a triatomic molecule, for instance, may be either linear or angular with a characteristic bond angle. The shape of a polyatomic molecule—the specification of its bond lengths and its bond angles—can be predicted by calculating the total energy of the molecule for a variety of nuclear positions, and then identifying the conformation that corresponds to the lowest energy.

11.6 The Hückel approximation

Molecular orbital theory takes large molecules and extended aggregates of atoms, such as solid materials, in its stride. First we shall consider conjugated molecules, in which there is an alternation of single and double bonds along a chain of carbon atoms. Although the classification of an orbital as σ or π is strictly valid only in linear molecules, as will be familiar from introductory chemistry courses, it is also used to denote the local symmetry with respect to a given A—B bond axis.

The π molecular orbital energy level diagrams of conjugated molecules can be constructed using a set of approximations suggested by Erich Hückel in 1931. In his approach, the π orbitals are treated separately from the σ orbitals, and the latter form a rigid framework that determines the general shape of the molecule. All the C atoms are treated identically, so all the Coulomb integrals α for the atomic orbitals that contribute to the π orbitals are set equal. For example, in ethene, we take the σ bonds as fixed, and concentrate on finding the energies of the single π bond and its companion antibond.

(a) Ethene and frontier orbitals

We express the π orbitals as LCAOs of the C2p orbitals that lie perpendicular to the molecular plane. In ethene, for instance, we would write

$$\psi = c_A A + c_B B \tag{11.36}$$

where the A is a C2p orbital on atom A, and so on. Next, the optimum coefficients and energies are found by the variation principle as explained in Section 11.5. That is, we have to solve the secular determinant, which in the case of ethene is eqn 11.29 with $\alpha_A = \alpha_B = \alpha$:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{11.37}$$

The roots of this determinant can be found very easily (they are the same as those in *Illustration 11.2*). In a modern computation all the resonance integrals and overlap integrals would be included, but an indication of the molecular orbital energy level diagram can be obtained very readily if we make the following additional **Hückel approximations**:

1 All overlap integrals are set equal to zero.

2 All resonance integrals between non-neighbours are set equal to zero.

3 All remaining resonance integrals are set equal (to β).

These approximations are obviously very severe, but they let us calculate at least a general picture of the molecular orbital energy levels with very little work. The assumptions result in the following structure of the secular determinant:

1 All diagonal elements: $\alpha - E$.

2 Off-diagonal elements between neighbouring atoms: β.

3 All other elements: 0.
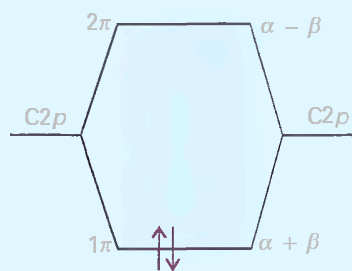
Fig. 11.38 The Hückel molecular orbital energy levels of ethene. Two electrons occupy the lower π orbital.

These approximations lead to

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0 \tag{11.38}$$

The roots of the equation are

$$E_{\pm} = \alpha \pm \beta \tag{11.39}$$

The + sign corresponds to the bonding combination (β is negative) and the − sign corresponds to the antibonding combination (Fig. 11.38). We see the effect of neglecting overlap by comparing this result with eqn 11.31.

The building-up principle leads to the configuration $1\pi^2$, because each carbon atom supplies one electron to the π system. The **highest occupied molecular orbital** in ethene, its HOMO, is the 1π orbital; the **lowest unfilled molecular orbital**, its LUMO, is the 2π orbital (or, as it is sometimes denoted, the $2\pi^*$ orbital). These two orbitals jointly form the **frontier orbitals** of the molecule. The frontier orbitals are important because they are largely responsible for many of the chemical and spectroscopic properties of the molecule. For example, we can estimate that $2\,|\beta|$ is the $\pi^* \leftarrow \pi$ excitation energy of ethene, the energy required to excite an electron from the 1π to the 2π orbital. The constant β is often left as an adjustable parameter; an approximate value for π bonds formed from overlap of two $C2p$ atomic orbitals is about −2.4 eV (−230 kJ mol^{-1}).

