8-2 THE ASSUMPTION OF \( \sigma-\pi \) SEPARABILITY

8-1 The Importance of Symmetry

Our discussions of the particle in a box, the harmonic oscillator, the hydrogen atom, and homonuclear diatomic molecules have all included emphasis on the role which symmetry plays in determining the qualitative nature of the eigenfunctions. When we encounter larger systems, detailed and accurate solutions become much more difficult to perform and interpret, but symmetry continues to exert strong control over the solutions.

In this chapter, we will describe a rather simple quantum chemical method which was formulated in the early 1930s by E. Hückel. One of the strengths of this method is that, by virtue of its crudeness and simplicity, the effects of symmetry and topology on molecular characteristics are easily seen. Also, the simplicity of the model makes it an excellent pedagogical tool for illustrating many quantum chemical concepts, such as bond order, electron densities, and orbital energies. Finally, the method and some of its variants continue to be useful for certain research applications. Indeed, it is difficult to argue against the proposition that every graduate student of organic and inorganic chemistry should be acquainted with the Hückel molecular orbital (HMO) method.

8-2 The Assumption of \( \sigma-\pi \) Separability

The simple Hückel method was devised to treat electrons in unsaturated molecules like ethylene and benzene. By 1930 it was recognized that unsaturated hydrocarbons are chemically more reactive than are alkanes, and that their spectroscopic and thermodynamic properties are different too. The available evidence suggested the existence of loosely held electrons in unsaturated molecules.

We have already seen that, when atoms combine to form a linear molecule, we can distinguish between MOs of type \( \sigma, \pi, \delta, \ldots \) depending on whether the MOs are associated with an \( m \) quantum number of 0, 1, 2, \ldots. Thus, in acetylene \( (C_2H_2) \), the minimal basis set of AOs on carbon and hydrogen lead to \( \sigma \) and \( \pi \) MOs. Let us imagine that our acetylene molecule is aligned along the \( z \) cartesian axis. Then the \( p_z \) \( \pi \)-type AOs on the carbons are antisymmetric for reflection through a plane containing the molecular axis and the \( y \) axis. The \( p_z \) \( \pi \)-type AOs are antisymmetric for reflection through a plane containing the molecular axis and the \( x \) axis. The \( p_z \) AOs, which are \( \sigma \)-type functions, are symmetric for reflection through any plane containing the molecular axis. It has become standard practice to carry over the \( \sigma-\pi \) terminology to planar (but nonlinear) molecules, where \( m \) is no longer a "good" quantum number. In this expanded usage, a \( \pi \) orbital is one that is antisymmetric for reflection through the plane of the molecule; a \( \sigma \) orbital being symmetric for that reflection.

Hückel found that, by treating only the \( \pi \) electrons explicitly, it is possible to reproduce theoretically many of the observed properties of unsaturated molecules such as the uniform C–C bond lengths of benzene, the high-energy barrier to internal rotation about double bonds, and the unusual chemical stability of benzene. Subsequent work by a large number of investigators has revealed many other useful correlations between experiment and this simple HMO method for \( \pi \) electrons.

Treating only the \( \pi \) electrons explicitly and ignoring the \( \sigma \) electrons is clearly an approximation, yet it appears to work surprisingly well. Physically, Hückel's approximation may be viewed as one which has the \( \pi \) electrons moving in a potential field due to the nuclei and a "\( \sigma \) core," which is assumed to be frozen as the \( \pi \) electrons move about. Mathematically, the \( \sigma-\pi \) separability approximation is

\[
E_{\text{tot}} = E_{\sigma} + E_{\pi}
\]  

(8-1)

where \( E_{\text{tot}} \) is taken to be the electronic energy \( E_{\text{el}} \) plus the internuclear repulsion energy \( V_{\text{nn}} \).

Let us consider the implications of Eq. (8-1). We have already seen (Chapter 5), that a sum of energies is consistent with a sum of Hamiltonians and a product-type wavefunction. This means that, if Eq. (8-1) is true, the wavefunction of our planar molecule should be of the form (see Problem 8-1)

\[
\psi(1, \ldots, n) = \psi_{\sigma}(1, \ldots, k)\psi_{\pi}(k + 1, \ldots, n)
\]

(8-2)

and our Hamiltonian should be separable into \( \pi \) and \( \sigma \) parts:

\[
\hat{H}(1, 2, \ldots, n) = \hat{H}_{\pi}(1, 2, \ldots, k) + \hat{H}_{\sigma}(k + 1, \ldots, n)
\]

(8-3)

Equations (8-2) and (8-3) lead immediately to Eq. (8-1):

\[
E = \int \psi_{\pi}^*\psi_{\pi}(\hat{H}_{\pi} + \hat{H}_{\sigma})\psi_{\pi}^*\psi_{\pi} \, dt(1, \ldots, n)
\]

\[
\int \psi_{\pi}^*\psi_{\pi} \, dt(1, \ldots, n)
\]

\[
\int \psi_{\pi}^*\psi_{\pi} \, dt(1, \ldots, k) + \int \psi_{\pi}^*\psi_{\pi} \, dt(k + 1, \ldots, n)
\]

\[
\int \psi_{\pi}^*\psi_{\pi} \, dt(k + 1, \ldots, n)
\]

\[
E_{\pi} + E_{\sigma}
\]

(8-4)
If these equations were valid, one could ignore $\psi_n$ and legitimately minimize $E_n$ by varying $\psi_n$, but the equations are not valid because it is impossible to rigorously satisfy Eq. (8-3). We cannot define $H_\sigma$ and $H_\pi$ so that they individually depend completely on separate groups of electrons and still sum to the correct total hamiltonian. Writing these operators explicitly gives

$$\hat{H}_n(1, \ldots, k) = -\frac{1}{2} \sum_{i=1}^{n} V_{i}^2 + \sum_{i=1}^{n} V_{m}(i) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j \neq i}^{n} 1/\eta_{ij}$$

$$\hat{H}_\pi(k + 1, \ldots, n)$$

$$= -\frac{1}{2} \sum_{i=k+1}^{n} V_{i}^2 + \sum_{i=k+1}^{n} V_{m}(i) + \frac{1}{2} \sum_{i=k+1}^{n} \sum_{j=k+1}^{n} (1/\eta_{ij}) + V_{nn}$$

where $V_{m}(i)$ represents the attraction between electron $i$ and all the nuclei. These hamiltonians do indeed depend on the separate groups of electrons, but they leave out the operators for repulsion between $\sigma$ and $\pi$ electrons:

$$\hat{H} - \hat{H}_n - \hat{H}_\pi = \frac{1}{2} \sum_{i=k+1}^{n} \sum_{j \neq i}^{n} 1/\eta_{ij}$$

In short, the $\sigma$ and $\pi$ electrons really do interact with each other, and the fact that the HMO method does not explicitly include such interactions must be kept in mind when we consider the applicability of the method to certain problems. Some account of $\sigma-\pi$ interactions is included implicitly in the method, as we shall see shortly.

