CHAPTER 1

Fundamental Models of Organic Chemistry

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1.1 ATOMS AND MOLECULES

Basic Concepts

Organic chemists think of atoms and molecules as basic units of matter. We work with mental pictures of atoms and molecules, and we rotate, twist, disconnect, and reassemble physical models in our hands.[1,2] Where do these mental images and physical models come from? It is useful to begin thinking about the fundamental models of organic chemistry by asking a simple question: What do we know about atoms and molecules, and how do we know it? As Kuhn pointed out,

> Though many scientists talk easily and well about the particular individual hypotheses that underlie a concrete piece of current research, they are little better than laymen at characterizing the established bases of their field, its legitimate problems and methods.[3]

Much of what we know in organic chemistry consists of what we were taught. Underlying that teaching are observations that someone has made and someone has interpreted. The most fundamental observations are those that can be made directly with human senses. We note the physical state of a substance—solid, liquid, or gas. We see its color or lack of color. We observe whether it dissolves in a given solvent and whether it evaporates if exposed to the atmosphere. We might get some sense of its density by seeing it float or sink when added to an immiscible liquid. These are qualitative observations, but they provide an important foundation for further experimentation.

It is only a modest extension of direct observation to the use of some simple experimental apparatus for quantitative measurements. A heat source and a thermometer allow determination of melting and boiling ranges. Other

[1] For a detailed discussion of physical models in chemistry, see Walton, A. *Molecular and Crystal Structure Models*; Ellis Horwood: Chichester, England, 1978.

[2] For applications of physical models to infer molecular properties, see Teets, D. E.; Andrews, D. H. *J. Chem. Phys.* **1935**, *3*, 175.

[3] Kuhn, T. S. *The Structure of Scientific Revolutions*, 2nd ed.; The University of Chicago Press: Chicago, 1970; p. 47.

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equipment allows measurement of indices of refraction, densities, surface tensions, viscosities, and heats of reaction. Classical elemental analysis indicates the elements present in a sample and their mass ratios. In all of these experiments, the experimenter uses some equipment but *still makes the actual experimental observations by eyes*. These simple techniques can provide essential data, nonetheless. For example, finding that 159.8 grams of bromine will always be decolorized by 82.15 grams of cyclohexene leads to the law of definite proportions. In turn, that suggests a model of matter in which submicroscopic particles combine with each other in characteristic patterns, just as the macroscopic samples do. It is then only a matter of definition to call the submicroscopic particles: atoms or molecules. It is essential, however, to remember that laboratory experiments are conducted with *materials*. The chemist may talk about the addition of bromine to cyclohexene in terms of individual molecules, but that can only be inferred from experimental data collected with macroscopic samples of the reactants.

Electronic instrumentation opened the door to a variety of investigations that expand the range of observations beyond those of the human senses. These instruments extend our eyes from seeing only a limited portion of the electromagnetic spectrum to detecting practically the entire spectrum, from X-rays to radio waves, and they let us "see" light in other ways (e.g. in polarimetry). They allow us to use entirely new tools, such as electron or neutron beams, magnetic fields, and electrical potential or current. They extend the range of conditions for studying matter from near atmospheric pressure to high vacuum or high pressure. They effectively expand and compress the time scale of the observations, allowing study of events that require eons or that occur in zeptoseconds.[4,5,6]

The unifying characteristic of modern instrumentation is that we no longer observe the chemical or physical change directly. Instead, it is detected only indirectly, such as through changes in pixels on a computer display. With such instruments, it is essential to recognize the difficulty in freeing the observations from constraints imposed by expectations. *To a layperson*, a UV-vis spectrum may not seem very different from an upside-down infrared spectrum, and a capillary gas chromatogram of a complex mixture may appear to resemble a mass spectrum. But the chemist sees these images not as lines on a paper or a computer display but as vibrating or rotating molecules, as electrons moving from one place to another, as substances separated from a mixture, or as fragments produced in a mass spectrometer. Thus, implicit assumptions about the origins of experimental data both make the observations interpretable and influence the interpretation of the data.[7]

With that caveat, what do we know about molecules and how do we know it? The first assumption is that all substances are composed of

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[4] A picosecond (ps) is 10^{-12} s. A femtosecond (fs) is 10^{-15} s. An attosecond (as) is 10^{-18} s. A zeptosecond (zs) is 10^{-21} s. For a table of metric prefixes for values ranging from 10^{30} to 10^{-30}, see Adam, A. *Science*, **2019**, *363*, 681. Rosker, M. J.; Dantus, M.; Zewail, A. H. *Science* **1988**, *241*, 1200 reported that the photodissociation of ICN to I and CN occurs in ca. 100 femtoseconds. See also Dantus, M.; Zewail, A. *Chem. Rev.* **2004**, *104*, 1717; Nisoli, M.; Decleva, P.; Calegari, F.; et al. *Chem. Rev.* **2017**, *117*, 10760.

[5] Baker, S.; Robinson, J. S.; Haworth, C. A.; et al. *Science* **2006**, *312*, 424; Osborne, I.; Yeston, J. *Science* **2007**, *317*, 765; Drescher, L.; Galbraith, M. C. E.; Reitsma, G. et al. *J. Chem. Phys.* **2016**, *145*, 011101.

[6] Grundmann, S.; Trabert, D.; Fehre, K. et al. *Science* **2020**, *370*, 6514 found the time for a photoionized electron to transverse a molecule to be 247 zs.

[7] "Innocent, unbiased observation is a myth." P. Medawar, quoted in *Science* **1985**, *227*, 1188.

atoms—indivisible particles that are the smallest units of that particular kind of matter that still retain all its properties.[8] As noted, it is convenient to correlate observations that substances combine only in certain proportions with the notion that these submicroscopic entities called atoms combine with each other only in certain ways.

Much fundamental information about molecules has been obtained from spectroscopy.[9] For example, a 4000 V electron beam has a wavelength of 0.06 Å, so it is diffracted by objects larger than that size.[10] Interaction of the electron beam with gaseous molecules produces characteristic circular patterns that can be interpreted in terms of molecular dimensions.[11] We can determine internuclear distance through infrared spectroscopy of diatomic molecules and can use X-ray or neutron scattering to calculate distances of atoms in crystals.

"Pictures" of atoms and molecules may be obtained through atomic force microscopy (AFM) and scanning tunneling microscopy (STM).[12,13] For example, investigators reported images of pentacene that displayed individual atoms,[14] polycyclic aromatic hydrocarbons that allowed determination of bond order,[15] products of single-molecule chemical reactions,[16] molecule-gears,[17] and a video of a single fullerene molecular shuttling in a vibrating carbon nanotube.[18] Investigators also reported visualizing atomic orbitals,[19] imaging the lateral profiles of individual sp^3 hybrid orbitals, and determining the electronegativity of individual surface atoms.[20,21] AFM was used to characterize the strength of intermolecular hydrogen bonds.[22] Some investigators reported imaging single organic molecules in motion with transmission electron microscopy,[23] and others reported studying electron transfer to single polymer molecules with single-molecule spectroelectrochemistry.[24]

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[8] This idea can be traced to ancient Greek philosophers. Cf. Asimov, I. *A Short History of Chemistry*; Anchor Books: Garden City, NY, 1965; pp. 8–14.

[9] For a review of structure determination methods, see Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991; pp. 25–39.

[10] Moore, W. J. *Physical Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1962; p. 575 ff.

[11] For discussions of structure determination with gas phase electron diffraction, see Karle, J. in Maksić, Z. B.; Eckert-Maksić, M., Eds. *Molecules in Natural Science and Medicine*; Ellis Horwood: Chichester, England, 1991; pp. 17–27; Hedberg, K. *ibid*.; pp. 29–42.

[12] Hou, J. G.; Wang, K. *Pure Appl. Chem.* **2006**, *78*, 905.

[13] See Ottensmeyer, F. P.; Schmidt, E. E.; Olbrecht, A. J. *Science* **1973**, *179*, 175 and references therein; Robinson, A. L. *Science* **1985**, *230*, 304; *Chem. Eng. News* **1986** (Sept. 1), 4; Hansma, P. K.; Elings, V. B.; Marti, O.; et al. *Science* **1988**, *242*, 209; Parkinson, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 1030; Frommer, J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1298.

[14] Gross, L.; Mohn, F.; Moll, N.; et al. *Science* **2009**, *325*, 1110.

[15] Gross, L.; Mohn, F.; Moll, N.; et al. *Science* **2012**, *337*, 1326.

[16] de Oteyza, D. G.; Gorman, P.; Chen, Y.-C.; et al. *Science* **2013**, *340*, 1434. Albrecht, F.; Fatayer, S.; Pozo, I. et al. *Science* **2022**, *377*, 298 reported switching among three different structures with voltage applied by an STM tip.

[17] Soe, W.-H.; Srivastava, S.; Joachim, C. *J. Phys. Chem. Lett.* **2019**, *10*, 6462.

[18] Shimizu, T.; Lungerich, D.; Stuckner, J.; et al. *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1079.

[19] Pardini, L.; Löffler, S.; Biddau, G.; et al. *Phys. Rev. Lett.* **2016**, *117*, 036801.

[20] Chen, J. C. *Nanotechnology* **2006**, *17*, S195.

[21] Onoda, J.; Ondráček, M.; Jelinek, P.; et al. *Nature Commun.* **2016**, *8*, 15155.

[22] Zhang, J.; Chen, P.; Yuan, B.; et al. *Science* **2013**, *342*, 611; Monig, H.; Amirjalayer, S.; Timmer, A.; et al. *Nature Nanotech.* **2018**, *13*, 371.

[23] Koshino, M.; Tanaka, T.; Solin, N.; et al. *Science* **2007**, *316*, 853.

[24] Palacios, R. E.; Fan, F.-R. F.; Bard, A. J.; et al. *J. Am. Chem. Soc.* **2006**, *128*, 9028.

Even though "seeing is believing," it is important to remember that these experiments do not really show molecules—just computer graphics. Some examples illustrate this point: STM features that had been associated with DNA molecules were later assigned to the surface used to support the DNA.[25] An STM image of benzene molecules was reinterpreted as possibly showing groups of acetylene molecules instead.[26] AFM images suggesting the visualization of intermolecular hydrogen bonds were questioned when it was shown that similar images could be observed when such hydrogen bonding should not be possible.[27,28]

Organic chemists also reach conclusions about molecular structure on the basis of logic. For example, the fact that one and only one substance has been found to have the molecular formula CH_3Cl is consistent with a structure in which three hydrogen atoms and one chlorine atom are attached to a carbon atom in a tetrahedral arrangement. If methane were a trigonal pyramid, then two different compounds with the formula CH_3Cl might be possible—one with chlorine at the apex of the pyramid and another with chlorine in the base of the pyramid. The existence of only one isomer of CH_3Cl does not require a tetrahedral arrangement; however, since there could also be only one isomer if the four substituents to the carbon atom were arranged in a square pyramid with a carbon atom at the apex or in a square planar structure with a carbon atom at the center. Since no one has identified more than one CH_2Cl_2 molecule, the latter two geometries seem unlikely. Therefore, the parent compound, methane, may be tetrahedral as well. This view is reinforced by the existence of two different structures (enantiomers) with the formula CHClBrF. Similarly, we infer the flat, aromatic structure for benzene by noting that there are three and only three isomers of dibromobenzene.[29]

Organic chemists do not think of molecules only in terms of atoms, however. We often envision molecules as collections of nuclei and electrons and consider the electrons to be constrained to certain regions of space (orbitals) around the nuclei. Thus, we interpret UV-vis absorption and emission spectroscopy in terms of movement of electrons from one orbital to another. These concepts resulted from the development of quantum mechanics. The Bohr model of the atom, the Heisenberg uncertainty principle, and the Schrödinger equation laid the foundation for current ways of thinking about chemistry. Although there may be some truth in the statement that

> The why? and how? as related to chemical bonding were in principle answered in 1927; the details have been worked out since that time.[30]

there are still uncharted frontiers of those details to explore in organic chemistry.

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[25] Clemmer, C. R.; Beebe, T. P, Jr. *Science* **1991**, *251*, 640.

[26] Moler, J. L.; McCoy, J. R. *Chem. Eng. News* **1988** (Oct. 24), 2.

[27] Hämäläinen, S. I.; van der Heijden, N.; van der Lit, J.; et al. *Phys. Rev. Lett.* **2014**, *113*, 186102; Guo, C.-S.; Xin, X.; Van Hove, M. A.; et al. *J. Phys. Chem. C* **2015**, *119*, 14195.

[28] Reports that orbitals can be imaged were challenged because molecular orbitals "are not unique and are not observable." Pham, B. Q.; Gordon, M. S. *J. Phys. Chem. A* **2017**, *121*, 4851. See also Autschbach, J. *J. Chem. Educ.* **2012**, *89*, 1032.

[29] These examples were discussed in an analysis of "topological thinking" in organic chemistry by Turro, N. J. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 882.

[30] Ballhausen, C. J. *J. Chem. Educ.* **1979**, *56*, 357.

Molecular Dimensions

Data from spectroscopy or from X-ray, electron, or neutron diffraction measurements allow us to determine the distance between atomic centers as well as to measure the angles between sets of atoms in covalently bonded molecules.[31] The most detailed information comes from microwave spectroscopy, although that technique is more useful for lower molecular weight than higher molecular weight molecules because the sample must be in the gas phase.[32] Diffraction methods locate a center of electron density instead of a nucleus, but center of electron density is close to the nucleus for atoms that have electrons below the valence shell. For hydrogen, however, the electron density is shifted toward the atom to which it is bonded, and bonds to hydrogen are determined by diffraction methods to be shorter than bond lengths determined with spectroscopy.[33] With solid samples, the possible effect of crystal-packing forces must also be considered. Therefore, the various techniques give slightly different measures of molecular dimensions.

Table 1.1 shows data for the interatomic distances and angles of the methyl halides.[34,35] These distances and angles only provide geometric information about the location of nuclei (or local centers of electron density) as points in space. Chemists infer that those points are connected by chemical bonds, so the distance $r_{C–H}$ is the length of a C–H bond and the angle $\angle_{H–C–H}$ is the angle between two C–H bonds on the same carbon atom.

We may also define atomic dimensions, including the ionic radius (r_i), the covalent radius (r_c), and the van der Waals radius (r_{vdW}) of an atom.[36] The ionic radius is the apparent size of the electron cloud around an ion as deduced from the packing of ions into a crystal lattice.[37] As might be expected, this value varies with the charge on the ion. The ionic radius for a C^{4+} ion is

TABLE 1.1 Bond Lengths and Bond Angles for Methyl Halides

Molecule	$r_{C–H}$ (Å)	$r_{C–X}$ (Å)	$\angle_{H–C–H}$	$\angle_{H–C–X}$
CH_3F	1.105	1.385	109°54′	109°2′
CH_3Cl	1.096	1.781	110°52′	108°0′
CH_3Br	1.10	1.939	111°38′	107°14′
CH_3I	1.096	2.139	111°50′	106°58′

Source: Adapted from reference 34.

[31] A tabulation of common bond length values was provided by Allen, F. H.; Kennard, O.; Watson, D. G.; et al. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[32] Wilson, E. B. *Chem. Soc. Rev.* **1972**, *1*, 293 and references therein; see also Harmony, M. D. *Acc. Chem. Res.* **1992**, *25*, 321.

[33] Clark, T. *A Handbook of Computational Chemistry*; John Wiley & Sons: New York, 1985; chapter 2.

[34] (a) Tabulations of bond length and bond angle measurements for specific molecules are available in *Tables of Interatomic Distances and Configuration in Molecules and Ions*; compiled by Bowen, H. J. M.; Donohue, J.; Jenkin, D. G.; et al. Special Publication No. 11, Chemical Society (London): Burlington House, W1, London, 1958. (b) See also the 1965 Supplement.

[35] See Johnson, R. D., III, Ed. *NIST Computational Chemistry Comparison and Benchmark Database*. NIST Standard Reference Database Number 101, Release 21, August 2020, http://cccbdb.nist.gov/.

[36] Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[37] For an extensive discussion of ionic radii, see Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.

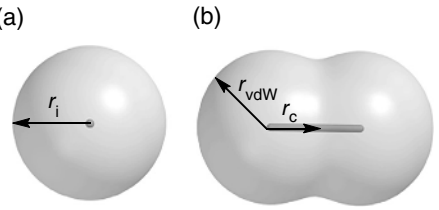


FIGURE 1.1
Radii values for chlorine.

0.15 Å, while that for a C^{4-} ion is 2.60 Å.[36] The van der Waals radius is the effective size of the electron cloud around a covalently bonded atom as perceived by another atom to which it is not bonded, and it also is determined from interatomic distances found in crystals. Note that the van der Waals radius is not the distance at which the repulsive interactions of the electrons on the two atoms outweigh the attractive forces between them, as is often assumed. Rather, it is a crystal packing measurement that gives a smaller value.[38,39] The term van der Waals *radius* implies a spherical electron density distribution, but calculations indicate that many electron density distributions are spheroidal.[40,41,42] The covalent radius of an atom indicates the size of an atom when it is part of a covalent bond, and this distance is much less than the van der Waals radius.[43] Figure 1.1 illustrates these radii for chlorine. The computer-drawn plots of electron density surfaces represent Figure 1.1(a) r_i for chloride ion; Figure 1.1(b) r_c and r_{vdW} for chlorine in Cl_2.[44]

Table 1.2 lists ionic and covalent radii values for several atoms.[45] Note that the covalent radius for an atom depends on its bonding pattern. A carbon atom with four single bonds has a covalent radius of 0.76 Å. The value is 0.73 Å for a carbon atom with one double bond, while the covalent radius for a triple-bonded carbon atom is 0.69 Å. We can also assign an r_{vdW} to a group of atoms. The value for a CH_3 or CH_2 group is 2.0 Å, while the van der Waals thickness of half the electron cloud in an aromatic ring is 1.85 Å.[36] Knowledge of van der Waals radii is important in calculations of molecular structure and reactivity, particularly with regard to proteins.[46]

Atomic radii may be used to calculate the volume and the surface area of an atom. Such calculations were described by Bondi, and a selected set of atomic volume and surface areas is given in Table 1.3. The **principle of additivity** then allows calculation of the volumes and surface areas of molecules.[47] For example, the molecular volume of propane is estimated by counting $2 \times 13.67\ cm^3/mol$ for the two methyl groups plus $10.23\ cm^3/mol$ for the methylene group, giving a total volume of $37.57\ cm^3/mol$. Similarly, we

[38] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[39] The difference is that distances between atoms in a crystal are determined by all of the forces acting on the molecules containing those atoms, not just the forces between those two atoms alone.

[40] Badenhoop, J. K.; Weinhold, F. *J. Chem. Phys.* **1997**, *107*, 5422.

[41] Eramian, H.; Tian, Y.-H.; Fox, Z.; et al. *J. Phys. Chem. A* **2013**, *117*, 14184.

[42] Grumman, A. S.; Carroll, F. A. *J. Chem. Educ.* **2019**, *96*, 1157.

[43] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; et al. *Dalton Trans.* **2008**, 2832.

[44] The images were produced with *Spartan '20*.

[45] Many sets of van der Waals radii are available in the literature. The data shown are values reported by Chauvin, R. *J. Phys. Chem.* **1992**, *96*, 9194. These values correlate well with—but are sometimes slightly different from—values given by Pauling (reference 36), Bondi (reference 38), and O'Keefe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226. A set of van der Waals radii of atoms found in proteins was reported by Li, A.-J.; Nussinov, R. *Proteins* **1998**, *32*, 111.

[46] For example, see Proserpio, D. M.; Hoffmann, R.; Levine, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 3217.

[47] Additivity means predicting a quantity by summing the contributions of its component parts.

TABLE 1.2 Comparison of van der Waals, Ionic, and Covalent Radii for Selected Atoms (Å)

		Ionic Radius (r_i)		Covalent Radii (r_c)		
Atom	van der Waals Radius (r_{vdW})[45]	Ion	r_i	Single Bonded[43]	Double Bonded	Triple Bonded
H	1.11 Å	H^-	2.08 Å	0.31 Å		
C	1.68	C^{4-}	2.60	0.76	0.73[43]	0.69[43]
N	1.53	N^{3-}	1.71	0.71		
O	1.50	O^{2-}	1.40	0.66		
F	1.51	F^-	1.36	0.57		
Cl	1.84	Cl^-	1.81	1.02	0.89	
Br	1.96	Br^-	1.95	1.20	1.04	
I	2.13	I^-	2.16	1.39	1.23	
P	1.85	P^{3-}	2.12	1.07	1.00	0.93
S	1.82	S^{2-}	1.64	1.05	0.94	0.87
Si	2.04	Si^{4-}	2.71	1.11	1.07	1.00

Source: Reference 36 except as noted/Cornell University Press.

