

The Simple Hückel Method and Applications

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 that 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 that 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 σ - π 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 σ , π , δ , ... depending on whether the MOs are associated with an m quantum number of 0, ± 1 , ± 2 , ... Thus, in acetylene (C_2H_2), the minimal basis set of AOs on carbon and hydrogen lead to σ and π MOs. Let us imagine that our acetylene molecule is aligned along the z Cartesian axis. Then the p_x π -type AOs on the carbons are antisymmetric for reflection through a plane containing the molecular axis and the y axis. Similarly, the p_y π -type AOs are antisymmetric for reflection through a plane containing the molecular axis and the x axis. The p_z AOs, which are σ -type functions, are symmetric for reflection through any plane containing

the molecular axis. It has become standard practice to carry over the σ - π terminology to planar (but nonlinear) molecules, where m is no longer a "good" quantum number. In this expanded usage, a π orbital is one that is antisymmetric for reflection through the plane of the molecule, a σ orbital being symmetric for that reflection.

Hückel found that, by treating only the π 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 π electrons.

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

$$E_{\text{tot}} = E_{\sigma} + E_{\pi} \quad (8-1)$$

where E_{tot} is taken to be the electronic energy E_{el} plus the internuclear repulsion energy V_{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)

$$\psi(1, \dots, n) = \psi_{\pi}(1, \dots, k) \psi_{\sigma}(k+1, \dots, n) \quad (8-2)$$

and our hamiltonian should be separable into π and σ parts:

$$\hat{\mathcal{H}}(1, 2, \dots, n) = \hat{\mathcal{H}}_{\pi}(1, 2, \dots, k) + \hat{\mathcal{H}}_{\sigma}(k+1, \dots, n) \quad (8-3)$$

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

$$\begin{aligned} \bar{E} &= \frac{\int \psi_{\pi}^* \psi_{\sigma}^* (\hat{\mathcal{H}}_{\pi} + \hat{\mathcal{H}}_{\sigma}) \psi_{\pi} \psi_{\sigma} d\tau(1, \dots, n)}{\int \psi_{\pi}^* \psi_{\sigma}^* \psi_{\pi} \psi_{\sigma} d\tau(1, \dots, n)} \\ &= \frac{\int \psi_{\pi}^* \hat{\mathcal{H}}_{\pi} \psi_{\pi} d\tau(1, \dots, k)}{\int \psi_{\pi}^* \psi_{\pi} d\tau(1, \dots, k)} + \frac{\int \psi_{\sigma}^* \hat{\mathcal{H}}_{\sigma} \psi_{\sigma} d\tau(k+1, \dots, n)}{\int \psi_{\sigma}^* \psi_{\sigma} d\tau(k+1, \dots, n)} \\ &= E_{\pi} + E_{\sigma} \end{aligned} \quad (8-4)$$

If these equations were valid, one could ignore ψ_{σ} and legitimately minimize E_{π} by varying ψ_{π} . But the equations are *not* valid because it is impossible to rigorously satisfy Eq. (8-3). We cannot define $\hat{\mathcal{H}}_{\pi}$ and $\hat{\mathcal{H}}_{\sigma}$ so that they individually depend completely on separate groups of electrons and still sum to the correct total hamiltonian. Writing these operators explicitly gives

$$\hat{\mathcal{H}}_{\pi}(1, \dots, k) = -\frac{1}{2} \sum_{i=1}^k \nabla_i^2 + \sum_{i=1}^k V_{\text{ne}}(i) + \frac{1}{2} \sum_{i=1}^k \sum_{j=1, j \neq i}^k \frac{1}{r_{ij}} \quad (8-5)$$

$$\hat{\mathcal{H}}_{\sigma}(k+1, \dots, n) = -\frac{1}{2} \sum_{i=k+1}^n \nabla_i^2 + \sum_{i=k+1}^n V_{\text{ne}}(i) + \frac{1}{2} \sum_{i=k+1}^n \sum_{j=k+1, j \neq i}^n \frac{1}{r_{ij}} + V_{\text{nn}} \quad (8-6)$$

where $V_{ne}(i)$ 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 σ and π electrons:

$$\hat{\mathcal{H}} - \hat{\mathcal{H}}_\pi - \hat{\mathcal{H}}_\sigma = \sum_{i=1}^k \sum_{j=k+1}^n \frac{1}{r_{ij}} \quad (8-7)$$

In short, the σ and π 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 σ - π interactions is included *implicitly* in the method, as we shall see shortly.