8-3 The Independent $\pi$-Electron Assumption

The HMO method assumes that the wavefunction $\psi_n$ is a product of one-electron functions and that the hamiltonian $\hat{H}_n$ is a sum of one-electron operators. Thus, for $n \pi$ electrons,

$$\psi_n(1, 2, \ldots, n) = \phi_1(1)\phi_2(2) \cdots \phi_n(n)$$

$$\hat{H}_n(1, 2, \ldots, n) = \hat{H}_n(1) + \hat{H}_n(2) + \cdots + \hat{H}_n(n)$$

and

$$\int \phi_i^*(1)\hat{H}_n(1)\phi_i(1) d\tau(1)/\int \phi_i^*(1)\phi_i(1) d\tau(1) \equiv E_i$$

It follows that the total $\pi$ energy $E_n$ is a sum of one-electron energies:

$$E_n = E_i + E_j + \cdots + E_i$$

This means that the $\pi$ electrons are being treated as though they are independent of each other, since $E_i$ depends only on $\phi_i$ and is not influenced by the presence or absence of an electron in $\phi_j$. However, this cannot be correct because $\pi$

electrons in fact interact strongly with each other. Once again, such interactions will be roughly accounted for in an implicit way by the HMO method.

The implicit inclusion of interelectronic interactions is possible because we never actually write down a detailed expression for the $\pi$ one-electron hamiltonian operator $\hat{H}_n(i)$. We cannot write it down because it results from a $\pi-\sigma$ separability assumption and an independent $\pi$-electron assumption, and both assumptions are incorrect. $\hat{H}_n(i)$ is considered to be an "effective" one-electron operator—an operator that somehow includes the important physical interactions of the problem so that it can lead to a reasonably correct energy value $E_i$.

A key point is that the HMO method ultimately evaluates $E_i$ via parameters that are evaluated by appeal to experiment. Hence, it is a semiempirical method. Since the experimental numbers must include effects resulting from all the interelectronic interactions, it follows that these effects are implicitly included to some extent in the HMO method through its parameters.

It was pointed out in Chapter 5 that, when the independent electron approximation [Eqs. (8-8)-(8-11)] is taken, all states belonging to the same configuration become degenerate. In other words, considerations of space–spin symmetry do not affect the energy in that approximation. Therefore, the HMO method can make no explicit use of spin orbitals or Slater determinants, and so $\psi_n$ is normally taken to be a single product function as in Eq. (8-8). The Pauli principle is provided for by assigning no more than two electrons to a single MO.

8-4 Setting up the Hückel Determinant

A. Identifying the Basis Atomic Orbitals and Constructing a Determinant

The allyl radical, $C_3H_5$, is a planar molecule\(^1\) with three unsaturated carbon centers (see Fig. 8-1). The minimal basis set of AOs for this molecule consists of a 1s AO on each hydrogen and 1s, 2s, 2p\(_x\), 2p\(_y\), and 2p\(_z\) AOs on each carbon. Of all these AOs only the 2p\(_z\) AOs at the three carbons are antisymmetric for reflection through the molecular plane.

Following Hückel, we ignore all the $\sigma$-type AOs and take the three 2p\(_z\) AOs as our set of basis functions. Notice that this restricts us to the carbon atoms. The hydrogens are not treated explicitly in the simple HMO method. We label our three basis functions $\chi_1$, $\chi_2$, $\chi_3$ as indicated in Fig. 8-2. We will assume these AOs to be normalized.

Suppose that we now perform a linear variation calculation using this basis set. We know this will lead to a $3 \times 3$ determinant whose roots will be MO

\(^1\) The minimum energy conformation of the allyl system is planar. We will ignore the deviations from planarity resulting from vibrational bending of the system.
8. THE SIMPLE HÜCKEL METHOD AND APPLICATIONS

8-4 SETTING UP THE HÜCKEL DETERMINANT

B. The Quantity \( \alpha \)

We have already indicated that there is no way to write an explicit expression for \( \tilde{H}_e \) that is both consistent with our separability assumptions and physically correct. But, without an expression for \( \tilde{H}_e \), how can we evaluate the integrals \( H_{ij} \)? The HMO method sidesteps this problem by carrying certain of the \( H_{ij} \) integrals along as symbols until they can be evaluated empirically by matching theory with experiment.

Let us first consider the integrals \( H_{11}, H_{22}, \) and \( H_{33} \). The interpretation consistent with these integrals is that \( H_{ij} \), for instance, is the average energy of an electron in AO \( \chi_i \) experiencing a potential field due to the entire molecule. Symmetry requires that \( H_{11} = H_{33} \). \( H_{22} \) should be different since an electron in AO \( \chi_2 \) experiences a different environment than it does when in \( \chi_1 \) or \( \chi_3 \). It seems likely, however, that \( H_{22} \) is not very different from \( H_{11} \). In each case, we expect the dominant part of the potential to arise from interactions with the local carbon atom, with more distant atoms playing a secondary role. Hence, one of the approximations made in the HMO method is that all \( H_{ij} \) are identical if \( \chi_i \) is on a carbon atom. The symbol \( \alpha \) is used for such integrals. Thus, for the example at hand, \( H_{11} = H_{22} = H_{33} = \alpha \). The quantity \( \alpha \) is often called the coulomb integral.

C. The Quantity \( \beta \)

Next, we consider the resonance integrals or bond integrals \( H_{12}, H_{23}, \) and \( H_{13} \). (The requirement that \( \tilde{H}_e \) be hermitian plus the fact that the \( \chi_i \)'s and \( H_{ij} \) are real suffices to make these equal to \( H_{21}, H_{32}, \) and \( H_{31} \), respectively.) The interpretation consistent with these integrals is that \( H_{12} \), for instance, is the energy of the overlap charge between \( \chi_1 \) and \( \chi_2 \). Symmetry requires that \( H_{12} = H_{23} \) in the allyl system. However, even when symmetry does not require it, the assumption is made that all \( H_{ij} \) are equal to the same quantity (called \( \beta \)) when \( i \) and \( j \) refer to "neighbors" (i.e., atoms connected by a \( \sigma \) bond). It is further assumed that \( H_{ij} = 0 \) when \( i \) and \( j \) are not neighbors. Therefore, in the allyl case, \( H_{12} = H_{23} = \beta, H_{13} = 0 \).

D. Overlap Integrals

Since the \( \chi_i \)'s are normalized, \( S_{ii} = 1 \). The overlaps between neighbors are typically around 0.3. Nevertheless, in the HMO method, all \( S_{ij} (i \neq j) \) are taken to be zero. Although this seems a fairly drastic approximation, it has been shown to have little effect on the qualitative nature of the solutions.

\[ H_{ij} = \int \chi_i \tilde{H} \chi_j d\nu \]  

\[ S_{ij} = \int \chi_i \chi_j d\nu \]  

Since \( H_{ij} \) and \( S_{ij} \) are integrals over the space coordinates of a single electron, the electron index is suppressed in Eqs. (8-13) and (8-14).

