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Chemical Bonding and Structure

Introduction

Organic chemistry is a broad field which intersects with such diverse areas as biology, medicine and pharmacology, polymer technology, agriculture, and petroleum engineering. At the heart of organic chemistry are fundamental concepts of molecular structure and reactivity of carbon-containing compounds. The purpose of this text is to explore this central core, which is concerned with how the structures of organic compounds are related to reactivity. Reactivity, in turn, determines the methods that can be used for synthesis. Understanding of *structure*, *reactivity*, and *synthesis* can be used within organic chemistry or applied to other fields, such as those named above, which require contributions from organic chemistry. *Structure* includes the description of bonding in organic molecules and the methods for determining, analyzing, and predicting molecular structure. Dynamic aspects of structure, such as conformational equilibria, are also included. Stereochemistry is also a crucial aspect of structure in organic chemistry. *Reactivity* pertains to the aspects of a given structure that determine its chemical transformations. Is the molecule electron-rich or electron-poor? Is it easily reduced or oxidized? What is the distribution of the most reactive electrons? Which bonds are weakest and therefore most likely to engage in reactions? Unlike structure, which is an inherent property of the molecule, reactivity usually describes an interaction with other molecules. Understanding reactivity includes describing the mechanisms, that is, the stepwise process by which reactions occur. Reactivity also encompasses the *stereochemical aspects* of the transformation. *Synthesis* encompasses those activities which are directed toward finding methods that convert existing substances into different compounds. Synthesis involves the control of reactivity to achieve specified transformations. It involves the choice of reagents, catalysts, and reaction conditions that will accomplish a given transformation within the required parameters. In various circumstances, the limiting parameters might include yield, purity of product, stereochemical control, availability or cost of reagents, or safety and environmental consequences. Structure, reactivity, and synthesis are all interrelated.

Synthesis is built on knowledge of both structure and reactivity, and understanding reactivity ultimately rests on detailed knowledge about molecular structure. A firm grounding in the principles of structure and chemical bonding is therefore an essential starting point for fuller appreciation of reactivity and synthesis. In this first chapter, we will discuss the ideas that have proven most useful to organic chemists for describing and organizing facts, concepts, and theories about the structure of organic molecules.

Structural formulas serve as key devices for communication of chemical information, and it is important to recognize the symbolic relationship between structural formulas and molecular structure. The current system of structural formulas arose largely as a result of research done in the last half of the 19th century. Elemental analyses, interrelation of various compounds, and systematic investigation of the reactivity of various "functional groups" permitted chemists to correctly deduce much information about molecular structure. For most molecules, it became possible to draw conclusions as to which atoms were directly connected (*constitution*). Lines drawn between atoms were used to represent direct connections or bonds. It was recognized that the various elements formed a characteristic numbers of bonds. The capacity of an element to form bonds was called valence, and the number of bonds a given element could form was called its *valence number*. These structural deductions predated modern electronic concepts of atomic and molecular structure and the nature of the forces that bind atoms together in molecules. Nevertheless, structural formulas proved to be readily adaptable to description of chemical bonding in terms of electron-pair bonds since the bonds came to symbolize the shared pair of electrons.

The precise description of molecular structure specifies nuclear positions with respect to other nuclei in the molecule and the distribution of the electrons associated with the nuclei. Because chemical properties are primarily determined by the outer shell of valence electrons, chemists focus attention primarily on these electrons. Spectroscopic methods and diffraction methods, especially X-ray crystal structure determination, have provided a large amount of information about atomic positions and bond lengths. Dynamic aspects of molecular structure involving such issues as alternative molecular shapes arising by bond rotations (*conformations*) can also be characterized by spectroscopic methods, especially nuclear magnetic resonance (NMR) spectroscopy. These *experimental methods* for structure determination have been joined by *computational methods*. Computational approaches for calculating molecular structures are based on systematic searching for the most stable arrangement of the atoms having a particular bonding pattern (molecular connectivity). Computational methods can be based on observed relationships between energy and structure (*molecular mechanics*) or on theoretical descriptions of bonding based on quantum chemistry.

Theories of molecular structure attempt to describe the nature of chemical bonding both qualitatively and quantitatively. To be useful to chemists, the bonding theories must provide insight into the properties and reactivity of molecules. The structural theories and concepts that are most useful in organic chemistry are the subject of this chapter. Our goal is to be able to relate molecular structure, as depicted by structural formulas and other types of structural information, such as bond lengths and electronic distributions, to the chemical reactivity and physical properties of molecules.

1.1. Valence Bond Approach to Chemical Bonding

The idea put forth by G. N. Lewis in 1916 that chemical bonding results from a sharing of electron pairs between two atoms was a fundamental advance in bonding

theory.[1] The concept of valence is related to the number of electrons available to each atom and, for the second-row elements, to the "octet rule," that is, to the stability associated with four pairs of electrons. Lewis's proposal was put on the sound ground of quantum mechanics by Heitler and London's treatment of the hydrogen molecule in 1927. This treatment marked the beginning of what we now know as *valence bond theory*.[2] A central feature of this theory was the conclusion that most of the binding energy between the two atoms at the most stable internuclear separation results from sharing of the electrons between the two nuclei. This conclusion arose in a direct way from the Heitler–London calculations. If electron 1 were constrained to be associated only with nucleus l, and electron 2 with nucleus 2, then the calculated binding energy was only a small fraction of the experimentally determined bond energy. If this constraint was removed so that the electrons were indistinguishable and permitted to interact equally with both nuclei, the calculated potential energy curve exhibited a deep minimum at the equilibrium internuclear distance. The bonding energy associated with this minimum corresponded quite well with the experimental bond energy. The covalent bond represented by a line in the simple notation H−H then takes on more precise meaning. It symbolizes the presence of *two bonding electrons* in the region between the two nuclei. The region of space occupied by an electron is called an *orbital*. In the H_2 molecule, the bonding arises from the two electrons in an orbital formed by overlap of the spherically symmetrical $1s$ atomic orbital of each hydrogen atom, as shown in Fig. 1.1. Similarly, the bonding orbitals of other molecules arise from the atomic orbitals of the constituent atoms.

Application of valence bond theory to more complex molecules involves writing as many plausible Lewis structures as possible that correspond to the correct molecular connectivity. Valence bond theory assumes that the actual molecule is a hybrid of these "canonical forms." As a simple example, the hydrogen chloride molecule is considered to be a hybrid of the limiting canonical forms H−Cl, H^+Cl^-, and H^-Cl^+. In mathematical terms, the molecule can be represented as the weighted combination of the contributing structures. Unfortunately, the extension of this approach to larger molecules results in a large number of canonical structures, which makes both conceptual and computational interpretation difficult. For example, more than 175 individual structures, most with charge separation, can be written for benzene.[3] For this reason, qualitative concepts which arise from the valence bond treatment of simple molecules are applied to larger molecules. The key ideas that are used to adapt the concepts of valence bond theory to complex molecules are *hybridization* and *resonance*. In this qualitative form, valence bond theory describes molecules in terms of orbitals that are mainly localized between two atoms. The shapes of these orbitals are assumed to be similar to those of orbitals described by more quantitative
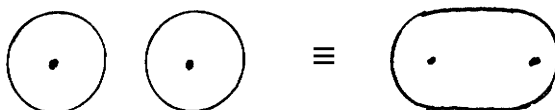
Fig. 1.1. Representation of σ bond of H_2 formed by overlap of $1s$ orbitals.

1. G. N. Lewis, *J. Am. Chem. Soc.* **38:**762 (1916).
2. W. Heitler and F. London, *Z. Phys.* **44:**455 (1927). For a historical review, see M. Simonetta, in *Structural Chemistry and Molecular Biology*, A. Rich and N. Davidson, eds., W. H. Freeman, San Francisco, 1968, pp. 769–782.
3. C. Amovilli, R. D. Harcourt, and R. McWeeny, *Chem. Phys. Lett.* **187:**494 (1991).

treatment of simpler molecules. The properties of complex molecules are regarded as derived from the combination of the properties of the constituent bonds. This conceptual approach is in accord with a large body of chemical knowledge which indicates that structure and reactivity of similar bonds and groups are relatively constant in different molecules.

1.1.1. Orbital Hybridization

The concepts of *directed valence* and *orbital hybridization* were developed by Linus Pauling soon after the description of the hydrogen molecule by the valence bond theory. These concepts were applied to an issue of specific concern to organic chemistry, the tetrahedral orientation of the bonds to tetracoordinate carbon.[4] Pauling reasoned that because covalent bonds require mutual overlap of orbitals, stronger bonds would result from better overlap. Orbitals that possess directional properties, such as p orbitals, should therefore be more effective than spherically symmetric s orbitals.

The electronic configuration of a carbon atom in its ground state is $1s^2 2s^2 2p^2$, and is not consistent with a simple rationalization of the tetrahedral bonding at carbon. Pauling suggested that four atomic orbitals ($2s$, $2p_x$, $2p_y$, $2p_z$) are replaced by a set of four equivalent *hybrid orbitals*, designated sp^3. The approximate shapes of these orbitals are shown in Fig. 1.2. Notice particularly that the probability distribution is highly directional for the sp^3 orbitals, with the region of greatest probability concentrated to one side of the nucleus.

Orbital hybridization has two important consequences. First, four bonds, rather than two, can be formed to carbon. Second, the highly directional sp^3 orbitals provide for more effective overlap and stronger bonds. Thus, although an isolated carbon atom with one electron in each of four equivalent sp^3-hybridized orbitals would be of higher energy than the ground state, the energy required in a formal sense to promote two electrons from a $2s$ orbital to sp^3 orbitals is more than compensated for by the formation of four bonds rather than two. In addition, each of the bonds is stronger owing to the directional properties of the hybrid orbitals. Tetrahedral geometry is predicted by the mathematical description of hybridization. Methane is found experimentally to be a perfect tetrahedron, with each H−C−H bond angle equal to 109.5°. The valence bond representation of methane in Fig. 1.3 shows the orbital overlaps that give rise to four equivalent C−H bonds. These bonds, in which the electron density is cylindrically symmetric about the internuclear axis are called σ bonds.

The hybridization concept can also be applied to molecules containing double and triple bonds. The descriptive valence bond approach to the bonding in ethylene and
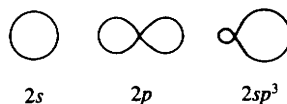

$2s$ $\quad$ $2p$ $\quad$ $2sp^3$

Fig. 1.2. Cross section of angular dependence of orbitals.

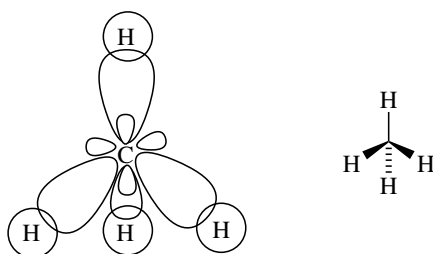4. L. Pauling, *J. Am. Chem. Soc.* **53:**1367 (1931).

Fig. 1.3. Valence bond structural representation of methane resulting from overlap of H $1s$ orbitals with four equivalent sp^3 orbitals of carbon.

acetylene and their congeners is analogous to that for methane. In ethylene (Fig. 1.4), each carbon bears three ligands and is sp^2 hybridized. Three sp^2 orbitals are generated from the $2s$ and two of the $2p$ orbitals. The three sp^2 orbitals are coplanar and orthogonal to the remaining $2p$ orbital. A bond is formed between the two carbon atoms by overlap of an sp^2 orbital of each. The four hydrogens are bonded by σ bonds involving hydrogen $1s$ orbitals and the remaining two sp^2 hybrid orbitals. Additional bonding between the two carbon atoms is portrayed as resulting from overlap of the unhybridized p orbitals on each carbon atom, each of which contains one electron. This overlap is somewhat less effective than that of a σ bond and corresponds to a π bond. The electron distribution in a π bond is concentrated above and below the plane of the σ framework. The molecule is planar, and the plane defined by the nuclei is a nodal plane for the π system. The hybridization at each carbon atom of acetylene is sp, and the two carbon atoms are considered as bonded by a σ bond and two π bonds, as shown in Fig. 1.4.

The concept of hybrid orbitals is deeply ingrained in the thinking of organic chemists, as widely reflected in texts and the research literature. However, Pauling and others recognized that there was a different conceptual starting point in which multiple bonds can be represented as bent bonds.[4]

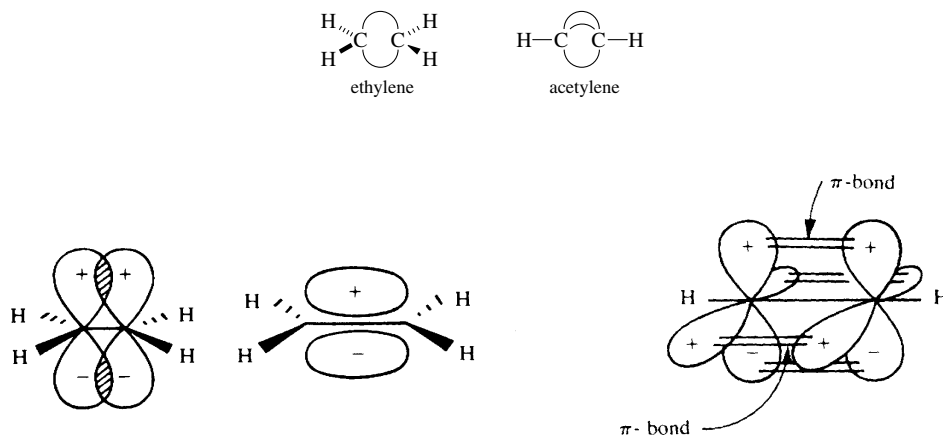ethylene   acetylene

Fig. 1.4. The π bond in ethylene and the π bonds in acetylene.

It has been shown that description of bonding based on the bent-bond concept can be just as successful in describing molecular structure as the hybridization concept.[5] We will, however, use the hybridization terminology.

The relation between the number of ligands on carbon (its coordination number), hybridization, and molelcular geometry is summarized in Table 1.1. Unless all the ligands on a particular carbon atom are identical, there will be deviations from the perfectly symmetrical structures implied by the hybridization schemes. For example, whereas methane and carbon tetrachloride are tetrahedral with bond angles of 109.5°, the C−C−C angle in cyclohexane is 111.5°. The H−C−H angle in formaldehyde is 118° rather than 120°. Benzene, however, is a regular hexagon with 120° bond angles.

Large deviations in bond angles from the normal values are found in cyclopropane, cyclobutane, and other molecules containing three- and four-membered rings. These molecules are less stable than molecules with larger rings, and the difference in energy is referred to as *angle strain*. Because the three carbon atoms of a cyclopropane ring are required by symmetry to be at the vertices of an equilateral triangle, the internuclear angles are 60°. This arrangement represents a serious distortion of the normal tetrahedral bond angle and engenders unique chemical and physical properties. To develop a valence bond model of the bonding in cyclopropane, it is assumed than the carbon atoms will adopt the hybridization that produces the most stable bonding arrangement.[6] The orbitals used for forming the carbon–carbon bonds in cyclopropane can overlap more effectively if they have more p character than normal sp^3 bonds, since additional p character corresponds to a reduced bond angle. Consequently, the orbitals used for bonding to hydrogen must have increased s character. This adjustment in hybridization can be described quantitatively by assignment of numerical values to the "percent s character" in the C−H bonds. Values of 33% and 17%, respectively, have been suggested for the C−H and C−C bonds of cyclopropane, on the basis of NMR measurements.[7] The picture of the bonding in cyclopropane indicates that the region of maximum orbital overlap would not correspond to the internuclear axis. The C−C bonds are described as "bent bonds" (Fig. 1.5).

The change in hybridization is associated with a change in electronegativity. The greater the s character of a particular carbon orbital, the greater is its electronegativity. As a result, carbon atoms that are part of strained rings are more electronegative than normal toward hydrogen.[8] Figure 1.6 shows some calculated charges for cyclopropane and other

Table 1.1. Dependence of Structure on Hybridization of Carbon

Number of ligands	Hybridization	Geometry	Examples
4	sp^3	Tetrahedral	Methane, cyclohexane, methanol, carbon tetrachloride
3	sp^2	Trigonal	Ethylene, formaldehyde, benzene methyl cation, carbonate ion
2	sp	Linear	Acetylene, carbon dioxide, hydrogen cyanide, allene (C-2)

5. P. A. Shultz and R. P. Messmer, *J. Am. Chem. Soc.* **115:**10925, 10938, 10943 (1993).
6. For a review of various descriptions of the bonding in cyclopropane, see A. de Meijer, *Angew. Chem. Int. Ed. Engl.* **18:**809 (1979); K. B. Wiberg, in *The Chemistry of the Cyclopropyl Group*, Z. Rappoport, ed., John Wiley & Sons, New York, Chapter 1, 1987; B. Rozsondai, in *The Chemistry of the Cyclopropyl Group*, Vol. 2, Z. Rappoport (ed.), John Wiley & Sons, New York, Chapter 3, 1995.
7. F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.* **89:**5962 (1967).
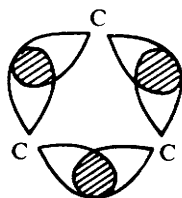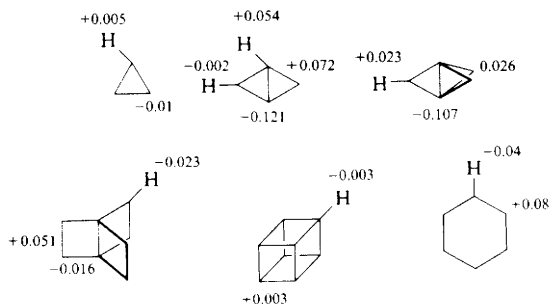8. K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am. Chem. Soc.* **109:**1001 (1987).

Fig. 1.5. Bent bonds in cyclopropane.

Fig. 1.6. Charge distributions in strained cyclic hydro-
carbons in comparison with cyclohexane. Data are from
K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am.
Chem. Soc.* **109:**1001 (1987).

strained hydrocarbons in comparison with the unstrained reference cyclohexane. Notice that the greater the distortion from the normal tetrahedral angle, the greater is the negative charge on carbon. This relative electronegativity is reflected in both the acidity and the NMR chemical shifts of hydrogens attached to strained ring systems.

Even more drastic distortions from ideal geometry are found when several small rings are assembled into bicyclic and tricyclic molecules. The synthesis of such highly strained molecules is not only a challenge to the imagination and skill of chemists, but also provides the opportunity to test bonding theories by probing the effects of unusual bonding geometry on the properties of molecules. One series of such molecules is the *propellanes*.[9] The structures of some specific propellanes and the strain energies of the molecules are shown in Fig. 1.7. Each of the molecules in Fig. 1.7 has been synthesized, and some of their physical and structural properties have been analyzed. In the propellanes with small rings, the bridgehead must be severely flattened to permit bonding. In order to attain this geometry, the hybridization at the bridgehead carbons must change as the size of the bridges decreases. Whereas the hybridization at the bridgehead carbons in [4.4.4]propel-lane can be approximately the normal sp^3, in [2.2.2]propellane the flattening of the bridgehead must result in a change to approximately sp^2 hybridization, with the central bond between the two bridgehead carbons being a σ bond formed by overlap of two p orbitals. The distortion is still more extreme in [1.1.1]propellane, in which the bridgehead

9. K. B. Wiberg, *Acc. Chem. Res.* **17:**379 (1984); K. B. Wiberg, *Chem. Rev.* **89:**975 (1989).
10. J. E. Jackson and L. C. Allen, *J. Am. Chem. Soc.* **106:**591 (1984); K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am. Chem. Soc.* **109:**985 (1987); K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am. Chem. Soc.* **109:**1001 (1987).

[3.3.3]   [3.2.2]   [3.2.1]   [2.2.2]   [2.1.1]   [1.1.1]
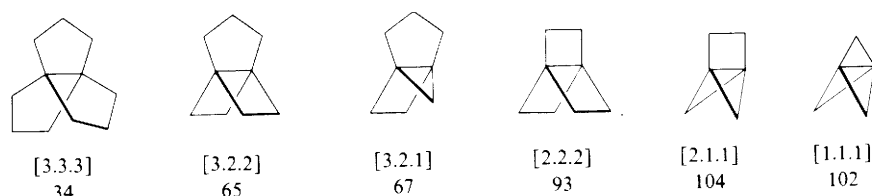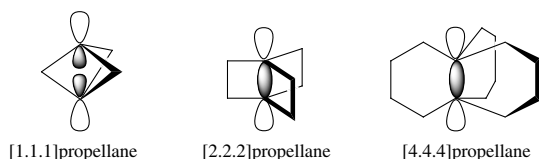 34   65   67   93   104   102

Fig. 1.7. Strain energies of some propellanes in kcal/mol.

carbon is an "inverted carbon" with all four bonds to one side. The resulting bond has quite special characteristics and is not adequately described as a localized bond.[10]

[1.1.1]propellane   [2.2.2]propellane   [4.4.4]propellane

The distortion of the bond angles in propellanes leads both to strain and to unusual chemical reactivity. [3.2.1]Propellane, for example, is found to have a strain energy of 67 kcal/mol, as compared to 27 kcal/mol for cyclopropane. The molecule is exceptionally reactive and undergoes a variety of reactions involving the cleavage of the central bond under mild conditions. For example, it undergoes bromination instantaneously at $-50°C$.[11] The strain should be less in [3.3.3]propellane, in which a smaller distortion at the bridgehead carbons is required to permit bonding. This is reflected by the lower strain energy of 34 kcal/mol. On the other hand, the smaller bridges lead to increased strain. [2.2.1]Propellane conforms to the expectation that it would be highly reactive. It can be observed when isolated in solid argon at 45 K but decomposes at temperatures higher than this and cannot be isolated as a pure substance.[12] [1.1.1]Propellane is a surprisingly stable substance. Although the strain is comparable to that of [3.1.1]- and [2.2.1]propellane, the relief of strain on rupture of the center bond is quite small, leading to greater thermal stability.[13] The "inverted" center bond is largely p in character, and, as a result, there is a considerable charge density external to the ring. This permits a variety of radical and electrophilic addition reactions to occur.[14]
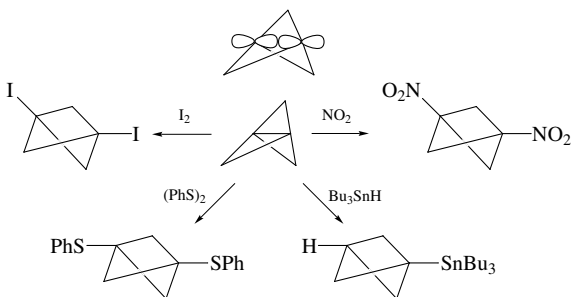
11. K. B. Wiberg and G. J. Burgmaier, *J. Am. Chem. Soc.* **94:**7396 (1972).
12. K. B. Wiberg, C. M. Breneman, and T. J. LePage, *J. Am. Chem. Soc.* **112:**61 (1990); A. Gobbi and G. Frenking, *J. Am. Chem. Soc.* **116:**9275 (1994).
13. K. B. Wiberg and F. H. Walker, *J. Am. Chem. Soc.* **104:**5239 (1982); C. Y. Zhao, Y. Zhang, and X. Z. You, *J. Phys. Chem.* **101:**3174 (1997).
14. K. B. Wiberg and S. T. Waddell, *J. Am. Chem. Soc.* **112:**2194 (1990); D. S. Toops and M. R. Barbachyn, *J. Org. Chem.* **58:**6505 (1993).
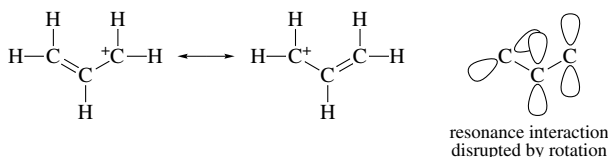
1.1.2. Resonance

A second concept that makes valence bond theory useful for the structural description of complex molecules is *resonance theory*. Resonance theory is an extension of valence bond theory which recognizes that, for many molecules, more than one Lewis structure can be written. Its usefulness in organic chemistry lies in its being a convenient way of depicting electron delocalization. Resonance theory is particularly useful in describing conjugated compounds and reactive intermediates. Arguments based on resonance theory are usually made in a qualitative way, although a mathematical treatment can be applied.[15] The elements of resonance theory that are necessary for qualitative applications can be summarized as follows:

a. Whenever alternative Lewis structures can be written for a molecule that differ only in assignment of electrons among the nuclei, with the nuclear positions being constant for all the structures, then the molecule is not adequately represented by a single Lewis structure but has weighted properties of all of the alternative Lewis structures.

b. All structures are restricted to the maximum number of valence electrons that is appropriate for each atom, that is, two for hydrogen and eight for the first-row elements.

c. Some individual Lewis structures are more stable than others. The structures that approximate the actual molecule most closely are those that incorporate the following features: maximum number of covalent bonds, minimum separation of unlike charges, and placement of any negative charges on the most electronegative atom (or any positive charge on the most electropositive atom). Stated in another way, the most favorable (lowest-energy) resonance structure makes the greatest contribution to the true (hybrid) structure.

d. In most cases, the delocalization of electrons, as represented by the writing of alternative Lewis structures, is associated with enhanced stability relative to a single localized structure. This is not always true, however, since molecules and ions are known in which electron delocalization produces an increase in energy relative to a localized model.