TABLE 1.3 Group Contributions to van der Waals Atomic Volume (V_{vdW}) and Surface Area (A_{vdW})

Group	V_{vdw} (cm^3/mol)	A_{vdw} ($cm^2/mol \times 10^9$)
Alkane, C bonded to four other carbon atoms	3.33	0
Alkane, CH bonded to three other carbon atoms	6.78	0.57
Alkane, CH_2 bonded to two other carbon atoms	10.23	1.35
Alkane, CH_3 bonded to one other carbon atom	13.67	2.12
CH_4	17.12	2.90
F, bonded to a 1° carbon atom	5.72	1.10
F, bonded to a 2° or 3° carbon atom	6.20	1.18
Cl, bonded to a 1° carbon atom	11.62	1.80
Cl, bonded to a 2° or 3° carbon atom	12.24	1.82
Br, bonded to a 1° carbon atom	14.40	2.08
Br, bonded to a 2° or 3° carbon atom	14.60	2.09
I, bonded to a 1° carbon atom	19.18	2.48
I, bonded to a 2° or 3° carbon atom	20.35	2.54

Source: Adapted with permission from reference 38. © 1964 American Chemical Society.

calculate that the volume of the atoms in hexane is $2 \times 13.67\ cm^3/mol$ for the two methyl groups plus $4 \times 10.23\ cm^3/mol$ for the four methylene groups, making a total volume of $68.26\ cm^3/mol$. The volume of one mole of liquid hexane at 20° is 130.5 mL, which means that much of the volume occupied by liquid hexane corresponds to space that is outside the boundaries of the carbon and hydrogen atoms as defined above.[48]

Values for atomic and molecular volume are increasingly available from theoretical calculations. The calculated values vary somewhat, depending on

[48] Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Comp. Chem.* **1995**, *16*, 385 calculated that the volume of a mole of hexane molecules corresponds to about 71% of the volume of a mole of liquid hexane.

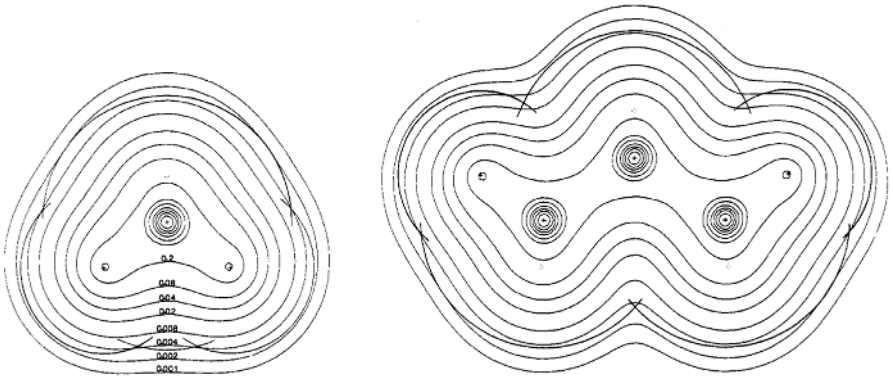


FIGURE 1.2
Contour maps and van der Waals radii arcs for methane (left) and propane (right). (Reprinted with permission from reference 49. © 1987 American Chemical Society.)

the definition of the surface of the atom or molecule. Usually the boundary of an atom is defined as a certain minimum value of electron density in units of au, where 1.00 au = 6.748 e/Å^3. Bader and co-workers determined that the 0.001 au volumes of methane and ethane are 25.53 and 39.54 cm^3/mol, respectively, while the corresponding 0.002 au volumes are 19.58 and 31.10 cm^3/mol.[49] Thus, it appears that the 0.002 au values are closer to, but still somewhat larger than, those calculated empirically using the values in Table 1.3. The relationships between atomic volumes and van der Waals radii are illustrated for cross sections through methane and propane in Figure 1.2. The contour lines represent the electron density contours and the intersecting arcs represent the van der Waals radii of the atoms.

1.2 HEATS OF FORMATION AND REACTION

Experimental Determination of Heats of Formation

Thermochemical measurements provide valuable insights into organic reactions. The **heat of formation** (ΔH_f°) of a compound is defined as the difference in enthalpy between the compound and the starting elements in their standard states.[50] For a hydrocarbon with molecular formula (C_mH_n), ΔH_f° is the heat of reaction for the reaction

$$mC_{(\text{graphite})} + (n/2)H_{2(\text{gas})} \rightarrow C_mH_n \tag{1.1}$$

The heat of formation of an organic compound can be found indirectly by determining the heat of reaction of the compound to form other

[49] Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; et al. *J. Am. Chem. Soc.* **1987**, *109*, 7968. See the discussion of the theory of atoms in molecules in Chapter 2.

[50] Mortimer, C. T. *Reaction Heats and Bond Strengths*; Pergamon Press: New York, 1962; Clark, T.; McKervey, M. A. in Stoddart, J. F., Ed. *Comprehensive Organic Chemistry*, Vol. 1; Pergamon Press: Oxford, England, 1979; p. 66 ff. For a discussion of the experimental techniques involved in calorimetry experiments, see (a) Wiberg, K. in Liebman, J. F.; Greenberg, A., Eds. *Molecular Structure and Energetics*, Vol. 2; VCH Publishers: New York, 1987; p. 151; (b) Sturtevant, J. M. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. I, Part V; Wiley-Interscience: New York, 1971; p. 347. For a discussion of experimental and theoretical methods, see Rogers, D. W.; Zavitsas, A. A.; Matsunaga, N. *WIREs Comput. Mol. Sci.* **2013**, *3*, 21.

substances for which the heats of formation are known. The heat of combustion ($\Delta H^\circ_{\text{combustion}}$) of a substance is often used for this purpose. Consider the combustion of a compound with the formula C_mH_n. The balanced chemical equation is

$$C_mH_n + (m + n/4)O_2 \rightarrow mCO_2 + (n/2)H_2O \tag{1.2}$$

We know the heats of formation of CO_2 and H_2O:

For the reaction $$C_{(\text{graphite})} + O_{2\,(\text{gas})} \rightarrow CO_{2\,(\text{gas})} \tag{1.3}$$

$$\Delta H^\circ_r = \Delta H^\circ_f(CO_2) \tag{1.4}$$

And for the reaction $$H_{2\,(\text{gas})} + \frac{1}{2}O_{2\,(\text{gas})} \rightarrow H_2O_{(\text{liquid})} \tag{1.5}$$

$$\Delta H^\circ_r = \Delta H^\circ_f(H_2O) \tag{1.6}$$

Combining the above equations leads to

$$\Delta H^\circ_f(C_mH_n) = m\Delta H^\circ_f(CO_2) + (n/2)\Delta H^\circ_f(H_2O) - \Delta H^\circ_{(\text{combustion})}(C_mH_n) \tag{1.7}$$

As an example, the heat of combustion of 1,3-cyclohexanedione was found to be −735.9 kcal/mol.[51,52] Taking −94.05 kcal/mol and −68.32 kcal/mol as the standard heats of formation of CO_2 and H_2O, respectively, gives a standard heat of formation for crystalline 1,3-cyclohexanedione of 6(−94.05) + 4(−68.32) − (−735.9) = −101.68 kcal/mol. It is sometimes necessary to correct heats of reaction for the heats associated with phase changes in the reactants or products. To convert from a condensed phase to the gas phase (e.g. for comparison with values calculated theoretically), the relevant terms are the heat of vaporization (ΔH°_v) of a liquid or heat of sublimation (ΔH°_s) of a solid.[53,54,55] Correcting for the standard heat of sublimation of 1,3-cyclohexanedione, +21.46 kcal/mol, gives its standard heat of formation in the gas phase as −80.22 kcal/mol.

The relative enthalpies of two compounds can be determined more accurately by measuring ΔH values of a reaction in which the two different reactants combine with identical reagents to give the same product(s). Figure 1.3 illustrates how the difference in enthalpy of reactants A and B can be calculated in this manner. If the reaction of A and C to give D has a ΔH_r

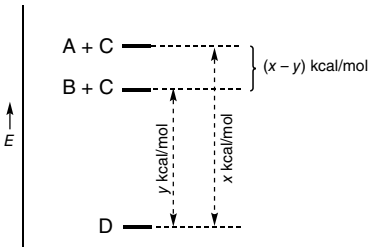


FIGURE 1.3
Calculation of the enthalpy difference of isomers.

[51] Pilcher, G.; Parchment, O. G.; Hillier, I. H.; et al. *J. Phys. Chem.* **1993**, *97*, 243.

[52] The reported value (converted from kJ/mol) was −735.9 ± 0.2 kcal/mol. Experimental uncertainties will not be carried through this discussion because the emphasis is on the calculation procedure and not the precision of the experimental method.

[53] Determination of heats of sublimation was discussed by Chickos, J. S. in Liebman, J. F.; Greenberg, A., Eds. *Molecular Structure and Energetics*, Vol. 2; VCH Publishers: New York, 1987; p. 67.

[54] The enthalpy associated with transformation of a solid to a liquid is the **heat of fusion**. For a discussion, see Chickos, J. S.; Braton, C. M.; Hesse, D. G.; et al. *J. Org. Chem.* **1991**, *56*, 927.

[55] Data for heat capacity can be used to correct ΔH values measured at one temperature to another temperature. See Orchin, M.; Kaplan, F.; Macomber, R. S.; et al. *The Vocabulary of Organic Chemistry*; Wiley-Interscience: New York, 1980; pp. 255–256.

of $-x$ kcal/mol, and if the reaction of B and C to give D has a ΔH_r of $-y$ kcal/mol, then the difference in energy between A and B must be $(x - y)$ kcal/mol. For example, ΔH_r values for the reaction of trifluoroacetic acid with 2-methyl-1-butene and with 2-methyl-2-butene were −10.93 and −9.11 kcal/mol, respectively.[56] Therefore, the 2-alkene is judged to be 1.82 kcal/mol lower in energy than the 1-alkene. Heats of hydrogenation are also used to determine the difference in heats of formation of alkenes even though heats of combustion may be measured much more *precisely* than heats of hydrogenation. Heats of hydrogenation are smaller in magnitude than are heats of combustion, so small enthalpy differences between isomers may be determined more *accurately* by hydrogenation.[57]

Bond Increment Calculation of Heats of Formation

Table 1.4 shows experimental ΔH_f° values for some linear alkanes.[58] There is a general trend in the data, with each homolog higher than ethane having a ΔH_f° value about 5 kcal/mol more negative than the previous alkane. This observation suggests that it should be possible to use the principle of additivity to predict the heat of formation of an organic compound by summing the contribution each component makes to ΔH_f°.[59] Benson published extensive tables of **bond increment contributions** to heats of formation and other thermodynamic properties.[59,60,61,62,63,64] A portion of one such table is reproduced as Table 1.5.

The heats of formation of some linear alkanes calculated by the bond increment method are shown in Table 1.4. Consider the calculation of ΔH_f° values for methane and ethane. Methane has four C—H bonds, each contributing −3.83 kcal/mol, so the ΔH_f° value is −15.32 kcal/mol. For ethane, the ΔH_f° value is 6×-3.83 for the six C—H bonds plus 1×2.73 for the one C–C bond, and the total is −20.25 kcal/mol. As the chain is extended, each additional CH_2 group contributes $2 \times (-3.83) + 1 \times (2.73) = -4.93$ kcal/mol to the ΔH_f° value.

There is a problem with the ΔH_f° values obtained from the bond increment data in Table 1.5. The five isomers of hexane listed in Table 1.6 all have five C—C bonds and fourteen C—H bonds. The bond increment values in Table 1.5 thus predict each of them to have the same heat of formation (−39.97 kcal/mol). As shown in Table 1.6, however, the experimental heats of formation become more negative as the branching increases. The structure with a quaternary carbon atom is more stable than an isomeric structure with two tertiary carbon atoms, and it is more stable than structures with only one

[56] Wiberg, K. B.; Hao, S. *J. Org. Chem.* **1991**, *56*, 5108.

[57] Davis, H. E.; Allinger, N. L.; Rogers, D. W. *J. Org. Chem.* **1985**, *50*, 3601.

[58] Experimental data for ΔH_f° at 298 K are from tabulations in Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969; pp. 243–245.

[59] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; p. 24.

[60] Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1959**, *29*, 546.

[61] Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; et al. *Chem. Rev.* **1969**, *69*, 279.

[62] For a discussion of the development of bond increment and group increment calculations, see Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

[63] Calculation of group increments to heats of formation of linear hydrocarbons was reported by Pitzer, K. S. *J. Chem. Phys.* **1940**, *8*, 711 and to nonlinear hydrocarbons by Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.

[64] Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

TABLE 1.4 Experimental and Calculated Heats of Formation of Linear Alkanes at 298 K

Compound	ΔH_f° (kcal/mol) obs.	ΔH_f° (kcal/mol) calc.[a]
Methane	−17.89	−15.32
Ethane	−20.24	−20.25
Propane	−24.82	−25.18
Butane	−30.15	−30.11

[a]Calculations are based on bond increment values in Table 1.5.

TABLE 1.5 Bond Increment Contributions to ΔH_f°

Bond	ΔH_f° (kcal/mol)	Bond	ΔH_f° (kcal/mol)
C–H	−3.83	N–H	−2.6
C–D	−4.73	S–H	−0.8
C–C	2.73	S–S	−6.0
C–F	−52.5	C–S	6.7
C–Cl	−7.4	C_d–C	6.7
C–Br	2.2	C_d–H	3.2
C–I	14.1	C_d–F	−39.0
C–O	−12.0	C_d–Cl	−5.0
O–H	−27.0	C_d–Br	9.7
O–D	−27.9	C_d–I	21.7
O–O	21.5	C_d–C_d	7.5

Source: Reference 59/John Wiley & Sons.

TABLE 1.6 Heats of Formation (kcal/mol) of Isomeric C_6H_{14} Structures

Compound	ΔH_f°, obs.[a]	ΔH_f°, calc.[b]	ΔH_f°, corr.[c]
Hexane	−39.96	−39.96	−39.96
2-Methylpentane	−41.66	−42.04	−41.24
3-Methylpentane	−41.02	−42.04	−41.24
2,2-Dimethylbutane	−44.35	−44.77	−43.16
2,3-Dimethylbutane	−42.49	−44.12	−42.52

[a]Experimental data for ΔH_f° at 298 K are from reference 58/John Wiley & Sons.

[b]Calculated from group increments in Table 1.7 without correcting for gauche interactions.

[c]Data from the previous column corrected for gauche interactions. See Table 1.7 and Figure 1.4.

tertiary carbon atom. This leads to the conclusion that the heat of formation of a compound depends not only on the number of carbon–carbon bonds but also on the pattern of carbon–carbon bonding.

Group Increment Calculation of Heats of Formation

An alternative to the bond increment method is the **group increment** approach, which allows calculation of enthalpy differences that result from different arrangements of bonds within molecules.[65] That means considering

[65] Holmes, J. L.; Aubry, C. *J. Phys. Chem. A* **2011**, *115*, 10576 reported updated group additivity values.

TABLE 1.7 Group Increment Contributions to Heats of Formation

Group	$\Delta H^\circ_{f\,298}$ (kcal/mol)	Group	$\Delta H^\circ_{f\,298}$ (kcal/mol)
$C–(H)_3(C)$	−10.08	$C_d–(C_B)(C)$	8.64
$C–(H)_2(C)_2$	−4.95	$C–(C_B)(C)(H)_2$	−4.86
$C–(H)(C)_3$	−1.90	$C–(C_B)(C)_2(H)$	−0.98
$C–(C)_4$	0.50	$C_t–(H)$	26.93
$C_d–(H)_2$	6.26	$C_t–(C)$	27.55
$C_d–(H)(C)$	8.59	$C_t–(C_d)$	29.20
$C_d–(C)_2$	10.34	$C_B–(H)$	3.30
$C_d–(C_d)(H)$	6.78	$C_B–(C)$	5.51
$C_d–(C_d)(C)$	8.88	$C_B–(C_d)$	5.68
$[C_d–(C_B)(H)]$	6.78		

Source: Adapted from reference 61.

not only the bonds holding atoms together but also the groups that result from these bonds. Table 1.7 lists the group increment values for a series of organic functional groups.[61] These data lead to a close approximation of the heats of formation of the isomeric hexanes. Consider 2-methylpentane. Three methyl groups [$C–(H)_3(C)$ in the table] contribute −10.08 kcal/mol each to the heat of formation; two methylene units [$C–C(H)_2(C)_2$] contribute −4.95 kcal/mol each; and one methine unit [$C–(H)(C)_3$] contributes −1.90 kcal/mol. Thus, the estimated heat of formation is

$$\Delta H^\circ_f = 3 \times (-10.08) + 2 \times (-4.95) + 1 \times (-1.90) = -42.04\ \text{kcal/mol} \quad (1.8)$$

The experimental value is −41.66 kcal/mol.[58]

The heats of formation calculated in this way assign the same contribution to each group without regard to its position in the molecule and without regard to strain. In branched acyclic alkanes, the major form of strain is van der Waals repulsion due to *unavoidable* butane gauche interactions, which may be assigned 0.8 kcal/mol each.[66] Figure 1.4 shows a Newman projection and gives the minimum number of gauche interactions for each hexane. Correcting the initial ΔH°_f of 2-methylpentane for one such interaction gives −41.24 kcal/mol, which is closer to the experimental value. Angle strain corrections must be applied for ring compounds. For example, cyclopropane, cyclobutane, and cyclopentane rings add 27.6, 26.2, and 6.3 kcal/mol, respectively, to a heat of formation calculated from the data in Table 1.7.[61,67]

[66] Deviations from staggered dihedral angles may also contribute somewhat to steric energy. Energies of different conformations will be discussed in Chapter 4.

[67] These examples only hint at the analysis of heats of formation of organic compounds that is possible. Benson and co-workers summarized the methods and data for calculations for the major functional groups in organic chemistry.[59,61] In addition, the data allow calculation of heat capacities and entropies of these compounds in the same manner in which heats of formation are determined. Heats of formation are valuable reference points in discussing the stabilities of various isomers or products of reactions, whether they are calculated by bond increments or group increments or are derived as part of a theoretical calculation.

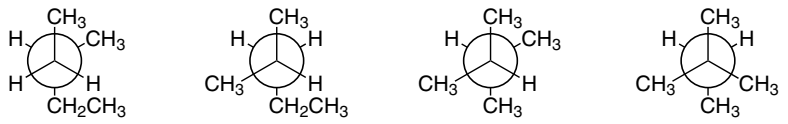


FIGURE 1.4
Gauche interactions in branched hexane isomers.

Heats of Formation and the Concept of Protobranching

The origin of the increased stability of branched alkanes relative to nonbranched isomers has been the subject of some debate. Benson and Luria proposed that alkanes have polarized $C^{\delta-}$—$H^{\delta+}$ bonds and that the sum of the electrostatic interactions of a branched compound is lower in energy than the sum of electrostatic interactions in a linear structure.[68] Laidig calculated that branched hydrocarbons have overall smaller distances between atoms than do linear isomers and that the resulting increase in nucleus–electron attraction in a branched compound outweighs the increase in nuclear–nuclear and electron–electron repulsion.[69] Schreiner attributed the stabilization of branched alkanes to attractive interactions involving alkyl groups bonded to the same carbon atom.[70]

Gronert proposed a different explanation based on the observation that van der Waals interactions between nonbonded groups that are closer than the sum of their van der Waals radii, such as C1 and C4 in the gauche conformation of butane, are known to be repulsive.[71] Since C1 and C3 in neopentane are even closer to each other than are C1 and C4 in gauche butane, he suggested that their interaction should be repulsive as well. Moreover, the interactions between two hydrogen atoms bonded to the same carbon as well as those between hydrogen and carbon atoms bonded to the same carbon were also suggested to be repulsive. The effect of branching (e.g. conversion of butane to isobutane) is to reduce the number of H–C–C interactions while increasing the number of H–C–H and C–C–C interactions. Gronert proposed that the steric energy of an H–C–C interaction is less than the average of those for the H–C–H and C–C–C interactions, so the effect of the branching is to decrease overall intramolecular repulsion and produce a more stable isomer. Using equations 1.9 and 1.10, along with the interaction values (E) for C–H and C–C bonding and specific values for repulsive 1,3 interactions shown in Table 1.8, Gronert was able to reproduce the observed gas phase ΔH_f° values of a series of alkanes quite well. For example, the ΔH_f° of *n*-pentane in kcal/mol is calculated as shown in equation 1.11.

$$\Delta H_f = n_{C-C}E_{C-C} + n_{C-H}E_{C-H} + n_{C-C-C}E_{C-C-C} + n_{C-C-H}E_{C-C-H} + n_{H-C-H}E_{H-C-H} + f(C,H) \quad (1.9)$$

[68] Benson, S. W.; Luria, M. *J. Am. Chem. Soc.* **1975**, *97*, 704.

[69] Laidig, K. E. *J. Phys. Chem.* **1991**, *95*, 7709.

[70] Schreiner, P. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 4217.

[71] Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209; 9560. The literature values in Table 1.8 are from this source. The values of the E parameters at the bottom of the table are shown to two decimal places, while those in the sources cited here were reported to one decimal place.