\footnote{The term "coulomb integral" for \( \alpha \) is unfortunate since the same name is used for repulsion integrals of the form \( \int \frac{\rho_i(1)\rho_j(2)}{r_{ij}} \) \( 1/r_{ij} \) \( 1/r_{ij} \). The quantity \( \alpha \) also contains kinetic energy and nuclear--electronic attraction energy.}
8. THE SIMPLE HÜCKEL METHOD AND APPLICATIONS

E. Further Manipulation of the Determinant

Our determinantal equation for the allyl system is now much simplified. It is

\[
\begin{vmatrix}
\alpha - E & \beta & 0 \\
\beta & \alpha - E & \beta \\
0 & \beta & \alpha - E
\end{vmatrix} = 0
\]  
(8-15)

Dividing each row of the determinant by \( \beta \) corresponds to dividing the whole determinant by \( \beta^3 \). This will not affect the equality. Letting \( (\alpha - E)/\beta = x \), we obtain the result

\[
\begin{vmatrix}
x & 1 & 0 \\
1 & x & 1 \\
0 & 1 & x
\end{vmatrix} = 0
\]  
(8-16)

which is the form we will refer to as the HMO determinantal equation. Notice that \( x \) occurs on the principal diagonal, \( 1 \) appears in positions where the indices correspond to a bond, \( 0 \) appears in positions (e.g., 1, 3) corresponding to no bond. This gives us a simple prescription for writing the HMO determinant for any unsaturated hydrocarbon system directly from a sketch of the molecular structure. The rules are (1) sketch the framework defined by the \( n \) unsaturated carbons; (2) number the atoms \( 1, \ldots, n \) (the ordering of numbers is arbitrary); (3) fill in the \( n \times n \) determinant with \( x \)'s on the diagonal, \( 1 \)'s in positions where row-column indices correspond to bonds, \( 0 \)'s elsewhere. See Fig. (8-3) for examples. As a check, it is useful to be sure the determinant is symmetric for reflection through the diagonal of \( x \)'s. This is necessary since, if atoms \( i \) and \( j \) are neighbors, \( 1 \)'s must appear in positions \( i, j \) and \( j, i \) of the determinant.

Since the Hückel determinant contains only information about the number of unsaturated carbons and how they are connected together, it is sometimes referred to as a topological determinant. (Topology refers to properties that are due to the connectedness of a figure, but are unaffected by twisting, bending, etc.)

8-5 Solving the HMO Determinantal Equation

for Orbital Energies

The HMO determinantal equation for the allyl system (8-16) can be expanded to give

\[ x^3 - 2x = 0 \]  
(8-17)

or

\[ x(x^2 - 2) = 0 \]  
(8-18)

Thus, the roots are \( x = 0 \), \( x = \sqrt{2} \), and \( x = -\sqrt{2} \). Recalling the definition of \( x \), these roots correspond respectively to the energies \( E = \alpha \), \( E = \alpha - \sqrt{2} \beta \), \( E = \alpha + \sqrt{2} \beta \).

How should we interpret these results? Since \( x \) is supposed to be the energy of a \( \pi \) electron in a carbon \( 2p \) AO in the molecule, we expect this quantity to be negative (corresponding to a bound electron). Since \( \beta \) refers to an electron in a bond region, it too should be negative. Therefore, the lowest-energy root should be \( E_1 = \alpha + \sqrt{2} \beta \), followed by \( E_2 = \alpha \), with \( E_3 = \alpha - \sqrt{2} \beta \) being the highest-energy root. (It is convenient to number the orbital energies sequentially, starting with the lowest, as we have done here.)

We have just seen that bringing three \( 2p_{\pi} \) AOs together in a linear arrangement causes a splitting into three MO energy levels. This is similar to the splitting into two energy levels produced when two \( 1s \) AOs interact, discussed in connection with \( H_2^+ \). In general, \( n \) linearly independent separated AOs will lead to \( n \) linearly independent MOs.

The ground-state \( \pi \)-electron configuration of the allyl system is built up by putting electrons in pairs into the MOs, starting with those of lowest energy. Thus far, we have been describing our system as the allyl radical. However, since we have as yet made no use of the number of \( \pi \) electrons in the system, our results so far apply equally well for the allyl cation, radical, or anion.

---

**FIG. 8-3** HMO determinants for some small systems.

---

**FIG. 8-4** \( \pi \)-Electron configurations and total energies for the ground states of the allyl cation, radical, and anion.
Configurations and total $\pi$ energies for these systems in their ground states are depicted in Fig. 8-4. The total $\pi$-electron energies are obtained by summing the one-electron energies, as indicated earlier.

### 8-6 Solving for the Molecular Orbitals

We still have to find the coefficients which describe the MOs as linear combinations of AOs. Recall from Chapter 7 that this is done by substituting energy roots of the secular determinant back into the simultaneous equations. For the allyl system, the simultaneous equations corresponding to the secular determinant (8-16) are

\[
\begin{align*}
c_1 x + c_2 &= 0 \quad (8-19) \\
c_1 + c_2 x + c_3 &= 0 \quad (8-20) \\
c_2 + c_3 x &= 0 \quad (8-21)
\end{align*}
\]

(Compare these equations with the secular determinant in Eq. (8-16) and note the obvious relation.) As we noted in Chapter 7, homogeneous equations like these can give us only ratios between $c_1$, $c_2$, and $c_3$, not their absolute values. So we anticipate using only two of these equations and obtaining absolute values by satisfying the normality condition. Because we are neglecting overlap between AOs, this corresponds to requiring

\[
c_1^2 + c_2^2 + c_3^2 = 1 \quad (8-22)
\]

The roots $x$ are, in order of increasing energy, $-\sqrt{2}$, $0$, $+\sqrt{2}$. Let us take $x = -\sqrt{2}$ first. Then

\[
\begin{align*}
-\sqrt{2}c_1 + c_2 &= 0 \quad (8-23a) \\
c_1 - \sqrt{2}c_2 + c_3 &= 0 \quad (8-23b) \\
c_2 - \sqrt{2}c_3 &= 0 \quad (8-23c)
\end{align*}
\]

Comparing Eqs. (8-23a) and (8-23c) gives $c_1 = c_3$. Equation (8-23a) gives $c_2 = \sqrt{2}c_1$. Inserting these relations into the normality equation (8-22) gives

\[
c_1^2 + (\sqrt{2}c_1)^2 + c_3^2 = 1 \quad (8-24)
\]

\[
4c_1^2 = 1, \quad c_1 = \pm \frac{1}{2} \quad (8-25)
\]

It makes no difference which sign we choose for $c_1$ since any wavefunction is equivalent to its negative. (Both give the same $\psi^2$.) Choosing $c_1 = +\frac{1}{2}$ gives

\[
c_1 = \frac{1}{2}, \quad c_2 = 1/\sqrt{2}, \quad c_3 = \frac{1}{2} \quad (8-26)
\]

These coefficients define our lowest-energy MO, $\phi_1$:

\[
\phi_1 = \frac{1}{2}x_1 + (1/\sqrt{2})x_2 + \frac{1}{2}x_3 \quad (8-27)
\]

A similar approach may be taken for $x = 0$ and $x = +\sqrt{2}$. The results are

\[
\begin{align*}
(x = 0): \quad &\phi_2 = (1/\sqrt{2})x_1 - (1/\sqrt{2})x_3 \\
(x = +\sqrt{2}): \quad &\phi_3 = \frac{1}{2}x_1 - (1/\sqrt{2})x_2 + \frac{1}{2}x_3
\end{align*}
\]

The allyl system MOs are sketched in Fig. 8-5.

