

## CHAPTER 5

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# SIMPLE HÜCKEL MOLECULAR ORBITAL THEORY

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In this chapter, simple Hückel molecular orbital (SHMO) theory is developed. The reference energy,  $\alpha$ , and the energy scale in units of  $\beta$  are introduced.

### SIMPLE HÜCKEL ASSUMPTIONS

The SHMO theory was originally developed to describe planar hydrocarbons with conjugated  $\pi$  bonds. Each center is  $sp^2$  hybridized and has one unhybridized  $p$  orbital perpendicular to the trigonal  $sp^2$  hybrid orbitals. The  $sp^2$  hybrid orbitals form a rigid unpolarizable framework of equal C—C bonds. Hydrogen atoms are part of the framework and are not counted. The Hückel equations (3.3) described in the first part of Chapter 3 apply, namely,

$$F(1) \approx h^{\text{eff}}(1) \quad h^{\text{eff}}(1)\phi_a(1) = \varepsilon_a\phi_a(1) \quad E_{\text{IEA}} = 2 \sum_{a=1}^M \varepsilon_a \quad (5.1)$$

Each MO is expanded in terms of the unhybridized  $p$  orbitals, one per center. The overlap integral between two parallel  $p$  orbitals is small and is approximated to be exactly zero. Thus,

$$\phi(1) = \sum_{A=1}^{N_N} c_A \chi_A(1) \quad \int \chi_A(1)\chi_B(1) d\tau_1 = \delta_{AB} \quad (5.2)$$

where  $N_N$  is the number of carbon atoms which is the same as the number of orbitals. Equation (5.2) is just a generalization of equation (3.4). The subsequent steps are precisely those which were followed in Chapter 3. The energy is expressed as an expectation value of the MO [equation (5.2)] with the effective hamiltonian

$$\begin{aligned}
\varepsilon &= \frac{\int \phi(1) h^{\text{eff}}(1) \phi(1) d\tau_1}{\int |\phi(1)|^2 d\tau_1} \\
&= \frac{\sum_{A=1}^{N_N} \sum_{B=1}^{N_N} c_A c_B \int \chi_A(1) h^{\text{eff}} \chi_B(1) d\tau_1}{\sum_{A=1}^{N_N} \sum_{B=1}^{N_N} c_A c_B \int \chi_A(1) \chi_B(1) d\tau_1} \\
&= \frac{\sum_{A=1}^{N_N} c_A^2 h_{AA} + \sum_{A=1}^{N_N} \sum_{B \neq A}^{N_N} c_A c_B h_{AB}}{\sum_{A=1}^{N_N} c_A^2 + \sum_{A=1}^{N_N} \sum_{B \neq A}^{N_N} c_A c_B S_{AB}} \quad (5.3)
\end{aligned}$$

$$= \frac{\sum_{A=1}^{N_N} [c_A^2 h_{AA} + \sum_{B \neq A}^{N_N} c_A c_B h_{AB}]}{\sum_{A=1}^{N_N} c_A^2} = \frac{\mathcal{N}}{\mathcal{D}} \quad (5.4)$$

and the variational method applied. Differentiating equation (5.4) with respect to each of the coefficients,  $c_A$ ,

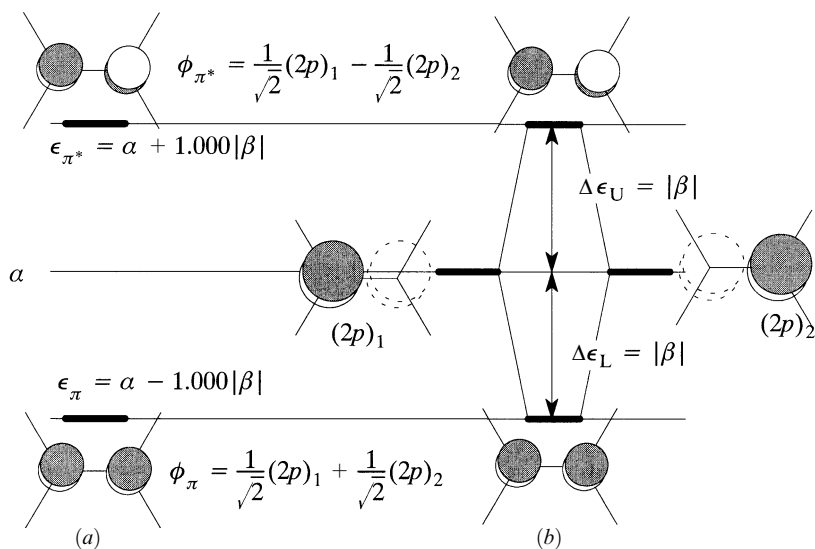
$$\begin{aligned}
\frac{\partial}{\partial c_A} (\mathcal{N} \mathcal{D}^{-1}) &= \frac{\partial \mathcal{N}}{\partial c_A} \mathcal{D}^{-1} - \mathcal{N} \mathcal{D}^{-2} \frac{\partial \mathcal{D}}{\partial c_A} = 0 \\
\frac{\partial \mathcal{N}}{\partial c_A} - \varepsilon \frac{\partial \mathcal{D}}{\partial c_A} &= 0 \\
(h_{AA} - \varepsilon) c_A + \sum_{B \neq A}^{N_N} h_{BA} c_B &= 0 \quad \text{for each } A = \{1, \dots, N_N\} \quad (5.5)
\end{aligned}$$