Some fundamental structure–stability relationships can be employed to illustrate the use of resonance concepts. The allyl cation is known to be a particularly stable carbocation. This stability can be understood by recognizing that the positive charge is delocalized between two carbon atoms, as represented by the two equivalent resonance structures. The delocalization imposes a structural requirement. The *p* orbitals on the three contiguous carbon atoms must all be aligned in the same direction to permit electron delocalization. As a result, there is an energy barrier to rotation about the carbon–carbon

15. For a classical presentation of resonance theory, see G. W. Wheland, *Resonance Theory in Organic Chemistry*, John Wiley & Sons, New York, 1955. Models of molecular structure based on mathematical description of valence bond theory have been developed: F. W. Bodrowicz and W. A. Goddard III, in *Modern Theoretical Chemistry, Methods of Electronic Structure Theory*, Vol. 3, H. F. Schaefer III, ed., Plenum Press, New York, 1977, Chapter 4; A. Voter and W. A. Goddard III, *Chem. Phys.* **57:**253 (1981); N. D. Epiotis, *Unified Valence Bond Theory of Electronic Structure*, Springer-Verlag, Berlin, 1983; D. J. Klein and N. Trinajstic, eds., *Valence Bond Theory and Chemical Structure*, Elsevier, Amsterdam, 1990; D. L. Cooper, J. Gerratt, and M. Raimondi, *Chem. Rev.* **91:**929 (1991).

bonds in the allyl cation. The most stable geometry is planar, and the barrier to rotation is estimated to be 36–38 kcal/mol.[16]

resonance interaction
disrupted by rotation

Another important and familiar example of resonance is the stabilization of the enolate anions formed by deprotonation of carbonyl compounds. This can be illustrated by considering the relative acidity of 2-methylpropene (isobutene) and 2-propanone (acetone). The relative acidity is indicated by the pK values, which are $\sim$25 and $\sim$45, respectively. The difference of $\sim$20 pK units (20 powers of 10) shows that it is much easier for a proton to be removed from acetone than from isobutene. The main reason for the difference in acidity is the difference in stability of the two conjugate bases. A resonance-stabilized anion is generated in each case, but one of the contributing structures for the acetone anion has a negative charge on oxygen. In both resonance structures for the anion of isobutene, the negative charge is on carbon. Because oxygen is a more electronegative element than carbon, application of resonance theory leads to the conclusion that the acetone anion will be more stable than the isobutene anion and that acetone will therefore be more acidic.
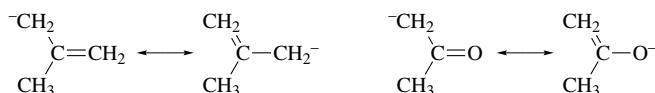
Another example of the effect of resonance is in the relative acidity of carboxylic acids as compared to alcohols. Carboxylic acids derived from saturated hydrocarbons have pK_a values near 5, whereas saturated alcohols have pK_a values in the range 16–18. This implies that the carboxylate anion can accept negative charge more readily than an oxygen on a saturated carbon chain. This can be explained in terms of stabilization of the negative charge by resonance.[17]


Resonance stabilization of
carboxylate anion.

Alcoholate anions have negative
charge localized on a single oxygen.
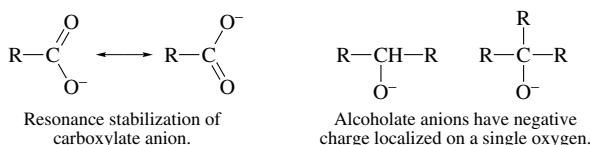
One of the structural implications of the delocalization of the negative charge, the identity of the two C−O bond lengths, intermediate between those of single and double bonds, has been verified by many crystal structure determinations.

Dynamic structural characteristics can also be interpreted in terms of resonance. There is a substantial barrier to rotation about the C−N single bonds in carboxamides. A frequently observed consequence is the nonidentity of NMR peaks due to the *syn* and *anti*

16. K. B. Wiberg, C. M. Breneman, and T. J. LePage, *J. Am. Chem. Soc.* **112:**61 (1990); A. Gobbi and G. Frenking, *J. Am. Chem. Soc.* **116:**9275 (1994).

17. F. G. Bordwell and A. V. Satish, *J. Am. Chem. Soc.* **116:**8885 (1994); P. C. Hiberty and C. P. Byrman, *J. Am. Chem. Soc.* **117:**9875 (1995); J. D. da Motta Neto and M. A. C. Nascimento, *J. Phys. Chem.* **100:**15105 (1996).

substituents on nitrogen. The barrier is in the range of 15–20 kcal/mol.[18] A planar structure is imposed by the necessity of *p*-orbital overlap for delocalization. Other structural parameters of amides, such as bond lengths and bond force constants, are also consistent with the resonance model.[19]
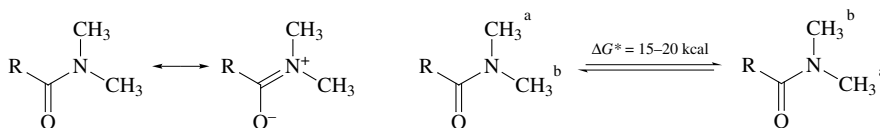
Resonance concepts are especially important in systems in which two or more double bonds are in conjugation. Resonance structures permit a description of the interaction between the bonds. Carbonyl compounds having a carbon–carbon double bond adjacent to the carbonyl group provide a good example of how structural features can be related to resonance interactions. While only a single uncharged stucture can be drawn, two structures with charges can be drawn. The structure with a negative charge on oxygen is far more important because of the higher electronegativity of oxygen relative to carbon. The structure with a positive charge on oxygen is unfavorable and would make only a minor contribution.
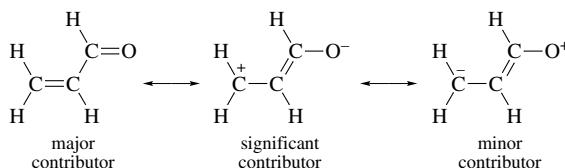
Some of the structural features of this class of compounds which are in accord with the resonance picture are as follows:

a. The C=O bond is not as strong as in saturated carbonyl compounds. This is revealed by the infrared stretching frequency, which comes at lower energy (typically $1690\,cm^{-1}$ versus $1730\,cm^{-1}$ for saturated compounds).
b. Carbon-13 NMR spectroscopy also reveals that the β carbon is less shielded (lower electron density) than is the case for a simple alkene. This results from the delocalization of π electrons from this carbon to the carbonyl oxygen.
c. The chemical reactivity of the double bond is also affected by the presence of the conjugated carbonyl group. Simple alkenes are not very reactive toward nucleophiles. In contrast, double bonds adjacent to carbonyl groups do react with nucleophiles. The partial positive charge depicted by the resonance structure makes the β carbon subject to nucleophilic attack.

18. B. M. Pinto, in *Acyclic Organonitrogen Stereodynamics*, J. B. Lambert and Y. Takeuchi, eds., VCH Publishers, New York, 1992, pp. 149–175.
19. The issue of resonance in carboxamides has recently been reexamined. Most of the structural consequences predicted by resonance are consistent with a stabilizing interaction which results in a net shift of electron density from nitrogen to carbon and oxygen; A. J. Bennet, V. Somayaji, R. S. Brown, and B. D. Santarsiero, *J. Am. Chem. Soc.* **113:**7563 (1991); A. Greenberg, T. D. Thomas, C. R. Bevilacqua, M. Coville, D. Ji, J.-C. Tsai, and G. Wu, *J. Org. Chem.* **57:**7093 (1992).

Also, the carbonyl group stabilizes the negative charge that develops at the α carbon as a result of nucleophilic attack. All of these effects are summed up by saying that the carbonyl group acts as an *electron-withdrawing group* toward the double bond, as is depicted in the most important of the charged resonance structures.

There are also substituents that can act as electron-releasing groups through resonance. Among familiar examples are alkoxy and amino groups in vinyl ethers and enamines, respectively.

We might wonder how important such resonance effects are since the resonance structures have the unfavorable feature of charge separation and place a positive charge on electronegative atoms. Several approaches have been taken to determining the importance of these interactions. Most are based on molecular orbital theory (see Sections 1.3 and 1.6). Typically, the results reveal only small ground-state structural changes, but parameters which reflect reactivity do indicate that these molecules are very much enhanced in reactivity toward electrophiles.[20] Carbon and proton NMR shifts are also upfield in vinyl ethers and enamines, as implied by the charged resonance structures. The most detailed analyses suggest that there is indeed a π polarization of the type indicated, but that it is compensated by a σ polarization in the opposite sense.[21]
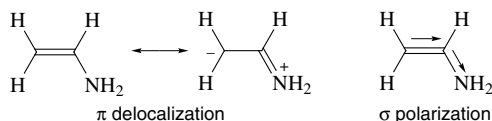
The most impressive example of resonance stabilization is benzene, in which the delocalization is responsible for a stabilization of 30–36 kcal/mol, the *resonance energy* of benzene.
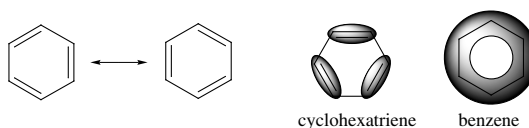

We will return to the aromatic stabilization of benzene in more detail in Chapter 9, but substituted benzenes provide excellent examples of how proper use of the resonance concept can be valuable in predicting reactivity. Many substituents can be readily classified

20. A. R. Katritzky and M. Karelson, *Tetrahedron Lett.* **31:**2987 (1990); K. B. Wiberg, R. E. Rosenberg, and P. R. Rablen, *J. Am. Chem. Soc.* **113:**2890 (1991).
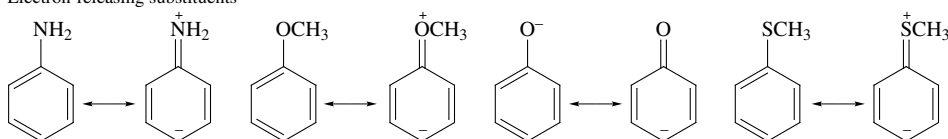21. K. B. Wiberg and P. R. Rablen, *J. Am. Chem. Soc.* **115:**9234 (1993).

as electron-releasing or electron-withdrawing simply by noting whether the substituent can donate or accept electrons by π-orbital interaction with the ring.

Electron-withdrawing substituents
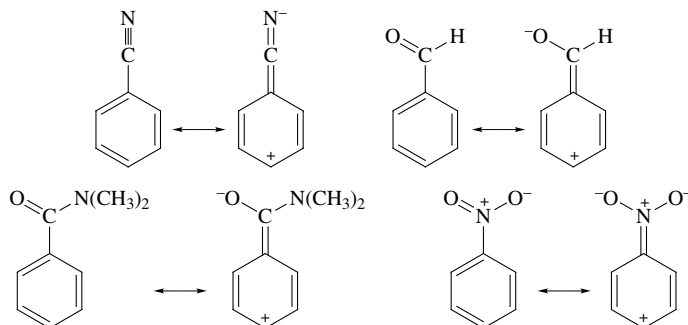
Electron-releasing substituents

We will address this issue further in Chapter 10, where the polar effects of the substituents on both the σ and π electrons will be considered. For the case of electrophilic aromatic substitution, where the energetics of interaction of an approaching electrophile with the π system determines both the rate of reaction and position of substitution, simple resonance arguments are extremely useful.

1.2. Bond Energy, Polarity, and Polarizability

1.2.1. Bond Energies

Of the various geometric parameters associated with molecular shape, the one most nearly constant from molecule to molecule and most nearly independent of substituent effects is bond length. Bond lengths to carbon depend strongly on the hybridization of the carbon involved but are little influenced by other factors. Table 1.2 lists the interatomic distances for some of the most common bonds in organic molecules. The near constancy of bond lengths from molecule to molecule reflects the fact that the properties of individual bonds are, to a good approximation, independent of the remainder of the molecule.

Table 1.3 gives some bond-energy data. Part A includes bond energies for some simple diatomic molecules and generalized values for some of the types of bonds found

Table 1.2. Bond Lengths (Å)[a]

sp^3	C–H	1.09	sp^3–sp^3	C–C	1.54	sp^2–sp^2	C–C	1.46	C–O	1.42
sp^2	C–H	1.086	sp^3–sp^2	C–C	1.50	sp^2–sp^2	C=C	1.34	C=O	1.22
sp	C–H	1.06	sp^3–sp	C–C	1.47	sp–sp	C≡C	1.20		

a. From experimental values tabulated for simple molecules by M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99:**4907 (1977).

most often in organic molecules. The assumption that bond energies are independent of the remainder of the molecule is a rather rough one. Part B of Table 1.3 lists some specific C−H, C−C, and other bond energies. It is apparent that some are substantially different from the generalized values. For example, the CH_2−H bond dissociation energies listed for propene and toluene are 85 kcal/mol, which is significantly less than for a C−H bond in ethane (98 kcal/mol). The reason for the relative weakness of these particular bonds is that the allyl and benzyl radicals that are produced by the bond dissociations are stabilized by resonance.

$$H_2C{=}CH{-}CH_2\bullet \longleftrightarrow \bullet H_2C{-}CH{=}CH_2$$
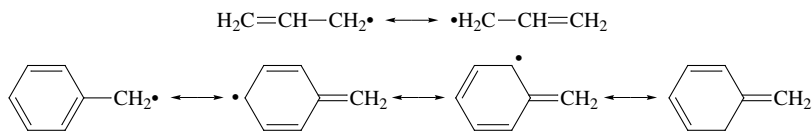
A similar explanation lies behind the diminished strength of the sp^3–sp^3 carbon–carbon bond in ethylbenzene. The general trend toward weaker C−C bonds with increased substitution that can be recognized in Table 1.3 reflects the increased stability of substituted radicals relative to primary radicals.

The bond energies in Table 1.3 refer to *homolytic* bond dissociation to uncharged radical fragments. Many reactions involve heterolytic bond cleavages. The energy for heterolytic cleavage of C−H or C−C bonds in the gas phase is very high, largely because of the energy required for charge separation. However, in solution, where stabilization of the ions by solvation becomes possible, heterolytic bond dissociation can become energetically feasible. Heterolytic bond dissociations are even more sensitive to structural changes than homolytic ones. Table 1.4 gives a series of comparable ionization energies for cleavage of H^- from hydrocarbons and Cl^- from chlorides in the gas phase. Besides

Table 1.3. Bond Energies (kcal/mol)

A. Some common bond energies[a]					
H−H	103	C−H	98	C=C	145
C−C	81	N−H	92	C≡C	198
O−O	34	O−H	109	N≡N	225
Cl−Cl	57	Cl−H	102	C=O	173
Br−Br	45	Br−H	87	C−O	79
I−I	36	I−H	71	C−N	66

B. Some specific bond dissociation energies[b]					
H_3C−H	104	H_3C−CH_3	88	H_3C−F	108
CH_3CH_2−H	98	H_5C_2−CH_3	85	H_3C−Cl	84
$H_2C{=}CH$−H	110[c]	$(CH_3)_2CH$−CH_3	83	H_3C−Br	70
HC≡C−H	131	$PhCH_2$−CH_3	70	H_3C−I	56
$H_2C{=}CHCH_2$−H	85	H_5C_2−C_2H_5	82	H_3C−OH	91
$PhCH_2$−H	85	$(CH_3)_2CH$−$CH(CH_3)_2$	78		
H_2N−H	103	$H_2C{=}CH_2$	171[c]		
CH_3NH−H	92	HC≡CH	228[c]		
CH_3O−H	102				

a. From Table 1, G. J. Janz, *Thermodynamic Properties of Organic Compounds*, Academic Press, New York, 1967.
b. Except where noted, from J. A. Kerr, *Chem. Rev.* **66:**465 (1966).
c. K. M. Ervin, S. Gronert, S. E. Barlow, M. K. Gilles, A. G. Harrison, V. M. Bierbaum, C. H. DePuy, W. C. Lineberger, and G. B. Ellison, *J. Am. Chem. Soc.* **112:**5750 (1990).

**Table 1.4. Heterolytic Bond Dissociation Energies for
Some C−H and C−Cl Bonds**[a]

R	$R-H \rightarrow R^+ + H^-$ ΔE_{C-H} (kcal/mol)	$R-Cl \rightarrow R^+ + Cl^-$ ΔE_{C-Cl} (kcal/mol)
CH_3	312.2	227.1
CH_3CH_2	272.6	190.3
$(CH_3)_2CH$	249.9	171.0
$CH_2=CH$	290.2	
$CH_2=CHCH_2$	255.3	

a. Data from C. G. Screttas, *J. Org. Chem.* **45:**333 (1980).

noting the higher energies in comparison with the homolytic bond dissociation energies, one can see that branching decreases the energy requirement for heterolytic bond cleavage more dramatically than for homolytic cleavage. These bond-energy relationships are consistent with the familiar order of carbocation stability, *tert* > *sec* > *pri* > methyl. Note also that the heterolytic bond dissociation energies for allyl and vinyl bonds reflect the stability of allyl cations and the instability of vinyl cations.

Smaller, but nevertheless significant, differences in energies of organic molecules also result from less obvious differences in structure. Table 1.5 gives the heats of formation of some hydrocarbons. These energy values represent the heat evolved on formation of the compound from its constituent elements under standard conditions. The heats of formation therefore permit precise comparison of the stability of *isomeric compounds*. The more negative the heat of formation, the greater is the stability. Direct comparison of compounds having different elemental composition is not meaningful, because the total number of bonds formed is then different.

Part A of Table 1.5 shows all the acyclic C_4–C_6 and some of the C_8 hydrocarbons. A general trend is discernible in the data. Branched-chain hydrocarbons are more stable than straight-chain hydrocarbons. For example, ΔH_f° for *n*-octane is −49.82 kcal/mol, whereas the most highly branched isomer possible, 2,2,3,3-tetramethylbutane, is the most stable of the octanes, with ΔH_f° of −53.99 kcal/mol. Similar trends are observed in the other series.

Part B of Table 1.5 gives heats of formation for the C_4, C_5, and some of the C_6 alkenes. A general relationship is also observed for the alkenes. The more highly substituted the double bond, the more stable is the compound. There are also other factors that enter into alkene stability. *trans*-Alkenes are usually more stable than *cis*-alkenes, probably largely because of increased nonbonded repulsion in the *cis* isomer.[22]

1.2.2. Electronegativity and Polarity

Another fundamental property of chemical bonds is *polarity*. In general, it is to be expected that the distribution of the pair of electrons in a covalent bond will favor one of the two atoms. The tendency of an atom to attract electrons is called *electronegativity*. There are a number of different approaches to assigning electronegativity, and most are numerically scaled to a definition originally proposed by Pauling.[23] Part A of Table 1.6

22. For a theoretical discussion of this point, see N. D. Epiotis, R. L. Yates, and F. Bernardi, *J. Am. Chem. Soc.* **97:**5961 (1975).
23. For leading references, see G. Simons, M. E. Zandler, and E. R. Talaty, *J. Am. Chem. Soc.* **98:**7869 (1976).

Table 1.5. Standard Enthalpies of Formation of Some Hydrocarbons (kcal/mol)[a]

A. Saturated hydrocarbons

C_4		C_8	
Butane	−30.15	Octane	−49.82
2-Methylpropane	−32.15	2-Methylheptane	−51.50
		3-Methylheptane	−50.82
C_5		4-Methylheptane	−50.69
Pentane	−35.00	2,2,-Dimethylhexane	−53.71
2-Methylbutane	−36.90	2,3-Dimethylhexane	−51.13
2,2-Dimethylpropane	−36.97	2,4-Dimethylhexane	−52.44
		3,3-Dimethylhexane	−52.61
C_6		2,2,3-Trimethylpentane	−52.61
Hexane	−39.96	2,2,4-Trimethylpentane	−53.57
2-Methylpentane	−41.66	2,2,3,3-Tetramethylbutane	−53.99
3-Methylpentane	−41.02		
2,3-Dimethylbutane	−42.49		
2,2-Dimethylbutane	−44.35		

B. Alkenes

C_4		C_6	
1-Butene	−0.03	1-Hexene	−9.96
trans-2-Butene	−2.67	*trans*-2-Hexene	−12.56
cis-2-Butene	−1.67	*cis*-2-Hexene	−11.56
2-Methylpropene	−4.04	*trans*-3-Hexene	−12.56
		cis-3-Hexene	−11.56
C_5		2-Methyl-1-pentene	−13.56
1-Pentene	−5.00	3-Methyl-pentene	−11.02
trans-2-Pentene	−7.59	4-Methyl-1-pentene	−11.66
cis-2-Pentene	−6.71	2-Methyl-2-pentene	−14.96
2-Methyl-1-butene	−8.68	3- Methyl-2-pentene	−14.32
3-Methyl-1- butene	−6.92	2,3-Dimethyl-1-butene	−14.78
2- Methyl-2-butene	−10.17	3,3-Dimethyl-1-butene	−14.25
		2,3-Dimethyl-2-butene	−15.91

a. From F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953.

gives the original Pauling values and also a more recent set based on theoretical calculation of electron distributions. The concept of electronegativity can also be expanded to include functional groups. Part B of Table 1.6 gives some values which are scaled to be numerically consistent with elemental electronegativities, as well as a set based on theoretical electron distribution calculations. These electronegativity values can serve to convey a qualitative impression of the electron-attracting capacity of these groups.

The unequal distribution of electron density in covalent bonds produces a *bond dipole*, the magnitude of which is expressed by the dipole moment, having the units of charge times distance.[24] Bonds with significant bond dipoles are described as being polar. The bond and group dipole moments of some typical substituents are shown in Table 1.7.

24. For more detailed discussion of dipole moments, see L. E. Sutton, in *Determination of Organic Structures by Physical Methods*, Vol. 1, E. A. Braude and F. C. Nachod, eds., Academic Press, New York, 1955, Chapter 9; V. I. Minkin, O. A. Osipov, and Y. A. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, 1970.

Table 1.6. Atomic and Group Electronegativities

A. Atomic electronegativities[a]				
H 2.1	C 2.5; **2.35**	N 3.0; **3.16**	O 3.5; **3.52**	F 4.0; **4.00**
	Si 1.8; **1.64**	P 2.1; **2.11**	S 2.5; **2.52**	Cl 3.0; **2.84**
		As 2.0; **1.99**	Se 2.4; **2.40**	Br 2.8; **2.52**
				I 2.5

B. Empirical electronegativities for some organic functional groups[b]		
CH_3 2.3; **2.55**	H 2.28; **1.20**	F 3.95; **4.00**
CH_2Cl 2.75; **2.61**	NH_2 3.35; **3.12**	Cl 3.03; **3.05**
$CHCl_2$ 2.8; **2.66**	$^+NH_3$ 3.8; **3.21**	Br 2.80; **2.75**
CCl_3 3.0; **2.70**	NO_2 3.4; **3.22**	I 2.28;
CF_3 3.35; **2.71**	OH 3.7; **3.55**	
Ph 3.0; **2.58**		
$CH{=}CH_2$ 3.0; **2.58**		
$C{\equiv}CH$ 3.3; **2.66**		
$C{\equiv}N$ 3.3; **2.69**		

a. From L. Pauling, *The Nature of the Chemical Bond*, 3rd edition, Cornell University Press, Ithaca, New York, 1960. Boldface values from G. Simons, M. E. Zandler, and E. R. Talaty, *J. Am. Chem. Soc.* **98:**7869 (1976).

b. From P. R. Wells, *Prog. Phys. Org. Chem.* **6:**111 (1968). Boldface values from R. J. Boyd and S. L. Boyd, *J. Am. Chem. Soc.* **114:**1652 (1992).

It is possible to estimate with a fair degree of accuracy the dipole moment of a molecule as the vector sum of the component bond dipoles. A qualitative judgment of bond polarity can be made by comparing the electronegativities of the bound atoms or groups. The larger the difference in electronegativity, the greater will be the bond dipole.

For most purposes, hydrocarbon groups can be considered to be nonpolar. There are, however, small dipoles associated with C−H bonds and bonds between carbons of different hybridization or substitution pattern. For normal sp^3 carbon, the carbon is found to be slightly negatively charged relative to hydrogen.[25] The electronegativity order for hybridized carbon orbitals is $sp > sp^2 > sp^3$. Scheme 1.1 lists the dipole moments of some hydrocarbons and some other organic molecules.

Electronegativity is a fundamental characteristic of atoms that is transferred into functional groups. Electronegativity correlates strongly with position in the periodic table.

**Table 1.7. Bond and Group Dipoles for Some
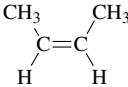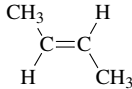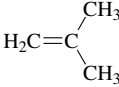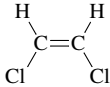Organic Functional Groups[a]**
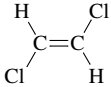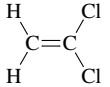
Bond moments[b]		Bond moments[b]		Group moments[b]	
C−H	0.4	C−N	0.22	MeO	1.3
C−F	1.41	C−O	0.74	NH_2	1.2
C−Cl	1.46	C=O	2.3	CO_2H	1.7
C−Br	1.38	C≡N	3.5	COMe	2.7
C−I	1.19			NO_2	3.1
				CN	4.0

a. From C. P. Smyth, *Dielectric Behavior and Structure*, McGraw-Hill Book Company, New York, 1955, pp. 244, 253.

b. In e.s. units $\times 10^{18}$.

25. K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am. Chem. Soc.* **109:**1001 (1987).

Scheme 1.1. Dipole Moments for Some Organic Compounds[a]

A. Hydrocarbons

$H_2C{=}CHCH_2CH_3$ $HC{\equiv}CCH_2CH_3$

CH$_3$ CH$_3$
    C=C
H   H

CH$_3$ H
    C=C
H   CH$_3$

0.34   0.800   0.253   0
                                                    (symmetry)

CH$_3$
H$_2$C=C
CH$_3$

$CH_3C{\equiv}CCH_3$ $H_2C{=}CHCH_3$ $HC{\equiv}CCH_3$

0.503   0   0.366   0.781
            (symmetry)

B. Substituted molecules

H   H
    C=C
Cl   Cl

H   Cl
    C=C
Cl   H

H   Cl
    C=C
H   Cl

(tetrahydrofuran ring with O)

1.90   0   1.34   1.63
            (symmetry)

| | | | | O ‖ | O ‖ |
| CH$_3$CN | CH$_3$NO$_2$ | CH$_3$OCH$_3$ | CH$_3$OH | CH$_3$CO$_2$H | CH$_3$CCH$_3$ | CH$_3$SCH$_3$ |
| 3.92 | 3.46 | 1.30 | 1.70 | 1.74 | 2.88 | 3.96 |

a. Units are in debye. Data are from *Handbook of Chemistry and Physics*, 78th edition, CRC Press, Inc., Boca Raton, Florida, 1997.

Electronegativity increases going to the right in any row of the periodic table and decreases going down any column. Because electronegativity is such an important property in relation to chemical reactivity, there has been much effort to relate it to other atomic properties. Mulliken pointed out that there is a relationship between ionization energy and electron affinity and the numerical electronegativity scale.[26] The Mulliken electronegativity can be expressed as

$$\chi = \frac{I + A}{2}$$

where I is ionization potential and A is electron affinity. Ionization energy measures the energy required to remove an electron from an atom, whereas electron affinity is the energy released upon addition of an electron to an element. Both of these energies reflect the degree of attraction the atomic nucleus has for electrons and correlate with position in the periodic table. The metallic atoms readily release electrons, whereas the halogen atoms are avid electron acceptors.

The polarity of covalent bonds between carbon and substituents is the basis of important structure–reactivity relationships in organic chemistry. The effects of polar bonds are generally considered to be transmitted in two ways. Successive polarization through bonds is called the *inductive effect*. It is expected that such an effect would diminish as the number of intervening bonds increases.
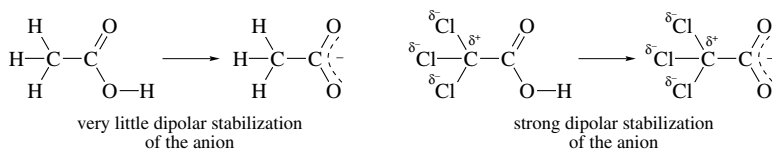
δ^-X $\overset{\delta^+}{\diagup}\overset{\delta\delta\delta^+}{\diagdown}$ Y
         $\underset{\delta\delta^+}{}$
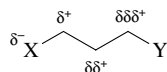
26. R. S. Mulliken, *J. Chem. Phys.* **2:**782 (1934); R. S. Mulliken, *J. Chem. Phys.* **3:**573 (1935).