**FIG. 8-5** Sketches of the allyl system MOs. (a) emphasizes AO signs and magnitudes. (b) resembles more closely the actual contours of the MOs.

The lowest-energy MO, $\phi_1$, has no nodes (other than the molecular-plane node common to all $\pi$ MOs) and is said to be bonding in the $C_1-C_2$ and $C_2-C_3$ regions. It is reasonable that such a bonding MO should have an energy wherein the bond-related term $\beta$ acts to lower the energy, as is true here. The second-lowest energy MO, $\phi_2$, has a nodal plane at the central carbon. Because there are no $\pi$ AOs on neighboring carbons in this MO, there are no interactions at all, and $\beta$ is absent from the energy expression. This MO is said to be nonbonding. The high-energy MO, $\phi_3$, has nodal planes intersecting both bonds. Because the $\pi$ AOs show sign disagreement across both bonds, this MO is everywhere antibonding and $\beta$ terms act to raise the orbital energy above $\alpha$. 
8.7 The Cyclopropenyl System: Handling Degeneracies

The allyl system results when three \( \pi \) AOs interact in a linear arrangement wherein \( H_{12} = H_{23} = \beta \), but \( H_{13} = 0 \). We can also treat the situation where the three \( \pi \) AOs approach each other on vertices of an ever-shrinking equilateral triangle. In this case, each AO interacts equally with the other two. This triangular system is the cyclopropenyl system \( \text{C}_3\text{H}_3 \) given in Fig. 8-6.

The HMO determinantal equation for this system is

\[
\begin{vmatrix}
  x & 1 & 1 \\
  1 & x & 1 \\
  1 & 1 & x \\
\end{vmatrix} = 0, \quad x^3 + 2 - 3x = 0 \tag{8-30}
\]

This equation can be factored as

\[
(x + 2)(x - 1)(x - 1) = 0 \tag{8-31}
\]

Therefore, the roots are \( x = -2, +1, +1 \).

**FIG. 8-6** The cyclopropenyl system (all nuclei are coplanar)

Since the root \( x = 1 \) occurs twice, we can expect there to be two independent HMOs having the same energy—a doubly degenerate level. The energy scheme and ground state electron configuration for the cyclopropenyl radical (three \( \pi \) electrons) (I) gives a total \( E_a \) of \( 3\alpha + 3\beta \). We can surmise from these orbital energies that \( \phi_1 \) is a bonding MO, whereas \( \phi_2 \) and \( \phi_3 \) are predominantly antibonding. To see if this is reflected in the nodal properties of the MOs, let us solve for the coefficients. The equations consistent with the HMO determinant and with orbital normality are

\[
\begin{align*}
  c_1 + c_2 + c_3 &= 0 \\
  c_1 + c_2x + c_3 &= 0 \\
  c_1 + c_2 + c_3x &= 0 \\
  c_1^2 + c_2^2 + c_3^2 &= 1
\end{align*} \tag{8-32}
\]

Setting \( x = -2 \) and solving gives

\[
\phi_1 = (1/\sqrt{3})\chi_1 + (1/\sqrt{3})\chi_2 + (1/\sqrt{3})\chi_3 \tag{8-33}
\]

For this MO, the coefficients are all of the same sign, so that the AOs show sign agreement across all bonds and all interactions are bonding.

To find \( \phi_2 \) and \( \phi_3 \) is trickier. We begin by inserting \( x = +1 \) into our simultaneous equations. This gives

\[
\begin{align*}
  c_1 + c_2 + c_3 &= 0 \quad \text{(three times)} \tag{8-34} \\
  c_1^2 + c_2^2 + c_3^2 &= 1 \tag{8-35}
\end{align*}
\]

With three unknowns and two equations, an infinite number of solutions is possible. Let us pick a convenient one: \( c_1 = -c_2, c_3 = 0 \). The normalization requirement then gives \( c_1 = 1/\sqrt{2}, c_2 = -1/\sqrt{2}, c_3 = 0 \). Let us call this solution \( \phi_2 \):

\[
\phi_2 = (1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_2 \tag{8-36}
\]

We still need to find \( \phi_3 \). There remain an infinite number of possibilities, so let us pick one: \( c_1 = 1/\sqrt{2}, c_2 = 0, c_3 = -1/\sqrt{2} \). We have used our experience with \( \phi_2 \) to choose \( c \)'s that guarantee a normalized \( \phi_3 \). Also, it is clear that \( \phi_3 \) is linearly independent of \( \phi_2 \) since they contain different AOs. But it is desirable to have \( \phi_3 \) orthogonal to \( \phi_2 \). Let us test \( \phi_2 \) and \( \phi_3 \) to see if they are orthogonal:

\[
S = \int \phi_2 \phi_3 \, dv = \frac{1}{2} \int \chi_1 \chi_1 dv - \frac{1}{2} \int \chi_2 \chi_2 dv - \frac{1}{2} \int \chi_3 \chi_3 dv = \frac{1}{2} \tag{8-37}
\]

Since \( S \neq 0 \), \( \phi_2 \) and \( \phi_3 \) are nonorthogonal. We can project out that part of \( \phi_3 \) which is orthogonal to \( \phi_2 \) by using the Schmidt orthogonalization procedure described in Section 6-10. We seek a new function \( \phi'_3 \), given by

\[
\phi'_3 = \phi_3 - S \phi_2 \tag{8-38}
\]

where

\[
S = \int \phi_2 \phi_3 \, dv = \frac{1}{2} \tag{8-39}
\]

Therefore,

\[
\phi'_3 = \phi_3 - \frac{1}{2} \phi_2 = 1/(2\sqrt{2})(\chi_1 + \chi_2 - 2\chi_3) \tag{8-40}
\]

This function is orthogonal to \( \phi_2 \) but is not normalized. Renormalizing gives

\[
\phi'^*_3 = (1/\sqrt{6})(\chi_1 + \chi_2 - 2\chi_3) \tag{8-41}
\]

In summary, to produce HMO coefficients for degenerate MOs, pick any two independent solutions from the infinite choice available, and orthogonalize them using the Schmidt (or any other) orthogonalization procedure.

The MOs for the cyclopropenyl system as seen from above the molecular plane are sketched in Fig. 8-7. The MO \( \phi_2 \) can be seen to have both antibonding
8.8 Charge Distributions from HMOs

Now that we have a method that provides us with orbitals and orbital energies, it should be possible to get information about the way the π-electron charge is distributed in the system by squaring the total wavefunction \( \psi_\pi \). In the case of the neutral allyl radical, we have (taking \( \psi_\pi \) to be a simple product of MOs)

\[
\psi_\pi = \phi_1(1)\phi_2(2)\phi_3(3).
\]

(8-42)

Hence, the probability for simultaneously finding electron 1 in \( dx(1) \), electron 2 in \( dx(2) \) and electron 3 in \( dx(3) \) is

\[
\psi_\pi^2(1, 2, 3) \, dx(1) \, dx(2) \, dx(3) = \phi_1^2(1)\phi_2^2(2)\phi_3^2(3) \, dx(1) \, dx(2) \, dx(3) \quad (8-43)
\]

For most physical properties of interest, we need to know the probability for finding an electron in a three-dimensional volume element \( dv \). Since the probability for finding an electron in \( dv \) is the sum of the probabilities for finding each electron there, the one-electron density function \( \rho \) for the allyl radical is

\[
\rho = 2\phi_1^2 + \phi_2^2.
\]

(8-44)

where we have suppressed the index for the electron. If we integrate \( \rho \) over all space, we obtain a value of three. This means we are certain of finding a total \( \pi \) charge corresponding to three \( \pi \) electrons in the system.