The condition that the  $N_N$  linear equations have a solution is that the determinant of coefficients (of the  $c$ 's) be equal to zero:

$$\begin{vmatrix}
h_{11} - \varepsilon & h_{12} & h_{13} & \cdots & h_{1N_N} \\
h_{21} & h_{22} - \varepsilon & h_{23} & \cdots & h_{2N_N} \\
h_{31} & h_{32} & h_{33} - \varepsilon & \cdots & h_{3N_N} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
h_{N_N 1} & h_{N_N 2} & h_{N_N 3} & \cdots & h_{N_N N_N} - \varepsilon
\end{vmatrix} = 0 \quad (5.6)$$

Within the SHMO approximations, all of the diagonal hamiltonian matrix elements,  $h_{AA}$ , are equal and are designated  $\alpha$ . The Hückel  $\alpha$  is the energy of an electron in a  $2p$  orbital of a trigonally ( $sp^2$ ) hybridized carbon atom. The off-diagonal matrix elements,  $h_{AB}$ , are all equal if the atoms involved are bonded together (since all bond distances are assumed to be equal) and these are designated  $\beta$ . The Hückel  $\beta$  is the energy of interaction of two  $2p$  orbitals of a trigonally ( $sp^2$ ) hybridized carbon atoms which are attached to each other by a  $\sigma$  bond. If the two atoms are not nearest neighbors, then  $h_{AB}$  is set equal to zero. In summary,

$$\begin{aligned}
h_{AA} &= \alpha \\
h_{AB} &= \beta \quad \text{if centers } A \text{ and } B \text{ are bonded} \\
h_{AB} &= 0 \quad \text{if centers } A \text{ and } B \text{ are not bonded}
\end{aligned}$$

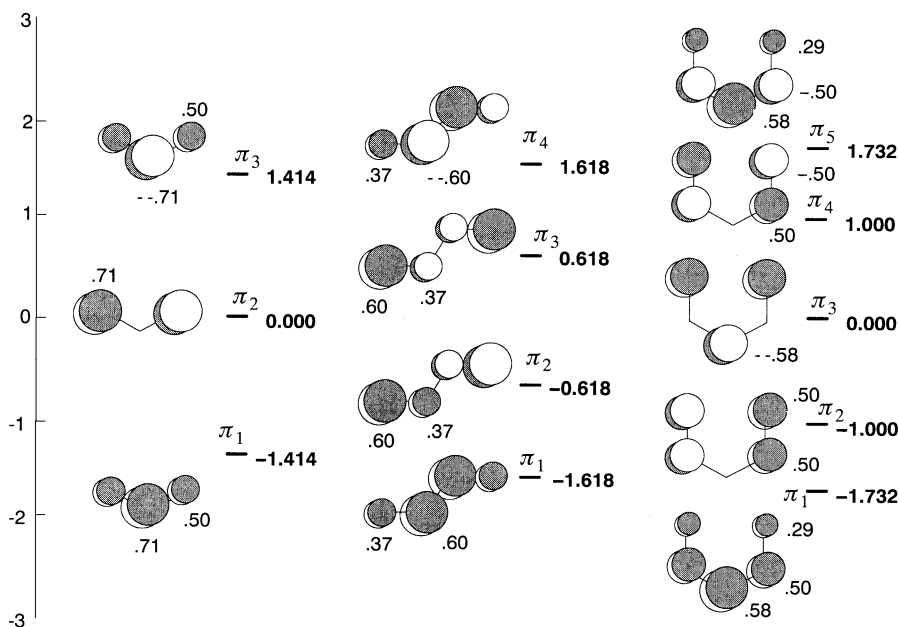


**Figure 5.1.** (a) SHMO results for ethylene. (b) The interaction diagram for ethylene: note that  $\Delta\epsilon_L = \Delta\epsilon_U$  because overlap is assumed to be zero in SHMO theory.

Thus, all of the diagonal elements are  $\alpha - \epsilon$ . The off-diagonal elements are  $\beta$  if the two atoms involved are bonded and zero if they are not. It is usual to divide each row of the determinant by  $\beta$ . This corresponds to a change of energy units and leaves either 1's or 0's in the off-diagonal positions which encode the connectivity of the molecule. The diagonal elements become  $(\alpha - \epsilon)/\beta$ , which is usually represented by  $x$ . While the determinant was expanded in Chapter 3 to yield the secular equation, it is more convenient in general to diagonalize the determinant using a computer. An interactive computer program, SHMO, has been written to accompany this book [102].