8-3 The Independent π -Electron Assumption

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

$$\psi_\pi(1, 2, \dots, n) = \phi_1(1)\phi_2(2) \dots \phi_n(n) \quad (8-8)$$

$$\hat{\mathcal{H}}_\pi(1, 2, \dots, n) = \hat{H}_\pi(1) + \hat{H}_\pi(2) + \dots + \hat{H}_\pi(n) \quad (8-9)$$

and

$$\frac{\int \phi_i^*(1) \hat{H}_\pi(1) \phi_i(1) d\tau(1)}{\int \phi_i^*(1) \phi_i(1) d\tau(1)} \equiv E_i \quad (8-10)$$

It follows that the total π energy E_π is a sum of one-electron energies:

$$E_\pi = E_i + E_j + \dots + E_l \quad (8-11)$$

This means that the π electrons are being treated as though they are independent of each other, since E_i depends only on ϕ_i and is not influenced by the presence or absence of an electron in ϕ_j . However, this cannot be correct because π 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 π one-electron hamiltonian operator $\hat{H}_\pi(i)$. (We *cannot* write it down because it results from a π - σ separability assumption and an independent π -electron assumption, and both assumptions are incorrect.) $\hat{H}_\pi(i)$ 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 ψ_π 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.

EXAMPLE 8-1 If O_2 were treated by the HMO method, what would be the form of the wavefunction and energy for the ground state?

SOLUTION ▶ The ground state configuration for O_2 is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,x}^2 1\pi_{u,y}^2 \times 1\pi_{g,x} 1\pi_{g,y}$, where we have shown the degenerate members of π levels explicitly and in their real forms. The HMO wavefunction is simply a product of the pi MOs, one for each of the six pi electrons: $1\pi_{u,x}(1)1\pi_{u,x}(2)1\pi_{u,y}(3)1\pi_{u,y}(4)1\pi_{g,x}(5)1\pi_{g,y}(6)$. The HMO energy is $2E_{\pi,u,x} + 2E_{\pi,u,y} + E_{\pi,g,x} + E_{\pi,g,y}$, which reduces to $4E_{\pi,u} + 2E_{\pi,g}$. Note that, because O_2 is linear, there is no unique molecular plane containing the internuclear axis. Therefore this molecule has two sets of π MOs, one pair pointing in the x direction, the other pair pointing along y . For a planar molecule, only one of these pairs would qualify as π MOs, as will be seen in the next section. ◀

8-4 Setting up the Hückel Determinant

8-4.A Identifying the Basis Atomic Orbitals and Constructing a Determinant

The allyl radical, C_3H_5 , is a planar molecule¹ 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.

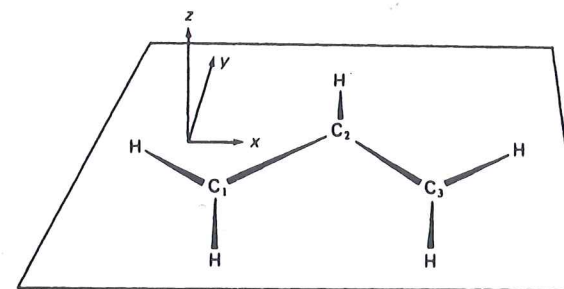


Figure 8-1 ▶ Sketch of the nuclear framework for the allyl radical. All the nuclei are coplanar. The z axis is taken to be perpendicular to the plane containing the nuclei.

¹The minimum energy conformation of the allyl system is planar. We will ignore the deviations from planarity resulting from vibrational bending of the system.

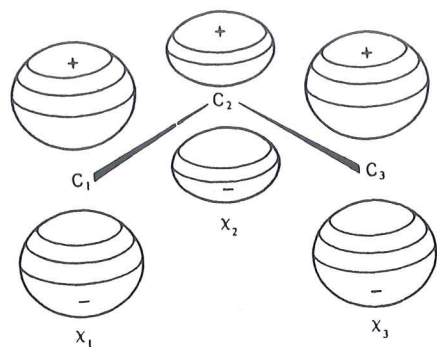


Figure 8-2 ► The three π -type AOs in the minimal basis set of the allyl radical.

Following Hückel, we ignore all the σ -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 χ_1, χ_2, χ_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 3×3 determinant having roots that are MO energies which can be used to obtain MO coefficients. The determinantal equation is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix} = 0 \quad (8-12)$$

where

$$H_{ij} = \int \chi_i \hat{H}_\pi \chi_j dv \quad (8-13)$$

$$S_{ij} = \int \chi_i \chi_j dv \quad (8-14)$$

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).