To find out how the \( \pi \) charge is distributed in the molecule, let us express \( \rho \) in terms of AOs. First, we write \( \phi_1^2 \) and \( \phi_2^2 \) separately:

\[
\phi_1^2 = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + \frac{1}{2}x_3^2 + (1/\sqrt{2})x_1x_2 + (1/\sqrt{2})x_1x_3 + (1/\sqrt{2})x_2x_3
\]

\[
\phi_2^2 = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 - x_1x_3
\]

(8-45)

If we were to integrate \( \phi_1^2 \), we would obtain

\[
\int \phi_1^2 \, dv = \int x_1^2 \, dv + \int x_2^2 \, dv + \int x_3^2 \, dv + \int (1/\sqrt{2})x_1x_2 \, dv + \int (1/\sqrt{2})x_1x_3 \, dv + \int (1/\sqrt{2})x_2x_3 \, dv
\]

\[
+ (1/\sqrt{2}) \int x_1x_2 \, dv + (1/\sqrt{2}) \int x_1x_3 \, dv + (1/\sqrt{2}) \int x_2x_3 \, dv
\]

\[
= \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1
\]

(8-46)

Thus, one electron in \( \phi_1 \) shows up, upon integration, as being "distributed" \( \frac{1}{2} \) at carbon 1, \( \frac{1}{2} \) at carbon 2, and \( \frac{1}{2} \) at carbon 3. We say that the atomic \( \pi \)-electron densities due to an electron in \( \phi_1 \) are \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \) at \( C_1, C_2 \), and \( C_3 \), respectively. If we accumulate these figures for all the electrons, we arrive at a total \( \pi \)-electron density for each carbon. For the allyl radical, Table 8-1 shows that each atom has a \( \pi \)-electron density of unity.

Generalizing this approach gives for the total \( \pi \)-electron density \( q_i \) on atom \( i \)

\[
q_i = \sum_{k}^{n_{\text{MOs}}} n_k c_{ik}^2
\]

(8-47)

Here \( k \) is the MO index, \( c_{ik} \) is the coefficient for an AO on atom \( i \) in MO \( k \), and
TABLE 8-1  
HMO \( \pi \) Electron Densities in the 
Allyl Radical

<table>
<thead>
<tr>
<th>Carbon atom</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 in ( \phi_1 )</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>2 in ( \phi_1 )</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>3 in ( \phi_2 )</td>
<td>0</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Sum</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\( n_k \), the "occupation number," is the number of electrons (0, 1, or 2) in MO \( k \). In those rare cases in which \( c_{1k} \) is complex, \( c_{1k}^\ast \) in Eq. (8-47) must be replaced by \( c_{2k}^\ast c_{1k} \).

If we apply Eq. (8-47) to the cyclopropenyl radical, we encounter an ambiguity. If the unpaired electron is assumed to be in MO \( \phi_2 \) of Fig. 8.7, we obtain \( q_1 = q_2 = 1/2, q_3 = 1/3 \). On the other hand, if the unpaired electron is taken to be in \( \phi_3 \), \( q_1 = q_2 = 1/3, q_3 = 1/3 \). The HMO method resolves this ambiguity by assuming that each of the degenerate MOs is occupied by half an electron. This has the effect of forcing the charge distribution to show the overall symmetry of the molecule. In this example, it follows that \( q_1 = q_2 = q_3 = 1/3 \). The general rule is that, for purposes of calculating electron distributions, the electron occupation is averaged in any set of partially occupied, degenerate MOs.

In actuality, the equilateral triangular structure for the cyclopropenyl radical is unstable, and therefore the above-described averaging process is only a theoretical idealization. It is fairly easy to see that a distortion from equilateral to isosceles form will affect the MO energies \( E_1, E_2, \) and \( E_3 \) differently. In particular, a distortion of the sort depicted in Fig. 8.8 would have little effect on \( E_1 \), but would raise \( E_2 \) (increased antibonding) and lower \( E_3 \) (decreased antibonding and increased bonding). Thus, there is good reason for the cyclopropenyl radical to be more stable in an isosceles rather than equilateral triangular form. This is an example of the Jahn–Teller theorem, which states, in fact, that a system having an odd number of electrons in degenerate MOs will change its nuclear configuration in a way to remove the degeneracy. The preference of the cyclopropenyl radical for a shape less symmetrical than what we might have anticipated is frequently called "Jahn–Teller distortion."4

Many times we are interested in comparing the \( \pi \)-electron distribution in the bonds instead of on the atoms. In the integrated expression (8-46) are cross terms that vanish under the HMO assumption of zero overlap. But the overlaps are not actually zero, especially between AOs on nearest neighbors. Hence, we might view the factors \( 1/\sqrt{2} \) as indicating how much overlap charge is being placed in the \( C_1-C_2 \) and \( C_2-C_3 \) bonds by an electron in \( \phi_1 \). The \( C_1-C_3 \) bond is usually ignored because these atoms are not nearest neighbors and therefore have much smaller AO overlap. Since \( S_{12} = S_{23} = S_{ij} \) for neighbors \( i \) and \( j \) in any \( \pi \) system (assuming equal bond distances), we need not include \( S_{ij} \) explicitly in our bond index. If we proceed in this manner, two electrons in \( \phi_1 \) would then give us a "bond order" of \( 2/\sqrt{2} = 1.414 \). It is more convenient in practice to divide this number in half, because then the calculated \( \pi \)-bond order for ethylene turns out to be unity rather than two. Since ethylene has one \( \pi \)-bond, this can be seen to be a more sensible index.

As a result of these considerations, the \( \pi \)-bond order (sometimes called "mobile bond order") of the allyl radical is \( \sqrt{2}/2 = 0.707 \) in each bond. (Electrons in \( \phi_2 \) make no contribution to bond order since \( c_2 \) vanishes. This is consistent with the "nonbonding" label for \( \phi_2 \).)

Generalizing the argument gives, for \( p_{ij} \), the \( \pi \)-bond order between nearest-neighbor atoms \( i \) and \( j \):

\[
p_{ij} = \sum \frac{\text{all} \text{ MOs}}{n_k c_{1k} c_{jk} (8-48)}
\]
where the symbols have the same meanings as in Eq. (8-46). In cases in which partially filled degenerate MOs are encountered, the averaging procedure described in connection with electron densities must be employed for bond orders as well.