The SHMO calculation on ethylene yields the results shown in Figure 5.1a. The  $\pi$  and  $\pi^*$  orbitals are precisely one  $\beta$  unit above and below  $\alpha$ . The SHMO results are presented in Figure 5.1b in the form of an interaction diagram. In this case,  $\Delta\epsilon_L$  and  $\Delta\epsilon_U$  are assigned the same value, namely  $|\beta|$ , in the spirit of SHMO theory, but we know that the effect of proper inclusion of overlap would yield  $\Delta\epsilon_U > \Delta\epsilon_L$ .

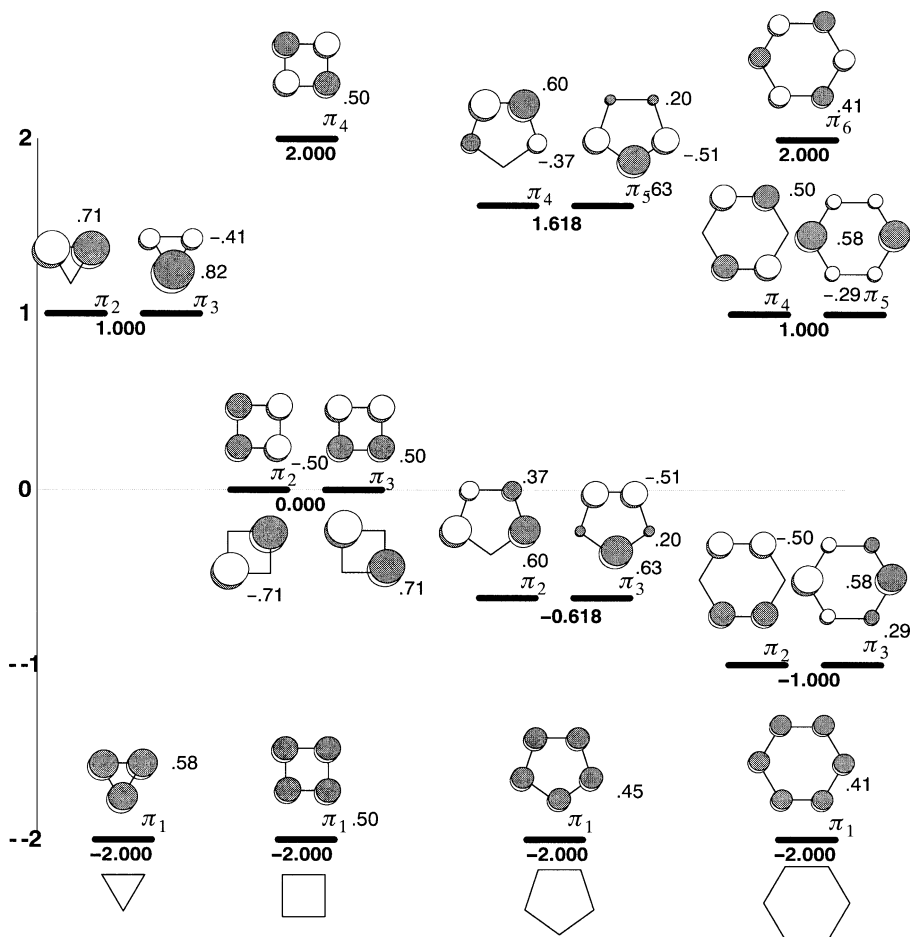
The SHMO results for the series of “linear”  $\pi$  systems allyl, butadiene, and penta-1,3-dienyl are shown in Figure 5.2. The molecular species are portrayed with realistic angles ( $120^\circ$ ) and, in the case of the last two, in a specific conformation. Simple Hückel MO theory does not incorporate any specific geometric information since all non-nearest-neighbor interactions are set equal to zero. As a result, the SHMO results (MO energies and coefficients) are independent of whether the conformation of butadiene is s-trans, as shown in Figure 5.2, or s-cis, as may be required for the Diels–Alder reaction. Likewise the results for the penta-1,3-dienyl system shown in the “U” conformation in Figure 5.2 are identical to the results for the “W” or “sickle” conformations. The MOs are displayed as linear combinations of  $2p$  atomic orbitals seen from the top on each center, with changes of phase designated by shading. The relative contribution of each atomic  $2p$  orbital to the  $\pi$  MO is given by the magnitude of the coefficient of the eigenvector from the solution of the SHMO equations. In the display, the size of the  $2p$  orbital is proportional



**Figure 5.2.** The SHMO orbitals of allyl, butadiene, and pentadienyl. The vertical scale is energy in units of  $|\beta|$ , relative to  $\alpha$ . Coefficients not specified may be obtained by symmetry.

