

# The Extended Hückel Method

## 10-1 The Extended Hückel Method

The extended Hückel (EH) method is much like the simple Hückel method in many of its assumptions and limitations. However, it is of more general applicability since it takes account of all valence electrons,  $\sigma$  and  $\pi$ , and it is of more recent vintage because it can only be carried out on a practical basis with the aid of a computer. The basic methods of extended Hückel calculations have been proposed at several times by various people. We will describe the method of Hoffmann [1], which, because of its systematic development and application, is the EHMO method in common use.

The method is described most easily by reference to an example. We will use methane ( $\text{CH}_4$ ) for this purpose.

### 10-1.A Selecting Nuclear Coordinates

The first choice we must make is the molecular geometry to be used. For methane, we will take the H–C–H angles to be tetrahedral and C–H bond distances of 1.1 Å. We can try altering these dimensions later.

Cartesian coordinates for the five atoms are listed in Table 10-1, and the orientation of the nuclei in Cartesian space is indicated in Fig. 10-1. (Even though the eigenvalues and MOs one finally obtains are independent of how  $\text{CH}_4$  is oriented in Cartesian space,<sup>1</sup> it is generally a good idea to choose an orientation that causes some Cartesian and symmetry axes to coincide. The resulting expressions for MOs in terms of AOs are generally much simpler to sketch and interpret.)

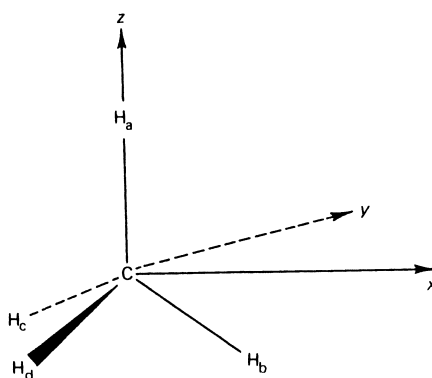
### 10-1.B The Basis Set

Next we must select the basis set of functions with which to express the MOs. The extended Hückel method uses the normalized valence AOs for this purpose. For  $\text{CH}_4$ , this means a 1s AO on each hydrogen and a 2s,  $2p_x$ ,  $2p_y$ , and  $2p_z$  AO on carbon. The inner-shell 1s AO on carbon is not included. The AOs are represented by Slater-type orbitals (STOs). Except for the 1s AOs on hydrogen, the exponential parameters of the STOs are determined from Slater's rules (Chapter 5). Various values for the hydrogen 1s AO exponent have been suggested. These have ranged from the 1.0 given by Slater's

<sup>1</sup>It sometimes happens that an approximation is made that causes the solution to depend on orientation. This is called "loss of rotational invariance."

**TABLE 10-1** ► Cartesian Coordinates (in Angstroms) for Atoms of Methane Oriented as Shown in Fig. 10-1

Atom	$x$	$y$	$z$
C	0.0	0.0	0.0
H <sub>a</sub>	0.0	0.0	1.1
H <sub>b</sub>	1.03709	0.0	-0.366667
H <sub>c</sub>	-0.518545	0.898146	-0.366667
H <sub>d</sub>	-0.518545	-0.898146	-0.366667

**Figure 10-1** ► Orientation of methane in a Cartesian axis system.

rules to a value of  $\sqrt{2}$ . We will use a value of 1.2, which is near the optimal value for H<sub>2</sub> (see Chapter 7). The STOs for methane are listed in Table 10-2.

### 10-1.C The Overlap Matrix

Knowing the AO functions and their relative positions enables us to calculate all of their overlaps. This would be a tedious process with pencil and paper. However, the formulas have been programmed for automatic computation, so this step is included in any EH computer program.<sup>2</sup> The computed overlap matrix for the methane molecule is shown in Table 10-3.

This matrix is symmetric (since the overlap between two AOs is independent of their numbering order) and has diagonal elements of unity since the AOs are normalized. The zero values in the first four rows and columns reflect the orthogonality between the s and all p AOs on carbon. Other zero values result when hydrogen 1s AOs are centered in nodal planes of carbon p AOs. The geometry of the system is clearly reflected in the overlap matrix. For instance, the overlap of the 2p<sub>z</sub> AO of carbon with the hydrogen 1s AO at H<sub>a</sub> is large and positive, while its overlaps with AOs on H<sub>b</sub>, H<sub>c</sub>, and H<sub>d</sub> are negative, equal, and of smaller magnitude. The 2s AO of carbon, on the other hand, overlaps all 1s AOs equally. Also, the overlap between every pair of hydrogen 1s AOs

<sup>2</sup>Several such programs are available from Quantum Chemistry Program Exchange, Chemistry Dept., Room 204, Indiana University, Bloomington, Indiana 47401. <http://www.QCPE.Indiana.edu>

**TABLE 10-2** ► Basis AOs for Methane

AO no.	Atom	Type	$n^a$	$l^a$	$m^a$	exp
1	C	2s	2	0	0	1.625
2	C	2p <sub>z</sub>	2	1	0	1.625
3	C	2p <sub>x</sub>	2	1	(1) <sup>b</sup>	1.625
4	C	2p <sub>y</sub>	2	1	(1) <sup>b</sup>	1.625
5	H <sub>a</sub>	1s	1	0	0	1.200
6	H <sub>b</sub>	1s	1	0	0	1.200
7	H <sub>c</sub>	1s	1	0	0	1.200
8	H <sub>d</sub>	1s	1	0	0	1.200

<sup>a</sup> $n, l, m$  are the quantum numbers described in Chapter 4.

<sup>b</sup>2p<sub>x</sub> and 2p<sub>y</sub> are formed from linear combinations of  $m = +1$  and  $m = -1$  STOs, and neither of these AOs can be associated with a particular value of  $m$ .

**TABLE 10-3** ► Overlap Matrix for STOs of Table 10-2

	1	2	3	4	5	6	7	8
1	1.0000	0.0	0.0	0.0	0.5133	0.5133	0.5133	0.5133
2	0.0	1.0000	0.0	0.0	0.4855	-0.1618	-0.1618	-0.1618
3	0.0	0.0	1.0000	0.0	0.0	0.4577	-0.2289	-0.2289
4	0.0	0.0	0.0	1.0000	0.0	0.0	0.3964	-0.3964
5	0.5133	0.4855	0.0	0.0	1.0000	0.1805	0.1805	0.1805
6	0.5133	-0.1618	0.4577	0.0	0.1805	1.0000	0.1805	0.1805
7	0.5133	-0.1618	-0.2289	0.3964	0.1805	0.1805	1.0000	0.1805
8	0.5133	-0.1618	-0.2289	-0.3964	0.1805	0.1805	0.1805	1.000

is the same. Features such as these provide a useful check on the correctness of our initial Cartesian coordinates.

### 10-1.D The Hamiltonian Matrix

We have the overlap matrix **S**. Next we must find the hamiltonian matrix **H**. Then we will be in a position to solve the equation  $\mathbf{HC} = \mathbf{SCE}$  for **C** and **E**. (See Chapter 9.) The matrix **H** is calculated from a very approximate but simple recipe. The basic ideas are similar in spirit to those described in connection with the interpretations of  $\alpha$  and  $\beta$  in the simple Hückel method. The energy integral  $H_{ii}$  in the EH method is taken to be equal to the energy of an electron in the  $i$ th AO of the isolated atom in the appropriate state. The various ionization energies of atoms are known,<sup>3</sup> so this presents no great difficulty. However, one special problem must be dealt with, namely, finding the

<sup>3</sup>See Moore [2].