8.9 Some Simplifying Generalizations

Thus far we have presented the bare bones of the HMO method using fairly small systems as examples. If we try to apply this method directly to larger molecules, it is very cumbersome. A ten-carbon-atom system leads to a $10 \times 10$ HMO determinant. Expanding and solving this for roots and coefficients is tedious. However, there are some short cuts available for certain cases. In the event that the system is too complicated to yield to these, one can use computer programs which are readily available.

For straight chain and monocyclic planar, conjugated hydrocarbon systems, simple formulas exist for HMO energy roots and coefficients. Those are derivable from the very simple forms of the HMO determinants for such systems.\(^5\) We state the results without proof.

For a straight chain of $n$ unsaturated carbons numbered sequentially,
\[
x = -2 \cos[\frac{kn}{(n+1)}], \quad k = 1, 2, \ldots, n
\]  
(8-49)

\[
c_{ik} = \frac{1}{2}^{(n+1)/2} \sin[\frac{kn}{(n+1)}] \]  
(8-50)

where $l$ is the atom index and $k$ the MO index.

For a cyclic polyene of $n$ carbons,
\[
x = -2 \cos(\frac{2nk}{n}), \quad k = 0, 1, \ldots, n-1
\]  
(8-51)

\[
c_{ik} = n^{-1/2} \exp[2\pi ik/(n-1)], \quad i = \sqrt{-1}
\]  
(8-52)

The coefficients derived from Eq. (8-52) for monocyclic polyenes will be complex when the MO is one of a degenerate pair. In such cases one may take linear combinations of these degenerate MOs to produce MOs with real coefficients, if one desires.

There is also a diagrammatic way to find the energy levels for linear and monocyclic systems. Let us consider monocycles first. One begins by drawing a circle of radius $2|\beta|$. Into this circle inscribe the cycle, point down, as shown in Fig. 8-9 for benzene. Project sideways the points where the polygon intersects the circle. The positions of these projections correspond to the HMO energy levels if the circle center is assumed to be at $E = \alpha$ (see Fig. 8-9). The number of intersections at a given energy is identical to the degeneracy. The numerical values for $E$ are often obtainable from such a sketch by inspection or simple trigonometry.

For straight chains, a modified version of the above method may be used.

\(^5\) See Coulson [2].

---

For an $n$-carbon chain, inscribe a cycle with $2n + 2$ carbons into the circle as before. Projecting out all intersections except the highest and lowest, and ignoring degeneracies gives the proper roots. This is exemplified for the allyl system in Fig. 8-10.

Examination of the energy levels in Figs. 8-9 and 8-10 reveals that the orbital energies are symmetrically disposed about $E = \alpha$. Why is this so? Consider the allyl system. The lowest-energy MO has two bonding interactions. The highest-energy MO differs only in that these interactions are now antibonding. [See Fig. 8-5 and note that the coefficients in $\phi_1$ and $\phi_2$ are identical except for sign in Eqs. (8-27) and (8-29).] The role of the $\beta$ terms is thus reversed and so they act to raise the orbital energy for $\phi_1$ just as much as they lower it for $\phi_1$. A similar situation holds for benzene. As we will see shortly, the lowest energy corresponds to an MO without nodes between atoms, so this is a totally bonding MO. The highest-energy MO has nodal planes between all neighbor carbons, and so every interaction is antibonding. An analogous argument holds for the degenerate pairs of benzene MOs. These observations suggest that the energy of an MO should be expressible as a function of the net bond order.

---

FIG. 8-9 HMO energy levels for benzene produced by projecting intersections of hexagon with a circle of radius $2|\beta|$.

FIG. 8-10 HMO energy levels for allyl system ($n = 3$) produced by projecting the intersections of octagon ($n = 2 \times 3 + 2$) with a circle of radius $2|\beta|$.
associated with it, and this is indeed the case. The energy of the \( i \)th MO is given by the expression

\[
E_i = \int \phi_i \hat{H} \phi_i \, dv = \sum_k c_{ki} \chi_k \hat{H} \sum_i c_{ii} \chi_i \, dv
\]

(8-53)

\[
= \sum_k \sum_i c_{ki} c_{ii} \int \chi_k \hat{H} \chi_i \, dv
\]

(8-54)

When the atom indices \( k \) and \( l \) are identical, the integral is equal to \( \alpha \); when \( k \) and \( l \) are neighbors, it equals \( \beta \). Otherwise it vanishes. Hence, we may write

\[
E_i = \sum_k c_{ki}^2 \alpha + \sum_{\text{neighbors}} c_{ki} c_{li} \beta
\]

(8-55)

However, \( c_{ki}^2 \) is the electron density at atom \( k \) due to one electron in MO \( \phi_i \), and \( c_{ki} c_{li} \) is \( p_{kl,i} \), the bond order between atoms \( k \) and \( l \) due to an electron in \( \phi_i \). Therefore,

\[
E_i = \sum_k q_{ki} \alpha + 2 \sum_{\text{neighbors}} p_{kl,i} \beta
\]

(8-56)

We have seen that the sum of electron densities must equal the total number of electrons present. For one electron in \( \phi_i \), this gives additional simplification.

\[
E_i = \alpha + 2 \beta \sum_{\text{bonds}} p_{kl,i}
\]

(8-57)

The total \( \pi \)-electron energy is the sum of one-electron energies. For \( n \) \( \pi \) electrons

\[
E_\pi = n \alpha + 2 \beta \sum_{\text{bonds}} p_{kl,i}
\]

(8-58)

where \( p_{kl,i} \) is the total \( \pi \)-bond order between neighbors \( k \) and \( l \). Hence, the individual orbital energies directly reflect the amount of bonding or antibonding described by the MOs, and the total energy reflects the net bonding or antibonding due to all the \( \pi \) electrons together.

Does this "pairing" of energy levels observed for allyl and benzene always occur? It is easy to show that it cannot in rings with an odd number of carbon centers. Consider the cyclopentenyl system. The lowest-energy MO is nodeless, totally bonding and has an energy of \( \alpha + 2\beta \). [Note from Eq. (8-51) and also from the diagram method that every monocyclic system has a totally bonding MO at this energy.] To transform these three bonding interactions into antibonding interactions of equal magnitude requires that we cause a sign reversal across every bond. This is impossible, for, if \( c_1 \) disagrees in sign with \( c_2 \) and \( c_3 \), then \( c_2 \) and \( c_3 \) must agree in sign and cannot yield an antibonding interaction.

Not surprisingly, this has all been considered in a rigorous mathematical fashion. Systems containing a ring with an odd number of atoms are "nonalternant" systems. All other homonuclear unsaturated systems are "alternant" systems. An alternant system can always have asterisks placed on some of the centers so that no two neighbors are both asterisked or unasterisked. For nonalternants, this is not possible (see Fig. 8-11). It is convenient to subdivide alternant systems into even alternants or odd alternants according to whether the number of centers is even or odd. With this terminology defined, we can now state the pairing theorem and some of its immediate consequences.

The theorem states that, for alternant systems, (1) energy levels are paired such that, for each level at \( \epsilon = \alpha + k\beta \) there is a level at \( \epsilon = \alpha - k\beta \); (2) MOs that are paired in energy differ only in the signs of the coefficients for one of the sets (asterisked or unasterisked) of AOs.

