sp^3 –N	1.47	Methylamine
sp^2 –N	1.38	Formamide
C=N		
sp^2 –N	1.28	Oximes, imines
C≡N		
sp –N	1.14	HCN
C–S		
sp^3 –S	1.82	Methanethiol
sp^2 –S	1.75	Diphenyl sulfide
sp –S	1.68	CH ₃ SCN
C=S		
sp –S	1.67	CS ₂

⁷⁶ Except where noted, values are from Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19 (follows p. 1914). In this source, values are given to three significant figures.

⁷⁷ Kaupp, G.; Boy, J. *Angew. Chem. Int. Ed.* **1997**, *36*, 48.

⁷⁸ Costain, C.C.; Stoicheff, B.P. *J. Chem. Phys.* **1959**, *30*, 777.

⁷⁹ For a full discussion of alkyne bond distances, see Simonetta, M.; Gavezzotti, A., in Patai, S. *The Chemistry of the Carbon–Carbon Triple Bond*, Wiley, NY, **1978**.

⁸⁰ See Henry, B.R. *Acc. Chem. Res.* **1987**, *20*, 429.

⁸¹ Bartell, L.S.; Roth, E.A.; Hollowell, C.D.; Kuchitsu, K.; Young Jr., J.E. *J. Chem. Phys.* **1965**, *42*, 2683.

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TABLE 1.4 (Continued)

C–halogen ⁸²	F	Cl	Br	I
<i>sp</i> ³ –halogen	1.40	1.79	1.97	2.16
<i>sp</i> ² –halogen	1.34	1.73	1.88	2.10
<i>sp</i> –halogen	1.27 ⁸³	1.63	1.79 ⁸⁴	1.99 ⁸⁴

^aThe values given are average lengths and do not necessarily apply exactly to the compounds mentioned.⁸⁴ Reproduced from Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19 with permission from the Royal Society of Chemistry.

that showed them to have long bond lengths, and an analysis of the X-ray structure for a photoisomer (**4**) of [2.2]-tetrabenzoparacyclophane, **3A** (also see Sec. 2.G), showed a C–C bond length of 1.77 Å.^{85,86} Note that **3A** is shown as the molecular model **3B** for comparison with photoisomer **4**, which has the two four-membered ring moieties. Long bond lengths have been observed in stable molecules such as benzocyclobutane derivatives.⁸⁶ A bond length of 1.729 Å was reliably measured in 1,1-di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobutan[*b*]naphthalene, **5**.⁸⁷ X-ray analysis of several of these derivations confirmed the presence of long C–C bonds, with **6** having a confirmed bond length of 1.734 Å.⁸⁸

A theoretical study has been reported, using computer simulation to apply encapsulation, strapping back, and stiffening to “squeeze” C–C bonds, leading to shorter bonds than would be observed if hybridization and conjugative effects operated alone.⁸⁹ The additional strain caused by threefold symmetric geometry constraints is believed responsible for this effect rather than changes in hybridization alone, as postulated by others.⁹⁰

There are indications that a C–D bond is slightly shorter than a corresponding C–H bond. Thus, electron-diffraction measurements of C₂H₆ and C₂D₆ showed a C–H bond distance of 1.1122 ± 0.0012 Å and a C–D distance of 1.1071 ± 0.0012 Å.⁸¹

As seen in Table 1.4, 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 (Sec. 2.C), and the matter is not completely settled. In general, molecules with one π bond (X=X) have shorter bond distances when compared to single bonds (X–X), and molecules with two π bonds (X≡X) have even shorter bond lengths. Indeed, the bond length clearly decreases in the molecules H₃C–CH₃, H₂C=CH₂, and HC≡CH, with C–C bond lengths

⁸² For reviews of carbon–halogen bonds, see Trotter, J., in Patai, S. *The Chemistry of the Carbon–Halogen Bond*, pt. 1; Wiley, NY, **1973**, pp. 49–62; Mikhailov, B.M. *Russ. Chem. Rev.* **1971**, *40*, 983.

⁸³ Lide Jr., D.R. *Tetrahedron* **1962**, *17*, 125.

⁸⁴ Rajput, A.S.; Chandra, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1854.

