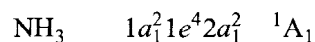Fig. 8.25 The symmetry classification of the nitrogen atomic orbitals in NH_3, a C_{3v} molecule, and the three symmetry-adapted linear combinations of the H1s orbitals.

energy levels shown in Fig. 8.26. There are eight electrons to accommodate, and so the configuration of the ground state is expected to be

$$NH_3 \qquad 1a_1^2 1e^4 2a_1^2 \qquad {}^1A_1$$

The HOMO is the $2a_1$-orbital, which is largely a nonbonding orbital composed of N2s- and N2p_z-orbitals: the electrons that occupy it therefore constitute a lone pair on the N atom.

8.9 Conjugated π-systems

A special class of polyatomic molecules consists of those containing π-bonded atoms, particularly conjugated polyenes and arenes. They fall into a unique class because the orbitals with local σ and π symmetry can be discussed separately. By 'local' symmetry we mean symmetry with respect to one internuclear axis rather than the global symmetry of the molecule. For global symmetry we have to classify orbitals according to the overall point group of the molecule, and the σ, π designation is relevant only for linear species. However, if we focus on an individual A—B fragment of the molecule, then the orbitals do have a characteristic rotational symmetry about that axis, and they can be classified as locally σ or π.

One reason for the separate treatment of locally σ- and π-orbitals is that the electrons in π-orbitals are typically less strongly bound than those in σ-orbitals, so there is little interaction between the two types of orbital (recall the principles set out in Section 8.6). Another reason for the separation is that as π-orbitals are typically found in planar molecules, they have global symmetry properties that distinguish them from σ-orbitals, and therefore span different irreducible representations of the molecular point group. As a consequence, they factorize and can be discussed separately.

The simplest organic π-system is the ethene molecule, CH_2=CH_2. The σ-orbitals in ethene are molecular orbitals composed of various symmetry-adapted linear combinations of C2s, C2p_x, C2p_y, and H1s orbitals; the π-orbitals are formed by overlap between C2p_z orbitals (Fig. 8.27). This model immediately accounts for the torsional rigidity of the molecule, because (C2p_z, C2p_z)-overlap is greatest when the molecule is planar. The π-orbital energies are found by solving a 2 × 2 secular determinant, and the solutions given in eqn 8.17 may be employed as the carbon–carbon fragment is homonuclear.

When the π-system is conjugated, which means that the π-system extends over several neighbouring atoms, the simplest description of the bonding is in terms of the **Hückel approximation**. This drastic approximation makes the following assumptions in the formulation of the secular determinant $\det |H - ES|$:

1. All overlap integrals are set equal to zero: $S_{ij} = \delta_{ij}$.

This is in fact a poor approximation, because actual overlap integrals are typically close to 0.2. Nevertheless, when the rule is relaxed, the energies are shifted in a simple way and their relative order is not greatly disturbed.

2. All diagonal matrix elements of the hamiltonian are ascribed the same value: $H_{ii} = \alpha$.
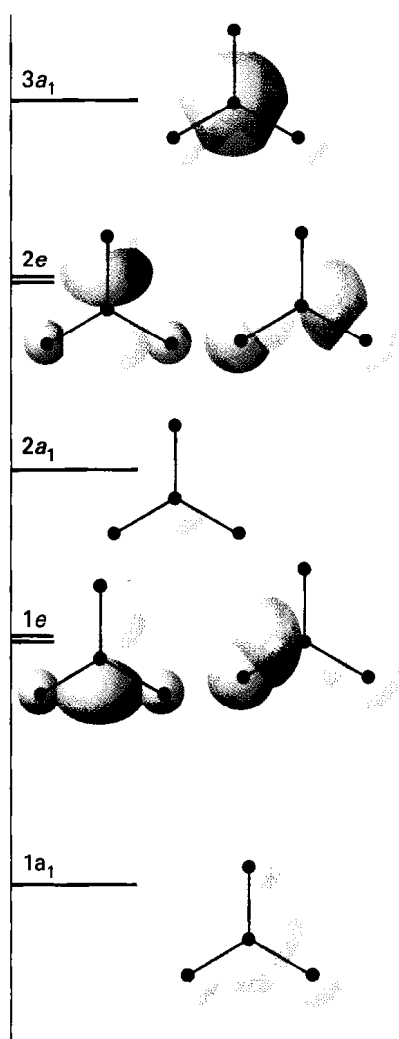
Fig. 8.26 The molecular orbitals of NH_3 at its equilibrium bond angle of $107°$.
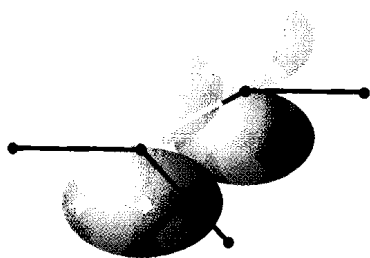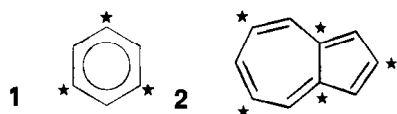

Figure 8.27 The structure of the π-orbital in ethene.

The parameter α is negative. This approximation is reasonable for species that do not contain heteroatoms because all the conjugated atoms are electronically similar. Some justification comes from the **Coulson–Rushbrooke theorem**, which states that in alternant hydrocarbons[5] the charge density on all the atoms is the same.

3. All off-diagonal elements of the hamiltonian are set equal to zero except for those between neighbouring atoms, all of which are set equal to β.

The parameter β is negative. It is the important parameter characteristic of Hückel theory, in so far as it governs the spacing of the molecular orbital energy levels.

Example 8.3 The implementation of the Hückel approximation

Set up and solve the secular determinant for π-orbitals of the butadiene molecule in the Hückel approximation.

Method. Construct the secular determinant by setting all diagonal elements equal to $\alpha - E$ and off-diagonal elements between neighbouring atoms equal to β; all other elements are zero. Set the secular determinant equal to zero, and solve the resulting quartic equation in $x = \alpha - E$ for x and hence E.

Answer. The equation to solve is

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

On setting $x = \alpha - E$ and expanding the determinant, we obtain

$$x^4 - 3\beta^2 x^2 + \beta^4 = 0$$

This quartic in x is in fact a quadratic equation in $y = x^2$, so its roots can be found by elementary methods:

$$x = \pm\left(\frac{3 \pm \sqrt{5}}{2}\right)^{1/2}\beta \qquad x = \pm\tfrac{1}{2}(\sqrt{5} \pm 1)\beta$$

We conclude that the energy levels are

$$E = \alpha \pm 1.618\beta \qquad \alpha \pm 0.618\beta$$

as shown in Fig. 8.28.

Comment. The secular determinant for butadiene is an example of a so-called 'tridiagonal determinant', in which the nonzero elements all lie along three neighbouring diagonal lines. From the theory of determinants, an $N \times N$ tridiagonal determinant has the following roots:

---

1   **2**

[5] An alternant hydrocarbon is one in which the atoms can be divided into two groups by putting a star on alternate atoms and not having any neighbouring stars when the numbering is complete. Benzene (1) is alternant, azulene (2) is nonalternant.
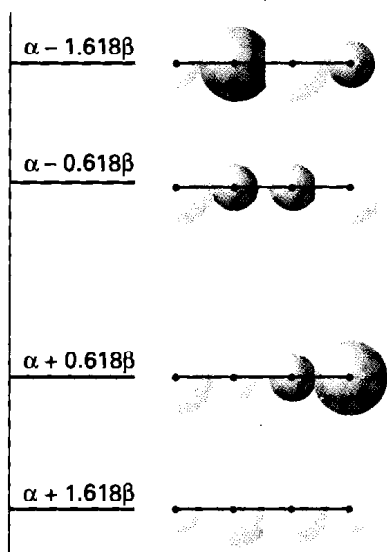
$\alpha - 1.618\beta$

$\alpha - 0.618\beta$

$\alpha + 0.618\beta$

$\alpha + 1.618\beta$

Fig. 8.28 The Hückel molecular orbitals and their energies in butadiene (as viewed down the axis of the p-orbitals).
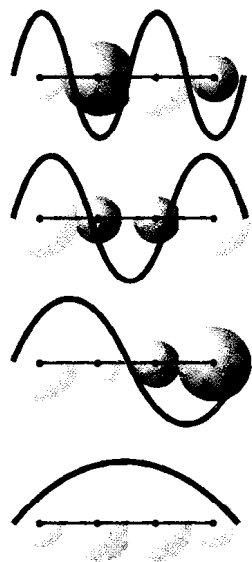

Fig. 8.29 The contributions of the p-orbitals to each π-orbital matches the amplitude of a sine wave (the wavefunction for a particle in a box) at the parent carbon atom.

$$E_k = \alpha + 2\beta\cos\left(\frac{k\pi}{N+1}\right) \qquad k = 1, 2, \ldots, N$$

Exercise 8.3. Find the roots of the secular determinant for the π-orbitals of cyclobutadiene. $[\ \alpha \pm 2\beta, \alpha \pm \beta]$

The worked example has shown how to calculate the molecular orbital energy levels in a simple case. The coefficients of the orbitals can be found by substituting these energies into the secular equations. However, in practice it is much easier to employ a computer: the roots we have found are the eigenvalues of the secular matrix and the corresponding eigenfunctions of the matrix are the coefficients of the atomic orbitals that contribute to each molecular orbital. For example, the four molecular orbitals of butadiene are found in this way to be

$$1\pi = 0.372\phi_A + 0.602\phi_B + 0.602\phi_C + 0.372\phi_D$$
$$2\pi = -0.602\phi_A - 0.372\phi_B + 0.372\phi_C + 0.602\phi_D$$
$$3\pi = -0.602\phi_A + 0.372\phi_B + 0.372\phi_C - 0.602\phi_D$$
$$4\pi = 0.372\phi_A - 0.602\phi_B + 0.602\phi_C - 0.372\phi_D$$

where the ϕ_J is a $2p_z$-orbital on atom J. The composition of these molecular orbitals is independent of the values of α and β. You should notice that the energy of the orbital increases with the number of nodes, and that the amplitude of each coefficient follows a sine wave fitted to the length of the molecule (Fig. 8.29).

The ground state configuration of the molecule is $1\pi^2 2\pi^2$, which corresponds to a total π-electron energy of $4\alpha + 2\sqrt{5}\beta$. The energy of a single unconjugated π-orbital is $\alpha + \beta$, and so if the molecule were described as having two unconjugated π-bonds, its total π-electron energy would have been $4\alpha + 4\beta$. The difference, which in this case is $2(\sqrt{5} - 2)\beta = 0.472\beta$, is called the **delocalization energy** of the molecule. The delocalization energy is independent of α within the Hückel approximation largely because all atoms are equivalent and the total electron density on them is the same regardless of the extent of delocalization of the orbitals.

The Hückel procedure leads to secular determinants of large dimension. However, they may often be factorized into more manageable dimensions by making use of the symmetry of the system beyond the simple mirror plane that enables the π-system to be distinguished from the σ-system. This additional factorization follows from the usual arguments about the hamiltonian having no nonzero elements between linear combinations of orbitals that belong to different symmetry species of the molecular point group. For benzene, for instance, the 6×6 determinant can be simplified very considerably by making use of the D_{6h} symmetry of the molecule. In fact, because every $2p_z$-orbital changes sign under reflection in the molecular plane, we lose no information by using the C_{6v} subgroup of the molecule. The procedure involves treating the C atoms as the peripheral atoms of a molecule, and setting up SALCs of their $2p_z$-orbitals; however as there is no 'central' atom, these SALCs are in this instance the actual π molecular orbitals of the molecule. The projection operator technique described in Section 5.12 leads to the fol-
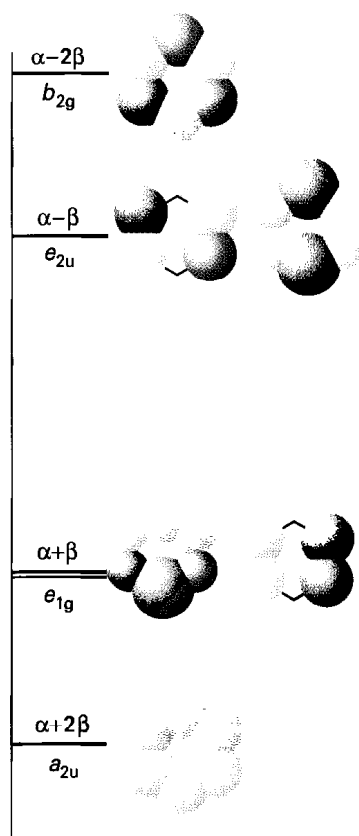
Fig. 8.30 The Hückel molecular orbitals and their energies in benzene.

lowing linear combinations (labelled according to the symmetry species of the group D_{6h}):

$$a_{2u} = \frac{1}{\sqrt{6}}(p_A + p_B + p_C + p_D + p_E + p_F)$$

$$e_{1g} = \begin{cases} (a) \ \frac{1}{\sqrt{12}}(2p_A + p_B - p_C - 2p_D - p_E + p_F) \\ (b) \ \frac{1}{2}(p_B + p_C - p_E - p_F) \end{cases}$$

$$e_{2u} = \begin{cases} (a) \ \frac{1}{\sqrt{12}}(2p_A - p_B - p_C + 2p_D - p_E - p_F) \\ (b) \ \frac{1}{2}(p_B - p_C + p_E - p_F) \end{cases}$$

$$b_{2g} = \frac{1}{\sqrt{6}}(p_A - p_B + p_C - p_D + p_E - p_F)$$

These orbitals are sketched in Fig. 8.30. Note that the form of the orbitals is determined solely by the symmetry of the molecule and makes no reference to the values of α or β. As we show in the following example, the energy levels are

$$E(a_{2u}) = \alpha + 2\beta \qquad E(e_{1g}) = \alpha + \beta \qquad E(e_{2u}) = \alpha - \beta \qquad E(b_{2g}) = \alpha - 2\beta$$

As we have already remarked, β is negative, so the orbitals lie in the order shown in the illustration.