to the *magnitude* of the coefficient. In some MOs, such as  $\pi_2$  of allyl, the node passes through a nucleus and a  $2p$  orbital is not shown because its coefficient is identically zero. The orbitals which are near  $\alpha$  will be of most interest in various applications. In the case of allyl, this orbital,  $\pi_2$ , is LUMO in the allyl cation, SOMO (singly occupied molecular orbital) in the allyl radical, and HOMO in the allyl carbanion. In the pentadienyl system,  $\pi_3$  plays the same role. In butadiene, the HOMO is  $\pi_2$ . Since the energy of the HOMO is higher than the energy of the HOMO of ethylene, one might conclude that butadiene is more basic than ethylene and more reactive toward electrophilic addition. Caution should be exercised in jumping to this conclusion, however, since the largest coefficient of butadiene's HOMO, 0.60, is smaller than the coefficient of the  $2p$  orbital of the HOMO of ethylene, 0.71. The smaller coefficient would imply a weaker intrinsic interaction ( $h_{AB}$ ) with Lewis acids and therefore reduced reactivity. Clearly, the energy factor and the intrinsic interaction (as judged from the coefficients) are in opposition, the first predicting higher reactivity and the second lower. As is often the case in orbital interaction theory, one must resort to experimental observations to evaluate the relative importance of opposed factors. Since, experimentally, dienes *are* more susceptible to electrophilic attack than unconjugated alkenes, we can conclude that the energy factor is more important than the relatively small difference in coefficients.

Simple Hückel MO results for the series of cyclic  $\pi$  systems cyclopropenyl, cyclobutadiene, cyclopentadienyl, and benzene are shown in Figure 5.3. Several points may be noted. The lowest MO in each case has energy identical to  $\alpha - 2|\beta|$ , a result which can be proved to be general for any regular polygon. Each ring has degenerate pairs of MOs as a consequence of the three- or higher-fold axis of symmetry. The orbitals of each



**Figure 5.3.** SHMO orbitals for cyclopropenyl, cyclobutadiene, cyclopentadienyl, and benzene. The energies are in units of  $|\beta|$  relative to  $\alpha$ . Two alternative but equivalent representations are shown for the degenerate  $\pi$  orbitals of cyclobutadiene. Sizes of the  $2p$  orbitals are shown proportional to the magnitudes of the coefficients whose numerical values are given. Coefficients not specified may be obtained by symmetry.

degenerate pair may appear very different. The orientation of the nodal surfaces of the degenerate MOs is entirely arbitrary. Two equivalent orientations are shown for cyclobutadiene. A perturbation at one of the vertices such as by a substituent will rotate the nodes of the degenerate set so that one node passes through that vertex. The orientations shown are those which should be adopted for the purposes of interaction diagrams involving a single substituent on the ring. The pairs of degenerate MOs which form the HOMO of benzene is at exactly the same energy as the HOMO of ethylene. In orbital interaction terms, we would predict that, even though the HOMOs are of the same energy, benzene would be less susceptible to electrophilic attack than ethylene for the reason that the

largest available coefficient, 0.58 in  $\pi_3$ , is smaller than 0.71, the coefficient in the HOMO of ethylene.

Conjugated  $\pi$  systems which do not contain any odd-membered rings are called *alternant*, and provided all the atoms are the same, alternant systems have a symmetrical distribution of orbital energies about the mean ( $\alpha$  for C). The coefficients also repeat in magnitude in MOs which are equidistant from the mean. These features are readily apparent in the orbitals portrayed in Figures 5.1–5.3.

Of the four cyclic conjugated  $\pi$  systems shown in Figure 5.3, only benzene, with six electrons in the  $\pi$  orbitals, is stable kinetically and thermodynamically. Neutral cyclopropenyl and cyclopentadienyl, with three and five  $\pi$  electrons, respectively, are free radicals. The cyclopropenyl cation, with two  $\pi$  electrons, and the cyclopentadienyl anion, with six, have filled shells and constitute aromatic systems in that they exhibit unusual stability, compared to other carbocations and carbanions, respectively. Cyclobutadiene is a special case. With two electrons in the degenerate HOMOs, one would expect that the electrons would separate and that the ground state would be a triplet. However, a distortion of the geometry from square to rectangular would eliminate the degeneracy and permit a singlet ground state. The ground state of cyclobutadiene has been shown experimentally to be singlet with a barrier for the rectangular-to-square deformation in the range  $7 \leq \Delta H^\ddagger \leq 42$  kJ/mol [103]. Theoretical computations suggest that the higher value may be correct [104].

### CHARGE AND BOND ORDER IN SHMO THEORY: ( $S_{AB} = 0$ , ONE ORBITAL PER ATOM)

It is of interest to enquire how the electrons are redistributed during an interaction and how a bond is affected. We use a simplified Mulliken population analysis [see Appendix A, equations (A.77)–(A.79)]. The simplification consists of dropping all terms involving the overlap of atomic orbitals and assuming that, in any given MO, there is only *one* atomic orbital on any given center). Thus, we may assume that the following relations hold:

$$\phi_a = \sum_{A=1}^n \chi_A c_{Aa} \quad S_{AB} = \delta_{AB} \quad \sum_{A=1}^n c_{Aa}^2 = 1 \quad (5.7)$$

where  $n$  is the number of atomic orbitals (which equals the number of nuclear centers, since there is one orbital per center). A measure of the *electron population* on each center is easily obtained as below.