(b) The matrix formulation of the Hückel method

In preparation for making Hückel theory more sophisticated and readily applicable to bigger molecules, we need to reformulate it in terms of matrices and vectors (see *Appendix 2*). We have seen that the secular equations that we have to solve for a two-atom system have the form

$$(H_{AA} - E_i S_{AA})c_{i,A} + (H_{AB} - E_i S_{AB})c_{i,B} = 0 \tag{11.40a}$$

$$(H_{BA} - E_i S_{BA})c_{i,A} + (H_{BB} - E_i S_{BB})c_{i,B} = 0 \tag{11.40b}$$

where the eigenvalue E_i corresponds to a wavefunction of the form $\psi_i = c_{i,A}A + c_{i,B}B$. (These expressions generalize eqn 11.25). There are two atomic orbitals, two eigenvalues, and two wavefunctions, so there are two pairs of secular equations, with the first corresponding to E_1 and ψ_1:

$$(H_{AA} - E_1 S_{AA})c_{1,A} + (H_{AB} - E_1 S_{AB})c_{1,B} = 0 \tag{11.41a}$$

$$(H_{BA} - E_1 S_{BA})c_{1,A} + (H_{BB} - E_1 S_{BB})c_{1,B} = 0 \tag{11.41b}$$

and another corresponding to E_2 and ψ_2:

$$(H_{AA} - E_2 S_{AA})c_{2,A} + (H_{AB} - E_2 S_{AB})c_{2,B} = 0 \tag{11.41c}$$

$$(H_{BA} - E_2 S_{BA})c_{2,A} + (H_{BB} - E_2 S_{BB})c_{2,B} = 0 \tag{11.41d}$$

If we introduce the following matrices and column vectors

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \qquad S = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \qquad c_i = \begin{pmatrix} c_{i,A} \\ c_{i,B} \end{pmatrix} \tag{11.42}$$

then each pair of equations may be written more succinctly as

$$(H - E_i S)c_i = 0 \qquad \text{or} \qquad Hc_i = Sc_i E_i \tag{11.43}$$

where H is the hamiltonian matrix and S is the overlap matrix. To proceed with the calculation of the eigenvalues and coefficients, we introduce the matrices

$$C = (c_1 \quad c_2) = \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} \qquad E = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \tag{11.44}$$

for then the entire set of equations we have to solve can be expressed as

$$HC = SCE \qquad (11.45)$$

Self-test 11.7 Show by carrying out the necessary matrix operations that eqn 11.45 is a representation of the system of equations consisting of eqns 11.41(a)–(d).

In the Hückel approximation, $H_{AA} = H_{BB} = \alpha$, $H_{AB} = H_{BA} = \beta$, and we neglect overlap, setting $S = 1$, the unit matrix (with 1 on the diagonal and 0 elsewhere). Then

$$HC = CE$$

At this point, we multiply from the left by the inverse matrix C^{-1}, and find

$$C^{-1}HC = E \qquad (11.46)$$

where we have used $C^{-1}C = 1$. In other words, to find the eigenvalues E_i, we have to find a transformation of H that makes it diagonal. This procedure is called **matrix diagonalization**. The diagonal elements then correspond to the eigenvalues E_i and the columns of the matrix C that brings about this diagonalization are the coefficients of the members of the **basis set**, the set of atomic orbitals used in the calculation, and hence give us the composition of the molecular orbitals. If there are N orbitals in the basis set (there are only two in our example), then there are N eigenvalues E_i and N corresponding column vectors c_i. As a result, we have to solve N equations of the form $Hc_i = Sc_iE_i$ by diagonalization of the $N \times N$ matrix H, as directed by eqn 11.46.

Example 11.4 *Finding the molecular orbitals by matrix diagonalization*

Set up and solve the matrix equations within the Hückel approximation for the π-orbitals of butadiene (3).