8-4.B The Quantity α

We have already indicated that there is no way to write an explicit expression for \hat{H}_π that is both consistent with our separability assumptions and physically correct. But, without an expression for \hat{H}_π , 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_{11} , for instance, is the average energy of an electron in AO χ_1 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 χ_2 experiences a different

environment than it does when in χ_1 or χ_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_{ii} are identical if χ_i is on a carbon atom. The symbol α is used for such integrals. Thus, for the example at hand, $H_{11} = H_{22} = H_{33} = \alpha$. The quantity α is often called the *coulomb integral*.²

8-4.C The Quantity β

Next, we consider the *resonance integrals* or *bond integrals* H_{12}, H_{23} , and H_{13} . (The requirement that \hat{H}_π be hermitian plus the fact that the χ 's and \hat{H}_π 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 χ_1 and χ_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 β) when i and j refer to "neighbors" (i.e., atoms connected by a σ bond). It is further assumed that $H_{ij} = 0$ when i and j are not neighbors. Therefore, in the allyl case,

$$H_{12} = H_{23} \equiv \beta, H_{13} = 0.$$

8-4.D Overlap Integrals

Since the χ '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.

8-4.E Further Manipulation of the Determinant

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

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

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

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

²The term "coulomb integral" for α is unfortunate since the same name is used for repulsion integrals of the form $\int \chi_1(1)\chi_2(2)(1/r_{12})\chi_1(1)\chi_2(2)dv$. The quantity α also contains kinetic energy and nuclear-electronic attraction energy.

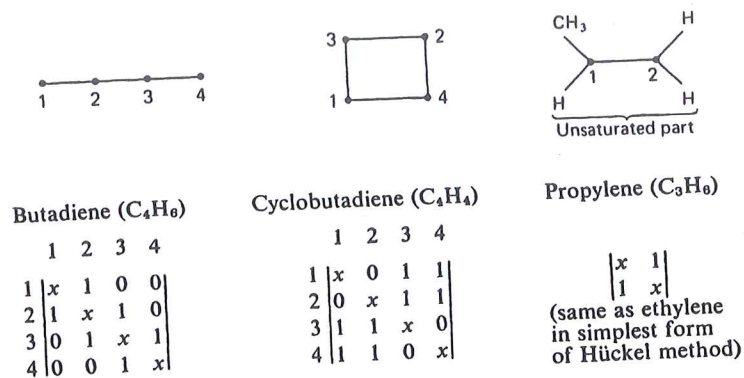


Figure 8-3 ► HMO determinants for some small systems.

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, ..., 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 that 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

$$x^3 - 2x = 0 \quad (8-17)$$

or

$$x(x^2 - 2) = 0 \quad (8-18)$$

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 α 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 β 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.

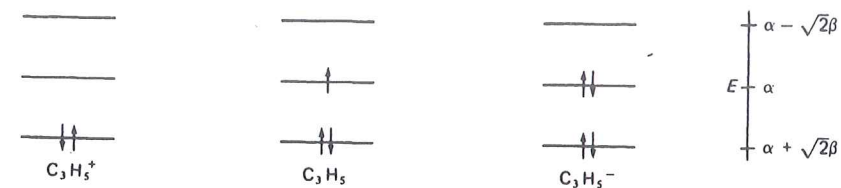


Figure 8-4 ► π -Electron configurations and total energies for the ground states of the allyl cation, radical, and anion.

(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 π -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 π electrons in the system, our results so far apply equally well for the allyl cation, radical, or anion.

Configurations and total π energies for these systems in their ground states are depicted in Fig. 8-4. The total π -electron energies are obtained by summing the one-electron energies, as indicated earlier.

EXAMPLE 8-2 For a planar, unsaturated hydrocarbon having formula C_xH_y , where all the carbons are part of the unsaturated framework, how many pi MOs are there?

SOLUTION ► Each carbon atom brings one $2p_\pi$ AO into the basis set, so there are x basis AOs. These x independent AOs mix to form x independent MOs. ◀

8-6 Solving for the Molecular Orbitals

We still have to find the coefficients that 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

$$c_1x + c_2 = 0 \quad (8-19)$$

$$c_1 + c_2x + c_3 = 0 \quad (8-20)$$

$$c_2 + c_3x = 0 \quad (8-21)$$

(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, the latter step 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

$$-\sqrt{2}c_1 + c_2 = 0 \quad (8-23a)$$

$$c_1 - \sqrt{2}c_2 + c_3 = 0 \quad (8-23b)$$

$$c_2 - \sqrt{2}c_3 = 0 \quad (8-23c)$$

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

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

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

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

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

These coefficients define our lowest-energy MO, ϕ_1 :

$$\phi_1 = \frac{1}{2}\chi_1 + \frac{1}{\sqrt{2}}\chi_2 + \frac{1}{2}\chi_3 \quad (8-27)$$