#### Electron Population and Net Charge of Center A

The electron population of center A is defined as

$$P_A = \sum_{a=1}^n n_a c_{Aa}^2 \quad (5.8)$$

where  $n_a$  ( $= 0, 1, 2$ ) is the number of electrons in the  $a$ th MO and the sum runs over the MOs (there are as many MOs as there are AOs and atomic centers). The *net charge* of

center A,  $C_A$ , depends on the number of electrons,  $n_A$ , which are required for a neutral atomic center A. Thus

$$C_A = n_A - P_A \quad (5.9)$$

Notice that  $C_A$  is negative if the population of A,  $P_A$ , exceeds the number of electrons required to give a neutral center. It is easily verified that

$$\sum_{A=1}^n P_A = N_e \quad \sum_{A=1}^n C_A = \text{net charge on molecule} \quad (5.10)$$

*Exercise 3.1.* Verify equations (5.10).

*Exercise 3.2.* Verify that the net charge at each carbon atom of each of the *neutral* ring systems shown in Figure 5.3 is zero (to two significant figures).

### Bond Order between Centers A and B

Strictly speaking, there should be no electron population between pairs of atoms in SHMO since orbitals are assumed not to overlap. However, it is conventional to set all overlap integrals to unity for the purpose of defining a “bond order.” The *bond order*,  $B_{AB}$ , between centers A and B is defined as

$$B_{AB} = \sum_{a=1}^n n_a c_{Aa} c_{Ba} \quad (5.11)$$

where the quantities are defined as above. A positive value indicates bonding. Small negative values of  $B_{AB}$  may result. These are indications of *antibonding* or *repulsive* interaction between the centers concerned.

*Exercise 3.3.* Show that the maximum value for the bond order due to a single bond is 1 and that it occurs when  $n_a = 2$  and  $c_A = c_B = 1/\sqrt{2}$ .

*Exercise 3.4.* Show that the bond order for benzene is 0.67 from the data in Figure 5.3.

## FACTORS GOVERNING ENERGIES OF MOs: SHMO THEORY

### Reference Energy and Energy Scale

Most organic molecules are made up of the elements C, H, N, and O, with lesser amounts of S, P, and X (Cl, Br, I). Molecular orbitals are built up by the interaction of the atomic orbitals of these elements held together at bonding separations. It is convenient at this point to adopt an energy scale derived from SHMO theory, in which the “Coulomb integral”  $\alpha$  ( $=\alpha_C$ ) is the reference point on the energy scale,

$$\alpha = \alpha_C = \int [2p_C(1)] h^{\text{eff}}(1) [2p_C(1)] d\tau_1 \quad (5.12)$$

and the absolute value of the “resonance integral”  $|\beta|$  ( $=|\beta_{CC}|$ ) is the unit of energy,

$$\beta = \beta_{CC} = \int [2p_C(1)]_A h^{\text{eff}}(1) [2p_C(1)]_B d\tau_1 \quad (5.13)$$

Thus,  $\alpha$  ( $=\alpha_C$ ) is the core energy of an electron localized to the  $2p$  atomic orbital of a carbon atom, and  $\beta$  ( $=\beta_{CC}$ ) is the energy associated with the interaction of two carbon  $2p$  orbitals overlapping in a  $\pi$  (parallel) fashion at the C—C separation of benzene (or ethylene).

## HETEROATOMS IN SHMO THEORY

In SHMO, the core energies of heteroatoms, X, are specified in terms of  $\alpha$  and  $\beta$ , and the interaction matrix elements for  $p$  orbitals overlapping in a  $\pi$  fashion on any pair of atoms, X and Y, are specified in terms of  $\beta$ . Thus,