appropriate state. In the isolated carbon atom, the lowest-energy states are associated with the configuration  $1s^2 2s^2 2p^2$ . In a saturated molecule such as methane, however, carbon shares electrons with four hydrogens, and calculations indicate that the 2s and all three 2p AOs are about equally involved in forming occupied MOs. That is, in the molecule, carbon behaves as though it were in the  $2s 2p^3$  configuration. This configuration (shortened to  $sp^3$ ) is referred to as the *valence state* of carbon in this molecule. Since this is an “open-shell” configuration (i.e., not all the electrons are spin-paired in filled orbitals), there are several actual physical states (corresponding to different spin and orbital angular momenta of an isolated carbon atom) that are associated with this configuration. Thus, there are several real physical states, with different ionization energies, associated with our mentally constructed  $sp^3$  valence state for the atom in a molecule. The question is, what real ionization energies should we use to evaluate our valence state ionization energy (VSIE)? The approach that is used is simply to *average* the real IEs for loss of a 2p or a 2s electron, the average being taken over all states associated with the  $sp^3$  configuration. Various authors recommend slightly different sets of VSIEs.<sup>4</sup> We use here the values tabulated by Pople and Segal [7]. Because of the rather crude nature of the EH method, the slight variations in VSIE resulting from different choices are of little consequence.<sup>5</sup> For methane, we have

$$(C_{2s}): H_{11} = -19.44 \text{ eV} = -0.7144 \text{ a.u.} \quad (10-1)$$

$$(C_{2p}): H_{22} = H_{33} = H_{44} = -10.67 \text{ eV} = -0.3921 \text{ a.u.} \quad (10-2)$$

$$(H_{1s}): H_{55} = H_{66} = H_{77} = H_{88} = -13.60 \text{ eV} = -0.50000 \text{ a.u.} \quad (10-3)$$

The off-diagonal elements of  $H$  are evaluated according to<sup>6</sup>

$$H_{ij} = K S_{ij} \left( \frac{H_{ii} + H_{jj}}{2} \right) \quad (10-4)$$

where  $K$  is an adjustable parameter. The rationalization for such an expression is that the energy of interaction should be greater when the overlap between AOs is greater, and that an overlap interaction energy between low-energy AOs should be lower than that produced by an equal amount of overlap between higher-energy AOs. We will discuss the energy *versus* overlap relation in more detail in a later section. The value of  $K$  suggested by Hoffmann [1] is 1.75. The reasons for choosing this value will be discussed shortly. For now, we accept this value and arrive at the hamiltonian matrix given in Table 10-4.

By examining  $H$  we can guess in advance some of the qualitative features of the MOs that will be produced. For instance, the value of  $H_{25}$  ( $-0.3790$  a.u.) indicates a strong energy-lowering interaction between the  $2p_z$  AO and the  $1s$  AO on  $H_a$ . This interaction refers to AOs with positive and negative lobes *as they are assigned in the basis set*. Therefore, we expect a low-energy (bonding) MO to occur where these AOs are mixed with coefficients of the same sign so as not to affect this AO sign relation. A high-energy MO should also exist where the mixing occurs through coefficients of opposite sign, producing an antibonding interaction. The values of  $H_{26}$ ,  $H_{27}$ , and  $H_{28}$  are positive,

<sup>4</sup>See Skinner and Pritchard [3], Hinze and Jaffé [4], Basch et al. [5], Anno [6], and Pople and Segal [7].

<sup>5</sup>The proper valence state for carbon in methane differs from that in ethylene, which in turn differs from that in acetylene. Generally, this is ignored in EHMO calculations and a compromise set of VSIEs is selected for use over the whole range of molecules.

<sup>6</sup>This formula is often called the Wolfsberg–Helmholtz relation.

**TABLE 10-4** ► The Extended Hückel Hamiltonian Matrix for CH<sub>4</sub><sup>a</sup>

	1	2	3	4	5	6	7	8
1	-0.7144	0.0	0.0	0.0	-0.5454	-0.5454	-0.5454	-0.5454
2	0.0	-0.3921	0.0	0.0	-0.3790	0.1263	0.1263	0.1263
3	0.0	0.0	-0.3921	0.0	0.0	-0.3573	0.1787	0.1787
4	0.0	0.0	0.0	-0.3921	0.0	0.0	-0.3094	0.3094
5	-0.5454	-0.3790	0.0	0.0	-0.5000	-0.1579	-0.1579	-0.1579
6	-0.5454	0.1263	-0.3573	0.0	-0.1579	-0.5000	-0.1579	-0.1579
7	-0.5454	0.1263	0.1787	-0.3094	-0.1579	-0.1579	-0.5000	-0.1579
8	-0.5454	0.1263	0.1787	0.3094	-0.1579	-0.1579	-0.1579	-0.5000

<sup>a</sup>All energies in a.u.

due to negative overlap in corresponding positions of **S**. In this case, energy lowering will be associated with mixing  $2p_z$  with  $1s$  AOs on hydrogens *b*, *c*, and *d*, *but now the mixing coefficients will have signs that reverse the AO sign relations from those pertaining in the original basis*. The AOs that are orthogonal have zero interaction, and so mixing between such AOs will not affect MO energies. (When such AOs are mixed in the same MO, it is often the result of arbitrary mixing between degenerate MOs. In such cases, one can find an orthogonal pair of MOs such that two noninteracting AOs do not appear in the same MO. Methane will be seen to provide an example of this.)

### 10-1.E The Eigenvalues and Eigenvectors

Having **H** and **S**, we now can use the appropriate matrix-handling programs to solve  $\mathbf{HC} = \mathbf{SCE}$  for the matrix eigenvalues on the diagonal of **E** and the coefficients for the MOs, which are given by the columns of **C**. The eigenvalues for methane, together with their occupation numbers, are given in Table 10-5. The corresponding coefficients are given in Table 10-6.

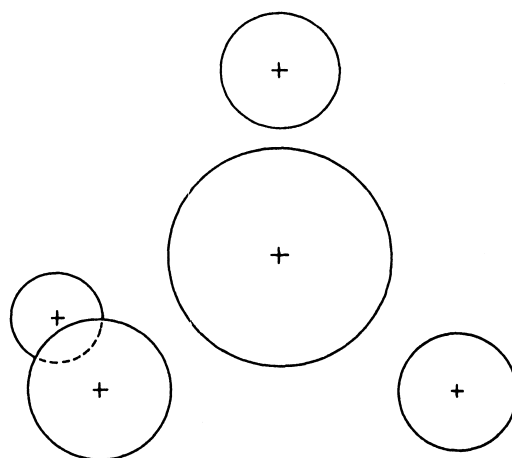
**TABLE 10-5** ► Energies for Methane by the Extended Hückel Method

MO no.	Energy (a.u.)	Occ. no.
8	1.1904	0
7	0.2068	0
6	0.2068	0
5	0.2068	0
4	-0.5487	2
3	-0.5487	2
2	-0.5487	2
1	-0.8519	2

**TABLE 10-6** ► Coefficients Defining MOs for Methane

	MO number							
	1	2	3	4	5	6	7	8
1(2s)	0.5842	0.0	0.0	0.0	0.0	0.0	0.0	1.6795
2(2p <sub>z</sub> )	0.0	0.5313	-0.0021	-0.0007	-0.0112	-0.0137	1.1573	0.0
3(2p <sub>x</sub> )	0.0	0.0021	0.5313	-0.0021	1.1573	-0.0178	0.0110	0.0
4(2p <sub>y</sub> )	0.0	0.0007	0.0021	0.5313	0.0176	1.1572	0.0139	0.0
5(1s <sub>a</sub> )	0.1858	0.5547	-0.0022	-0.0007	0.0105	0.0128	-1.0846	-0.6916
6(1s <sub>b</sub> )	0.1858	-0.1828	0.5237	-0.0019	-1.0260	0.0114	0.3518	-0.6916
7(1s <sub>c</sub> )	0.1858	-0.1853	-0.2589	0.4542	0.4943	-0.8977	0.3558	-0.6916
8(1s <sub>d</sub> )	0.1858	-0.1865	-0.2626	-0.4516	0.5213	0.8734	0.3770	-0.6916

Only two of the eight MOs are nondegenerate. These two MOs must be symmetric or antisymmetric for every symmetry operation of the molecule. This is easily checked by sketching the MOs, referring to the coefficients in the appropriate columns of Table 10-6. The lowest nondegenerate energy occurs in position 1 of our eigenvalue list (Table 10-5), and so the coefficients for this MO are to be found in column 1 of Table 10-6. This column indicates that the MO  $\phi_1$  is equal to  $0.5842 2s + 0.1858 1s_a + 0.1858 1s_b + 0.1858 1s_c + 0.1858 1s_d$ , where the symbols 2s, 1s<sub>a</sub>, etc., stand for AOs on carbon, H<sub>a</sub>, etc. A sketch of this MO appears in Fig. 10-2. It is obviously symmetric for all rotations and reflections of a tetrahedron. Notice that this MO is bonding in all four C–H bond regions since the 2s STO on carbon is in phase agreement with all the hydrogen 1s AOs. The higher-energy, nondegenerate MO  $\phi_8$  is qualitatively similar to  $\phi_1$  except that the signs are reversed on the 1s AOs (see Table 10-6). Hence, this MO has the same symmetry properties as  $\phi_1$ , but is antibonding in the C–H regions.