Example 8.4 The energy levels of the benzene molecule

Determine the π-electron energy levels of the benzene molecule within the Hückel approximation.

Method. The molecular orbitals are specified above. We need form secular determinants for each orbital species separately as the hamiltonian has no off-diagonal elements between orbitals of different symmetry species. Use the Hückel rules for writing the matrix elements after expanding the H_{ij} in terms of the linear combinations of $2p_z$-orbitals. The orbitals that span one-dimensional irreducible representations will give simple 1×1 determinants, which are trivial to solve. The orbitals that span two-dimensional irreducible representations will give 2×2 determinants, which will lead to quadratic equations. However, because the e-orbitals of each set have different reflection symmetry, they too give diagonal determinants, so the roots can be found trivially.

Answer. The matrix elements we require are as follows:

$$\langle a_{2u}|H|a_{2u}\rangle = \frac{1}{6}\langle p_A + \ldots + p_F|H|p_A + \ldots + p_F\rangle = \alpha + 2\beta$$

$$\langle b_{2g}|H|b_{2g}\rangle = \frac{1}{6}\langle p_A - \ldots - p_F|H|p_A - \ldots - p_F\rangle = \alpha - 2\beta$$

$$\langle e_{1g}(a)|H|e_{1g}(a)\rangle = \alpha + \beta$$

$$\langle e_{1g}(b)|H|e_{1g}(b)\rangle = \alpha + \beta$$

$$\langle e_{2u}(a)|H|e_{2u}(a)\rangle = \alpha - \beta$$

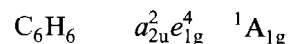$$\langle e_{2u}(b)|H|e_{2u}(b)\rangle = \alpha - \beta$$

$$\langle e(a)|H|e(b)\rangle = 0 \text{ for both types of } e \text{ orbital}$$

> The resulting energies are those quoted in the text and displayed in Fig. 8.30.
>
> **Exercise 8.4.** Use the C_{2v} subgroup of naphthalene to find the π-electron molecular orbital energy levels within the Hückel approximation.

The ground-state electron configuration of benzene is

$$C_6H_6 \qquad a_{2u}^2 e_{1g}^4 \qquad {}^1A_{1g}$$

and the delocalization energy is

$$E_{\text{deloc}} = (6\alpha + 8\beta) - 6(\alpha + \beta) = 2\beta$$

You should notice that the six electrons just complete the molecular orbitals with net bonding effect, leaving unfilled the orbitals with net antibonding character. To some extent this configuration echoes the configuration of N_2, and both molecules have a pronounced chemical inactivity. Another feature of the energy levels of benzene is that the array of levels is symmetrical: to every bonding level there corresponds an antibonding level. This symmetry is a characteristic feature of alternant hydrocarbons and can be traced to the topological character of the molecules. Indeed, many of the results of Hückel theory can be established on the basis of **graph theory**, the branch of topology concerned with the properties of networks. One particular result of this kind of analysis is the justification of the '$(4n + 2)$-rule' for the anticipation of aromatic character, where n is the number of π-electrons.

As we have stressed, Hückel theory, which virtually hijacks the disagreeable integrals that appear in a full treatment, is only the most primitive stage of discussing π-electron molecules. The modern, far more reliable numerical approaches are described in Chapter 9.

8.10 Ligand field theory

The success of Hückel theory is rooted in the fact that the orbitals themselves are determined by the symmetry of the system. These symmetry-determined orbitals are then put into an order of energies, essentially by counting the number and noting the importance of their nodes. The energy differences between the orbitals are typically so large that the coarseness of this procedure does not unduly misrepresent their order. A similar situation occurs in the complexes of d-metal ions. These complexes consist of a central metal ion surrounded by a three-dimensional array of ligands. The compositions of the orbitals of the complex are largely determined by the symmetry of the environment, and a single parameter can be used to give a rough indication of the order of the energies of the molecular orbitals of the complex. **Ligand field theory** is a kind of three-dimensional version of Hückel theory, in which symmetry plays a central role, and in which structural, spectroscopic, magnetic, and thermodynamic properties are parametrized in terms of the **ligand field splitting parameter, Δ.**

We shall denote the central metal ion by M and assume that it has the configuration d^n. The ligands will be denoted L, and we shall confine attention to ML_6 octahedral complexes with O_h symmetry. The orbitals of the ligands will be denoted λ. In particular, we shall suppose that each ligand i supplies an

The optimization of parameters is, in general, a difficult task for several reasons. For one, accurate experimental data are often not available. Also, the simultaneous optimization of several parameters for a large number of molecules is very time-consuming. The parameters are interconnected in the sense that significantly varying the value of one parameter in a nearly optimal parameter set needs to be accompanied by variations in several other parameters too. The successive optimization of each parameter is not feasible. Semiempirical methods were first developed for conjugated π-electron systems. We shall therefore begin our discussion with them and later describe more general methods.

9.12 Conjugated π-electron systems

We consider the case of a conjugated π-system with a total of n_π π-electrons. The π-electrons are dealt with separately from the σ-electrons partly because their energies are so different and partly on account of the different symmetries of their orbitals. The effective π-electron hamiltonian H_π is given by

$$H_\pi = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n_\pi}\nabla_i^2 + \sum_{i=1}^{n_\pi}V_i^{\pi,\text{eff}} + \frac{1}{2}\sum_{i,j}^{n_\pi}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{53}$$

where the first term is the kinetic energy operator for the π-electrons, $V_i^{\pi,\text{eff}}$ is the effective potential energy for π-electron i resulting from the potential field of the nuclei and all σ-electrons, and the final term represents the repulsive potential energy due to π-interelectronic interactions. The core hamiltonian h_i^π for π-electron i is defined by

$$h_i^\pi = -\frac{\hbar^2}{2m_e}\nabla_i^2 + V_i^{\pi,\text{eff}} \tag{54}$$

so we can write

$$H_\pi = \sum_{i=1}^{n_\pi}h_i^\pi + \frac{1}{2}\sum_{i,j}^{n_\pi}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{55}$$

The analogy with eqn 7.43 is apparent. The hamiltonian H_π is approximate because the π- and σ-electrons have been treated separately and the effect of the latter in H_π appears only in the effective potential $V_i^{\pi,\text{eff}}$. The use of an approximate form for the hamiltonian in eqn 9.1 is characteristic of semi-empirical methods.

The most famous semiempirical π-electron theory is **Hückel molecular orbital theory** (HMO). As this method has already been described in some detail in Section 8.9, here we shall only point out some of the features of this method that characterize it as semiempirical. In the HMO method, H_π is approximated as a sum of one-electron terms:

$$H_\pi = \sum_{i=1}^{n_\pi}h_i^{\pi,\text{eff}} \tag{56}$$

where $h_i^{\pi,\text{eff}}$ is an effective hamiltonian for π-electron i. The form of $h_i^{\pi,\text{eff}}$ is left unspecified; only its matrix elements appear in HMO. Because H_π is a sum of one-electron terms, the wavefunction Ψ_π can be written in terms of a product of one-electron (molecular) orbitals ψ_i, each of which is a solution of the eigenvalue equation

$$h_i^{\pi,\text{eff}}\psi_i = E_i\psi_i \tag{57}$$

where E_i is the energy associated with the molecular orbital labelled i. Each molecular orbital is written as a linear combination of atomic orbitals (LCAO). For example, in an HMO treatment of a conjugated hydrocarbon (such as benzene), the atomic orbitals are usually composed of the set of $C2p_z$ atomic orbitals. The variation principle is then applied, and gives rise to a set of secular equations, which have non-trivial solutions only if

$$\det |\mathbf{h}^{\pi,\text{eff}} - E\mathbf{S}| = 0 \tag{58}$$

where $h_{rs}^{\pi,\text{eff}}$ is the matrix element of $\mathbf{h}^{\pi,\text{eff}}$ between the atomic orbitals of the conjugated atoms r and s and S_{rs} is their overlap integral. This expression is the analogue of the Roothaan equations, eqn 9.21, but differs in the restriction of the hamiltonian to a sum of one-electron terms and the orbitals to π-orbitals. Solution of the secular determinant then yields the set of molecular orbital energies E_i as well as the expansion coefficients of the LCAO. As described in Section 8.9, HMO makes some assumptions about the values of the matrix elements $h_{rs}^{\pi,\text{eff}}$ and S_{rs}:

1. For all overlap integrals, $S_{rs} = \delta_{rs}$.
2. Diagonal elements $h_{rr}^{\pi,\text{eff}} = \alpha$.
3. Off-diagonal elements $h_{rs}^{\pi,\text{eff}} = \beta$ if atoms r and s are neighbours and 0 otherwise.

The setting of selected matrix elements to zero and the parametrizing of nonzero matrix elements are also common features in semiempirical methods.

Because H_π is written as a sum of one-electron terms with explicit forms left unspecified, the HMO method treats repulsions between the π-electrons very poorly (if at all!). As a result, it is only useful for qualitative discussions of π-conjugated systems.

The **Pariser–Parr–Pople method** (PPP) is a much more substantial procedure, but nevertheless quite primitive when compared with current semiempirical procedures. It starts with the hamiltonian H_π of eqn 9.55, which includes π-interelectronic repulsions, and writes the π-electron wavefunction Ψ_π as a Slater determinant of π-electron spinorbitals ϕ_i^π:

$$\Psi_\pi = (n_\pi!)^{-1/2} \det |\phi_a^\pi(1)\phi_b^\pi(2)\ldots\phi_z^\pi(n_\pi)| \tag{59}$$

The optimal spinorbitals are determined by using the variation principle, and satisfy

$$f_1^\pi \phi_a^\pi(1) = \varepsilon_a^\pi \phi_a^\pi(1) \tag{60}$$

where ε_a^π is the orbital energy of spinorbital ϕ_a^π, and where

$$f_1^\pi = h_1^\pi + \sum_u \{J_u(1) - K_u(1)\} \tag{61}$$

The Coulomb (J_u) and exchange (K_u) operators are defined as in eqns 9.9 and 9.10.

At this stage, the calculation is following the *ab initio* route described in Sections 9.1 and 9.2. Indeed, proceeding as in Section 9.4 for the closed-shell case, we can write the π-electron spinorbital as a product of a spin function and a space function; the space function is then expanded in a basis of known functions. The space functions are the π molecular orbitals and the known

basis functions are atomic orbitals θ_i centred on each π-conjugated atom i. For example, in a conjugated hydrocarbon, a basis set consisting of $C2p_z$ atomic orbitals is typically employed. The use of the basis set results in a set of equations analogous to the Roothaan equations, eqn 9.19, with F_{ij} in the latter replaced by the matrix elements F_{ij}^{π}:

$$F_{ij}^{\pi} = \int \theta_i^*(1) f_1^{\pi} \theta_j(1) \, dr_1 \tag{62}$$

and with ε_a replaced by ε_a^{π}. Next, we simplify the notation by defining the one-electron integral

$$h_{ij}^{\pi} = \int \theta_i^*(1) h_1^{\pi} \theta_j(1) \, dr_1 \tag{63}$$

and using the symbol $(ab|cd)$ to represent two-electron integrals over the atomic orbitals, we can write the matrix element F_{ij}^{π} as

$$F_{ij}^{\pi} = h_{ij}^{\pi} + \sum_{l,m} P_{lm}\{(ij|lm) - \tfrac{1}{2}(im|lj)\} \tag{64}$$

where P_{lm} is defined in eqn 9.27.

At this point the PPP method makes some approximations beyond the separation of π and σ orbitals. First, we set $S_{ij} = \delta_{ij}$, as in HMO theory. Then we set some of the two-electron integrals

$$(ab|cd) = \int \theta_a^*(1)\theta_b(1)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\theta_c^*(2)\theta_d(2) \, dr_1 dr_2$$

to zero too, but in a more subtle way than in HMO. The product $\theta_i^*(1)\theta_j(1)$ in which $i \neq j$ is designated a **differential overlap** term (it is the integrand of an overlap integral, so can formally be obtained from an overlap integral by differentiation; hence the name). In the **zero differential overlap approximation** (ZDO), the two-electron integral vanishes unless $a = b$ and $c = d$. In other words, we set the product of atomic orbitals

$$\theta_a^*(1)\theta_b(1) = 0 \qquad \text{if } a \neq b \tag{65}$$

As a result, the two-electron integrals are given by

$$(ab|cd) = \delta_{ab}\delta_{cd}(aa|cc) \tag{66}$$

and the integral $(aa|cc)$, which could be computed theoretically, is often treated as an empirical parameter. In the ZDO approximation, all three-centre and four-centre two-electron integrals are neglected.