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

$$(x = 0): \quad \phi_2 = \frac{1}{\sqrt{2}}\chi_1 - \frac{1}{\sqrt{2}}\chi_3 \quad (8-28)$$

$$(x = +\sqrt{2}): \quad \phi_3 = \frac{1}{2}\chi_1 - \frac{1}{\sqrt{2}}\chi_2 + \frac{1}{2}\chi_3 \quad (8-29)$$

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

The lowest-energy MO, ϕ_1 , has no nodes (other than the molecular-plane node common to all π 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 β acts to lower the energy, as is true here. The second-lowest energy MO, ϕ_2 , has a nodal plane at the central carbon. Because there are no π AOs on neighboring carbons in this MO, there are no interactions at all, and β is absent from the energy expression. This MO is said to be *nonbonding*. The high-energy MO, ϕ_3 has nodal planes intersecting both bonds. Because the π AOs show sign disagreement across both bonds, this MO is everywhere antibonding and β terms act to raise the orbital energy above α .

EXAMPLE 8-3 According to HMO theory, do the π electrons favor a linear, or a bent allyl radical?

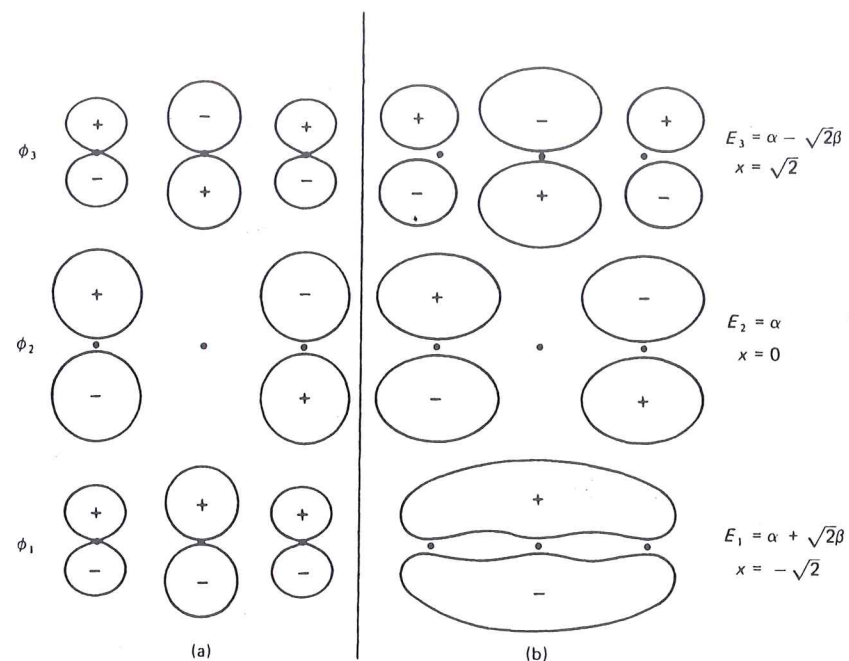


Figure 8-5 ► Sketches of the allyl system MOs. (a) emphasizes AO signs and magnitudes. (b) resembles more closely the actual contours of the MOs.

SOLUTION ► HMO theory favors neither. The difference between linear and bent allyl shows up as a difference in $C_1 - C_2 - C_3$ angle and in C_1 to C_3 distance. The HMO method has no angular-dependent features and explicitly omits interactions between non-neighbor carbons, like C_1 and C_3 .

8-7 The Cyclopropenyl System: Handling Degeneracies

The allyl system results when three π 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 π 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 C_3H_3 shown in Fig. 8-6.

The HMO determinantal equation for this system is

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0, \quad x^3 + 2 - 3x = 0 \quad (8-30)$$

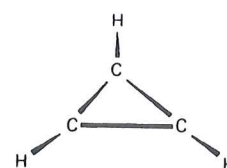


Figure 8-6 ► The cyclopropenyl system (all nuclei are coplanar).

This equation can be factored as

$$(x+2)(x-1)(x-1) = 0 \quad (8-31)$$

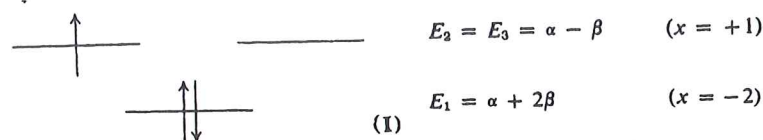
Therefore, the roots are $x = -2, +1, +1$.

