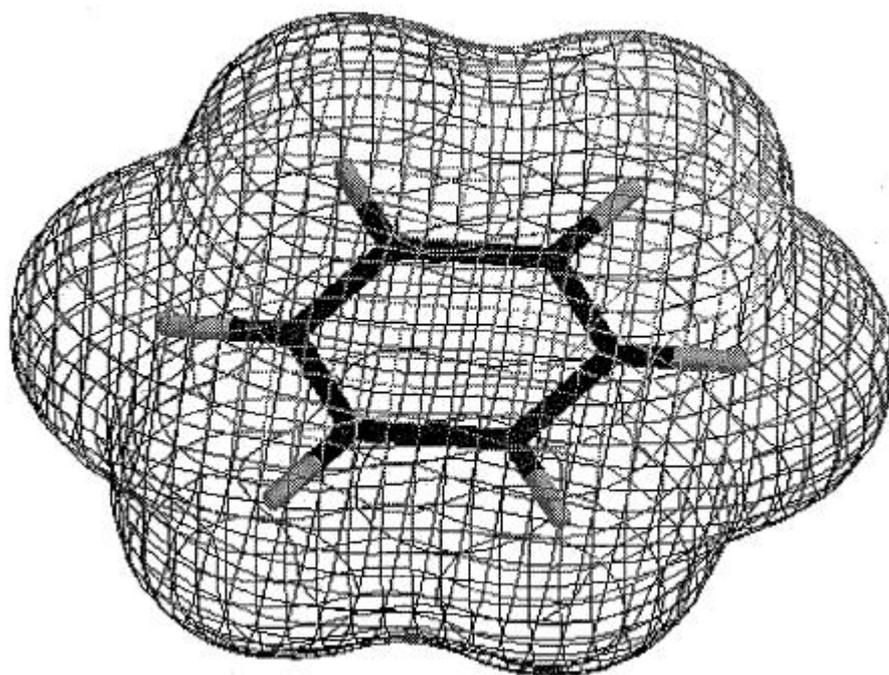


KEMS448 PHYSICAL CHEMISTRY
ADVANCED LABORATORY WORK



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 carbon 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).

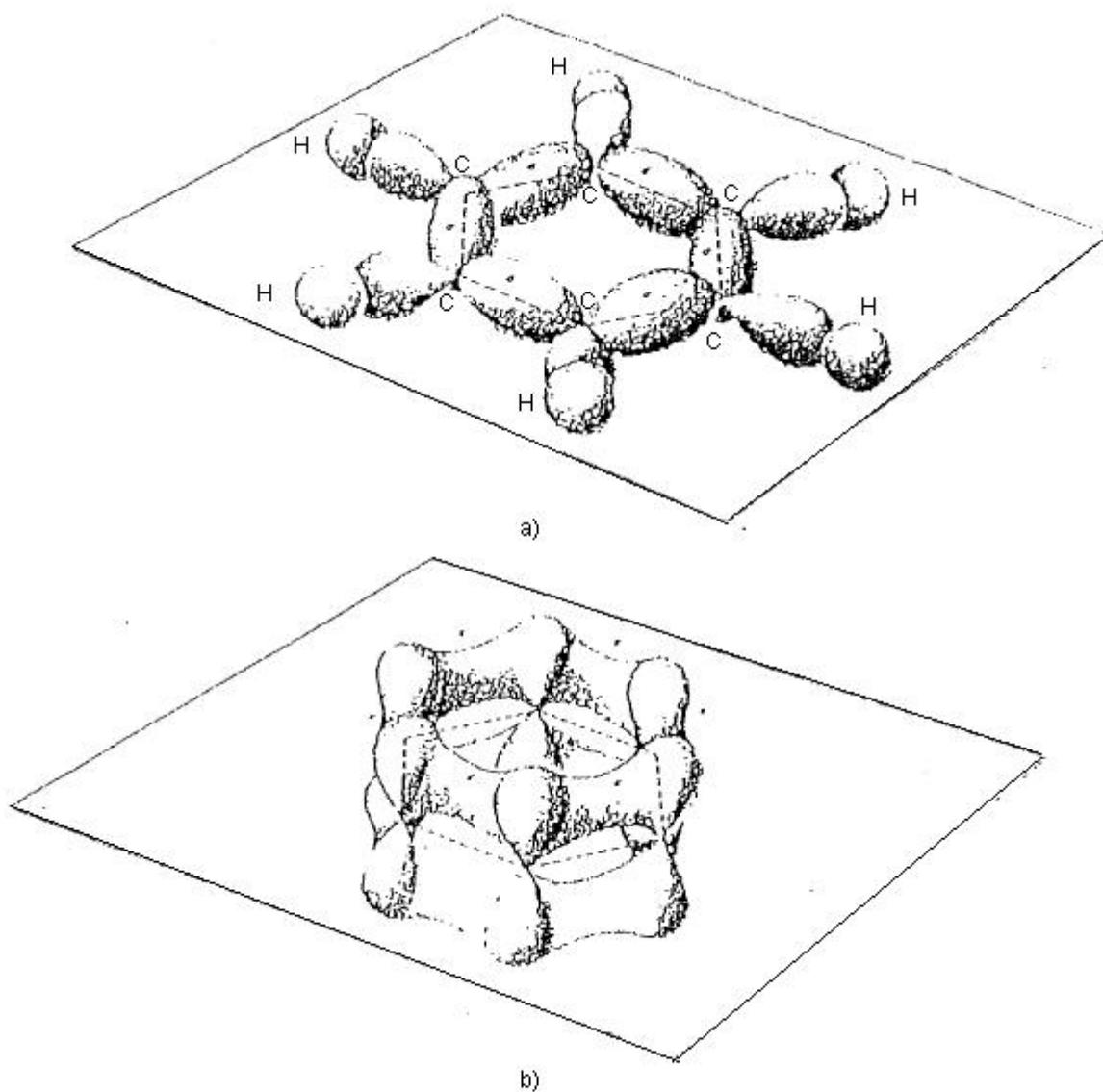


Figure 1: *The orbitals of a benzene molecule. a) The sp^2 -orbitals form σ -bonds. b) The delocalized π -bonds.*