In addition, the PPP method usually does not calculate the integrals h_{ij}^{π} theoretically but instead takes some to be empirical parameters and sets the remainder to zero. In particular, for atomic orbitals θ_i and θ_j centred on atoms i and j which are *not* bonded together, h_{ij}^{π} is set to zero, and for atomic orbitals centred on atoms which *are* bonded together, the matrix element is taken to be an empirical parameter β_{ij} which varies with the nature of the atoms i and j. The diagonal elements h_{ii}^{π} are usually set to an empirical parameter α_i. (Note the resemblance to HMO theory at this point.)

If all two-electron integrals $(ab|cd)$ are set to zero and the matrix elements h_{ij}^{π} replaced by the matrix elements $h_{ij}^{\pi,\text{eff}}$, then the PPP method (an SCF treatment) is 'reduced' to the HMO method (which is not an SCF treatment).
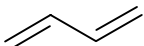
6   Hückel Theory

This theory was originally introduced to permit qualitative study of the π-electron systems in planar, conjugated hydrocarbon molecules (i.e. in "flat" hydrocarbon molecules which possess a mirror plane of symmetry containing all the carbon atoms, and in which the atoms of the carbon skeleton are linked by alternating double and single carbon-carbon bonds when the bonding is represented in a localised fashion). It is thus most appropriate for molecules such as benzene or butadiene, but the approach and concepts have wider applicability.

Basic Assumptions

1.   the atomic orbitals contributing to the π-bonding in a planar molecule (e.g. the so-called p_π orbitals in a molecule such as benzene) are antisymmetric with respect to reflection in the molecular plane; they are therefore of a different symmetry to the atomic orbitals contributing to the σ-bonding and may be treated independently.
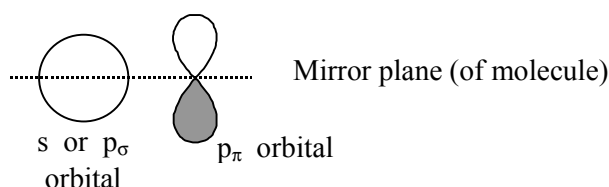
2.   the Coulomb integrals for all the carbon atoms are assumed to be identical.

   i.e. small differences in α-values due to the different chemical environment of C atoms in a molecule such as   are neglected.

3.   all resonance integrals between directly-bonded atoms are assumed to be the same; whilst those between atoms that are not directly bonded are neglected.

   i.e. $\int \phi_i \hat{H} \phi_j . d\tau$ $= \beta$: if atoms i and j are directly σ-bonded.

                                $= 0$: if atoms i and j are non-bonded.

4.   all overlap integrals representing the overlap of atomic orbitals centred on different atoms are neglected.

   i.e. $\int \phi_i \phi_j . d\tau$ $= 0$: if $i \neq j$

   (note - if $i = j$ then $\int \phi_i \phi_j . d\tau$ $= 1$ since it is assumed that the atomic orbitals are normalized)

A Closer Look at the Secular Determinant

The basic form of the secular determinant for the bonding arising from the overlap of two orbitals (from 4.9) is reproduced below.

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix}$$
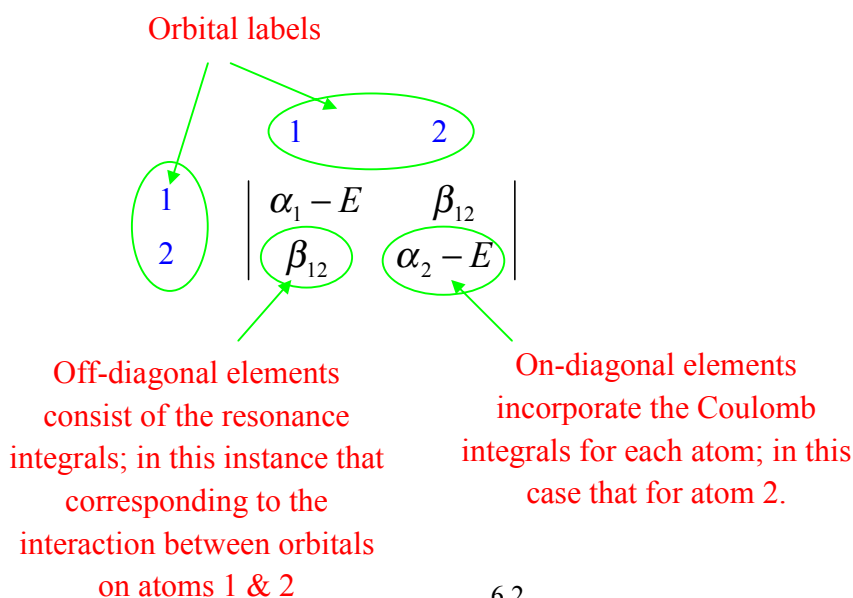
For three overlapping orbitals the approach outlined in Chapter 4 leads to a secular determinant of the form:

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} \\ \beta_{12} & \alpha_2 - E & \beta_{23} \\ \beta_{13} & \beta_{23} & \alpha_3 - E \end{vmatrix}$$

From a comparison of the two secular determinants given above, it is becoming clear that all such secular determinants have a characteristic structure:
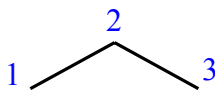
1. each row and column may be associated with one of the atomic orbitals; thus the first row and first column contain information about the nature of orbital 1 and its interactions with the other orbitals, the second row and second column contain information about the nature of orbital 2 and its interactions with the other orbitals.

2. The diagonal set of elements (comprised of those elements where row 1 intersects column 1, row 2 intersects column 2, ….. and so on) include the values of the relevant Coulomb integrals (α_1 , α_2 etc.).

3. The off-diagonal elements (comprised of those elements having different row numbers and column numbers) are equal to the relevant resonance integrals
(e.g. β_{12} at the intersection of row 1 and column 2)

This structure is summarised below, where the rows and columns have been labelled with numbers identifying the associated atomic orbital:

Orbital labels

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix}$$

Off-diagonal elements consist of the resonance integrals; in this instance that corresponding to the interaction between orbitals on atoms 1 & 2

On-diagonal elements incorporate the Coulomb integrals for each atom; in this case that for atom 2.

Linear Conjugated Hydrocarbons

C_3 Molecules (3-atom chain)

Secular Determinant / Equation

	1	2	3
1	$\alpha - E$	β	0
2	β	$\alpha - E$	β
3	0	β	$\alpha - E$

$= 0$

$\Rightarrow$
$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \qquad \text{where} \quad x = \frac{(\alpha - E)}{\beta}$$

$\Rightarrow \qquad x(x.x - 1.1) - 1(1.x - 1.0) + 0(1.1 - x.0) = 0$

$\Rightarrow \qquad x^3 - x - x = 0$

$\Rightarrow \qquad x^3 - 2x = 0$

$\Rightarrow \qquad x(x^2 - 2) = 0$

$\Rightarrow \qquad x = 0 \qquad \underline{\text{or}} \qquad x = \pm\sqrt{2}$

i.e. $\qquad x = +\sqrt{2} ,\ \ 0 ,\ -\sqrt{2}$

Now $\qquad E = \alpha - x\beta$

So the energies of the molecular orbitals are:

$$E = \alpha - \sqrt{2}.\beta \qquad \text{- Highest Energy}$$
$$E = \alpha$$
$$E = \alpha + \sqrt{2}.\beta \qquad \text{- Lowest Energy}$$

The secular equations are:

$$c_1(\alpha - E) \quad + \quad c_2\beta \quad + \quad 0 \quad = \quad 0$$
$$c_1\beta \quad + \quad c_2(\alpha - E) \quad + \quad c_3\beta \quad = \quad 0$$
$$0 \quad + \quad c_2\beta \quad + \quad c_3(\alpha - E) \quad = \quad 0$$

or, in terms of x,

$$c_1x \quad + \quad c_2 \quad + \quad 0 \quad = \quad 0 \qquad [1]$$
$$c_1 \quad + \quad c_2x \quad + \quad c_3 \quad = \quad 0 \qquad [2]$$
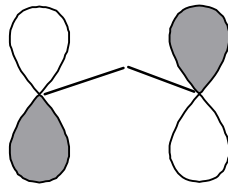$$0 \quad + \quad c_2 \quad + \quad c_3x \quad = \quad 0 \qquad [3]$$

For $\underline{x = 0}$ (i.e. $E = \alpha$)

     [1] $\Rightarrow$ $c_2 = 0$

     [2] $\Rightarrow$ $c_1 + c_3 = 0$ $\Rightarrow$ $c_1 = -c_3$

If we now apply the normalisation condition ($\sum_i c_i^2 = 1$ - see Appendix 2)

     $\Rightarrow$ $|c_1| = |c_3| = \dfrac{1}{\sqrt{2}}$

i.e.

For $\underline{x = -\sqrt{2}}$ (i.e. $E = \alpha + \sqrt{2}.\beta$)

     [1] $-$ [3] $\Rightarrow$ $c_1 - c_3 = 0$ $\Rightarrow$ $c_1 = c_3$

     [1] $\Rightarrow$ $-\sqrt{2}.c_1 + c_2 = 0$ $\Rightarrow$ $c_2 = \sqrt{2}.c_1$

If we now apply the normalisation condition ($\sum_i c_i^2 = 1$ - see Appendix 2)
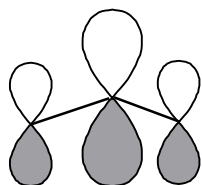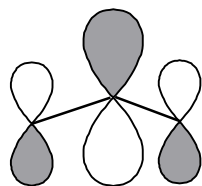
     $\sum c_i^2 = c_1^2 + c_2^2 + c_3^2 = c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 4c_1^2 = 1$

     $\Rightarrow$ $c_1^2 = \dfrac{1}{4}$

     $\Rightarrow$ $c_1 = c_3 = \dfrac{1}{2}$ (= 0.500)

     $\Rightarrow$ $c_2 = \sqrt{2}.\dfrac{1}{2} = \dfrac{1}{\sqrt{2}}$ (= 0.707)

i.e.

For $x = +\sqrt{2}$ (i.e. $E = \alpha - \sqrt{2}.\beta$)

     [1] − [3]   ⇒ $c_1 - c_3 = 0$ ⇒ $c_1 = c_3$

     [1] ⇒ $\sqrt{2}.c_1 + c_2 = 0$ ⇒ $c_2 = -\sqrt{2}.c_1$

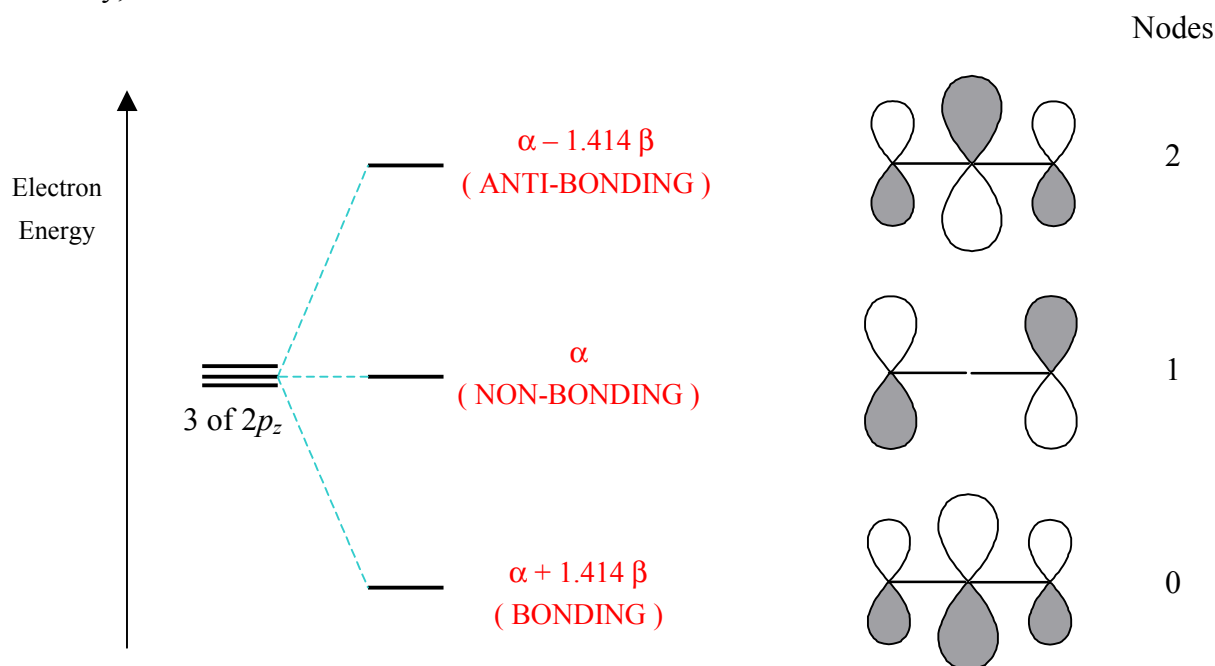If we now apply the normalisation condition ($\sum_i c_i^2 = 1$ - see Appendix 2)

    ⇒ $c_1 = c_3 = \dfrac{1}{2}$ (= 0.500)

    ⇒ $c_2 = \dfrac{-1}{\sqrt{2}}$ (= −0.707)

i.e.