**Figure 10-2** ► A drawing of the lowest-energy nondegenerate EHMO for methane. The AOs are drawn as though they do not overlap. This is done only to make the drawing simpler. Actually, the AOs overlap strongly.

Since these two MOs resemble the 2s STO in being symmetric for all the symmetry operations of a tetrahedron, we will refer to them as s-type MOs.

The remaining six MOs are grouped into two energy levels, each level being triply degenerate. (It is possible to predict from symmetry considerations alone that the energy levels resulting from this calculation will be nondegenerate and triply degenerate. This is discussed in a later chapter.) Because they are degenerate, the MOs cannot be expected to show *all* the symmetry of the molecule, but it should be possible for them to show *some* symmetry. Consider  $\phi_2$ , as given by column 2 of Table 10-6. This is mainly constructed from the  $2p_z$  AO on carbon and 1s AOs on the four hydrogens. Small contributions from  $2p_x$  and  $2p_y$  are also present, however. It would be nice to remove these small contributions and “clean up” the MO. We can do this, as mentioned earlier, by mixing  $\phi_2$  with appropriate amounts of  $\phi_3$  and  $\phi_4$  since these are all degenerate. The equations that our cleaned-up MO,  $\phi'_2$ , must satisfy are

$$\phi'_2 = d_2\phi_2 + d_3\phi_3 + d_4\phi_4 \quad (10-5)$$

where (in order to cause all  $2p_x$  and  $2p_y$  contributions to vanish)

$$\begin{aligned} 0.0021d_2 + 0.5313d_3 + -0.0021d_4 &= 0.0 \\ 0.0007d_2 + 0.0021d_3 + 0.5313d_4 &= 0.0 \\ d_2^2 + d_3^2 + d_4^2 &= 1 \end{aligned} \quad (10-6)$$

As a result,

$$\phi'_2 = 0.9999\phi_2 - 0.0040\phi_3 - 0.0013\phi_4 \quad (10-7)$$

A similar procedure to produce an orbital with no  $p_z$  or  $p_y$  contribution ( $\phi'_3$ ), and one with no  $p_z$  or  $p_x$  contribution ( $\phi'_4$ ) gives

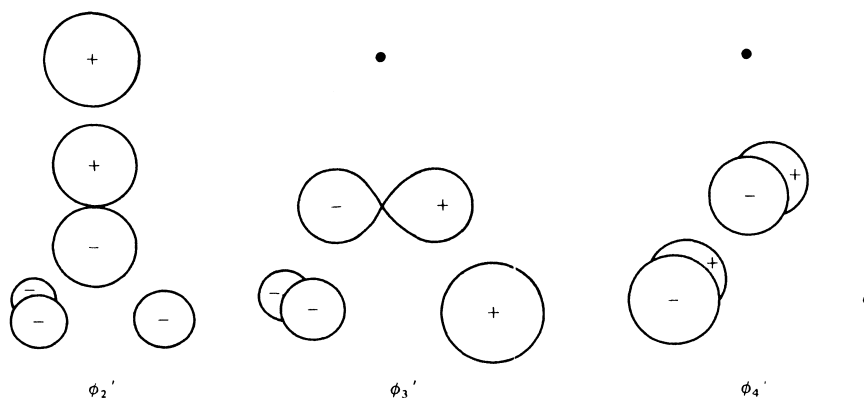
$$\phi'_3 = 0.9999\phi_3 + 0.0040\phi_2 - 0.0040\phi_4 \quad (10-8)$$

$$\phi'_4 = 0.9999\phi_4 + 0.0013\phi_2 + 0.0039\phi_3 \quad (10-9)$$

The coefficients for these MOs appear in Table 10-7.

**TABLE 10-7** ► Coefficients for MOs  $\phi'_2, \phi'_3, \phi'_4$

	$\phi'_2$	$\phi'_3$	$\phi'_4$
2s	0.0	0.0	0.0
2p <sub>z</sub>	0.5313	0.0	0.0
2p <sub>x</sub>	0.0	0.5313	0.0
2p <sub>y</sub>	0.0	0.0	0.5313
1s <sub>a</sub>	0.5547	0.0	0.0
1s <sub>b</sub>	-0.1849	0.5228	0.0
1s <sub>c</sub>	-0.1849	-0.2614	0.4529
1s <sub>d</sub>	-0.1849	-0.2614	-0.4529



**Figure 10-3** ► The three lowest-energy degenerate MOs of methane.

There is no fundamental change produced by intermixing degenerate MOs in this way. The total electronic density and the orbital energies are uninfluenced. The only advantage is that the cleaned-up MOs are easier to sketch and visualize. The MOs  $\phi'_2$ ,  $\phi'_3$ , and  $\phi'_4$  are sketched in Fig. 10-3.

Each of the MOs in Fig. 10-3 is symmetric or antisymmetric for some of the operations that apply to a tetrahedron.  $\phi'_2$  is symmetric for rotations about the  $z$  axis by  $2\pi/3$ , and also for reflection through the  $xz$  plane. This same reflection plane is a symmetry plane for  $\phi'_3$  and  $\phi'_4$ , but neither of these MOs shows symmetry or antisymmetry for rotation about the  $z$  axis. Each MO contains one p AO and, perforce, has the symmetry of that AO. We shall refer to these as p-type MOs. Note that hydrogen 1s AOs lying in the nodal plane of a p AO do not mix with that p AO in formation of MOs. This results from zero interaction elements in  $\mathbf{H}$ , which, in turn, results from zero overlap elements in  $\mathbf{S}$ . Note also that the MO  $\phi'_2$  is the MO that we anticipated earlier on the basis of inspection of the matrix  $\mathbf{H}$ . Because of phase agreements between the hydrogen 1s AOs and the adjacent lobes of the p AOs,  $\phi'_1$ ,  $\phi'_2$ , and  $\phi'_3$  are C–H bonding MOs.

A similar “cleaning up” procedure can be performed on  $\phi_5$ ,  $\phi_6$ , and  $\phi_7$ . These turn out to be the C–H antibonding mates to the MOs in Fig. 10-3.

The broad results of this calculation are that there are four occupied C–H bonding MOs, one of s type and three of p type. At higher energies are four unoccupied C–H antibonding MOs, again one of s type and three of p type.

Note that the s- and the three p-type MOs fall into the same energy pattern as the s and p AOs of isolated carbon. Because of their highly symmetric tetrahedral geometry, the hydrogen atoms do not lift the degeneracy of the p AOs. There are many molecules and complexes in which a cluster of atoms or molecules surrounds a central atom in such a highly symmetric way that the degeneracies among certain AOs on the central atom are retained.