The second component is called a *field effect* and is attributed to through-space interactions of the electric dipoles resulting from polar bonds.
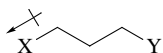
In Chapter 4, we will discuss the relative importance of inductive effects and field effects on reactivity. Generally, field effects appear to be the dominant mechanism for the transmission of electrostatic effects of polar bonds to other parts of a molecule.

One of the most extensively explored series of substituent effects involves the acidity of carboxylic acids. The pK_a values of some derivatives of acetic acid are presented in Table 1.8. These data illustrate that substitution of hydrogen by a more electronegative atom or group increases the equilibrium constant for ionization, that is, makes the derivative a stronger acid. The highly electronegative fluorine atom causes a larger increase in acidity than the somewhat less electronegative chlorine atom. A slight acid-weakening effect of a methyl substituent is observed when propanoic acid is compared with acetic acid. The pK_a data refer to measurements in solution, and some care must be taken in interpreting the changes in acidity solely on the basis of electronegativity. In fact, measurements in the gas phase show that propanoic acid is a slightly stronger acid than acetic acid.[27] In the case of acid dissociation in solution, both the proton and the carboxylate anion are strongly solvated, and this greatly favors the dissociation process in solution relative to the gas phase. We can discuss trichloroacetic acid, in which polar $C-Cl$ bonds have replaced $C-H$ bonds as an example.

very little dipolar stabilization of the anion   strong dipolar stabilization of the anion

Table 1.8. Acidity of Substituted Acetic Acids

	H_2O $(pK_a)^a$	Gas phase $(\Delta G)^b$
$(CH_3)_3CCO_2H$	5.0	337.6
$(CH_3)_2CHCO_2H$	4.9	339.0
$CH_3CH_2CO_2H$	4.9	340.4
CH_3CO_2H	4.8	341.5
HCO_2H	3.8	338.3
FCH_2CO_2H		331.6
$ClCH_2CO_2H$	2.7	329.0
F_3CCO_2H		317.4
Cl_3CCO_2H	0.7	
$NCCH_2CO_2H$	2.6	
$O_2NCH_2CO_2H$	1.3	

a. From *Stability Constants and Stability Constants*, *Supplement No. 1*, Special Publications 17 (1964) and 25 (1971), The Chemical Society, London.
b. ΔG for $AH \rightarrow H^+ + A^-$ in kcal/mol at 300 K; from G. Caldwell, R. Renneboog, and P. Kebarle, *Can. J. Chem.* **67:**611 (1989).

27. R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.* **95:**4050 (1973).

For the acid dissociation equilibrium,

$$RCO_2H \; + \; H_2O \; \rightleftharpoons \; RCO_2^- \; + \; H_3O^+$$

dissociation places a negative charge on the carboxylate residue and increases the electron density at the carboxyl group carbon and oxygen atoms. For acetic acid, where $R = CH_3$, this increase occurs adjacent to the carbon on the methyl group, which bears a very small negative charge. In the case of trichloroacetic acid, $R = CCl_3$, the corresponding carbon is somewhat positive as a result of the $C-Cl$ bond dipoles (inductive effect). The cumulative effect of the three $C-Cl$ bond dipoles establishes a strong dipole (field effect) associated with the CCl_3 group. As a result, the development of negative charge is more favorable, and trichloroacetic acid is a stronger acid than acetic acid.

It is always important to keep in mind the *relative* nature of substituent effects. Thus, the effect of the chlorine atoms in the case of trichloroacetic acid is primarily to stabilize the dissociated anion. The acid is more highly dissociated than in the unsubstituted case because there is a more favorable energy *difference* between the parent acid and the anion. It is the energy differences, not the absolute energies, that determine the equilibrium constant for ionization. As we will discuss more fully in Chapter 4, there are other mechanisms by which substituents affect the energy of reactants and products. The detailed understanding of substituent effects will require that we separate polar effects from these other factors.

It can be seen from the data in Table 1.8 that alkyl substituents slightly decrease the acidity of carboxylic acids in solution. This is a general effect and is attributable to two factors. One is a steric effect. The increasing steric bulk somewhat destabilizes the carboxylate anion by decreasing the effectiveness of solvation.[28] Alkyl groups also have an inductive/field effect that decreases acidity. This results from the weak electron-donating character of the alkyl substituent which causes acetic acid and other alkanoic acids to be weaker acids than formic acid both in solution and in the gas phase. The alkyl group donates charge density to the carbonyl carbon, thereby reducing the acidity of the carboxyl hydrogen.[29]

The second column in Table 1.8 shows the free energy for dissociation of some of the same acids in the gas phase. The effects of strongly electron-withdrawing groups are still evident. There is frequently a large difference in the energy of chemical processes in the gas and solution phases because of the importance of solvation. In the gas phase, alkyl groups enhance acidity. This is attributed to the greater polarizability of the larger substituents. In the case of molecules in the gas phase, any stabilization of the negative charge must be accomplished by internal charge redistribution.[30] With larger substituents, the larger molecular volume and the larger number of atoms that can participate lead to a greater stabilization.

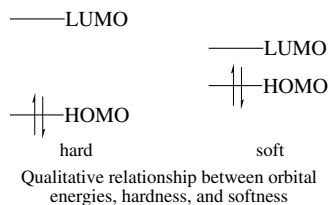### 1.2.3. Polarizability—Hardness and Softness

Another property that is closely related to electronegativity and position in the periodic table is polarizability. Polarizability is related to the size of atoms and ions and the

28. K. Bowden and R. G. Young, *Can. J. Chem.* **47:**2775 (1969).
29. A. D. Headley, M. E. McMurry, and S. D. Starnes, *J. Org. Chem.* **59:**1863 (1994); M. R. F. Siggel and T. D. Thomas, *J. Am. Chem. Soc.* **114:**5795 (1992).
30. G. Caldwell, R. Renneboog, and P. Kebarle, *Can. J. Chem.* **67:**611 (1989).

ease with which the electron cloud can be distorted. There is a mathematical correlation between polarizability and atomic volume, and polarizability is also related to the LUMO–HOMO energy gap. (See Section 1.6 if the terms HOMO and LUMO are unfamiliar.)

Qualitative relationship between orbital
energies, hardness, and softness

Numerical measures of polarizability analogous to electronegativity have been defined.[31] Hardness η is numerically expressed as

$$\eta = \tfrac{1}{2}(I - A)$$

where I is the ionization potential and A is the electron affinity. Softness σ is the opposite of hardness and is numerically expressed as

$$\sigma = 1/\eta$$

These two properties are closely related to the HOMO and LUMO energies of molecules and ions. The larger the HOMO–LUMO gap, the greater is the hardness. Numerically, hardness is approximately equal to half the energy gap, as defined above for atoms. In general, chemical reactivity increases as LUMO energies decrease and HOMO energies increase. The implication is that softer chemical species, those with smaller HOMO–LUMO gaps, will tend to be more reactive than harder ones. In qualitative terms, this can be described as the ability of nucleophiles or bases to donate electrons more readily to electrophiles and acids to begin the process of bond formation. Interactions between harder chemical entities are more likely to be dominated by electrostatic interactions. Table 1.9 gives some hardness values for atoms and common small molecules and ions.

Figure 1.8 shows the I–A gap (2η) for several radicals. Note that there is a correlation with electronegativity and position in the periodic table. The halogen anions and radicals become progressively softer from fluorine to iodine. Across the second row, softness decreases from carbon to fluorine. Highly electronegative atoms tend to be hard, whereas less electronegative atoms are softer. Polarizability is also a function of atomic number. Larger atoms are softer than smaller atoms of similar electronegativity. The charge on an atom also influences polarizability. Metal cations, for example, become harder as the oxidation number increases. Values for the hardness of some metal cations that are frequently of interest in organic chemistry are included in Table 1.9. A useful precept for understanding Lewis acid–base interactions is that hard acids prefer hard bases, and soft acids prefer soft bases. The hard–hard interactions are dominated by electrostatic attraction, whereas soft–soft interactions are dominated by mutual polarization.[32]

31. R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.* **105:**7512 (1983).
32. R. G. Pearson, *J. Am. Chem. Soc.* **85:**3533 (1963); T. L. Ho, *Hard and Soft Acids and Bases in Organic Chemistry*, Academic Press, New York, 1977; W. B. Jensen, *The Lewis Acid–Base Concept*, Wiley-Interscience, New York, 1980, Chapter 8.

**Table 1.9. Hardness of Some Atoms, Acids,
and Bases[a]**

Atom	η	Acid	η_A	Base	η_B
H	6.4	H^+	∞	H^-	6.8
Li	2.4	Li^+	35.1	F^-	7.0
C	5.0	Mg^{2+}	32.5	Cl^-	4.7
N	7.3	Na^+	21.1	Br^-	4.2
O	6.1	Ca^{2+}	19.7	I^-	3.7
F	7.0	Al^{3+}	45.8	CH_3^-	4.0
Na	2.3	Cu^+	6.3	NH_2^-	5.3
Si	3.4	Cu^{2+}	8.3	OH^-	5.6
P	4.9	Fe^{2+}	7.3	SH^-	4.1
S	4.1	Fe^{3+}	13.1	CN^-	5.3
Cl	4.7	Hg^{2+}	7.7		
		Pb^{2+}	8.5		
		Pd^{2+}	6.8		

a. From R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.*
105:7512 (1983).

Another useful generalization is the principle of maximum hardness.[33] This states that molecular arrangements that maximize hardness are preferred. Electronegativity and hardness determine the extent of electron transfer between two molecular fragments in a reaction. This can be approximated numerically by the expression

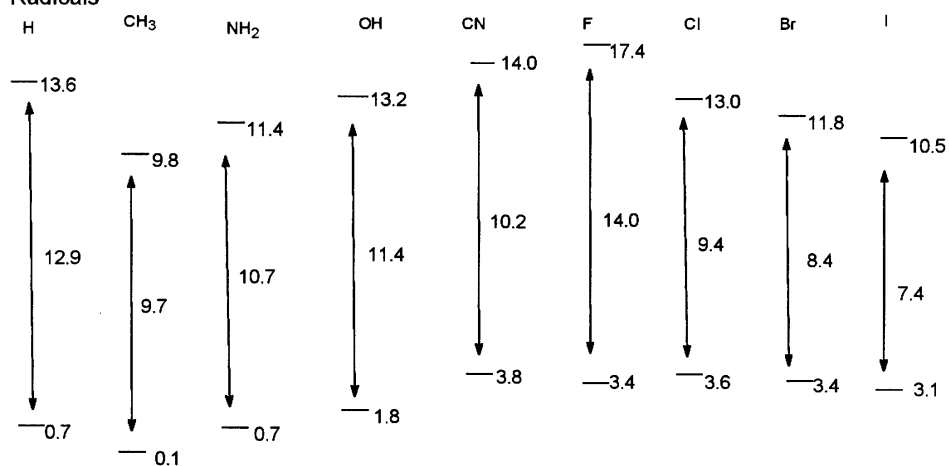$$\Delta N = \frac{\chi_X - \chi_Y}{2(\eta_X + \eta_Y)}$$

Fig. 1.8. Ionization energy (*I*) and electron affinity (*A*) gaps in eV for radicals. [Adapted from R. G. Pearson, *J. Am. Chem. Soc.* **110:**7684 (1988).]

33. R. G. Pearson, *Acc. Chem. Res.* **26:**250 (1993); R. G. Parr and Z. Zhou, *Acc. Chem. Res.* **26:**256 (1993); R. G. Pearson, *J. Org. Chem.* **54:**1423 (1989); R. G. Parr and J. L. Gazquez, *J. Phys. Chem.* **97:**3939 (1993).

where χ is absolute electronegativity and η is hardness for the reacting species. For example, one can calculate the values for each of the four halogen atoms reacting with the methyl radical to form the corresponding methyl halide.

$$X\cdot + CH_3\cdot \longrightarrow CH_3X$$
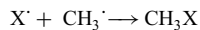
X	χ_X	η_X	ΔN	η_{CH_3X}
F·	10.4	7.0	0.23	9.4
Cl·	8.3	4.7	0.17	7.5
Br·	7.6	4.2	0.14	5.8
I·	6.8	3.7	0.10	4.7

According to this analysis, the C−X bond will be successively both more polar and harder in the order I < Br < Cl < F. This result is in agreement with both the properties and the reactivities of the methyl halides. When comparable bonds are considered, reacting species of greater hardness result in a larger net charge transfer, which adds an increment to the exothermicity of bond formation. That is, bonds formed between two harder reactants will be stronger than those between two softer reactants.[34] This is an example of a general relationship that recognizes that there is an increment to bond strength resulting from added ionic character. Indeed, quite accurate estimates of bond strength can be made by methods that add an increment due to the electronegativity difference between atoms.[35]

The concepts of electronegativity, hardness, and polarizability are all interrelated. For the kind of qualitative applications we will make in discussing reactivity, the concept that initial interactions between reacting molecules can be dominated by either partial electron transfer by bond formation (soft reactants) or by electrostatic interaction (hard reactants) is a useful generalization.

The ideas about bond length, bond energies, polarity, and polarizability discussed in this section are very useful because of the relative constancy of these properties from molecule to molecule. Thus, data obtained from simple well-characterized molecules can provide a good guide to the properties of substances whose structures are known but which have yet to be studied in detail. Organic chemists have usually discussed this transferability of properties in terms of valence bond theory. Thus, the properties are thought of as characteristic of the various types of atoms and bonds. The properties of the molecule are thought of as the sum of the properties of the bonds. This has been a highly fruitful conceptual approach in organic chemistry. As we shall see in the next section, there is an alternative description of molecules which is also highly informative and useful.

1.3. Molecular Orbital Theory and Methods

Another broad approach to the description of molecular structure that is of importance in organic chemistry is molecular orbital theory. Molecular orbital (MO) theory pictures electrons as being distributed among a set of molecular orbitals of discrete

34. P. K. Chattaraj, A. Cedillo, R. G. Parr, and E. M. Arnett, *J. Org. Chem.* **60:**4707 (1995).
35. R. R. Reddy, T. V. R. Rao, and R. Viswanath, *J. Am. Chem. Soc.* **111:**2914 (1989).

energies. In contrast to the orbitals described by valence bond theory, which are usually concentrated between two specific atoms, molecular orbitals can extend over the entire molecule. MO theory is based on the Schrödinger equation,

$$H\psi = E\psi$$

in which ψ is a wave function describing an orbital, H is the Hamiltonian operator, and E is the energy of an electron in a particular orbital. The wave function describes the interaction of the electron with the other electrons and nuclei of the molecule. The total electronic energy is the sum of the individual electron energies:

$$E = \int \psi H \psi \, d\tau \qquad \text{when } \int \psi^2 \, d\tau = 1$$

In order to make the mathematics tractable, approximations must be made. The choice of approximations has produced a variety of MO methods, the judicious application of which can provide valuable insight into questions of bonding, structure, dynamics, and reactivity. The discussion that follows will not be sufficiently detailed or complete for the reader to understand how the calculations are performed or the details of the approximations. Instead, the nature of the information that is obtained will be described, and the ways in which organic chemists have applied the results of MO theory will be illustrated. Several excellent books are available which provide detailed treatment of various aspects of MO methods.[36]

There is a trade-off between the accuracy of the calculation and the amount of computation required. In general, the more severe the approximations, the more limited is the range of applicability of the particular calculation. An organic chemist who wishes to make use of the results of MO calclulations must therefore make a judgment about the suitability of the various methods to the particular problem. The rapid increases that have occurred in computer speed and power have made the application of sophisticated methods practical for increasingly larger molecules.

Mathematically, the molecular orbitals are treated as linear combinations of atomic orbitals, so that the wave function, ψ, is expressed as a sum of individual atomic orbitals multiplied by appropriate weighting factors (atomic coefficients):

$$\psi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n$$

The coefficients indicate the contribution of each atomic orbital to the molecular orbital. This method of representing the molecular orbital wave function in terms of combinations of atomic orbital wave functions is known as the *linear combination of atomic orbitals* approximation (LCAO). The combination of atomic orbitals chosen is called the *basis set*.

36. M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969; W. T. Borden, *Modern Molecular Orbital Theory for Organic Chemists*, Prentice-Hall, Englewood Cliffs, New Jersey, 1975; H. E. Zimmerman, *Quantum Mechanics for Organic Chemists*, Academic Press, New York, 1975; I. G. Csizmadia, *Theory and Practice of MO Calculations on Organic Molecules*, Elsevier, Amsterdam, 1976; M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975; T. A. Albright, J. K. Burdett, and M.-H. Whangbo, *Orbital Interactions in Chemistry*, John Wiley & Sons, New York, 1985; W. G. Richards and D. L. Cooper, *Ab Initio Molecular Orbital Calculations for Chemists*, 2nd ed., Clarendon Press, Oxford, U.K., 1983; W. J. Hehre, L. Radom, P. Schleyer, and J. Pople, *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986.

A minimum basis set for molecules containing C, H, O, and N would consist of $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals for each C, N, and O and a $1s$ orbital for each hydrogen. The basis sets are mathematical expressions describing the properties of the atomic orbitals.

Two main streams of computational techniques branch out from this point. These are referred to as *ab initio* and *semiempirical* calculations. In both *ab initio* and semiempirical treatments, mathematical formulations of the wave functions which describe hydrogen-like orbitals are used. Examples of wave functions that are commonly used are Slater-type orbitals (abbreviated STO) and Gaussian-type orbitals (GTO). There are additional variations which are designated by additions to the abbreviations. Both *ab initio* and semiempirical calculations treat the linear combination of orbitals by iterative computations that establish a self-consistent electrical field (SCF) and minimize the energy of the system. The minimum-energy combination is taken to describe the molecule.

The various semiempirical methods differ in the approximations which are made concerning repulsions between electrons in different orbitals. The approximations are then corrected for by "parameterization," whereby parameters are included in the protocol to adjust the results to match more accurate calculations or experimental data. The reliability and accuracy of the semiempirical methods have evolved, and the increasing power of computers has permitted wider application of the more accurate methods. The earliest semiempirical methods to be applied extensively to organic molecules included the extended Hückel theory[37] (EHT) and the CNDO (complete neglect of differential overlap) methods.[38] These methods gave correct representations of the shapes and trends in charge distribution in the various molecular orbitals but were only roughly reliable in describing molecular geometry. These methods tend to make large errors in calculation of total energies of molecules. Improved semiempirical calculations give better representations of charge distributions, molecular geometry, and ground-state total energies. Among these methods are MINDO-3,[39] MNDO,[40] AM1,[41] and PM3.[42] (The acronyms refer to titles of the methods.) There are differences among the methods in the ranges of compounds for which the results are satisfactory.

Ab initio calculations are iterative procedures based on *self-consistent field* (SCF) methods. Normally, calculations are approached by the Hartree–Fock closed-shell approximation, which treats a single electron at a time interacting with an aggregate of all the other electrons. Self-consistency is achieved by a procedure in which a set of orbitals is assumed, and the electron–electron repulsion is calculated; this energy is then used to calculate a new set of orbitals, which in turn are used to calculate a new repulsive energy. The process is continued until convergence occurs and self-consistency is achieved.[43]

The individual *ab initio* calculations are further identified by abbreviations for the basis set orbitals that are used. These abbreviations include, for example, STO-3G,[44] 4-31G,[45] and 6-31G.[46] In general, the *ab initio* calculations make fewer assumptions than semiempirical methods, and therefore the computations are more demanding.

37. R. Hoffmann, *J. Chem. Phys.* **39:**1397 (1963).
38. J. A. Pople and G. A. Segal, *J. Chem. Phys.* **44:**3289 (1966).
39. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.* **97:**1285, 1294, 1302 (1975).
40. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99:**4907 (1977).
41. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.* **109:**3902 (1985).
42. J. J. P. Stewart, *J. Comput. Chem.* **10:**209, 221 (1989).
43. C. C. J. Roothaan, *Rev. Mod. Phys.* **23:**69 (1951); R. Pariser and R. G. Parr, *J. Chem. Phys.* **21:**767 (1953); J. A. Pople, *J. Phys. Chem.* **61:**6 (1957).
44. W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51:**2657 (1971).
45. R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* **54:**724 (1971).
46. W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56:**2257 (1972).

Another distinguishing aspect of MO methods is the extent to which they deal with *electron correlation*. The Hartree–Fock approximation does not deal with correlation between individual electrons, and the results are expected to be in error because of this, giving energies above the exact energy. MO methods that include electron correlation have been developed. The calculations are usually done using Møller–Plesset perturbation theory and are designated MP calculations.[47]

Among the most widely used *ab initio* methods are those referred to as G1[48] and G2.[49] These methods incorporate large basis sets including *d* and *f* orbitals, called 6-311**. The calculations also have extensive configuration interaction terms at the Møller–Plesset fourth order (MP4) and further terms referred to as quadratic configuration interaction (QCISD).[50] Finally, there are systematically applied correction terms calibrated by exact energies from small molecules.

Current MO methods give excellent results on ground-state molecular geometry and charge distribution. They can also give excellent agreement with experimental data in the calculation of relative molecular energies. The calculation of these quantities normally refers to isolated molecules; i.e., the calculated values correspond to those for the molecule in the gas phase. The energy changes associated with dynamic processes can be studied by calculation of molecular energy as a function of molecular distortion. Much effort is also being devoted to the description of reaction processes. This is an especially formidable task because information about solvent participation and exact separation of reacting molecules is imprecise. In cases where good assumptions about such variables can be made, *ab initio* MO calculations can give good estimates of the energy changes associated with chemical reactions.

The results of all types of MO calculations include the energy of each MO, the total electronic energy of the molecule relative to the separated atoms, and the coefficients of the atomic orbitals (AOs) contributing to each MO. Such information may be applied directly to a number of physical and chemical properties. The total electronic energy obtained by summing the energies of the occupied orbitals gives the calculated molecular energy. Comparison of isomeric molecules permits conclusions about the relative stabilities of the compounds. Conclusions about molecular stability can be checked by comparison with thermodynamic data when they are available. Conformational effects can be probed by calculating the total energy as a function of molecular geometry. The minimum energy should correspond to the most favorable conformation. Most calculations are done on single molecules, not an interacting array of molecules. Thus, the results are most comparable to the situation in the gas phase, where intermolecular forces are weak. The types of data which are obtained by MO calculations are illustrated in the following paragraphs.

The coefficients for the AOs that comprise each MO may be related to the electron density at each atom by the equation

$$q_r = \sum n_j c_{jr}{}^2$$

47. C. Møller and M. S. Plesset, *Phys. Rev.* **46:**618 (1934); J. S. Brinkley and J. A. Pople, *Int. J. Quantum Chem.* **9S:**229 (1975); K. Raghavachari and J. B. Anderson, *J. Phys. Chem.* **100:**12960 (1996).

48. J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90:**5622 (1989); M. Head-Gordon, *J. Phys. Chem.* **100:**13213 (1996).

49. L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94:**7221 (1991); L. A. Curtiss, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **98:**1293 (1993).

50. J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87:**5968 (1987).

which gives the electron density at atom r as the sum over all the occupied MOs of the product of the number of electrons in each orbital and the *square* of the coefficient at atom r for each orbital. To illustrate, the coefficients calculated for the methyl cation by the CNDO/2 method are given in Table 1.10. There are seven MOs generated from the three hydrogen $1s$ and the carbon $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The electron densities are calculated from the coefficients of ψ_1, ψ_2, and ψ_3 only, because these are the occupied orbitals for the six-electron system. The carbon atom is calculated to have 3.565 electrons (exclusive of the $1s$ electrons), and each hydrogen atom is calculated to have 0.812 electrons. Because neutral carbon has four valence electrons, its net charge in the methyl cation is +0.435. Each hydrogen atom has a charge of +0.188. The total charge is $0.435 + 3(0.188) = 1.000$ electron. A sample calculation of the hydrogen electron density from the orbital coefficients follows:

$$q_H = 2(0.3528)^2 + 2(0.0999)^2 + 2(0.5210)^2 = 0.812$$

Further examination of Table 1.10 reveals that the lowest unoccupied molecular orbital, ψ_4, is a pure p orbital, localized on carbon, since the coefficients are zero for all but the $2p_z$ orbital. The MO picture is in agreement with the usual qualitative hybridization picture for the methyl cation.

MO methods can also be used to calculate heats of formation (ΔH_f) of molecules or heats of reaction (ΔH) by comparing the heats of formation of reactants and products. The total stabilization energy calculated for even a small hydrocarbon, relative to the separated nuclei and electrons, is very large (typically, 50,000–100,000 kcal/mol for C_2 and C_4 compounds, respectively). The energy differences that are of principal chemical interest, such as ΔH for a reaction, are likely to be in the range of 0–50 kcal/mol. A very small error, relative to the total energy, in a MO calculation becomes an enormous error in a calculated ΔH. Fortunately, the absolute errors for compounds of similar structure are likely to be comparable so that the errors will cancel in calculation of the *energy differences* between related molecules. Calculation of heats of formation and heats of reaction is frequently done on the basis of *isodesmic reactions*[51] in order to provide for maximum cancellation of errors in total binding energies. An isodesmic reaction is defined as a process in which the number of formal bonds of each type is kept constant; that is, the numbers of C$-$H, C=C, C=O, etc., bonds on each side of the equation are identical.[52] Although the reaction may not correspond to any real chemical process, the calculation can

Table 1.10. Coefficients of Wave Functions Calculated for Methyl Cation by the CNDO/2 Approximation[a]

Orbital	C_{2s}	C_{2p_x}	C_{2p_y}	C_{2p_z}	H	H	H
ψ_1	0.7915	0.0000	0.0000	0.0000	0.3528	0.3528	0.3528
ψ_2	0.0000	0.1431	0.7466	0.0000	0.0999	0.4012	-0.5011
ψ_3	0.0000	0.7466	-0.1431	0.0000	0.5210	-0.3470	-0.1740
ψ_4	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000
ψ_5	-0.6111	0.0000	0.0000	0.0000	0.4570	0.4570	0.4570
ψ_6	0.0000	0.5625	-0.3251	0.0000	-0.5374	0.5377	-0.0003
ψ_7	0.0000	0.3251	0.5625	0.0000	-0.3106	-0.3101	0.6207

a. The orbital energies (eigenvalues) are not given. The lowest-energy orbital is ψ_1; the highest-energy orbital, ψ_7.

51. W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.* **92**:4796 (1970).
52. D. A. Ponomarev and V. V. Takhistov, *J. Chem. Educ.* **74**:201 (1997).