In summary,

Nodes

$\alpha - 1.414\,\beta$
(ANTI-BONDING)   2

α
(NON-BONDING)   1

Electron Energy
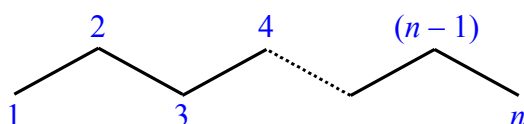
3 of $2p_z$

$\alpha + 1.414\,\beta$
(BONDING)   0

< *Lectures* - examples of bond order and charge distribution calculations for allylic species >

General Solution (n-atom chain ; e.g. $C_nH_{(n+2)}$ conjugated polyenes)

The secular determinant has the same basic form, whatever the chain length, as illustrated below:

	1	2	3			n
1	x	1	0	0	...	0
2	1	x	1			
3	0	1	x			
	0					
					x	1
n	0	...	...	...	1	x

$= 0$

Consequently the solutions also have the same basic form, whatever the chain length, and it can be demonstrated that:

<u>Orbital coefficients</u>: are given by

$$c_s \propto \sin\left(\frac{\pi k s}{n+1}\right) \qquad\qquad [4]$$

where n -   total number of atoms in the conjugated chain
         s -   atom number (i.e. 1, 2, ..., n)
         k -   quantum number, identifying the MO   (= 1, 2, ..., n)

and the constant of proportionality can be determined by applying the normalisation condition.

Example: consider the highest energy MO ($k = 3$) of the three carbon chain ($n = 3$).

$$\Rightarrow \qquad c_s \propto \sin\left(\frac{3\pi s}{4}\right)$$

i.e.

$$c_1 \propto \sin\left(\frac{3\pi}{4}\right) = \frac{1}{\sqrt{2}} \quad , \quad c_2 \propto \sin\left(\frac{6\pi}{4}\right) = -1 \quad , \quad c_3 \propto \sin\left(\frac{9\pi}{4}\right) = \frac{1}{\sqrt{2}}$$
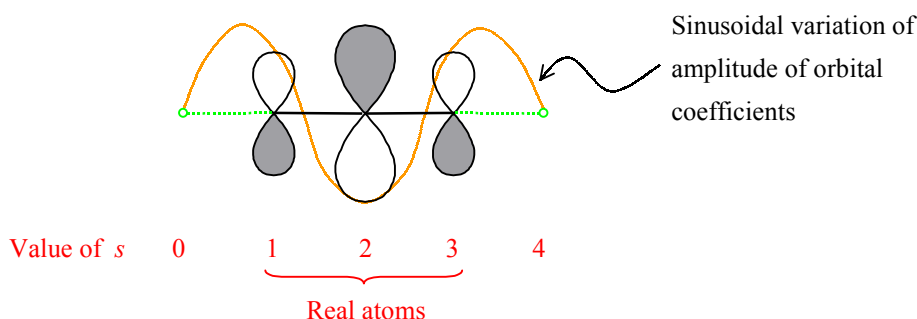
These coefficients are <u>not</u> normalized - to achieve this we need to multiply them all by the same constant value, chosen to ensure that the new values of the coefficients satisfy the condition that $\sum c_i^2 = 1$.

From the general expression for the coefficients given above it can be seen that the relative signs and sizes can also be visualised using the following trigonometric construction.

Procedure :

1. Draw the n-regularly spaced atoms (1, 2, ..., n) in a straight line and then add two imaginary atoms (labelled 0 and $(n + 1)$) at either end of the chain.

2. Sketch portions of sine waves between these two imaginary end atoms, ensuring that the imaginary end atoms correspond to nodes of the sine wave.

3. The lowest energy MO has no other nodes and corresponds to half a sine wave; the next MO has one additional node in the middle and corresponds to a complete sine wave; the next MO has two additional nodes .... and so on.

e.g. for the third MO ($k = 3$) of the three carbon chain ($n = 3$).

Sinusoidal variation of amplitude of orbital coefficients

Value of s 0   1   2   3   4

Real atoms

Orbital energies: are given by

$$E = \alpha + 2\beta \cos\left(\frac{\pi k}{n+1}\right)$$
[5]

where n -   total number of atoms in the conjugated chain

              k -   quantum number, identifying the MO   (= 1, 2, ..., n)

Note that the cosine function varies only between the limiting values of -1 and $+1$.

i.e. $-1 \le \cos\left(\frac{\pi k}{n+1}\right) \le +1$

hence $(\alpha + 2\beta) \le E \le (\alpha - 2\beta)$

Consequently all molecular orbital energies must lie within an energy range of 4β, $\pm 2\beta$ of the original atomic orbital energy.

Recall also that for an n-atom chain, in which each atom contributes one atomic orbital to the conjugated π-system, there will be n overlapping atomic orbitals giving rise to n molecular orbitals.

Since all these MOs are confined to a fixed energy range, it follows that the average energy separation must decrease as n increases. This is illustrated below in an electron energy diagram which also shows the electron occupancy (for the neutral molecule) for the first three members of the series :
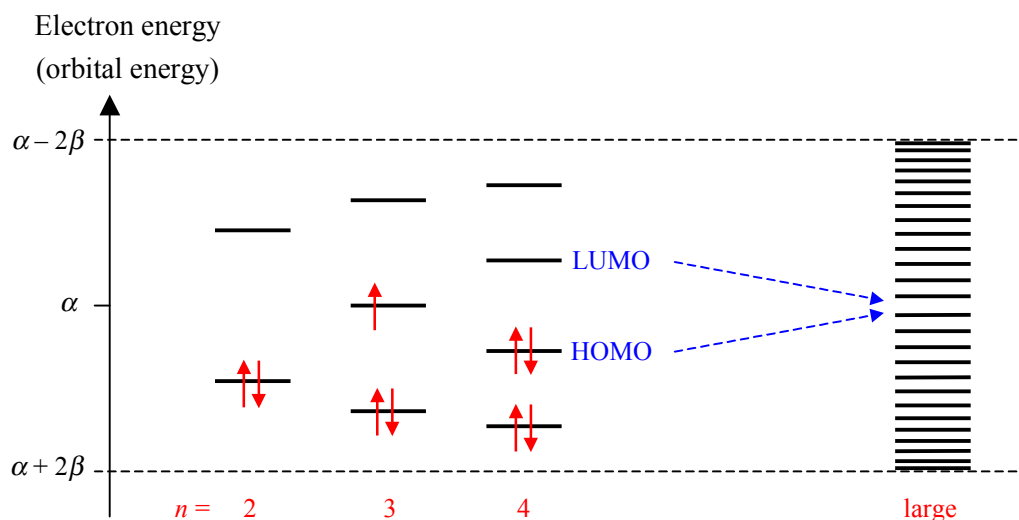
Note:

1. As n increases: the HOMO-LUMO separation decreases - consequently the photon energy required to excite an electron from the HOMO to LUMO also decreases.

    i.e. $h\nu = \Delta E = E_{HOMO} - E_{LUMO}$ decreases as n increases.

    For conjugated carbon atom chains the photon energy changes from the UV (for small n) to the visible (large n). Consequently, molecules with extended conjugated systems are coloured.

2. As $n \rightarrow \infty$: the separation between any two energy levels decreases towards zero and the energy levels (although still discrete in principle) effectively merge to give a continuous *band* of energy levels. The width of this band is 4β and is therefore determined by the effectiveness of overlap of the individual atomic orbitals and hence the strength of interaction and the magnitude of the resonance integral β. The system approaches the *metallic state* - that is to say that electrical conduction can readily occur (since the HOMO-LUMO separation is essentially zero) and all wavelengths of visible light are readily absorbed.

Cyclic Conjugated Hydrocarbons

General Solution (n-atom ring ; C_nH_n , cyclic conjugated hydrocarbons)
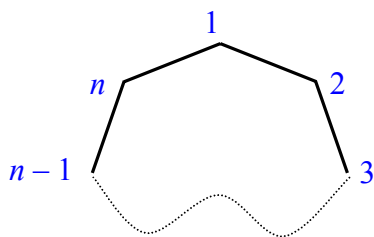
The secular determinant has the same basic form, whatever the ring size, as illustrated below:

	1	2	3			n
1	x	1	0	0	…	1
2	1	x	1			
3	0	1	x			
	0					
					x	1
n	1	…	…	…	1	x

$= 0$

Consequently the solutions also have the same basic form, whatever the ring size, and it can be demonstrated that the:

<u>Orbital energies</u>:   are given by

$$E = \alpha + 2\beta \cos\left(\frac{2\pi k}{n}\right) \qquad\qquad [6]$$

where n -   total number of atoms in the conjugated ring system
               k -   quantum number, identifying the MO   ($= 0, 1, 2, …., n{-}1$)

but, given the periodic and "even" (symmetrical about $\theta = 0$) nature of the cosine function, this permitted range of k-values may also be written in the form

$$k = 0, \pm1, \pm2, …., \left(\frac{n}{2}\right) \qquad\qquad \text{for even } n \text{ .}$$

$$k = 0, \pm1, \pm2, …., \pm\left(\frac{n-1}{2}\right) \qquad\qquad \text{for odd } n \text{ .}$$

Note that the cosine function varies only between the limiting values of -1 and $+1$, and because the cosine function is an even function, the energy depends only on $|k|$.

i.e.
$$-1 \le \cos\left(\frac{2\pi k}{n}\right) \le +1$$
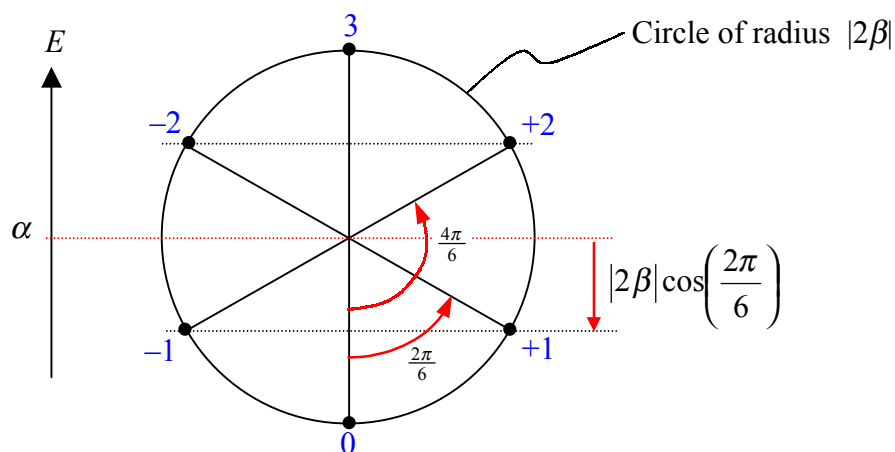
hence
$$(\alpha + 2\beta) \le E \le (\alpha - 2\beta)$$

It is possible to represent equation [6] as a geometrical construction, and this is illustrated below.

Consider $n = 6$ (e.g. C_6H_6 - benzene) ; then the expression for E is

$$E = \alpha + 2\beta \cos\left(\frac{2\pi k}{6}\right)$$

where
$$k = 0, \pm 1, \pm 2, 3 \qquad \text{(since } n \text{ is even).}$$

Whilst the above diagram highlights the relationship between the geometrical construction and the equation for E, it also suggests that the energies of the orbitals may also be obtained using a simpler construction - namely by drawing the corresponding regular polyhedron (i.e. a hexagon for $n = 6$) inscribed inside the circle with one apex coincident with the bottom of the circle.
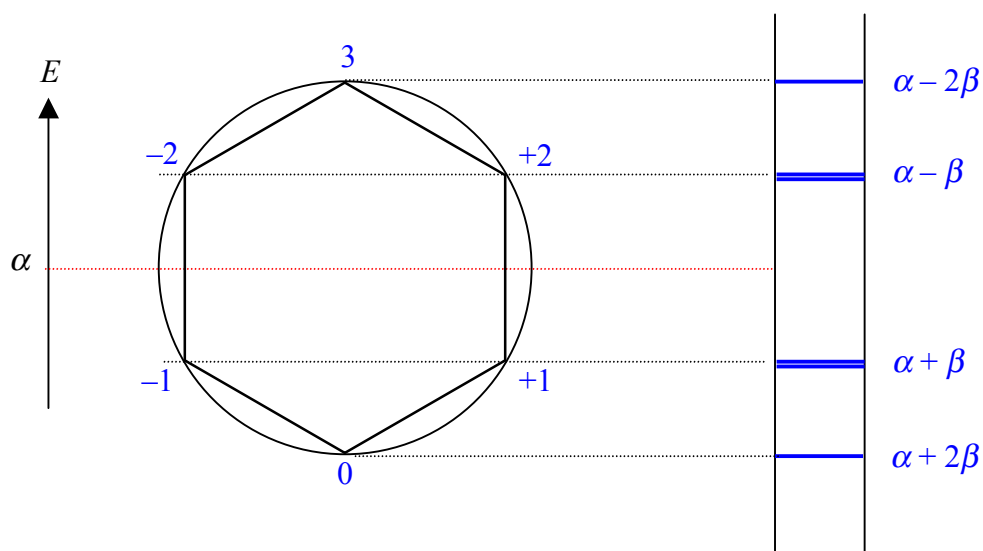
< *Lecture* - other examples, e.g. $n = 3$, $n = 5$ >

6.10

<u>Note</u> : for these cyclic conjugated systems
1. The lowest-energy MO is always non-degenerate
2. The highest-energy MO may be non-degenerate (if n is even) or degenerate (if n is odd).
3. All the remaining solutions form pairs of degenerate MOs

One consequence of this arrangement of the MOs is that only specific numbers of electrons can be accommodated if a stable molecule is to result - this is embodied in the ….