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:

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

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 inter-electronic 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

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

$$\Rightarrow E_i = \frac{\langle \Psi_i | \widehat{H}_{eff} | \Psi_i \rangle}{\langle \Psi_i | \Psi_i \rangle}, i = 1, 2, \dots \quad (3)$$

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 $c_{i\mu}$

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

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

1. The atomic orbitals are normalized:

$$\langle \phi_i | \phi_i \rangle = 1, i = 1, 2, \dots$$

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

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

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

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

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

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

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

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

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

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

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

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

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

If the expression of the i th 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:

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

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

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

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 be described by so called bond order

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

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 ($\mu = 1$):

$$\begin{aligned} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) + c_3(H_{13} - ES_{13}) + c_4(H_{14} - ES_{14}) &= 0 \\ \Rightarrow c_1(\alpha - E) + c_2(\beta - E \times 0) + c_3(0 - E \times 0) + c_4(0 - E \times 0) &= 0 \\ \Rightarrow c_1(\alpha - E) + c_2\beta &= 0 \end{aligned}$$

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

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

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

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

of which the determinant is

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0. \quad (14)$$

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,

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

$$x = \pm 1.618, \text{ or } x = \pm 0.618.$$

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

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

from which the conditions for the coefficients are determined:

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

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

$$\Psi_1 = 0.37\phi_1 + 0.60\phi_2 + 0.60\phi_3 + 0.37\phi_4; E_1 = \alpha + 1.618\beta. \quad (17)$$

Respectively, for the other three molecular orbitals

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

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

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

is the delocalization energy. If for β we use the value $-75 \frac{\text{kJ}}{\text{mol}}$, the delocalization energy for butadiene is about $-35 \frac{\text{kJ}}{\text{mol}}$, 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).

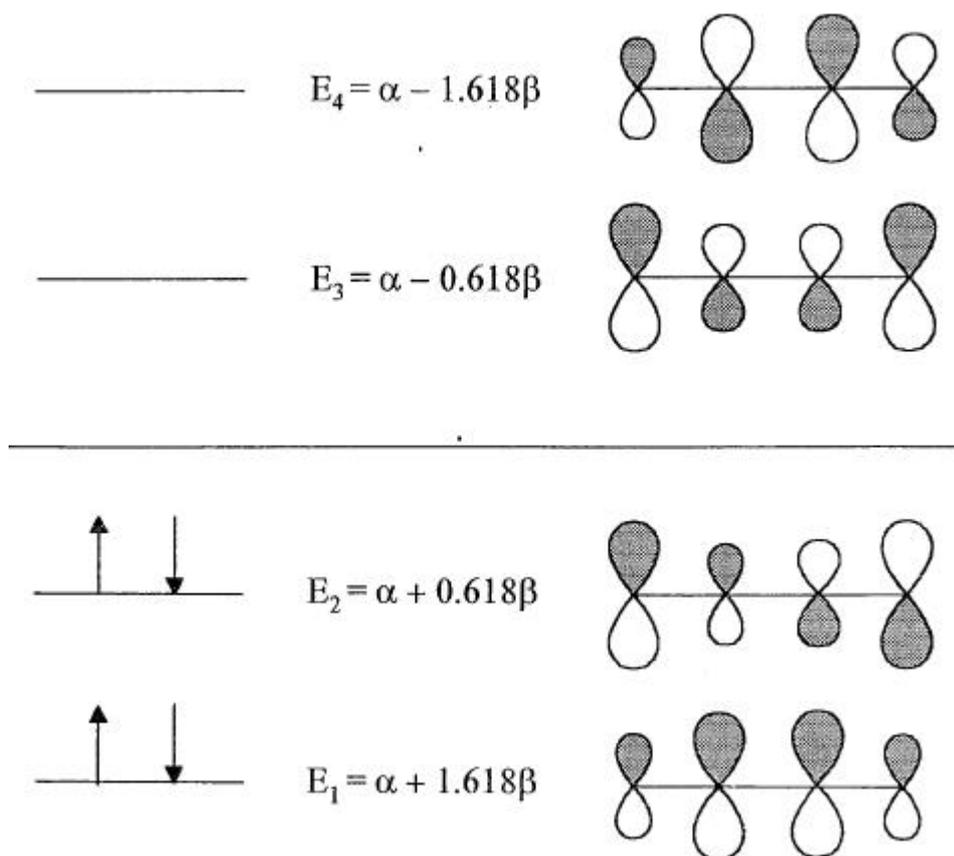


Figure 2: *The energy levels of butadiene and the Hückel molecular orbitals.*

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:

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix}. \quad (20)$$

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

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

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 $x_1 = -2$

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

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

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

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:

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

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

$$\begin{aligned} \langle \Psi_3 | \Psi_2 \rangle &= \frac{1}{\sqrt{2}} \langle c_1\phi_1 + c_2\phi_2 + c_3\phi_3 | \phi_1 - \phi_3 \rangle \\ &= \frac{1}{\sqrt{2}}c_1 - \frac{1}{\sqrt{2}}c_3 = 0, \end{aligned}$$

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

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

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

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

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 $\text{C}(1)\text{H}_2=\text{C}(2)=\text{O}(3)$:

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

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

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

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

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

which gives with the same method as previously

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

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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