⁸⁵ Ehrenberg, M. *Acta Crystallogr.* **1966**, *20*, 182.

⁸⁶ Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *Acta Crystallogr., Sect. C* **1996**, *52*, 177.

⁸⁷ Toda, F.; Tanaka, K.; Watanabe, M.; Taura, K.; Miyahara, I.; Nakai, T.; Hirotsu, K. *J. Org. Chem.* **1999**, *64*, 3102.

⁸⁸ Tanaka, K.; Takamoto, N.; Tezuka, Y.; Kato, M.; Toda, F. *Tetrahedron* **2001**, *57*, 3761.

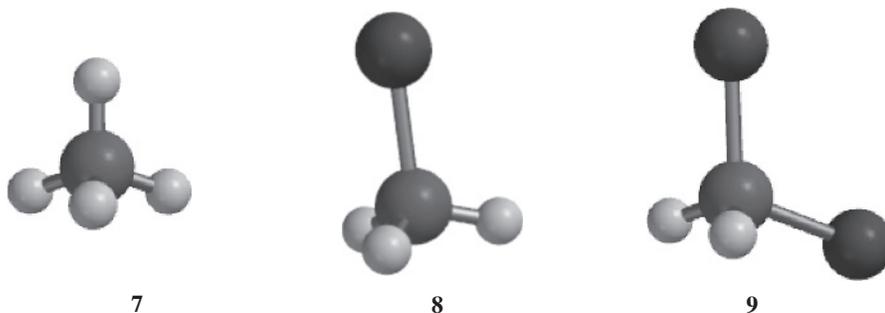
⁸⁹ Huntley, D.R.; Markopoulos, G.; Donovan, P.M.; Scott, L.T.; Hoffmann, R. *Angew. Chem. Int. Ed.* **2005**, *44*, 7549.

⁹⁰ See Tanaka, M.; Sekiguchi, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 5821.

of 1.538 Å, 1.338 Å, and 1.203 Å.⁹¹ There is work that suggests the absence of σ bonds may play a role in producing short bond distances in molecules that contain only π bonds.⁹² This suggests that σ bonds prevent π bonds from adopting their optimal shorter distances. Such bonds occur in some organometallic compounds.

1.K. BOND ANGLES

The bond angles of sp^3 carbon should be the tetrahedral angle $109^\circ 28'$ when the four atoms or groups are relatively small and identical, as in methane, neopentane, or carbon tetrachloride (Sec. 1.E). As atoms or groups become larger, bond angles are distorted to accommodate the larger size of the attached units. In most cases the angles deviate only a little from the pure tetrahedral value unless two or more units are very large. Molecular models **7–9** illustrate this phenomenon. The H–C–H bond angles in methane (**7**) are calculated for the model to be 109.47° , whereas the Br–C–H bond angle in **8** is calculated to be 108.08° and the Br–C–Br bond angle in **9** is calculated to be 113.38° . Note that the C–Br bond length is longer than the C–H bond lengths. As the bond angles expand to accommodate the larger atoms, the H–C–H bond angles in **8** and **9** must compress to a smaller angle. In 2-bromopropane, the methyl group can be compared with a H atom in bromomethane (**8**), so methyl replaces H, and the C–C–Br angle is 114.2° .⁹³



Variations are generally found from the ideal values of 120° and 180° for sp^2 and sp carbons, 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.⁹⁴ 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 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

⁹¹ Vannes, G.J.H.; Vos, A. *Acta Crystallogr. Sect. B* **1978**, B34, 1947; Vannes, G.J.H.; Vos, A. *Acta Crystallogr. Sect. B* **1979**, B35, 2593; McMullan, R.K.; Kvik, A. *Acta Crystallogr. Sect. B* **1992**, B48, 726.

⁹² Jemmis, E.D.; Pathak, B.; King, R.B.; Schaefer III, H.F. *Chem. Commun.* **2006**, 2164.

⁹³ Schwendeman, R.H.; Tobiason, F.L. *J. Chem. Phys.* **1965**, 43, 201.

⁹⁴ For a review of this concept, see Bingel, W.A.; Lüttke, W. *Angew. Chem. Int. Ed.* **1981**, 20, 899.

