Lecture 32 : The Hückel Method

The material in this lecture covers the following in Atkins.

14.0 The Hückel approximation
- (a)The secular determinant
- (b) Ethene and frontier orbitals
- (c) Butadiene and p-electron binding energy
- (d) benzene and aromatic stability

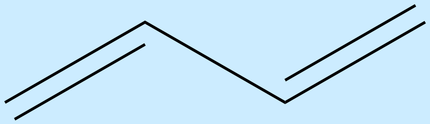
Lecture on-line
- Huckel Theory (PowerPoint)
- Huckel Theory (PDF)

Handout for this lecture

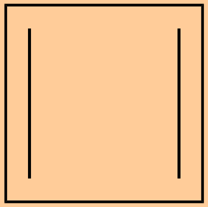
The Hückel method

The Hückel approximation can be used for conjugated molecules in which there is an alternation of single and double bonds along a chain

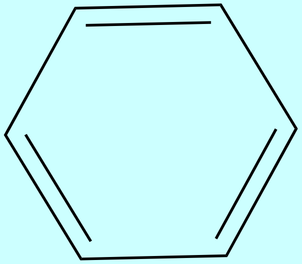
One example is the conjugated π - systems



Butadiene

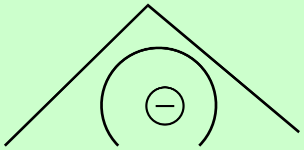


Cyclo-Butadiene



Benzene

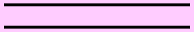
allyl cation



Conjugated systems

We shall also use it for the π - bond in ethylene

C_2H_4



Molecular orbital theory

In molecular orbital theory we write our orbitals as linear combinations of atomic orbitals :

$$\psi_k(1) = \sum_{i=1}^{i=n} C_i \chi_i(1)$$

We next require that the corresponding orbital energies

$$W(C_1, C_2, ..C_n) = \frac{\int \psi_k(1)\hat{H}\psi_k dv}{\int \psi_k(1)\psi_k(1)dv}$$

be optimal with respect to $\{C_1, C_2, ..C_n\}$

or :

$$\frac{\delta W}{\delta C_i} = 0; \; i = 1, .., n$$

This leads to the set of homogeneous equations :

$$\sum_{k=1}^{k=n} C_k \left| H_{ik} - WS_{ik} \right| = 0$$

$$i = 1, 2, ..., n.$$

For which the secular determinant must be zero

$$\left| H_{ik} - WS_{ik} \right| = 0$$

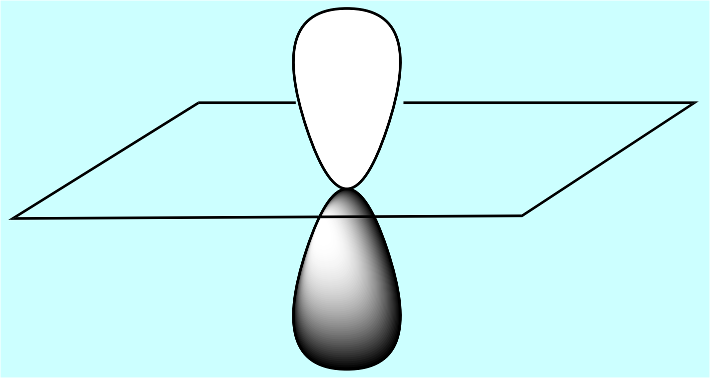
$$i = 1, 2, ..., n; \; k = 1, 2, ..., n$$

In order to obtain non-trivial solutions

The Hückel method

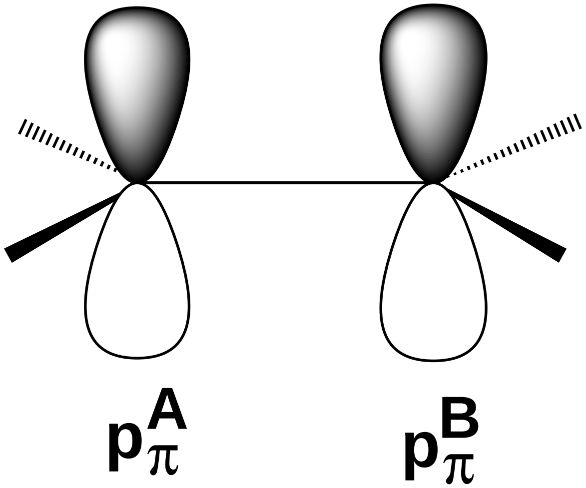
Conjugated systems

We are going to use as our atomic orbitals a single p π function on each carbon atom.