TABLE 1.8 Calculated Gas Phase ΔH_f° of Alkanes Assuming Repulsive Geminal Interactions[a]

Compound	n_{C-C}	n_{C-H}	n_{H-C-H}	n_{H-C-C}	n_{C-C-C}	n_C	n_H	ΔH_f (calc.)	ΔH_f (lit.)
Methane	0	4	6	0	0	1	4	−17.2	−17.9
Ethane	1	6	6	6	0	2	6	−20.4	−20.0
Propane	2	8	7	10	1	3	8	−25.3	−25.0
Butane	3	10	8	14	2	4	10	−30.2	−30.4
2-Methylpropane	3	10	9	12	3	4	10	−31.9	−32.1
n-Pentane	4	12	9	18	3	5	12	−35.1	−35.1
2-Methylbutane	4	12	10	16	4	5	12	−36.8	−36.7
2,2-Dimethylpropane	4	12	12	12	6	5	12	−40.3	−40.1
Hexane	5	14	10	22	4	6	14	−40.0	−40.0
Cyclohexane	6	12	6	24	6	6	12	−29.4	−29.4
	E_{C-C} −146.00	E_{C-H} −124.20	E_{H-C-H} 6.64	E_{H-C-C} 9.29	E_{C-C-C} 10.20	E_C 60.70	E_H 52.10		

[a]Energies are in kcal/mol.
Source: Adapted with permission from reference 71. © 2006 American Chemical Society.

where f(C, H) is given by equation 1.10.

$$f(\mathrm{C,H}) = (170.6 + E_C)n_C + 52.1n_H \tag{1.10}$$

$$\begin{aligned}\Delta H_f = {} & 4(-146) + 12(-124.2) + 9(6.64) + 18(9.29) + 3(10.2) \\ & + 5(231.3) + 12(52.1) = -35.1\ \mathrm{kcal/mol}\end{aligned} \tag{1.11}$$

Gronert's explanation for the stability of branched alkanes was supported by some investigators but questioned by others.[72,73] Wodrich and Schleyer pointed out that comparable results could be obtained by assuming that the interactions of geminal methyl groups are stabilizing, an interaction which was termed protobranching (equation 1.12).[74,75,76] Here n_{CH_2} is the number of methylene units conceptually added to methane to form the alkane, $n_{\text{primary branches}}$ is the number of C–CH_2–C units, $n_{\text{tertiary branches}}$ is the number of 3° carbon units, and $n_{\text{quaternary branches}}$ is the number of 4° carbons in the structure. Some results obtained with this approach are shown in Table 1.9, and a calculation of ΔH_f° for *n*-pentane is shown in equation 1.13.

$$\begin{aligned}\Delta H_f = {} & -17.89 - 2.15n_{CH_2} - 2.83n_{\text{primary branches}} - 7.74n_{\text{tertiary branches}} \\ & - 13.49n_{\text{quartenary branches}}\end{aligned} \tag{1.12}$$

$$\begin{aligned}\Delta H_f = {} & -17.89 + 4(-2.15) + 3(-2.83) + 0(-7.74) \\ & + 0(-13.49) = -34.98\ \mathrm{kcal/mol}\end{aligned} \tag{1.13}$$

[72] Mitoraj, M.; Zhu, H.; Michalak, A.; et al. *J. Org. Chem.* **2006**, *71*, 9208.

[73] Bartell, L. S. *J. Phys. Chem. A* **2012**, *116*, 10460 argued that the Gronert explanation makes the incorrect assumption that C–H interactions are more repulsive than the average of C–C and C–H interactions.

[74] Wodrich, M. D.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 2135.

[75] Wodrich, M. D.; Wannere, C. S.; Mo, Y.; et al. *Chem. Eur. J.* **2007**, *13*, 7731.

[76] Schleyer, P. v. R.; McKee W. C. *J. Phys. Chem. A* **2010**, *114*, 3737.

TABLE 1.9 Calculation of Gas Phase ΔH_f° Values of Alkanes Assuming Geminal Methyl Interactions Are Stabilizing[a]

Alkane	n_{CH2}	n primary branches	n tertiary branches	n quaternary branches	ΔH_f° (calc.)	ΔH_f° (lit)
Methane	0	0	0	0	–17.89	–17.89
Ethane	1	0	0	0	–20.04	–20.04
Propane	2	1	0	0	–25.02	–25.02
Butane	3	2	0	0	–30.00	–30.04
Isobutane	3	0	1	0	–32.08	–32.07
Pentane	4	3	0	0	–34.98	–35.08
Isopentane	4	1	1	0	–37.06	–36.73
Neopentane	4	0	0	1	–39.98	–40.14
Hexane	5	4	0	0	–39.96	–39.96

[a]Energies are in kcal/mol.
Source: Adapted from reference 74.

The two explanations produced a spirited discussion for several years.[77] It is sufficient here to note that sometimes opposite models can be used to predict the same experimental values. Even when only one model seems applicable, therefore, it is important to remember that a good correlation does not establish a cause-and-effect relationship.

Homolytic and Heterolytic Bond Dissociation Energies

Heats of reaction are important values for processes that involve reactive intermediates. For example, the **standard homolytic bond dissociation enthalpy** of compound A–B, denoted ΔH° (A–B) or ΔH_{298} (A–B), is the heat of reaction (ΔH_r°) at 298 K for the gas phase dissociation reaction in equation 1.14.

$$A - B_{(g)} \rightarrow A\bullet_{(g)} + B\bullet_{(g)} \tag{1.14}$$

ΔH°(A–B) values can be calculated from the relationship[78,79]

$$\Delta H^\circ(A - B) = \Delta H_{r\ (equation1.14)}^\circ = \Delta H_f^\circ(A\bullet) + \Delta H_f^\circ(B\bullet) - \Delta H_f^\circ(A - B) \tag{1.15}$$

Here $\Delta H_f^\circ(A\bullet)$ is the heat of formation of radical A•, and $\Delta H_f^\circ(B\bullet)$ is the heat of formation of radical B•. Table 1.10 gives a list of standard bond dissociation enthalpies for bonds involving hydrogen atoms, and Table 1.11 gives a list of

[77] Gronert, S. *Chem. Eur. J.* **2009**, *15*, 5372; Kemnitz, C. R.; Mackey, J. L.; Loewen, M. J.; et al. *Chem. Eur. J.* **2010**, *16*, 6942; reference 73; Kemnitz, C. R. *Chem. Eur. J.* **2013**, *19*, 11093; McKee, W. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2013**, *135*, 13008; Silva, A. F.; Duarte, L. J.; Popelier, P. L. A. *Struct. Chem.* **2020**, *31*, 507; Joyce, J. P.; Shores, M. P.; Rappè, A. K. *Phys. Chem. Chem. Phys.* **2020**, *22*, 16998.

[78] Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502.

[79] A standard bond dissociation energy is different from an **average** bond dissociation energy. The latter is just the value obtained by calculating the heat of atomization of a compound (the enthalpy change on converting the molecule to individual atoms) divided by the number of bonds from one atom to another in the molecule. For more details on this distinction, see reference 78.

TABLE 1.10 ΔH° Values (kcal/mol) for Bonds to Hydrogen

Compound	ΔH° (kcal/mol)	Compound	ΔH° (kcal/mol)
H–H	104.2	H–F	136.3
H–CN	126.3	H–Cl	103.2
H–NH_2	107.6	H–Br	87.5
HO–H	118.8	H–I	71.3
H–CH_2OH	96.1	HS–H	91.2
CH_3O–H	104.6	H–ONO_2	101.7
CH_3S–H	87.4	CH_3CH_2O–H	104.7
H–CH_2SH	94	$(CH_3)_2CHO$–H	105.7
HOO–H	87.8	$(CH_3)_3CO$–H	106.3
CH_3OO–H	88	C_6H_5O–H	90
H–CHO	88.1	CH_3CH_2OO–H	85
$CH_3C(O)$–H	89.4	$(CH_3)_3COO$–H	84
HCOO–H	112	CH_3COO–H	112
H–COOH	>96	C_6H_5COO–H	111

Source: Adapted with permission from reference 80. © 2003 American Chemical Society.

TABLE 1.11 ΔH° Values (kcal/mol) for Selected Bonds to Alkyl Groups

Subst.\R	CH_3	CH_3CH_2	$(CH_3)_2CH$	$(CH_3)_3C$	CH_2=CH	CH_2=$CHCH_2$	C_6H_5	$C_6H_5CH_2$	CH_3O	HC (O)	CH_3CH (O)
H	104.9	101.1	98.6	96.5	110.7	88.8	112.9	89.7	104.6	88.1	89.4
F	115	—	110.6	—	123.3	—	127.2	98.7	—	—	122.2
Cl	83.7	84.8	85.2	84.9	91.2	—	97.1	74	—	—	84.7
Br	72.1	72.4	73.9	72.6	80.8	59	84	63	—	—	71.7
I	57.6	56.9	57	55.6	—	45.6	67	51	—	—	53.8
HO	92.1	94.0	95.5	95.8	—	80.1	112.4	82.6	—	109.5	109.9
CH_3O	83.2	85	85.8	84	—	—	101	—	38	99.6	100
NH_2	85.2	84.8	86.0	85.7	—	—	104.2	71.7	—	—	99.1
CN	122.4	121.6	120.9	117.8	133	108.7	134	—	—	—	—
NO_2	61.0	61.6	62.9	62.8	—	—	72.5	50.5	42	—	—
CH_3	90.1	89.0	88.6	87.5	101.4	76.5	103.5	77.6	*	84.8	84.5
CH_3CH_2	*	87.9	87.1	85.6	100.0	75.4	102.2	76.7	*	83.3	83.5
$(CH_3)_2CH$	*	*	85.6	82.7	99.2	75.2	101.0	76.4	*	83.1	81.9
$(CH_3)_3C$	*	*	*	78.6	97.8	73.2	98.3	—	*	—	79.4
CH_2=CH	*	*	*	*	116	87.3	116	—	—	—	41
CH_2CHCH_2	*	*	*	*	*	62.7	—	—	—	—	—
HC≡C	126.5	125.1	124.5	122.3	—	—	—	—	—	—	—
HC≡CCH_2	78	77	—	—	—	—	—	—	—	—	—
C_6H_5	*	*	*	*	*	—	118	*	*	99.3	98.8
$C_6H_5CH_2$	*	*	*	—	—	—	97	65.2	—	—	71.4

Note: * Indicates a redundant entry. — Indicates not available.
Source: Adapted with permission from reference 80. © 2003 American Chemical Society.

ΔH° values for bonds between various alkyl groups and a number of common organic substituents.[80]

Values of ΔH_r° for dissociation reactions can be used to calculate heats of reaction. A familiar example is the calculation of ΔH_r° for the reaction of chlorine with methane to produce HCl plus methyl chloride using data in Table 1.11 and the bond dissociation enthalpies of Cl_2 and HCl.[81]

$$CH_3 - H \rightarrow CH_3\bullet + H\bullet \quad \Delta H_r^\circ = +104.9\ \text{kcal/mol} \tag{1.16}$$

$$Cl - Cl \rightarrow Cl\bullet + Cl\bullet \quad \Delta H_r^\circ = +58.0\ \text{kcal/mol} \tag{1.17}$$

$$Cl\bullet + CH_3\bullet \rightarrow CH_3Cl \quad \Delta H_r^\circ = -83.7\ \text{kcal/mol} \tag{1.18}$$

$$Cl\bullet + H\bullet \rightarrow H - Cl \quad \Delta H_r^\circ = -103.2\ \text{kcal/mol} \tag{1.19}$$

Summing these four equations and canceling the radicals that appear on both sides of the reaction arrows give

$$CH_3 - H + Cl - Cl \rightarrow CH_3Cl + HCl \quad \Delta H_r^\circ = -24.0\ \text{kcal/mol} \tag{1.20}$$

Note that the calculation of ΔH_r° does not require a radical mechanism because the difference in enthalpy between reactants and products is independent of the path of the reaction (Hess's law).[46]

If a bond dissociation occurs so that one of the species becomes a cation and the other becomes an anion, then the energy of the reaction is termed a **standard heterolytic bond dissociation energy**:

$$A - B_{(g)} \rightarrow A^+_{(g)} + B:^-_{(g)} \tag{1.21}$$

Therefore

$$\Delta H(A^+, B:^-) = \Delta H_{het}^\circ = \Delta H_f^\circ(A^+) + \Delta H_f^\circ(B:^-) - \Delta H_f^\circ(A - B) \tag{1.22}$$

As will be discussed in Chapter 7, it is possible to relate homolytic and heterolytic reaction enthalpies by using data for ionization potential (the energy required to remove an electron from a species) and electron affinity (the energy gained by adding an electron to a species).[82]

In the gas phase, heterolytic bond dissociation enthalpies are much higher than homolytic bond dissociation enthalpies because energy is needed to separate the two ions as well as to break the bond. For example, the heterolytic bond dissociation energy of HCl in the gas phase is 333.4 kcal/mol, which is more than three times the 103.2 kcal/mol homolytic bond dissociation energy.[83] Solvation of the ions can reduce the value of ΔH_{het}° dramatically, however, and HCl readily ionizes in aqueous solution. Similarly, the calculated homolytic dissociation energy of a C–Cl bond in 2,2′-dichlorodiethyl sulfide (**1**) decreases only slightly from the gas phase to a solvent with

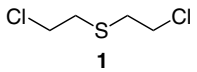
[80] Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255. This reference provides uncertainties for the values in Tables 1.10 and 1.11.

[81] Lide, D. R., Jr. *CRC Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, FL, 2003, Section 9.

[82] Arnett, E. M.; Flowers, R. A., II *Chem. Soc. Rev.* **1993**, *22*, 9.

[83] Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

ε = 5.9, while the heterolytic dissociation energy of that bond decreases from 154.8 kcal/mol in the gas phase to 138.5 kcal/mol in a solvent with the same polarity.[84,85,86] Even carbon–carbon σ bonds can heterolytically dissociate. One hydrocarbon was reported to exist as a covalently bonded compound in benzene, as a mixture of molecules and ions in acetonitrile, and as an ionic species in dimethyl sulfoxide.[87]



1

1.3 BONDING MODELS

The preceding discussion represented structures with bond-line formulas, which are implicitly based on the model of chemical bonding developed by G. N. Lewis.[88] Atoms are represented by element symbols with dots around them to indicate the number of electrons in the valence shell of the atom. Covalent bonds are formed by the sharing of one or more pairs of electrons between atoms so that both atoms achieve an electron configuration corresponding to a filled outer shell.[89] For example, combination of two chlorine atoms can produce a chlorine molecule, as shown in Figure 1.5.

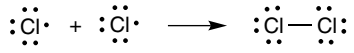


FIGURE 1.5
A Lewis structure representation of bonding of two chlorine atoms to form Cl_2.

This elementary description of bonding assumes some knowledge of electron shells of the atoms, but it does not require a detailed knowledge of the results of quantum mechanics. The representation of Cl_2 does not specify what orbitals are populated, the shapes of these orbitals, or the distribution of electrons in the final molecule of chlorine. This approach to describing chemical bonding might be adequate for some purposes, but it leaves many questions unanswered. In particular, this bonding description is purely qualitative. It would be desirable to have a mathematical description of bonding so that quantitative predictions about bonding can be compared with experimental observations.

[84] Politzer, P.; Habibollahzadeh, D. *J. Phys. Chem.* **1994**, *98*, 1576.

[85] The effects of solvent are thought to be negligible when carbon-centered radicals are formed, but solvent effects can be significant in the case of oxygen-centered radicals. Borges dos Santos, R. M.; Cabral, B. J. C.; Martinho Simões, J. A. *Pure Appl. Chem.* **2007**, *79*, 1369.

[86] In one case merely adding ether to a pentane solution of a compound was seen to produce heterolytic dissociation: Arnett, E. M.; Amarnath, K.; Harvey, N. G.; et al. *Science* **1990**, *247*, 423.

[87] Kitagawa, T.; Takeuchi, K. *J. Phys. Org. Chem.* **1998**, *11*, 157.

[88] The Lewis concept has been called "the most widely used model in contemporary chemistry." Frenking, G.; Shaik, S. *J. Comput. Chem.* **2007**, *28*, 1.

[89] Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762. It is interesting to note that Lewis proposed a model for bonding in which electrons were positioned at the corners of a cube, so an octet meant an electron at every corner. Single bonds were constructed by allowing two cubes to share one edge (and thus one pair of electrons). In the case of a double bond, the two cubes shared a face (and therefore two pairs of electrons). The cubical model offered no simple representation for triple bonds, but a model based on tetrahedral arrangement of carbon valences was able to do so. For a discussion of the role of G. N. Lewis in the development of structural theory in organic chemistry, see Calvin, M. *J. Chem. Educ.* **1984**, *61*, 14; Zandler, M. E.; Talaty, E. R. *J. Chem. Educ.* **1984**, *61*, 124; Saltzman, M. D. *J. Chem. Educ.* **1984**, *61*, 119; Stranges, A. N. *J. Chem. Educ.* **1984**, *61*, 185; Pauling, L. *J. Chem. Educ.* **1984**, *61*, 201; Shaik, S. *J. Comput. Chem.* **2007**, *28*, 51.

It is helpful to distinguish here two types of information about organic molecules. The first type is physically *observable* data that are characteristic of entire molecules or samples of molecules. A molecular dipole moment belongs to this category. The second kind of information includes those *non-observable* constituent properties of a structure that, taken together, gives rise to the overall molecular properties. Partial atomic charges and bond dipole moments belong to this category.

A dipole moment is a vector quantity that measures the separation of electrical charge. Dipole moments have units of electrical charge times distance, and they are usually expressed in units of debye (D), with 1 D = 10^{-18} esu-cm.[90,91,92] Thus, a system consisting of two atoms, one with a partial charge of +0.1 and the other a partial charge of −0.1, located 1.5 Å apart would have a dipole moment of

$$0.1 \times \left(4.8 \times 10^{-10}\ \text{esu}\right) \times \left(1.5 \times 10^{-8}\ \text{cm}\right) = 0.72 \times 10^{-18}\ \text{esu} - \text{cm} = 0.72\ \text{D} \tag{1.23}$$

Molecular dipole moments can be measured by several techniques, including the determination of the dielectric constant of a substance as a gas or in a nonpolar solution and the study of the effect of electrical fields on molecular spectra (Stark effect).

Molecular dipole moments reflect aspects of molecular structure and bonding that are not directly observable. While the center of charge need not coincide with the center of an atom, that is a convenient first approximation. For example, the dipole moment of CH_3F is 1.81 D.[93,94] Since those atoms are 1.385 Å apart (Table 1.1), the partial charge can be calculated to be +0.27 on one of the atoms and −0.27 on the other.

If there is more than one bond dipole moment in a molecule, then the molecular dipole moment is the vector sum of the bond dipole moments. This idea can be useful in determining the structures and bonding of molecules. For example, Smyth determined that the three isomers of dichlorobenzene have dipole moments of 2.30, 1.55, and 0 D.[95] The dipole moment of chlorobenzene was known to be 1.61 D. Smyth reasoned that two C—Cl bond dipole moments add to each other in one isomer of dichlorobenzene, cancel each other partially in a second isomer, and cancel each other completely in the third isomer. Using the relationship

$$\mu = 2 \times 1.61 \times 10^{-18} \times \cos(0.5A) \tag{1.24}$$

[90] A full plus charge corresponds to $+4.80 \times 10^{-10}$ esu.

[91] For background on the theory and measurement of dipole moments, see Minkin, V. I.; Osipov, O. A.; Zhdanov, Y. A.in Hazzard, B. J., trans. *Dipole Moments in Organic Chemistry*; Vaughan, W. E.; Plenum Press: New York, 1970.

[92] Smyth, C. P. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. 1, Part IV; Wiley-Interscience: New York, 1972; pp. 397–429.

[93] McClellan, A. L. *Tables of Experimental Dipole Moments*, Vol. 2; Rahara Enterprises: El Cerrito, CA, 1974; p. 167.

[94] A value of 1.857 D is given in reference 34b. That is a more recent value and may be more accurate than the number used here. The values for the other methyl fluorides there are very similar to those given in reference 93.

[95] Smyth, C. P.; Morgan, S. O. *J. Am. Chem. Soc.* **1927**, *49*, 1030.

where A is the angle between the two bond dipole moments, Smyth calculated that the three isomers of dichlorobenzene had A values of 89°, 122°, and 180° and that these values corresponded to the ortho, meta, and para isomers of dichlorobenzene, respectively. The expected angle for *o*-dichlorobenzene is 60°, but Smyth argued that the apparent angle is larger because repulsion of the two adjacent chlorines enlarges the angle between the dipoles but does not appreciably alter the geometry of the benzene ring.[96]

A dipole moment associated with a covalent bond suggests that the electrons in the bond are not shared equally between the two atoms because one atom has a greater ability to attract the pair of shared electrons than the other. As a result, a bond can be described as having a mixture of both ionic and covalent bonding. It is useful to define a weighting parameter, λ, to indicate how much ionic character is mixed into the covalent bond. Thus,

$$\text{Polar Bond} = [\text{Covalent Bond}] + \lambda\,[\text{Ionic Bond}] \tag{1.25}$$

The percentage ionic character in the bond is related to λ by equation 1.26.[97]

$$\%\text{Ionic Character} = \frac{\lambda^2}{(1+\lambda^2)} \times 100\% \tag{1.26}$$

In an HCl molecule with partial charges of +0.17 on the hydrogen atom and −0.17 on the chlorine atom, the value of λ is 0.45.