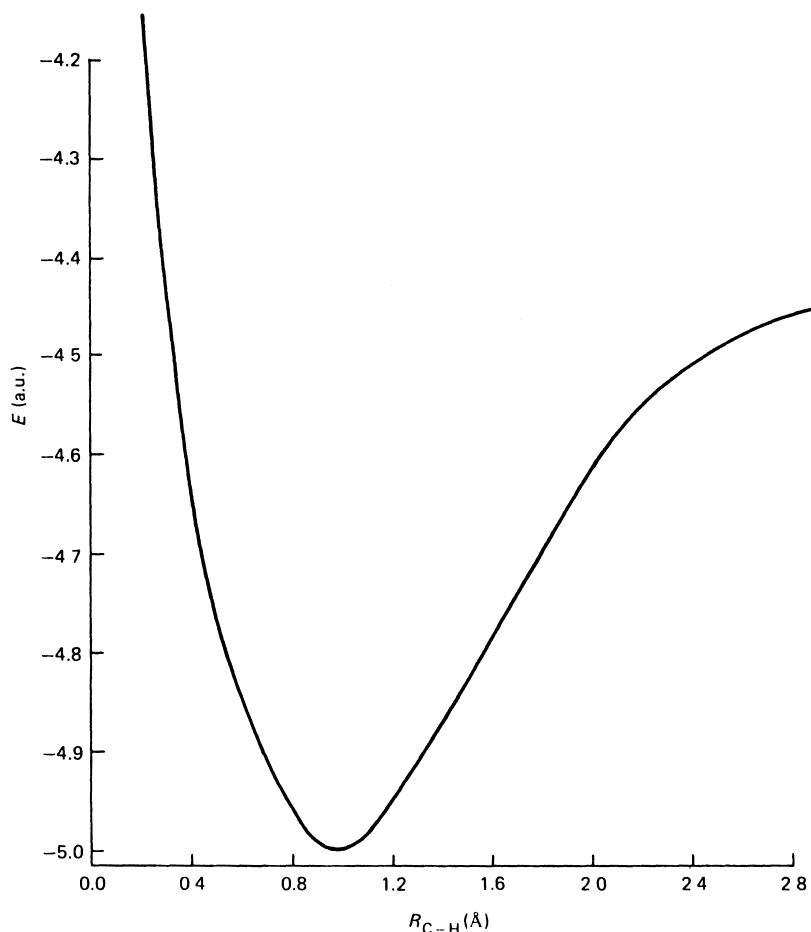
### 10-1.F The Total Energy

The total EH energy is taken as the sum of the one-electron energies. For methane, this is  $2 \times (-0.8519) + 6 \times (-0.5487)$ , or  $-4.9963$  a.u. There is some ambiguity as to how this energy is to be interpreted. For instance, does it include any of the internuclear repulsion energy? Also, what problems will arise from our neglect of inner-shell



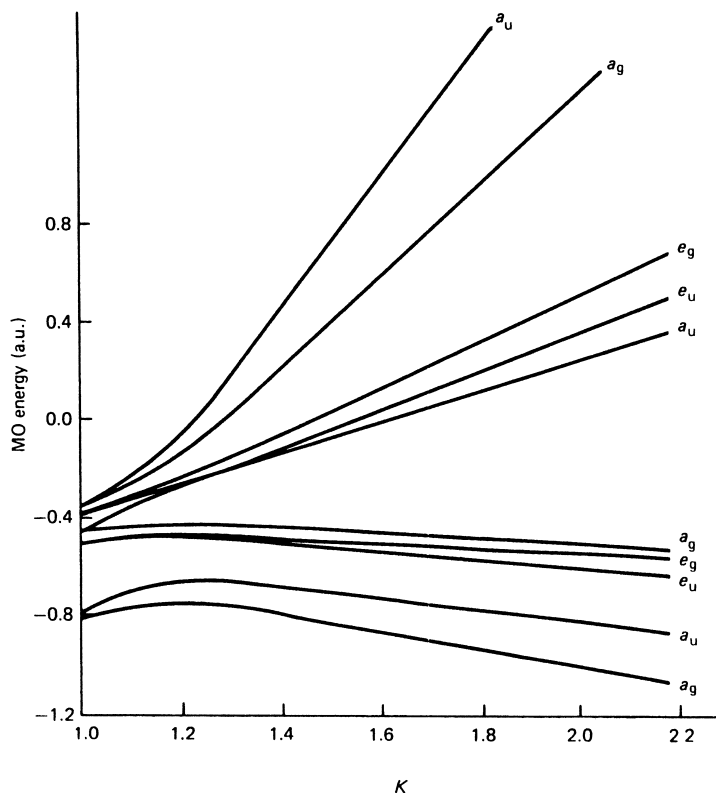
electrons? By comparing EH total energy changes with experimental energy changes, it has been decided<sup>7</sup> that the *change* in EH total energy upon change of geometry is approximately the same as the actual change in total electronic plus nuclear repulsion energy for the system. Thus, our value of  $-4.9963$  a.u. is not a realistic value for the total (nonrelativistic) energy of methane (the actual value is  $-40.52$  a.u.), but it is meaningful when compared to EH energies for methane at other geometries. For example, if we uniformly lengthen or shorten all the C–H bonds in methane and repeat our EH calculation several times, we can generate an energy curve versus  $R_{\text{C-H}}$  for the symmetrical stretch vibrational mode of methane. The resultant plot is given in Fig. 10-4. The EH total energy is minimized at about  $R_{\text{C-H}} = 1 \text{ \AA}$ , reasonably close to the experimentally observed  $1.1\text{-}\text{\AA}$  distance for the minimum *total* energy of methane.

The appearance of the curve in Fig. 10-4 does encourage us to equate EH total energy changes to changes in actual electronic-plus-nuclear-repulsion energies. As we shall see later, this procedure fails for some molecules (notably  $\text{H}_2$ ) and for methane may be regarded as fortuitous.



**Figure 10-4** ► Total extended Hückel energy for  $\text{CH}_4$  as a function of C–H bond length.

<sup>7</sup>See Hoffmann [1].

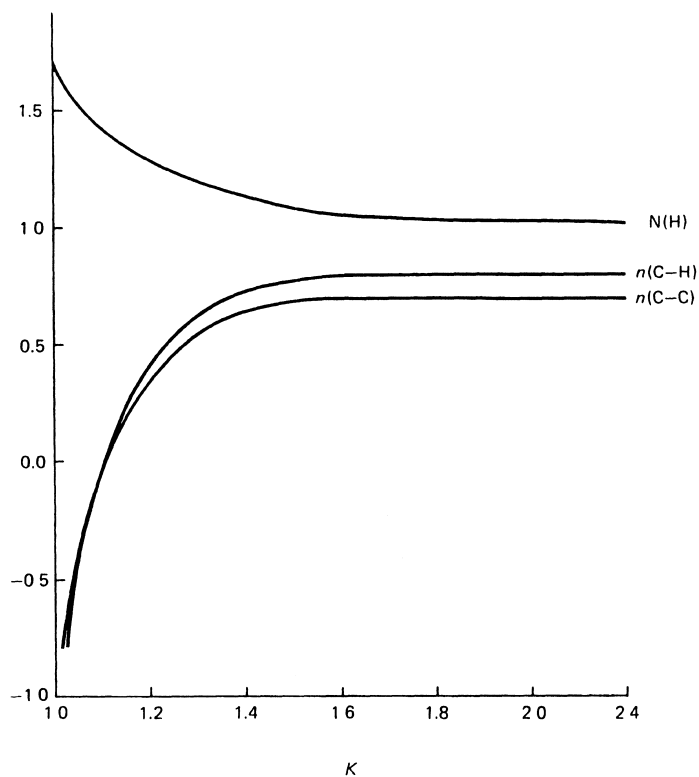


**Figure 10-5** ► Staggered ethane MO energies versus  $K$ . C–H distances are 1.1 Å; C–C distance is 1.54 Å; all angles are tetrahedral.

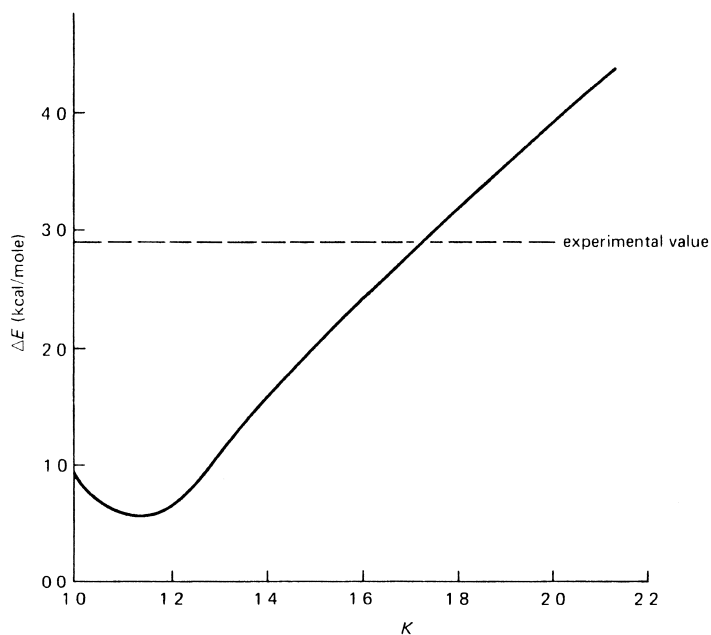
### 10-1.G Fixing the Parameter $K$

We mentioned earlier that Hoffmann suggested a value of 1.75 for  $K$ . We will now indicate the considerations behind this suggestion.