Table 1.11. Calculated and Experimental ΔH Values for Some Isodemic Reactions

Reaction	Calculated ΔH (4-31G)[a] (kcal/mol)	Calculated ΔH (6-31G)[b] (kcal/mol)	Experimental ΔH (kcal/mol)
$CH_3CH_2CH_3 + CH_4 \rightarrow 2CH_3CH_3$	1.0	0.8	2.6
$\triangle + 3CH_4 \rightarrow 2CH_3CH_3 + CH_2{=}CH_2$	-58	-50.4	-43.9
$H_2C{=}C{=}O + CH_4 \rightarrow CH_2{=}CH_2 + H_2C{=}O$	12.8	13.3	15.0
$CH_3CN + CH_4 \rightarrow CH_3CH_3 + HCN$	12.0	11.7	14.4

a. Data from W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.* **92:**4796 (1970).
b. From W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986, pp. 299–305.

provide a test of the reliability of the computational methods because of the comparability of ΔH_f data. The "experimental" ΔH for a reaction can be obtained by summation of tabulated ΔH_f for reactants and products. Table 1.11 gives some ΔH values calculated at the 4-31G and 6-31G level of theory for some isodesmic reactions.

The relative merits of various MO methods have been discussed in the literature.[53] In general, the *ab initio* type of calculations will be more reliable, but the semiempirical calculations are faster in terms of computer time. The complexity of calculation also increases rapidly as the number of atoms in the molecule increases. The choice of a method is normally made on the basis of evidence that the method is adequate for the problem at hand and the availability of appropriate computer programs and equipment. Results should be subjected to critical evaluation by comparison with experimental data or checked by representative calculations using higher-level methods. Table 1.12 lists some reported deviations from experimental ΔH_f for some small hydrocarbons. The extent of deviation gives an indication of the accuracy of the various types of MO calculations in this application.

The use of MO methods to probe the relationship between structure and energy can be illustrated by a study of CH_3^+, $CH_3\cdot$, and CH_3^-. The study employed *ab initio* calculations and the 4-31G basis set and was aimed at exploring the optimum geometry and resistance to deformation in each of these reaction intermediates.[54] Figure 1.9 is a plot of the calculated energy as a function of deformation from planarity for the three species. Whereas CH_3^+ and $CH_3\cdot$ are found to have minimum energy at $\theta = 0°$, that is, when the molecule is planar, CH_3^- is calculated to have a nonplanar equilibrium geometry. This calculated result is in good agreement with a variety of experimental observations which will be discussed in later chapters where these intermediates are discussed in more detail.

53. J. A. Pople, *J. Am. Chem. Soc.* **97:**5306 (1975); W. J. Hehre, *J. Am. Chem. Soc.* **97:**5308 (1975); T. A. Halgren, D. A. Kleier, J. H. Hall, Jr., L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.* **100:**6595 (1978); M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.* **101:**5558 (1979); W. J. Hehre, *Acc. Chem. Res.* **9:**399 (1976); M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.* **107:**3902 (1985); J. N. Levine, *Quantum Chemistry*, 3rd ed., Allyn and Bacon, Boston, 1983, pp. 507–512; W. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Calculations*, John Wiley & Sons, New York, 1986, Chapter 6; B. H. Besler, K. M. Merz, Jr., and P. Kollman, *J. Comput. Chem.* **11:**431 (1990); M. Sana and M. T. Nguyen, *Chem. Phys. Lett.* **196:**390 (1992).
54. E. D. Jemmiss, V. Buss, P. v. R. Schleyer, and L. C. Allen, *J. Am. Chem. Soc.* **98:**6483 (1976).

Table 1.12. Deviations of Calculated ΔH_f Values from Experimental ΔH_f Data[a]

Hydrocarbon	MNDO	AM1	PM3[b]	3-21G	6-31G	G2[c]	MP4/QCI[d]
Methane	5.9	9.0	4.9	−0.9	−0.5	0.7	−0.6
Ethane	0.3	2.6	2.1	0.2	1.9	−0.2	−0.7
Ethene	3.1	4.0	4.2	−1.6	−2.4	0.3	0.1
Allene	−1.6	0.6	1.5	−2.6	−6.8	0.0[e]	
1,3-Butadiene	2.7	3.6	5.0	−4.7	−2.9[f]	0.5[g]	
Cyclopropane	−1.5	5.1	3.5		−2.4		
Cyclobutane	−18.7	0.2	−10.6				
Cyclopentane	−12.0	−10.5	−5.6		−6.1[f]		
Cyclohexane	−5.3	−9.0	−1.5		−9.1[f]		
Benzene	1.5	2.2	3.6			4.0[h]	

a. Except as noted, energy (kcal/mol) comparisons are from M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.* **107:**3902 (1985).
b. J. J. P. Stewart, *J. Comput. Chem.* **10:**221 (1989).
c. J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90:**5622 (1989); L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94:**7221 (1991).
d. M. Sana and M. T. Nguyen, *Chem. Phys. Lett.* **196:**390 (1992).
e. D. W. Rogers and F. W. McLafferty, *J. Phys. Chem.* **99:**1375 (1993).
f. M. Selmi and J. Tomasi, *J. Phys. Chem.* **99:**5894 (1995).
g. M. N. Glukhovtsev and S. Laiter, *Theor. Chim. Acta* **92:**327 (1995).
h. A. Nicolaides and L. Radom, *J. Phys. Chem.* **98:**3092 (1994).

Substituent effects on intermediates can also be analyzed by MO methods. Take, for example, methyl cations where adjacent substituents with lone pairs of electrons can form π bonds, as can be expressed in either valence bond or MO terminology.
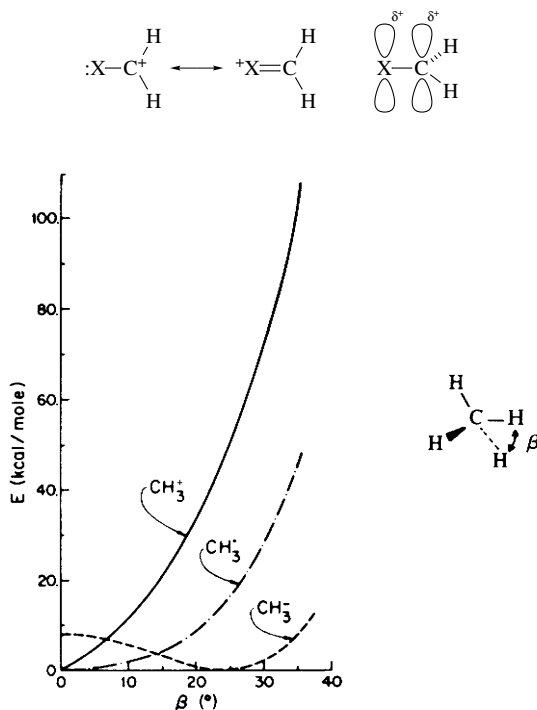
Fig. 1.9. Total energy as a function of distortion from planarity for methyl cation, methyl radical, and methyl anion. [Reproduced from *J. Am. Chem. Soc.* **98:**6483 (1976) by permission of the American Chemical Society.]

Table 1.13. Calculated Stabilization Resulting from Substituents on the Methyl Cation

Substituent	Stabilization in kcal/mol			
	4-31G[a]	6-31G*[b,c]	MP2/6-31G**[c]	MP3/6-31G*[d]
F	2.1	14.16		21.5
OH	48.0	53.77		62.7
NH_2	93.0	87.33		97.8
CH_3	30.0	30.2	41.5	34.1
$CH=CH_2$		53.9	66.1	
$CH=O$		−5.2	0.2	
CN		−13.0	−4.3	
NO_2		−40.7	−22.3	

a. Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.* **99:**1291 (1977).
b. F. Bernardi, A. Bottoni, and A. Venturini, *J. Am. Chem. Soc.* **108:**5395 (1986).
c. X. Creary, Y.-X. Wang, and Z. Jiang, *J. Am. Chem. Soc.* **117:**3044 (1995).
d. Y. Apeloig, in *Heteroatom Chemistry*, E. Block, ed., VCH Press, Weinheim, 1990, p. 27.

An *ab initio* study using 4-31G basis set orbitals gave the stabilization energies shown in Table 1.13.[55] The table shows the calculated stabilization, relative to the methyl cation, that results from electron release by the substituent. The π-donor effects of the fluorine, oxygen, and nitrogen atoms are partially counterbalanced by the inductive electron withdrawal through the σ bond. In the case of the oxygen and nitrogen substitutents, the π-donor effect is dominant, and these substituents strongly stabilize the carbocation. For the fluorine substituent, the balance is much closer and the overall stabilization is calculated to be quite small. We will return to the case of the methyl group and its stabilizing effect on the methyl cation a little later.

In the case of the methyl anion, stabilization will result from electron-accepting substituents. Table 1.14 gives some stabilization energies calculated for a range of substituents.[56] Those substituents that have a low-lying π orbital capable of accepting electrons from the carbon $2p_z$ orbital (BH_2, $C\equiv N$, NO_2, and $CH=O$) are strongly stabilizing. Electronegative substituents without π-acceptor capacity reveal a smaller stabilization of the methyl anion. The order is $F > OH > NH_2$, which parallels the ability of these substituents to act as σ-electron acceptors. The strong effect of the trifluoromethyl group is a combination of both σ- and π-bond effects.

The substituent stabilization effects calculated for the methyl cation and the methyl anion refer to the gas phase, where no solvation effects are present, and therefore are substantially larger, in terms of energy, than would be the case in solution, where solvation contributes to stabilization and attenuates the substituent effects.

The allyl carbocation is an example of an intermediate whose structure has been extensively investigated by MO methods. The hybridization/resonance approach discussed earlier readily rationalizes some of the most prominent features of the allyl carbocation. The resonance structures suggest a significant stabilization and imply that the molecule would be planar in order to maximize the overlap of the π system.
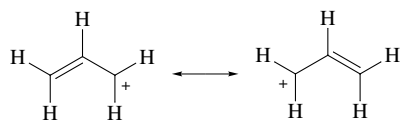
55. Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.* **99:**1291 (1977).
56. A. Pross, D. J. DeFrees, B. A. Levi, S. K. Pollack, L. Radom, and W. J. Hehre, *J. Org. Chem.* **46:**1693 (1981).

Table 1.14. Calculated Stabilization of Methyl Anion by Substituents

Substituent	Stabilization in kcal/mol		
	4-31G[a]	6-31G*[b]	QC150[c]
BH_2	68	61.4	54.0
CH_3	2	1.4	-3.2
NH_2	5	3.3	-0.5
F	25	14.6	10.4
$CH=CH_2$	38		
$CH=O$	72		
CN	61		
CF_3	57		
NO_2	98		

a. A. Pross, D. J. DeFrees, B. A. Levi, S. K. Pollack, L. Radom, and W. J. Hehre, *J. Org. Chem.* **46:**1693 (1981).
b. G. W. Spitznagel, T. Clark, J. Chandrasekhar, and P. v. R. Schleyer, *J. Comput. Chem.* **3:**363 (1982).
c. A. M. El-Nahas and P. v. R. Schleyer, *J. Comput. Chem.* **15:**596 (1994).

These structural effects are also found by MO calculations. Calculations at the MP4/6-311++G** level have been performed on the allyl cation and indicate a rotation barrier of 36–38 kcal/mol.[57]

1.4. Hückel Molecular Orbital Theory

Before computers enabled elaborate MO calculations to be performed routinely, it was essential that greatly simplifying approximations be applied to the molecules of interest to organic chemists. The most useful of these approximations were those incorporated in Hückel molecular orbital (HMO) theory for treatment of conjugated systems. HMO theory is based on the assumption that the π system can be treated independently of the σ framework in conjugated planar molecules and that it is the π system that is of paramount importance in determining the chemical and spectroscopic properties of conjugated polyenes and aromatic compounds. The basis for treating the σ and π systems as independent of each other is their orthogonality. The σ skeleton of a planar conjugated system lies in the nodal plane of the π system and does not interact with it. Because of its simplicity, HMO theory has been extremely valuable in the application of MO concepts to organic chemistry. It provides a good qualitative description of the π molecular orbitals in both cyclic and acyclic conjugated systems. In favorable cases such as aromatic ring systems, it provides a quite thorough analysis of the relative stability of related structures.

In the HMO approximation, the π-electron wave function is expressed as a linear combination of the p_z atomic orbitals (for the case in which the plane of the molecule coincides with the x–y plane). Minimizing the total π-electron energy with respect to the coefficients leads to a series of equations from which the atomic coefficients can be extracted. Although the mathematical operations involved in solving the equation are not

57. K. B. Wiberg, C. M. Breneman, and T. J. LePage, *J. Am. Chem. Soc.* **112:**61 (1990); A. Gobbi and G. Frenking, *J. Am. Chem. Soc.* **116:**9275 (1994).

difficult, we will not describe them in detail but will instead concentrate on the interpretation of the results of the calculations. For many systems, the Hückel MO energies and atomic coefficients have been tabulated.[58]

The most easily obtained information from such calculations is the relative orderings of the energy levels and the atomic coefficients. Solutions are readily available for a number of frequently encountered delocalized systems, which we will illustrate by referring to some typical examples. Consider, first, *linear polyenes* of formula C_nH_{n+2} such as 1,3-butadiene, 1,3,5-hexatriene, and so forth. The energy levels for such compounds are given by the expression

$$E = \alpha + m_j\beta$$

where

$$m_j = 2\cos\frac{j\pi}{n+1} \qquad \text{for } j = 1, 2, \ldots, n$$

and n is the number of carbon atoms in the conjugated chain. This calculation generates a series of MOs with energies expressed in terms of the quantities α and β, which symbolize the *Coulomb integral* and *resonance integral*, respectively. The Coulomb integral, α, is related to the binding of an electron in a $2p$ orbital, and this is taken to be a constant for all carbon atoms but will vary for heteroatoms as a result of the difference in electronegativity. The resonance integral, β, is related to the energy of an electron in the field of two or more nuclei. In the Hückel method, β is assumed to be zero when nuclei are separated by distances greater than the normal bonding distance. The approximation essentially assumes that the electron is affected only by nearest-neighbor nuclei. Both α and β are negative numbers and represent unspecified units of energy.

The coefficient corresponding to the contribution of the $2p$ AO of atom r to the jth MO is given by

$$c_{rj} = \left(\frac{2}{n+1}\right)^{1/2}\left(\sin\frac{rj\pi}{n+1}\right)$$

Carrying out the numerical operations for 1,3,5-hexatriene gives the results shown in Table 1.15. Because the molecule is a six-π-electron system, ψ_1, ψ_2, and ψ_3 are all doubly

Table 1.15. Energy Levels and Coefficients for HMOs of 1,3,5-Hexatriene

π-Orbital:

ψ_j	m_j	c_1	c_2	c_3	c_4	c_5	c_6
ψ_1	1.802	0.2319	0.4179	0.5211	0.5211	0.4179	0.2319
ψ_2	1.247	0.4179	0.5211	0.2319	-0.2319	-0.5211	-0.4179
ψ_3	0.445	0.5211	0.2319	-0.4179	-0.4179	0.2319	0.5211
ψ_4	-0.445	0.5211	-0.2319	-0.4179	0.4179	0.2319	-0.5211
ψ_5	-1.247	0.4179	-0.5211	0.2319	0.2319	-0.5211	0.4179
ψ_6	-1.802	0.2319	-0.4179	0.5211	-0.5211	0.4179	-0.2319

58. C. A. Coulson and A. Streitwieser, Jr., *Dictionary of π-Electron Calculations*, W. H. Freeman, San Francisco, 1965; E. Heilbronner and P. A. Straub, *Hückel Molecular Orbitals*, Springer-Verlag, Berlin, 1966.

occupied, giving a total π-electron energy of $6\alpha + 6.988\beta$. The general solution for this system is based on the assumption that the electrons are delocalized. If this assumption were not made and the molecule were considered to be composed of alternating single and double bonds, the total π-electron energy would have been $6\alpha + 6\beta$, identical to that for three ethylene units. The differences between the electron energy calculated for a system of delocalized electrons and that calculated for alternating single and double bonds is referred to as the *delocalization energy* and is a measure of the extra stability afforded a molecule containing delocalized electrons compared to a molecule containing localized bonds. The calculated delocalization energy (DE) for 1,3,5-hexatriene is 0.988β. The value of β (as expressed in conventional energy units) is not precisely defined. One of the frequently used values is 18 kcal/mol, which is based on the value of 36 kcal/mol for the resonance energy of benzene, for which the calculated DE is 2β.

Inspection of the coefficients and a familiarity with the way they translate into symmetry properties of orbitals can be used in an extremely powerful way to aid in understanding a number of aspects of the properties of conjugated unsaturated compounds. Such considerations apply particularly well to the class of reactions classified as *concerted*, which will be described in detail in Chapter 11. It can be seen in Table 1.15 that the coefficients are all of like sign in the lowest-energy orbital, ψ_1, and that the number of times that a sign *change* occurs in the wave function increases with the energy of the orbital. A change in sign of the coefficients of the AOs on adjacent atoms corresponds to an antibonding interaction between the two atoms, and a node exists between them. Thus, ψ_1 has no nodes, ψ_2 has one, ψ_3 has two, and so on up to ψ_6, which has five nodes and no bonding interactions in its combination of AOs. A diagrammatic view of the bonding and antibonding interactions among the AOs of 1,3,5-hexatriene is presented in Fig. 1.10. Notice that for the bonding orbitals ψ_1, ψ_2, and ψ_3, there are more bonding interactions than antibonding interactions, whereas the opposite is true of the antibonding orbitals.

The success of simple HMO theory in dealing with the relative stabilities of cyclic conjugated polyenes is impressive. Simple resonance arguments do not explain the unique stability of benzene as compared with the elusive and unstable nature of cyclobutadiene. (Two apparently analogous resonance structures can be drawn in each case.) This contrast in stability is readily explained by Hückel's rule, which states that a species will be strongly stabilized (aromatic) if it is composed of a planar monocyclic array of atoms, each of which contributes a p orbital to the π system, when the number of electrons in the π system is $4n + 2$, where n is an integer. By this criterion, benzene, with six π electrons, is aromatic, whereas cyclobutadiene, with four, is not. An understanding of the theoretical basis for Hückel's rule can be gained by examining the results of HMO calculations. For cyclic polyenes, the general solution for the energy levels is

$$E = \alpha + m_j\beta$$

where

$$m_j = 2\cos\frac{2j\pi}{n} \qquad \text{for } j = 0, \pm 1, \pm 2, \ldots, \begin{cases} \pm(n-1)/2 \text{ for } n \text{ odd} \\ \pm n/2 \text{ for } n \text{ even} \end{cases}$$

and n is the number of carbon atoms in the ring. This solution gives the energy level diagrams for cyclobutadiene and benzene shown in Fig. 1.11.

The total π-electron energy of benzene is $6\alpha + 8\beta$, corresponding to a DE of 2β. Cyclobutadiene is predicted to have a triplet ground state (for a square geometry) and zero

DE, since the π-electron energy is $4\alpha + 4\beta$, the same as that for two independent double bonds. Thus, at this level of approximation, HMO theory predicts no stabilization for cyclobutadiene from delocalization and furthermore predicts that the molecule will have unpaired electrons, which would lead to very high reactivity. In addition, cyclobutadiene would suffer angle strain, which is not present in benzene. The extreme instability of cyclobutadiene is then understandable. Higher-level MO calculations modify this picture somewhat and predict that cyclobutadiene will be a rectangular molecule, as will be discussed in Chapter 9. These calculations, nevertheless, agree with simple HMO theory in

bonding orbitals   antibonding orbitals
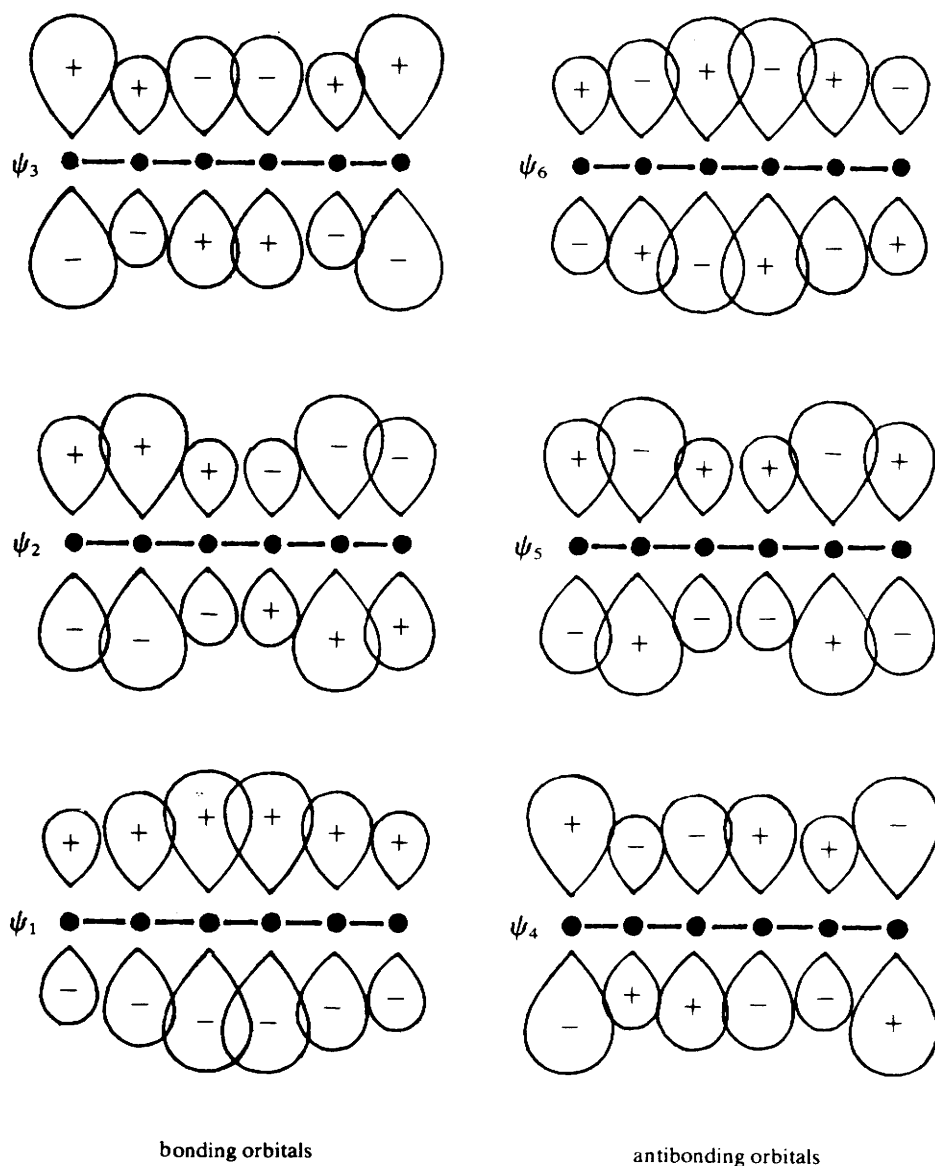
Fig. 1.10. Graphic representation of π-molecular orbitals of 1,3,5-hexatriene as combinations of $2p$ AOs. The sizes of the orbitals are roughly proportional to the coefficients of the Hückel wave functions.
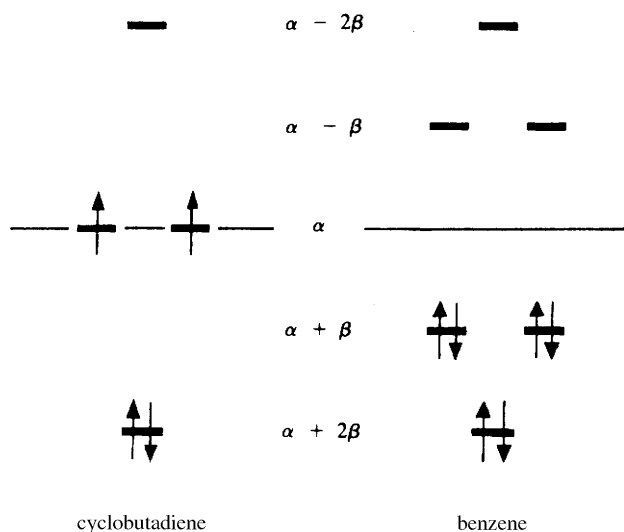
Fig. 1.11. Energy level diagrams for cyclobutadiene and benzene.

concluding that there will be no stabilization of butadiene resulting from delocalization of the π electrons of the conjugated double bonds.

A useful mnemonic device for quickly setting down the HMOs for cyclic systems is *Frost's circle*.[59] If a regular polygon of n sides is inscribed in a circle of diameter 4β with one corner at the lowest point, the points at which the corners of the polygon touch the circle define the energy levels. The energy levels obtained for benzene and cyclobutadiene with Frost's circle are shown in Fig. 1.12.

The energy level diagrams for charged C_3H_3 and C_5H_5 systems are readily constructed and are presented in Fig. 1.13. Cyclopropenyl cation has a total of two π electrons, which occupy the bonding HMO, and a total π-electron energy of $2\alpha + 4\beta$. This gives a DE of 2β and is indicative of a stabilized species. Addition of two more π electrons to the system to give cyclopropenide anion requires population of higher-energy anti-bonding orbitals and results in a net destabilization of the molecule. The opposite is true for the C_5H_5 case, where the anionic species is stabilized more than the cation and the cation is predicted to have unpaired electrons.
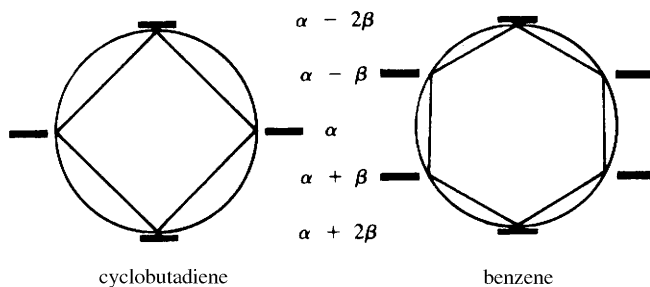
Fig. 1.12. Energy level diagrams for cyclobutadiene and benzene, illustrating the application of Frost's circle.

59. A. A. Frost and B. Musulin, *J. Chem. Phys.* **21:**572 (1953).

$$\alpha - 1.618\beta$$

$$\alpha - \beta$$

$$\alpha + 0.618\beta$$

$$\alpha + 2\beta \qquad \alpha + 2\beta$$
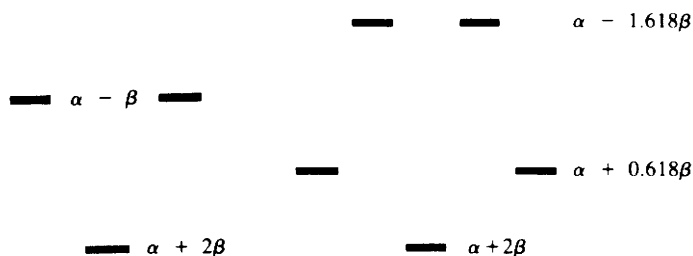
Fig. 1.13. Energy level diagrams for C_3H_3 and C_5H_5 systems.