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 π electrons) (I) gives a total E_π of $3\alpha + 3\beta$. We can surmise from these orbital energies that ϕ_1 is a bonding MO, whereas ϕ_2 and ϕ_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

$$\begin{aligned} c_1x + c_2 + c_3 &= 0 \\ c_1 + c_2x + c_3 &= 0 \\ c_1 + c_2 + c_3x &= 0 \\ c_1^2 + c_2^2 + c_3^2 &= 1 \end{aligned} \quad (8-32)$$

Setting $x = -2$ and solving gives

$$\phi_1 = \frac{1}{\sqrt{3}}\chi_1 + \frac{1}{\sqrt{3}}\chi_2 + \frac{1}{\sqrt{3}}\chi_3 \quad (8-33)$$



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

To find ϕ_2 and ϕ_3 is trickier. We begin by inserting $x = \pm 1$ into our simultaneous equations. This gives

$$c_1 + c_2 + c_3 = 0 \quad (\text{three times}) \quad (8-34)$$

$$c_1^2 + c_2^2 + c_3^2 = 1 \quad (8-35)$$

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 ϕ_2 :

$$\phi_2 = \frac{1}{\sqrt{2}}\chi_1 - \frac{1}{\sqrt{2}}\chi_2 \quad (8-36)$$

We still need to find ϕ_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 ϕ_2 to choose c 's that guarantee a normalized ϕ_3 . Also, it is clear that ϕ_3 is linearly independent of

ϕ_2 since they contain different AOs. But it is desirable to have ϕ_3 orthogonal to ϕ_2 . Let us test ϕ_2 and ϕ_3 to see if they are orthogonal:

$$\begin{aligned} S &= \int \phi_2 \phi_3 dv = \frac{1}{2} \int (\chi_1 - \chi_2)(\chi_1 - \chi_3) dv \\ &= \frac{1}{2} \left\{ \int \chi_1^2 dv - \int \chi_1 \chi_3 dv - \int \chi_1 \chi_2 dv + \int \chi_2 \chi_3 dv \right\} = \frac{1}{2} \end{aligned} \quad (8-37)$$

Since $S \neq 0$, ϕ_2 and ϕ_3 are nonorthogonal. We can project out that part of ϕ_3 that is orthogonal to ϕ_2 by using the Schmidt orthogonalization procedure described in Section 6-10. We seek a new function ϕ_3' given by

$$\phi_3' = \phi_3 - S\phi_2 \quad (8-38)$$

where

$$S = \int \phi_2 \phi_3 dv = \frac{1}{2} \quad (8-39)$$

Therefore,

$$\phi_3' = \phi_3 - \frac{1}{2}\phi_2 = \frac{1}{2\sqrt{2}}(\chi_1 + \chi_2 - 2\chi_3) \quad (8-40)$$

This function is orthogonal to ϕ_2 but is not normalized. Renormalizing gives

$$\phi_3'' = \frac{1}{\sqrt{6}}(\chi_1 + \chi_2 - 2\chi_3) \quad (8-41)$$

In summary, to produce HMO coefficients for degenerate MOs, pick any two independent solutions from the infinite choice available, and orthogonalize one of them to the other 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 ϕ_2 can be seen to have both antibonding (C_1-C_2) and nonbonding (C_1-C_3, C_2-C_3) interactions. ϕ_3'' has antibonding (C_1-C_3, C_2-C_3) and bonding (C_1-C_2) interactions. The interactions are of such size and number as to give an equal net energy value ($\alpha - \beta$) in each case. Since nodal planes produce antibonding or nonbonding situations, it is not surprising that higher and higher-energy HMOs in a

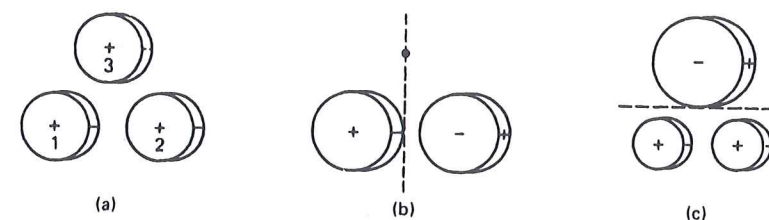


Figure 8-7 ▶ The HMOs for the cyclopropenyl system: (a) $\phi_1 = (1/\sqrt{3})(\chi_1 + \chi_2 + \chi_3)$; (b) $\phi_2 = (1/\sqrt{2})(\chi_1 - \chi_2)$ (c) $\phi_3'' = (1/\sqrt{6})(\chi_1 + \chi_2 - 2\chi_3)$. The nodal planes intersect the molecular plane at the dashed lines.

system display more and more nodal planes. Notice that the MOs ϕ_2 and ϕ_3'' have the same number of nodal planes (one, not counting the one in the molecular plane) but that these planes are perpendicular to each other. This is a common feature of some degenerate, orthogonal MOs in cyclic molecules.

