

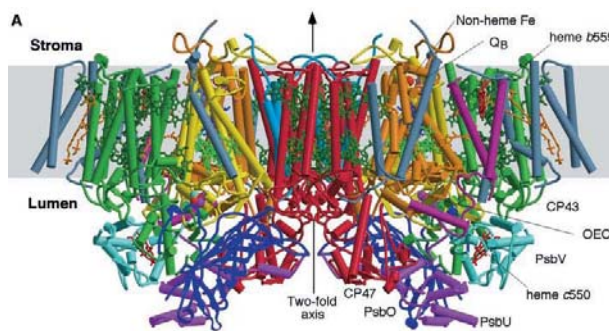
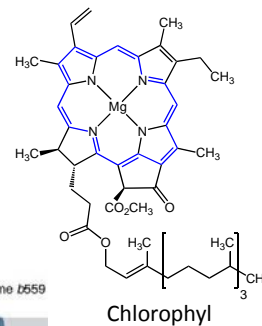
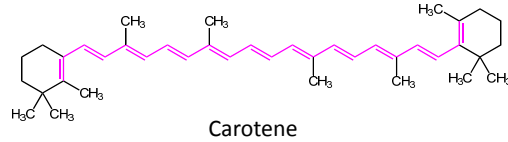
Hückel Molecular Orbital (HMO) Theory

A simple quantum mechanical concept that gives important insight into the properties of large molecules

Why HMO theory

- The first MO theory that could be applied to large molecules.
- A theory that can be implemented without the aid of a computer.
- Has been the starting point for very successful theoretical interpretation of electronic (UV-vis) spectra of conjugated and aromatic hydrocarbons.
- Has been the starting point for more advanced theories.

Important conjugated and aromatic compounds



Molecular electronics

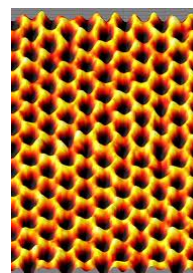
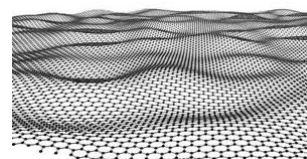
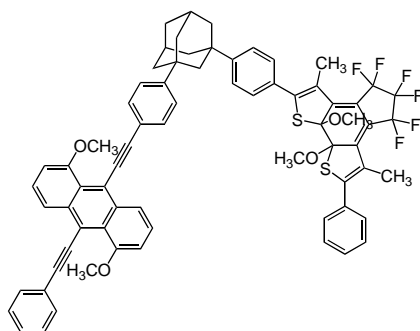
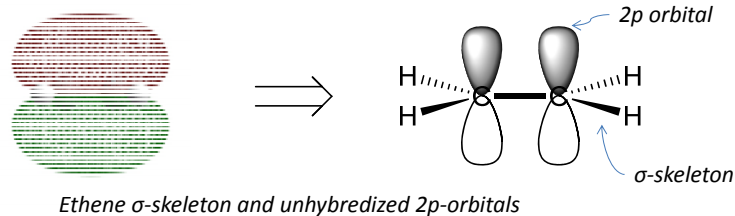


Image of graphene taken with TEAM 0.5
NANO LETTERS, 2008, 8, 3582-3586

The basis of the Hückel approach 1

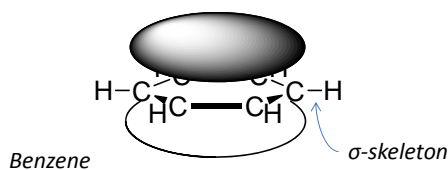


- The geometries and special properties of **conjugated** and **aromatic** compounds may be interpreted in terms of the sp²-hybridization.
- The unhybridized 2p AOs perpendicular to the sp² hybrid orbitals are available for the formation of the π -electron structure.
- The σ -electrons are disregarded, except for their role in establishing the molecular geometry.