Electronegativity and Bond Polarity

The polarity of covalent bonds is attributed to **electronegativity**, which Pauling defined as "the power of an atom in a molecule to attract electrons to itself."[98] It is generally the case that the bond dissociation energy of a polar diatomic molecule A–B is greater than the average of the bond dissociation energies of A–A and B–B.[99] For example, the average of the bond strengths of H_2 and Cl_2 is 81.1 kcal/mol, but the homolytic dissociation energy of H–Cl is 103.2 kcal/mol.[100,101] The increased bond dissociation energy can be attributed to the ionic character of the polar bond if the dissociation must overcome Coulombic effects in addition to covalent bonding interaction. Pauling obtained a set of electronegativity values (χ_P) by correlating standard bond dissociation energies between different atoms (A–B) with the average of the standard bond dissociation energies of identical atoms (A–A and B–B)

[96] Not only did this study identify which isomer of dichlorobenzene was which, but it also reinforced the view that benzene is a planar molecule. Alternative structures, such as Baeyer, Körner, or Ladenburg benzene, would have given different molecular dipole moments.

[97] Coulson, C. A. *Valence*; Clarendon Press: Oxford, England, 1952; p. 128.

[98] Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570.

[99] This idea was called the "postulate of the additivity of normal covalent bonds" by Pauling (reference 36).

[100] The premise that covalent bonds between atoms with different electronegativity values are stronger than the corresponding bonds between identical atoms is not always found to be true. Benson (reference 78) pointed out that the reaction of Hg_2 with Cl_2 to produce 2HgCl, is endothermic by at least 10 kcal/mol.

[101] Reddy, R. R.; Rao, T. V. R.; Viswanath, R. *J. Am. Chem. Soc.* **1989**, *111*, 2914.

TABLE 1.12 Comparison of Electronegativity Values[a]

Atom	χ_P	χ_M	χ_{spec}	χ_α	V_x	χ_{TO}
H	2.20	3.059	2.300	2.27	2.70	3.04
Li	0.91	1.282	0.912	0.94	0.75	2.17
Be	1.57	1.987	1.576	1.55	2.08	2.42
B	2.04	1.828	2.051	2.02	3.66	3.04
C	2.55	2.671	2.544	2.56	5.19	3.15
N	3.04	3.083	3.066	3.12	6.67	3.56
O	3.44	3.215	3.610	3.62	8.11	3.78
F	3.98	4.438	4.193	4.23	9.915	4.00
Na	0.93	1.212	0.869	0.95	0.65	2.15
Mg	1.31	1.630	1.293	1.32	1.54	2.39
Al	1.61	1.373	1.613	1.55	2.40	2.52
Si	1.90	2.033	1.916	1.87	3.41	2.82
P	2.19	2.394	2.253	2.22	4.55	3.16
S	2.58	2.651	2.589	2.49	5.77	3.44
Cl	3.16	3.535	2.869	2.82	7.04	3.50
K	0.82	1.032	0.734	0.84	0.51	2.07
Ca	1.00	1.303	1.034	1.11	1.15	2.20
Br	2.96	3.236	2.685	2.56	6.13	3.45
I	2.66	2.880	2.359	2.27	5.25	3.20

[a]Values for χ_P, χ_M, and χ_{spec} are from the compilation of Allen (reference 108). Values for χ_α are taken from reference 107; values of V_x are from reference 112, and values of χ_{TO} are from reference 114.

as shown in equation 1.27, where $\Delta\chi_P$ is the difference in χ values of A and B.[98] The electronegativity of fluorine was arbitrarily set to 4.0, and the electronegativities of other atoms were then determined (Table 1.12).

$$D_{A-B} = \sqrt{D_{A-A}D_{B-B}} + 30(\Delta\chi_P)^2 \tag{1.27}$$

On the one hand, the concept of electronegativity has been called "perhaps the most popular intuitive concept in chemistry."[102] On the other hand, it is difficult to determine precise values for electronegativity because a set of electronegativity values amounts to "a chemical pattern recognition scheme which is not amenable to direct physical measurement."[103] As seen above, different models can produce equivalent predictions, and many other approaches have been taken to describe and quantify electronegativity.[104]

The Pauling electronegativity scale is inherently dependent on measurements made on molecules, but there have been many attempts to define electronegativity as an atomic property. Sanderson's definition of electronegativity as "the effectiveness of the nuclear charge as sensed within an outer orbital vacancy" of an atom suggests that some atomic properties could be related to electronegativity.[105] Mulliken introduced an electronegativity scale (χ_M) based on the average of the ionization potential (I) and electron affinity

[102] Sen, K. D. in the Editor's Note to reference 110.

[103] Allen, L. C.; Egolf, D. A.; Knight, E. T.; et al. *J. Phys. Chem.* **1990**, *94*, 5602.

[104] Accorinti, H. L. *Found. Chem.* **2019**, *21*, 71.

[105] Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112, 227. See also Pauling, L. *J. Chem. Educ.* **1988**, *65*, 375.

(A) of atoms, that is $\chi = (I + A)/2$.[106] The rationale for this definition is that a greater electron affinity means a greater attraction of an atom for an electron from outside the atom; a greater ionization potential means a greater affinity of an atom for a nonbonded electron localized on the atom. Nagle introduced an electronegativity value based on atomic polarizability.[107] Allen proposed electronegativity values based on the average ionization potential of all of the *p* and *s* electrons on an atom.[108,109,110,111] Building on a suggestion of Yuan, Benson proposed another measure of electronegativity, V_x, which is calculated by dividing the number of valence electrons about an atom by its covalent radius.[112,113] Thus, seven electrons in the valence shell of a fluorine atom, divided by 0.706 Å, gives a V_x value of 9.915 for fluorine. Values of V_x were found to correlate well with a number of physical properties.[112] Tantardini and Oganov proposed a revised set of electronegativity values (designated here as χ_{TO}), based on a modification of Pauling's approach, that are more consistent with some thermochemical data.[114,115]

Table 1.12 compares the electronegativity values reported by Pauling (χ_P), Mulliken (χ_M), Allen (χ_{spec}), Nagle (χ_α), Benson (V_x), and Tantardini and Oganov (χ_{TO}).[112,116] The Pauling, Allen, and Nagle values are usually quite similar, suggesting that the properties of atoms in molecules may indeed be related to the properties of isolated atoms. However, while the Mulliken values are similar to the other values, there are some differences, particularly for hydrogen.[117] The Benson values are likewise larger in magnitude, but (except for hydrogen) they generally correlate well with the Pauling values. Finally, the Tantardini and Oganov values also correlate well ($R^2 = 0.97$) with the Pauling values for the atoms included in Table 1.12.

Theoretical studies provide additional perspectives on electronegativity. Parr and co-workers[118] defined a quantity, μ, as the "electronic chemical potential," which measures "the escaping tendency" of the electrons in the

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[106] Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782; **1935**, *3*, 573.

[107] Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741.

[108] Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003. Allen called this definition of electronegativity "the third dimension of the periodic table." For a summary, see Borman, S. A. *Chem. Eng. News* **1990** (Jan 1), 18. Also see Politzer, P.; Murray, J. S.; Grice, M. E. *Collect. Czech. Chem. Commun.* **2005**, *70*, 550; Murphy, L. R.; Meek, T. L.; Allred, A. L.; et al. *J. Phys. Chem. A* **2000**, *104*, 5867.

[109] For other treatments of electronegativity, see Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182; Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 223; Li, K.; Wang, X.; Xue, D. *J. Phys. Chem. A* **2008**, *112*, 7894.

[110] For a summary of these electronegativity scales, see Mullay, J. in Sen, K. D.; Jorgensen, C. K., Eds. *Electronegativity*; Springer-Verlag: Berlin, 1987.

[111] Campanelli, A. R.; Domenicano, A.; Ramondo, F.; et al. *J. Phys. Chem. A.* **2004**, *108*, 4940 developed a set of group electronegativities based on the effect of a substituent on a benzene ring.

[112] Yuan, H. C. *Acta Chim. Sin.* **1964**, *30*, 341; cf. reference 112; *Chem. Abstr.* **1965**, *62*, 2253h.

[113] Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255; *J. Am. Chem. Soc.* **1989**, *111*, 2480; *J. Phys. Chem.* **1989**, *93*, 3304. See also Luo, Y.-R.; Pacey, P. D. *J. Am. Chem. Soc.* **1991**, *113*, 1465 and references therein; Luo, Y.-R.; Benson, S. W. *Acc. Chem. Res.* **1992**, *25*, 375.

[114] Tantardini, C.; Oganov, A. R. *Nature Commun.* **2021**, *12*, 2087.

[115] See also the commentary by Accorinti, H.; Labarca, M. *J. Chem. Educ.* **2020**, *97*, 3474.

[116] Table 1.12 lists χ values for atoms only, but it is also possible to calculate "group electronegativities" to reflect the net effect of a group of atoms. For a tabulation of group electronegativities calculated by a variety of methods, see Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101. As an example, the group electronegativity of the CH_3 group is about 2.3, while that for CF_3 is about 3.5.

[117] Franco-Pérez, M.; Gázquez, J. L. *J. Phys. Chem. A* **2019**, *123*, 10065 analyzed Pauling and Mulliken electronegativity values using DFT calculations (to be discussed in Chapter 2).

[118] Parr, R. G.; Donnelly, R. A.; Levy, M.; et al. *J. Chem. Phys.* **1978**, *68*, 3801.

system.[119] The value of μ is approximately the same as $(I + A)/2$, the Mulliken electronegativity, so the value χ_M has been termed *absolute* electronegativity.[119] Closely related to the concept of electronegativity is the concept of **chemical potential**, which is also given the symbol μ and which is defined as $\partial E/\partial N$, where E is the energy of the system and N is the number of electrons.[120,121,122] Parr and co-workers defined

$$\chi = -\mu = -\delta E/\delta\rho \tag{1.28}$$

where the energy is related to a theoretical treatment of electron density.[123,124]

As a result of the many theoretical treatments, chemists now find themselves using one term to mean different things, since "the electronic chemical potential, μ, … is an entirely different chemical quantity" from the concept of electronegativity as the origin of bond polarity.[122] As Pearson noted,

> The fact that there are two different measures both called (electronegativity) scales creates considerable opportunity for confusion and misunderstanding. Since the applications are so different, it is not a meaningful question to ask which scale is more correct. Each scale is more correct in its own area of use.[119]

Usually organic chemists use the term *electronegativity* in the sense originally proposed by Pauling. Still, the discussion here illustrates that a simple idea that is intuitively useful in understanding some problems of structure and bonding may become more difficult to apply with attempts to define it more fully.

Complementary Theoretical Models of Bonding

The Lewis model assumes that electron pairs are localized between two specific atoms (for bonds) or on an individual atom (for a nonbonded electron pair). The theoretical basis for this model is known as **valence bond (VB) theory**, which describes formation of a structure by bringing together complete atoms that then interact to form bonds.[125] In **molecular orbital (MO) theory** on the other hand, molecules are thought to assemble when nuclei (or nuclei and filled inner shells) and electrons are brought together to produce orbitals for the entire array of atomic particles.[97] MO theory does not generate discrete chemical bonds. Rather, it generates a set of orbitals that allow electrons to roam over many nuclei, perhaps an entire molecule, without being restricted to any particular pair of nuclei.

Both VB and MO theories utilize mathematical expressions that can rapidly become complex, even for simple organic molecules. Furthermore, VB

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[119] Pearson, R. G. *Acc. Chem. Res.* **1990**, *23*, 1.

[120] Pritchard, H. O.; Sumner, F. H. *Proc. Roy. Soc. (London)* **1956**, *A235*, 136.

[121] Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

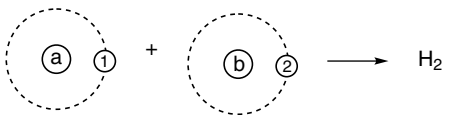
[122] Allen, L. C. *Acc. Chem. Res.* **1990**, *23*, 175.

[123] Here ρ is actually a functional (Chapter 2). For an introduction, see (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; (b) March, N. H. *Electron Density Theory of Atoms and Molecules*; Academic Press: New York, 1991.

[124] For a theoretical approach to electronegativity and hardness, see Sánchez-Márquez, J.; Garcia, V.; et al. *J. Phys. Chem. A* **2020**, *124*, 4700.

[125] A summary of the development of VB theory and a discussion of the merits of VB and MO theories was given by Klein, D. J.; Trinajstić, N. *J. Chem. Educ.* **1990**, *67*, 633.

FIGURE 1.6
Schematic representation for formation of a hydrogen molecule from two hydrogen atoms.



theory and MO theory are usually described with different symbols, so it can be difficult to distinguish their similarities and differences. Therefore, it may be useful to consider first a very simple bonding problem, the formation of a hydrogen molecule from two hydrogen atoms. The principles will be the same as for larger molecules, but the comparison of the two approaches will be more apparent in the case of H_2.

The discussion that follows has been adapted from several introductory texts on bonding, which may be consulted for more details.[126] Consider two isolated hydrogen atoms, as shown in Figure 1.6. Each atom has one electron in its 1*s* orbital, and the wave equation for that orbital is known from quantum mechanics. Electron 1 is initially associated with hydrogen nucleus *a*, and electron 2 is associated with hydrogen nucleus *b*. Bringing the two atoms together allows bonding to occur, as shown in Figure 1.6.

The valence bond method initially used by Heitler and London proposed one possible equation to describe the electron distribution in the hydrogen molecule as[127]

$$\Psi_1 = ca(1)b(2) \tag{1.29}$$

in which c is a constant, $a(1)$ is the wave function for electron 1 in a 1*s* orbital on hydrogen nucleus *a*, and $b(2)$ is the wave function for electron 2 in a 1*s* orbital on hydrogen nucleus *b*. Since the electrons are indistinguishable, it should be equally acceptable to write

$$\Psi_2 = ca(2)b(1) \tag{1.30}$$

Both descriptions are possible, so both need to be included in the wave function for the molecule. Therefore, Heitler and London wrote that

$$\Psi_{VB} = ca(1)b(2) + ca(2)b(1) \tag{1.31}$$

The constants are chosen so that the overall wave function is properly normalized and antisymmetric with respect to spin.

The molecular orbital approach to describing hydrogen also starts with two hydrogen nuclei (*a* and *b*) and two electrons (1 and 2), but it makes no initial assumption about the location of the two electrons.[126] Solving (in principle) the Schrödinger equation for the molecular orbitals around the pair of nuclei would lead to a wave equation for *one* electron in a resulting MO:

$$\Psi = c_1a(1) + c_2b(1) \tag{1.32}$$

Note that electron 1 is associated with both nuclei. Similarly,

[126] For examples, see reference 10, p. 517 ff.; Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; John Wiley & Sons, Inc.: New York, 1944; p. 212 ff. The mathematics is described in some detail in Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. I. Electronic Structure of Molecules*; McGraw-Hill: New York, 1963.

[127] Heitler, W.; London, F. *Z. Physik* **1927**, *44*, 455.

$$\Psi = c_1 a(2) + c_2 b(2) \tag{1.33}$$

The combined MO wave function was taken to be the product of the two one-electron wave functions:

$$\Psi_{MO} = \Psi_1 \Psi_2 = c_1^2 a(1)a(2) + c_2^2 b(1)b(2) + c_1 c_2 [a(1)b(2) + a(2)b(1)] \tag{1.34}$$

Ψ_{MO} is more complex than Ψ_{VB}; in fact, Ψ_{VB} is incorporated into Ψ_{MO}. Specifically, the third term of Ψ_{MO} in equation 1.34 is the same as Ψ_{VB} if the product of $c_1 c_2$ constants is numerically the same as c in equation 1.31. What is the physical significance of the differences in Ψ_{VB} and Ψ_{MO}? Ψ_{MO} includes two terms that Ψ_{VB} does not: $a(1)a(2)$ and $b(1)b(2)$. Each of these terms represents a **configuration** (arrangement of electrons in orbitals) in which *both* electrons are formally localized in what had been a 1*s* orbital on *one* of the hydrogen atoms. Therefore, these terms describe ionic structures. In other words, $a(1)a(2)$ represents $a{:}^- b^+$, and $b(1)b(2)$ represents $a^+ b{:}^-$. The MO treatment appears to give large weight to terms that represent electronic configurations in which both electrons are on one nucleus, while the VB treatment ignores these terms.

Which approach is correct? The usual measure of the "correctness" of any calculation is how well it agrees with a reported physical property. In the case of H_2, a relevant property is the homolytic bond dissociation energy. The simple VB calculation described here gave a value of 3.14 eV (72.4 kcal/mol) for H_2 dissociation.[126] The simple MO calculation gave a value of 2.70 eV (62.3 kcal/mol). The experimental value is 4.75 eV (109.5 kcal/mol).[126] Obviously, neither calculation is correct—unless one takes order of magnitude agreement as satisfactory; in that case, both calculations are correct.

It may seem reasonable that the MO method gives a result that underestimates the H_2 bond dissociation energy because the wave equation includes patterns of electron density that resemble ionic species such as $a^+ b{:}^-$. But why is the VB result also in error? The answer seems to be that, while the MO approach places too much emphasis on these ionic electron distributions, the VB approach underutilizes them. A strong bond may require that both electrons spend a lot of time in the region of space between the two nuclei. That arrangement may then make it more likely that the two electrons will, at some instant, be on the same atom.[128] Thus, the accuracy of the VB calculation might improve with the addition of terms that keep the electrons closer together between the nuclei.

Similarly, the MO calculation could be improved by adding some terms that would decrease the ionic character of the bonding orbital. For example, including a description of the hydrogen atoms in which each electron has some probability of being in an orbital higher than the 1*s* orbital would decrease excessively repulsive interactions in the final molecular orbital.[129] Other changes are possible as well. Table 1.13 shows how the calculated stability of H_2 varies according to the complexity of the MO calculation.[130,131] Including 13 terms makes a major improvement. From that point on almost

[128] Colloquial terminology is used here to be consistent with the level of presentation of the theory.

[129] This procedure is called *configuration interaction* (to be discussed in Chapter 2); cf. Coffey, P.; Jug, K. *J. Chem. Educ.* **1974**, *51*, 252. See also Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.

[130] (a) Data from McWeeny, R. *Coulson's Valence*, 3rd ed.; Oxford University Press: Oxford, England, 1979; p. 120 and references therein. (b) See also Davis, J. C., Jr. *Advanced Physical Chemistry*; Ronald Press: New York, 1965; p. 426.

[131] For additional references, see King, G. W. *Spectroscopy and Molecular Structure*; Holt, Rinehart and Winston: New York, 1964; p. 149.

TABLE 1.13 Calculated Values for H_2 BDE

Calculation Method	*DE* (Calc.)
Simple valence bond theory	3.14 eV
Simple molecular orbital theory	2.70 eV
James-Coolidge (13 terms)	4.72 eV
Kolos-Wolniewicz (100 terms)	4.7467 eV
Experimental value	4.7467 eV

Source: Reference 130.

any change decreases the stability of the calculated structure almost as much as it increases it, but small gains can be won. An MO equation with 50 terms did quite well. Similarly, a VB calculation with a large number of terms can also produce an answer that is within experimental error of the measured value.[132,133] If enough terms are included, therefore, the two methods can produce equivalent results.[97,134,135]

Several conclusions may be drawn from this analysis:

1. Neither *simple* VB theory nor *simple* MO theory produces a value for the dissociation energy (*DE*) that is very close to the experimental value.
2. Both VB and MO theories can be modified to produce more accurate results. Even for a simple molecule such as H_2, however, many terms may be required to produce an acceptable value for the property of interest.
3. As both simple VB theory and simple MO theory are modified to agree more closely with experimental data, they must necessarily begin to provide more similar descriptions of an observable property. Hiberty noted that "Done well, done rigorously, VB and MO theory converge to the same exact description."[136,137]

Computational chemistry has advanced far beyond simple VB and simple MO theories. They still play important roles in organic chemistry, however, because their conceptual accessibility provides a foundation for understanding more advanced theoretical results. It is easy to visualize the interactions represented by equation 1.34, as well as the physical situation suggested by equation 1.31. It is much more difficult for us to envision the interactions

[132] For a study involving more than 7000 terms, see Sims, J. S.; Hagstrom, S. A. *J. Chem. Phys.* **2006**, *124*, 094101.

[133] For a discussion of results obtained with different theoretical methods, see Rychlewski, J. *Explicitly Correlated Wave Functions in Chemistry and Physics*; Springer Science+Business Media: Dordrecht, The Netherlands, 2003; pp. 107–110.