It is important to notice the symmetry characteristics of these MOs. ϕ_1 is either symmetric or antisymmetric for every symmetry operation of the molecule. (It is antisymmetric for reflection through the molecular plane, symmetric for rotation about the threefold axis, etc.) This must be so for any nondegenerate MO. But the degenerate MOs ϕ_2 and ϕ_3'' are neither symmetric nor antisymmetric for certain operations. (ϕ_2 is antisymmetric for reflection through the plane indicated by the dashed line in Fig. 8-7, but is neither symmetric nor antisymmetric for rotation about the threefold axis by 120° .) In fact, one can easily show that, given a cycle with an odd number of centers, each with one AO of a common type, there is but *one* way to combine the AOs (to form a *real* MO) so that the result is symmetric or antisymmetric for all rotations and reflections of the cycle. Hence, an HMO calculation for a three-, five, seven-, ... membered ring can give only *one* nondegenerate MO. However, for a cycle containing an *even* number of centers, the analogous argument shows that *two* nondegenerate MOs exist.

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 ψ_π . In the case of the neutral allyl radical, we have (taking ψ_π to be a simple product of MOs)

$$\psi_\pi = \phi_1(1)\phi_1(2)\phi_2(3) \quad (8-42)$$

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

$$\psi_\pi^2(1, 2, 3)dv(1)dv(2)dv(3) = \phi_1^2(1)\phi_1^2(2)\phi_2^2(3)dv(1)dv(2)dv(3) \quad (8-43)$$

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* ρ for the allyl radical is

$$\rho = 2\phi_1^2 + \phi_2^2 \quad (8-44)$$

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

To find out how the π charge is distributed in the molecule, let us express ρ in terms of AOs. First, we write ϕ_1^2 and ϕ_2^2 separately:

$$\begin{aligned} \phi_1^2 &= \frac{1}{4}x_1^2 + \frac{1}{2}x_2^2 + \frac{1}{4}x_3^2 + \frac{1}{\sqrt{2}}x_1x_2 + \frac{1}{\sqrt{2}}x_2x_3 + \frac{1}{2}x_1x_3 \\ \phi_2^2 &= \frac{1}{2}x_1^2 + \frac{1}{2}x_3^2 - x_1x_3 \end{aligned} \quad (8-45)$$

If we were to integrate ϕ_1^2 we would obtain

$$\begin{aligned} \int \phi_1^2 dv &= \frac{1}{4} \int x_1^2 dv + \frac{1}{2} \int x_2^2 dv + \frac{1}{4} \int x_3^2 dv + \frac{1}{\sqrt{2}} \int x_1x_2 dv \\ &\quad + \frac{1}{\sqrt{2}} \int x_2x_3 dv + \frac{1}{2} \int x_1x_3 dv \\ &= \frac{1}{4} + \frac{1}{2} + \frac{1}{4} = 1 \end{aligned} \quad (8-46)$$

Thus, one electron in ϕ_1 shows up, upon integration, as being "distributed" $\frac{1}{4}$ at carbon 1, $\frac{1}{2}$ at carbon 2, and $\frac{1}{4}$ at carbon 3. We say that the *atomic π -electron densities* due to an electron in ϕ_1 are $\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{4}$ at C_1 , C_2 , and C_3 , respectively. If we accumulate these figures for all the electrons, we arrive at a total π -electron density for each carbon. For the allyl radical, Table 8-1 shows that each atom has a π -electron density of unity.

Generalizing this approach gives for the total π -electron density q_i on atom i

$$q_i = \sum_k^{\text{all MOs}} n_k c_{ik}^2 \quad (8-47)$$

Here k is the MO index, c_{ik} is the coefficient for an AO on atom i in MO k , and n_k , the "occupation number," is the number of electrons (0, 1, or 2) in MO k . (In those rare cases where c_{ik} is complex, c_{ik}^2 in Eq. (8-47) must be replaced by $c_{ik}^* c_{ik}$.)