S. M. Lindsay *Introduction to Nanoscience* pp 279-284

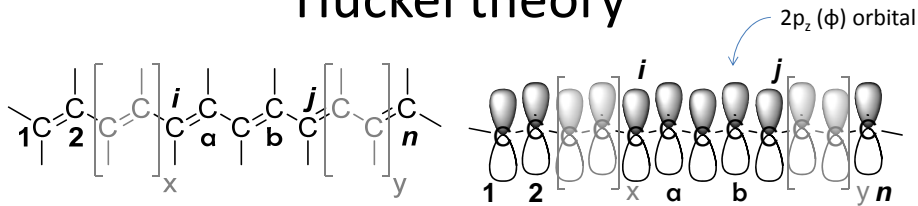
B.H. Bransden and C.J. Joachain *Physics of Atoms and Molecules* 2nd Edn. pp 533-537

The basis of the Hückel approach 2



- There is **no bonding interaction between σ - and π -orbitals in planar conjugated molecules.**
 - The σ -bonds between the sp²-hybridized atoms and their neighbours (the σ -orbitals) lie in the molecular plane. The σ -orbitals are **symmetrical** with respect to reflection in the plane of the molecule.
 - The unhybridized 2p AOs are perpendicular to the molecular skeleton made up by the sp² hybridized atoms. Any MO (π -orbital) formed from them will therefore be **antisymmetrical** with respect to reflection in the plane of the molecule.
- The two types of electrons move in different regions of space: the σ -electrons occupy the space in the plane of the conjugated molecule, the π -electrons are located above and below that plane.
- (The energies of the σ -electrons are on the whole lower than those of the π -electrons. The σ -electrons are involved in strong bonds and the π -electrons in weaker ones.)

Hückel theory

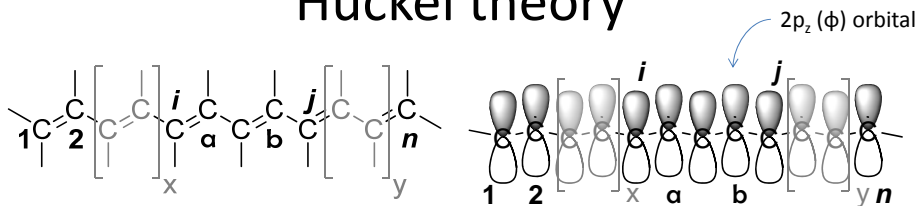


The total π -electron energy E_π is:

$$E_\pi = \sum_{l=1}^{N=n} r_l \varepsilon_l$$

Where r_l is the number of electrons in molecular orbital l .

Hückel theory



The problem: find the set of π -electron MOs (ψ_l) formed as linear combinations of the $2p_z(\phi)$ orbitals at the atoms in the conjugated system.

$$\psi_l = c_{l1}\phi_1 + c_{l2}\phi_2 + c_{l3}\phi_3 + \dots + c_{ln}\phi_n = \sum_i^n c_{li}\phi_i$$

The variation theorem gives that the best wave function is the one that gives the lowest energy E_l .

S. M. Lindsay *Introduction to Nanoscience* pp 279-284
B.H. Bransden and C.J. Joachain *Physics of Atoms and Molecules* 2nd Edn. pp 130-135

Expectation value of the MO energy ε_l

The expectation value of the energy ε_l is:

$$\begin{aligned}\varepsilon_l &= \frac{\langle \Psi_l | \hat{H} | \Psi_l \rangle}{\langle \Psi_l | \Psi_l \rangle} = \frac{\langle \sum_i^n c_{li} \phi_i | \hat{H} | \sum_j^n c_{lj} \phi_j \rangle}{\langle \sum_i^n c_{li} \phi_i | \sum_j^n c_{lj} \phi_j \rangle} = \left\langle \sum_{i=1}^n c_{li} \phi_i \left| \hat{H} \right| \sum_{j=1}^n c_{lj} \phi_j \right\rangle \left/ \left\langle \sum_{i=1}^n c_{li} \phi_i \left| \sum_{j=1}^n c_{lj} \phi_j \right. \right\rangle \right. \\ &= \frac{\sum_{i=1}^n c_{li}^* \sum_{j=1}^n c_{lj} \langle \phi_i | \hat{H} | \phi_j \rangle}{\sum_{i=1}^n c_{li}^* \sum_{j=1}^n c_{lj} \langle \phi_i | \phi_j \rangle} \equiv \frac{\sum_{i=1}^n c_{li}^* \sum_{j=1}^n c_{lj} H_{ij}}{\sum_{i=1}^n c_{li}^* \sum_{j=1}^n c_{lj} S_{ij}}\end{aligned}$$

Where $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$ is the **resonance or interaction integral** and $S_{ij} = \langle \phi_i | \phi_j \rangle$ is the **overlap integral**.