[134] Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1968**, *49*, 404.

[135] For a theoretical discussion of the origin of bonding in H_2, see Bacskay, G. B.; Nordholm, S. *J. Phys. Chem. A* **2017**, *121*, 9330; Nordholm, S.; Bacskay, G. B. *Molecules* **2020**, *25*, 2667.

[136] For a conversation about VB and MO theories, see Hoffmann, R.; Shaik, S.; Hiberty, P. C. *Acc. Chem. Res.* **2003**, *36*, 750.

[137] Hiberty, P. C.; Shaik, S. in Frenking, G.; Shaik, S., Eds. *The Chemical Bond: Fundamental Aspects of Chemical Bonding*; John Wiley & Sons: Hoboken, NJ, 2014; pp. 69–90. "Simple MO level describes the H_2 bond as being too ionic, while the simple HLVB level defines it as being purely covalent. Both theories converge to the right description when CI is introduced. It follows that the *accurate description of two-electron bonding is half-way in-between the simple MO and simple HLVB levels; elaborated MO and VB levels become equivalent and converge to the same description, in which the bond is mostly covalent but has a substantial contribution from ionic structures*."

involved in a 50- or 100-term wave function.[138] Therefore, the most useful model may be one that is sufficiently accurate for the purpose at hand yet is still simple enough to provide an understanding of what the model describes.[139] Otherwise the model is a "black box," and the chemist has no understanding of what it does and cannot be confident that the answers it produces are physically reasonable.

Pictorial Representations of Bonding Concepts

The MO and VB methods described above illustrate the use of mathematical models in chemistry. Chemists often use pictorial representations of computational results. Figure 1.7 shows the combination of two atomic hydrogen 1*s* orbitals to make two new molecular orbitals, the familiar σ and σ* orbitals of H_2. Each horizontal line represents the energy associated with a particular atomic wave function. The small arrows represent electrons, and the direction of each arrow indicates the spin quantum number of the electron it represents. There can be no more than two arrows on each horizontal line (i.e. two electrons in the same atomic orbital), and then only if the arrows point in opposite directions (meaning that the two electrons have paired spins). The σ MO is lower in energy than the original hydrogen 1*s* orbitals, and the σ* orbital is higher in energy.[140] The σ orbital is a bonding orbital, and population of the σ MO with two electrons produces a stable H_2 molecule. On the other hand, σ* is an antibonding orbital, and population of this orbital with an electron destabilizes the molecule.

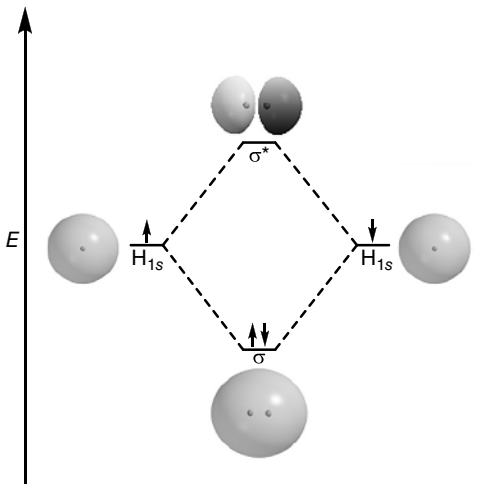


FIGURE 1.7
Combination of atomic hydrogen orbitals to produce molecular hydrogen.

[138] Coulson, C. A. *Rev. Mod. Phys.* **1960**, *32*, 170 noted that "Even in the five-term James-Coolidge function… there is nothing easily visualized about the wave function."

[139] Weisberg, M. *When Less is More: Tradeoffs and Idealization in Model Building*; Ph.D. Dissertation, Stanford University, 2003. See also Weisberg, M. *Phil. Sci.* **2004**, *71*, 1071.

[140] This figure is somewhat stylized since it shows the σ and σ* orbitals symmetrically displaced above and below the energy of the initial hydrogen 1*s* orbitals. The σ* should be more antibonding than the σ orbital is bonding. For details, see Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; p. 12 ff. In addition, Willis, C. J. *J. Chem. Educ.* **1988**, *65*, 418 calculated that the H–H bond energy is only about 19% of the energy gained by moving two electrons from hydrogen 1*s* orbitals to the H_2 σ bonding orbital. The other 81% of that energy is consumed in offsetting electrical repulsion within the molecule.

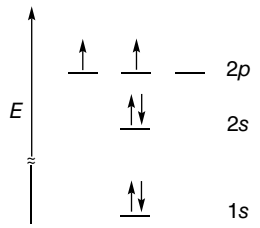


FIGURE 1.8
Energy levels of atomic carbon orbitals.

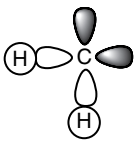


FIGURE 1.9
A simple bonding model of "methane" as CH_2.

Figure 1.8 shows the atomic orbitals of an isolated carbon atom. Combining this energy level diagram for carbon with the bonding model shown schematically in Figure 1.7 suggests that C–H bonds could be formed by pairing an unpaired electron in a 2*p* orbital on carbon with an electron from a hydrogen 1*s* orbital (Figure 1.9). While this result is the logical extension of the bonding model illustrated in Figure 1.8, there is abundant experimental data indicating that methane has the molecular formula CH_4, not CH_2.

sp^3 Hybridization

Once a model is fixed in our minds, it is almost impossible to discard it unless another model is available to take its place. Instead, models are almost always modified to fit new data—and that is the case here. The concept of **hybridization**, which was introduced by Pauling, changes our mental picture of atomic orbitals of carbon to a more useful model.[141,142,143,144,145,146] Figure 1.10(a) shows promotion of an electron from a 2*s* orbital to a 2*p* orbital, leading to the configuration in Figure 1.10(b). Combining the *s* and *p* orbitals produces four sp^3 hybrid orbitals that are equal in energy, as shown in Figure 1.10(c).[147,148,149] Promotion of the electron requires about 96 kcal/mol, but this is more than offset by the additional stabilization (about 200 kcal/mol) gained by forming two additional C—H bonds.[150] Figure 1.11 shows the contours of one of the sp^3 orbitals as well as those of carbon 2*s*, 2*p*, *sp*, and sp^2 hybrids.[151]

The wave functions of the hybrid orbitals are shown in equations 1.35–1.38 (where C_{2s} represents the wave function for a 2*s* orbital on carbon, etc.).[152] Each of the sp^3 orbitals in equations 1.35–1.38 has a large lobe and a small lobe. The two lobes have a different mathematical sign, and the four large lobes point toward the corners of a regular tetrahedron.[153]

$$\phi_{sp^3_{(1)}} = \frac{1}{2}\left(C_{2s} + C_{2p_x} + C_{2p_y} + C_{2p_z}\right) \tag{1.35}$$

[141] (a) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367; reference 36, p. 118; (b) See also Slater, J. C. *Phys. Rev.* **1931**, *37*, 481.

[142] Barbier, C.; Berthier, G. *Adv. Quantum Chem.* **2000**, *36*, 1.

[143] Hsu, C.-Y.; Orchin, M. *J. Chem. Educ.* **1973**, *50*, 114.

[144] Root, D. M.; Landis, C. R.; Cleveland, T. *J. Am. Chem. Soc.* **1993**, *115*, 4201.

[145] Bingel, W. A.; Lüttke, W. *Angew. Chem. Int. Ed.* **1981**, *20*, 899.

[146] For a reconsideration of the concept of hybridization, see Magnusson, E. *J. Am. Chem. Soc.* **1984**, *106*, 1177. Lamoureux, G.; Ogilvie, J. F. *Quim. Nova* **2019**, *42*, 812; *ibid*, 817.

[147] Matteson, D. S. *Organometallic Reaction Mechanisms of the Nontransition Elements*; Academic Press: New York, **1974**; p. 5.

[148] Ogilvie, J. F. *J. Chem. Educ.* **1990**, *67*, 280.

[149] Strictly speaking, there are hybridized *orbitals* but not hybridized *atoms*. However, organic chemists frequently use the term "sp^3-hybridized carbon" to refer to a carbon atom with four single bonds.

[150] See the discussion in Hameka, H. F. *Quantum Theory of the Chemical Bond*; Hafner Press: New York, 1975; p. 216 ff.

[151] The orbital contours were generated with *CAChe*™ visualization software.

[152] Bernett, W. A. *J. Chem. Educ.* **1969**, *46*, 746.

[153] The shapes of these orbitals are quite different from the representations shown in many chemistry textbooks. See Allendoerfer, R. D. *J. Chem. Educ.* **1990**, *67*, 37.

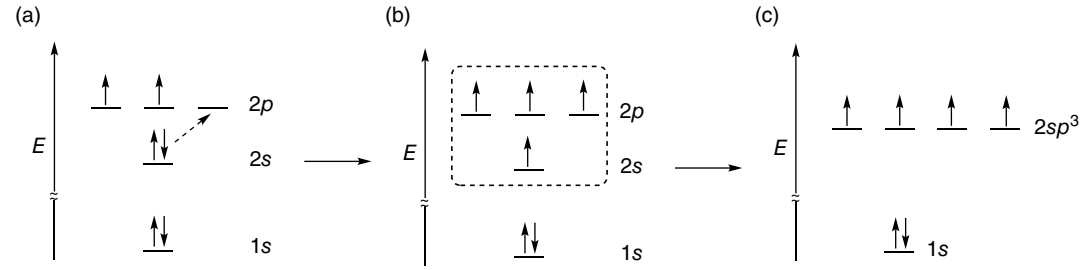


FIGURE 1.10
Hybridization of carbon orbitals to produce sp^3 hybrid orbitals.

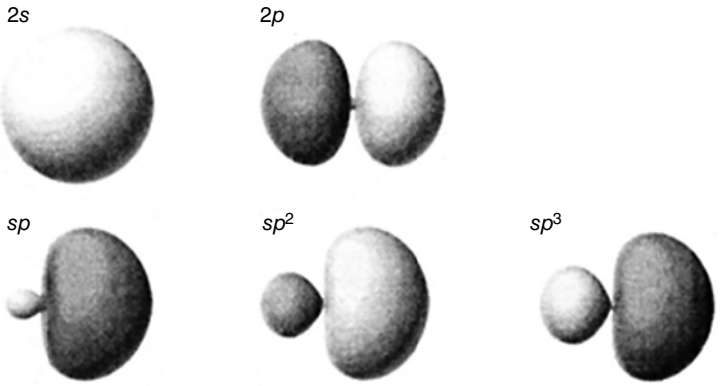


FIGURE 1.11
Shapes and relative sizes of carbon orbitals.

$$\phi_{sp^3_{(2)}} = \frac{1}{2}\left(C_{2s} + C_{2p_x} - C_{2p_y} - C_{2p_z}\right) \quad (1.36)$$

$$\phi_{sp^3_{(3)}} = \frac{1}{2}\left(C_{2s} - C_{2p_x} + C_{2p_y} - C_{2p_z}\right) \quad (1.37)$$

$$\phi_{sp^3_{(4)}} = \frac{1}{2}\left(C_{2s} - C_{2p_x} - C_{2p_y} + C_{2p_z}\right) \quad (1.38)$$

Now bonding in methane can be described as a set of four C—H bonding orbitals formed by combining each of the four carbon sp^3 hybrid orbitals with a 1*s* orbital on hydrogen. A qualitative energy diagram for the process is shown in Figure 1.12. The four sp^3 hybrid orbitals point to the corners of a tetrahedron, which is consistent with CH_4 having tetrahedral geometry (Figure 1.13).[34,154]

It is important to note in this discussion that *we* hybridize the atomic orbitals to produce a different model. As Ogilvie noted,

> According to *Coulson's Valence*, "hybridization is not a physical effect but merely a feature of [a] theoretical description"…. Despite the fact that many authors of textbooks of general chemistry have written that CH_4 has a tetrahedral structure because of sp^3 hybridization, there neither exists now, nor has ever existed, any quantitative experimental or theoretical justification of such a statement.[148]

[154] Although it is usually rounded to 109.5°, the tetrahedral bond angle is 109°28′, which corresponds to 109.47°. A method for the calculation of *sp*, sp^2, and sp^3 interorbital angles was given by Duffey, G. H. *J. Chem. Educ.* **1992**, *69*, 171.

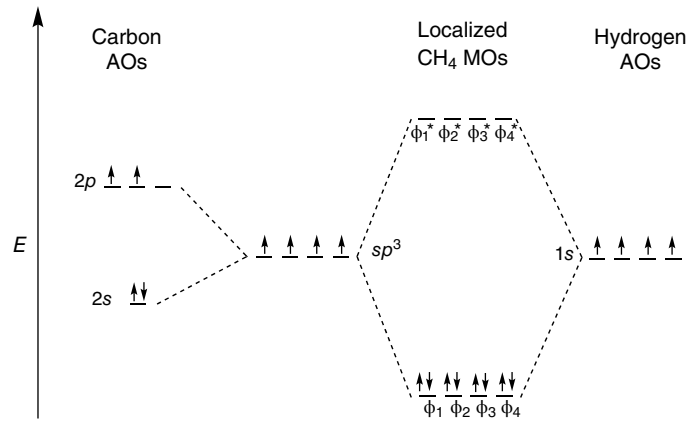
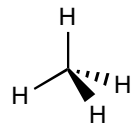


FIGURE 1.12
Schematic representation of mixing of hydrogen 1*s* and carbon sp^3 orbitals to make localized MOs of methane. (Adapted with permission from reference 172. © 1977 American Chemical Society.)



$l_{C\text{-}H}$ = 1.091 Å

FIGURE 1.13
Experimental geometry of methane.

In addition, Matteson noted that

> Hybridization is not something that atoms do or have done to them. It is purely a mental process gone through by the chemist, who wants to group atomic orbitals according to their symmetry properties so he can talk about one localized bond and ignore the rest. Hybridization does not change the shape of the electron distribution in any atom.[147]

Some have proposed that the concept of orbital hybridization should be "retired," but Pauling and others strongly opposed this view.[155,156,157,158,159] In addition, the widespread use of natural bond orbital (NBO) analysis has given a new utility to the concept of hybrid orbitals.[157,160,161]

Are There sp^3 Hybrid Orbitals in Methane?

The hybridization model is so ingrained in organic chemistry that the concepts of sp^3 hybridization and tetrahedral geometry are often used interchangeably.[144] There is an experimental result that initially may seem inconsistent with that equivalence, however. **Photoelectron spectroscopy** (PES) is a method to determine the energies of electrons ejected from molecules or atoms by high-energy photons.[162,163] As shown in Figure 1.14, the difference between the energies of an ejected electron (energy out) and the energy of

[155] Grushow, A. *J. Chem. Educ.* **2011**, *88*, 860.

[156] Pauling, L. *J. Chem. Educ.* **1992**, *69*, 519.

[157] Landis, C. R.; Weinhold, F. *J. Chem. Educ.* **2012**, *89*, 570.

[158] Hiberty, P. C.; Volatron, F.; Shaik, S. *J. Chem. Educ.* **2012**, *89*, 575.

[159] Alabugin, I. V.; Bresch, S.; dos Passos Gomes, G. *J. Phys. Org. Chem.* **2015**, *28*, 147.

[160] Weinhold, F.; Landis, C. R. *Chem. Educ. Res. Pract.* **2001**, *2*, 91.

[161] See, for example, Stewart, J. J. P. *J. Mol. Model.* **2019**, *25*, 7.

[162] A related procedure is called electron spectroscopy for chemical analysis **(ESCA)**. For a discussion of PES, ESCA, and similar techniques, see Baker, A. D.; Brundle, C. R.; Thompson, M. *Chem. Soc. Rev.* **1972**, *1*, 355; Baker, A. D. *Acc. Chem. Res.* **1970**, *3*, 17; Hercules, D. A. *J. Chem. Educ.* **2004**, *81*, 1751. Another technique, Auger spectroscopy, is discussed in reference 164.

[163] Bock, H.; Mollère, P. D. *J. Chem. Educ.* **1974**, *51*, 506; Baker, A. D. *Acc. Chem. Res.* **1970**, *3*, 17; Ballard, R. E. *Photoelectron Spectroscopy and Molecular Orbital Theory*; John Wiley & Sons: New York, 1978.

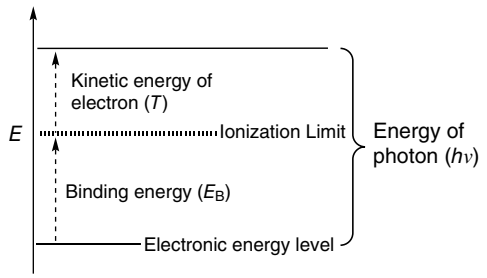


FIGURE 1.14
Energy relationships in photoelectron spectroscopy.

the photon causing the displacement (energy in) is taken to be a measure of the binding energy (E_B) that holds an electron in the molecule or atom. This relationship is shown in equation 1.39, where $h\nu$ is the energy of the photon, T is the kinetic energy of the electron ejected from the molecule, and E_B is the binding energy of the electron in the molecule. It seems intuitive to associate the number and position of binding energy levels in a structure with the energies of its atomic or molecular orbitals.[164] It is important to note, however, that PES does not directly measure energy levels of electrons in the pre-ionized state. Rather, the experiments indicate how the electron distribution in the molecule changes upon ionization.[165]

$$h\nu = T + E_B \tag{1.39}$$

Figure 1.15 shows a photoelectron spectrum of methane.[166] One peak at very high binding energy (>290 eV) is characteristic of molecules with electrons in carbon 1*s* orbitals. The other two peaks are at lower binding energy: one is at 23.0 eV, and the other is at 12.7 eV. Therefore, this experiment might suggest that the electrons in methane are in three different energy levels, one energy level corresponding to the carbon 1*s* electrons, and two different energy levels corresponding to the other electrons in the molecule. That conclusion conflicts with a simple bonding model in which methane is constructed of four equivalent C(sp^3)–H(1*s*) bonds, each produced by overlap of an sp^3 hybrid orbital on a carbon atom with a 1*s* orbital (Figure 1.12). Such a bonding model suggests only two peaks in the photoelectron spectrum, one corresponding to C_{1s} and the other to the four equivalent H_{1s}–C_{sp^3} bonding pairs.

One important aspect of MO theory—the concept of **symmetry-correct molecular orbitals**—not only makes it possible to explain the PES spectrum of methane but, in fact, requires it. A fundamental property of MOs is that they have the full symmetry of the basis set of atomic orbitals used to generate the molecular orbitals.[167] This means that the molecular orbitals must be either symmetric or antisymmetric with respect to the symmetry operations

[164] This relationship is known as Koopmans' theorem. Cf. Albridge, R. G. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. I, Part IIID; Wiley-Interscience: New York, 1972; p. 307.

[165] Truhlar, D. G.; Hiberty, P. C.; Shaik, S.; et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 12332.

[166] Hamrin, K.; Johansson, G.; Gelius, U.; et al. *Chem. Phys. Lett.* **1968**, *1*, 613.

[167] The term *basis set* refers to the set of atomic orbitals used to construct the molecular orbitals.

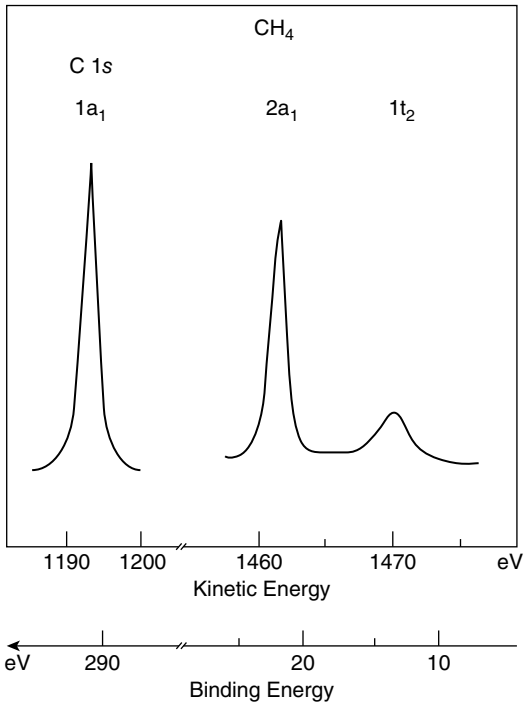


FIGURE 1.15
PES spectrum of methane. (Adapted with permission from reference 166. © 1968 Elsevier.)

provided for by the symmetry group of the atomic orbitals.[168] If each C—H σ bond formed by overlap of an sp^3 orbital on a carbon atom with a 1*s* orbital on a hydrogen atom is considered to be an MO, then each of these MOs lacks the full symmetry of the basis set of *s* and *p* atomic orbitals.[169,170]

Symmetry-correct MOs for methane can be calculated directly from the unhybridized orbitals: a carbon 2*s* orbital, three carbon 2*p* orbitals, and four hydrogen 1*s* orbitals.[152,171,172,173,174] The resulting molecular orbitals are given in equations 1.40–1.43, where H_1 is the hydrogen 1*s* orbital on hydrogen 1, and so on.[152] Figure 1.16 shows a qualitative MO energy level diagram, and

[168] The terms *symmetric* and *antisymmetric* mean that the result of any symmetry operation will be an orbital of the same type and in the same location as before the transformation. If the orbital is symmetric with respect to that transformation, then the orbital produced will also have + and − lobes in the same locations as before; if the orbital is antisymmetric, then the resulting orbital will have + lobes where − lobes were, and vice versa. All MOs must be either symmetric or antisymmetric. If a symmetry operation that corresponds to an element of symmetry of the basis set of atomic orbitals transforms a lobe to a position in space in which there was not a lobe beforehand, that MO is said to be **asymmetric** (without symmetry) and is not allowable as a symmetry-correct MO for the molecule. These topics will be discussed in more detail in Chapters 2 and 11.