Monocyclic conjugated polyenes are referred to as *annulenes*, and there exists ample experimental evidence to support the conclusions based on application of HMO theory to neutral and charged annulenes. The relationship between stability and structure in cyclic conjugated systems will be explored more fully in Chapter 9.

While Hückel's $4n + 2$ rule applies only to monocyclic systems, HMO theory is applicable to many other systems. HMO calculations of fused-ring systems are carried out in much the same way as for monocyclic species and provide energy levels and atomic coefficients for the systems. The incorporation of heteroatoms is also possible. Because of the underlying assumption of orthogonality of the σ and π systems of electrons, HMO theory is restricted to planar molecules.

Although the Hückel method has now been supplanted by more complete treatments for theoretical analysis of organic reactions, the pictures of the π orbitals of both linear and cyclic conjugated polyene systems that it provides are correct as to symmetry and the relative energy of the orbitals. In many reactions where the π system is the primary site of reactivity, these orbitals correctly describe the behavior of the systems. For that reason, the reader should develop a familiarity with the qualitative description of the π orbitals of typical linear polyenes and conjugated cyclic hydrocarbons. These orbitals will be the basis for further discussion in Chapters 9 and 11.

1.5. Qualitative Application of Molecular Orbital Theory

As with valence bond theory, the full mathematical treatment of MO theory is too elaborate to apply to many situations. It is important to be able to develop qualitative approaches based on the fundamental concepts of MO theory that can be applied without the need for detailed calculations. A key tool for this type of analysis is a molecular orbital energy diagram. The construction of an approximate energy level diagram can be accomplished without recourse to detailed calculations by keeping some basic principles in mind. These principles can be illustrated by referring to some simple examples. Consider, first, diatomic species formed from atoms in which only the $1s$ orbitals are involved in the bonding scheme. The two $1s$ orbitals can combine in either a bonding or an antibonding manner to give two molecular orbitals, as indicated in Fig. 1.14.

The number of molecular orbitals (bonding + nonbonding + antibonding) is equal to the sum of the atomic orbitals in the basis set from which they are generated. The bonding combination is characterized by a positive overlap in which the coefficients are of like sign, while the antibonding combination is characterized by a negative overlap with coefficients of opposite sign.
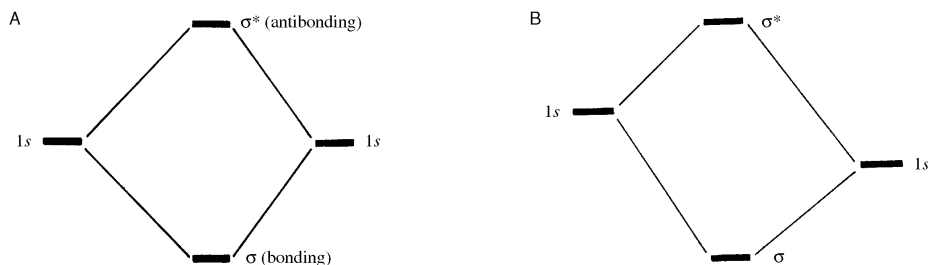
A
σ* (antibonding)

1s   1s

σ (bonding)

B
σ*

1s

1s

σ

Fig. 1.14. Graphic description of combination of two $1s$ orbitals to give two molecular orbitals for H_2 (A) and HHe^+ (B).

Orbitals are occupied by a maximum of two electrons, beginning with the orbital of lowest energy (the Aufbau principle). The number of electrons is determined by the number of electrons present on the interacting atoms. The orbitals in Fig. 1.14A could be applied to systems such as H_2^+ (one electron), H_2 (two electrons), He_2^+ (three electrons), or He_2 (four electrons). A reasonable conclusion would be that H_2 would be the most stable of these diatomic species because it has the largest net number of electrons in the bonding orbital (two). The He_2 molecule has no net bonding because the antibonding orbital contains two electrons and cancels the bonding contribution of the occupied bonding orbital. Both H_2^+ and He_2^+ have one more electron in bonding orbitals than in antibonding orbitals. These species have been determined to have bond energies of 61 and 60 kcal/mol, respectively. The bond energy of H_2, for comparison, is 103 kcal/mol.

A slight adjustment in the energy level diagram allows it to be applied to hetero-nuclear diatomic species such as HHe^+. The diagram that results from this slight modification is shown in Fig. 1.14B. Rather than being a symmetrical diagram, this diagram shows the He $1s$ level to be lower than the H $1s$ level, owing to the increased nuclear charge on helium. Calculations for the HHe^+ ion indicate a bond energy of 43 kcal/mol.[60]

The second-row elements, including carbon, oxygen, and nitrogen, involve p atomic orbitals as well as $2s$ orbitals. An example of a heteronuclear diatomic molecule involving these elements is carbon monoxide, CO. The carbon monoxide molecule has 14 electrons, and the orbitals for each atom are $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$. For most chemical purposes, the carbon $1s$ and oxygen $1s$ electrons are ignored. This simplification is valid because the energy gap between the $1s$ and $2s$ levels is large and the effect of the $1s$ levels on the valence electrons is very small. The 10 valence electrons are distributed among eight MOs generated by combining the four valence AOs from carbon with the four from oxygen, as illustrated in Fig. 1.15.

Figure 1.16 illustrates in a qualitative way the interactions between the AOs that give rise to the MOs. Each pair of AOs leads to a bonding and an antibonding combination. The $2s$ orbitals give the σ and σ^* orbitals. The $2p_x$ and $2p_y$ combinations form MOs that are π in character. The $2p_z$ combination gives a σ-type orbital labeled σ' as well as the corresponding antibonding orbital. The lower five orbitals are each doubly occupied, accounting for the 10 valence-shell electrons in the molecule. Of these five occupied orbitals, one is antibonding; thus, the net number of bonding electrons is six, consistent with the triple bond found in the Lewis structure for carbon monoxide. The shapes of the

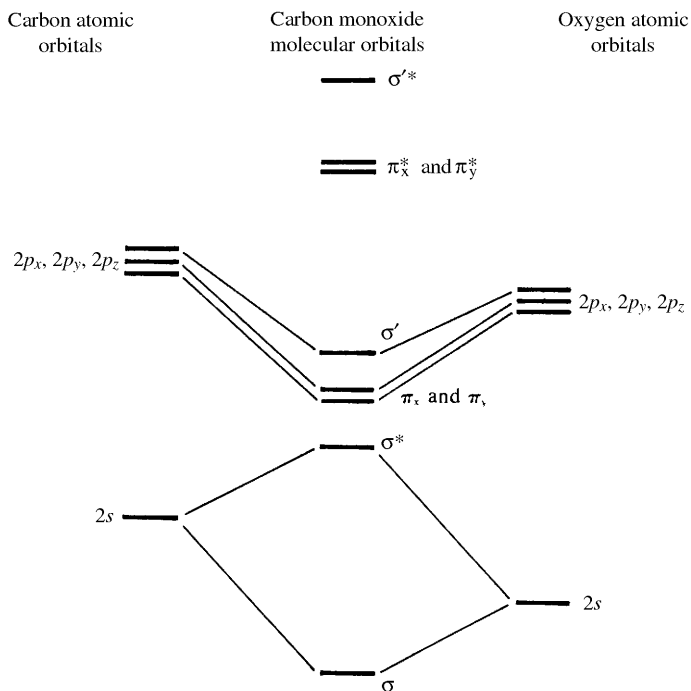60. H. H. Michels, *J. Chem. Phys.* **44:**3834 (1966).

Fig. 1.15. Energy levels in the carbon monoxide molecule. (Adapted from H. B. Gray and G. P. Haight, *Basic Principles of Chemistry*, W. A. Benjamin, New York, 1967, p. 289.)

molecular orbitals can also be depicted as in Fig. 1.17. Here the nodes in the MOs are represented by a change from solid to dashed lines, and the sizes of the lobes are scaled to represent the distribution of the orbital. One gains from these pictures an impression of the distortion of the bonding orbital toward oxygen as a result of the greater electronegativity of the oxygen atom.
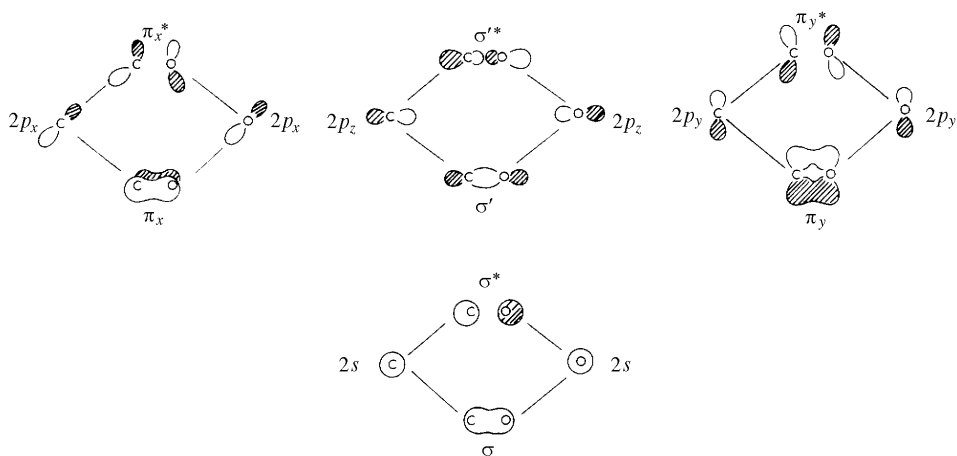
Fig. 1.16. Interaction of atomic orbitals of carbon and oxygen leading to molecular orbitals of carbon monoxide.

$\sigma'* \ E=0.2755$

$\pi_x^* \ E=0.1268$

$\pi_y^* \ E=0.1268$

$\sigma' \ E=-0.5544$

$\pi_x \ E=-0.6395$

$\pi_y \ E=-0.6395$

$\sigma* \ E=-0.8038$

$\sigma \ E=-1.5210$
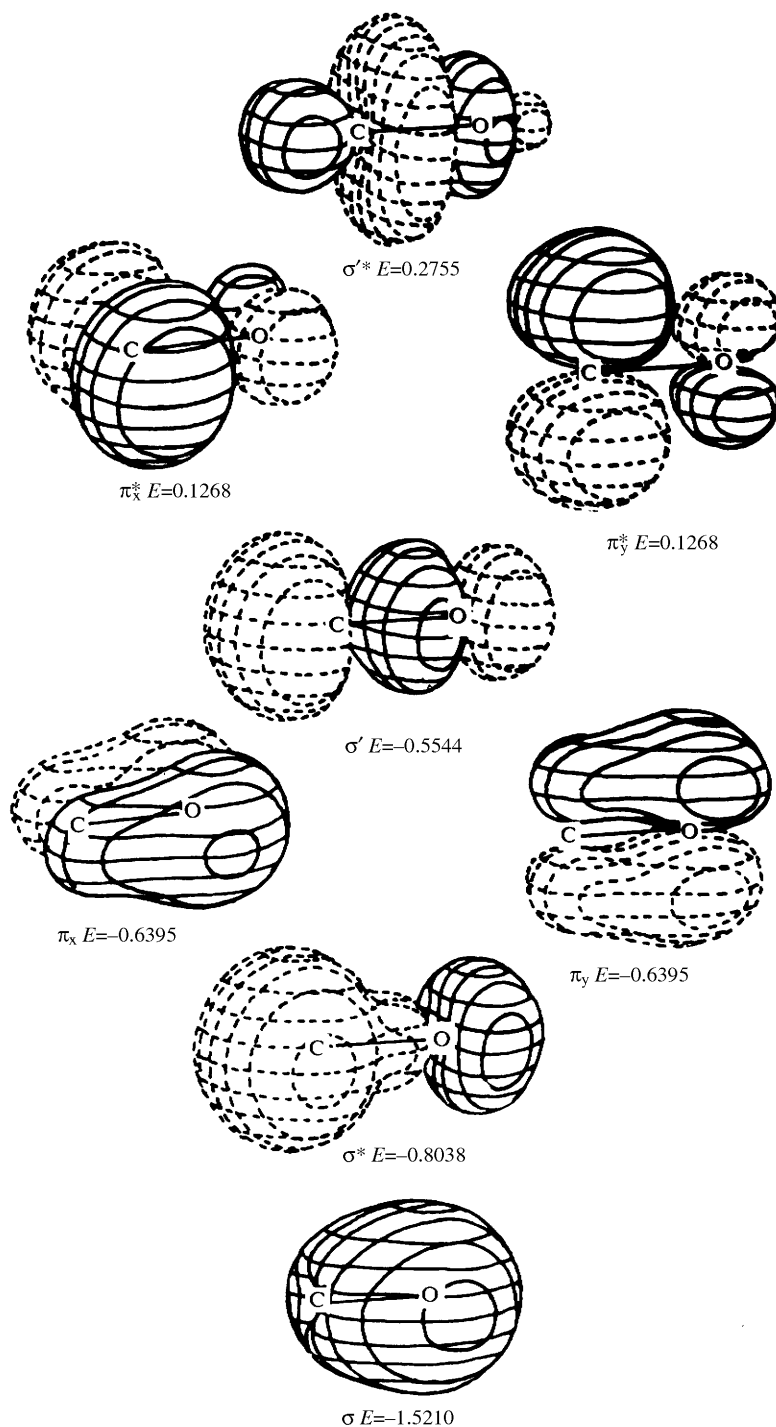
Fig. 1.17. Representation of the molecular orbitals of carbon monoxide. Energies are given in atomic units (1 a.u. 27.21 eV). (From W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973. Reproduced with permission.)

Just as we were able to state some guiding rules for application of resonance theory, it is possible to state some conditions by which to test the correctness of an MO energy level diagram derived by qualitative considerations.

a. The total number of MOs must equal the number of AOs from which they were constructed.

b. The symmetry of the MOs must conform to the symmetry of the molecule. That is, if a molecule possesses a plane of symmetry, for example, *all* the MOs must be either symmetric (unchanged) or antisymmetric (unchanged except for sign) with respect to that plane.

c. AOs that are orthogonal to one another do not interact. Thus, two different carbon $2p$ orbitals will not contribute to the same MO.

d. The energies of similar AOs (s or p) are lower for elements of higher electronegativity. MOs will reflect these differences in energy.

e. The relative energy of MOs in a molecule increases with the number of nodes in the orbital.

By applying these rules and recognizing the elements of symmetry present in the molecule, it is possible to construct MO diagrams for more complex molecules. In the succeeding paragraphs, the MO diagrams of methane and ethylene are constructed on the basis of these kinds of considerations.

To provide a basis for comparison, Fig. 1.18 gives the results of an *ab initio* calculation on the methane molecule.[61] This particular calculation used as a basis set the $1s$, $2s$, and three $2p$ orbitals of carbon and the $1s$ orbitals of the four hydrogens. The lowest MO is principally $1s$ in character. A significant feature of this and other MO calculations of methane is that, unlike a picture involving localized bonds derived from sp^3 hybrid carbon orbitals, there are not four equivalent orbitals. We can obtain an understanding of this feature of the MO picture by a qualitative analysis of the origin of the methane MOs. We will consider the orbitals to be derived from the carbon $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals and ignore the carbon $1s$ orbital. The most convenient frame of reference for the tetrahedral methane molecule is a cube with hydrogen atoms at alternate corners and the carbon atom centered in the cube, as shown in Fig. 1.19. This orientation of the molecule reveals that methane possesses three twofold symmetry axes, one each along the x, y, and z axes. Because of this molecular symmetry, the proper MOs of methane must possess symmetry with respect to these same axes. There are two possibilities: the orbital may be unchanged by 180° rotation about the axis (symmetric), or it may be transformed into an orbital of identical shape but opposite sign by the symmetry operation (antisym-
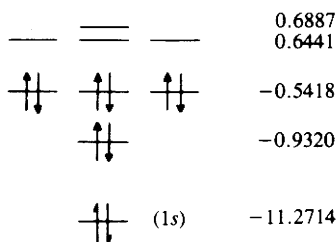
Fig. 1.18. Molecular orbital energy diagram for methane. Energies are in atomic units.

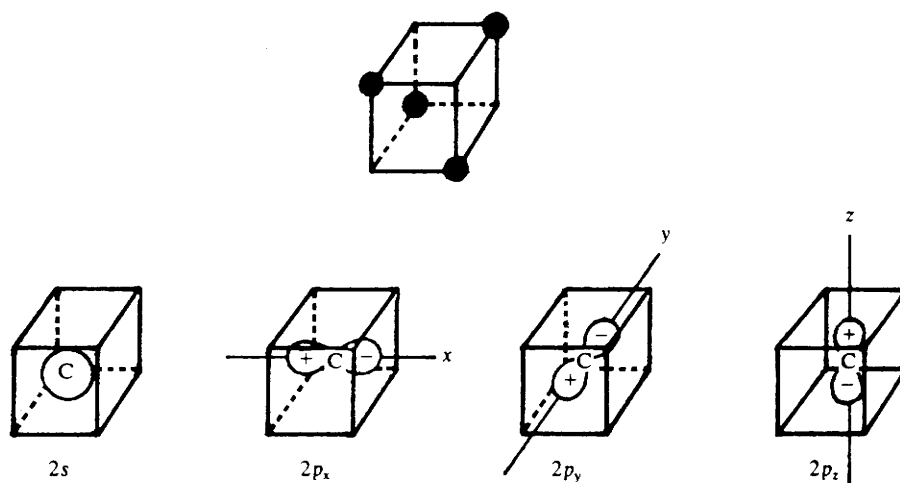61. W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.* **88:**2384 (1966).

Fig. 1.19. Atomic orbitals of carbon relative to methane in a cubic frame of reference.

metric). The carbon $2s$ orbital is symmetric with respect to each axis, but the three $2p$ orbitals are each antisymmetric with respect to two of the axes and symmetric with respect to one. The combinations that give rise to MOs that meet these symmetry requirements are shown in Fig. 1.20.

The bonding combination of the carbon $2s$ orbital with the four $1s$ hydrogen orbitals leads to an MO that encompasses the entire molecule and has no nodes. Each of the MOs derived from a carbon $2p$ orbital has a node at carbon. The three combinations are equivalent, but higher in energy than the MO with no nodes. The four antibonding orbitals arise from similar combinations, but with the carbon and hydrogen orbitals having opposite signs in the region of overlap. Thus, the MO diagram arising from these considerations shows one bonding MO with no nodes and three degenerate (having the same energy) MOs with one node. The diagram is given in Fig. 1.21. Note that except for
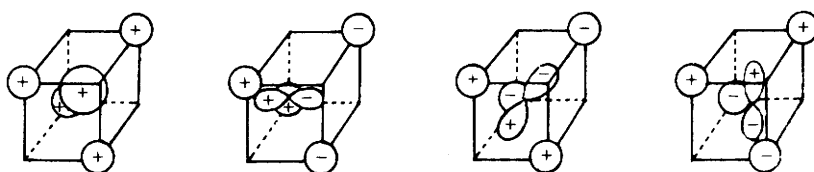
Fig. 1.20. Atomic orbital combinations giving rise to bonding molecular orbitals for methane.

three identical orbitals (one node)

single unique orbital (no nodes)
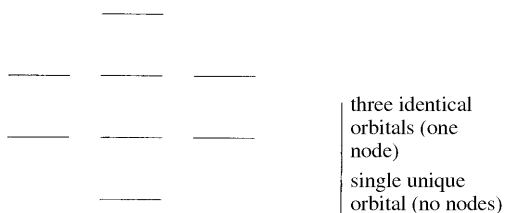
Fig. 1.21. Qualitative molecular orbital diagram for methane.

inclusion of the 1s orbital, this qualitative picture corresponds to the calculated orbital diagram in Fig. 1.18.

A qualitative approach cannot assign energies to the orbitals. In many cases, it is, however, possible to assign an ordering of energies. The relationship between relative energy and number of nodes has already been mentioned. In general, σ-type orbitals are lower in energy than π-type orbitals because of this factor. Conversely, antibonding σ^* orbitals are higher in energy than antibonding π^* orbitals. Orbitals derived from more electronegative atoms are lower in energy than those derived from less electronegative atoms.

The process of constructing the MOs of ethylene is similar to that used for carbon monoxide, but the total number of AOs is greater, 12 instead of 8, because of the additional AOs from hydrogen. We must first define the symmetry of ethylene. Ethylene is known from experiment to be a planar molecule.
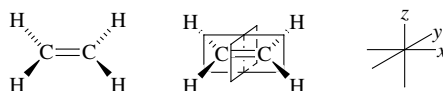
This geometry possesses three important elements of symmetry, the molecular plane and two planes that bisect the molecule. All MOs must be either symmetric or antisymmetric with respect to each of these symmetry planes. With the axes defined as in the diagram above, the orbitals arising from carbon $2p_z$ have a node in the molecular plane. These are the familiar π and π^* orbitals.
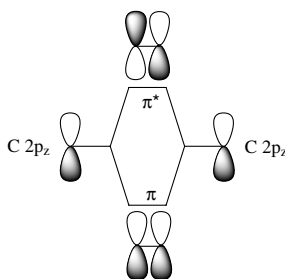
The π orbital is symmetric with respect to both the x–z plane and the y–z plane. It is antisymmetric with respect to the molecular (x–y) plane. On the other hand, π^* is antisymmetric with respect to the y–z plane.

The remaining AOs are the four H 1s, two C 1s, and four C 2p orbitals. All lie in the molecular plane. Only two combinations of the C 2s and H 1s orbitals meet the molecular symmetry requirements. One of these, σ, is bonding between all atoms, whereas σ^* is antibonding between all nearest-neighbor atoms. No other combination corresponds to the symmetry of the ethylene molecule.
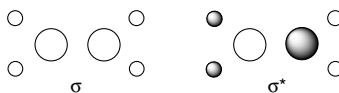
Let us next consider the interaction of $2p_y$ with the four hydrogen $1s$ orbitals. There are four possibilities that conform to the molecular symmetry:
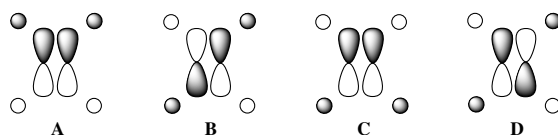
Orbital **A** is bonding between all nearest-neighbor atoms, whereas **B** is bonding within the CH_2 units but antibonding with respect to the two carbons. The orbital labeled **C** is C$-$C bonding but antibonding with respect to the hydrogens. Finally, orbital **D** is antibonding with respect to all nearest-neighbor atoms. Similarly, when the $2p_x$ orbitals are considered, four possible combinations arise. Notice that the nature of the overlap of the $2p_x$ orbitals is different from that in the $2p_y$ case, so that the two sets of MOs should have different energies.
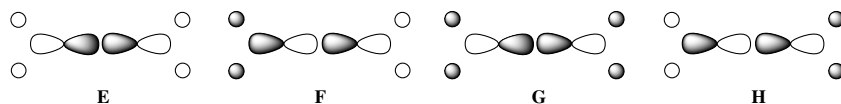
The final problem in construction of a qualitative MO diagram for ethylene is the relative placement of the orbitals. There are some guidelines which are useful. First, because π-type interactions are normally weaker than σ-type, we expect the separation between σ and σ^* to be greater than that between π and π^*. Within the sets **ABCD** and **EFGH**, the orbitals can be placed in the order $\mathbf{A} < \mathbf{B} < \mathbf{C} < \mathbf{D}$ and $\mathbf{E} < \mathbf{F} < \mathbf{G} < \mathbf{H}$ on the basis that C$-$H bonding interactions will outweigh C$-$C antibonding interactions arising from relatively weak p–p overlaps. The placement of the set **ABCD** in relation to **EFGH** is not qualitatively obvious. Calculations give the results shown in Fig. 1.22.[62] Pictorial representations of the orbitals are given in Fig. 1.23.

The kind of qualitative considerations that have been used to construct the ethylene MO diagram do not give an indication of how much each AO contributes to the individual

D	———	0.89
σ^*	———	0.84
H	———	0.63
G	———	0.62
C	———	0.59
π^*	———	0.24
π	———	-0.37
B	———	-0.51
F	———	-0.56
A	———	-0.64
E	———	-0.78
σ	———	-1.0

Fig. 1.22. Ethylene molecular orbital energy levels. Energies are given in atomic units.

62. W. L. Jorgensen and L. Salem, *The Organic Chemists's Book of Orbitals*, Academic Press, New York, 1973.

MOs. This information is obtained from the coefficients provided by an MO calculation. Without these coefficients, we cannot specify the shapes of the MOs very precisely. However, the qualitative ideas do permit conclusions about the *symmetry* of the orbitals. As will be seen in Chapter 11, just knowing the symmetry of the MOs provides very useful insight into many chemical reactions.
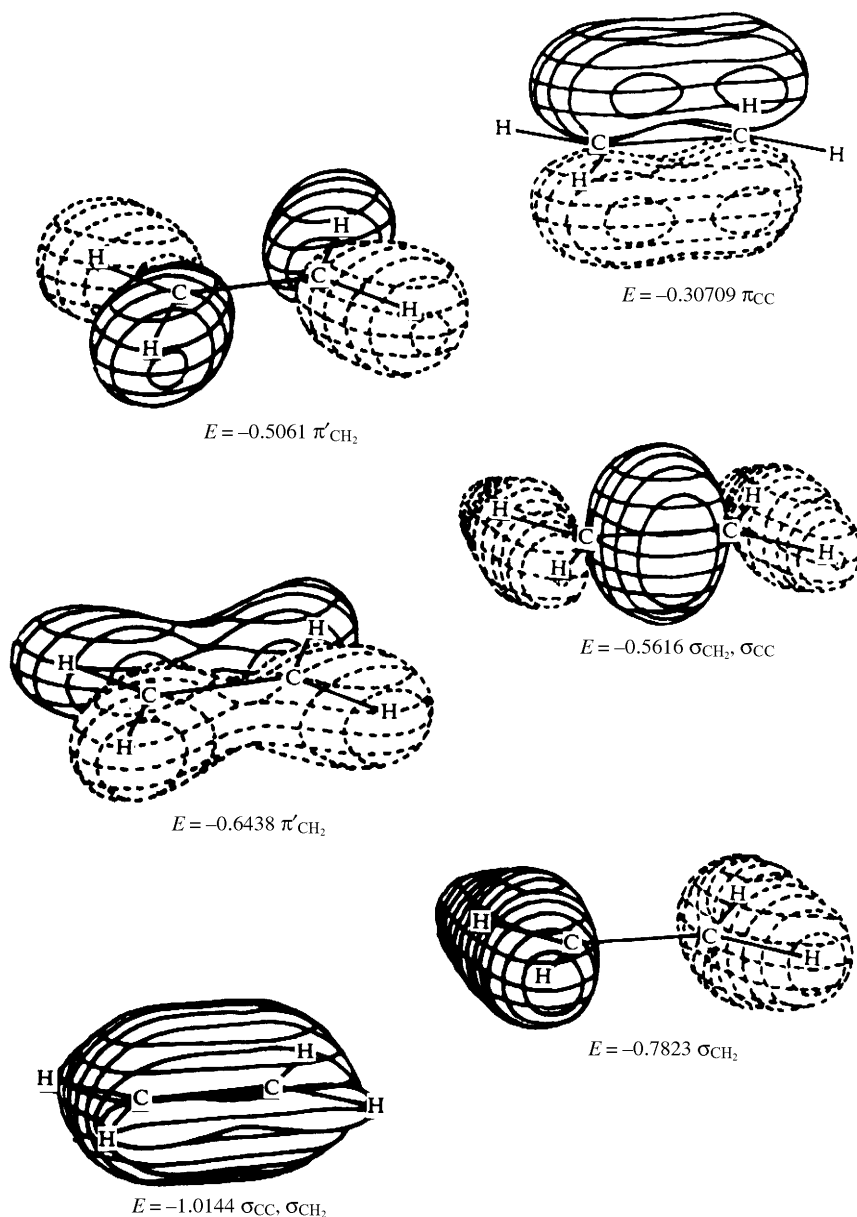
$E = -0.30709\ \pi_{CC}$

$E = -0.5061\ \pi'_{CH_2}$

$E = -0.5616\ \sigma_{CH_2},\ \sigma_{CC}$

$E = -0.6438\ \pi'_{CH_2}$

$E = -0.7823\ \sigma_{CH_2}$

$E = -1.0144\ \sigma_{CC},\ \sigma_{CH_2}$

Fig. 1.23. Representation of the molecular orbitals of ethylene. (From W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973. Reproduced with permission.)