Rearrange and drop the index l since the equation applies to any of the π molecular orbitals

$$\varepsilon = \frac{\sum_{i=1}^n c_i^* \sum_{j=1}^n c_j H_{ij}}{\sum_{i=1}^n c_i^* \sum_{j=1}^n c_j S_{ij}}$$

Variational approach

To find the minimum energy, differentiate both sides of the expression for ε_l with respect to the coefficients c_a , where a runs from 1 to n .

$$\frac{\partial \varepsilon}{\partial c_a} = 0$$

Rearrange and differentiate

$$\varepsilon \left(\sum_i^n c_i^* \sum_j^n c_j S_{ij} \right) = \sum_i^n c_i^* \sum_j^n c_j H_{ij}$$

$$\frac{\partial \varepsilon}{\partial c_a} \left(\sum_{i=1}^n c_i^* \sum_{j=1}^n c_j S_{ij} \right) + \varepsilon \frac{\partial (\sum_i^n c_i^* \sum_j^n c_j S_{ij})}{\partial c_a} = \frac{\partial \sum_i^n c_i^* \sum_j^n c_j H_{ij}}{\partial c_a}$$

$$\frac{\partial \varepsilon}{\partial c_a} = 0, \text{ including } \frac{\partial \varepsilon}{\partial c_a^*} = 0, \text{ thus } \varepsilon \frac{\partial (\sum_i^n c_i^* \sum_j^n c_j S_{ij})}{\partial c_a} = \frac{\partial \sum_i^n c_i^* \sum_j^n c_j H_{ij}}{\partial c_a}$$

The derivative will be non-zero *only* for those terms where $j = a$.

S. M. Lindsay *Introduction to Nanoscience* pp 63 and 268-270

$$\varepsilon \left(\sum_i^n c_i^* S_{ia} \right) = \sum_i^n c_i^* H_{ia}$$

Take the complex conjugate of each side.

$$\varepsilon^* \left(\sum_i^n c_i S_{ia}^* \right) = \sum_i^n c_i H_{ia}^*$$

But $\varepsilon = \varepsilon^*$, $S_{ia} = S_{ai}^*$ and $H_{ia} = H_{ai}^*$

$$\varepsilon \left(\sum_i^n c_i S_{ai} \right) = \sum_i^n c_i H_{ai}$$

Rearrange.

$$\sum_{i=1}^n c_i (H_{ai} - \varepsilon S_{ai}) = 0$$

There are n simultaneous equations, **one for each coefficient** – a set of homogeneous linear equations – the secular equations.

Secular equations

There are n simultaneous equations, **one for each coefficient** – a set of homogeneous linear equations – the secular equations.

$$\begin{aligned} c_1(H_{11} - \varepsilon S_{11}) + c_2(H_{12} - \varepsilon S_{12}) + \dots + c_n(H_{1n} - \varepsilon S_{1n}) &= 0 \\ c_1(H_{21} - \varepsilon S_{21}) + c_2(H_{22} - \varepsilon S_{22}) + \dots + c_n(H_{2n} - \varepsilon S_{2n}) &= 0 \\ \vdots & \\ c_1(H_{n1} - \varepsilon S_{n1}) + c_2(H_{n2} - \varepsilon S_{n2}) + \dots + c_n(H_{nn} - \varepsilon S_{nn}) &= 0 \end{aligned}$$

Rewritten in matrix notation

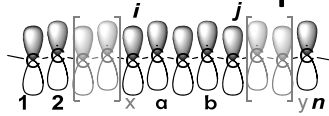
$$\begin{pmatrix} (H_{11} - \varepsilon S_{11}) & (H_{12} - \varepsilon S_{12}) & \dots & (H_{1n} - \varepsilon S_{1n}) \\ (H_{21} - \varepsilon S_{21}) & (H_{22} - \varepsilon S_{22}) & \dots & (H_{2n} - \varepsilon S_{2n}) \\ \vdots & \vdots & \ddots & \vdots \\ (H_{n1} - \varepsilon S_{n1}) & (H_{n2} - \varepsilon S_{n2}) & \dots & (H_{nn} - \varepsilon S_{nn}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

or

$$(H - \varepsilon S)C' = 0$$

where C' is a column vector.