Method The matrices will be four-dimensional for this four-atom system. Ignore overlap, and construct the matrix H by using the Hückel values α and β. Find the matrix C that diagonalizes H: for this step, use mathematical software. Full details are given in *Appendix 2*.
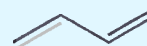
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Solution

$$H = \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}$$

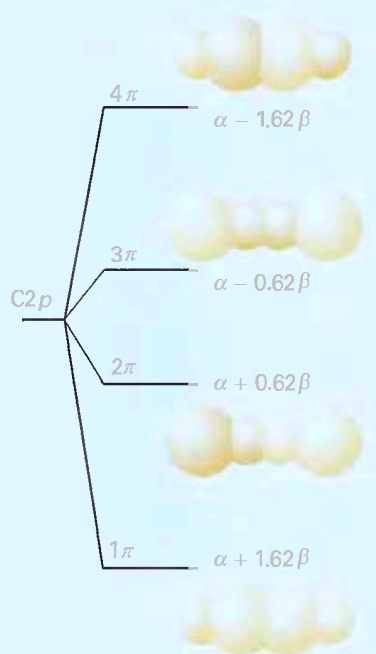Mathematical software then diagonalizes this matrix to

$$E = \begin{pmatrix} \alpha + 1.62\beta & 0 & 0 & 0 \\ 0 & \alpha + 0.62\beta & 0 & 0 \\ 0 & 0 & \alpha - 0.62\beta & 0 \\ 0 & 0 & 0 & \alpha - 1.62\beta \end{pmatrix}$$

and the matrix that achieves the diagonalization is

$$C = \begin{pmatrix} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{pmatrix}$$

We can conclude that the energies and molecular orbitals are

$$E_1 = \alpha + 1.62\beta \qquad \psi_1 = 0.372\chi_A + 0.602\chi_B + 0.602\chi_C + 0.372\chi_D$$
$$E_2 = \alpha + 0.62\beta \qquad \psi_2 = 0.602\chi_A + 0.372\chi_B - 0.372\chi_C - 0.602\chi_D$$
$$E_3 = \alpha - 0.62\beta \qquad \psi_3 = 0.602\chi_A - 0.372\chi_B - 0.372\chi_C + 0.602\chi_D$$
$$E_4 = \alpha - 1.62\beta \qquad \psi_4 = -0.372\chi_A + 0.602\chi_B - 0.602\chi_C - 0.372\chi_D$$

where the C2p atomic orbitals are denoted by $\chi_A, \ldots, \chi_D$. Note that the orbitals are mutually orthogonal and, with overlap neglected, normalized.

Self-test 11.8 Repeat the exercise for the allyl radical, $\cdot CH_2{-}CH{=}CH_2$.
$$[E = \alpha + 2^{1/2}\beta,\ \alpha,\ \alpha - 2^{1/2}\beta;\ \psi_1 = \tfrac{1}{2}\chi_A + (\tfrac{1}{2})^{1/2}\chi_B + \tfrac{1}{2}\chi_C,$$
$$\psi_2 = (\tfrac{1}{2})^{1/2}\chi_A - (\tfrac{1}{2})^{1/2}\chi_C,\ \psi_3 = \tfrac{1}{2}\chi_A - (\tfrac{1}{2})^{1/2}\chi_B + \tfrac{1}{2}\chi_C]$$

(c) Butadiene and π-electron binding energy

As we saw in the preceding example, the energies of the four LCAO-MOs for butadiene are

$$E = \alpha \pm 1.62\beta, \qquad \alpha \pm 0.62\beta \tag{11.47}$$

These orbitals and their energies are drawn in Fig. 11.39. Note that the greater the number of internuclear nodes, the higher the energy of the orbital. There are four electrons to accommodate, so the ground-state configuration is $1\pi^2 2\pi^2$. The frontier orbitals of butadiene are the 2π orbital (the HOMO, which is largely bonding) and the 3π orbital (the LUMO, which is largely antibonding). 'Largely' bonding means that an orbital has both bonding and antibonding interactions between various neighbours, but the bonding effects dominate. 'Largely antibonding' indicates that the antibonding effects dominate.