It is easy to see that an immediate result of this theorem is that an odd-alternant system, which must have an odd number of MOs, must have a nonbonding \( (E = \alpha) \) MO that is not paired with another MO. It is also possible to show that the electron density is unity at every carbon for the neutral ground state of an alternant system. The proofs of the pairing theorem and some of its consequences are given in Appendix 5.

Another useful short cut exists that enables one to sketch qualitatively the MOs for any linear polynye. The HMOs for the allyl and butadiene systems are given in Fig. 8-12. Notice that the envelopes of positive (or negative) sign in these MOs are similar in appearance to the particle in a one-dimensional "box" solutions described in Chapter 2. This similarity makes it fairly easy to guess the first few MOs for pentadieny1, hexatriene, etc. Also, if one knows the lowest-energy half of the MOs for such molecules, one can generate the remaining MOs by appeal to the second part of the pairing theorem. (The edges of the one-dimensional box should extend one C-C bond length beyond the terminal atoms.)

For larger, more complicated systems, like naphthalene, it is possible to use symmetry properties of the molecule to help choose a basis of symmetry orbitals. As was mentioned in our discussion of homonuclear diatomic molecules, this has the effect of partitioning the secular determinant into a set of smaller determinants, thereby making the problem computationally less tedious. This
8. THE SIMPLE HÜCKEL METHOD AND APPLICATIONS

FIG. 8-12 MOs for the allyl and butadiene systems. The dashed lines emphasize the similarity between an envelope, or contour, of positive $\psi_+$ for these systems and the particle in a one-dimensional box solutions.

procedure is described by Streitwieser [3] and Levine [4] and will not be described here since, in recent times, it has become common practice to do only the simplest HMO calculations by hand. Complicated systems are subjected to solution by computer6 or else by appeal to HMO tabulations in print.7

8-10 HMO Calculations on Some Simple Molecules

Thus far, we have used the allyl and cyclopropenyl systems as examples. We will now describe the results of HMO calculations on some other simple but important systems.

A. Ethylene (Even Alternant)

The Hückel determinantal equation is

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

6 Many types of quantum-chemical computer programs are available from: Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana, 47401.

7 See Coulson and Streitwieser [5], Streitwieser and Brauman [6], and Heilbronner and Straub [7]. See also Appendix 6 of this text.

and so $x^2 - 1 = 0; x = +1, -1$. The resulting orbital energies and coefficients are

$$E_1 = \alpha + \beta, \quad \phi_1 = (1/\sqrt{2})\chi_1 + (1/\sqrt{2})\chi_2$$
$$E_2 = \alpha - \beta, \quad \phi_2 = (1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_2$$

These, with the ground state electronic configuration indicated, are shown in (II). $\pi$-Electron densities and $\pi$-bond order are indicated in the diagram beneath the MO sketches. Ethylene is an even alternant, so it has paired energies, unit electron densities, and coefficients related by a sign change.

$$E_4 = \alpha - \beta$$

$$E_1 = \alpha + \beta$$

$$E_x = 2\alpha + 2.00\beta$$

(II)

B. Butadiene (Even Alternant)

This problem can be solved by expansion to a polynomial in $x$ and factoring, but it is simpler to use Eq. (8-49) or the decagon in a circle of radius $2|\beta|$. The coefficients are obtainable from Eq. (8-50). The results are

$$E_4 = \alpha - 1.618\beta, \quad E_5 = \alpha - 0.618\beta, \quad E_2 = \alpha + 0.618\beta,$$

$$E_1 = \alpha + 1.618\beta, \quad E_n = 4\alpha + 4.472\beta$$

$$\phi_1 = 0.372\chi_1 + 0.602\chi_2 + 0.602\chi_3 + 0.372\chi_4$$

$$\phi_2 = 0.602\chi_1 + 0.372\chi_2 - 0.372\chi_3 - 0.602\chi_4$$

(8-60)

$$\begin{bmatrix}
0.894 & 0.447 & 0.894 \\
1 & 1 & 1
\end{bmatrix}$$
The MOs are given in Fig. 8.12. \( \phi_1 \) is bonding in all bonds, \( \phi_2 \) is bonding in the outer bonds, antibonding in the central bond. As a result, butadiene has a lower \( \pi \)-bond order in the central bond than in the outer bonds. This is in pleasing accord with the experimental observation that the central bond in butadiene is significantly longer than the outer bonds.

The formal structural formula for butadiene (III), indicating two pure double bonds and one pure single bond, is clearly not an adequate description since we have just found the central bond to have some \( \pi \)-bonding order (0.447) and the outer bonds to be less \( \pi \) bonding than ethylene (0.894). The MO parlance is that the \( \pi \) electrons in butadiene are delocalized over the entire carbon system rather than being restricted to the formal double bonds only.

Because the HMO method allows for no interaction between terminal carbons (i.e., \( H_{1,4} = 0 \)), there is no distinction between cis- and trans-butadiene in this calculation. However, if a weak interaction were postulated, it is not difficult to see that \( \phi_1 \) would give a bonding end-to-end contribution, \( \phi_2 \) a substantially larger antibonding interaction, leading to a prediction (in agreement with experiment) that trans-butadiene is the more stable form.

C. Cyclobutadiene (Even Alternant)

Inscribing this molecule in a circle gives us the orbital energies immediately (IV).

\[
E_4 = \alpha - 2\beta \\
E_{2,\alpha} = \alpha \\
E_1 = \alpha + 2\beta \\
E_\alpha = 4\alpha + 4\beta
\]

Since \( \phi_1 \) and \( \phi_4 \) are nondegenerate, they must be symmetric or antisymmetric for the various rotations and reflections of the molecule. Also, \( \phi_1 \) and \( \phi_4 \) must have the same coefficients, except for sign changes.

It follows at once that

\[
\phi_1 = \frac{x_1}{2} + \frac{x_2}{2} + \frac{x_3}{2} + \frac{x_4}{2}, \quad \phi_4 = \frac{x_1}{2} - \frac{x_2}{2} + \frac{x_3}{2} - \frac{x_4}{2}
\]

\( \phi_2 \) and \( \phi_3 \) are degenerate, so there is some arbitrariness here. However, we expect each of these MOs to have a nodal plane, and these planes should be perpendicular to each other if \( \phi_2 \) and \( \phi_3 \) are to be orthogonal. Therefore, we choose the pair having nodal planes indicated by dashed lines (V). The four MOs for cyclobutadiene as seen from above are shown in (VI). It is clear that \( \phi_2 \) and \( \phi_3 \) are nonbonding because the nodal planes prevent interactions between neighbors, but it looks like \( \phi_2 \) and \( \phi_3 \) violate the pairing theorem since they cannot be interchanged by changing signs of coefficients. This is only an apparent violation, because it is easy to find an equivalent pair of MOs that follow the rule. We need only choose nodal planes that are rotated 45° (VII) from those we selected previously. These MOs are linear combinations of \( \phi_2 \) and \( \phi_3 \) and are equivalent to them for purposes of calculating electron densities and bond orders. They are still nonbonding MOs (E still equals \( \alpha \)), but now it is not because of a nodal plane preventing nearest-neighbor interactions, but because bonding and antibonding interactions occur in equal number and magnitude.