Hückel's assumptions



- The **overlap integral** S_{ij} is a measure of the extent of overlap between the $2p_z$ AOs on carbon atoms i and j .
 - $i = j$: $S_{ij} = 1$, because the overlap of an AO with itself is unity for a normalized wave function.
 - $i \neq j$: $S_{ij} = 0$. A drastic assumption*
- The **resonance integral** H_{ij} represents the energy of a single electron moving in the average field of all the nuclei, all the σ -electrons and all other π -electrons.
 - $i = j$: $H_{ij} = \alpha$. The integral represents the energy of an electron in a "free" carbon $2p_z$ AOs in a molecule.
 - Carbon i adjacent to $j = i \pm 1$: $H_{i(i \pm 1)} = \beta$.**
 - H_{ij} negligible (= 0) if the two carbons i and j are separated by two or more bonds.**

* The overlap integral for two $2p_z$ orbitals, one each on two adjacent carbon atoms in a conjugated compound, is approximately 0.25. It falls off rapidly with increasing distance.

** The molecular structure (connectivity) has to be known on beforehand.

Apply Hückel's approximations

The secular equations.

$$\begin{pmatrix} (H_{11} - \epsilon S_{11}) & (H_{12} - \epsilon S_{12}) & \cdots & (H_{1n} - \epsilon S_{1n}) \\ (H_{21} - \epsilon S_{21}) & (H_{22} - \epsilon S_{22}) & \cdots & (H_{2n} - \epsilon S_{2n}) \\ \vdots & \vdots & \ddots & \vdots \\ (H_{n1} - \epsilon S_{n1}) & (H_{n2} - \epsilon S_{n2}) & \cdots & (H_{nn} - \epsilon S_{nn}) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

Simplifies to:

$$\begin{pmatrix} (\alpha - \epsilon) & (\beta - \epsilon) & \cdots & (\beta/0 - \epsilon) \\ (\beta - \epsilon) & (\alpha - \epsilon) & \cdots & (\beta/0 - \epsilon) \\ \vdots & \vdots & \ddots & \vdots \\ (\beta/0 - \epsilon) & (\beta/0 - \epsilon) & \cdots & (\alpha - \epsilon) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

Equals:

$$\begin{pmatrix} (\alpha - \epsilon) & \beta & \cdots & \beta/0 \\ \beta & (\alpha - \epsilon) & \cdots & \beta/0 \\ \vdots & \vdots & \ddots & \vdots \\ \beta/0 & \beta/0 & \cdots & (\alpha - \epsilon) \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

Divide by β and define $x = -\frac{(\alpha - \epsilon)}{\beta}$.

Matrix algebra

$$\begin{pmatrix} -x & 1 & \cdots & 1/0 \\ 1 & -x & \cdots & 1/0 \\ \vdots & \vdots & \ddots & \vdots \\ 1/0 & 1/0 & \cdots & -x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

$$\left[\begin{pmatrix} 0 & 1 & \cdots & 1/0 \\ 1 & 0 & \cdots & 1/0 \\ \vdots & \vdots & \ddots & \vdots \\ 1/0 & 1/0 & \cdots & 0 \end{pmatrix} - \begin{pmatrix} x & 0 & \cdots & 0 \\ 0 & x & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & x \end{pmatrix} \right] \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

$$\left[\begin{pmatrix} 0 & 1 & \cdots & 1/0 \\ 1 & 0 & \cdots & 1/0 \\ \vdots & \vdots & \ddots & \vdots \\ 1/0 & 1/0 & \cdots & 0 \end{pmatrix} - \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} x \right] \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

Extrapolate to solve for all orbital coefficients c_{ij} and orbital energies ϵ_i [all $x(n)$] for all n π -orbitals simultaneously.

Topology matrix

$$\left[\begin{pmatrix} 0 & 1 & \cdots & 1/0 \\ 1 & 0 & \cdots & 1/0 \\ \vdots & \vdots & \ddots & \vdots \\ 1/0 & 1/0 & \cdots & 0 \end{pmatrix} - \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} x \right] \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$

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$$\left[\begin{pmatrix} 0 & 1 & \cdots & 1/0 \\ 1 & 0 & \cdots & 1/0 \\ \vdots & \vdots & \ddots & \vdots \\ 1/0 & 1/0 & \cdots & 0 \end{pmatrix} - \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} \begin{pmatrix} x(1) & 0 & \cdots & 0 \\ 0 & x(2) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & x(n) \end{pmatrix} \right] \begin{pmatrix} c(1)_1 c(2)_1 \cdots c(n)_1 \\ c(1)_2 c(2)_2 \cdots c(n)_2 \\ \vdots \\ c(1)_n c(2)_n \cdots c(n)_n \end{pmatrix} = 0$$