Hoffmann used the ethane molecule  $C_2H_6$  to evaluate  $K$ . A plot of the orbital energies of staggered ethane as a function of  $K$  is shown in Fig. 10-5. The energies are linearly dependent on  $K$  at values of  $K$  greater than about 1.5. At lower values, the lines curve and some crossing occurs. Hence, in order that the MO energy order not be highly sensitive to  $K$ , its value should exceed 1.5. A plot of the amount of electronic charge in a bond or at an atom in ethane, as calculated by the EHMO method, versus  $K$  is shown in Fig. 10-6. We will describe the details of such calculations shortly, but for now, we merely note that the disposition of charge in ethane becomes rather insensitive to  $K$  at values of  $K$  greater than about 1.5. In Fig. 10-7 a plot of the EH total energy difference between staggered and eclipsed ethanes versus  $K$  is given. This energy difference has an experimentally determined value of  $2.875 \pm 0.025$  kcal/mole, the staggered form being more stable. To give reasonable agreement with this experimental value,  $K$  should be about 1.75. Thus, the value  $K = 1.75$  is selected because the MO energy order and charge distribution are not sensitive to  $K$  in this region and because this value of  $K$  gives the correct total energy change for a known physical process. We have also seen earlier that this same value of  $K$  leads to a reasonable prediction for the equilibrium bond length in  $CH_4$ . Notice that the evaluation of  $K$  comes by matching the



**Figure 10-6** ► Mulliken gross population on H [ $N(H)$ ] and Mulliken overlap populations in C-C and C-H bonds [ $n(C-C)$  and  $n(C-H)$ ] of ethane as calculated by the EH method with various values of  $K$ .



**Figure 10-7** ► Extended Hückel energy difference between staggered and eclipsed ethanes as a function of  $K$ .

EH total energy *change* to the total (nuclear repulsion plus electronic) observed energy *change* for internal rotation in ethane. This is consistent with our earlier interpretation of EH total energy.

## 10-2 Mulliken Populations

We found that the electron densities and bond orders calculated in the simple Hückel method were extremely useful for relating theory to observable molecular properties such as electron spin-resonance splittings or bond lengths. Hence, it is desirable that we find analogous quantities to describe the distribution of electrons in an all-valence-electron method like the EH method. A number of suggestions have been made. The one we use is due to Mulliken [8]. It is the most widely used, and, as we shall see, it has an especially direct and useful connection with the EH method.

Consider a real, normalized MO,  $\phi_i$ , made up from two normalized AOs,  $\chi_j$  and  $\chi_k$ :

$$\phi_i = c_{ji}\chi_j + c_{ki}\chi_k \quad (10-10)$$

We square this MO to obtain information about electronic distribution:

$$\phi_i^2 = c_{ji}^2\chi_j^2 + c_{ki}^2\chi_k^2 + 2c_{ji}c_{ki}\chi_j\chi_k \quad (10-11)$$

If we integrate Eq. (10-11) over the electronic coordinates, we obtain (since  $\phi_i$ ,  $\chi_j$ , and  $\chi_k$  are normalized)

$$1 = c_{ji}^2 + c_{ki}^2 + 2c_{ji}c_{ki}S_{jk} \quad (10-12)$$

where  $S_{jk}$  is the overlap integral between  $\chi_j$  and  $\chi_k$ . Mulliken suggested that one electron in  $\phi_i$  should be considered to contribute  $c_{ji}^2$  to the electron *net AO population* of  $\chi_j$ ,  $c_{ki}^2$  to the population of  $\chi_k$ , and  $2c_{ji}c_{ki}S_{jk}$  to the *overlap population* between  $\chi_j$  and  $\chi_k$ . If there are two electrons in  $\phi_i$ , then these populations should be doubled.

Let  $q_j^i$  symbolize the net AO population of  $\chi_j$  due to one electron in MO  $\phi_i$ , and  $p_{jk}^i$  symbolize the overlap population between  $\chi_j$  and  $\chi_k$  due to this same electron. The above example leads to the following general definitions:

$$q_j^i = c_{ji}^2 \quad (10-13)$$

$$p_{jk}^i = 2c_{ji}c_{ki}S_{jk} \quad (10-14)$$

We can now sum the contributions due to all the electrons present in the model system, obtaining a *Mulliken net AO population*  $q_j$  for each AO  $\chi_j$ , and a *Mulliken overlap population*  $p_{jk}$ , for each distinct AO pair  $\chi_j$  and  $\chi_k$ :

$$q_j = \sum_i^{\text{MOs}} n_i c_{ji}^2 \equiv \sum_i^{\text{MOs}} n_i q_j^i \quad (10-15)$$

$$P_{jk} = 2 \sum_i^{\text{MOs}} n_i c_{ji} c_{ki} S_{jk} \equiv \sum_i^{\text{MOs}} n_i p_{jk}^i \quad (10-16)$$

Notice that the sum of all the net AO *and* overlap populations must be equal to the total number of electrons in the model system. (In the EH method, this is the total number



**TABLE 10-9** ► Reduced Net AO and Overlap Population Matrix for Methane

	C	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>d</sub>
C	2.3762	0.7952	0.7952	0.7952	0.7952
H <sub>a</sub>		0.6844	-0.0491	-0.0491	-0.0491
H <sub>b</sub>			0.6844	-0.0491	-0.0491
H <sub>c</sub>				0.6844	-0.0491
H <sub>d</sub>					0.6844

by summing all the carbon atom AO contributions together to give a reduced overlap population matrix, shown in Table 10-9. The reduced population matrix makes evident the equivalence of the four C–H bonds, all of which have a total overlap population of 0.7952 electrons.

The Mulliken population scheme described above assigns some electronic charge to AOs, the rest to overlap regions. An alternative scheme, which assigns all the charge to AOs, was also proposed by Mulliken. One simply divides each overlap population in half, assigning half of the charge to each of the two participating AOs. When all the overlap populations have been reassigned in this way, the electronic charge is all in the AOs, and the sum of these AO charges still equals the total number of electrons. Mulliken called the AO populations resulting from this procedure *gross AO populations*. We will use the symbol  $N(X)$  for the gross population in  $X$ , where  $X$  can be an AO or an atom (i.e., the sum of all gross AO populations on one atom). Clearly

$$N(X) = q_x + \frac{1}{2} \sum_{j \neq x} p_{xj} \quad (10-21)$$

The gross AO populations, gross atomic populations, and the resultant atomic charges (obtained by combining electronic and nuclear charges) for methane are listed in Table 10-10. These data suggest that the carbon has lost a very small amount of charge to hydrogen upon formation of the molecule. It would be very risky, however, to place much faith in such an interpretation. It turns out that populations are rather sensitive to choice of VSIEs. For example, Hoffmann's original choice of VSIEs differs from that

**TABLE 10-10** ► Gross AO Populations, Gross Atomic Populations, and Net Atomic Charges for Methane

	Gross AO population	Gross atom population	Net atomic charge
C <sub>2s</sub>	1.128	3.966	+0.0334
C <sub>2p</sub> <sup>a</sup>	0.946		
H <sup>a</sup>	1.008	1.008	-0.0083

<sup>a</sup>All 2p AOs and all H AOs have identical values because they are equivalent through symmetry.

used here, and he obtained gross populations for hydrogen atoms of around 0.9, giving net positive charges of 0.1. Thus, absolute values are not very useful, but *changes* in gross population as we go from one hydrogen to another in the same hydrocarbon molecule or in closely related molecules do appear to be rather insensitive to VSIE choice and are often in accord with results of more accurate calculations.