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TABLE 1.5 Oxygen, sulfur, and nitrogen bond angles in some compounds

Angle	Value	Compound	Ref.
H—O—H	104°27'	Water	9
C—O—H	107–109°	Methanol	70
C—O—C	111°43'	Dimethyl ether	95
C—O—C	124° ± 5°	Diphenyl ether	96
H—S—H	92.1°	Hydrogen sulfide	84
C—S—H	99.4°	Methanethiol	84
C—S—C	99.1°	Dimethyl sulfide	97
H—N—H	106°46'	Ammonia	9
H—N—H	106°	Methylamine	98
C—N—H	112°	Methylamine	91
C—N—C	108.7°	Trimethylamine	99

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orbitals.¹⁰⁰ Of course, in strained molecules, such as **3–6**, the bond angles may be greatly distorted from the ideal values (also see Sec. 4.Q).

For molecules that contain oxygen and nitrogen, angles of 90° are predicted from p^2 bonding. However, as seen in Section 1.B, the angles of water and ammonia are much larger than this, as are the angles of other organic molecules that contain oxygen and nitrogen (Table 1.5). In fact, they are much closer to the tetrahedral angle of 109°28' than to 90°. These facts have led to the suggestion that in these compounds oxygen and nitrogen use sp^3 bonding. Using the hybridization model, these atoms are said to form bonds by the overlap of two (or three) p orbitals with $1s$ orbitals of the hydrogen atoms, which means that 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, with 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,¹⁰¹ it becomes necessary to explain why the angles of these two compounds are in fact not 109°28' but a few degrees smaller. One explanation that has been offered is that the unshared electron pair actually has a greater steric requirement (Sec. 4.Q) than the electrons 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 bonds¹⁰² and the explanation

⁹⁵ Blukis, V.; Kasai, P.H.; Myers, R.J. *J. Chem. Phys.* **1963**, *38*, 2753.

⁹⁶ Abrahams, S.C. *Q. Rev. Chem. Soc.* **1956**, *10*, 407.

⁹⁷ Iijima, T.; Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2564.

⁹⁸ Lide, Jr., D.R. *J. Chem. Phys.* **1957**, *27*, 343.

⁹⁹ Lide, Jr., D.R.; Mann, D.E. *J. Chem. Phys.* **1958**, *28*, 572.

¹⁰⁰ This assumption has been challenged: see Pomerantz, M.; Liebman, J.F. *Tetrahedron Lett.* **1975**, 2385.

¹⁰¹ 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, M. *J. Chem. Educ.* **1987**, *64*, 124.

¹⁰² See Blackburne, I.D.; Katritzky, A.R.; Takeuchi, Y. *Acc. Chem. Res.* **1975**, *8*, 300; Aaron, H.S.; Ferguson, C.P. *J. Am. Chem. Soc.* **1976**, *98*, 7013; Anet, F.A.L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 2794; Vierhapper, F.W.; Eliel, E.L. *J. Org. Chem.* **1979**, *44*, 1081; Gust, D.; Fagan, M.W. *J. Org. Chem.* **1980**, *45*, 2511. For other views, see Lambert, J.B.; Featherman, S.I. *Chem. Rev.* **1975**, *75*, 611; Breuker, K.; Kos, N.J.; van der Plas, H.C.; van Veldhuizen, B. *J. Org. Chem.* **1982**, *47*, 963.

most commonly accepted is that the hybridization is not pure sp^3 . As seen above, an atom supplies more p character when it is bonded to more electronegative 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 character and the bonds more p character than pure sp^3 orbitals, making the bonds somewhat more like p^2 bonds and reducing the angle. However, these arguments ignore the steric effect of the atoms or groups attached to oxygen or nitrogen. As seen in Table 1.5, 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.

1.L. BOND ENERGIES¹⁰³

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 $118 \text{ kcal mol}^{-1}$ (494 kJ mol^{-1}). 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 $100 \text{ kcal mol}^{-1}$ (418 kJ mol^{-1}). The average of these two values, $109 \text{ kcal mol}^{-1}$ (456 kJ mol^{-1}), is taken as the *bond energy*, E . In diatomic molecules, of course, $D = E$.