Topology matrix

T

I

Eigenvalue matrix

X

Eigenvector matrix

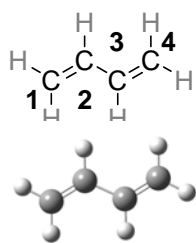
C

or

$$(T - X)C = 0 \Rightarrow TC = XC$$

Solved according to $C^{-1}TC = X$

Butadiene as an example



C no.	1	2	3	4
1	$S_{11} = 1$ $H_{11} = \alpha$	$S_{12} = 0$ $H_{12} = \beta$	$S_{13} = 0$ $H_{13} = 0$	$S_{14} = 0$ $H_{14} = 0$
2	$S_{21} = 0$ $H_{21} = \beta$	$S_{22} = 1$ $H_{22} = \alpha$	$S_{23} = 0$ $H_{23} = \beta$	$S_{24} = 0$ $H_{24} = 0$
3	$S_{31} = 0$ $H_{31} = 0$	$S_{32} = 0$ $H_{32} = \beta$	$S_{33} = 1$ $H_{33} = \alpha$	$S_{34} = 0$ $H_{34} = \beta$
4	$S_{41} = 0$ $H_{41} = 0$	$S_{42} = 0$ $H_{42} = 0$	$S_{43} = 0$ $H_{43} = \beta$	$S_{44} = 1$ $H_{44} = \alpha$

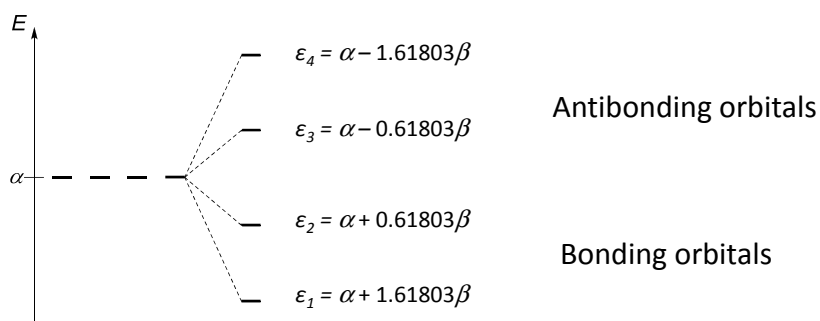
The topology matrix:

$$T = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

The π -orbital energies

$$x = -\frac{(\alpha - \epsilon_l)}{\beta} = \pm 0.61803 \text{ and } \pm 1.61803$$

$$\epsilon_l = \alpha \pm 0.61803\beta \text{ and } \alpha \pm 1.61803\beta$$



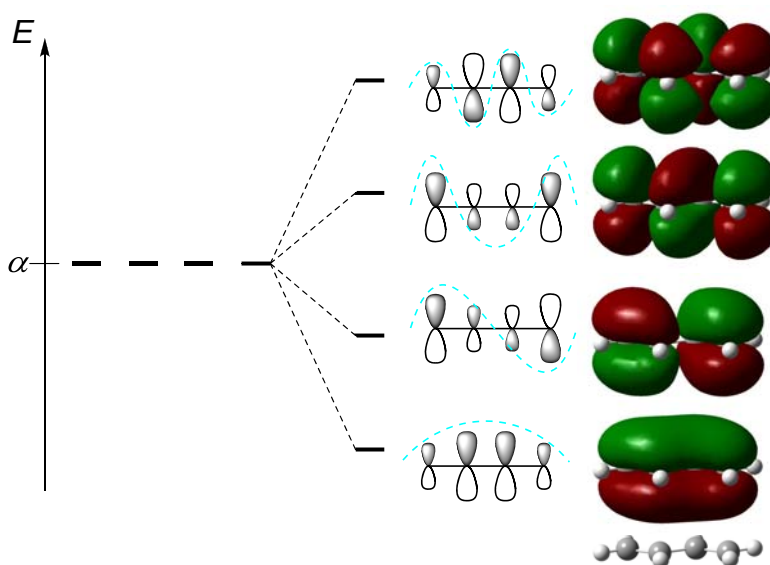
Next, determine the shape of the π -orbitals