If we apply Eq. (8-47) to the cyclopropenyl radical, we encounter an ambiguity. If the unpaired electron is assumed to be in MO ϕ_2 of Fig. 8-7, we obtain $q_1 = q_2 = \frac{7}{6}$, $q_3 = \frac{4}{6}$. On the other hand, if the unpaired electron is taken to be in ϕ_3'' , $q_1 = q_2 = \frac{5}{6}$, $q_3 = \frac{8}{6}$. 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 $q_1 = q_2 = q_3 = 1$. The general rule is that, for purposes of calculating electron distributions, the electron occupation is averaged in any set of partially occupied, degenerate MOs.

TABLE 8-1 ► HMO π Electron Densities in the Allyl Radical

Electron	Carbon atom		
	1	2	3
1 in ϕ_1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$
2 in ϕ_1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$
3 in ϕ_2	$\frac{1}{2}$	0	$\frac{1}{2}$
Sum	1	1	1

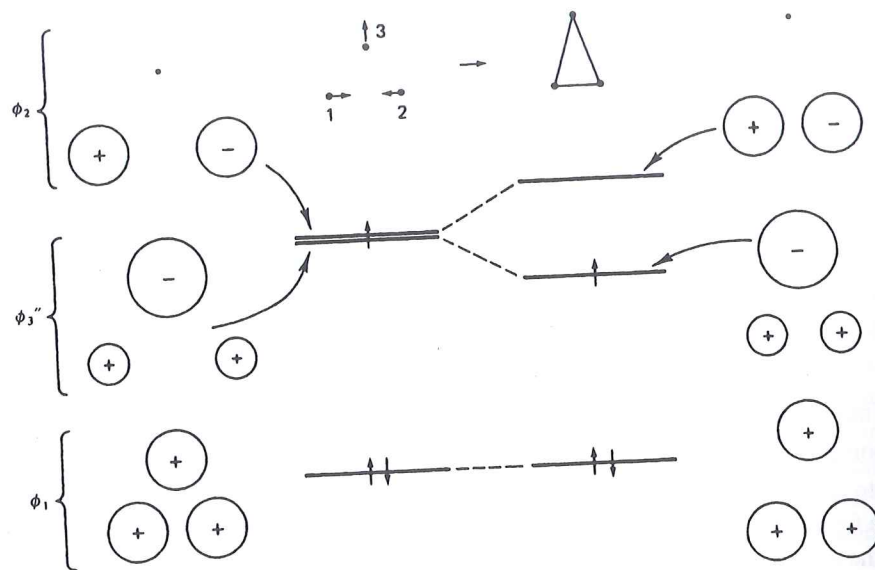


Figure 8-8 ▶ When the equilateral structure is distorted by decreasing R_{12} and increasing R_{13} , R_{23} , the energies associated with ϕ_1 , ϕ_2 , ϕ_3'' shift as shown.

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 effect, that a system having an odd number of electrons in degenerate MOs will change its nuclear configuration in a way to remove the degeneracy.³ 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 π -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 ϕ_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 π 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

³Linear systems are exceptions to this rule. Problems are also encountered if there is an odd number of electrons and spin-orbit coupling is substantial. The reader should realize that the above statement of the theorem is a little misleading inasmuch as it makes it sound like the molecule finds itself in a symmetric geometry that produces degenerate MOs and then “distorts” to a lower-energy geometry. It is actually we who have guessed a geometry that is too symmetric. When our calculations reveal that this results in degenerate orbital energies containing an odd number of electrons, we are alerted that we have erred in our assumption, and that the molecule is really in a less symmetric, lower energy geometry.

⁴See Salem [1, Chapter 8].

ϕ 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 π -bond order for ethylene turns out to be unity rather than two. Since ethylene has one π -bond, this can be seen to be a more sensible index.

As a result of these considerations, the π -bond order (sometimes called *mobile bond order*) of the allyl radical is $1/\sqrt{2} = 0.707$ in each bond. (Electrons in ϕ_2 make no contribution to bond order since c_2 vanishes. This is consistent with the *nonbonding* label for ϕ_2 .)

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

$$p_{ij} = \sum_k^{\text{all MOs}} n_k c_{ik} c_{jk} \quad (8-48)$$

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.

EXAMPLE 8-4 Calculate p_{13} for the cyclopropenyl radical, using data in Fig. 8-7.