The D values may be easy or difficult to measure, and they can be estimated by various techniques.¹⁰⁴ When properly applied, “Pauling’s original electronegativity equation accurately describes homolytic bond dissociation enthalpies of common covalent bonds, including highly polar ones, with an average deviation of ($1.5 \text{ kcal mol}^{-1}$ [$\approx 6.3 \text{ kJ mol}^{-1}$] from literature values).”¹⁰⁵ Whether measured or calculated, there is no question as to what D values mean. With E values the matter is not so simple. For methane, the total energy of conversion from CH_4 to $\text{C} + 4 \text{ H}$ (at 0 K) is $393 \text{ kcal mol}^{-1}$ (1644 kJ mol^{-1}).¹⁰⁶ Consequently, E for the C—H bond in methane is 98 kcal mol^{-1} (411 kJ mol^{-1}) at 0 K. The more usual practice 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 1.12.

Heats of combustion are very accurately known for hydrocarbons.¹⁰⁷ For methane the value at 25°C is $212.8 \text{ kcal mol}^{-1}$ ($890.4 \text{ kJ mol}^{-1}$), which leads to a heat of atomization of $398.0 \text{ kcal mol}^{-1}$ (1665 kJ mol^{-1}) or a value of E for the C—H bond at 25°C of

¹⁰³ Blanksby, S.J.; Ellison, G.B. *Acc. Chem. Res.* **2003**, *36*, 255. For reviews including methods of determination, see Wayner, D.D.M.; Griller, D. *Adv. Free Radical Chem. (Greenwich, Conn.)* **1990**, *1*, 159; Kerr, J.A. *Chem. Rev.* **1966**, *66*, 465; Wiberg, K.B., in Nachod, F.C.; Zuckerman, J.J. *Determination of Organic Structures by Physical Methods*, Vol. 3, Academic Press, NY, **1971**, pp. 207–245.

¹⁰⁴ Cohen, N.; Benson, S.W. *Chem. Rev.* **1993**, *93*, 2419; Korth, H.-G.; Sicking, W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 715.

¹⁰⁵ Matsunaga, N.; Rogers, D.W.; Zavitsas, A.A. *J. Org. Chem.* **2003**, *68*, 3158.

¹⁰⁶ For the four steps, D values are 101 to 102, 88, 124, and 80 kcal mol^{-1} (423 – 427 , 368 , 519 , and 335 kJ mol^{-1}), respectively, though the middle values are much less reliable than the other two: Knox, B.E.; Palmer, H.B. *Chem. Rev.* **1961**, *61*, 247; Brewer, R.G.; Kester, F.L. *J. Chem. Phys.* **1964**, *40*, 812; Linevsky, M.J. *J. Chem. Phys.* **1967**, *47*, 3485.

¹⁰⁷ See Cox, J.D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, NY, **1970**; Domalski, E.S. *J. Phys. Chem. Ref. Data* **1972**, *1*, 221–277; Stull, D.R.; Westrum Jr., E.F.; Sinke, G.C. *The Chemical Thermodynamics of Organic Compounds*, Wiley, NY, **1969**.

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				kcal	kJ
C_2H_6 (gas)	+ 3.5 O_2	= 2 CO_2 (gas)	+ 3 H_2O (liq)	+372.9	+1560
	2 CO_2 (gas)	= 2 C (graphite)	+ 2 O_2 (gas)	-188.2	-787
	3 H_2O (liq)	= 3 H_2 (gas)	+ 1.5 O_2 (gas)	-204.9	-857
	3 H_2 (gas)	= 6 H (gas)		-312/5	-1308
	2 C (graphite)	= 2 C (gas)		-343.4	-1437
	C_2H_6 (gas)	= 6 H (gas)	+ 2 C (gas)	-676.1 kcal	-2829 kJ

FIGURE 1.12 Calculation of the heat of atomization of ethane at 25 °C.