An important point emerges when we calculate the total π-electron binding energy, E_π, the sum of the energies of each π electron, and compare it with what we find in ethene. In ethene the total energy is

$$E_\pi = 2(\alpha + \beta) = 2\alpha + 2\beta$$

In butadiene it is

$$E_\pi = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

Therefore, the energy of the butadiene molecule lies lower by 0.48β (about 110 kJ mol^{-1}) than the sum of two individual π bonds. This extra stabilization of a conjugated system is called the **delocalization energy**. A closely related quantity is the **π-bond formation energy**, the energy released when a π bond is formed. Because the contribution of α is the same in the molecule as in the atoms, we can find the π-bond formation energy from the π-electron binding energy by writing

$$E_{bf} = E_\pi - N\alpha \tag{11.48}$$

where N is the number of carbon atoms in the molecule. The π-bond formation energy in butadiene, for instance, is 4.48β.

Fig. 11.39 The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π orbitals. The four p electrons (one supplied by each C) occupy the two lower π orbitals. Note that the orbitals are delocalized.

$4\pi \qquad \alpha - 1.62\beta$

$3\pi \qquad \alpha - 0.62\beta$

C2p

$2\pi \qquad \alpha + 0.62\beta$

$1\pi \qquad \alpha + 1.62\beta$

Example 11.5 *Estimating the delocalization energy*

Use the Hückel approximation to find the energies of the π orbitals of cyclobutadiene, and estimate the delocalization energy.

Method Set up the secular determinant using the same basis as for butadiene, but note that atoms A and D are also now neighbours. Then solve for the roots of the secular equation and assess the total π-bond energy. For the delocalization energy, subtract from the total π-bond energy the energy of two π-bonds.

Answer The hamiltonian matrix is

$$H = \begin{pmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{pmatrix}$$

Diagonalization gives the energies of the orbitals as

$$E = \alpha + 2\beta, \qquad \alpha, \qquad \alpha, \qquad \alpha - 2\beta$$

Four electrons must be accommodated. Two occupy the lowest orbital (of energy $\alpha + 2\beta$), and two occupy the doubly degenerate orbitals (of energy α). The total energy is therefore $4\alpha + 4\beta$. Two isolated π bonds would have an energy $4\alpha + 4\beta$; therefore, in this case, the delocalization energy is zero.

Self-test 11.9 Repeat the calculation for benzene.   [See next subsection]

(d) Benzene and aromatic stability

The most notable example of delocalization conferring extra stability is benzene and the aromatic molecules based on its structure. Benzene is often expressed in a mixture of valence-bond and molecular orbital terms, with typically valence-bond language used for its σ framework and molecular orbital language used to describe its π electrons.

First, the valence-bond component. The six C atoms are regarded as sp^2 hybridized, with a single unhydrized perpendicular $2p$ orbital. One H atom is bonded by $(Csp^2, H1s)$ overlap to each C carbon, and the remaining hybrids overlap to give a regular hexagon of atoms (Fig. 11.40). The internal angle of a regular hexagon is 120°, so sp^2 hybridization is ideally suited for forming σ bonds. We see that benzene's hexagonal shape permits strain-free σ bonding.

Now consider the molecular orbital component of the description. The six $C2p$ orbitals overlap to give six π orbitals that spread all round the ring. Their energies are calculated within the Hückel approximation by diagonalizing the hamiltonian matrix