$E = 0.8917 \ \pi^*_{CH_2}$

$E = 0.8453 \ \sigma^*_{CC}, \ \sigma^*_{CH_2}$

$E = 0.6395 \ \sigma^*_{CH_2}, \ \sigma^*_{CC}$

$E = 0.6206 \ \sigma^*_{CH_2}$

$E = 0.5868 \ \sigma^*_{CH_2}$

$E = 0.2426 \ \pi^*_{CC}$
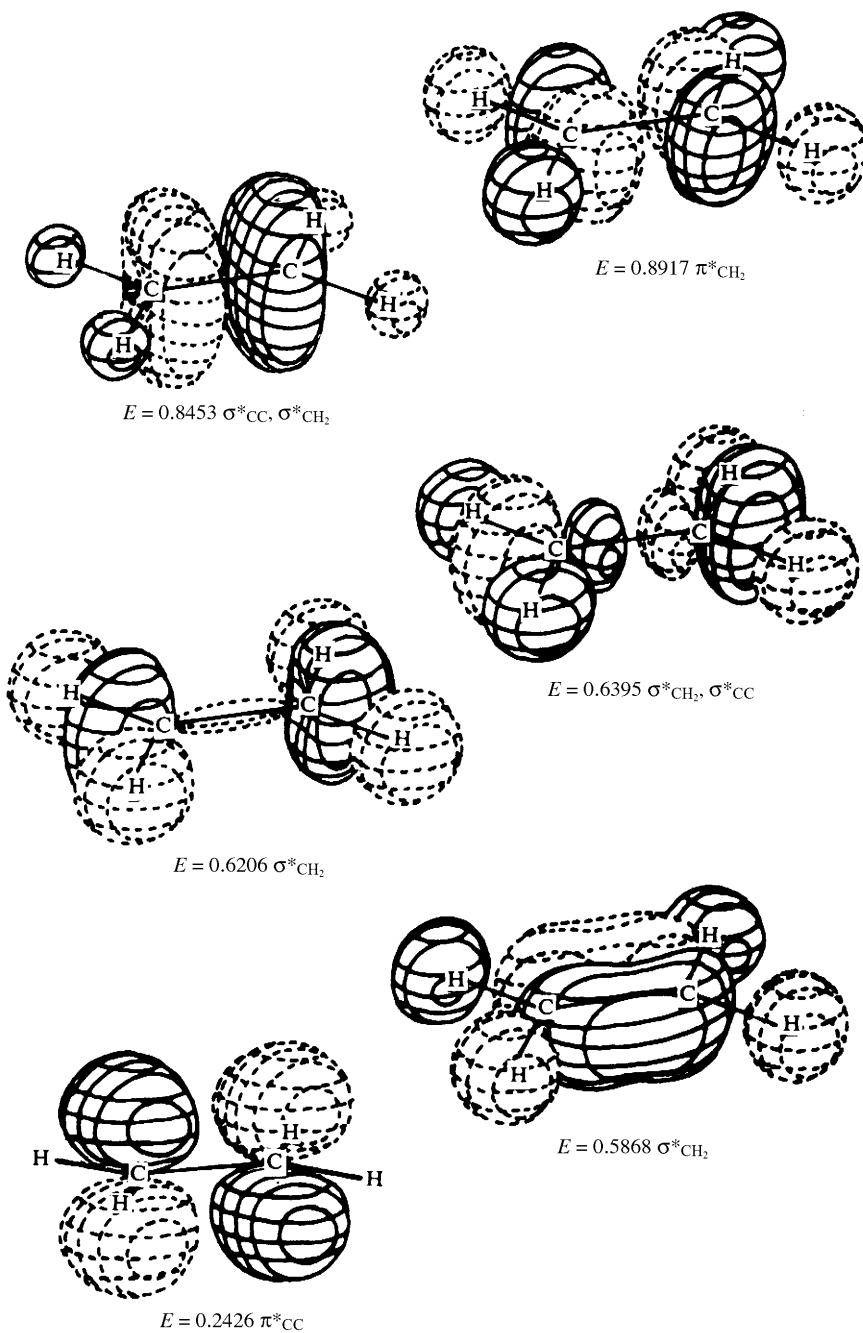
Fig. 1.23. (*continued*)

1.6. Application of Molecular Orbital Theory to Reactivity

The construction of MO diagrams under the guidance of the general principles and symmetry restrictions which have been outlined can lead to useful insights into molecular structure. Now we need to consider how these structural concepts can be related to reactivity. In valence bond terminology, structure is related to reactivity in terms of substituent effects. The impact of polar and resonance effects on the electron distribution and stability of reactants, transition states, and intermediates is assessed. In MO theory, reactivity is related to the relative energies and shapes of the orbitals that are involved as the reactants are transformed to products. Reactions which can take place through relatively stable transition states and intermediates are more favorable and faster than reactions which proceed through less stable ones. The *symmetry* of the MOs is a particularly important feature of many analyses of reactivity based on MO theory. The shapes of orbitals also affect the energy of reaction processes. Orbital shapes are quantified by the atomic coefficients. The strongest interaction (bonding when the overlapping orbitals have the same sign) occurs when the orbitals on two reaction centers have high coefficients on the atoms which undergo bond formation.

The qualitative description of reactivity in MO terms must begin with a basic understanding of the MOs of the reacting systems. At this point, we have developed a familiarity with the MOs of ethylene and conjugated unsaturated systems from the discussion of Hückel MO theory and the construction of the ethylene MOs from AOs. To apply these ideas to new systems, we need to be able to understand how a change in structure will affect the MOs. One approach to this problem is called *perturbation molecular orbital theory* or PMO for short.[63] In this approach, a system under analysis is compared to another related system for which the MO pattern is known, and the MO characteristics of the new system are deduced by analyzing how the change in structure affects the MO pattern. The types of changes that can be handled in a qualitative way are substitution of atoms by other elements, with the resulting change in electronegativity and changes in connectivity that revise the pattern of direct orbital overlap. The fundamental thesis of PMO theory is that the resulting changes in the MO energies are relatively small and can be treated as adjustments on the original MO system.

Another aspect of qualitative application of MO theory is the analysis of interactions of the orbitals in reacting molecules. As molecules approach one another and reaction proceeds, there is a mutual perturbation of the orbitals. This process continues until the reaction is complete and the new product (or intermediate in a multistep reaction) is formed. PMO theory incorporates the concept of *frontier orbital control*. This concept proposes that the most important interactions will be between a particular pair of orbitals.[64] These orbitals are the highest filled orbital of one reactant (the HOMO, highest occupied molecular orbital) and the lowest unfilled (LUMO, lowest unoccupied molecular orbital) orbital of the other reactant. The basis for concentrating attention on these two orbitals is that they will be the closest in energy of the interacting orbitals. A basic postulate of PMO

63. C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A* **192:**16 (1947); L. Salem, *J. Am. Chem. Soc.* **90:**543 (1968); M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975; G. Klopman, *Chemical Reactivity and Reaction Paths*, Wiley-Interscience, New York, 1974, Chapter 4.
64. K. Fukui, *Acc. Chem. Res.* **4:**57 (1971); I. Fleming, *Frontier Orbital and Organic Chemical Reactions*, John Wiley & Sons, New York, 1976; L. Salem, *Electrons in Chemical Reactions*, John Wiley & Sons, New York, 1982, Chapter 6.

theory is that interactions are strongest between orbitals that are close in energy. Frontier orbital theory proposes that these strong initial interactions will guide the course of the reaction as it proceeds to completion. A further general feature of MO theory is that only MOs of matching symmetry can interact so as to lead to bond formation. Thus, analysis of a prospective reaction path will direct attention to the *relative energy* and *symmetry* of the interacting orbitals.

These ideas can be illustrated here by considering some very simple cases. Let us consider the fact that the double bonds of ethylene and formaldehyde have very different chemical reactivities. Formaldehyde reacts readily with nucleophiles whereas ethylene does not. The π bond in ethylene is more reactive toward electrophiles than the formaldehyde C=O π bond. We have already described the ethylene MOs in Figs. 1.22 and 1.23. How will those of formaldehyde differ? In the first place, the higher atomic number of oxygen provides two additional electrons so that in place of the CH_2 group of ethylene, the oxygen of formaldehyde has two pairs of nonbonding electrons. The key change, however, has to do with the frontier orbitals, the π (HOMO) and π^* (LUMO) orbitals. These are illustrated in Fig. 1.24. One significant difference between the two molecules is the lower energy of the π and π^* orbitals in formaldehyde. These are lower in energy than the corresponding ethylene orbitals because they are derived in part from the lower-lying (more electronegative) $2p_z$ orbital of oxygen. Because of its lower energy, the π^* orbital is a better acceptor of electrons from the HOMO of any attacking nucleophile than is the LUMO of ethylene. On the other hand, we also can see why ethylene is more reactive toward electrophiles than formaldehyde. In electrophilic attack, it is the HOMO that is involved as an electron donor to the approaching electrophile. In this case, the fact that the HOMO of ethylene lies higher in energy than the HOMO of formaldehyde will mean that electrons can be more easily attracted by the approaching electrophile. The unequal electronegativities of the oxygen and carbon atoms also distort the π-MOs. Whereas the π-MO has a symmetrical distribution in ethylene, the formaldehyde π-MO has a higher atomic coefficient at oxygen. This results in a net positive charge in the vicinity of the carbon atom, which is a favorable circumstance for approach by a nucleophilic reactant.

One principle of PMO theory is that the degree of perturbation is a function of the degree of overlap of the orbitals. Thus, in the qualitative application of MO theory, it is important to consider the shapes of the orbitals (as indicated quantitatively by their atomic coefficients) and the proximity that can be achieved within the limits of the geometry of the reacting molecules. Secondly, the strength of the interaction between orbitals depends on their relative energy. The closer the orbitals are in energy, the greater will be their mutual interaction. This principle, if used in conjunction with reliable estimates of relative orbital energies, can be of value in predicting the relative importance of various possible interactions.
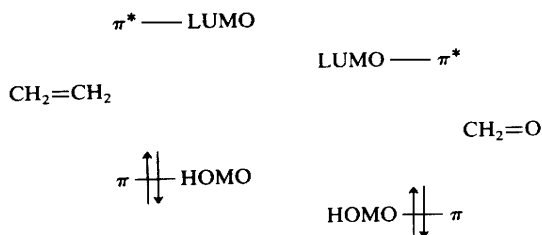

Fig. 1.24. Relative energy of the π and π^* orbitals in ethylene and formaldehyde.

Let us illustrate these ideas by returning to the comparisons of the reactivity of ethylene and formaldehyde toward a nucleophilic species and an electrophilic species. The perturbations which arise as both a nucleophile and an electrophile approach are sketched in Fig. 1.25. The electrophilic species $\mathbf{E}^+$ must have a low-lying empty orbital. The strongest interaction will be with the ethylene π orbital, and this leads to a stabilizing effect on the complex because the electrons are located in an orbital that is stabilized. The same electrophilic species would lie further from the π orbital of formaldehyde because the formaldehyde orbitals are shifted to lower energy. As a result, the mutual interaction with the formaldehyde HOMO will be weaker than in the case of ethylene. The conclusion is that such an electrophile will undergo a greater stabilizing attraction on approaching within bonding distance of ethylene than on approaching within bonding distance of formaldehyde. In the case of $\mathbf{Nu}^-$, a strong bonding interaction with π^* of formaldehyde is possible (Fig. 1.25D). In the case of ethylene, there may be a stronger interaction with the HOMO, but this is a destabilizing interaction because both orbitals are filled and the lowering of one orbital is canceled by the raising of the other. Thus, we conclude that a nucleophile with a high-lying HOMO will interact more favorably with formaldehyde than with ethylene.

The ideas of MO theory can be used in a slightly different way to describe substituent effects. Let us consider, for example, the effect of a π-donor substituent or a π-acceptor substituent on the MO levels of ethylene and upon the reactivity of substituted ethylenes. We can take the amino group as an example of a π-donor substituent. The nitrogen atom provides an additional $2p_z$ orbital and two electrons to the π system. The π orbitals of aminoethylene are very similar to those of an allyl anion but with some distortion because the system is no longer symmetrical. The highest charge density is on the terminal atoms, that is, the nitrogen atom and the β carbon, since the HOMO has a node at the center carbon. Furthermore, the HOMO is considerably higher in energy than the HOMO in ethylene. The HOMO in aminoethylene resembles ψ_2 of the allyl anion. It is not quite so high in energy as the allyl ψ_2 because of the greater electronegativity of the nitrogen atom, but is substantially higher than the HOMO of ethylene. Thus, we expect aminoethylene, with its high-lying HOMO, to be more reactive toward electrophiles than ethylene. Furthermore, the HOMO has the highest coefficients on the terminal atoms, so we expect an electrophile to become bonded to the β carbon or nitrogen, but not to the α carbon. On the other hand, the LUMO will now correspond to the higher-energy ψ_3 of the


Interaction of ethylene frontier orbitals with $\mathbf{E}^+$ and $\mathbf{Nu}^-$
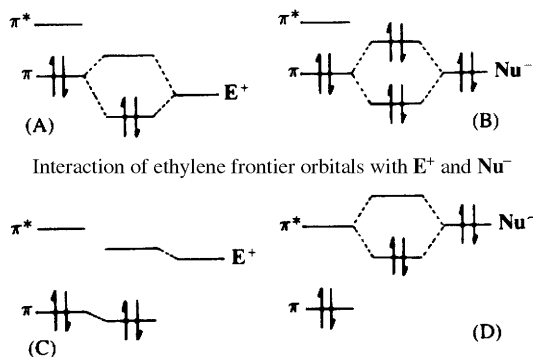
Interaction of formaldehyde frontier orbitals with $\mathbf{E}^+$ and $\mathbf{Nu}^-$

Fig. 1.25. PMO description of interaction of ethylene and formaldehyde with an electrophile ($\mathbf{E}^+$) and a nucleophile ($\mathbf{Nu}^-$).

allyl anion, so we expect aminoethylene to be even less reactive toward nucleophiles than is ethylene.

$$\pi \text{ MO energy levels for ethylene with a } \pi\text{-donor substituent.}$$
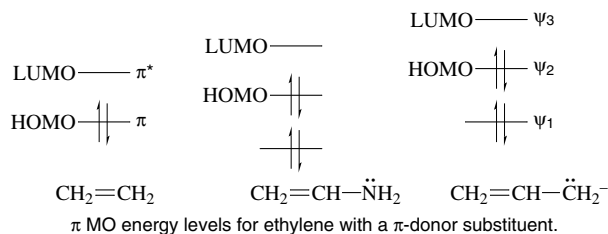
An example of a π-acceptor group is the formyl group as in acrolein.

$$CH_2=CHCH=O$$

In this case, the π-MOs resemble those of butadiene. Relative to the butadiene orbitals, however, the acrolein orbitals lie somewhat lower in energy because of the effect of the more electronegative oxygen atom. This factor also increases the electron density at oxygen relative to carbon.

$$\pi \text{ MO energy levels for ethylene with a } \pi\text{-acceptor substituent.}$$
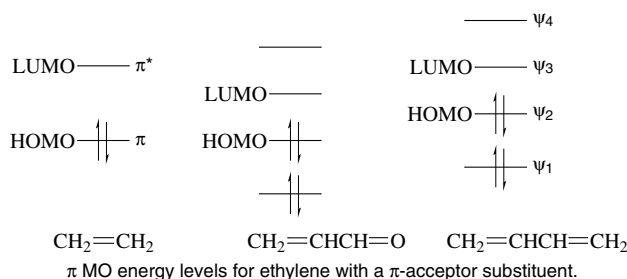
The LUMO, which is the frontier orbital in reactions with nucleophiles, has a larger coefficient on the β-carbon atom, whereas the two occupied orbitals are distorted in such a way as to have larger coefficients on oxygen. The overall effect is that the LUMO is relatively low-lying and has a high coefficient on the β-carbon atom. The frontier orbital theory therefore predicts that nucleophiles will react preferentially at the β-carbon atom.

MO calculations at the 6-31G** level have been done on both acrolein and aminoethylene. The resulting MOs were used to calculate charge distributions. Figure 1.26 gives the π-electron densities calculated for butadiene, acrolein, and aminoethylene.[65] Inclusion of the hydrogen and σ orbitals leads to overall charges as shown. These charge distributions result from σ polarization which is counter to the π polarization.

Notice that the MO picture gives the same qualitative picture of the substituent effects as described by resonance structures. The amino group is pictured by resonance as an electron donor which causes a buildup of electron density at the β carbon, whereas the formyl group is an electron acceptor which diminishes electron density at the β carbon.

$$CH_2=CH-\ddot{N}H_2 \longleftrightarrow {}^{-}CH_2-CH=NH_2{}^{+} \qquad CH_2=CH-CH=O \longleftrightarrow {}^{+}CH_2-CH=CH-O^{-}$$

65. K. B. Wiberg, R. E. Rosenberg, and P. R. Rablen, *J. Am. Chem. Soc.* **113:**2890 (1991).
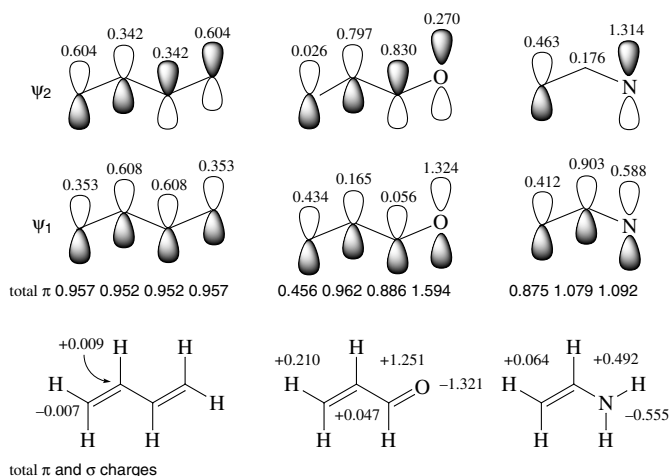
Fig. 1.26. Charge distribution in butadiene, acrolein, and aminoethylene. Data are from K. B. Wiberg, R. E. Rothenberg, and P. R. Rablen, *J. Am. Chem. Soc.* **113:**2890 (1991).

The chemical reactivity of these two substituted ethylenes is in agreement with the ideas encompassed by both the MO and resonance descriptions. Enamines, as amino-substituted alkenes are called, are very reactive toward electrophilic species, and it is the β carbon that is the site of attack. For example, enamines are protonated on the β carbon. Acrolein is an electrophilic alkene, as predicted, and the nucleophile attacks the β carbon.

Both MO theory and experimental measurements provide a basis for evaluation of the energetic effects of conjugation between a double bond and adjacent substituents. Table 1.16 gives some representative values. The theoretical values ΔE are for the isodesmic reaction

$$CH_2{=}CH{-}X \ + \ CH_4 \ \rightarrow \ CH_3{-}X \ + \ CH_2{=}CH_2$$
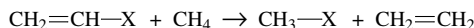
and are calculated at the *ab initio* 4-31G level of theory. These values refer to the gas phase. The ΔH values are based on the experimentally determined thermodynamic ΔH_f of the compounds. Notice that both electron-withdrawing and electron-accepting substituents result in a net stabilization of the conjugated system. This stabilization results from the lowering in energy of the lowest-lying MO in each case. The effect on the HOMO is

Table 1.16. Stabilization Resulting from Conjugation of Ethylene with Substituents[a]

Substituent	ΔE (kcal/mol)	ΔH (kcal/mol)	Substituent	ΔE (kcal/mol)	ΔH (kcal/mol)
H	0	0	NH_2	13.3	13.3
F	6.4	6.7 (3.4)	CN	3.3	4.8
CH_3	4.3	5.4	$COCH_3$	4.0	10.5 (3.8)
OCH_3	10.9	12.3 (4.9)	CO_2CH_3	8.0	11.9 (3.4)

a. From A. Greenberg and T. A. Stevenson, *J. Am. Chem. Soc.* **107:**3488 (1985). Values in parentheses are from J. Hine and M. J. Skoglund, *J. Org. Chem.* **47:**4766 (1982) and are based on experimental equilibrium measurement values. These measurements are in solution, and the difference between the two sets of values may reflect the effect of solvent.

different for electron-withdrawing as compared with electron-accepting substituents. For donor substituents, the HOMO is raised in energy, relative to the HOMO in ethylene. For electron-accepting substituents, it is lowered relative to the HOMO in ethylene.

Frontier orbital theory also provides the basic framework for analysis of the effect that the symmetry of orbitals has upon reactivity. One of the basic tenets of MO theory is that the symmetries of two orbitals must match to permit a strong interaction between them. This symmetry requirement, when used in the context of frontier orbital theory, can be a very powerful tool for predicting reactivity. As an example, let us examine the approach of an allyl cation and an ethylene molecule and ask whether the following reaction is likely to occur.
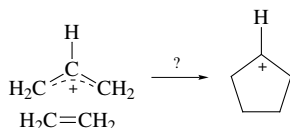
The positively charged allyl cation would be expected to be the electron acceptor in any initial interaction with ethylene. Therefore, to consider this reaction in terms of frontier orbital theory, the question we need to answer is, "do the ethylene HOMO and allyl cation LUMO interact favorably as the reactants approach one another?" The orbitals that are involved are shown in Fig. 1.27. If we analyze a symmetrical approach, which would be necessary for the simultaneous formation of the two new bonds, we see that the symmetries of the two orbitals do not match. Any bonding interaction developing at one end would be canceled by an antibonding interaction at the other end. The conclusion that is drawn from this analysis is that this particular reaction process is not favorable. We would need to consider other modes of approach to analyze the problem more thoroughly, but this analysis indicates that simultaneous (concerted) bond formation between ethylene and an allyl cation to form a cyclopentyl cation is not possible.
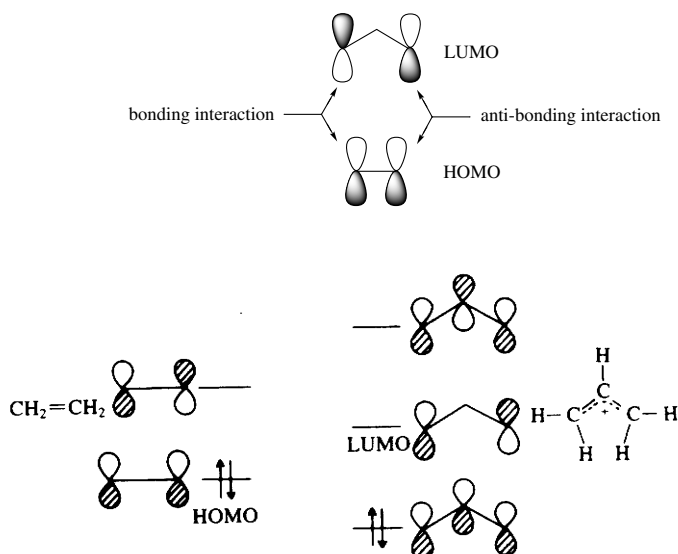
Fig. 1.27. MOs for ethylene and allyl cation.