Notice that this is an example of an even alternant system with nonbonding MOs. Thus, whereas an odd alternant system must have an unpaired nonbonding MO, even alternants may have nonbonding MOs in pairs.
Since this system is alternant, it must have π-electron densities of unity in its ground neutral state. This would be necessary however, even if the molecule were not alternant, due to the fact that all carbons are equivalent by symmetry. Hence, they must all have the same electron density. Since it must sum to four electrons, the density of each atom must be unity. The same argument applies to the cyclopropenyl radical, a nonalternant; that, nevertheless, has all electron densities equal to unity (if the unpaired electron is divided between degenerate MOs).

Symmetry also requires all four bonds to be identical. Since the total energy, \(4\alpha + 4\beta\), is related to bond order through Eq. (8-58), it follows at once that the total bond order is 2, and so each bond has order \(\frac{1}{2}\).

**D. Benzene (Even Alternant)**

Benzene is another molecule whose high symmetry enables one to use shortcuts. The orbital energies have already been found from the hexagon-in-a-circle diagram (see Fig. 8-9). The lowest- and highest-energy MOs must show all the symmetry of the molecule, as they are nondegenerate. Therefore,

\[
\phi_1^{(6)} = (1/\sqrt{6})(\chi_1(-) + \chi_2(-) + \chi_3(-) + \chi_4 - \chi_5 + \chi_6)
\]

where the carbon atoms are numbered sequentially around the ring.

The degenerate MOs \(\phi_2\) and \(\phi_3\) should have one nodal plane each, and these should be perpendicular to each other.\(^8\) If we take one plane as shown in (VIII), we can immediately write down \(\phi_2\). The node for \(\phi_3\) is given in (IX). It is obvious that \(\chi_6\), \(\chi_5\), \(\chi_2\) have coefficients of the same sign, and that \(c_2 = c_6 = -c_5 = -c_3\), and also \(c_1 = -c_4\). However, \(c_1\) need not equal \(c_2\) as these atoms are differently placed with respect to the nodal plane. To determine these coefficients, we will use the fact that the neutral ground-state π densities are all unity in this system. We consider first atom number 1. Its electron density due to two electrons in \(\phi_1\) and two electrons in \(\phi_2\) is \(\frac{1}{6} + \frac{1}{6} + 0 + 0 = \frac{1}{3}\).

\[
\phi_2 = \frac{1}{2}(\chi_2 + \chi_3 - \chi_4)
\]

(VIII)

(IX)

Therefore, two electrons in \(\phi_3\) must produce a contribution of \(\frac{2}{3}\). Hence the coefficient for this atom in \(\phi_3\) must be \(1/\sqrt{3}\). A similar argument for atom 2 gives a coefficient of \(1/\sqrt{12}\) (or, one can use the normality condition for \(\phi_3\)). As a result,

\[
\phi_3^{(5)} = (1/\sqrt{3})(\chi_1(-) + \chi_2(-) - \chi_3(-) + \chi_4 - \chi_5 + \chi_6)
\]

Appeal to the pairing theorem generates \(\phi_4\) and \(\phi_5\), as indicated.

By symmetry, all bond orders must be identical, and their sum must be 4, since \(E = 6\alpha + 8\beta\). Therefore, \(P_{12} = P_{23} = \cdots = P_{61} = \frac{4}{6} = 0.667\).

The hexagon in a circle applies to ethylene \((n = 2, 2n + 2 = 6)\) as well as to benzene. As a result, the orbital energies for \(\phi_2, \phi_3\) of benzene are identical to \(E_1\) for ethylene. Examination of these MOs (Fig. 8-13) makes the reason for their energy agreement clear. Molecular orbital \(\phi_2\) of benzene is more revealing than \(\phi_1\) in this context. The nodal plane produces an MO corresponding to two noninteracting ethylene MOs. Hence, an electron in this MO is always in a situation that is indistinguishable (under HMO approximations) from that in \(\phi_1\) of ethylene.

**FIG. 8-13** \(\phi_2\) for benzene and \(\phi_1\) for ethylene have the same HMO energy. The MOs are sketched as seen from above.

In this section, we have tried to illustrate some of the properties of HMO solutions for simple systems and to indicate how symmetry and other relations are useful in producing and understanding HMO results. It is often convenient to have HMO results for various simple systems readily available in a condensed form. Therefore, a summary of results for a number of molecules is provided in Appendix 6.

**8-11 Summary: The Simple HMO Method for Hydrocarbons**

1. The assumption is made that the π-electron energy can be minimized independently of σ electrons. This is an approximation.

2. The assumption is made that each π electron sees the same field (the repulsion due to the other π electrons is presumably included “in effect,” in a time averaged way) so that the π electrons are treated as independent particles. This approximation leads to a total wavefunction that is a simple product of one-electron MOs and a total π energy that is a sum of one-electron energies. Except for use of the Pauli principle to build up configurations, no explicit treatment is made of electron spin.
The basis set is chosen to be a $2p_x$ AO from each carbon atom in the unsaturated system. Choosing a basis set of AOs means our MOs will be linear combinations of AOs, and so this is an LCAO–MO method.

(4) The Hückel determinant summarizes the connectedness of the unsaturated system, and is independent of cis–trans isomerism or bond length variation.

(5) The energy of each MO is expressed in terms of atomic terms, $\alpha$, and bond terms, $\beta$. The amount of $\alpha$ in each MO energy is always unity because the sum of $\pi$-electron densities for one electron in the MO is always unity. The amount of $\beta$ present is related to the net bonding or antibonding character of the MO.

(6) Alternant systems display paired energy levels and corresponding MOs having coefficients related by simple sign reversals. For ground-state neutral alternants, the electron densities are all unity.

(7) A caveat: One can perform HMO calculations on very large systems such as pentahelicene (X) thereby making the implicit assumption that this is a planar molecule. But repulsion between protons on the terminal rings is sufficient to cause this molecule to deviate from planarity. Hence, one must recognize that, in certain cases, an HMO calculation refers to a planar "ideal" not actually achieved by the molecule.

8-12 Relation between Bond Order and Bond Length

In this and following sections we will describe some of the relations between HMO theoretical quantities and experimental observations.\textsuperscript{9}

It is natural to look for a correlation between calculated $\pi$-bond orders and experimentally determined bond lengths. A high bond order should correspond to a large $\pi$ charge in the bond region, which should yield a shorter, stronger bond. The bond-order–bond-length results for certain simple systems, given as a graph in Fig. 8-14, do indeed show the anticipated behavior. However, as more and more data are added (Fig. 8-15) it becomes clear that an exact linear relation between these quantities does not exist at this level of refinement. Efforts to improve the situation by refining the theory have been made, but the relatively large uncertainty in experimentally determined bond lengths has been a severe handicap. Nevertheless, the correlation between bond order and bond length is good enough to make it useful for rough predictions of bond length variations. An example of this is given in Fig. 8-16, where calculated and observed bond

\textsuperscript{9}For a more complete discussion of these phenomena as well as many others, see Streitwieser