$$H = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

The MO energies, the eigenvalues of this matrix, are simply

$$E = \alpha \pm 2\beta, \alpha \pm \beta, \alpha \pm \beta \tag{11.49}$$

as shown in Fig. 11.41. The orbitals there have been given symmetry labels that we explain in Chapter 12. Note that the lowest energy orbital is bonding between all neighbouring atoms, the highest energy orbital is antibonding between each pair of neighbours, and the intermediate orbitals are a mixture of bonding, nonbonding, and antibonding character between adjacent atoms.
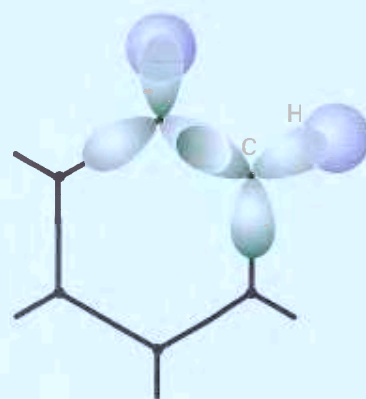
Fig. 11.40 The σ framework of benzene is formed by the overlap of Csp^2 hybrids, which fit without strain into a hexagonal arrangement.
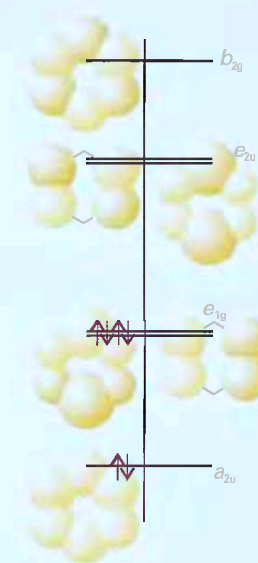
Fig. 11.41 The Hückel orbitals of benzene and the corresponding energy levels. The symmetry labels are explained in Chapter 12. The bonding and antibonding character of the delocalized orbitals reflects the numbers of nodes between the atoms. In the ground state, only the bonding orbitals are occupied.

We now apply the building-up principle to the π system. There are six electrons to accommodate (one from each C atom), so the three lowest orbitals (a_{2u} and the doubly-degenerate pair e_{1g}) are fully occupied, giving the ground-state configuration $a_{2u}^2 e_{1g}^4$. A significant point is that the only molecular orbitals occupied are those with net bonding character.

The π-electron energy of benzene is

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

If we ignored delocalization and thought of the molecule as having three isolated π bonds, it would be ascribed a π-electron energy of only $3(2\alpha + 2\beta) = 6\alpha + 6\beta$. The delocalization energy is therefore $2\beta \approx -460$ kJ mol^{-1}, which is considerably more than for butadiene. The π-bond formation energy in benzene is 8β.

This discussion suggests that aromatic stability can be traced to two main contributions. First, the shape of the regular hexagon is ideal for the formation of strong σ bonds: the σ framework is relaxed and without strain. Second, the π orbitals are such as to be able to accommodate all the electrons in bonding orbitals, and the delocalization energy is large.

11.7 Computational chemistry

The difficulties arising from the severe assumptions of Hückel method have been overcome by more sophisticated theories that not only calculate the shapes and energies of molecular orbitals but also predict with reasonable accuracy the structure and reactivity of molecules. The full treatment of molecular electronic structure is quite easy to formulate but difficult to implement. However, it has received an enormous amount of attention by chemists, and has become a keystone of modern chemical research. John Pople and Walter Kohn were awarded the Nobel Prize in Chemistry for 1998 for their contributions to the development of computational techniques for the elucidation of molecular structure and reactivity.

(a) The Hartree–Fock equations

The starting point is to write down the many-electron wavefunction as a product of one-electron wavefunctions:

$$\Psi = \psi_{a,\alpha}(1)\psi_{a,\beta}(2)\ldots\psi_{z,\beta}(N)$$

This is the wavefunction for an N-electron closed-shell molecule in which electron 1 occupies molecular orbital ψ_a with spin α, electron 2 occupies molecular orbital ψ_a with spin β, and so on. However, the wavefunction must satisfy the Pauli principle and change sign under the permutation of any pair of electrons. To achieve this behaviour, we write the wavefunction as a sum of all possible permutations with the appropriate sign:

$$\Psi = \psi_{a,\alpha}(1)\psi_{a,\beta}(2)\ldots\psi_{z,\beta}(N) - \psi_{a,\alpha}(2)\psi_{a,\beta}(1)\ldots\psi_{z,\beta}(N) + \cdots$$

There are $N!$ terms in this sum, and the entire sum can be written as a determinant:

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{a,\alpha}(1) & \psi_{a,\beta}(1) & \cdots & \cdots & \psi_{z,\beta}(1) \\ \psi_{a,\alpha}(2) & \psi_{a,\beta}(2) & \cdots & \cdots & \psi_{z,\beta}(2) \\ \vdots & \vdots & & & \vdots \\ \psi_{a,\alpha}(N) & \psi_{a,\beta}(N) & \cdots & \cdots & \psi_{z,\beta}(N) \end{vmatrix} \tag{11.50a}$$