Hückel Rule

A stable, closed-shell conjugated cyclic structure is obtained for ($4N + 2$) electrons.

i.e. stable structures are obtained for 2, 6, 10, …. electrons.

< *Lecture* - examples of stable cyclic systems >
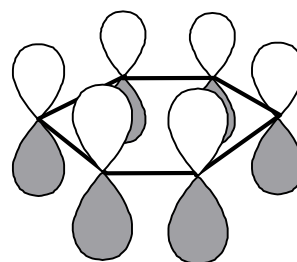
What are the Wavefunctions ?

The wavefunctions are generally complex (i.e. contain imaginary parts), the exceptions being the non-degenerate solution(s).

- The MO of lowest energy ($k = 0$) is always non-degenerate (irrespective of whether n is even or odd) and has the same coefficient for each and every contributing atomic orbital - there are therefore no angular nodes in the wavefunction.

    e.g. for $n = 6$
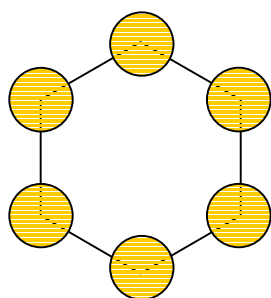
Top view   Side view

The molecular plane is a nodal plane for all the π-MOs , but for this particular MO there are no angular nodal planes in the wavefunction and all the interactions between orbitals on adjacent atoms are of a bonding nature.

- The highest-energy MO of even n systems is also non-degenerate.

  The magnitude of the coefficient is the same for each and every contributing atomic orbital but the sign changes between adjacent atoms.

  e.g. for $n = 6$
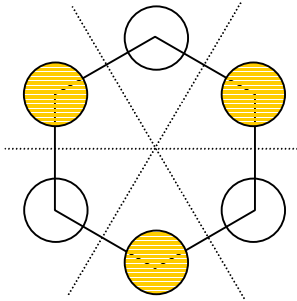
  In this case there are three angular nodal planes as marked (---) on the diagram - the wavefunction thus changes sign between each pair of atoms and all the interactions between orbitals on adjacent atoms are of an anti-bonding nature.

- The remaining degenerate pairs of solutions are complex wavefunctions but it is possible to generate completely real linear combinations of these which are still solutions of the Schrödinger equation with the same energies (in the same way that the p_x and p_y atomic orbitals may be constructed from the p_+ and p_- atomic orbitals).

  The coefficients for the real functions are:

$$\psi_{k+} \propto \sum_s \left(\cos\left(\frac{2\pi ks}{n} \right) \right) \phi_s$$

$$\psi_{k-} \propto \sum_s \left(\sin\left(\frac{2\pi ks}{n} \right) \right) \phi_s$$

  e.g. for $n = 6$

$k = \pm 2$

$s = 0$

$k = \pm 1$

$s = 0$
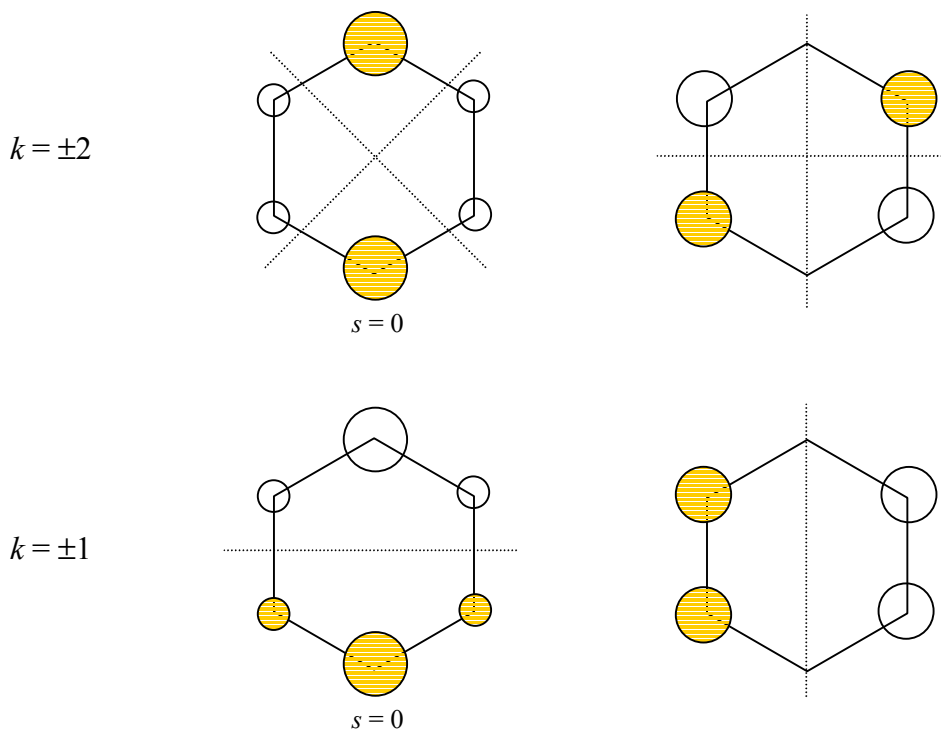
HÜCKEL MOLECULAR ORBITAL THEORY

In general, the vast majority polyatomic molecules can be thought of as consisting of a collection of two-electron bonds between pairs of atoms. So the qualitative picture of σ and π-bonding and antibonding orbitals that we developed for a diatomic like CO can be carried over give a qualitative starting point for describing the C=O bond in acetone, for example. One place where this qualitative picture is extremely useful is in dealing with conjugated systems – that is, molecules that contain a series of alternating double/single bonds in their Lewis structure like 1,3,5-hexatriene:


Now, you may have been taught in previous courses that because there are other resonance structures you can draw for this molecule, such as:

that it is better to think of the molecule as having a series of bonds of order 1 ½ rather than 2/1/2/1/… **MO theory actually predicts this behavior, and this prediction is one of the great successes of MO theory as a descriptor of chemistry**. In this lecture, we show how even a very simple MO approximation describes conjugated systems.

Conjugated molecules of tend to be planar, so that we can place all the atoms in the x-y plane. Thus, the molecule will have reflection symmetry about the z-axis:
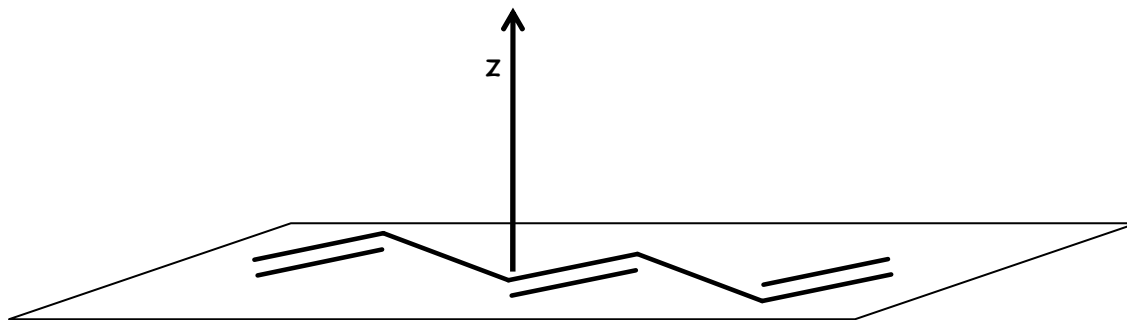
Now, for diatomics, we had reflection symmetry about x and y and this gave rise to π_x and π_y orbitals that were odd with respect to reflection and σ orbitals that were even. In the same way, for planar conjugated systems the orbitals will separate into σ orbitals that are even with respect to reflection

and π_z orbitals that are odd with respect to reflection about z. These π_z orbitals will be linear combinations of the p_z orbitals on each carbon atom:
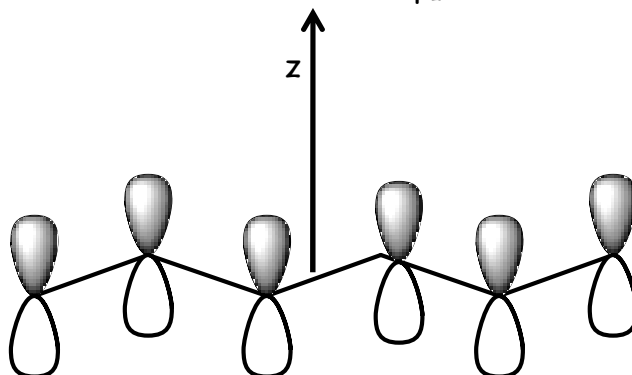
In trying to understand the chemistry of these compounds, it makes sense to focus our attention on these π_z orbitals and ignore the σ orbitals. The π_z orbitals turn out to be the highest occupied orbitals, with the σ orbitals being more strongly bound. Thus, the forming and breaking of bonds – as implied by our resonance structures – will be easier if we talk about making and breaking π bonds rather than σ. Thus, at a basic level, we can ignore the existence of the σ-orbitals and deal only with the π-orbitals in a qualitative MO theory of conjugated systems. This is the basic approximation of Hückel theory, which can be outlined in the standard 5 steps of MO theory:

1) **Define a basis of atomic orbitals**. Here, since we are only interested in the π_z orbitals, we will be able to write out MOs as linear combinations of the p_z orbitals. If we assume there are N carbon atoms, each contributes a p_z orbital and we can write the μth MOs as:

$$\pi^\mu = \sum_{i=1}^{N} c_i^\mu p_z^i$$

2) **Compute the relevant matrix representations**. Hückel makes some radical approximations at this step that make the algebra much simpler without changing the qualitative answer. We have to compute two matrices, **H** and **S** which will involve integrals between p_z orbitals on different carbon atoms:

$$H_{ij} = \int p_z^i \ \hat{H} \ p_z^j d\tau \qquad\qquad S_{ij} = \int p_z^i \ p_z^j d\tau$$

The first approximation we make is that **the p_z orbitals are orthonormal**. This means that:

$$S_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$

Equivalently, this means **S** is the identity matrix, which reduces our generalized eigenvalue problem to a normal eigenvalue problem

$$\mathbf{H} \cdot \mathbf{c}^{\alpha} = E_{\alpha} \mathbf{S} \cdot \mathbf{c}^{\mu} \quad \Rightarrow \quad \mathbf{H} \cdot \mathbf{c}^{\mu} = E_{\mu} \mathbf{c}^{\mu}$$

The second approximation we make is to assume that **any Hamiltonian integrals vanish if they involve atoms i,j that are not nearest neighbors.** This makes some sense, because when the p_z orbitals are far apart they will have very little spatial overlap, leading to an integrand that is nearly zero everywhere. We note also that the diagonal (i=j) terms must all be the same because they involve the average energy of an electron in a carbon p_z orbital:

$$H_{ii} = \int p_z^i \ \hat{H} \ p_z^i d\tau \equiv \alpha$$

Because it describes the energy of an electron on a single carbon, α is often called the on-site energy. Meanwhile, for any two nearest neighbors, the matrix element will also be assumed to be constant:

$$H_{ij} = \int p_z^i \ \hat{H} \ p_z^j d\tau \equiv \beta \quad \text{i,j neigbors}$$

This last approximation is good as long as the C-C bond lengths in the molecule are all nearly equal. If there is significant bond length alternation (e.g. single/double/single…) then this approximation can be relaxed to allow β to depend on the C-C bond distance. As we will see, β allows us to describe the electron delocalization that comes from multiple resonance structures and hence it is often called a resonance integral. There is some debate about what the "right" values for the α, β parameters are, but one good choice is α=-11.2 eV and β=-.7 eV.

3) **Solve the generalized eigenvalue problem.** Here, we almost always need to use a computer. But because the matrices are so simple, we can usually find the eigenvalues and eigenvectors very quickly.

4) **Occupy the orbitals according to a stick diagram.** At this stage, we note that from our N p_z orbitals we will obtain N π orbitals. Further, each carbon atom has one free valence electron to contribute, for a total of N electrons that will need to be accounted for (assuming the molecule is neutral). Accounting for spin, then, there will be $N/2$ occupied molecular orbitals and $N/2$ unoccupied ones. For the ground state, we of course occupy the lowest energy orbitals.

5) **Compute the energy.** Being a very approximate form of MO theory, Hückel uses the non-interacting electron energy expression:

$$E_{tot} = \sum_{i=1}^{N} E_i$$

where E_i are the MO eigenvalues determined in the third step.