[169] For the VB explanation of the methane PES spectrum, see (a) reference 156; (b) Shaik, S. S.; Hiberty, P. C. *A Chemist's Guide to Valence Bond Theory*; Wiley-Interscience: New York, 2008; pp. 104–106.

[170] For a detailed discussion, see reference 160.

[171] Flurry, R. L., Jr. *J. Chem. Educ.* **1976**, *53*, 554; Cohen, I.; Del Bene, J. *J. Chem. Educ.* **1969**, *46*, 487.

[172] Hoffman, D. K.; Ruedenberg, K.; Verkade, J. G. *J. Chem. Educ.* **1977**, *54*, 590.

[173] Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975; p. 21 ff.

[174] Note that the four molecular orbitals are not tetrahedral in shape. Rather, each is either symmetric or antisymmetric with respect to the symmetry operations of the T_d point group.

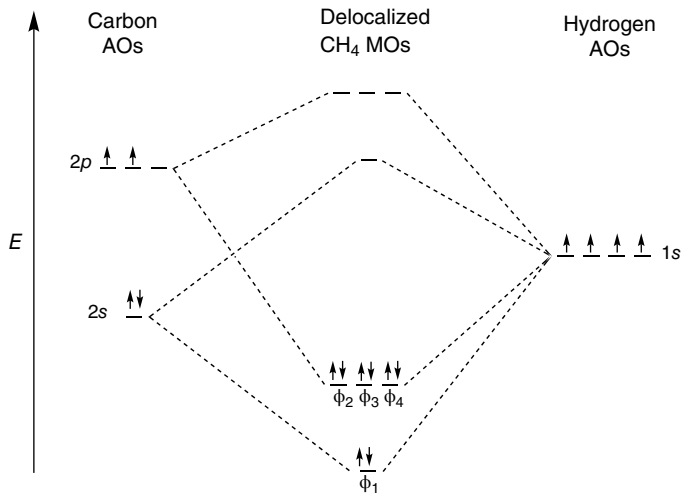


FIGURE 1.16
Mixing of atomic orbitals on carbon with hydrogen 1*s* orbitals to make molecular orbitals of methane. (Adapted with permission from reference 172. © 1977 American Chemical Society.)

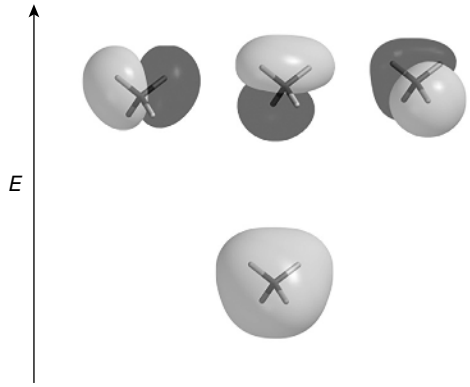


FIGURE 1.17
Bonding MOs for methane.

Figure 1.17 represents the three-dimensional electron contour plot for the orbitals.[175] One MO (ϕ_1) represents a bonding interaction of the carbon 2*s* orbital with all four of the hydrogen 1*s* orbitals, while the other orbitals each have bonding over only a portion of the structure. Therefore, ϕ_1 is lower in energy than the other three. These figures indicate two different energy levels for the bonding electrons, consistent with the two PES bands observed.

$$\phi_1 = 0.545C_{2s} + 0.272(H_1 + H_2 + H_3 + H_4) \quad (1.40)$$

$$\phi_2 = 0.545C_{2p_x} + 0.272(H_1 + H_2 - H_3 - H_4) \quad (1.41)$$

$$\phi_3 = 0.545C_{2p_y} + 0.272(H_1 - H_2 + H_3 - H_4) \quad (1.42)$$

$$\phi_4 = 0.545C_{2p_z} + 0.272(H_1 - H_2 - H_3 + H_4) \quad (1.43)$$

[175] Images were prepared using semiempirical MO calculations with *Spartan '20*. For a more complete discussion of the molecular orbitals of methane, see Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; p. 68.

It is important to recognize that this discussion is not a rejection of valence bond theory.[176] As Shaik and Hiberty pointed out, a correct valence bond theory description of the bonding in methane also produces a result that is consistent with the PES experiment.[177] Rather, the PES result is a reminder that simple illustrations of C–H bonds formed by overlap of hydrogen 1*s* and carbon sp^3 orbitals should not be considered pictures of reality.[178]

Hybridization and Molecular Geometry

The sp^3 hybridization model is often associated with the tetrahedral geometry of methane, but that does not mean that the geometry results from the hybridization. The geometry could be explained just as well from the Lewis structure of methane with **valence shell electron pair repulsion** (VSEPR) theory.[179,180,181] The VSEPR method does not require the use of atomic or molecular orbitals; it is simply a solution to a problem in which the mutually repulsive points (electron pairs) are arranged as far apart from each other as possible on the surface of a sphere.[182,183,184]

Using the VSEPR theory to predict the geometry of methane involves asking one question: What is the most stable arrangement for four pairs of electrons bonded to a central atom? The tetrahedral arrangement provides for the maximum distance between each electron pair and the other three electron pairs, so this arrangement should be the most stable.[185,186] Methane does not have a molecular dipole moment, even though each C—H bond might be slightly polar. Any bond dipole moment corresponding to one C–H bond aligned with the *x*-axis must therefore be canceled by the vector sum of the projections of the other three C–H bond dipole moments along the *x*-axis. Thus, the cosine of an H–C–H bond angle must be $-\frac{1}{3}$, making the bond angle 109°28′.

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[176] Pauling, L. *J. Chem. Educ.* **1992**, *69*, 519 argued that the photoelectron spectrum of methane is consistent with sp^3 hybridization for methane.See also the discussion by Simons, J. *J. Chem. Educ.* **1992**, *69*, 522.

[177] For a conversation about VB and MO theories, see Hoffmann, R.; Shaik, S.; Hiberty, P. C. *Acc. Chem. Res.* **2003**, *36*, 750.

[178] Hoffmann, R. *C&EN* **2013**, *91* (issue 36), 28 wrote "Accept that at the limits a bond will be a bond by some criteria, maybe not others. Respect chemical tradition, relax, and instead of wringing your hands about how terrible it is that this concept cannot be unambiguously defined, have fun with the fuzzy richness of the idea."

[179] For a discussion of VSEPR, see reference 9; Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295; Burdett, J. K. *Chem. Soc. Rev.* **1978**, *7*, 507. Gillespie, R. J. *Coord. Chem. Rev.* **2008**, *252*, 1315; Esselman, B. J.; Block, S. B. *J. Chem. Educ.* **2019**, *96*, 75.

[180] Gillespie, R. J. *Chem. Soc. Rev.* **1992**, *21*, 59.

[181] Hall, M. B. *J. Am. Chem. Soc.* **1978**, *100*, 6333.

[182] The model may be more intuitively useful if the electron points are considered to be three-dimensional objects with shapes similar to those calculated for hybrid atomic orbitals. See Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295.

[183] Tykodi, R. J. *J. Chem. Educ.* **1994**, *71*, 273 described VSEPR as it is usually presented as an "incomplete theory."

[184] Clauss, A. D.; Nelsen, S. F.; Ayoub, M.; et al. *Chem. Educ. Res. Pract.* **2014**, *15*, 417 discussed issues arising from the use of VSEPR theory in undergraduate education.

[185] The repulsion is attributed to the Pauli exclusion principle and not Coulombic repulsion of the electron pairs. For a discussion, see Allen, L. C. *Theor. Chim. Acta (Berlin)* **1972**, *24*, 117.

[186] A simple method to calculate the bond angles of the resulting regular tetrahedron was reported by Ferreira, R. *J. Chem. Educ.* **1998**, *75*, 1087.

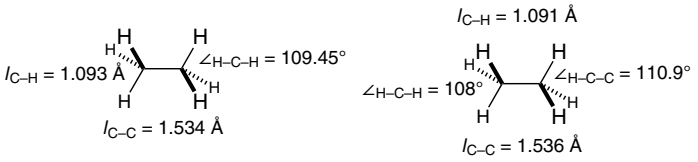


FIGURE 1.18
Predicted (left) and experimental (right) geometry of ethane.

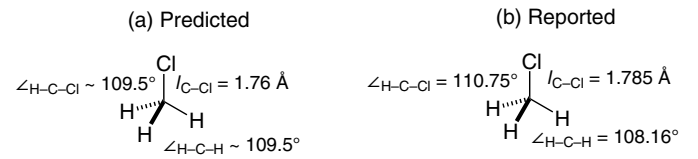


FIGURE 1.19
Predicted (a) and reported (b) geometry of CH_3Cl.

The VSEPR approach can be extended to ethane. Since each carbon atom has four substituents and since the electronegativity of carbon is close to that of hydrogen, the H–C–H and H–C–C bond angles should remain 109.5°. The experimental bond angles are close to but not exactly 109.5° (Figure 1.18).[34,35,187]

Now consider methyl chloride. The covalent radius of chlorine (Table 1.2) is about 0.22 Å greater than that of carbon, so the C–Cl bond distance should be about 1.76 Å. If all else is the same, the molecular geometry of methyl chloride might be expected to be that shown in Figure 1.19(a). Spectroscopic data indicate, however, that the structure is similar to that shown in Figure 1.19(b).[35,188] While the C–Cl bond length is reasonable, the H–C–H bond angle is greater than 109.5°, and the H–C–Cl angle is smaller than 109.5°.

The difference between prediction and experiment can be rationalized with VSEPR theory by noting that the electronegativity of chlorine is greater than that of carbon (Table 1.12). In a methane C–H bond, the carbon atom and the hydrogen atom attract the electron pair approximately equally. In CH_3Cl, however, the electrons in the C–Cl bond will be pulled toward the chlorine atom and away from the carbon atom. In terms of VSEPR theory, points on a sphere representing pairs of electrons used for bonding to more electronegative groups can be considered less repulsive to other points (electron pairs) than are points corresponding to bonds to less electronegative atoms.[180] This should decrease the Cl–C–H bond angle, as is observed. In turn, the carbon atom will pull electron density from the hydrogen atoms attached to it. Since electron density associated with the C–H bonds has been increased near the carbon nucleus, the repulsion between pairs of C–H bonds is now increased, at least by comparison with C–H bond repulsion by the C–Cl bond. Therefore, the H–C–H bond angle is expanded relative to that of methane.

Variable Hybridization

The qualitative VSEPR explanation of the geometry of methyl chloride can be made quantitative by a modification of the concept of hybrid orbitals. Because methyl chloride is less symmetric than methane, the hybrid orbitals on carbon

[187] Bartell, L. S. *Struct. Chem.* **2011**, *22*, 247 argued that, for molecules with central atoms that are not very large, molecular geometry is better explained by forces among geminal atoms bonded to the central atom than by either hybridization or VSEPR.

[188] See also Wiberg, K. B. *J. Am. Chem. Soc.* **1979**, *101*, 1718 and references therein.

should be somewhat dissimilar.[189] Carbon 2*p* orbitals are higher in energy than 2*s* orbitals (Figure 1.8) because electrons in a 2*p* orbital are further from the carbon nucleus than electrons in a 2*s* orbital. Since the chlorine will pull some electron density away from the less electronegative carbon atom, these electrons will be further from the carbon nucleus and will best be described as being in an orbital having less *s* character and more *p* character than sp^3.[190,191,192] As a result, there must be more *s* character in the carbon orbitals used for the three C–H bonds, so the H–C–H bond angles are expanded from 109.5° to 110.5°.

To make this bonding description quantitative, it is useful to describe an sp^n orbital in terms of its **hybridization parameter**, λ, and its **hybridization index**, n, which is defined as $n = \lambda^2$. Now the fractional *s*-character of the *i*th orbital is given by the expression $1/(1 + \lambda_i^2)$.[193,194] For example, the fraction of *s* character of an sp^3 hybrid orbital is $1/(1 + 3) = 1/4$. Since the total *s*-character of all the hybrid orbitals must sum to 1, equation 1.44 holds.

$$\sum_i \frac{1}{1 + \lambda_i^2} = 1 \tag{1.44}$$

The total *p* character of the hybrid orbitals must equal the number of *p* orbitals involved in the hybridization. For an sp^3-hybridized carbon, equation 1.45 applies, where $\lambda_i^2/(1 + \lambda_i^2)$ is the fractional *p*-character of the *i*th hybrid orbital.

$$\sum_i \frac{\lambda_i^2}{(1 + \lambda_i^2)} = 3 \tag{1.45}$$

Hybridization parameters can be related to molecular geometry. The interorbital angle θ_{ab} between hybrid orbitals from carbon to atom *a* and to atom *b* can be determined from equation 1.46.[195] If atoms *a* and *b* are identical, then equation 1.47 applies.

$$1 + \lambda_a \lambda_b \cos\theta_{ab} = 0 \tag{1.46}$$

$$1 + \lambda_a^2 \cos\ \theta_{aa} = 0 \tag{1.47}$$

---

[189] For further reading, see (a) Breslow, R. *Organic Reaction Mechanisms*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1969; p. 3; (b) Coulson, C. A.; Stewart, E. T. in Patai, S., Ed. *The Chemistry of Alkenes*, Vol. 1; Wiley-Interscience: London, 1964; p. 98 ff.

[190] The generalization that there is more atomic *s* character in orbitals directed toward electropositive substituents is known as Bent's Rule: Bent, H. A. *Chem. Rev.* **1961**, *61*, 275; *J. Chem. Educ.* **1960**, *37*, 616.

[191] See also Walsh, A. D. *Discuss. Faraday Soc.* **1947**, *2*, 18; *J. Chem. Soc.* **1948**, 398.

[192] The lower energy of *s* orbitals results because their average distance from the nucleus is less than is the average distance from the nucleus for *p* orbitals of the same principal quantum number (reference 141a).

[193] Coulson, C. A. *J. Chem. Soc.* **1955**, 2069.

[194] (a) Mislow, K. *Introduction to Stereochemistry*; W. A. Benjamin: New York, 1966; pp. 13–23; (b) reference 130a, p. 195 ff.

[195] For strained molecules, such as those with small rings, the interorbital bond angle may not be the same as that of the internuclear bond angle. See the discussions of bent bonds later in this chapter.

Note that these equations predict that the interorbital angle will increase with greater *s* character, which is consistent with the increase in bond angle from 109.5° to 120° to 180° as the hybridization changes from sp^3 to sp^2 to *sp*, respectively.

For a monosubstituted methane such as methyl chloride, denoted here as CA_3B, there are only two different bond angles: θ_{aa} and θ_{ab}. They are related by the expression[196]

$$3\sin^2\theta_{ab} = 2(1 - \cos\theta_{aa}) \tag{1.48}$$

so knowledge of only one of these bond angles is sufficient to calculate the other. In the case of methyl chloride, the H–C–Cl bond angle is 108°, so the H–C–H bond angle is found from equation 1.49.

$$\cos\theta_{aa} = 1 - \frac{3\sin^2\theta_{ab}}{2} \tag{1.49}$$

Using the θ_{aa} value of 110.9°, λ_a^2 can be calculated from the formula

$$\lambda_a^2 = -\frac{1}{\cos\theta_{aa}} = 2.80 \tag{1.50}$$

Thus, the orbitals used to bond hydrogen to carbon in methyl chloride are $sp^{2.80}$. Since the total *s* character in all four orbitals to carbon must sum to 1.00, equation 1.51 holds.

$$3\left[\frac{1}{1+2.80}\right] + \frac{1}{1+\lambda_b^2} = 1 \tag{1.51}$$

Rearranging equation 1.51 and solving for λ_b^2 gives a value of 3.75. Therefore, the C–Cl bond uses a $sp^{3.75}$ hybrid orbital on carbon (Figure 1.20).

The association of tetravalent carbon with sp^3 hybridization is so instilled into introductory organic chemistry students that it may be surprising that C–C–C bond angles are 109.47° only for carbon atoms with four identical substituents. The C–C–C angle of propane is 112.4°,[197] and the C–C–C angles in pentane, hexane, and heptane are similar.[198] A survey of 3431 X-ray crystallography measurements revealed a range of C–C–C bond angles from 74.88° to 159.66°, with the mean being 113.5° ± 4.5°.[199] The data also showed that the mean C–C–X angle in a series of ethyl derivatives varies with the electronegativity of the group X, with compounds having a more electronegative X (e.g. F, OH) having smaller C–C–X angles than compounds with less electronegative X groups (e.g. Na, Li).[200]

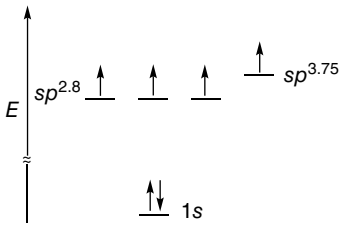


FIGURE 1.20
Hybridization of carbon orbitals proposed for CH_3Cl.

[196] If there are two sets of identical ligands, CA_2B_2, there will be three bond angles: θ_{aa}, θ_{ab}, and θ_{bb}. They are related by the formula $\cos\theta_{ab} = -\cos 2\theta_{aa} \cos 2\theta_{bb}$. For further details and examples, see reference 194a.

[197] Lide, D. R., Jr. *J. Chem. Phys.* **1960**, *33*, 1514.

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

[199] Boese, R.; Bläser, D.; Niederprüm, N.; et al. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 314.

[200] Because the C–C–X bond angle also varied with rotation about the C–X bond, electronegativity was judged not to be the only determinant of bond angles. A role was also described for hyperconjugation, a concept that will be discussed in later chapters.

Now consider CH_2Cl_2. The microwave spectra of isotopically substituted methylene chlorides indicated that the C–Cl distance is 1.772 Å and the C–H distance is 1.082 Å. The Cl–C–Cl angle was determined to be 111°47′, while the H–C–H angle was found to be 112°0′.[201] From equation 1.50, λ^2_{Cl} is 2.69, so the C–Cl bonding uses a carbon orbital that is an $sp^{2.69}$ hybrid. Equation 1.44 then leads to a value of 3.37 for λ^2_H. That corresponds to an H–C–H angle of 107°. Clearly, there is an inconsistency between the experimental and calculated values.

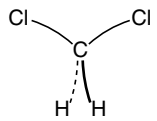


FIGURE 1.21
Cartoon representation of curved bonds in CH_2Cl_2.

This result prompts a reconsideration of the intuitive view of a covalent bond as a straight line between two atoms and raises the possibility that the C–Cl or C–H bonds (or both) may be curved.[202] Figure 1.21 shows the proposed curved bond structure for CH_2Cl_2. The apparent conflict between geometry and hybridization parameters can be resolved by distinguishing two different meanings of the term *bond angle*. The **internuclear** bond angle is the angle measured by the shortest distance lines between pairs of nuclei. The **interorbital** bond angle is the angle between pairs of hybrid orbitals make as they leave the carbon atom. Experimental geometry measurements provide internuclear bond angles, while the variable hybridization analysis considers interorbital bond angles. Thus, the H–C–H and Cl–C–Cl inter*nuclear* angles could both be greater than 109°, but the inter*orbital* angles could still be 107°.

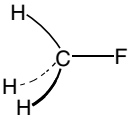


FIGURE 1.22
Curved paths suggested for C–H bonds in CH_3F. (Adapted with permission from reference 205. © 1996 American Chemical Society.)

Curved bonds have also been proposed for CH_3F. Because of the greater electronegativity of fluorine than chlorine, C–F bond should utilize even more *p* character on carbon than does the C–Cl bond in CH_3Cl. This should decrease the H–C–F bond angle even more than the H–C–Cl angle in CH_3Cl. However, the H–C–F bond angle in CH_3F is found to be 108.9°.[203] Wiberg and coworkers explained this apparent anomaly by suggesting that there is considerable curvature in the C–H bonds, as shown in Figure 1.22.[204,205,206] The H–C–F angle made by the C–F bond path and by one of the C–H bond paths *as they leave the carbon atom* is estimated to be 106.7°, which is, as expected, smaller than the H–C–Cl bond angle in methyl chloride.[207,208]

The idea of curved bonds in CH_2Cl_2 and CH_3F may seem unfamiliar, but this explanation has long been invoked to describe bonding in cyclopropane.[209] In this valence bond model, each carbon is assumed to have sp^3

[201] Myers, R. J.; Gwinn, W. D. *J. Chem. Phys.* **1952**, *20*, 1420.