### 10-3 Extended Hückel Energies and Mulliken Populations

In Chapter 8 it was shown that a simple quantitative relation exists between the energy of a simple Hückel MO and the contributions of the MO to bond orders [Eq. (8-56)]. The more bonding such an MO is, the lower is its energy. A similar relationship will now be shown to hold for extended Hückel energies and Mulliken populations.

The orbital energy for the real MO  $\phi_i$  is (ignoring the spin variable)

$$E_i = \frac{\int \phi_i \hat{H} \phi_i dv}{\int \phi_i^2 dv} \quad (10-22)$$

$$= \frac{\sum_{j,k}^{\text{AOs}} c_{ji} c_{ki} H_{jk}}{\sum_{j,k}^{\text{AOs}} c_{ji} c_{ki} S_{jk}} \quad (10-23)$$

Assume that  $\phi_i$  is normalized: The denominator is unity. The numerator of Eq. (10-23) contains diagonal and off-diagonal terms. If we separate these, and substitute the relation (10-4) for the off-diagonal terms, we obtain

$$E_i = \sum_{j,k}^{\text{AOs}} c_{ji}^2 H_{jj} + 2 \sum_{j<k}^{\text{AOs}} c_{ji} c_{ki} K S_{jk} \frac{H_{jj} + H_{kk}}{2} \quad (10-24)$$

Comparison with Eqs. (10-13) and (10-14) shows that the first sum contains contributions to net AO populations and the second sum contains overlap population contributions. That is,

$$E_i = \sum_j^{\text{AOs}} q_j^i H_{jj} + \sum_{j<k}^{\text{AOs}} p_{jk}^i K \frac{H_{jj} + H_{kk}}{2} \quad (10-25)$$

This equation indicates that the energy of an extended Hückel MO is equal to its net contributions to AO populations times AO energy weighting factors plus its contributions to overlap populations times overlap energy weighting factors.

By summing over all MOs times occupation numbers, we arrive at a relation between *total* EH energy and net AO and overlap populations:

$$E = \sum_j^{\text{AOs}} q_j H_{jj} + \sum_{j<k}^{\text{AOs}} p_{jk} K \frac{H_{jj} + H_{kk}}{2} \quad (10-26)$$

Equations (10-25) and (10-26) are useful because they permit us to understand computed energies in terms of electron distributions. This is helpful when we seek to understand energy changes which occur as molecules are stretched, bent, or twisted.

There is an important difference between the extended Hückel formulas (10-25) and (10-26) and their simple Hückel counterparts. In a simple Hückel MO, the charge density contributions  $q^i$  always add up to unity, contributing  $\alpha$  to the MO energy (omitting heteroatom cases). The deviation of the MO energy from  $\alpha$  is thus due only to the bond-order contributions  $p^i$ . As a result, for hydrocarbons, the simple Hückel MO that is the more bonding of a pair is *always* lower in energy. This is not so, however, in extended Hückel MOs. Since the sum of AO and overlap populations must equal the number of electrons present, we can increase the total amount of overlap population *only* at the expense of net AO populations. Therefore, energy lowering due to the second sum of Eq. (10-25) is purchased at the expense of that due to the first sum. This complicates the situation and requires that we take a more detailed look before issuing any blanket statements.

The following simple example provides a convenient reference point for discussion. Consider two identical 1s AOs,  $\chi_a$  and  $\chi_b$ , on identical nuclei separated by a distance  $R$ . These AOs combine to form MOs of  $\sigma_g$  and  $\sigma_u$  symmetry. The  $\sigma_g$  MO has an associated positive overlap population and equal positive net AO populations for  $\chi_a$  and  $\chi_b$ . If  $R$  now is decreased slightly, the overlap population increases slightly (say by  $2\delta$ ), so the net AO populations must each decrease by  $\delta$ . The energy change for the MO, then, is

$$\Delta E_{\sigma_g} = -\delta(H_{aa} + H_{bb}) + 2\delta K \frac{H_{aa} + H_{bb}}{2} \quad (10-27)$$

Since the molecule is homonuclear,  $H_{aa} = H_{bb}$ , and

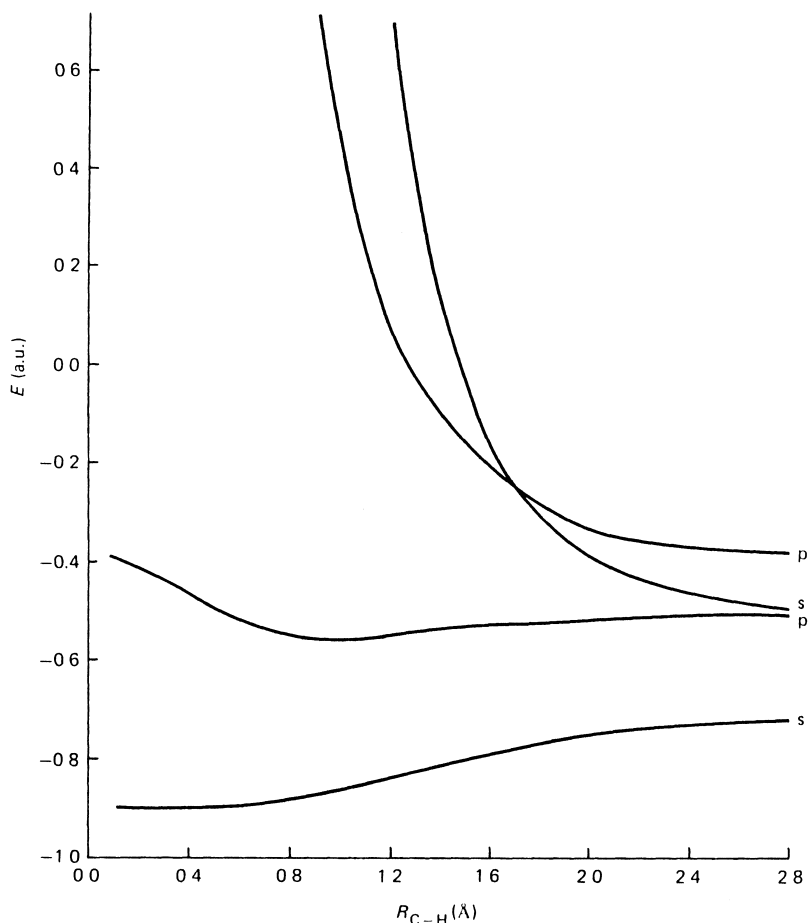
$$\Delta E_{\sigma_g} = 2\delta H_{aa} (K - 1) \quad (10-28)$$

If  $K > 1$ ,  $\Delta E_{\sigma_g}$  is negative (since  $H_{aa}$  is negative). This analysis shows that the choice of 1.75 as the value for  $K$  has the effect of making the increase in overlap population dominate the energy change. If  $K$  were less than unity, the net AO population changes would dominate.

The above example suggests that the EHMO method lowers the energy by maximizing weighted overlap populations at the expense of net AO populations. It also suggests that the EH energy should be lowered whenever a molecule is distorted in a way that enables overlap population to increase. These are useful rules of thumb, but some caution must be exercised since the existence of several different kinds of atom in a molecule leads to a more complicated relation than that in the above example.

Our methane example illustrates the above ideas. We have already seen that the total EH energy for methane goes through a minimum around  $R_{C-H} = 1 \text{ \AA}$ . Let us see how the individual MO energies change as a function of  $R_{C-H}$  and try to rationalize their behaviors in terms of the overlap population changes. A plot of the MO energies is given in Fig. 10-8. The lowest-energy MO is s type and C-H bonding. The overlap between H 1s AOs and the C 2s STO increases as  $R_{C-H}$  decreases. As a result, the energy of this MO decreases as  $R_{C-H}$  decreases, favoring formation of the united atom. The second-lowest energy level is triply degenerate and belongs to p-type C-H bonding MOs. A glance at Fig. 10-3 indicates that overlap between AOs will first increase in magnitude as  $R_{C-H}$  decreases. But ultimately, at small  $R_{C-H}$  this behavior must be reversed because the 1s and 2p AOs are orthogonal when they are isocentric. Therefore, as  $R_{C-H}$  decreases, the overlap population first increases, then decreases toward zero. Consequently, the EH energy of this level first decreases, then increases. Since there are six electrons in this





**Figure 10-8** ► Extended Hückel MO energies for methane as a function of  $R_{C-H}$ .

level and only two in the lowest-energy MO, this one dominates the total energy and is responsible for the eventual rise in total energy at small  $R$  that creates the minimum in Fig. 10-4. The two remaining (unoccupied) levels belong to antibonding MOs, and the overlap population becomes more negative as  $R_{C-H}$  decreases. The p-type level rises less rapidly and eventually passes through a maximum (not shown), again because the overlap population must ultimately approach zero as  $R_{C-H}$  approaches zero.