Let us now consider another reaction, this time between the allyl cation and butadiene. Again, the assumption will be made that it is the frontier π orbitals that will govern the course of the reaction. We will also be slightly more formal about the issue of symmetry. This can be done by recognizing the elements of symmetry that would be maintained as the reaction proceeds. If the reaction is to proceed in a single step, the geometry must permit simultaneous overlap of the orbitals on the carbons where new bonds are being formed. A geometry of approach that permits such a simultaneous overlap is shown below.
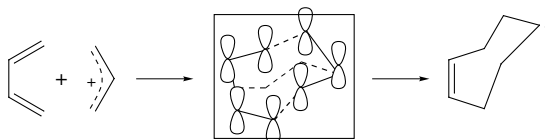
The allyl cation could approach from the the top (or bottom) of the *s-cis* conformation of butadiene, and the new bonds would be formed from the π orbitals. This arrangement would maintain a plane of summetry during the course of the reaction. The plane bisects butadiene between C-2 and C-3 and the allyl cation at C-2. The orbitals can be classified as symmetric (*S*) or antisymmetric (*A*) with respect to this plane. This gives rise to the MO diagram shown in Fig. 1.28. Because strong interactions will occur only between orbitals of the same symmetry, the mutual perturbation of the approaching reactants will affect the orbital energy levels as shown in the diagram. As in all such perturbations, one orbital of the interacting pair will be stabilized and the other will move to higher energy. The
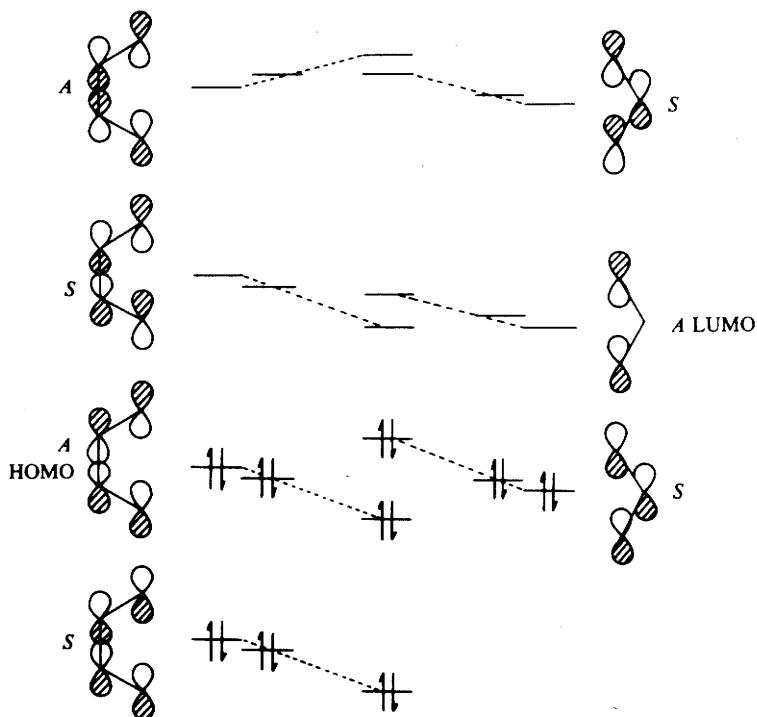
Fig. 1.28. MO diagram showing mutual perturbation of MOs of butadiene and allyl cation.

perturbed orbitals at some point on the way to the transition state are shown in the diagram. Eventually, when the reaction has proceeded to completion, a new set of orbitals belonging to the product will have been formed. These are shown in the center of the diagram, but we will be considering only the initial perturbed set. The lowest-lying π orbitals of both butadiene and the allyl cation are filled. These will interact, with one moving down in energy and the other up. These two changes in energy are partially compensating, with the total energy change being a net increase in the energy of the system. Both the HOMO and LUMO are antisymmetric and will interact strongly, but in this case, because only two electrons are involved, only the energy of the stabilized orbital will affect the total energy since the destabilized orbital is empty. This HOMO–LUMO interaction then contributes a net bonding contribution as the transition state is approached. From this analysis, we conclude that there is the possibility of a favorable bonding interaction between the two reactant species. Notice that the reaction is only *permitted* and that nothing can be said about its actual rate or position of equilibrium on the basis of the analysis given. Such matters as steric hindrance to approach of the reactants and the geometric requirements for satisfactory overlap of the orbitals could still cause the reaction to proceed with difficulty. The analysis does establish, however, that there is a pathway by which the orbitals of the reactants can interact in a way that is favorable for reaction.

A more complete analysis of interacting molecules would examine all of the involved MOs in a similar way. A *correlation diagram* would be constructed to determine which reactant orbital is transformed into which product orbital. Reactions which permit smooth transformation of the reactant orbitals to product orbitals without intervention of high-energy transition states or intermediates can be identified in this way. If no such transformation is possible, a much higher activation energy is likely since the absence of a smooth transformation implies that bonds must be broken before they can be re-formed. This treatment is more complete than the frontier orbital treatment because it focuses attention not only on the reactants but also on the products. We will describe this method of analysis in more detail in Chapter 11. The qualitative approach that has been described here is a useful and simple way to apply MO theory to reactivity problems, and we will employ it in subsequent chapters to problems in reactivity that are best described in MO terms.

It is worth noting that in the case of the reactions of ethylene and butadiene with the allyl cation, the MO description has provided a prediction that would not have been recognized by a pictorial application of valence bond terminology. Thus, we can write an apparently satisfactory description of both reactions.
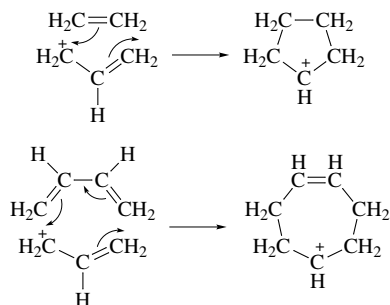

It is only on considering the symmetry of the interacting orbitals that we find reason to suspect that only the second of the two reactions is possible.

1.7. Interactions between σ and π Systems—Hyperconjugation

One of the key assumptions of the Hückel approximation is the noninteracton of the π-orbital system with the σ-molecular framework. This is a good approximation for planar π molecules in which the σ framework is in the nodal plane of the π system. For other molecules, as for example when an sp^3 carbon is added as a substituent group, this approximation is no longer entirely valid. Qualitative application of MO theory can be enlightening in describing interactions between the π system and substituent groups. In valence bond theory, a special type of resonance called *hyperconjugation* is used to describe such interactions. For example, much chemical and structural evidence indicates that alkyl substituents on a carbon–carbon double bond act as electron donors to the π system. In valence bond language, "no bond" resonance structures are introduced to indicate this electronic interaction.
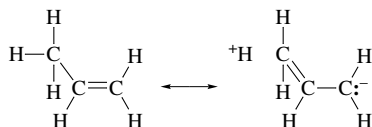
The MO picture of such interactions flows from the idea that individual orbitals encompass the entire molecule. Thus, while the MO description of ethylene involved no interaction between the C $2p_z$ orbitals and the H $1s$ orbitals (see p. 43 to recall this discussion), this strict separation would not exist in propene because the hydrogens of the methyl group are not in the nodal plane of the π bond. The origin of interactions of these hydrogens with the π orbital can be indicated as in Fig. 1.29, which shows propene in a geometry in which two of the hydrogen $1s$ AOs are in a position to interact with the $2p_z$ orbital of carbon 2. An *ab initio* calculation using a STO-3G basis set was carried out on propene in two distinct geometries, eclipsed and staggered.
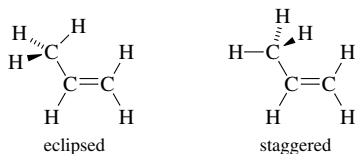
The calculations of the optimum geometry show a slight lenghthening of the C−H bonds because of the electron release to the π system. These calculations also reveal a barrier to rotation of the methyl group of about 1.5–2.0 kcal/mol. Interaction between the hydrogens and the π system favors the eclipsed conformation to this extent.[66] Let us examine the
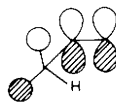

Fig. 1.29. Interactions between two hydrogen $1s$ orbitals and carbon $2p_z$ orbitals stabilize the eclipsed conformation of propene.

66. W. J. Hehre, J. A. Pople, and A. J. P. Devaquet, *J. Am. Chem. Soc.* **98:**664 (1976); A. Pross, L. Radom, and N. V. Riggs, *J. Am. Chem. Soc.* **102:**2253 (1980); K. B. Wiberg and E. Martin, *J. Am. Chem. Soc.* **107:**5035 (1985); A. E. Dorigo, D. W. Pratt, and K. N. Houk, *J. Am. Chem. Soc.* **109:**6589 (1987).

reason for the preference for the eclipsed conformation. This issue can be approached by analyzing the interactions between the carbon $2p_z$ orbitals and the CH_3 fragment in a little more detail. The bonding and antibonding combinations that arise from interaction of the appropriate CH_3-π and CH_3-π* orbitals with the $2p_z$ orbitals are shown in Fig. 1.30. The strongest interaction is a repulsive one between the filled CH_3-π and $C=C$-π orbitals. It is this interaction which is primarily responsible for the favored eclipsed conformation. The eclipsed structure minimizes the repulsion by maximizing the separation between the hydrogens and the π bond. The second interaction is the stabilizing hyperconjugative one between CH_3-π and $C=C$-π*. This is a bonding interaction because π* is an empty orbital and can accept electron density from CH_3-π. It is this bonding interaction which transfers electron density from the methyl group to the terminal carbon of the double bond. Notice that there is a correspondence between the MO picture and the valence bond resonance structure in that both specify a net transfer of electron density from C—H bonds to the π system with a net strengthening of the bond between C-2 and C-3 but a weakening of the C(1)—C(2) π bond.
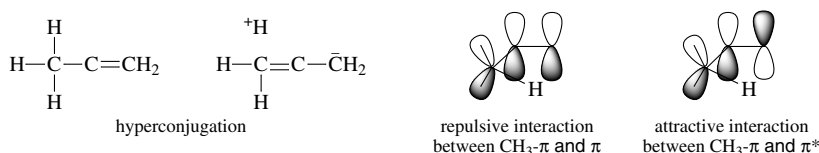
One of the fundamental structural facets of organic chemistry, which has been explained most satisfactorily in MO terms, is the existence of a small barrier to rotation about single bonds. In ethane, for example, it is known that the staggered conformation is about 3 kcal/mol more stable than the eclipsed conformation so that the eclipsed conformation represents a transition state for transformation of one staggered conformation into another by rotation.
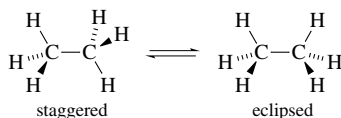
Valence bond theory offers no immediate qualitative explanation since the σ bond that is involved is cylindrically symmetrical. A steric argument based on repulsions between hydrogens also fails because on detailed examination of this hypothesis, it is found that the
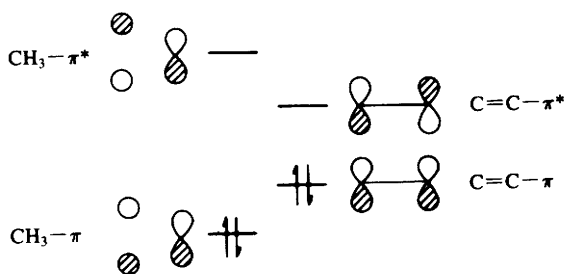

Fig. 1.30. Interactions between CH_3-π and CH_3-π* orbitals and carbon $2p_z$ orbitals.

hydrogens are too small and too distant from one another to account for the observed energy. MO ideas, however, succeed in correctly predicting and calculating the magnitude of the ethane rotational barrier.[67] The origin of the barrier is a repulsive interaction between the filled C$-$H orbitals which is maximal in the eclipsed geometry.

The interaction can be further examined by consideration of the ethane MOs.[68] Because ethane contains two carbon atoms and six hydrogens, the MOs are constructed from six H $1s$, two C $2s$, and six C $2p$ orbitals. Figure 1.31 depicts the seven bonding MOs, assuming the staggered geometry. The σ, σ', and σ_x orbitals are not affected much by the rotation of the two CH_3 groups with respect to one another because the H $1s$ orbitals all have the same sign within each CH_3 group. The other MOs, however, are of a π type, having a nodal plane derived from the nodal plane of the C $2p_z$ orbitals. The extent of the overlap in these orbitals clearly changes as the two CH_3 groups are rotated with respect to one another. Analysis of the relative magnitudes of the bonding and antibonding interactions that take place as rotation occurs indicates that the change in energy of these two pairs of MOs is the source of the ethane rotational barrier.

The interaction of the lone-pair electrons on an amine nitrogen with adjacent C$-$H bonds is another example of a hyperconjugative effect that can be described in MO language. The lone-pair electrons, when properly aligned with the C$-$H bond, lead to a
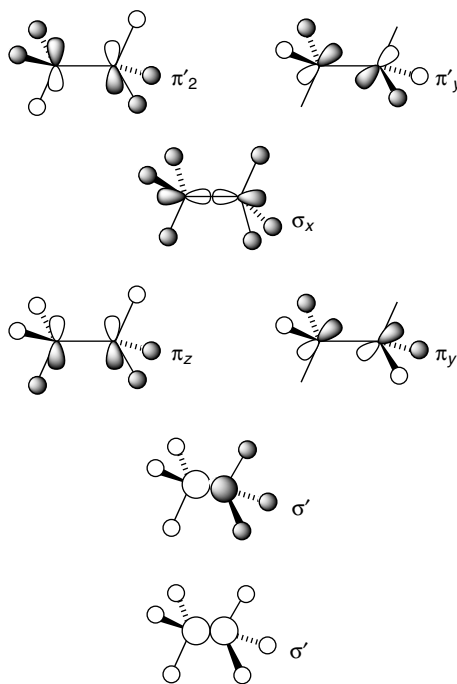
Fig. 1.31. Molecular orbitals of ethane revealing π character of π_z, π_y, π'_z, and π'_y orbitals. Only the filled orbitals are shown.

67. R. M. Pitzer, *Acc. Chem. Res.* **16:**207 (1983); R. Hoffmann, *J. Chem. Phys.* **39:**1397 (1963); R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.* **39:**1995 (1963); J. A. Pople and G. A. Segal, *J. Chem. Phys.* **43:**5136 (1956).
68. J. P. Lowe, *Prog. Phys. Org. Chem.* **6:**1 (1968); J. P. Lowe, *J. Am. Chem. Soc.* **92:**3799 (1970); J. P. Lowe, *Science* **179:**527 (1973).

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donation of electron density from the lone-pair orbital to the antibonding C−H orbital. The overall effect is to weaken the C−H bond.

representation
by hyperconjugation

Electron donation from N *n* orbital to C−H σ* orbital.
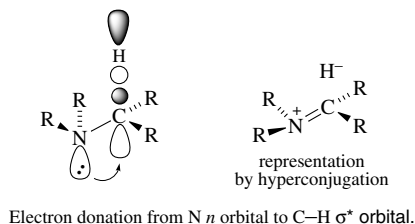
In acyclic structures, such effects are averaged by rotation, but in cyclic structures differences in C−H bond strengths based on the different alignments can be recognized.[69] The C−H bonds that are in an *anti* orientation to the lone pair are weaker than the C−H bonds in other orientations.

The examples that have been presented in this section illustrate the approach that is used to describe structure and reactivity effects within the framework of MO description of structure. In the chapters that follow, both valence bond theory and MO theory will be used in the discussion of structure and reactivity. Qualitative valence bond terminology is normally most straightforward for saturated systems. MO theory provides useful insights into conjugated systems and into effects that depend upon the symmetry of the molecules under discussion.

1.8. Other Quantitative Descriptions of Molecular Structure

One of the difficulties of MO computations is that the concept of the electron-pair bond disappears. The bonding between individual atoms appears as a contribution from several MOs. Thus, while MO theory is valuable in describing overall molecular characteristics such as structure, total energy, and charge distribution, it is less useful for focusing attention on individual parts of a molecule. Although the frontier orbital concept is a useful guide to reactivity, MO theory provides no unambiguous method to relate the MOs to properties of a particular atom or functional group. For this reason, many chemists have pursued theoretical descriptions of molecules that would lend themselves more readily to the concepts of transferable structural units and functional groups which arise from qualitative valence bond theory. Although we do not have space here to fully develop these approaches, we can describe some of the key ideas and illustrate specific applications.

1.8.1. Atoms in Molecules

MO calculations can provide the minimum-energy structure, total energy, and overall electron density of a given molecule. However, this information is in the form of the sum of the individual MOs and cannot be easily dissected into contributions by specific atoms or groups. How can the properties described by the MOs be related to our concept of molecules as a collection of atoms or functional groups held together by chemical bonds?

69. A. Pross, L. Radom, and N. V. Riggs, *J. Am. Chem. Soc.* **102:**2253 (1980); T. Laube and T.-K. Ha, *J. Am. Chem. Soc.* **110:**5511 (1988).

One approach is to define critical bond points and surfaces that subdivide molecules into the constituent atoms. R. F. W. Bader has developed such an approach.[70] The total electron density obtained from MO or other computational methods is partitioned among atoms. The quantitative results can be depicted qualitatively in the form of *molecular graphs*. The atoms are connected by atomic interaction lines that define maximum charge density between neighboring atoms. The atomic interaction lines correspond to chemical bonds by revealing accumulation of electron density between nuclei. The network of lines constitutes a molecular graph. In addition, the graphs locate *critical points* where electron density is either at a maximum or a minimum with respect to dislocation in any of the directions of three- dimensional space. The similarity to a classical structural formula is clear, but the molecular graphs are based on quantum-chemical theory rather than the qualitative concepts of valence bonds and hybridized orbitals. Figure 1.32 gives some representative molecular graphs and shows the bond critical points in these structures.

The subunits which can be defined can include atoms or collections of atoms corresponding to functional groups. The subunits can be represented as regions of space defined by electon density. These representations correspond well with the qualitative concepts that arise from valence bond structures. The mathematical evaluation can assign shape and charge density to atoms. Table 1.17 gives the C and H charge densities in some

a.

pentane   hexane

b.

Bicyclo[1.1.1]pentane   Bicyclo[2.1.1]hexane   Bicyclo[2.2.1]heptane
and [1.1.1]propellane   and [2.1.1]propellane   and [2.2.1]propellane
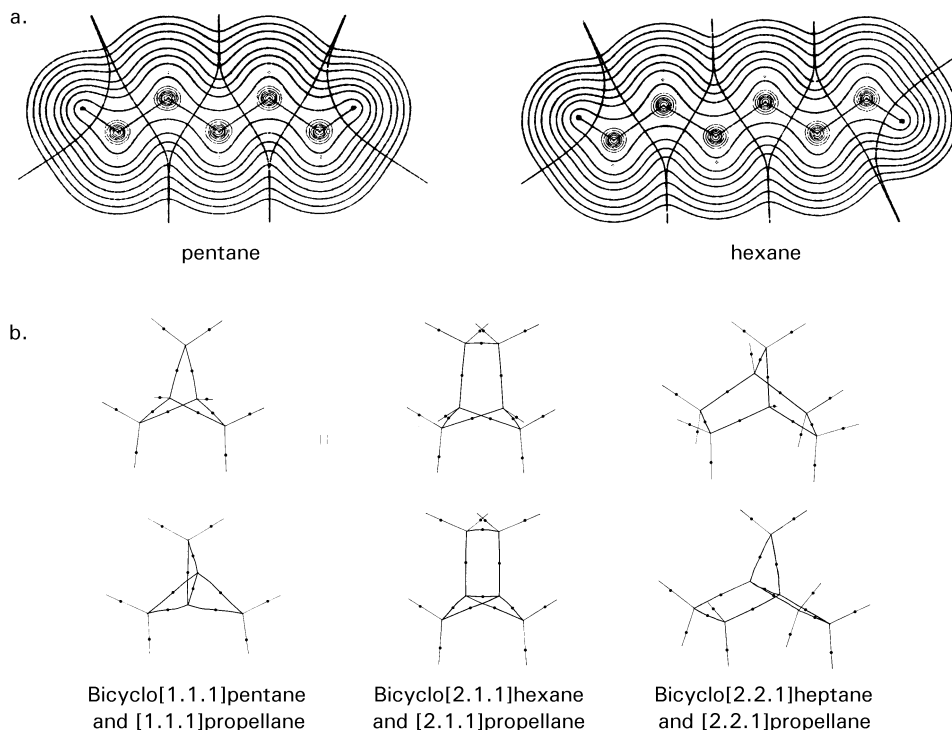
Fig. 1.32. (a) Molecular graphs and electron density contours for pentane and hexane. Dots on bond paths represent critical points. (b) Comparison of molecular graphs for bicycloalkanes and corresponding propellanes. (Reproduced from *Chem. Rev.* **91**:893 (1991) with permission of the American Chemical Society.)

70. R. F. W. Bader, *Atoms in Molecules—A Quantum Theory*, Oxford University Press, Oxford, U.K., 1990; R. F. W. Bader, *Chem. Rev.* **91**:893 (1991).

Table 1.17. Atomic Charges in Organic Structures[a]

	$q(C)$	$q(H)$
CH_4	$+0.175$	-0.044
C_2H_6	$+0.184$	-0.061
C_2H_4	$+0.035$	-0.017
C_6H_6	$+0.020$	-0.020
C_2H_2	-0.136	$+0.136$
CH_3^+	$+0.179$	$+0.274$
$CH_3\cdot$	-0.035	$+0.012$
CH_3^-	-0.422	-0.193

a. From R. F. W. Bader, P. L. A. Popelier, and T. A. Keith, *Angew. Chem. Int. Ed. Engl.* **33:**620 (1994).

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fundamental organic molecules and intermediates.[71] Figure 1.33 shows the carbon and hydrogen atoms dissected from ethane, ethylene, ethyne, and benzene. Especially noteworthy is the decreasing size of hydrogen as the carbon electronegativity changes with hybridization in the order $sp > sp^2 > sp^3$. Figure 1.34 shows the shape of carbon in CH_3^+, CH_3^-, and $CH_3\cdot$.

Figure 1.35 shows the second-row elements Li through F in their compounds with hydrogen. Note the transformation of hydrogen from "hydride" in LiH to a much smaller, protonlike entity in HF as the electronegativity of the heavier atom increases.

The lesson in these figures is that the qualitative concepts of chemical structures can be given a pictorial representation based on the quantitative application of the principles of quantum chemistry. Various, indeed all, molecular properties can, in principle, be calculated from the electronic distribution these pictures represent.

1.8.2. Electron Density Functionals

Another approach to calculating molecular geometry and energy is based on *density functional theory* (DFT).[72] DFT focuses on the electron cloud corresponding to a molecule. The energy of a molecule is uniquely specified by the electron density functional.[73] The calculation involves the construction of an expression for the electron density. The energy of the system is then expressed as

$$E = T + v_{en} + J_{ee} + v_{xc}$$

where T is the kinetic energy, v_{en} and J_{ee} are Coulombic electron–nuclear and electron–electron interactions, respectively, and v_{xc} are correlation and exchange effects. As in the Hartree–Fock MO approach, the minimization of energy should provide the most accurate description of the electronic field. The mathematical problem is to define each of the terms, with v_{xc} being the most challenging. The formulation cannot be done exactly, but various approaches have been developed and calibrated by comparison with experimental data. The methods used most frequently by chemists were developed by A. D. Becke.[74] This approach is often called the B3LYP method. The computations can be done with

71. R. F. W. Bader, P. L. A. Popelier, and T. A. Keith, *Angew. Chem. Int. Ed. Engl.* **33:**620 (1994).

72. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, U.K., 1989.

73. P. Hohenberg and W. Kohn, *Phys. Rev. A* **136:**864 (1964); M. Levy, *Proc. Natl. Acad. Sci. U.S.A.* **76:**6062 (1979).

74. A. D. Becke, *Phys. Rev. A* **38:**3098 (1988); A. D. Becke, *J. Chem. Phys.* **96:**2155 (1992); A. D. Becke, *J. Chem. Phys.* **97:**9173 (1992); A. D. Becke, *J. Chem. Phys.* **98:**5648 (1993).
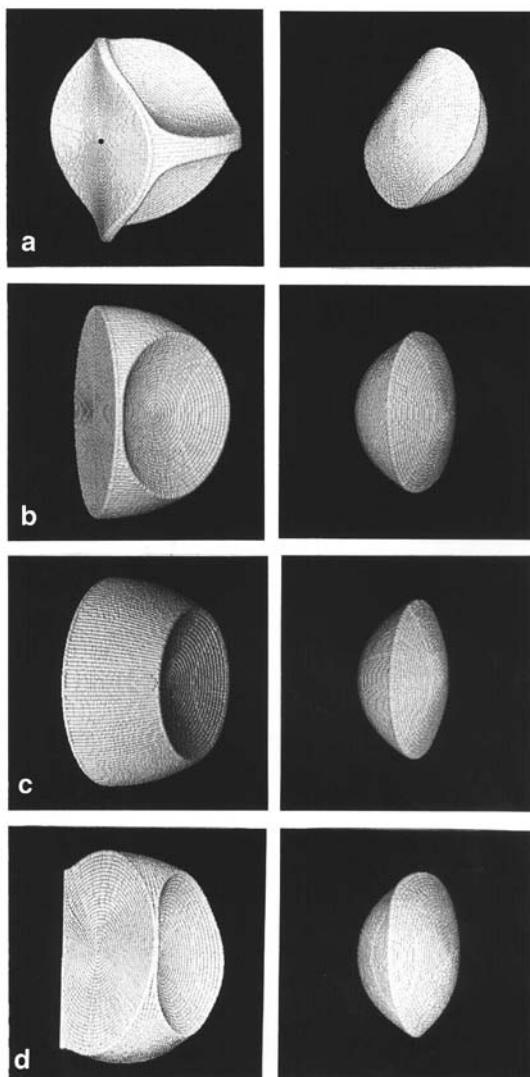
Fig. 1.33. The C and H atoms in ethane (a), ethene (b),
ethyne (c), and benzene (d), respectively. Note that the
H atom is largest in ethane and smallest in ethyne.
(Reproduced from *Angew. Chem. Int. Ed. Engl.* **33:**620
(1994) by permission of Wiley-VCH.)

considerably less computer time than required by the most advanced (G2) *ab initio* MO
methods (see Section 1.3), and there has been considerable interest in comparing B3LYP
results to MO calculations.

Table 1.18 gives total bonding energies in kilocalories per mole for some simple
molecules. The B3LYP results are comparable in accuracy to G1 and G2 results. Another
comparison was done with a series of cyclic hydrocarbons as the test case. The calculations
were done using an isodesmic reaction scheme. The results are given in Table 1.19. Density
functional calculations have also been successfully extended to functionalized molecules.[75]

75. A. St. Amant, W. D. Cornell, P. A. Kollmar, and T. A. Halgren, *J. Comput. Chem.* **16:**1483 (1995).

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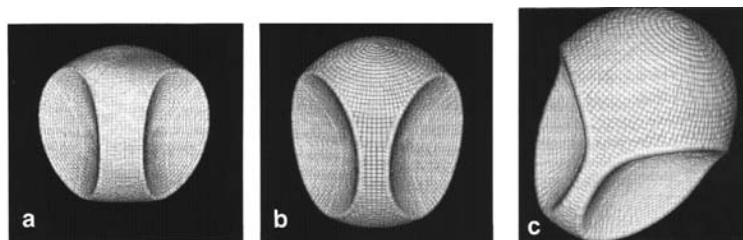
Fig. 1.34. The carbon atoms in the methyl cation (a), radical (b), and anion (c), respectively. (Reproduced from *Angew. Chem. Int. Ed. Engl.* **33:**620 (1994) by permission of Wiley-VCH.)

DFT turns out to be well suited to quantitative expression of some of the qualitative concepts introduced in Section 1.2, such as electronegativity, hardness, and softness.[76] The principle of maximum hardness[77] (p. 22) can be derived as a consequence of DFT, as can the concepts of hardness and softness.[78]

A very simple definition of electronegativity also finds a foundation in DFT. The definition is

$$V = n/r$$

which relates electronegativity to the number of valence-shell electrons and the effective atomic radius.[79] This measure of electronegativity is both empirically correlated and theoretically related to the Mulliken electronegativity χ, defined as $\chi = (I + A)/2$.[80] The values assigned for some of the atoms of most interest in organic chemistry are given in Table 1.20.