[202] An alternative possibility is that the hybrid orbitals in CH_2Cl_2 involve some *d* orbital character, but this was discounted because of the much higher energy of *d* orbitals (reference 201).

[203] Clark, W. W.; De Lucia, F. C. *J. Mol. Struct.* **1976**, *32*, 29.

[204] The curved bond line follows the path of maximum electron density from one atom to another and is known as a **bond path**. See Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040. For a discussion, see Krug, J. P.; Popelier, P. L. A.; Bader, R. F. W. *J. Phys. Chem.* **1992**, *96*, 7604. Bader, R. F. W. *J. Phys. Chem. A* **2009**, *113*, 10391 emphasized that a bond path is not the same thing as a chemical bond.

[205] Wiberg, K. B. *Acc. Chem. Res.* **1996**, *29*, 229.

[206] Wiberg, K. B.; Murcko, M. A. *J. Mol. Struct. (Theochem)* **1988**, *169*, 355.

[207] Wiberg, K. B.; Hadad, C. M.; Breneman, C. M.; et al. *Science* **1991**, *252*, 1266.

[208] For a discussion of theories concerning the stability and geometry of carbon atoms with two, three, or four fluorine substituents, see Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

[209] For a leading reference to some theoretical treatments for the bonding in cyclopropane, see (a) Bernett, W. A. *J. Chem. Educ.* **1967**, *44*, 17; (b) Hamilton, J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.

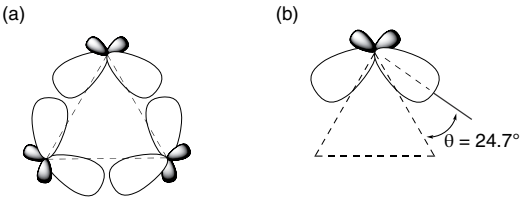


FIGURE 1.23
Valence bond model of C–C bonding in cyclopropane based on sp^3 hybridization (a) and calculation of orbital misalignment resulting from 109.47° interorbital angles (b).

hybridization. Figure 1.23(a) shows a schematic representation of C–C bond formation involving sp^3 hybrid orbitals on adjacent carbon atoms.[210,211] C–H bonding, not shown in the figure, then arises from a pair of C_{sp^3}–H_{1s} interactions on each carbon. Each of the resulting H–C–H groups is perpendicular to the plane defined by the three carbon atoms.

Figure 1.23(b) shows that each sp^3 hybrid orbital in the molecular plane is oriented nearly 25° outside the dashed carbon–carbon internuclear bond. Since this is much larger than the 60° internuclear angle required for an equilateral triangle, the orbitals used for C–C bonding must lie considerably outside the internuclear lines (the dashed lines in Figure 1.23). In addition, strict sp^3 hybridization would be expected to produce an H–C–H bond angle of 109.5°. The experimental value for the H–C–H bond angle is 115.1°, so the hybridization of the orbital on carbon used for C–H bonding is calculated to be $sp^{2.36}$.[212,213] The hybridization used for C–C bonds is then calculated to be $sp^{3.94}$, which predicts a C–C–C *interorbital* value of 104.7°. That reduces the internuclear and interorbital deviation to about 22.2°.

An alternative description of carbon–carbon bonding in cyclopropane was proposed by Walsh.[214] This approach assumes sp^2 hybridization for each carbon, so a bonding interaction arises from three sp^2 hybrid orbitals directed toward the center of the cyclopropane ring (Figure 1.24(a)) and also from three *p* orbitals oriented tangentially to the (Figure 1.24(b)).[215] Each C–H bond then arises from overlap of an H_{1s} orbital with one of the remaining sp^2 hybrid orbitals on each carbon atom. Interestingly, rehybridization of a *p* orbital on carbon with the sp^2 hybrid orbital oriented into the ring can produce a pair of sp^5 hybrid orbitals (Figure 1.25).[216,217] The sp^5 hybrid orbitals have an interorbital angle of 105°, which corresponds even more closely to the internuclear angle of cyclopropane.[218]

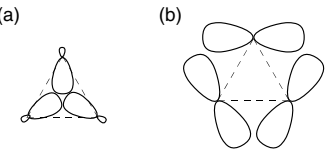


FIGURE 1.24
Walsh model for C–C bonding in cyclopropane. (a) Interaction of three sp^2 hybrid orbitals directed toward the center of the ring. (b) Interaction of three *p* orbitals oriented tangentially to the ring.

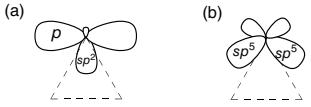


FIGURE 1.25
Rehybridization of a *p* orbital and an sp^2 orbital of cyclopropane (a) to produce a pair of sp^5 hybrid orbitals (b).

[210] For clarity, the orbital shapes are arbitrarily sized and do not overlap in this drawing.

[211] This bonding model is based on the work of Förster, Coulson, and Moffitt and is often called the Coulson-Moffitt model or the Förster-Coulson-Moffitt model. Förster, T. *Z. Phys. Chem.* **1939**, *B43*, 58; Coulson, C. A.; Moffitt, W. E. *J. Chem. Phys.* **1947**, *15*, 151; Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1.

[212] Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.

[213] Literature values can vary somewhat, leading to differences in calculated *s* and *p* contributions. An H–C–H bond angle of 113.6° was reported by Almenningen, A.; Bastiansen, O.; Skancke, P. N. *Acta Chem. Scand.* **1961**, *15*, 711. See Klasinc, L.; Maksić, Z.; Randić, M. *J. Chem. Soc. (A)* **1966**, 755.

[214] Walsh, A. D. *Nature* **1947**, *159*, 167; ibid, 712; *Trans. Faraday Soc.* **1949**, *45*, 179.

[215] For simplicity, the orbitals are arbitrarily sized and only their shapes are represented here.

[216] The rehybridization involves combining one orbital that is 1/3 *s* and 2/3 *p* with an orbital that is entirely 3/3 *p* to produce equivalent orbitals that are 1/6 *s* and 5/6 *p* (reference 209).

[217] For a discussion of rehybridization, see Alabugin, I. V.; Manoharan, M. *J. Comp. Chem.* **2007**, *28*, 373.

[218] Honegger, E.; Heilbronner, E.; Schmelzer, A.; et al. *Israel J. Chem.* **1982**, *22*, 3 discussed some differences between the two bonding models for cyclopropane.

The hybridization parameter is useful as a tool to describe molecular bonding, but it is not an "observable" because it cannot be measured directly. It can only be inferred from physically observable values that are said to correlate with it.[219] It is generally accepted that NMR coupling constants involving hydrogen provide a measure of the density of bonding electrons at the nucleus.[220] Since *s* orbitals have electron density at the nucleus but *p* orbitals do not, the coupling constant reflects the *s* character of the orbital used for bonding to hydrogen. Equation 1.52 shows a useful empirical relationship between $J_{13_{C-H}}$(the NMR coupling constant for ^{13}C and H) and the hybridization parameter.[194,221]

$$J_{13_{C-H}}(\text{cps}) = \frac{500}{1 + \lambda_a^2} \tag{1.52}$$

Electron density at hydrogen is thought to be related to the acidity of a C–H bond, and Streitwieser and co-workers demonstrated a correlation between $J_{13_{C-H}}$ and the kinetic acidities (the rates of exchange of C–H protons for tritium catalyzed by cesium cyclohexylamide). The data in Table 1.14 show a good correlation of log k_{rel} (rate constant relative to that of cyclohexane) with $J_{13_{C-H}}$ as shown in equation 1.53.[219,222]

$$\log k_{rel} = 0.129 J_{13_{C-H}} - 15.9 \tag{1.53}$$

An explanation for the correlation of acidity with $J_{13_{C-H}}$ is that both are related to the hybridization of the carbon orbital used for C–H bonding. Because *s* orbitals are lower in energy than *p* orbitals, a hybrid orbital with more *s* character will be lower in energy and thus have electron density closer to the nucleus than a hybrid orbital with less *s* character. This lower energy orbital will be more electronegative and will be better able to stabilize a negative charge when a proton is removed in an acid–base reaction.[190]

TABLE 1.14 Correlation of Rate Constants of Proton Exchange with $J_{13_{C-H}}$

Compound	Relative Rate	$J_{13_{C-H}}$
Cyclopropane	7.0×10^4	161
Cyclobutane	28.0	134
Cyclopentane	5.7	128
Cyclohexane	1.00	123, 124
Cycloheptane	0.76	123
Cyclooctane	0.64	122

Source: Adapted with permission from reference 222. © 1969 American Chemical Society.

[219] For a discussion and references, see Ferguson, L. N. *Highlights of Alicyclic Chemistry*, Part 1; Franklin Publishing Company: Palisade, NJ, 1973; p. 52 ff.

[220] Crăciun, L.; Jackson, J. E. *J. Phys. Chem. A* **1998**, *102*, 3738.

[221] Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 1471 found that better correlations were obtained when calculated atomic charges were included in the equation. Gil, V. M. S. *J. Chem. Educ.* **2001**, *78*, 31 reported an alternative correlation of $^1J_{CH}$ with percent *s* character in an orbital.

[222] Streitwieser, A., Jr.; Caldwell, R. A.; Young, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 529.

It must be emphasized that hybridization is a theoretical construct that facilitates calculation of some molecular parameters. Varying the hybridization index simply means modifying a prior model to suit a current need, just as the concept of hybridization represents only a change to the model of orbital energy levels in an isolated carbon atom. Variable hybridization should not be considered more fundamental than the VSEPR model, just more mathematical. The ability to make quantitative predictions of molecular geometry and physical properties makes the variable hybridization model quite useful for some problems. On the other hand, the VSEPR model is also valuable as an intuitive basis for qualitatively correct predictions. As is so often the case, the model of choice is the one that best serves a particular purpose at a given time.

1.4 COMPLEMENTARY MODELS FOR THE DOUBLE BOND

The σ,π Description of Ethene

Contemporary introductory organic chemistry textbooks describe the double bond in terms of the σ,π formulation.[223,224] The simplest example of such bonding is ethene, in which a C–C σ is bond formed through overlap of an sp^2 hybrid orbital (Figure 1.26) on each of the carbon atoms, while the π bond results from overlap of two parallel 2*p* orbitals (one on each of the carbon atoms, Figure 1.27).[225] A familiar pictorial representation of the carbon–carbon σ and π bonds is shown in Figure 1.28, and the geometry implied by sp^2 hybridization is shown in Figure 1.29. This description of the carbon–carbon double bond is very familiar, but is it correct?[226]

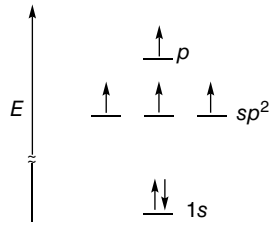


FIGURE 1.26
Depiction of carbon orbital energy levels with sp^2 hybridization.

The σ,π model has qualitative utility because it predicts the carbon–carbon bond length of ethene to be shorter than the carbon–carbon bond length of ethane. The reason is that the overlap of sp^2 orbitals (which have more *s* character and are therefore closer to the carbon nucleus than are sp^3 hybrids) makes a shorter bond, and the additional π bond pulls the two atoms even closer. On the other hand σ,π model predicts the H–C–H and H–C–C bond angles to be 120° because of sp^2 hybridization. Figure 1.30 shows the geometry of ethene determined from spectroscopic measurements, and the H–C–H bond angles are 117°, not 120°.[34]

[223] One text that presented the bent bond formulation was Roberts, J. D.; Stewart, R.; Caserio, M. C. *Organic Chemistry*; W. A. Benjamin: Menlo Park, CA, 1971.

[224] For a discussion of the origin of the σ and π labels, see Jensen, W. B. *J. Chem. Educ.* **2013**, *90*, 802.

[225] It is more complete to say that overlap of the two sp^2 hybrids produces both a σ bonding and a σ* antibonding orbital. Similarly, overlap of the two *p* orbitals produces both a π bonding and a π* antibonding molecular orbital, with energies shown qualitatively in Figure 1.27.

[226] Frenking, G.; Krapp, A. *J. Comput. Chem.* **2007**, *28*, 15 described π bonding as one of the "unicorns in the world of chemical bonding models," meaning that everyone knows what a unicorn looks like even though no one has ever seen one.

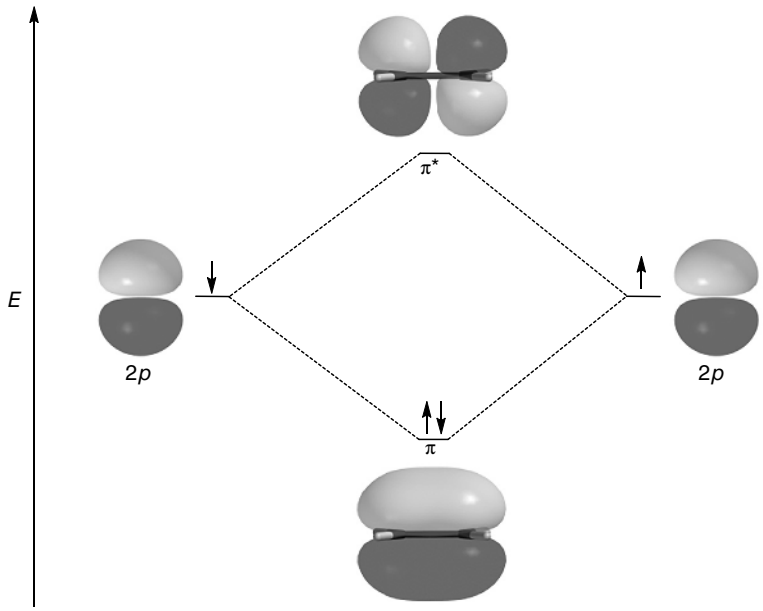


FIGURE 1.27
Energies of ethene π and π* orbitals.



FIGURE 1.28
The σ,π formulation for ethene.

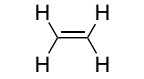


FIGURE 1.29
Predicted geometry of ethene.

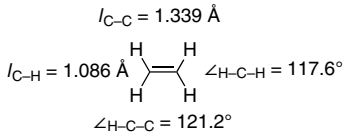


FIGURE 1.30
Experimental geometry of ethene (reference 35).

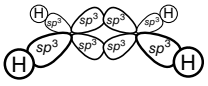


FIGURE 1.31
Overlap of sp^3 hybrid orbitals in the bent bond description of ethene.

The Bent Bond Description of Ethene

A much older description of ethene is based on the concept of bent bonds.[227,228] The double bond is described as the result of overlap of two sp^3 hybrid orbitals on *each* of the two carbon atoms, as shown in Figure 1.31. This model also predicts that ethene should be a planar molecule. However, it predicts H–C–H bond angles of 109.5°—which is even further from the observed 117° than was the prediction based on sp^2 hybridization. Nevertheless, one advocate of the bent bond description was Linus Pauling, who wrote:

> There may be chemists who would contend that one innovation of great significance has been made—the introduction of the σ,π description of the double bond and the triple bond and of conjugated systems, in place of the bent bond description. I contend that the σ,π description is less satisfactory than the bent bond description, that this innovation is only ephemeral, and that the use of the σ,π description will die out before long…[229]

Predictions of Physical Properties with the Two Models

Geometry of Alkenes

Although Pauling's prediction has not yet come true, there are advantages in using the bent bond formulation. One advantage is conceptual simplicity. If the sp^3 hybridization model can give the correct answer, why use a whole

[227] Flygare, W. H. *Science* **1963**, *140*, 1179.

[228] Bent bonds are also known as banana bonds or τ (tau) bonds. For a discussion of the utility of this model in explaining molecular conformation and reactivity, see Wintner, C. E. *J. Chem. Educ.* **1987**, *64*, 587 and references therein.

[229] Pauling, L. in *Theoretical Organic Chemistry, The Kekulé Symposium*; Butterworths Scientific Publications: London, 1959; p. 1.

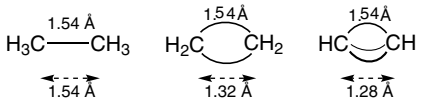


FIGURE 1.32
Quantitative predictions of the bent bond formulation.

TABLE 1.15 Gas Phase Acidities of C_2 Hydrocarbons

Compound	ΔH°_{acid} (kcal/mol)
Ethane	420.1 ± 2.0
Ethene	409.4 ± 0.6
Ethyne	378.5 ± 0.2

Source: Reference 231.

family of explanations (sp^3, sp^2, and sp) for bonding questions? A practical advantage is the ease of construction of physical models. Many molecular model kits designed for introductory organic chemistry courses use bent bonds as the physical model of the double bond. Such models give acceptable structural geometries, require fewer parts in the model set, and are easier for novices to use than are model kits that attempt to represent both σ and π bonds. Still another advantage is that the bent bond formulation seems to provide more quantitative predictions about geometry than does the σ,π formulation. Consider the measurement of the carbon–carbon distances illustrated in Figure 1.32. Taking the C–C bond length of ethane, l.54 Å, as the length of an arc formed by overlap of sp^3 orbitals outside the internuclear line, Pauling calculated that ethene should have an internuclear distance of 1.32 Å, which is close to the experimental value.[36] Similarly, three bent bonds arranged as 1.54 Å arcs directed 109.47° apart produce a C–C internuclear distance of 1.18 Å for ethyne, which is very close to the experimental value.[230] The σ,π formulation makes no quantitative prediction about the length of the double or triple bond.

Acidities of Hydrocarbons

The alkanes, alkenes, and alkynes are not usually considered to be acidic, but it is possible to measure rates and equilibria of proton removal in solution and in the gas phase. Table 1.15 shows some experimental values of ΔH°_{acid}, the enthalpy change for detachment of a proton from the hydrocarbon in the gas phase. The data indicate that ethyne is more acidic than ethene, which in turn is more acidic than ethane.[231]

These results are consistent with the relative stabilities of the carbanions formed by removal of a proton from each structure. In the σ,π formulation, the hybridization of the carbon orbital with the nonbonded electron pair changes from sp^3 to sp^2 to sp as a proton is removed ethane to ethene to ethyne, respectively (Figure 1.33). Again, the more s character in an atomic orbital, the greater is the electron-attracting power of that orbital, and the more stable

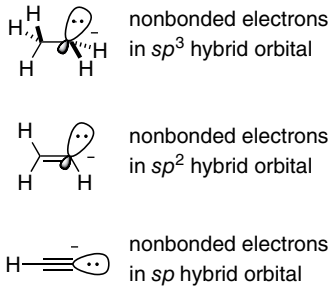


FIGURE 1.33
σ,π rationalization of carbanion stabilities.

[230] Robinson, E. A.; Gillespie, R. J. *J. Chem. Educ.* **1980**, *57*, 329 described these calculations as well as the use of molecular models with bent bonds to measure the internuclear distances.

[231] Data from the compilation by Bartmess, J. E. in Mallard, W. G.; Linstrom, P. J., Eds. *NIST Webbook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov).

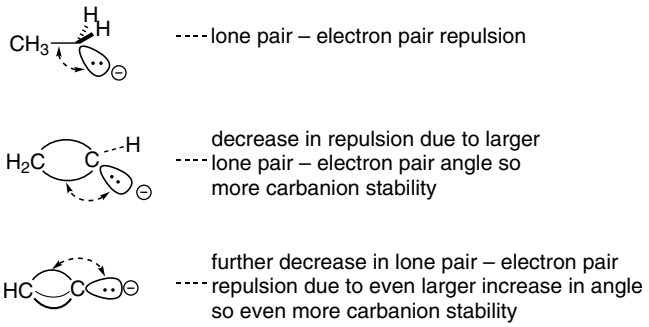


FIGURE 1.34
Bent bond rationalization of acidities.

should be an anion produced by removing a proton and leaving a nonbonded pair of electrons in that orbital.[190] Thus, the order of carbanion stability should be $(sp)C:^- > (sp^2)C:^- > (sp^3)C:^-$, which is the same as the ranking of hydrocarbon acidities: $(sp)C–H > (sp^2)C–H > (sp^3)C–H$.

The bent bond formulation can rationalize the same results by noting the effect of curved C–C bonds on the electron pair repulsions around each carbon atom. As Figure 1.34 shows, formation of bent bonds in ethene pulls the double bond electrons closer to the center of the C–C internuclear line. In turn, this decreases the repulsion between a C–H bond electron pair and the bent C–C bond electrons. The C–H electrons thus experience a less-shielded carbon nucleus, so they are attracted more strongly to it. An unshared pair of electrons left by removal of a proton from ethene is much more stable than is a pair of electrons left by removal of a proton from ethane. For the same reason, a nonbonded pair of electrons is more stable on a triple-bonded carbon than on a double-bonded carbon. Thus, the bent bond formulation as well as the σ,π description can rationalize these experimental observations at least qualitatively.