It is important to remember that all these remarks apply to the EH method only. The relationships between the EH method and other methods or with experimental energies is yet to be discussed.

## 10-4 Extended Hückel Energies and Experimental Energies

We have seen that a change in EH energy reflects certain changes in calculated Mulliken populations. We now consider the circumstances that should exist in order that such EH energy changes agree roughly with actual total energy changes for various systems.

In essence, there are two requirements. First, the population changes calculated by the EH method ought to be in qualitative agreement with the charge shifts that actually occur in the real system. This condition is not always met. Some systems, especially those having unpaired electrons, are not accurately representable by a single-configuration wavefunction (that is, by a single product or a single Slater determinant). An example of this was seen for some  $1s2s$  states of helium (see Chapter 5). Since the EHMO method is based on a single configuration, it is much less reliable for treating such systems. Special methods exist for handling such systems, but they normally are not applied at the Hückel level of approximation.

The second requirement is that, as the charge shifts in the real system, the total energy should change in the way postulated by the EH method. For instance, if the charge increases in bond regions, this should tend to lower the total energy. In actuality, this does not always happen. We can see this by returning to our example of two identical  $1s$  AOs separated by  $R$ . The associated  $\sigma_g$  MO increases its overlap population monotonically as  $R$  decreases. Therefore, the EH postulate predicts that the total energy should decrease monotonically. It is clear, however, that this does not happen in any real system. If our system is  $H_2$ , we know that the experimental energy decreases with decreasing  $R$  until  $R = R_e$ , and increases thereafter (Fig. 7-18). If our system is  $He_2^{2+}$ , the experimental total energy *increases* as  $R$  decreases, due to the dominance of internuclear repulsion.<sup>8</sup> Consideration of many examples such as these indicates that the postulate is usually qualitatively correct when we are dealing with interactions between neutral, fairly nonpolar systems that are separated by a distance greater than a bond length typical for the atoms involved. These, then, are circumstances under which the EHMO method might be expected to be qualitatively correct.

In brief, we find two kinds of condition limiting the applicability of the EH method. The first is that the system must be reasonably well represented by a single configuration. Hence, closed-shell systems are safest. The second condition is that we apply the method to uncharged nonpolar systems where the nuclei that are undergoing relative motion are not too close to each other.

These conditions are often satisfied by molecules undergoing internal rotation about single bonds. Thus, it is indeed appropriate that the internal rotation barrier in ethane was used to help calibrate the method. A comparison of other EH calculated barriers with experimental values (Table 10-11) gives us some idea of the capabilities and limitations of the method. For all the molecules listed, the most stable conformation predicted by the EH method agrees with experiment. This suggests that one can place a fair amount of reliance on the conformational predictions of the method, at least for threefold symmetric rotors. Also, certain gross quantitative trends, such as the significant reduction as we proceed down the series ethane, methylamine, methanol, are displayed in the EH results, but it is evident that the quantitative predictions of barrier height are not very good. This is not too surprising since the method was calibrated on hydrocarbons. Introduction of halogens, nitrogen, or oxygen produces greater polarity and might be expected to require a different parametrization.

For reasons outlined earlier, we expect even less accuracy in EH calculations of molecular deformations involving bond-angle or bond-length changes. This expectation is generally reinforced by calculation. Molecular shape predictions become poorer

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<sup>8</sup>Actually,  $He_2^{2+}$  has a minimum at short  $R$  in its energy curve due to an avoidance of curve crossing (discussed in Chapter 14), but this minimum is unstable with respect to the separated ions. See Pauling [9].

**TABLE 10-11** ► Energy Barriers for Internal Rotation about Single Bonds<sup>a</sup>

Molecule	Barrier (kcal/mole) <sup>b</sup>	
	Calculated	Experiment
CH <sub>3</sub> -CH <sub>3</sub>	3.04	2.88
CH <sub>3</sub> -NH <sub>2</sub>	1.66	1.98
CH <sub>3</sub> -OH	0.45	1.07
CH <sub>3</sub> -CH <sub>2</sub> F	2.76	3.33
CH <sub>3</sub> -CHF <sub>2</sub>	2.39	3.18
CH <sub>3</sub> -CF <sub>3</sub>	2.17	3.25
CH <sub>3</sub> -CH <sub>2</sub> Cl	4.58	3.68
CH <sub>3</sub> -CHCH <sub>2</sub>	1.20	1.99
<i>cis</i> -CH <sub>3</sub> -CHCHCl	0.11	0.62
CH <sub>3</sub> -CHO	0.32	1.16
CH <sub>3</sub> -NCH <sub>2</sub>	0.44	1.97

<sup>a</sup>Calculated barriers are for rigid rotation, where no bond length or angle changes occur except for the torsional angle change about the internal axis.

<sup>b</sup>The stable form for the first seven molecules has the methyl C-H bonds staggered with respect to bonds across the rotor axis. For the last four molecules, the stable form has a C-H methyl bond eclipsing the double bond.

for more polar molecules (water is calculated to be most stable when it is linear), and bond-length predictions are quite poor too.

Results such as these have tended to restrict use of the EH method to qualitative predictions of conformation in molecules too large to be conveniently treated by more accurate methods. However, just as the simple Hückel method underwent various refinements (such as the  $\omega$  technique) to patch up certain inadequacies, so has the EH method been refined. Such refinements<sup>9</sup> have been shown to give marked improvement in numerical predictions of various properties. The EH method has been overtaken in popularity by a host of more sophisticated computational methods. (See Chapter 11.) However, it is still sometimes used as a first step in such methods as a way to produce a starting set of approximate MOs. The EHMO method also continues to be important as the computational equivalent of qualitative MO theory (Chapter 14), which continues to play an important role in theoretical treatments of inorganic and organic chemistries (as, for example, in Walsh's Rules and in Woodward-Hoffmann Rules).

### 10-4.A Problems

The following output is produced by an EH calculation on the formaldehyde molecule, and is referred to in Problems 10-1 to 10-10.

<sup>9</sup>See Kalman [10], Boyd [11], and the references cited in these papers. Also, see Anderson and Hoffmann [12] and Anderson [13].

## Formaldehyde (Ground State) Orbital Numbering

Orbital	Atom	<i>n</i>	<i>l</i>	<i>m</i>	<i>x</i>	<i>y</i>	<i>z</i>	exp <i>H<sub>ii</sub></i>
1	H-1	1	0	0	-0.550000	0.952600	0.0	1.200-13.60
2	H-2	1	0	0	-0.550000	-0.952600	0.0	1.200-13.60
3	C-3	2	0	0	0.0	0.0	0.0	1.625-19.44
4	C-3	2	1	0	0.0	0.0	0.0	1.625-10.67
5	C-3	2	1	1	0.0	0.0	0.0	1.625-10.67
6	C-3	2	1	1	0.0	0.0	0.0	1.625-10.67
7	O-4	2	0	0	1.220000	0.0	0.0	2.275-32.38
8	O-4	2	1	0	1.220000	0.0	0.0	2.275-15.85
9	O-4	2	1	1	1.220000	0.0	0.0	2.275-15.85
10	O-4	2	1	1	1.220000	0.0	0.0	2.275-15.85

$$H_{ij} = K S_{ij}(H_{ii} + H_{jj})/2, \text{ with } K = 1.75.$$

## Distance Matrix (a.u.)

	1	2	3	4
1	0.0	3.6004	2.0787	3.7985
2	3.6004	0.0	2.0787	3.7985
3	2.0787	2.0787	0.0	2.3055
4	3.7985	3.7985	2.3055	0.0

Total effective nuclear repulsion = 17.69537317 a.u.