To illustrate how we apply Hückel in practice, let's work out the energy of benzene as an example.
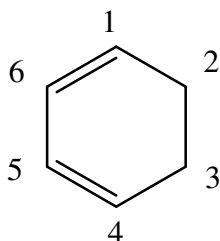
1) Each of the MOs is a linear combination of 6 pz orbitals

$$\psi^{\mu} = \sum_{i=1}^{6} c_i^{\mu} p_z^i \qquad \rightarrow \qquad \mathbf{c}^{\mu} = \begin{pmatrix} c_1^{\mu} \\ c_2^{\mu} \\ c_3^{\mu} \\ c_4^{\mu} \\ c_5^{\mu} \\ c_6^{\mu} \end{pmatrix}$$

2) It is relatively easy to work out the Hamiltonian. It is a 6-by-6 matrix. The first rule implies that every diagonal element is α:

$$\mathbf{H} = \begin{pmatrix} \alpha & & & & & \\ & \alpha & & & & \\ & & \alpha & & & \\ & & & \alpha & & \\ & & & & \alpha & \\ & & & & & \alpha \end{pmatrix}$$

The only other non-zero terms will be between neighbors: 1-2, 2-3, 3-4, 4-5, 5-6 and 6-1. All these elements are equal to β:

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

All the rest of the elements involve non-nearest neighbors and so are zero:

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

3) Finding the eigenvalues of $\mathbf{H}$ is easy with a computer. We find 4 distinct energies:

$E_6 = \alpha - 2\beta$ _____

$E_4 = E_5 = \alpha - \beta$ _____   _____

....

$E_2 = E_3 = \alpha + \beta$ _____   _____

$E_1 = \alpha + 2\beta$ _____

The lowest and highest energies are non-degenerate. The second/third and fourth/fifth energies are degenerate with one another. With a little more work we can get the eigenvectors. They are:

$$\mathbf{c}^6 = \frac{1}{\sqrt{6}} \begin{pmatrix} +1 \\ -1 \\ +1 \\ -1 \\ +1 \\ -1 \end{pmatrix} \quad \mathbf{c}^5 = \frac{1}{\sqrt{12}} \begin{pmatrix} +1 \\ -2 \\ +1 \\ +1 \\ -2 \\ +1 \end{pmatrix} \quad \mathbf{c}^4 = \frac{1}{\sqrt{4}} \begin{pmatrix} +1 \\ 0 \\ -1 \\ +1 \\ 0 \\ -1 \end{pmatrix} \quad \mathbf{c}^3 = \frac{1}{\sqrt{4}} \begin{pmatrix} +1 \\ 0 \\ -1 \\ -1 \\ 0 \\ +1 \end{pmatrix} \quad \mathbf{c}^2 = \frac{1}{\sqrt{12}} \begin{pmatrix} +1 \\ +2 \\ +1 \\ -1 \\ -2 \\ -1 \end{pmatrix} \quad \mathbf{c}^1 = \frac{1}{\sqrt{6}} \begin{pmatrix} +1 \\ +1 \\ +1 \\ +1 \\ +1 \\ +1 \end{pmatrix}$$
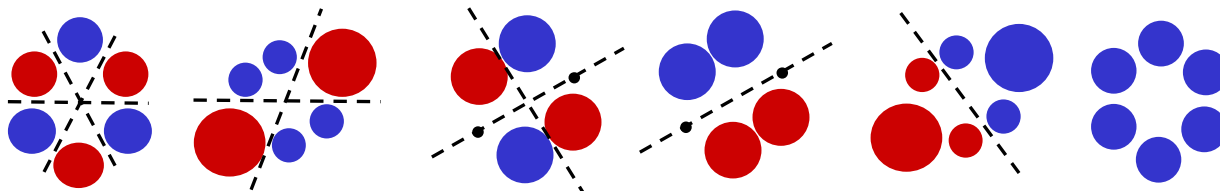
The pictures at the bottom illustrate the MOs by denting positive (negative) lobes by circles whose size corresponds to the weight of that particular p_z orbital in the MO. The resulting phase pattern is very reminiscent of a particle on a ring, where we saw that the ground state had no nodes, the first and second excited states were degenerate (sine and cosine) and had one node, the third and fourth were degenerate with two nodes. The one

difference is that, in benzene the fifth excited state is the only one with three nodes, and it is non-degenerate.

4) There are 6 π electrons in benzene, so we doubly occupy the first 3 MOs:

$E_6 = \alpha - 2\beta$ _____

$E_4 = E_5 = \alpha - \beta$ _____   _____

$E_2 = E_3 = \alpha + \beta$ ↓↑   ↓↑

$E_1 = \alpha + 2\beta$ ↓↑
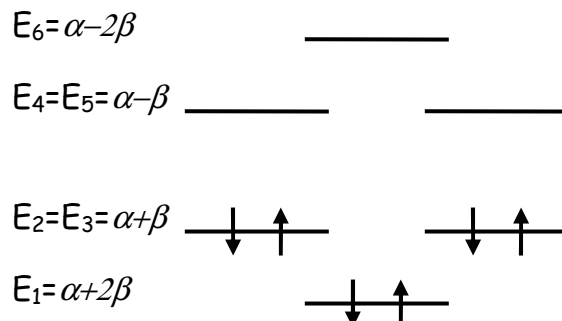
5) The Hückel energy of benzene is then:
$$E = 2E_1 + 2E_2 + 2E_3 = 6\alpha + 8\beta$$

Now, we get to the interesting part. What does this tell us about the bonding in benzene? Well, first we note that benzene is somewhat more stable than a typical system with three double bonds would be. If we do Hückel theory for ethylene, we find that a single ethylene double bond has an energy
$$E_{C=C} = 2\alpha + 2\beta$$

Thus, if benzene simply had three double bonds, we would expect it to have a total energy of
$$E = 3E_{C=C} = 6\alpha + 6\beta$$

which is off by 2β. We recall that β is negative, so that **the π-electrons in benzene are more stable than a collection of three double bonds**. We call this *aromatic stabilization*, and Hückel theory predicts a similar stabilization of other cyclic conjugated systems with 4N+2 electrons. This energetic stabilization explains in part why benzene is so unreactive as compared to other unsaturated hydrocarbons.

We can go one step further in our analysis and look at the bond order. In Hückel theory the bond order can be defined as:
$$O_{ij} \equiv \sum_{\mu=1}^{occ} c_i^{\mu} c_j^{\mu}$$

This definition incorporates the idea that, if molecular orbital μ has a bond between the ith and j^{th} carbons, then the coefficients of the MO on those carbons should both have the same sign (e.g. we have $p_z^i + p_z^j$). If the orbital

is antibonding between i and j, the coefficients should have opposite signs(e.g. we have $p_z^i - p_z^j$). The summand above reflects this because

$$c_i^\mu c_j^\mu > 0 \qquad \text{if } c_i^\mu, c_j^\mu \text{ have same sign}$$

$$c_i^\mu c_j^\mu < 0 \qquad \text{if } c_i^\mu, c_j^\mu \text{ have opposite sign}$$

Thus the formula gives a positive contribution for bonding orbitals and a negative contribution for antibonding. The summation over the occupied orbitals just sums up the bonding or antibonding contributions from all the occupied MOs for the particular ij-pair of carbons to get the total bond order. Note that, in this summation, a doubly occupied orbital will appear twice. Applying this formula to the 1-2 bond in benzene, we find that:

$$O_{12} \equiv 2c_1^{\mu=1} c_2^{\mu=1} + 2c_1^{\mu=2} c_2^{\mu=2} + 2c_1^{\mu=3} c_2^{\mu=3}$$

$$= 2\left(\frac{+1}{\sqrt{6}}\right) \times \left(\frac{+1}{\sqrt{6}}\right) + 2\left(\frac{+1}{\sqrt{12}}\right) \times \left(\frac{+2}{\sqrt{12}}\right) + 2\left(\frac{+1}{\sqrt{4}}\right) \times \left(\frac{0}{\sqrt{4}}\right)$$

$$= 2\frac{1}{6} + 2\frac{2}{12} = \frac{2}{3}$$

Thus, the C_1 and C_2 formally appear to share 2/3 of a π-bond [Recall that we are omitting the σ-orbitals, so the total bond order would be 1 2/3 including the σ bonds]. We can repeat the same procedure for each C-C bond in benzene and we will find the same result: there are 6 equivalent π-bonds, each of order 2/3. This gives us great confidence in drawing the Lewis structure we all learned in freshman chemistry:
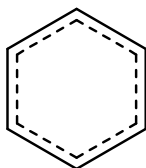
You might have expected this to give a bond order of 1/2 for each C-C π-bond rather than 2/3. The extra 1/6 of a bond per carbon comes directly from the aromatic stabilization: because the molecule is more stable than three isolated π-bonds by 2β, this effectively adds another π-bond to the system, which gets distributed equally among all six carbons, resulting in an increased bond order. This effect can be confirmed experimentally, as benzene has slightly shorter C-C bonds than non-aromatic conjugated systems, indicating a higher bond order between the carbons.

Just as we can use simple MO theory to describe resonance structures and aromatic stabilization, we can also use it to describe crystal field and ligand field states in transition metal compounds and the sp, sp^2 and sp^3 hybrid

orbitals that arise in directional bonding. These results not only mean MO theory is a useful tool – in practice these discoveries have led to MO theory becoming part of the way chemists **think** about molecules.

KEMS448 Physical Chemistry Advanced Laboratory Work
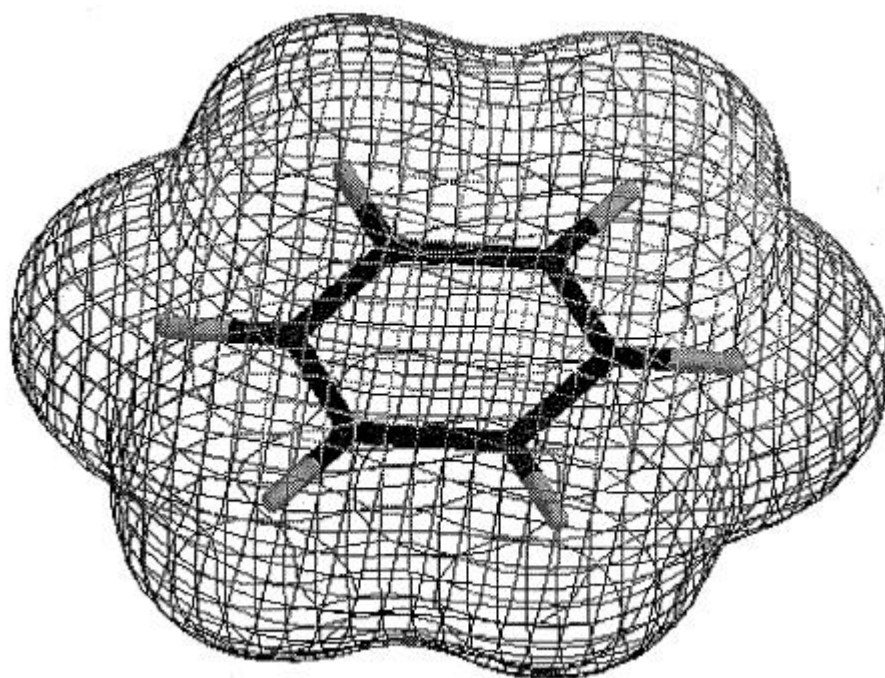
Hückel Molecular Orbital Method

1 Introduction

Quantum chemists often find themselves using a computer to solve the Schrödinger equation for a molecule they want to examine. Nowadays, the computational methods give, in addition to the answer - total energy, orbital energies, and the molecular orbitals - a great number of results derived directly from the answer. These include, for example, bond dipole moments, polarizability, rotational constants, and vibrational frequencies, among many others.

The input data required by the computations may easily be rather complex. Modern chemists use modelling software to automatically produce input data files for the computational software. The results are also, usually, a vast numerical table of data, and interpreting it can be quite complicated. Again, modelling software comes to the rescue: the numerical data can be easily visualized.

In this work, molecular orbital calculations are executed with a method that allows manual calculations, and the results can be simply represented by drawings. This method is called the Hückel Molecular Orbital Method. With this method, despite its simplicity, reasonably accurate results can be derived, when compared to the more advanced computational methods of quantum chemistry. These results include wave functions, energies, atomic charges, and, to some extent, the bond order. The Hückel Molecular Orbital Method contains the most fundamental parts of computational chemistry, and therefore it has a significant role as a visualizing tool.

2 Theoretical basis

2.1 General

The Hückel Molecular Orbital Method (HMO) is a very simple calculative process and it applies only to systems that include conjugated double bonds. Even though the HMO as a calculative method is only an estimate, it is rather useful and educational, because the calculations for small molecules can be done manually.