99.5 kcal mol⁻¹ (416 kJ mol⁻¹). 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⁻¹ or 2829 kJ mol⁻¹ (Figure 1.12), and it must be decided 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 the assumption is made 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⁻¹ or 416 kJ mol⁻¹), then 6×99.5 (or 416) = 597.0 (or 2498), leaving 79.1 kcal mol⁻¹ (331 kJ mol⁻¹) 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. The E values for the C–C bonds in pentane, isopentane, and neopentane, similarly calculated from heats of atomization, are (at 25 °C) 81.1, 81.8, and 82.4 kcal mol⁻¹ (339, 342, 345 kJ mol⁻¹), respectively, even though all of them have twelve C–H bonds and four C–C bonds. The bond dissociation enthalpies for bridgehead C–H bonds have been determined.¹⁰⁸ The allylic C–H bond dissociation energy of cyclopropene was measured to be 104.4 kcal mol⁻¹ (435 kJ mol⁻¹), and there is evidence that the radical is nonaromatic.¹⁰⁹

These differences have been attributed to various factors caused by the introduction of new structural features. Thus isopentane (2-methylbutane) 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 5.2). There is also the steric factor (Sec. 4.Q). Hence it is certainly incorrect to use the value of 99.5 kcal mol⁻¹ (416 kJ mol⁻¹) 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 computed¹¹⁰ 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 that contain the structural feature.

The literature contains charts that take hybridization into account (thus an sp^3 C–H bond does not have the same energy as an sp^2 C–H bond).¹¹¹ Bond dissociation energies, both

¹⁰⁸ Fattahi, A.; Lis, L.; Tehrani, Z.A.; Marimannikkuppam, S.S.; Kass, S.R. *J. Org. Chem.* **2012**, *77*, 1909.

¹⁰⁹ Tian, Z.; Lis, L.; Kass, S.R. *J. Org. Chem.* **2013**, *78*, 12650.

¹¹⁰ For a review, see Cox, J.D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, NY, **1970**, pp. 531–597. See also, Gasteiger, J.; Jacob, P.; Strauss, U. *Tetrahedron* **1979**, *35*, 139.

¹¹¹ Cox, J.D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, NY, **1970**, pp. 531–597; Cox, J.D. *Tetrahedron* **1962**, *18*, 1337.

calculated and experientially determined, are constantly being refined. Improved values are available for the O—O bond of peroxides,¹¹² the C—H bond in alkyl amines,¹¹³ the N—H bond in aniline derivatives,¹¹⁴ the N—H bond in protonated amines,¹¹⁵ the O—H bond in phenols,¹¹⁶ the C—H bond in alkenes,¹¹⁷ amides, and ketones,¹¹⁸ and in CH₂X₂ and CH₃X derivatives (X=COOR, C=O, SR, NO₂, etc.),¹¹⁹ the O—H and S—H bonds of alcohols and thiols,¹²⁰ and the C—Si bond of aromatic silanes.¹²¹ Solvent plays a role in the *E* values. When phenols bearing electron-releasing groups are in aqueous media, calculations show that the bond dissociation energies decrease due to hydrogen-bonding interactions with water molecules, while electron-withdrawing substituents on the phenol increase the bond dissociation energies.¹²² The bond dissociation energy of 1-phenylcyclopropane was determined to be 93.0 kcal mol⁻¹ (389.1 kJ mol⁻¹).¹²³

Certain generalizations can be derived from bond energy data.

1. There is a correlation of bond strengths with bond distances. In general, *shorter bonds are stronger bonds*. Since it is known that increasing *s* character shortens bonds (Sec. 1.J), it follows that bond strengths increase with increasing *s* character. Calculations show that ring strain has a significant effect on bond dissociation energy, particularly the C—H bond of hydrocarbons, because it forces the compound to adopt an undesirable hybridization.¹²⁴
2. Bonds become weaker moving down the periodic table. Compare C—O and C—S, or the carbon–halogen bonds C—F, C—Cl, C—Br, C—I. This is a consequence of the first generalization, since bond distances must increase going down the periodic table because the number of inner electrons increases. However, it is noted that “high-level *ab initio* molecular orbital calculations confirm that the effect of alkyl substituents on R—X bond dissociation energies varies according to the nature of X (the stabilizing influence of the ionic configurations to increase in the order Me < Et < *i*-Pr < *t*-Bu), accounting for the *increase* (rather than expected decrease) in the R—X bond dissociation energies with increasing alkylation in the R—OCH₃, R—OH, and R—F molecules. This effect of X has been explained in terms of the increasing contribution of the ionic R⁺X⁻ configuration for electronegative X substituents.”¹²⁵

¹¹² Bach, R.D.; Ayala, P.Y.; Schlegel, H.B. *J. Am. Chem. Soc.* **1996**, *118*, 12758.