Orbital coefficients

i	Coefficient C_{ij} for carbon number				Energy
	1	2	3	4	
4	0.3718	-0.6015	0.6015	-0.3718	$\alpha - 1.61803\beta$
3	0.6015	-0.3718	-0.3718	0.6015	$\alpha - 0.61803\beta$
2	0.6015	0.3718	-0.3718	-0.6015	$\alpha + 0.61803\beta$
1	0.3718	0.6015	0.6015	0.3718	$\alpha + 1.61803\beta$

- β is a negative quantity representing the (π) bonding energy between two adjacent carbon atoms.
- The order of the energy levels follows the number of nodes.
- The term α is common to all energies. It is the energy of a non-bonded $2p_z$ electron **IN** the molecule.
- MOs of energy of lower energy than α are **bonding** and those of energy greater than α are **antibonding**.

Orbital shapes



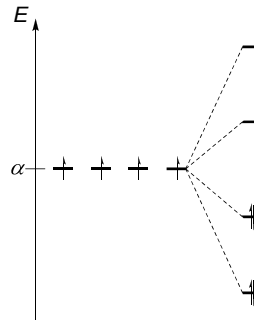
Add in the electrons

Total energy is equal to the sum of orbital energies times the occupation

$$E_{\pi} = \sum_{I=1}^{N=n} r_I \varepsilon_I$$

Add in electrons according to:

1. Aufbau principle
2. Pauli principle
3. Hund's rule

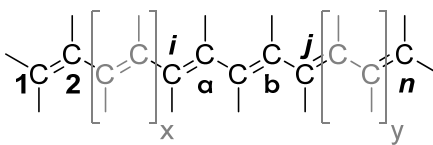


- Each carbon contributes with one electron. The **stabilization** due to the π -electrons is: $4\alpha - 2(\alpha + 1.61803\beta) - 2(\alpha + 0.61803\beta)$
 $= -4.47212\beta$

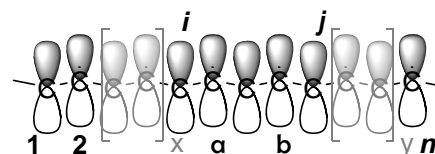
S. M. Lindsay *Introduction to Nanoscience* pp 35-36 and 58.

General solutions

Linear polyenes



$$\varepsilon_I = \alpha + 2\beta \cos \frac{I\pi}{(n+1)}$$



$$c_{j,I} = \left(\frac{2}{n+1} \right)^{1/2} \sin \frac{jI\pi}{(n+1)}$$

j = atom number in linear π -system.

$I = 1, 2, 3, \dots, n$ (MO number).