The necessary assumption, here called the Hückel approximation, is that in canonical structures (conjugated systems) the σ- and π-electrons can be considered separately. For unsaturated molecules, the basic geometry is usually defined by its sigma bonds and the "spine" they form. The $2p_z$-orbitals of the molecule are orthogonal to the spine of the molecule and they form the π part of the bonds. For example, in a benzene molecule, the carbon atoms form σ-bonds to their nearest neighbours through the sp^2-hybrid orbitals, which gives rise to a planar

hexagonal shape (figure 1a). The non-hybridized $2p$-orbital of each carbom atom is orthogonal to the spine of the molecule and can form a π-bond between two neighbouring carbon atoms, with their respective $2p$-orbitals (figure 1b).
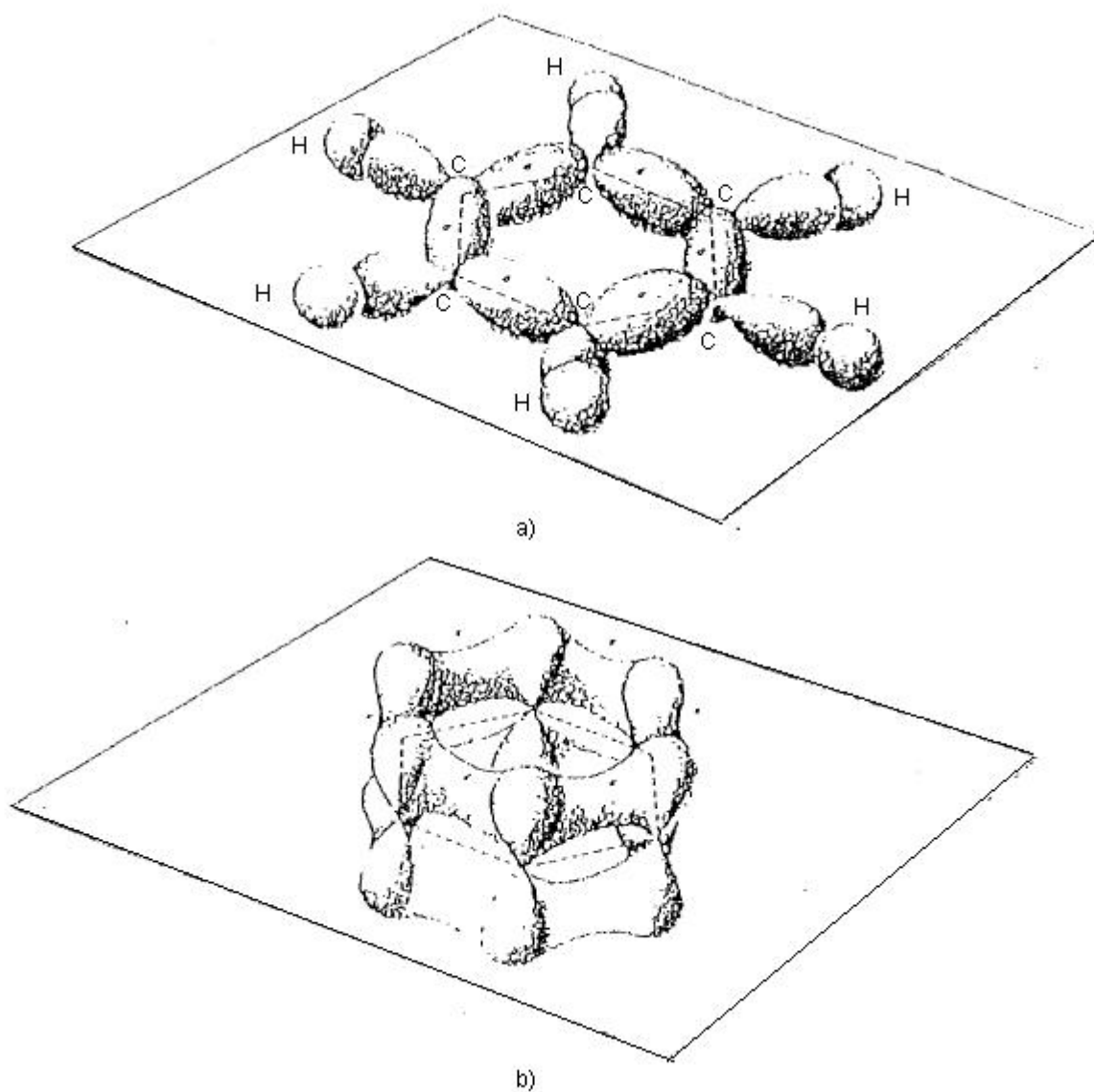

a)

b)

Figure 1: *The orbitals of a benzene molecule. a) The sp^2-orbitals form σ-bonds. b) The delocalized π-bonds.*

2.2 Energy levels and molecular orbitals

In the HMO method, every π- molecular orbital, Ψ_i, is represented by the LCAO principles, as a linear combination of the molecule's atomic p-orbitals, ϕ_i's:

$$\Psi_i = c_{i1}\phi_1 + c_{i2}\phi_2 + \ldots + c_{in}\phi_n = \sum_{\mu=1}^{n} c_{i\mu}\phi_\mu \qquad (1)$$

These orbitals represent the π-electron behaviour in a field formed by the nuclei of the atoms, the shell electrons, and the electrons partaking in σ-bonds or non-bonding pairs. In surroundings like this, the Hamiltonian of a single electron's Schrödinger equation becomes very complicated. Let us discard the interelectronic interactions by assuming the π-electrons move only in the effective field formed by the σ-bonds. Now we form a single-electron Schrödinger equation that can be divided for each separate π- molecular orbital

$$\widehat{H}_{eff}\Psi_i = E_i\Psi_i \qquad (2)$$

$$\Rightarrow E_i = \frac{\left\langle \Psi_i | \widehat{H}_{eff} | \Psi_i \right\rangle}{\langle \Psi_i | \Psi_i \rangle}, i = 1,2,\ldots. \qquad (3)$$

The Hamiltonian is an energy operator that gives out energy values. Minimizing these energies, the LCAO coefficients $c_{i\mu}$ (Equation (1)) can be determined. The π-electron energy levels of the system can be calculated from Equation (3) by using the variation principle to minimize the energy eigenvalues relating them to the atomic orbital coefficients $c_{i\mu}$

$$\frac{\partial E_i}{\partial c_{i\mu}} = 0, \mu = 1,2,\ldots,n. \qquad (4)$$

To calculate the energies E_i, two necessary assumptions are made:

1. The atomic orbitals are normalized:

$$\langle \phi_i | \phi_i \rangle = 1, i = 1,2,\ldots.$$

2. Non-concentric atomic orbitals ϕ_i and ϕ_j are orthogonal, and therefore

$$\langle \phi_i | \phi_j \rangle = 0, i \neq j; i,j = 1,2,\ldots.$$

With the assumptions above, and by substituting molecular orbitals in the form of Equation (1) into Equation (3), we get for the energies

$$E_i = \frac{\sum_\mu c_{i\mu}^2 H_{\mu\mu} + 2\sum_{\mu<\nu} c_{i\mu}c_{i\nu}H_{\mu\nu}}{\sum_\mu c_{i\mu}^2 S_{\mu\mu} + 2\sum_{\mu<\nu} c_{i\mu}c_{i\nu}S_{\mu\nu}}. \tag{5}$$

The following notation was used in Equation (5) for simplicity:

1. $H_{\mu\mu} = \left\langle \phi_\mu | \widehat{H} | \phi_\mu \right\rangle$, which is the coulomb integral representing the energy of a π-electron on an atomic orbital ϕ_μ.

2. $H_{\mu\nu} = \left\langle \phi_\mu | \widehat{H} | \phi_\nu \right\rangle$, when $\mu \neq \nu$, is the resonance integral representing the electronic interactions of the electrons on an atomic orbital.

3. $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$, which is the overlap integral of two different atomic orbitals.

Now, by differentiating the energy with respect to the coefficients $c_{i\mu}$ and finding the points where the derivative is zero, we get a system of equations comprised of n equations.

$$\sum_{\nu=1}^{n} c_\nu \left(H_{\mu\nu} - ES_{\mu\nu} \right) = 0, \mu = 1, \dots, n \tag{6}$$

The system of equations has, in addition to trivial solution, other solutions if the secular determinant formed from the coefficients equals to zero.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \tag{7}$$

To simplify these secular Equations (6), the following approximations are made in the HMO Method:

1. The coulomb integrals $H_{\mu\mu}$ are equal for all carbon atoms ($= \alpha < 0$).
2. The resonance integral $H_{\mu\nu}$ is a constant $\beta < 0$, when atoms μ and ν are bonded.
3. The resonance integral $H_{\mu\nu} = 0$ when there is no bond between atoms μ and

ν.

4. It is assumed that the orbitals of neighbouring atoms do not overlap, therefore $S_{\mu\nu} = 0$ and $S_{\mu\mu} = 1$.

After the following, the secular determinant in Equation (7) gets the form

$$\begin{vmatrix} (\alpha - E) & \beta_{12} & \cdots & \beta_{1n} \\ \beta_{21} & (\alpha - E) & \cdots & \beta_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ \beta_{n1} & \beta_{n2} & \cdots & (\alpha - E) \end{vmatrix} = 0, \tag{8}$$

where $\beta_{\mu\nu} = \beta$, when μ and ν are bonded and $\beta_{\mu\nu} = 0$ when there is no bond between μ and ν.

When the energies have been calculated through the secular determinant, the π-electrons are placed on the energy levels, according to the Pauli principle. On the degenerate energy levels, the Hund rule is applied, placing as many electrons with parallel spins as possible. The molecule has degenerate energy levels when Equation (8) has multiple root solutions. The method presented represents the principle atoms are formed by. The total energy of the molecule can, in this simplified case, be calculated as the sum of the energies of the occupied molecular orbitals.

When calculating for a hydrocarbon molecule, the energy difference between a structure where the π-electrons are delocalized and the structure where they are localized, is called the delocalization energy. Usually, the values of the delocalization energy tell of the stability of the delocalized electronic structure.

Because of the simplicity of the Hückel model, and the Hamiltonian being unaffected by bond lengths and angles, the model does not tell anything of the molecule's structure. Through the model it is possible, however, to determine the energetically most favorable structure, if there are known alternative structures. Because only the bond locations with respect to one another are considered, the model is topological. The matrix representation of the secular equations is called the topological matrix.

2.3 π-electron density and bond order

The molecular orbitals represent the distribution of electrons in the molecule. The shape of the orbital indicates the reaction mechanisms taking place in substitution reactions. The squares and the products of the coefficients can be used to calculate

5

useful quantities of the molecule, and to get an impression of the molecule's properties given by the model.

If the expression of the ith HMO is written in the form of Equation (1), the square of this expression is a quantity describing the electron occurrence probability, i.e. the electron density on the molecular orbital in question:

$$\langle \Psi_i | \Psi_i \rangle = \sum_\mu c_{i\mu}^2, \tag{9}$$

because it was assumed that the overlap integrals are zero when the atoms are not the same. The squares of the coefficients $c_{i\mu}$ are the Hückel molecular orbital electron densities. If the squares of the coefficients are summed up over all occupied molecular orbitals, the total electron density for the atom μ can be calculated from

$$q_\mu = \sum_r^{occ.} n_r c_{r\mu}^2, \tag{10}$$

where n_r is the amount of electrons on the orbital r. For every electrically neutral carbon atom, there is one π-electron in the molecule.

When the atoms μ and ν are bonded, their bond strength can de described by so called bond order

$$p_{\mu\nu} = \sum_r^{occ.} n_r c_{r\mu} c_{r\nu}, \tag{11}$$

where the sum is again over all occupied molecular orbitals. The bond order tells of the electron density between the bonded atoms μ and ν.

These properties have spectroscopic applications, for example in EPR (Electron paramagnetic resonance) spectroscopy. In EPR, the coupling between the pairless electron and the nuclei can be reduced into the spin density at the atom in question. Also for carbon-NMR spectra, the chemical transitions have been discovered to follow the order of magnitude of the atomic charges.

3   Examples

3.1   Butadiene

First we shall look at butadiene, C(1)=C(2)-C(3)=C(4), and how it behaves under the HMO method. First, finding the secular equations. Butadiene has four carbon atoms, so a system of four equations and a 4×4 secular determinant is formed. The secular equations can be written using Equation (6) with the simplifying assumptions. For example, for the first carbon atom ($\mu = 1$):

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) + c_3(H_{13} - ES_{13}) + c_4(H_{14} - ES_{14}) = 0$$

$$\Rightarrow c_1(\alpha - E) + c_2(\beta - E \times 0) + c_3(0 - E \times 0) + c_4(0 - E \times 0) = 0$$

$$\Rightarrow c1(\alpha - E) + c_2\beta = 0$$

Respectively, for the other carbon atoms ($\mu = 2,3,4$), so the system of equations for butadiene is

$$
\begin{cases}
(\alpha - E)c_1 & +\beta c_2 & & & = 0 \\
\beta c_1 & +(\alpha - E)c_2 & +\beta c_3 & & = 0 \\
& \beta c_2 & +(\alpha - E)c_3 & +\beta c_4 & = 0 \\
& & \beta c_3 & +(\alpha - E)c_4 & = 0
\end{cases}
\tag{12}
$$

Let's form a smaller determinant by dividing all equations with β and assigning $x := \frac{\alpha - E}{\beta}$, so the secular equations get the form

$$
\begin{cases}
xc_1 & +c_2 & & & = 0 \\
c_1 & +xc_2 & +c_3 & & = 0 \\
& c_2 & +xc_3 & +c_4 & = 0 \\
& & +c_3 & +xc_4 & = 0
\end{cases}
\tag{13}
$$

of which the determinant is

$$
\begin{vmatrix}
x & 1 & 0 & 0 \\
1 & x & 1 & 0 \\
0 & 1 & x & 1 \\
0 & 0 & 1 & x
\end{vmatrix}
= 0.
\tag{14}
$$

The secular determinant (14) is easy to write directly without solving the system of equations. The number of atoms on the spine of the molecule determines the

size of the determinant. In the case of butadiene, a 4×4 determinant is formed, and i.e. for benzene, the secular determinant would be 6×6. The elements a_{ij} of the determinant can be found with the above x-substitution written onto the diagonal, and the other elements being determined according the bonding in the molecule's spine.