## Formaldehyde Eigenvalues

Eigenvalues (a.u.)	Occ. no.	Eigenvalues (a.u.)	Occ. no.
$E(1) = 1.039011$	0	$E(6) = -0.587488$	2
$E(2) = 0.472053$	0	$E(7) = -0.597185$	2
$E(3) = 0.314551$	0	$E(8) = -0.611577$	2
$E(4) = -0.342162$	0	$E(9) = -0.755816$	2
$E(5) = -0.517925$	2	$E(10) = -1.242836$	2

Sum = -8.625654 a.u.

Total Overlap Matrix

	1	2	3	4	5	6	7	8	9	10
1	1.0000	0.1534	0.5133	0.0	-0.2428	0.4204	0.0813	0.0	-0.0729	0.0392
2	0.1534	1.0000	0.5133	0.0	-0.2428	-0.4204	0.0813	0.0	-0.0729	-0.0392
3	0.5133	0.5133	1.0000	0.0	0.0	0.0	0.3734	0.0	-0.3070	0.0
4	0.0	0.0	0.0	1.0000	0.0	0.0	0.0	0.2146	0.0	0.0
5	-0.2428	-0.2428	0.0	0.0	1.0000	0.0	0.4580	0.0	-0.3056	0.0
6	0.4204	-0.4204	0.0	0.0	0.0	1.0000	0.0	0.0	0.0	0.2146
7	0.0813	0.0813	0.3734	0.0	0.4580	0.0	1.0000	0.0	0.0	0.0
8	0.0	0.0	0.0	0.2146	0.0	0.0	0.0	1.0000	0.0	0.0
9	-0.0729	-0.0729	-0.3070	0.0	-0.3056	0.0	0.0	0.0	1.0000	0.0
10	0.0392	-0.0392	0.0	0.0	0.0	0.2146	0.0	0.0	0.0	1.0000

Eigenvectors

	1	2	3	4	5	6	7	8	9	10
1	0.5279	0.7683	0.8924	0.0	-0.4281	-0.2016	0.0	-0.2141	-0.2721	0.0011
2	0.5279	0.7683	-0.8924	0.0	0.4281	-0.2016	0.0	0.2141	-0.2721	0.0011
3	-1.3964	-0.5553	0.0000	0.0	-0.0000	-0.0460	0.0	-0.0000	-0.4875	0.2550
4	0.0	0.0	0.0	0.9940	0.0	0.0	0.2456	0.0	0.0	0.0
5	-0.6043	1.1727	-0.0000	0.0	0.0000	0.2768	0.0	0.0000	0.2245	0.0685
6	0.0000	-0.0000	-1.2519	0.0	-0.3813	0.0000	0.0	-0.3179	0.0000	0.0000
7	0.8367	-0.4799	0.0000	0.0	0.0000	-0.0884	0.0	-0.0000	0.3066	0.8481
8	0.0	0.0	0.0	-0.4532	0.0	0.0	0.9181	0.0	0.0	0.0
9	-0.6960	0.3412	-0.0000	0.0	0.0000	-0.8317	0.0	-0.0000	0.3327	0.0252
10	-0.0000	0.0000	0.2511	0.0	0.6475	0.0000	0.0	-0.7600	-0.0000	-0.0000

Mulliken Overlap Populations for 12 Electrons

	1	2	3	4	5	6	7	8	9	10
1	0.6876	-0.0702	0.2920	0.0	0.1134	0.3890	-0.0210	0.0	-0.0225	-0.0180
2	-0.0702	0.6876	0.2920	0.0	0.1134	0.3890	-0.0210	0.0	-0.0225	-0.0180
3	0.2920	0.2920	0.6097	0.0	0.0	0.0	0.1058	0.0	0.1443	0.0
4	0.0	0.0	0.0	0.1207	0.0	0.0	0.0	0.1936	0.0	0.0
5	0.1134	0.1134	0.0	0.0	0.2634	0.0	0.1876	0.0	0.1880	0.0
6	0.3890	0.3890	0.0	0.0	0.0	0.4929	0.0	0.0	0.0	-0.0046
7	-0.0210	-0.0210	0.1058	0.0	0.1876	0.0	1.6420	0.0	0.0	0.0
8	0.0	0.0	0.0	0.1936	0.0	0.0	0.0	1.6857	0.0	0.0
9	-0.0225	-0.0225	0.1443	0.0	0.1880	0.0	0.0	0.0	1.6061	0.0
10	-0.0180	-0.0180	0.0	0.0	0.0	-0.0046	0.0	0.0	0.0	1.9939

Charge Matrix for MOs with Two Electrons in Each

	1	2	3	4	5	6	7	8	9	10
1	0.1664	0.3881	0.4266	0.0	0.4258	0.1088	0.0	0.1476	0.3363	0.0004
2	0.1664	0.3881	0.4266	0.0	0.4258	0.1088	0.0	0.1476	0.3363	0.0004
3	0.9171	0.0561	0.0000	0.0	0.0000	0.0028	0.0	0.0000	0.7358	0.2882
4	0.0	0.0	0.0	1.7825	0.0	0.0	0.2175	0.0	0.0	0.0
5	0.3198	1.1155	0.0000	0.0	0.0000	0.3257	0.0	0.0000	0.1775	0.0614
6	0.0000	0.0000	1.1204	0.0	0.4593	0.0000	0.0	0.4203	0.0000	0.0000
7	0.2082	0.0241	0.0000	0.0	0.0000	0.0021	0.0	0.0000	0.1123	1.6534
8	0.0	0.0	0.0	0.2175	0.0	0.0	1.7825	0.0	0.0	0.0
9	0.2220	0.0282	0.0000	0.0	0.0000	1.4518	0.0	0.0000,	0.3017	-0.0037
10	0.0000	0.0000	0.0264	0.0	0.6891	0.0000	0.0	1.2845	0.0000	0.0000

Reduced Overlap Population Matrix Atom by Atom

	1	2	3	4
1	0.6876	-0.0702	0.7945	-0.0615
2	-0.0702	0.6876	0.7945	-0.0615
3	0.7945	0.7945	1.4866	0.8148
4	-0.0615	-0.0615	0.8148	6.9277

Orbital Charges

1	1.018973	6	0.879574
2	1.018973	7	1.767672
3	1.026764	8	1.782529
4	0.217471	9	1.749778
5	0.564637	10	1.973630

Net Charges

1	-0.018973	3	1.311555
2	-0.018973	4	-1.273609

Total charge = 0.000000.

- 10-1.** Use the output to determine the orientation of the molecule with respect to Cartesian coordinates. Sketch the molecule in relation to these axes and number the *atoms* in accord with their numbering in the output.
- 10-2.** Use the orbital numbering data together with the overlap matrix to figure out which of the labels 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> goes with each of the ten AOs (i.e., it is obvious that AO 1 is a 1s AO, but it is not so obvious what AO 5 is).
- 10-3.** Use your conclusions from above, together with coefficients in the eigenvector matrix, to sketch the MOs having energies of -0.756, -0.611, and -0.597 a.u. Which of these are  $\pi$  MOs? Which are  $\sigma$  MOs?
- 10-4.** Label each of the ten MOs " $\pi$ " or " $\sigma$ " by inspecting the coefficient matrix.
- 10-5.** What is the Mulliken overlap population between C and O 2p <sub>$\pi$</sub>  AOs in this molecule? Should removal of an electron from MO 7 cause the C=O bond to shorten or to lengthen?
- 10-6.** Demonstrate that MO 7 satisfies Eq. (10-24). (Note that  $H_{ii}$  values in the first table are in units of electron volts, while orbital energies are in atomic units.)
- 10-7.** Use the reduced overlap population matrix to verify that the sum of AO and overlap populations is equal to the number of valence electrons.
- 10-8.** Using MO 7 as your example, verify that the charge matrix table is a tabulation of the contributions of each MO to *gross* atom populations.
- 10-9.** In the list of "orbital charges," are the "orbitals" MOs or AOs? Demonstrate how these numbers are derived from those in the charge matrix.

- 10-10.** What is the physical meaning of the “net charges” in the data? Would you characterize these results as indicative of low polarity? Which end of the molecule should correspond to the negative end of the dipole moment?
- 10-11.** How many MOs will be produced by an EHMO calculation on butadiene?

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