Concepts such as relative acidity and carbocation stability can be fundamentally related to hardness and electronegativity as defined by DFT.

$$R{-}H$$

$$_{-H^-} \diagup \quad \Big| _{-H\cdot} \quad \diagdown _{-H^+}$$

$$R^+ \rightleftharpoons R\cdot \rightleftharpoons R^-$$
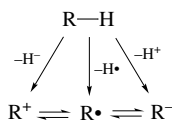
The energy difference between R^+ and R^- can be expressed as

$$\Delta G = -23.06[E_{red}(R^+) - E_{red}(R\cdot)]$$

where the E_{red} are the reduction potentials of R^+ and $R\cdot$. This energy is approximately the same as 2χ, since it represents the HOMO–LUMO gap for $R\cdot$.[81]

76. P. W. Chattaraj and R. G. Parr, *Struct. Bonding* **80:**11 (1993); G.-H. Liu and R. G. Parr, *J. Am. Chem. Soc.* **117:**3179 (1995).

77. R. G. Parr and P. K. Chattaraj, *J. Am. Chem. Soc.* **113:**1854 (1991); T. K. Ghanty and S. K. Ghosh, *J. Phys. Chem.* **100:**12295 (1996).

78. P. K. Chattaraj, H. Lee, and R. G. Parr, *J. Am. Chem. Soc.* **113:**1855 (1991).

79. Y.-R. Luo and S. W. Benson, *J. Phys. Chem.* **92:**5255 (1988); Y.R. Luo and S. W. Benson, *J. Am. Chem. Soc.* **111:**2480 (1989); Y.R. Luo and S. W. Benson, *J. Phys. Chem.* **94:**914 (1990); Y.R. Luo and S. W. Benson, *Acc. Chem. Res.* **25:**375 (1992).

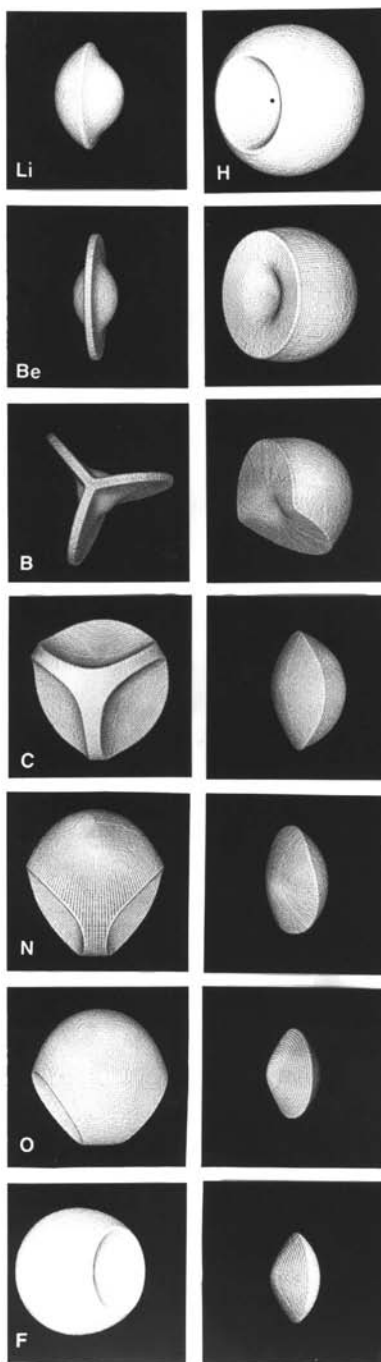80. Y.-R. Luo and P. D. Pacey, *J. Am. Chem. Soc.* **113:**1465 (1991).

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Fig. 1.35. Representations of the atoms in the second-row hydrides AH_n. In the hydridic members LiH, BeH_2, and BH_3, the A atom consists primarily of a core of decreasing radius, dressed with some residual valence density. The form and properties of the atoms undergo a marked change at methane, a nonpolar molecule: no core is visible on the C atom, and the H atoms, considerably reduced in size and population, now lie on the convex side of the interatomic surface. The increasing polarity of the remaining members is reflected in the decreasing size of the H atom and the increasing convexity of its interatomic surface. (Reproduced from *Angew. Chem. Int. Ed. Engl.* **33:**620 (1994) by permission of Wiley-VCH.)

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Table 1.18. Comparison of *Ab Initio* and DFT Calculations of Atomization Energies in kcal/mol.

	Exp	G1[a]	G2[b]	DFT[c]	B3LYP[d]
H_2O	219.3	218.4	219.3	217.0	220.7
NH_3	276.7	275.4	276.6	276.8	279.7
CH_4	392.5	393.1	393.3	393.5	393.0
C_2H_6	666.3	667.6	666.6	668.7	667.5
C_2H_4	531.9	533.5	531.4	534.3	532.1
C_2H_2	388.9	391.2	386.6	389.0	391.0
CH_3OH	480.8	482.6	481.9	480.8	481.3
$CH_2{=}O$	357.2	362.2	358.7	357.9	356.7

a. J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90:**5622 (1989).
b. L. A. Curtiss, J. E. Carpenter, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **96:**9030 (1992).
c. A. D. Becke, *J. Chem. Phys.* **98:**5648 (1993).
d. C. W. Bauschlicher, Jr., and H. Partridge, *Chem. Phys. Lett.* **240:**533 (1995).

Table 1.19. Comparison of *Ab Initio* and DFT Enthalpies with Experimental Values in kcal/mol for the Isodemic Reaction:[a]

$$C_nH_m + (3n - m)CH_4 \rightarrow (2n - m/2)C_2H_6$$

Structure	ΔH_f (exp)	*Ab Initio*[b]	DFT
	6.99	5.79	5.12
	11.51	11.87	9.94
	13.12	5.39	5.14
	10.43	12.37	8.99
	14.21	3.16	1.47
	21.73	6.41	3.00
	−7.66	12.23	9.11

a. A. Fortunelli and M. Selmi, *Chem. Phys. Lett.* **223:**390 (1994).
b. Gaussian 92.

81. E. M. Arnett and R. T. Ludwig, *J. Am. Chem. Soc.* **117:**6627 (1995).
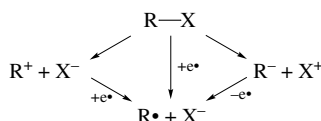
**Table 1.20. Electronegativity of Some Atoms by
the Definition n/r^a**

Atom	Single bond	Double bond	Triple bond
C	5.18	6.00	6.63
N	6.67	8.1	
O	8.11	9.7	
F	9.92		
Cl	7.04		
Br	6.13		
I	5.25		

a. Based on covalent radii given by W. Gordy and R. L. Cook, in *Microwave Molecular Spectroscopy*, John Wiley & Sons, New York, 1984.

The same concept can be applied to carbon radicals bound to atoms other than hydrogen.[82]

The energy for the electron transfer

$$2R\cdot \rightarrow R^+ + R^-$$

is given by

$$\Delta E = I - A = 2\eta \approx \text{HOMO–LUMO gap}$$

These relationships also underlie observed correlations between acidity, hydride affinity, or heterolytic bond energies and oxidation potentials. Table 1.21 gives some hardness values for simple compounds of hydrogen, carbon, and the halogens. Note particularly the trend towards greater softness in the hydrogen halides and methyl halides as the halogen becomes larger.

Table 1.21. Hardness for Some Small Molecules^a

H_2	8.7	HF	11.0	F_2		CH_4	10.3	CH_3F	9.4
H_2O	9.5	Cl	8.0	Cl_2	4.6	$CH_2{=}CH_2$	6.2	CH_3Cl	7.5
NH_3	8.2	HBr		Br_2	4.0	$HC{\equiv}CH$	7.0	CH_3Br	5.8
H_2S	6.2	HI	5.3	I_2	3.4	C_6H_6	5.3	CH_3I	4.7

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1.8.3. Modern Valence Bond Approaches

Several methods of quantitative description of molecular structure based on the concepts of valence bond theory have been developed.[83–87] These methods employ orbitals similar to localized valence bond orbitals, but permitting modest delocalization. These orbitals allow many fewer structures to be considered and remove the need for incorporating many ionic structures, in agreement with chemical intuition. To date, these methods have not been as widely applied in organic chemistry as MO calculations. They have, however, been successfully applied to fundamental structural issues. For example, successful quantitative treatments of the structure and energy of benzene and its heterocyclic analogs have been developed.[88] It remains to be seen whether computations based on DFT and modern valence bond theory will come to rival the widely used MO programs in analysis and interpretation of structure and reactivity.

General References

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W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. Pople, *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986.
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R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970.
H. E. Zimmerman, *Quantum Mechanics for Organic Chemists*, Academic Press, New York, 1975.

Problems

(References for these problems will be found on page 791.)

1. Use thermochemical relationships to obtain the required information.

   (a) The heats of formation of cyclohexane, cyclohexene, and benzene are, respectively, -29.5, -1.1, and $+18.9$ kcal/mol. Estimate the resonance energy of benzene using these data.

88. D. L. Cooper, S. C. Wright, J. Gerratt, and M. Raimondi, *J. Chem. Soc.*, *Perkin Trans. 2* **1989:**255; D. L. Cooper, S. C. Wright, J. Gerratt, P. A. Hyams, and M. Raimondi, *J. Chem. Soc.*, *Perkin Trans. 2* **1989:**719; C. Amovilli, R. D. Harcourt, and R. McWeeny, *Chem. Phys. Lett.* **187:**494 (1991); J. Gerratt, D. L. Cooper, P. B. Karadakov, and M. Raimondi, *Chem. Soc. Rev.* **26:**87 (1997).

(b) Calculate ΔH for the air oxidation of benzaldehyde to benzoic acid given that the heats of formation of benzaldehyde and benzoic acid are -8.8 and $-70.1\,\text{kcal/mol}$, respectively.

(c) Using the appropriate heats of formation in Table 1.5, calculate the heat of hydrogenation of 2-methyl-1-pentene.

2. Suggest an explanation for the following observations:

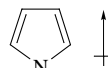(a) The dipole moment of the hydrocarbon calicene has been estimated to be as large as 5.6 D.
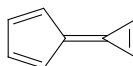
calicene

(b) The measured dipole moment of *p*-nitroaniline (6.2 D) is larger than the value calculated using empirical group moments (5.2 D).

(c) The dipole moment of furan is smaller than and in the opposite direction from that of pyrrole.
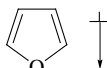
0.71 D   1.80 D

3. Predict the energetically preferred site of protonation for each of the following molecules and explain the basis of your prediction.

(a)

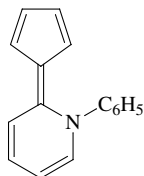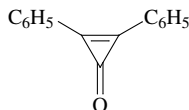$C_6H_5CH{=}N{-}C_6H_5$
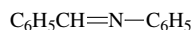
(c)

(b)
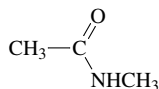
(d)
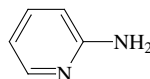
4. What physical properties, such as absorption spectra, bond length, dipole moment, etc., could be examined to obtain evidence of resonance interactions in the following molecules? What deviations from "normal" physical properties would you expect to find?
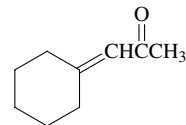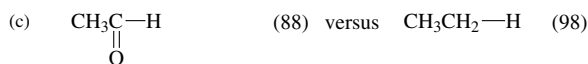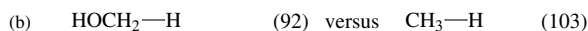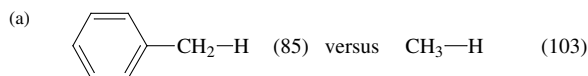
(a)

(b)

(c)

5. Certain C$-$H bonds have significantly lower bond dissociation energies than do the "normal" C$-$H bonds in saturated hydrocarbons. Offer a structural rationalization of the lowered bond energy in each of the following compounds, relative to the saturated

hydrocarbon C–H bond taken as a reference. (The bond dissociation energies are given in kcal/mol.)

(a)

Ph—CH_2—H (85) versus CH_3—H (103)

(b) $HOCH_2$—H   (92) versus CH_3—H (103)

(c) $CH_3\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}$—H   (88) versus CH_3CH_2—H (98)

6. (a) Carboxamides have substantial rotational barriers on the order of 20 kcal/mol for the process
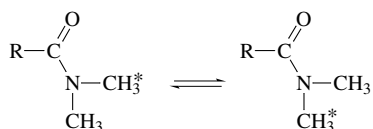
   Develop a structural explanation for the existence of this barrier in both resonance and molecular orbital terminology.

   (b) In the gas phase the rotational barrier of *N*,*N*-dimethylformamide is about 19.4 kcal/mol, which is about 1.5 kcal/mol less than in solution. Is this change consistent with the ideas you presented in (a)? Explain.

   (c) Explain the relative rates of alkaline hydrolysis of the following pairs of carboxamides.
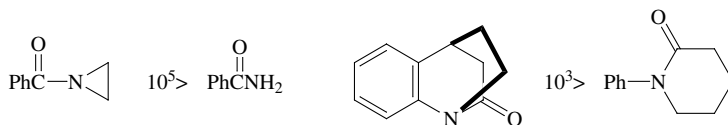
7. Construct a qualitative MO diagram showing how the π-molecular orbitals in the following molecules are modified by the addition of the substituent:

   (a) vinyl fluoride, compared to ethylene
   (b) acrolein, compared to ethylene
   (c) acrylonitrile, compared to ethylene
   (d) benzyl cation, compared to benzene
   (e) propene, compared to ethylene
   (f) fluorobenzene, compared to benzene

8. The data below give the stabilization calculated in kcal/mol by MO methods for the reaction:

$$CH_3{-}X \; + \; CH_2{=}CH_2 \; \longrightarrow \; CH_4 \; + \; CH_2{=}CH{-}X$$
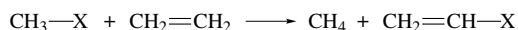
X	ΔH
F	− 6.4
OCH_3	− 10.9
NH_2	− 13.3

    (a) Demonstrate that this indicates that there is a stabilizing interaction between the substituent and a carbon–carbon double bond.

    (b) Draw resonance structures showing the nature of the interaction.

    (c) Construct a qualitative MO diagram which rationalizes the existence of a stabilizing interaction.

    (d) Both in resonance and molecular orbital terminology, explain the order of the stabilization $N > O > F$.

9. Construct a qualitative MO diagram for the H-bridged ethyl cation by analyzing the interaction of the ethylene MOs given in Fig. 1.23 with a proton approaching the center of the ethylene molecule from a direction perpendicular to the molecular plane. Indicate which ethylene orbitals will be lowered by this interaction and which will be raised or left relatively unchanged. Assume that the hydrogens of ethylene are slightly displaced away from the direction of approach of the proton.

10. In the Hückel treatment, atomic orbitals on nonadjacent atoms are assumed to have no interaction. They are neither bonding nor antibonding. The concept of *homoconjugation* suggests that such orbitals may interact, especially in rigid structures which direct orbitals toward one another. Consider, for example, bicyclo[2.2.1]hepta-2,5-diene:
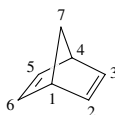
    (a) Construct the MO diagram according to simple Hückel theory and assign energies to the orbitals.

    (b) Extend the MO description by allowing a significant interaction between the C-2 and C-6 and between the C-3 and C-5 orbitals. Construct a qualitative MO diagram by treating the interaction as a perturbation on the orbitals shown for (a).

11. (a) Sketch the nodal properties of the highest occupied molecular orbital of pentadienyl cation ($CH_2=CHCH=CHCH_2^+$).

    (b) Two of the π-MOs of pentadienyl are given below. Specify which one is of lower energy, and classify each as to whether it is bonding, nonbonding, or antibonding. Explain your reasoning.
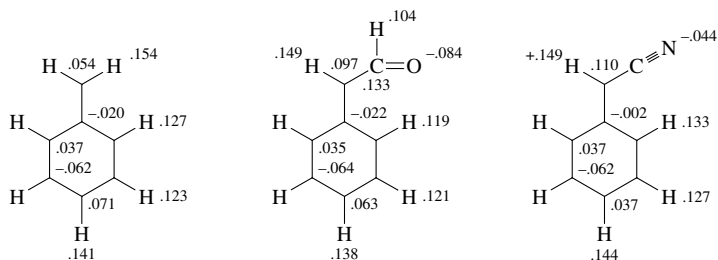
$$1\ \ 2\ \ 3\ \ 4\ \ 5$$
$$o-o-o-o-o$$

$$\psi_x = 0.50\phi_1 + 0.50\phi_2 - 0.50\phi_4 - 0.50\phi_5$$
$$\psi_y = 0.58\phi_1 - 0.58\phi_3 + 0.58\phi_5$$

12. The diagrams below give STO-3G calculated charge densities for the benzyl cation and its α-formyl and α-cyano derivatives. Analyze the effect of these substituents on

the charge density.

H .054 H .154
H
.020
H .127
.037
−.062
H
H .071 H .123
H
.141

H .104
.149 H .097 C=O −.084
.133
H
−.022 H .119
.035
−.064
H
H .063 H .121
H
.138

−.044
+.149 H .110 C≡N
H
−.002 H .133
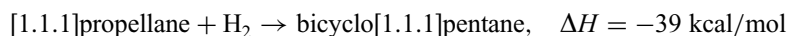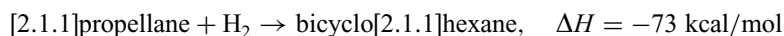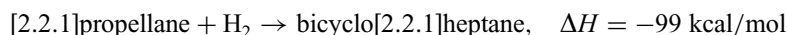.037
−.062
H
H .037 H .127
H
.144

13. Calculate the energy levels and coefficients for 1,3-butadiene using Hückel MO theory.

14. (a) Estimate from HMO theory the delocalization energy, expressed in units of β, of cyclobutadienyl dication ($C_4H_4^{2+}$).
    (b) Estimate, in units of β, the energy associated with the long-wavelength UV-VIS absorption of 1,3,5,7-octatetraene. Does it appear at longer or shorter wavelengths than the corresponding absorption for 1,3,5-hexatriene?

15. Addition of methylmagnesium bromide to 2-methylcyclohexanone followed by iodine-catalyzed dehydration of the resulting alcohol gave three alkenes in the ratio $A:B:C = 3:31:66$. Each isomer gave a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane on catalytic hydrogenation. When the alkene mixture is heated with a small amount of sulfuric acid, the ratio $A:B:C$ is changed to $0.0:15:85$. Assign structures to A, B, and C.

16. The propellanes are highly reactive substances which readily undergo reactions involving rupture of the central bond. It has been suggested that the polymerization of propellanes occurs by a dissociation of the central bond:

$(CH_2)_n$
$(CH_2)_n$—C—$(CH_2)_n$
$\longrightarrow$
$(CH_2)_n$
$(CH_2)_n$—C·—$(CH_2)_n$
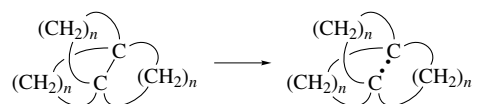
Somewhat surprisingly perhaps, it has been found that [1.1.1]propellane is considerably *less reactive* than [2.2.1]propellane. Use the theoretically calculated enthalpy data below to estimate the bond dissociation energy of the central bond in each of the three propellanes shown. How might this explain the relative reactivity of the [1.1.1]- and [2.2.1]propellanes?

Enthalpy for addition of hydrogen to give the corresponding bicycloalkane

$[2.2.1]\text{propellane} + H_2 \rightarrow \text{bicyclo}[2.2.1]\text{heptane}, \quad \Delta H = -99 \text{ kcal/mol}$

$[2.1.1]\text{propellane} + H_2 \rightarrow \text{bicyclo}[2.1.1]\text{hexane}, \quad \Delta H = -73 \text{ kcal/mol}$

$[1.1.1]\text{propellane} + H_2 \rightarrow \text{bicyclo}[1.1.1]\text{pentane}, \quad \Delta H = -39 \text{ kcal/mol}$

Assume that the bond dissociation energy of the bridgehead hydrogens in each bicycloalkane is 104 kcal/mol. Indicate and discuss any other assumptions you have made.

17. Examine the following thermochemical data pertaining to hydrogenation of unsaturated eight-membered ring hydrocarbons to give cyclooctane:

Unsaturated ring hydrocarbon	$-\Delta H$ (kcal/mol)
cis,cis,cis,cis-1,3,5,7-Cyclooctatetraene	97.96
cis,cis,cis-1,3,5-Cyclooctatriene	76.39
cis,cis,cis-1,3,6-Cyclooctatriene	79.91
cis,cis-1,5-Cyclooctadiene	53.68
cis,cis-1,4-Cyclooctadiene	52.09
cis,cis-1,3-Cyclooctadiene	48.96
trans-Cyclooctene	32.24
cis-Cyclooctene	22.98

(a) Discuss the differences observed in each isomeric series of compounds, and offer an explanation for these differences.

(b) Comment on whether the conjugation present in cyclooctatetraene has a stabilizing or destabilizing effect on the C=C bonds.

18. Cyclic amines such as piperidine and its derivatives show substantial differences in the properties of the axial C-2 and C-6 versus the equatorial C-2 and C-6 C−H bonds.
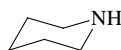
The axial C−H bonds are *weaker* than the equatorial C−H bonds as can be demonstrated by a strongly shifted C−H stretching frequency in the IR spectrum. Axial C-2 and C-6 methyl groups *lower* the ionization potential of the lone-pair electrons on nitrogen substantially more than do equatorial C-2 or C-6 methyl groups. Discuss the relationship between these observations and provide a rationalization in terms of qualitative MO theory.

19. (a) The strain energy of spiropentane (62.5 kcal/mol) is considerably greater than twice that of cyclopropane (27.5 kcal/mol). Suggest an explanation.
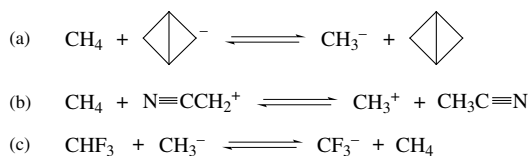

(b) The fractional *s* character in bonds to carbon in organic molecules may be estimated by its relation to $^{13}C-^{13}C$ coupling constants, as determined by NMR. Estimate the fractional *s* character of C-1 in its bond to C-3 of spiropentane, given

$$s_{1(3)} = \frac{J_{^{13}\mathrm{C}-^{13}\mathrm{C}}}{Ks_{3(1)}}$$

where K is a constant equal to 550 Hz, the $^{13}\mathrm{C}-^{13}\mathrm{C}$ coupling constant J between C-1 and C-3 is observed to be 20.2 Hz, and $s_{3(1)}$ is the s character at C-3 in its bond to C-1.

20. Predict which direction will be favored in the thermodynamic sense for each of the following reactions:

(a) CH_4 + $\rightleftharpoons$ CH_3^- +

(b) CH_4 + $N{\equiv}CCH_2^+$ $\rightleftharpoons$ CH_3^+ + $CH_3C{\equiv}N$

(c) CHF_3 + CH_3^- $\rightleftharpoons$ CF_3^- + CH_4

21. Predict which compound would give the faster (k) or more complete (K) reaction. Explain the basis for your prediction.

(a)

or

(b) Ph_3CH + $^-NH_2$ $\xrightarrow{\;K\;}$ Ph_3C^- + NH_3
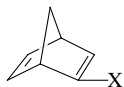
or

(c)

or
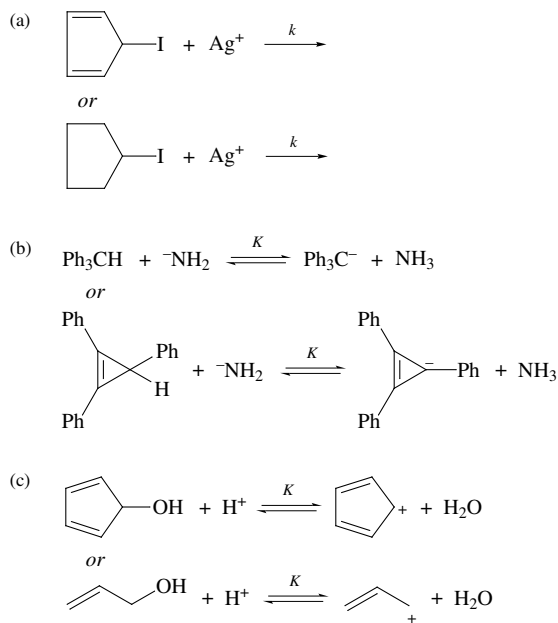
22. Computational comparison of structures of the benzyl cation (**A**) and singlet phenylcarbene (**B**) indicates a much greater double-bond character for the exocyclic

bond in **A** than in **B**.

A   B
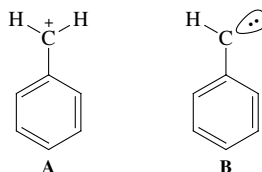
Can you provide a rationalization of this difference in terms of both valence bond-resonance and PMO considerations? Explain.

23. The ionization potentials of some substituted norbornadienes have been measured by photoelectron spectroscopy. The values which pertain to the π orbitals are shown:

	IP (eV)	
X	1	2
H	8.69	9.55
CH$_3$O	8.05	9.27
CN	9.26	10.12

Use PMO theory to describe the effect of the substituents on the ionization potential. Use an MO diagram to explain the interaction of the substituents with the π bonds. Explicitly take into account the fact that the two orbitals interact and therefore cannot be treated as separate entities (see Problem 10).

24. *Ab initio* MO calculations using 4-31G orbitals indicate that the eclipsed conformation of acetaldehyde is more stable than the staggered conformation.

$E = -152.685$ au $E = -152.683$ au
H/C = O eclipsed   H/C = O staggered
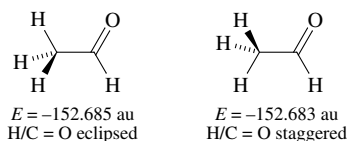
Provide a rationalization of this structural effect in terms of MO theory. Construct a qualitative MO diagram for each conformation, and point out the significant differences that can account for the preference for the eclipsed conformation.

25. Interesting stabilization and structural trends have been noted using MP2/6-31G* calculations on the effect of substituents on imines. The data below give ΔE for the isodesmic reaction and show that stabilization tends to increase with χ_{BE}, the group electronegativity of the substituent. The X–N=CH$_2$ bond angle decreases with χ_{BE}.

Account for these trends.

$$X\!-\!N\!=\!CH_2 + CH_3CH\!=\!CH_2 \longrightarrow CH_3N\!=\!CH_2 + XCH\!=\!CH_2$$

Discuss these trends in relation to the interaction of the nitrogen unshared pair and the C=N electrons with the substituent.

Substituent	χ_{BE}	ΔE (kcal/mol)	$\angle XN\!=\!CH_2$ (°)
H	2.20	+ 4.1	110
CH_3	2.55	0.0	116
CH=O	2.66	+ 3.6	114
CN	2.69	− 4.8	117
CF_3·	2.71	+ 4.7	118
NO_2	3.22	− 10.0	111
OH	3.55	− 20.5	110
F	4.00	− 29.0	108
SiH_3	1.90	+ 13.2	120