¹¹³ Wayner, D.D.M.; Clark, K.B.; Rauk, A.; Yu, D.; Armstrong, D.A. *J. Am. Chem. Soc.* **1997**, *119*, 8925. For the α C—H bond of tertiary amines, see Dombrowski, G.W.; Dinnocenzo, J.P.; Farid, S.; Goodman, J.L.; Gould, I.R. *J. Org. Chem.* **1999**, *64*, 427.

¹¹⁴ Bordwell, F.G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410. See also, Li, Z.; Cheng, J.-P. *J. Org. Chem.* **2003**, *68*, 7350.

¹¹⁵ Liu, W.-Z.; Bordwell, F.G. *J. Org. Chem.* **1996**, *61*, 4778.

¹¹⁶ Lucarini, M.; Pedrielli, P.; Pedulli, G.F.; Cabiddu, S.; Fattuoni, C. *J. Org. Chem.* **1996**, *61*, 9259. For the O—H *E* of polymethylphenols, see de Heer, M.I.; Korth, H.-G.; Mulder, P. *J. Org. Chem.* **1999**, *64*, 6969.

¹¹⁷ Zhang, X.-M. *J. Org. Chem.* **1998**, *63*, 1872. See Langler, R.F. *Aust. J. Chem.* **2011**, *64*, 324.

¹¹⁸ Bordwell, F.G.; Zhang, X.-M.; Filler, R. *J. Org. Chem.* **1993**, *58*, 6067.

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¹²⁴ Feng, Y.; Liu, L.; Wang, J.-T.; Zhao, S.-W.; Guo, Q.X. *J. Org. Chem.* **2004**, *69*, 3129; Song, K.-S.; Liu, L.; Guo, Q.X. *Tetrahedron* **2004**, *60*, 9909. See De Lio, A.M.; Durfey, B.L.; Gilbert, T.M. *J. Org. Chem.* **2015**, *80*, 10234.

¹²⁵ Coote, M.L.; Pross, A.; Radom, L. *Org. Lett.* **2003**, *5*, 4689.

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3. Double bonds are both shorter and stronger than the corresponding single bonds, but not twice as strong, because π overlap is less than σ overlap. This means that a σ bond is stronger than a π 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.¹²⁶

Calculations suggest that covalent bond strength and also equilibrium bond length are not determined by maximum overlap of the σ valence orbitals, as described in previous sections.¹²⁷ Rather, orbital interactions, Pauli repulsion, and quasi-classical electrostatic attraction determine both.

Solvents are thought to play a role in bond dissociation energy of molecules, as noted for phenol above, and also for intermediates (see Chapter 5). It has been assumed that the solvation enthalpies were small and they have been largely ignored in calculations involving various reactions. Solvent effects on the bond dissociation energy of a molecule may arise from the difference in solvation enthalpies between the molecule and the key intermediate. For radical reactions that involve polar molecules, the radical–solvent interaction may be larger.¹²⁸

The relation of energy and bond length has been discussed.¹²⁹ It is noted that the bond energy of the C–S bond¹³⁰ is 61 kcal mol^{-1} (255 kJ mol^{-1}), that of the C–N bond¹³¹ is $69\text{--}75 \text{ kcal mol}^{-1}$ ($290\text{--}315 \text{ kJ mol}^{-1}$), and a reported value for the O–O bond¹³² is $42.9 \text{ kcal mol}^{-1}$ ($179.6 \pm 4.5 \text{ kJ mol}^{-1}$).

¹²⁶ See Miller, S.I. *J. Chem. Educ.* **1978**, *55*, 778.

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¹³² The average of the values obtained was ΔH° (O–O). dos Santos, R.M.B.; Muralha, V.S.F.; Correia, C.F.; Simões, J.A.M. *J. Am. Chem. Soc.* **2001**, *123*, 12670.