n = total number of atoms in π -system

Cyclic polyenes

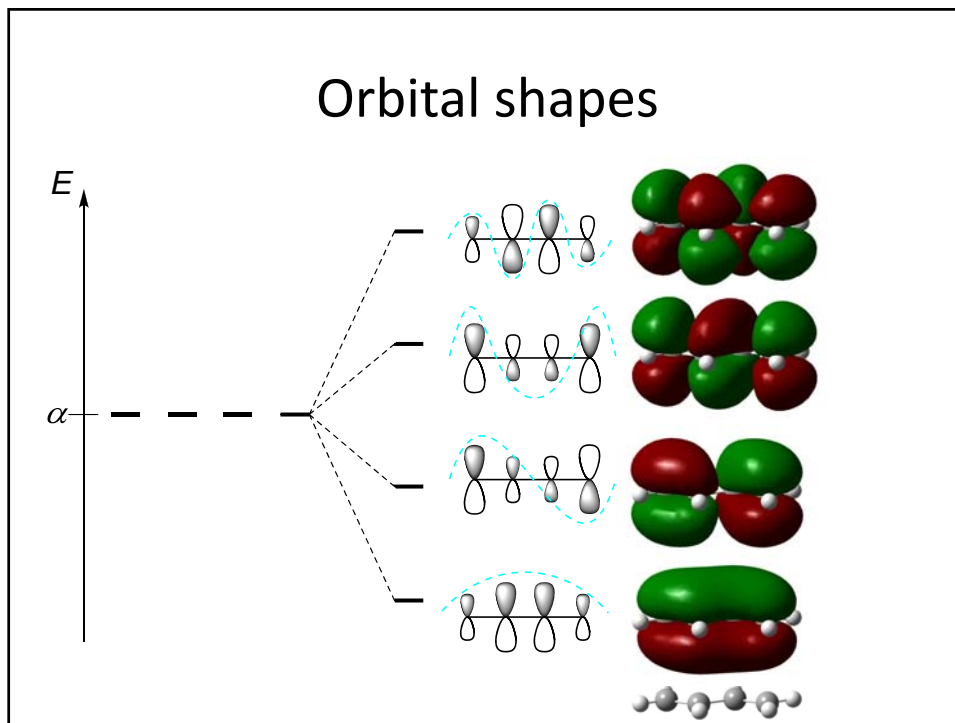
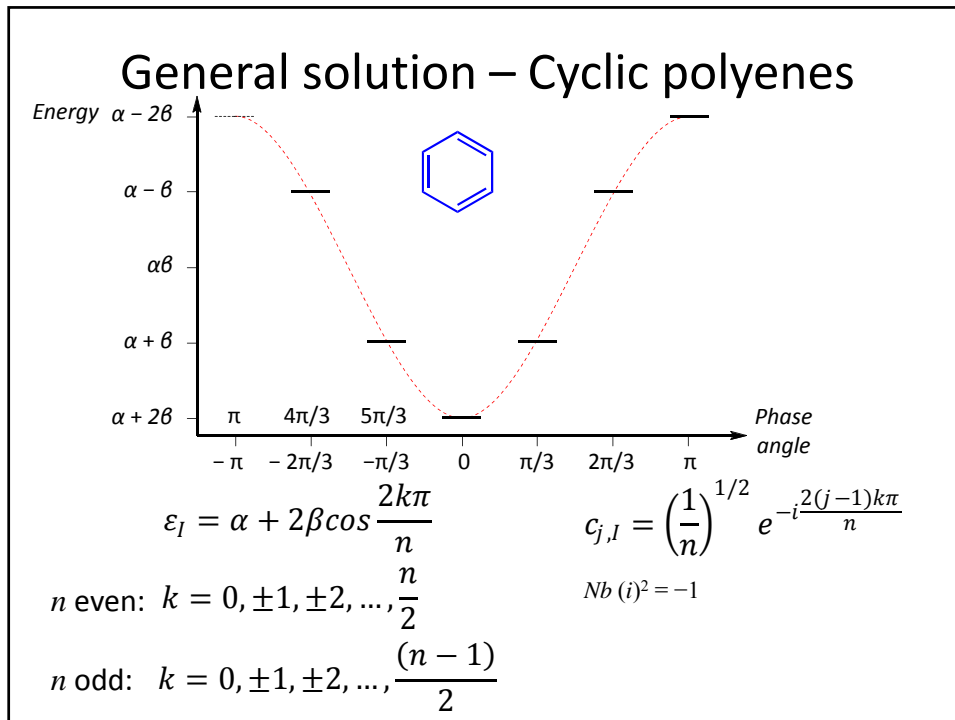