$$\alpha_X = \alpha + h_X |\beta| \quad (5.14)$$

$$\beta_{XY} = k_{XY} |\beta| \quad (5.15)$$

In SHMO theory the energy of  $\pi$  bond formation in ethylene is  $2\beta$  (since the strength of a C—C  $\pi$  bond is about 280 kJ/mol, one may consider  $|\beta|$  to be about 140 kJ/mol). The energies of electrons in  $2p$  orbitals of N and O, normally found in  $\pi$  bonding environments (i.e., as *dicoordinated* N and *monocoordinated* O) are given by  $h_{N2} = -0.51$  and  $h_{O1} = -0.98$ . These are suitable values for a pyridine N and a carbonyl O. The  $\pi$ -type interaction matrix elements of most pairs, except those involving F, are approximately given by  $k_{XY} = -1$ . The energies of electrons in  $2p$  orbitals of N and O in normal (saturated) bonding environments (i.e., as *tricoordinated* N and *dicoordinated* O) are given by  $h_{N3} = -1.37$  and  $h_{O2} = -2.05$ . Thus a tricoordinated N is more electronegative than a dicoordinated N, and similarly for dicoordinated versus monocoordinated O. The  $\pi$ -type interaction matrix elements of these kinds of orbitals with the normal C  $2p$  orbitals are approximately given by  $k_{CN} = -0.8$  and  $k_{CO} = -0.67$ , reflecting the smaller size of the orbitals. The value for the C—F interaction,  $k_{CF} = -0.5$ , is small for the same reasons. The change in effective electronegativity of the  $2p$  orbitals is a consequence of the increase in the number of atoms to which they are coordinated (see below), although in usual SHMO usage, the distinction is made in terms of the number of electrons which the atom contributes to the  $\pi$  system. A more complete list of  $h_X$  and  $k_{XY}$  parameters, derived on the basis of Pariser-Parr-Pople (PPP) calculations by Van Catledge [105], is given in Table 5.1.

### Effect of Coordination Number on $\alpha$ and $\beta$

A decrease in the coordination number at N from three to two reduces the effective electronegativity of the remaining nonbonded  $p$  orbitals at the center. The change in  $h_N$  is  $0.86|\beta|$ . A decrease in the coordination number at O from 2 to 1 similarly reduces the effective electronegativity of the remaining nonbonded  $p$  orbitals at the O center. The change in  $h_O$  is larger,  $1.12|\beta|$ . Within the same molecule, the coordination number of N or O may readily be changed by the process of protonation or deprotonation, as



TABLE 5.1. SHMO Values for Heteroatoms:  $a_X = a + h_X|\beta|$ ,  $\beta_{XY} = k_{XY}|\beta|^a$ 

X	Number of Electrons	$h_X$	$k_{XY}$ by Y Atoms																		
			C <sup>b</sup>	B <sup>b</sup>	N2 <sup>c</sup>	N3 <sup>b</sup>	O1 <sup>d</sup>	O2 <sup>c</sup>	F <sup>d</sup>	Si <sup>b</sup>	P2 <sup>c</sup>	P3 <sup>b</sup>	SI <sup>d</sup>	S2 <sup>c</sup>	Cl <sup>d</sup>						
C <sup>b</sup>	1	0.00	-1.00																		
B <sup>b</sup>	0	0.45	-0.73	-0.87																	
N2 <sup>c</sup>	1	-0.51	-1.02	-0.66	-1.09																
N3 <sup>b</sup>	2	-1.37	-0.89	-0.53	-0.99	-0.98															
O1 <sup>d</sup>	1	-0.97	-1.06	-0.60	-1.14	-1.13	-1.26														
O2 <sup>c</sup>	2	-2.09	-0.66	-0.35	-0.80	-0.89	-1.02	-0.95													
F <sup>d</sup>	2	-2.71	-0.52	-0.26	-0.65	-0.77	-0.92	-0.94	-1.04												
Si <sup>b</sup>	1	0.00	-0.75	-0.57	-0.72	-0.43	-0.65	-0.24	-0.17	-0.64											
P2 <sup>c</sup>	1	-0.19	-0.77	-0.53	-0.78	-0.55	-0.75	-0.31	-0.21	-0.62	-0.63										
P3 <sup>b</sup>	2	-0.75	-0.76	-0.54	-0.81	-0.64	-0.82	-0.39	-0.22	-0.52	-0.58	-0.63									
SI <sup>d</sup>	1	-0.46	-0.81	-0.51	-0.83	-0.68	-0.84	-0.43	-0.28	-0.61	-0.65	-0.65	-0.68								
S2 <sup>c</sup>	2	-1.11	-0.69	-0.44	-0.78	-0.73	-0.85	-0.54	-0.32	-0.40	-0.48	-0.60	-0.58	-0.63							
Cl <sup>d</sup>	2	-1.48	-0.62	-0.41	-0.77	-0.80	-0.88	-0.70	-0.51	-0.34	-0.35	-0.55	-0.52	-0.59	-0.68						

<sup>a</sup>Ref. 105.<sup>b</sup>Ttricoordinated, planar geometry.<sup>c</sup>Dicoordinated.<sup>d</sup>Monocoordinated.