SOLUTION ▶ There are 2 electrons in ϕ_1 and the coefficients on atoms 1 and 3 are $\frac{1}{\sqrt{3}}$, so this MO contributes $2 \times (\frac{1}{\sqrt{3}})^2 = 2/3$. We allocate $\frac{1}{2}$ electron to ϕ_2 . Since $c_3 = 0$ in this MO, the contribution to p_{13} is zero. The remaining $\frac{1}{2}$ electron goes to ϕ_3 , yielding a contribution of $\frac{1}{2} \times \frac{1}{\sqrt{6}} \times \frac{-2}{\sqrt{6}} = -\frac{1}{6}$. So $p_{13} = \frac{2}{3} - \frac{1}{6} = \frac{1}{2}$. ◀

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 10×10 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. These 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,

$$x = -2 \cos[k\pi/(n+1)], \quad k = 1, 2, \dots, n \quad (8-49)$$

$$c_{lk} = [2/(n+1)]^{1/2} \sin[kl\pi/(n+1)] \quad (8-50)$$

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

⁵See Coulson [2].

For a cyclic polyene of n carbons,

$$x = -2 \cos(2\pi k/n), \quad k=0, 1, \dots, n-1 \quad (8-51)$$

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

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.⁶ 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: 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 ϕ_1 and ϕ_3 are identical except for sign in Eqs. (8-27) and (8-29).] The role of the β terms is thus reversed and so they act to raise the orbital energy for ϕ_3 just as much as they lower it for ϕ_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

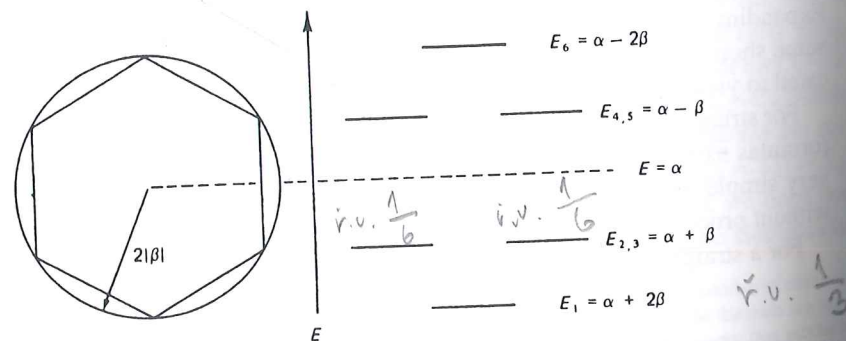


Figure 8-9 ► HMO energy levels for benzene produced by projecting intersections of a hexagon with a circle of radius $2|\beta|$.

⁶See Frost and Musulin [3].

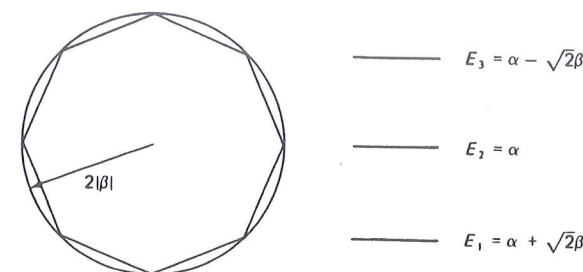


Figure 8-10 ► HMO energy levels for the allyl system ($n=3$) produced by projecting the intersections of an octagon ($n=2 \times 3 + 2$) with a circle of radius $2|\beta|$.

MO should be expressible as a function of the net bond order associated with it, and this is indeed the case. The energy of the i th MO is given by the expression

$$E_i = \int \phi_i \hat{H}_\pi \phi_i dv = \int \sum_k c_{ki} \chi_k \hat{H}_\pi \sum_l c_{li} \chi_l dv \quad (8-53)$$

$$= \sum_k \sum_l c_{ki} c_{li} \int \chi_k \hat{H}_\pi \chi_l dv \quad (8-54)$$

When the atom indices k and l are identical, the integral is equal to α ; when k and l are neighbors, it equals β . Otherwise it vanishes. Hence, we may write

$$E_i = \sum_k c_{ki}^2 \alpha + \sum_{k,l}^{\text{neighbors}} c_{ki} c_{li} \beta \quad (8-55)$$

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

$$E_i = \sum_k q_{k,i} \alpha + 2 \sum_{k<l}^{\text{neighbors}} p_{kl,i} \beta \quad (8-56)$$

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

$$E_i = \alpha + 2\beta \sum_{k<l}^{\text{bonds}} p_{kl,i} \quad (8-57)$$

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

$$E_\pi = n\alpha + 2\beta \sum_{k<l}^{\text{bonds}} p_{kl} \quad (8-58)$$

where p_{kl} is the total π -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 π electrons together.