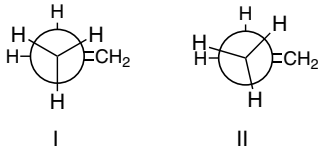


FIGURE 1.35
Conformations of propene: σ,π description. (Adapted with permission from reference 232. © 1966 American Chemical Society.)

Conformations of Propene

Now consider which bonding model is more amenable to qualitative predictions of molecular conformation. Specifically, what should be the preferred conformation of propene? Walters noted that two conformers of propene (designated as I and II) can be visualized as Newman projections observed by sighting down the C3–C2 bond (Figure 1.35).[232,233] In conformer I, a C–H bond eclipses a carbon–carbon double bond. In conformer II, a C–H bond eclipses a C–H bond. Based on the assumption of greater electron density in a carbon–carbon double bond than in a C–H single bond, conformer II is predicted to be more stable. Experimentally, however, conformer I was found to be more stable by about 2 kcal/mol.[234]

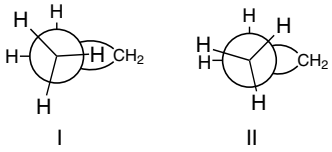


FIGURE 1.36
Conformations of propene: bent-bond formulation. (Adapted with permission from reference 232. © 1966 American Chemical Society.)

A different picture emerges when the same Newman projections are constructed with bent bonds, as shown in Figure 1.36. Conformer II is now seen to be essentially an all-eclipsed conformation. Thus, it should be less stable than I, which is an all-staggered arrangement. If utility is the main criterion for adopting conceptual models, then this result would seem to argue

[232] Walters, E. A. *J. Chem. Educ.* **1966**, *43*, 134.

[233] Newman projections and other stereochemical representations will be discussed in Chapter 3.

[234] Herschbach, D. R.; Krisher, L. C. *J. Chem. Phys.* **1958**, *28*, 728.

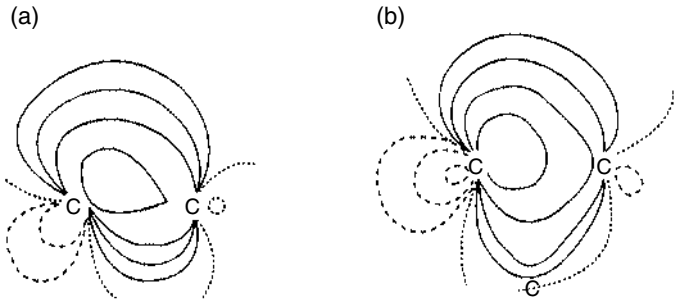


FIGURE 1.37
Contour lines for a bonding orbital on one carbon in (a) ethene and (b) cyclopropane. (Adapted with permission from reference 209b. © 1993 American Chemical Society.)

persuasively for using the bent bond formulation.[235] Chapter 4 will revisit the question of conformational preference in propene.[236] However, the advantage of the bent bond model here is that it leads directly to a correct prediction of conformational stability.[237]

Pauling's prediction that the use of the σ,π description will fade may yet come true, at least in part. In recent years some theoreticians have determined that calculations of molecular structure are in better agreement with the bent bond description than with the σ,π description. Figure 1.37(a) shows calculated contour lines of a carbon orbital in a plane that is perpendicular to the molecular plane of ethene, and Figure 1.37(b) shows contour lines for an orbital in a plane containing the carbon atoms of cyclopropane. Clearly, much of the orbital lies outside the internuclear bond line in each case. It is generally agreed that the bonds in cyclopropane are bent; the picture from this theoretical calculation reinforces the view that they are bent in ethene also.

This conclusion was reinforced by a number of investigations. The title of one publication was "Double Bonds Are Bent Equivalent Hybrid (Banana) Bonds."[238] Another study concluded that "the GVB description of the double bond in (C_2F_4) is *not* the traditional picture of σ and π bonds but rather a representation in terms of two bent bonds."[239] Still another paper comparing the bent bond and σ,π models concluded that "… from an energetical point of view, both constructions provide an equally good starting point for the treatment of correlation effects beyond the one-electron configuration."[240] Another study concluded that "our results yield bent bonds as the favored bonding description, showing that the σ,π bond descriptions of multiple bonds are artifacts of approximations to the full independent-particle equations."[241] For systems that exhibit resonance, such as benzene and the allyl radical, these

[235] The emphasis in the present discussion is on the application of two very simple conceptual models to a particular problem. High level calculations provide a much deeper analysis of the conformations of propene and other molecules. For a discussion, see Bond, D.; Schleyer, P. v. R. *J. Org. Chem.* **1990**, *55*, 1003.

[236] See also Lin, B.-L.; Xie, Z.; Liu, R.; et al. *J. Mol. Struct. (Theochem)* **2003**, *633*, 15.

[237] Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687.

[238] This discussion implicitly treats the methyl group as interacting with the vinyl group only through steric interactions. This assumption ignores the electronic interactions inherent in any molecular entity. See, for example, Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

[239] GVB is a type of VB calculation. Cf. Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1988**, *110*, 8258.

[240] Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; et al. *J. Am. Chem. Soc.* **1993**, *115*, 6863.

[241] Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10925.

authors stated the conclusion even more succinctly: "bent bonds are better."[242,243]

The distinction between the bent bond and σ,π formulations of the double bond is not as distinct as the discussion above might suggest, because the two representations are merely different conceptual representations of the same quantum mechanical result.[28,244] As Schultz and Messmer put it, "no experiment can possibly distinguish between a σ,π double bond and double bent bonds in any system, and therefore neither can be proven to be 'right' in an absolute sense; both are approximate descriptions."[241] The σ,π model for the double bond and the bent bond description should each be taken as viable *starting points* to describe molecular structure but not as complete descriptions.[36,245] Each approach has its advantages and disadvantages. It is important to keep in mind that straight or curved lines are not depictions of quantum mechanical realities. They are simply pictorial devices for summarizing quantum mechanical interactions.

1.5 THE ROLE OF COMPLEMENTARY MODELS IN ORGANIC CHEMISTRY

Conceptual, mathematical, and physical models are essential tools in organic chemistry because they help rationalize the results of experiments (observables) with theory (nonobservables). Yet the paradox is that these models may be most useful to us when they are oversimplified to the point of being incorrect in some way. It would be difficult to communicate organic structures without using a bond line or pair of dots. Yet sometimes it may be advantageous to draw those lines curved instead of straight, and hybrid orbitals are not always the best explanation for molecular properties. A more detailed description of that line and of those orbitals can be made only with the help of computers and high level mathematics.

If any organic chemistry model is asked to give a more correct answer to a problem, it quickly becomes more complex. Electronegativity is useful in a qualitative sense, but attempts to make it more quantitative led to different conclusions about what it means and how it should be determined. Elementary VB theory and MO theory are intuitively reasonable, but further development complicates the mathematics and obscures the simple mental pictures each provides. Chemists feel a need to retain these simple pictures, even when it is clear they cannot be totally accurate. As Bent noted,[246]

> Indeed, to be useful, *a model must be wrong, in some respects*—else it would be the thing itself. The trick is to see—with the help of a teacher—*where it's right*.

One solution to the use of oversimplified models in organic chemistry is to hybridize complementary conceptual models, just as two Kekulé structures for benzene can be hybridized mentally in order to understand and describe

[242] Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10943.

[243] For a different view, see Carter, E. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1988**, *110*, 4077.

[244] Gallup, G. A. *J. Chem. Educ.* **1988**, *65*, 671 and references therein.

[245] England, W. *J. Chem. Educ.* **1975**, *52*, 427; Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

[246] Bent, H. A. *J. Chem. Educ.* **1984**, *61*, 774.

aromaticity. The σ,π and bent bond descriptions represent a pair of models that serve as useful beginning points to the description of the double bond, and visualizing a hybrid of these two mental pictures may be more nearly correct than is thinking in terms of either model alone. More important, deliberately considering a chemical concept using more than one model serves as a useful reminder that no model is complete by itself. Keeping that in mind prevents overreliance on a single way of thinking about chemistry.

Perhaps another metaphor may be useful. In the end, models must be described in a language of some kind, whether it is English, French, German, Spanish, Russian, Chinese, or another language. There are nuances to the words different languages use to describe something, and those nuances are not always captured in translations. Thus, having *a* language to describe something does not necessarily make an explanation complete. If complementary models are considered different languages to describe chemistry, it is better to be multilingual—to converse in many languages, to translate from one language to another, and to think in more than one language.

Problems

1.1. Kuhn (reference 3) wrote that scientists "are little better than laymen at characterizing the established bases of their field." Briefly summarize the physical phenomena that support your belief in atomic and molecular theory.

1.2. Find a popular or scientific article that refers to observations of a single atom or atoms.

a. What is the nature of the experiment?

b. What observations are made directly with the human senses?

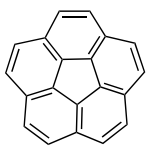
1.3. **a.** Consider two geometries for methane other than the regular tetrahedron. Show how each alternative geometry is inconsistent with the known number of isomers of some derivative of methane.

b. Consider at least four structures with the molecular formula C_6H_6 and show how each is inconsistent with the known number of isomers of benzene substitution products having a given molecular formula.

c. In parts a and b of this problem, you assumed that the structure of a derivative (e.g. bromobenzene) is essentially the same as that of the parent structure (e.g. benzene). Is that assumption valid? For example, how can it be certain that methane is not planar even though chloromethane is roughly tetrahedral?

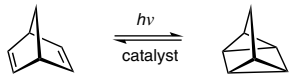
1.4. Use the values in Table 1.3 to determine the van der Waals volume and surface area for each of the pentanes. Verify that for *n*-pentane the values are correctly predicted by the formulas $V_{vdw} = 6.88 + 10.23\,N_c$ and $A_w = 1.54 + 1.35N_c$, where N_c is the number of carbon atoms in the molecule.

1.5. The heat of formation of corannulene (**2**) in the crystal state is 81.81 kcal/mol. Its heat of sublimation has been calculated to be 29.01 kcal/mol. What is ΔH_f° of **2** in the vapor phase?



2

1.6. A proposed system for the conversion and storage of solar energy was based on the photochemical isomerization of norbornadiene (**3**) to quadricyclane (**4**) during sunny periods, with catalytic conversion of **4** to **3** and release of energy at a later time. The heats of hydrogenation of **3** and **4** (both in the liquid phase) to norbornane are −68.0 and −92.0 kcal/mol, respectively. What is the potential for energy storage (in kcal/mol) for the photochemical conversion of **3** to **4**?



3 **4** (1.54)

1.7. The standard heat of combustion of 4,4-dimethyl-1,3-cyclohexanedione was determined to be −1042.90 kcal/mol. Its standard heat of sublimation is +23.71 kcal/mol. What is the ΔH_f° (gas phase) of this compound?

1.8. The heat of hydrogenation of phenylethyne was found to be −66.12 kcal/mol, and the heat of formation of phenylethane is 7.15 kcal/mol. What is ΔH_f° of phenylethyne?

1.9. **a.** The heat of formation of 2,5-thiophenedicarboxylic acid at 298.15 K is −772.4 ± 2.2 kJ/mol. Its heat of sublimation is 139.8 ± 0.4 kJ/mol. What is ΔH_f° of the compound in the gas phase?

b. The heat of formation of liquid 2-acetylthiophene at 298.15 K is −118.0 ± 1.7 kJ/mol, while that of crystalline 3-acetylthiophene is −129.1 ± 1.4 kJ/mol. The heat of vaporization of 2-acetylthiophene at 298.15 K is 58.8 ± 1.2 kJ/mol, and the heat of sublimation of 3-acetylthiophene at 298.15 K is 74.6 ± 1.1 kJ/mol. What is the difference in the gas phase heats of formation of these two compounds?

1.10. *cis*-3-Methyl-2-pentene has a ΔH_f° that is 1.65 kcal/mol more negative than that of 2-ethyl-1-butene. The ΔH_r° of 2-ethyl-1-butene with trifluoroacetic acid is −10.66 kcal/mol. Predict the heat of reaction of *cis*-3-methyl-2-pentene with trifluoroacetic acid under the same conditions.

1.11. The heat of hydrogenation of *cis*-1,3,5-hexatriene to hexane is −81 kcal/mol, while that of the trans isomer is −80.0 kcal/mol. Under the same conditions the heat of hydrogenation of 1,5-hexadiene is −60.3 kcal/mol. What would be the heat of hydrogenation for just the middle double bond of the cis and trans isomers of 1,3,5-hexatriene?

1.12. Calculate ΔH_f° for heptane using both equations 1.9 and 1.12. How do these predictions compare with literature values?

1.13. The dipole moments of CH_3F, CH_3Cl, CH_3Br, and CH_3I are reported to be 1.81, 1.87, 1.80, and 1.64 D, respectively.[69]

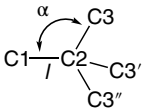
a. Calculate the partial charge on the halogen in each of the methyl halides (assuming that the halogen bears the partial negative charge and that the partial positive charge is centered on the carbon atom) using the C–X bond lengths listed in Table 1.1.

b. What trend, if any, do you see in the dipole moments of the methyl halides? How do you rationalize this result?

1.14. For what category of atoms could Allen or Nagle but not Pauling electronegativity values be determined?

1.15. The C–C–C bond angle of propane was reported to be 112.4°. What is the hybridization of the orbitals on C2 used for C–C and C–H bonding?

1.16. Both experimental and theoretical studies indicate that the C1–C2 bond length (l) and the C1–C2–C3 bond angle (α) in molecules having the following general structure below



are strongly correlated. (The C1–C2–C3′ and the C1–C2–C3″ bond angles are also α.) One study found that they could be related by the equation

$$l = 2.0822 - 0.0049\alpha \tag{1.55}$$

where distances are in Å and angles are in degrees.

a. What does this equation indicate about the change in bond length expected when the adjacent angle changes to a value greater than or less than 109.5°?

b. Rationalize the form of equation 1.55 in terms of both variable hybridization theory and VSEPR theory.

1.17. **a.** Arrange the following compounds in order of increasing length of C–H bonds and rationalize your answer: ethane, ethene, ethyne, cyclopropane, and cyclobutane.

b. Arrange these compounds in order of increasing length of C–C single bonds and explain your answer: ethane, 2-methylpropane, 2-methylpropene, 1,3-butadiene, 1,3-butadiyne, 1-butene-3-yne.

1.18. **a.** Use the bent bond description of double bonds to rationalize that the H–C–H bond angles in ethene are 117° and not 109.5°.

b. Modify your explanation to predict the H–C–H angle of formaldehyde. Specifically, should it be larger or smaller than the H–C–H angle of ethene?

1.19. Consider again ethene and formaldehyde, this time analyzing the double bond in each as a two-membered ring. Calculate the fractional s character and hybridization parameter for the C–H bond in each.

1.20. **a.** Consider the formula $J_{^{13}C-H} = 5.7 \times (\%\ s) - 18.4$ Hz. Determine whether this formula is equivalent to that in equation 1.52, and explain your reasoning.

b. Muller and Pritchard (reference 221) determined that the lengths of C–H bonds correlate with values of $J_{^{13}C-H}$ according to equation 1.56.

$$r_{C-H} = 1.1597 - 4.17 \times 10^{-4} J_{^{13}C-H} \tag{1.56}$$

Use equations 1.52 and 1.56 to relate the length of a C–H bond directly to λ^2.

1.21. Analyze cyclopropane, cyclobutane, and cyclopentane according to both the bent bond (using sp^3 hybrid orbitals) and variable hybridization descriptions.

a. For each compound, use the literature value for the H–C–H bond angle to calculate the fractional s and p character of the carbon orbitals used for C–H bonds, then use the result to calculate the interorbital C–C–C bond angle. How do the calculated values differ from the literature values of the internuclear bond angles? What does that tell you about the nature of the strain in the molecule? What does that suggest to you about the chemical properties of cyclobutane (e.g. reaction with electrophiles).

b. What does each model suggest to you about the acidities of the C–H bonds? How do the literature data for the acidity of cyclopropane agree with the predictions?

1.22. Some investigators noted that the sum of the six bond angles (109.5° each) around a tetrahedral carbon atom is 657° and postulated that the bond angles in other tetraligant species should sum to that same value.[247] For example, the H–C–F bond angle in fluoromethane was reported to be 109°2′ (Table 1.1). Since there are three H–C–F and three H–C–H angles, the "657" method predicts the H–C–H bond angle to be ⅓ (657° – 3 × 109.03°) = 110°.

a. How does this result compare with an experimental value?

b. Does the predictive ability of the "657" method depend on the extent to which the geometry at a carbon atom is nearly tetrahedral? If so, determine the range of $\angle_{H-C-F}$ values for which the "657" method produces a predicted H–C–H angle that is less than 10° different from the value calculated using the trigonometric relationships.

1.23. The C–H coupling constants for ethane, ethene, and ethyne are 125.2, 156, and 249 Hz, respectively. Do these values correlate with the gas phase acidity values in Table 1.15? If so, use the correlation to estimate the gas phase acidity of cyclopropane ($J_{^{13}C-H}$ = 161 Hz).

1.24. In bicyclo[1.1.0]butane (**5**), the $^{13}C–^{1}H$ coupling constant for the bridgehead C–H groups is 202 Hz. Calculate the % *s* character in the bond from carbon to hydrogen at this position. Would you expect the acidity of the bridgehead protons to be greater or less than that of the protons in acetylene?



5

1.25. If λ is a function of molecular geometry and $J_{^{13}C-H}$ is also a function of λ, then is not $J_{^{13}C-H}$ really a function of geometry? Is λ an observable? If not, is λ really needed?

1.26. Zavitsas et al. reported that the enthalpies of formation of an alkane could be correlated with equation 1.57, which is based on the number of hydrogen atoms of different types in a structure.[248]

$$\Delta H_f^\circ(\text{alkane}) = (-3.345)n_1 + (-2.490)n_2 + (-1.590)n_3 \qquad (1.57)$$

Here n_1 is the number of 1° hydrogen atoms in the alkane, n_2 is the number of 2° hydrogen atoms, and n_3 is the number of 3° hydrogen atoms. Use this equation to calculate the ΔH_f° values for the alkanes in Table 1.9 and compare the accuracy of this approach with that in Tables 1.8 and 1.9. What does the result suggest to you about the theoretical bases of the calculation methods on which those tables were based?

1.27. Evidence discussed in this chapter suggested that some familiar views of hybridization are at best oversimplified. In view of this result, can you justify the continued use of hybridized orbitals as a conceptual model in organic chemistry?

1.28. Greenberg and Liebman stated that "we believe organic chemistry is essentially a pictorial and not a mathematical science."[249] Do you agree with this statement? Do you think organic chemistry should be a mathematical science? Do you believe it will become so in the future?

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[247] McNelis, E.; Blandino, M. *New J. Chem.* **2001**, *25*, 772. More precisely, 6 × 109.47° = 656.82°.

[248] Zavitsas, A. A.; Matsunaga, N.; Rogers, D. W. *J. Phys. Chem. A* **2008**, *112*, 5734.

[249] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978, p. 37.

1.29. Respond to Coulson's observation about the nature of theory in chemistry:

> Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly that I can almost see it. And then I awake with a little shock: for a chemical bond is not a real thing: it does not exist: no one has ever seen it, no-one ever can. It is a figment of our own imagination… Here is a strange situation. The tangible, the real, the solid, is explained by the intangible, the unreal, the purely mental.[193]

1.30. Respond to Roald Hoffmann's statement that

> …much that goes into the acceptance of theories has little to do with rationalization and prediction. Instead, I will claim, what matters is a heady mix of factors in which psychological attitudes figure prominently.[250]

Hoffmann also wrote that

> …explanations are almost always stories. Indeed, moralistic and deterministic stories. For to be satisfying they don't just say A→B→C→D, but A→B→C→D *because* of such and such properties of A, B and C. The implicit strong conviction of causality, justified by seemingly irrefutable reason, may be dangerously intoxicating. This is one reason why I wouldn't like scientists and engineers to run this world.[250]

Do you think scientists who understand the limitations of human knowledge discussed in this chapter would be better able to run the world than Hoffmann imagines?

1.31. Weisberg argued that there is a trade-off between precision and generality in the models that scientists use and that "sacrificing precision in model descriptions can often add explanatory depth to the models picked out by these descriptions."[251] Cite examples from this chapter that are consistent with Weisberg's statement. Are any examples inconsistent with Weisberg's conclusion?

1.32. Accorinti wrote about electronegativity (EN) that "…the different models used to describe and quantify EN are incompatible but, in a certain sense, equivalent because the same EN scale results in all of them."[104] Are two models actually incompatible if they produce the same numerical values for physical property measurements?

1.33. Schleyer and McKee wrote "Regard molecules in many different ways. Each provides instructive insights. The protobranching concept enriches understanding."[76] In what ways has this chapter prompted new ways of thinking about molecular structure?

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[250] Hoffmann, R. *Am. Sci.* **2003**, *91*, 9.

[251] Weisberg, M. *Philos. Sci.* **2004**, *71*, 1071.