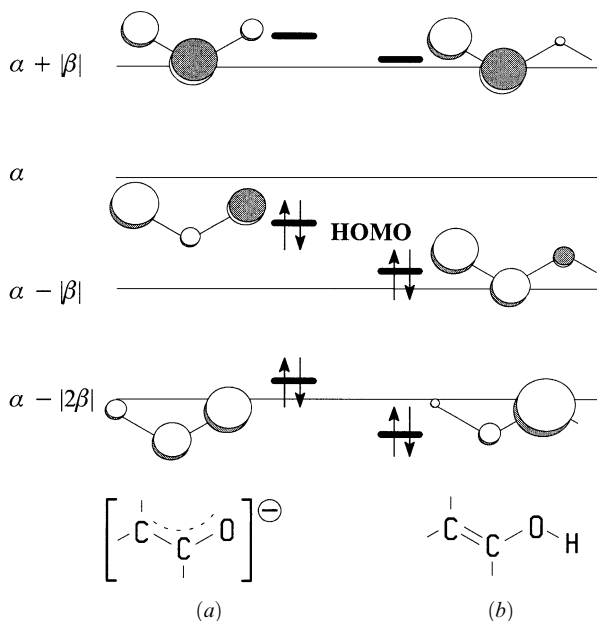


Figure 5.4. SHMO results for enolate (a, using O1 parameters) and enol (b, with O2 parameters).

a consequence of a change of pH, for instance. The results of SHMO calculations on the enolate anion and on enol are shown in Figure 5.4. In the enolate case,  $h_{O1} = -0.97$ ,  $k_{CO} = -1.06$ , while for enol, the values  $h_{O2} = -2.09$ ,  $k_{CO} = -0.66$  were used according to Table 5.1. The contributions of the individual  $2p$  orbitals of C and O are displayed with sizes proportional to the magnitudes of the coefficients. The effect of the protonation can be seen as a lowering of the energy and changed polarization of all of the MOs, including the HOMO.

Normally, no distinction is made between the kind of atom or group which is coordinated to the center of interest, but this may be a gross oversimplification in extreme cases. It is not reasonable to expect that the  $2p$  orbital of a methyl group will have approximately the same energy as the  $2p$  orbital of a trifluoromethyl group (assuming it were planar). Because of the strong inductive effect of the electronegative fluorine atoms acting in the  $\sigma$  framework, the carbon atom of trifluoromethyl would be significantly denuded of electrons. The  $2p$  orbital is in effect more electronegative and falls below  $\alpha$ .

Can one deduce reasonable values for the effective electronegativity of the  $p$  orbitals of C upon reduction of the coordination number from 3 to 2 (i.e., C2), as in alkynes, allenes, nitriles (R—CN), or carbenes, or even to 1, as in CO, isonitriles (R—NC), or acetylides? A linear extrapolation from dicoordinated O ( $\alpha_{O2} = \alpha - 2.09|\beta|$ ) and dicoordinated N ( $\alpha_{N2} = \alpha - 0.51|\beta|$ ) to dicoordinated C yields an estimate of the energy of the  $2p$  orbital as  $\alpha + 0.86|\beta|$ . This value is probably too high. It places the energy of the  $2p$  orbital of a dicoordinated carbon above that of the  $2p$  of a tricoordinated boron, but the same is not true in the case of a dicoordinated N and a tricoordinated C, and the

electronegativity differences in the series B, N, C (Table 5.1) are very similar. A reasonable compromise is to place  $\alpha_{C2}$  midway between  $\alpha_B$  and  $\alpha_C$ ,

$$\alpha_{C2} = \alpha + 0.23|\beta| \quad (5.16)$$

### Hybridization at C in Terms of $\alpha$ and $\beta$

The  $2s$  to  $2p$  promotion energy of atomic C is about 800 kJ/mol. In a molecular environment, this value is expected to be somewhat less where the presence of other nuclei may stabilize  $p$  orbitals relative to  $s$ . The coordination number of the carbon atom has a direct effect on the orbital energies, just as it had on the energies of heteroatom orbitals discussed in the previous section. Mullay has estimated the group electronegativities of  $\text{CH}_3$ ,  $\text{CHCH}_2$ , and  $\text{CCH}$  to be 2.32, 2.56, and 3.10, respectively [106]. The last value is similar to his estimate for  $\text{NH}_2$ . Boyd and Edgcombe have placed all three values near 2.6 [107]. Reed and Allen, using their bond polarity index, have assigned values of 0.000, 0.027, and 0.050, respectively (compared to H  $-0.032$  and F 0.189) [108]. Without attempting to be too quantitative, convenient values of the core energies of “hybrid” atomic orbitals, in  $|\beta|$  units, recognizing that changes in coordination number also occur, are approximately

$$\alpha_{sp} = \alpha - 0.50|\beta| \quad (\text{coordination number 1}) \quad (5.17)$$

$$\alpha_{sp^2} = \alpha - 0.33|\beta| \quad (\text{coordination number 2}) \quad (5.18)$$

$$\alpha_{sp^3} = \alpha - 0.25|\beta| \quad (\text{coordination number 3}) \quad (5.19)$$