Let's review the secular determinant of butadiene (Equation 14). The diagonal will be marked as x. For the first row, the other elements come from the bonding of the first carbon atom:

- C(1) bonds with C(2) $\rightarrow$ element $a_{12} = 1$
- C(1) doesn't form a bond with C(3) or C(4) $\rightarrow$ element $a_{13} = a_{14} = 0$

Respectively for the second row:

- C(2) bonds with C(1) and C(3) $\rightarrow$ element $a_{21} = a_{23} = 1$
- C(2) doesn't form a bond with C(4) $\rightarrow$ element $a_{24} = 0$.

This way, by only considering the bonding of the atoms in the molecule's spine, the molecular secular determinant can be formed. And, by advancing through Equations (12)-(14) in reverse order, the molecular secular equations can also be found.

The next step is to solve Equation (14), to get the energies and the coefficients. By unwrapping the determinant,

$$x^4 - 3x^2 + 1 = 0 \Rightarrow x^2 = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \pm 1.618, \, or \, x = \pm 0.618.$$

From above, the notation $x = \frac{\alpha - E}{\beta}$ was used, so the energies can be calculated directly from there. The energies are $E = \alpha \pm 0.618\beta$ and $E = \alpha \pm 1.618\beta$. The molecular orbital coefficients $c_{i\mu}$ are found by directly substituting one of the solutions for x into Equation (13), giving the system of equations

$$\begin{cases} -1.618c_1 & +c_2 & & & = 0 \\ c_1 & -1.618c_2 & +c_3 & & = 0 \\ & c_2 & -1.618c_3 & +c_4 & = 0 \\ & & +c_3 & -1.618c_4 & = 0 \end{cases}, \qquad (15)$$

from which the conditions for the coefficients are determined:

$$\begin{cases} 1.618c_1 & = c_2 \\ c_3 & = 1.618c_2 - c_1 = 1.618c_1 \\ c_4 & = c_1 \end{cases} \qquad (16)$$

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From the normalization, $c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$, which finally gives $c_1 = \pm 0.37$.

Because the sign of the wave function does not matter, the positive solution is selected, which gives the values $c_1 = 0.37$, $c_2 = 0.60$, $c_3 = 0.60$ and $c_4 = 0.37$ for the coefficients.

Therefore, the expression for the molecular orbital Ψ_1 is

$$\Psi_1 = 0.37\phi_1 + 0.60\phi_2 + 0.60\phi_3 + 0.37\phi_4; E_1 = \alpha + 1.618\beta. \tag{17}$$

Respectively, for the other three molecular orbitals

$$\begin{cases} \Psi_2 = \quad 0.60\phi_1 \quad +0.37\phi_2 \quad -0.37\phi_3 \quad -0.60\phi_4; \quad E_2 = \alpha + 0.618\beta \\ \Psi_3 = \quad 0.60\phi_1 \quad -0.37\phi_2 \quad -0.37\phi_3 \quad +0.60\phi_4; \quad E_3 = \alpha - 0.618\beta \\ \Psi_4 = \quad 0.37\phi_1 \quad -0.60\phi_2 \quad +0.60\phi_3 \quad -0.37\phi_4; \quad E_4 = \alpha - 1.618\beta \end{cases} \tag{18}$$

Let's draw the energy level diagram for butadiene, place the four π-electrons on the lowest energy levels, and sketch the molecular orbitals.

The total π-electron energy for butadiene is the sum of the molecular orbital energies, $4\alpha + 4.4472\beta$. If butadiene didn't have energy delocalization, the system would comprise of two ethene units. The binding molecular orbital energy for ethene is $\alpha + \beta$ [1], and therefore the energy difference

$$E_\pi(butadiene) - 2 \times E_\pi(ethene) = 0.472\beta \tag{19}$$

is the delocalization energy. If for β we use the value $-75 \frac{kJ}{mol}$, the delozalization energy for butadiene is about $-35 \frac{kJ}{mol}$, which is the extent of the stability of butadiene when compared to a structure with two non-conjugated double bonds. The stabilization is the consequence of π-electrons delocalizing over the whole carbon spine.

Let us calculate the π-electron densities and bond orders for butadiene. The total energy density can be calculated from Equation (10), which gives for butadiene $q_1 = q_2 = 1.00$. Because of symmetry, the atoms 3 and 4 have the same charges as the atoms 1 and 2, so the π-electron density is one on every atom. This means that an electron can be found with equal probability next to any of the four atoms.

The bond orders can be calculated from Equation (11). For butadiene, $p_{12} = p_{34} = 0.89$ and $p_{23} = 0.45$. According to the bond orders, butadiene has double bond character between atoms C(1) and C(2), and between C(3) and C(4).
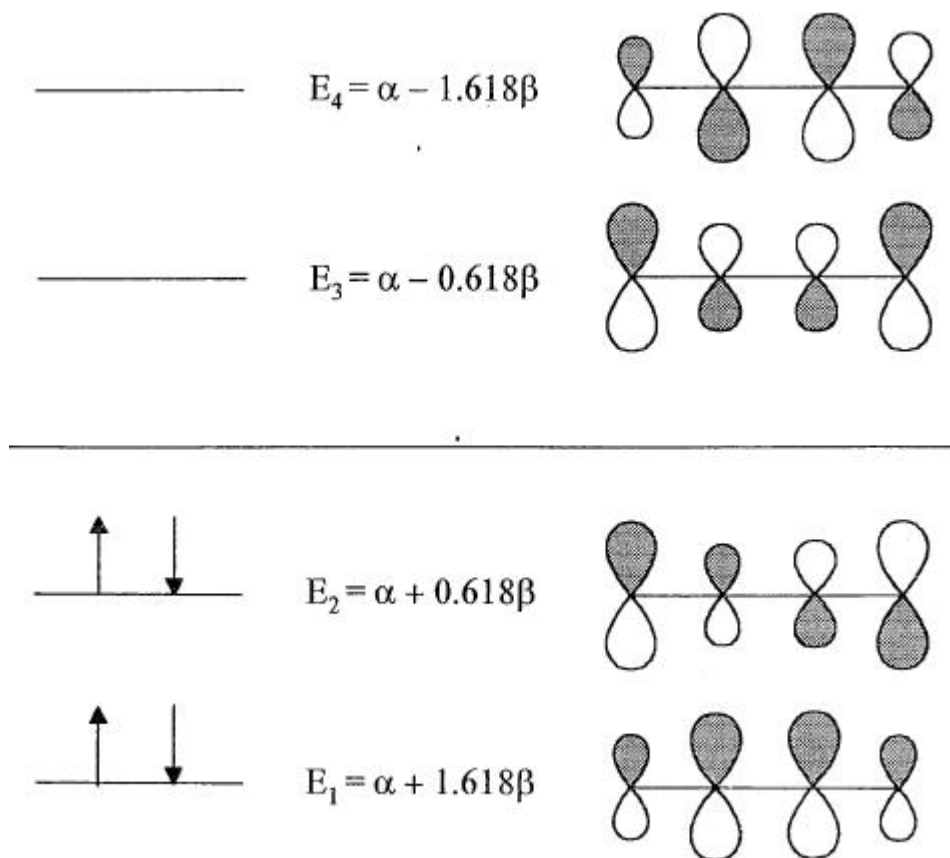
Figure 2: *The energy levels of butadiene and the Hückel molecular orbitals.*

3.2 Cyclopropenyl

As another example, let us examine cyclopropenyl, and find the energy levels and molecular orbitals. First, let us write the secular determinant, with the same choice for x as previously:

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix}. \tag{20}$$

Solving for the energies, we get $E_1 = \alpha + 2\beta$, $E_2 = \alpha \pm \beta$ and $E_3 = \alpha \pm \beta$. We get three energy levels, of which two are degenerate. Cyclopropenyl has three π-electrons, of which two are to be placed on the lowest energy level with opposite spins and the third going to the energy level E_2. Therefore, the total π-electron

energy for cyclopropenyl is $E_\pi = 3\alpha + 3\beta$. The secular equations for cyclopropenyl are

$$\begin{cases} xc_1 & +c_2 & +c_3 & = 0 \\ c_1 & +xc_2 & +c_3 & = 0 \\ c_1 & +c_2 & +xc_3 & = 0 \end{cases} \qquad (21)$$

Substituting the x's we solved earlier into the secular equations, the coefficients for the molecular orbitals can be calculated. This results in $c_1 = c_2 = c_3$, and from the normalization, $c_1 = \pm\frac{1}{\sqrt{3}}$. Therefore, for the first molecular orbital, for $x_1 = -2$

$$\Psi_1 = \frac{1}{\sqrt{3}}\phi_1 + \frac{1}{\sqrt{3}}\phi_2 + \frac{1}{\sqrt{3}}\phi_3. \qquad (22)$$

For the second molecular orbital, $x_2 = 1$, the situation is a bit more complicated, because of the degeneration of the orbital energies. By substituting it into the secular equations, three similar equations will be gotten, for which $c_1 + c_2 + c_3 = 0$.

For degenerate orbitals, the molecular orbital theory does not give separate solutions for the coefficients. They can be chosen freely, as long as they follow the orthogonality rule of the secular equations. For the second molecular orbital of cyclopropenyl, Ψ_2, it can simply be chosen that $c_1 = c_1$, $c_2 = 0$ and $c_3 = -c_1$. Again, through the normalization, $c_1 = \frac{1}{\sqrt{2}}$, and for the molecular orbital

$$\Psi_2 = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_3, \qquad (23)$$

which is orthogonal to Ψ_1. In finding the third molecular orbital, Ψ_3 we cannot choose the coefficients freely anymore, but the orthogonality rules must be followed:

$$\langle \Psi_3 | \Psi_1 \rangle = 0, \langle \Psi_3 | \Psi_2 \rangle = 0. \qquad (24)$$

For the third molecular orbital, through Equation (1),

$$\langle \Psi_3 | \Psi_2 \rangle = \frac{1}{\sqrt{2}} \langle c_1\phi_1 + c_2\phi_2 + c_3\phi_3 | \phi_1 - \phi_3 \rangle$$

$$= \frac{1}{\sqrt{2}}c_1 - \frac{1}{\sqrt{2}}c_3 = 0,$$

so $c_1 = c_3$. Substitute this into the secular equation, which gives $c_2 = -2c_1$. From normalization, $c_1 = \frac{1}{\sqrt{6}} = c_3$ and $c_2 = -\frac{2}{\sqrt{6}}$. Therefore the third molecular orbital for cyclopropenyl is

$$\Psi_3 = \frac{1}{\sqrt{6}}\phi_1 - \frac{2}{\sqrt{6}}\phi_2 + \frac{1}{\sqrt{6}}\phi_3, \tag{25}$$

which is orthogonal also with Ψ_1.

3.3 Heteroatoms

The HMO method can be expanded to heteroatomic systems. In this case, for heteroatom X, in place of the coulombic integral $\alpha = \alpha_C$, and the resonance integral $\beta = \beta_{CC}$ we'll use

$$\begin{cases} \alpha_x & = \alpha_C + h_x \beta_{CC} \\ \beta_{Rx} & = k_{Rx}\beta_{CC} \end{cases}, \tag{26}$$

where the constants h_x and k_{Rx} are dependent of the heteroatom and the bond between the two atoms. Some values for these constants for different heteroatoms can be found in Table 1.

As an example, let us form the secular determinant of $C(1)H_2=C(2)=O(3)$:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta_{CO} \\ 0 & \beta_{CO} & \alpha_O - E \end{vmatrix} \tag{27}$$

Table 1: Values for the heteroatomic constants h_x and k_{Rx}

Atom X	h_x	bond R-X	k_{Rx}
N-	0.5	C-N	0.8
N=	1.5	C=N	1.0
N$^+$	2.0	N-O	0.7
O-	1.0	C-O	0.8
O=	2.0	C=O	1.0

By using the constants in Table 1, we'll get

$$\begin{cases} \alpha_O & = \alpha + 2.0\beta \\ \beta_{CO} & = 1.0\beta \end{cases},$$ (28)

where $\alpha = \alpha_C$ and $\beta = \beta_{CC}$. The secular determinant is therefore

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & 1{,}0\beta \\ 0 & 1.0\beta & \alpha - E + 2.0\beta \end{vmatrix} = 0,$$ (29)

which gives with the same method as previously

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1{,}0 \\ 0 & 1.0 & x + 2.0\beta \end{vmatrix} = 0,$$ (30)

which can be solved as before.

4 Calculations and results

First, manually calculate, for a small molecule given to you by the assistant, the π-electron energies, the orbital coefficients $c_{i\mu}$, π-electron densities and bond orders for each atom and bond. In the report, a sufficient amount of intermediate steps in calculations must be provided, in addition to written comments about the steps made. Discuss and comment on the results.

Then, draw an energy level diagram, and place the π-electrons according to rules and principles. Sketch the molecular orbitals, taking note on the signs.

References

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[2] Murrell J.N., Kettle S.F.A., Tedder J.M., *Valence Theory*, 2nd Edition, 1970, John Wiley & Sons Ltd.

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