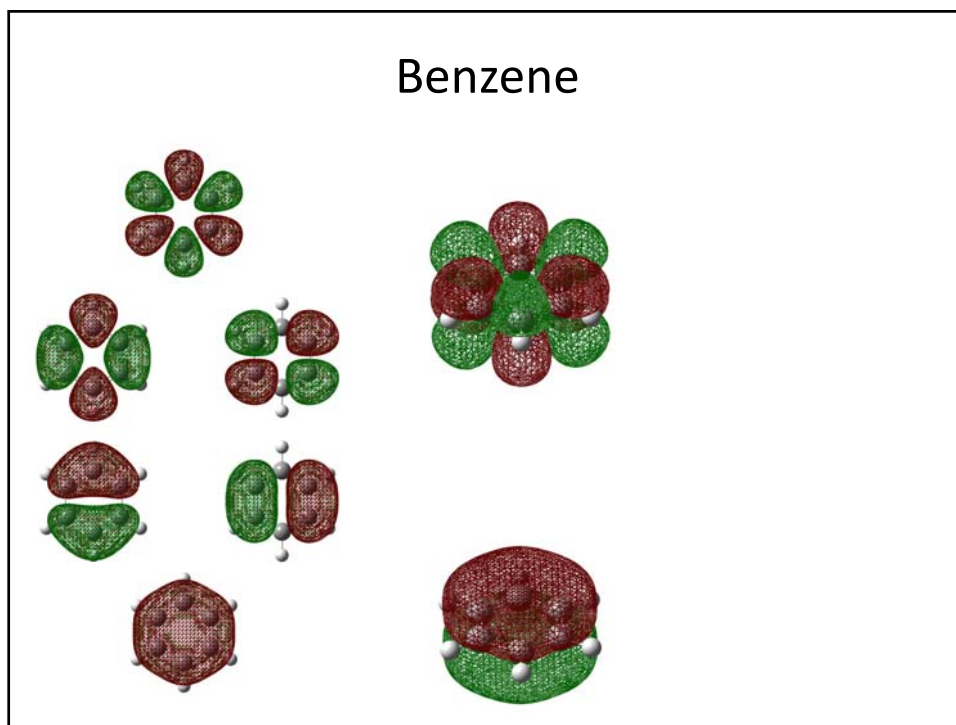
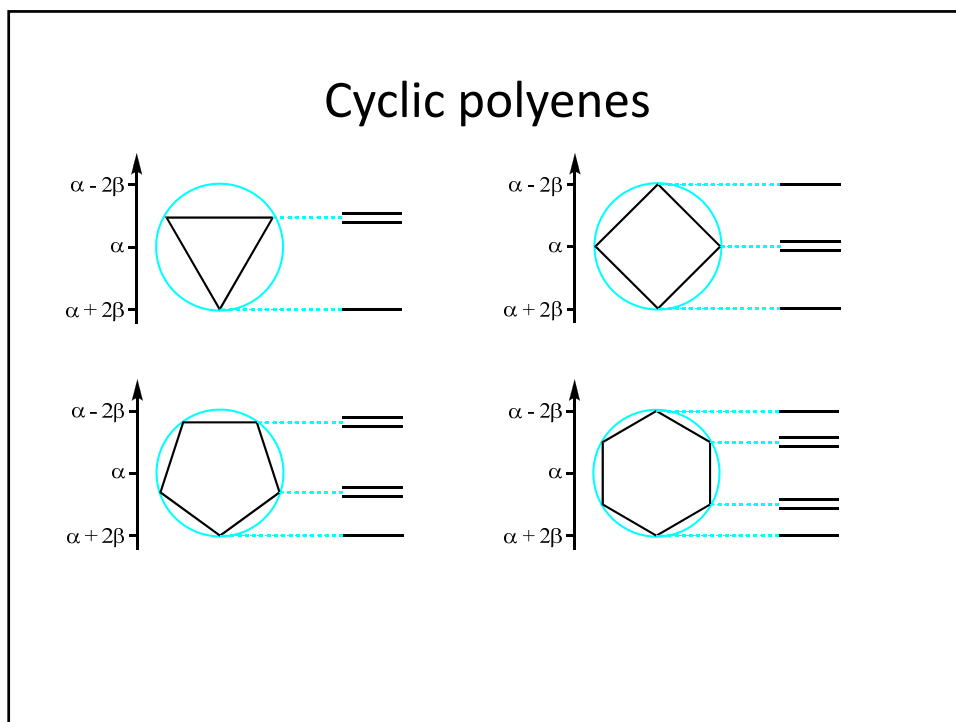
$$\varepsilon_I = \alpha + 2\beta \cos \frac{2(I-1)\pi}{n}$$

$$c_{j,I} = \left(\frac{1}{n} \right)^{1/2} e^{-i \frac{2(j-1)(I-1)\pi}{n}}$$

$Nb (i)^2 = -1$

$I = 1, 2, 3, \dots, n$ (MO number)





Aromaticity

For a molecule to experience the stabilization of aromaticity it must fulfill the following requirements:

- It must contain a cyclic sequence of atoms.
- All the atoms of the cyclic sequence must lie in the same plane, or nearly so.
- Each atom in the cyclic sequence must “contribute with a p-orbital” aligned perpendicular to the plane of the cyclic structure.
- The cyclic, conjugated system must contain $(4n + 2)$ electrons.

Parameterized method

- The parameter β is composite parameter representing the electron-nucleus attraction, the interelectronic repulsion and the kinetic energy.

The atomic 2p energy level for carbon:

$$E(2p_z) = \alpha \quad (\sim -11.4 \text{ eV})$$

The resonance integral for adjacent 2p orbitals

$$H_{ij}(\text{C=C}) = \beta \quad (\sim -3 \text{ eV})$$