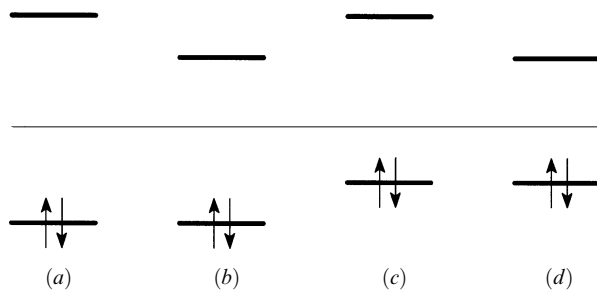
The interaction energies of the pairs of hybridized orbitals interacting in a  $\sigma$  fashion would be strongly distance dependent. At typical single-bond distances, one may adopt  $k_\sigma = 1.5k_\pi|\beta|$  for all of them, but the value rises steeply as the separation is decreased. When the separation is that of a double bond, a value of  $k_\sigma = -2.0k_\pi|\beta|$  is more appropriate. These values are suggested only to help place  $\sigma$  bonds or  $\sigma^*$  orbitals more or less correctly relative to  $\pi$  bonds and  $\pi^*$  orbitals when both may have similar energies.

### GROSS CLASSIFICATION OF MOLECULES ON THE BASIS OF MO ENERGIES

Frontier orbital energy is not the only criterion which governs the chemical characteristics of a compound. For example, the magnitudes of the atomic orbital coefficients on any given atom may be responsible for the reduced basicity of benzene relative to ethylene, both of which have the same HOMO energy. Nevertheless, the energy criterion may be applied to deduce gross features. In Figure 5.5 are shown four extreme cases into which molecules can be categorized on the basis of their frontier orbital energies. Compounds which have a large HOMO–LUMO gap ( $>1.5|\beta|$ ) will be stable against self-reaction, for example, dimerization, polymerization, and intramolecular rearrangements. If the HOMO is low in an absolute sense ( $<\alpha - 1|\beta|$ , the HOMO of ethylene), the compound will be chemically resistant to reaction with Lewis acids. If the LUMO is high in an absolute sense ( $>\alpha + 1|\beta|$ , the LUMO of ethylene), the compound will be chemically resistant to reaction with Lewis bases:

- Compounds with a high LUMO and a low HOMO (Figure 5.5a) will be chemically inert. Saturated hydrocarbons, fluorocarbons, and to some extent ethers fall in this category.

- Compounds with a low HOMO and LUMO (Figure 5.5*b*) tend to be stable to self-reaction but are chemically reactive as Lewis acids and electrophiles. The lower the LUMO, the more reactive. Carbocations, with LUMO near  $\alpha$ , are the most powerful acids and electrophiles, followed by boranes and some metal cations. Where the LUMO is the  $\sigma^*$  of an H—X bond, the compound will be a Lowry–Bronsted acid (proton donor). A Lowry–Bronsted acid is a special case of a Lewis acid. Where the LUMO is the  $\sigma^*$  of a C—X bond, the compound will tend to be subject to nucleophilic substitution. Alkyl halides and other carbon compounds with “good leaving groups” are examples of this group. Where the LUMO is the  $\pi^*$  of a C=X bond, the compound will tend to be subject to nucleophilic addition. Carbonyls, imines, and nitriles exemplify this group.
- Compounds with a high HOMO and LUMO (Figure 5.5*c*) tend to be stable to self-reaction but are chemically reactive as Lewis bases and nucleophiles. The higher the HOMO, the more reactive. Carbanions, with HOMO near  $\alpha$ , are the most powerful bases and nucleophiles, followed by amides and alkoxides. The neutral nitrogen (amines, heteroaromatics) and oxygen bases (water, alcohols, ethers, and carbonyls) will only react with relatively strong Lewis acids. Extensive tabulations of gas-phase basicities or *proton affinities* (i.e.,  $-\Delta G^\circ$  of protonation) exist [109, 110]. These will be discussed in subsequent chapters.
- Compounds with a narrow HOMO–LUMO gap (Figure 5.5*d*) are kinetically reactive and subject to dimerization (e.g., cyclopentadiene) or reaction with Lewis acids or bases. Polyenes are the dominant *organic* examples of this group. The difficulty in isolation of cyclobutadiene lies not with any intrinsic instability of the molecule but with the self-reactivity which arises from an extremely narrow HOMO–LUMO gap. A second class of compounds also falls in this category, coordinatively unsaturated transition metal complexes. In transition metals, the atomic  $n d$  orbital set may be partially occupied and/or nearly degenerate with the partially occupied  $n + 1 sp^n$  set. Such a configuration permits exceptional reactivity, even toward C—H and C—C bonds. These systems are treated separately in Chapter 13.



**Figure 5.5.** (a) High LUMO, low HOMO, large HOMO–LUMO gap; thermodynamically stable and chemically inert. (b) Low LUMO, low HOMO, large HOMO–LUMO gap; thermodynamically stable and chemically reactive as Lewis acid. (c) High LUMO, high HOMO, large HOMO–LUMO gap; thermodynamically stable and chemically reactive as Lewis base. (d) Low LUMO, high HOMO, small HOMO–LUMO gap; may be thermodynamically stable but chemically amphoteric and self-reactive.