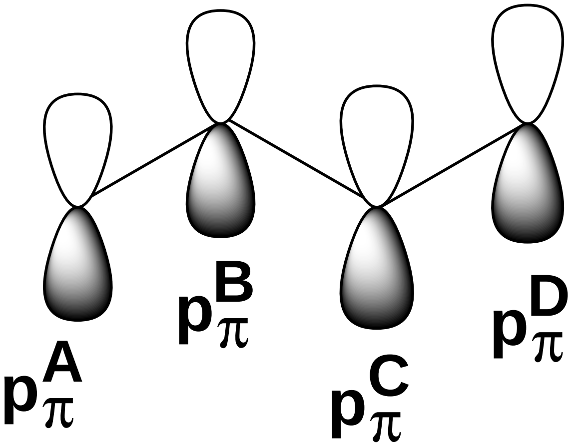


The p_π orbital is the p - function perpendicular to the molecular plane

For ethylene we have two p_π orbitals

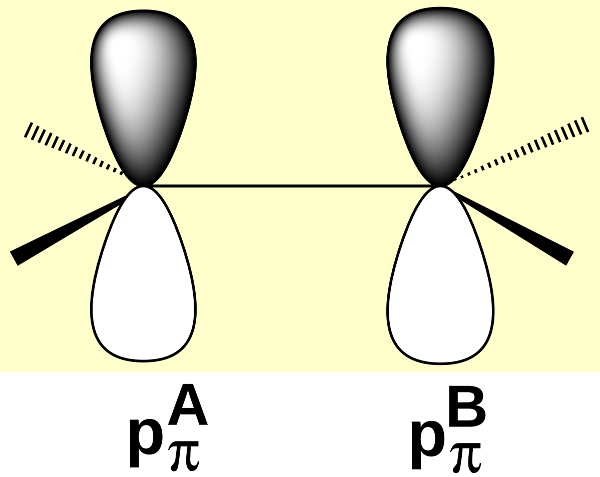


For butadiene we have four p_π orbitals



The Hückel method Ethylene

For ethylene we have two p_π orbitals



For ethylene we can use linear variation theory to obtain a set of linear homogeneous equations

$$\sum_{k=1}^{k=n} C_k \left| H_{ik} - WS_{ik} \right| = 0$$

$i = 1, 2$ and $n = 1, 2$

Non - trivial solutions are only possible if the secular determinant is zero

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{11} - E \end{vmatrix} = 0$$

Each of the two roots $W = E_i$ $i = 1, 2$ can be substituted into the set of linear equations to obtain orbital coefficients

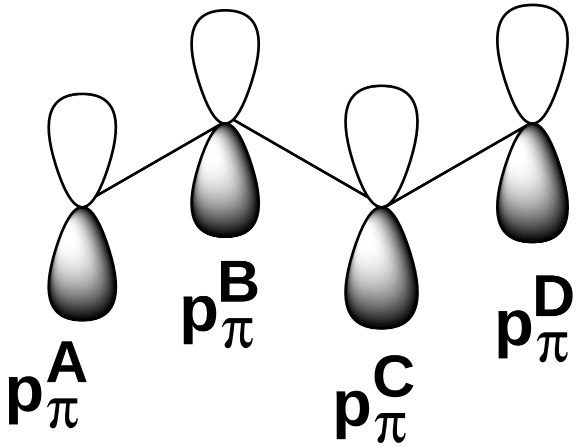
$$\psi^i = \sum_{k=1}^{k=n} C_i^k p_\pi^k$$

$k = 1, 2$; $i = 1, 2$

The Hückel method

Butadiene

For butadiene we have four p_π orbitals



For butadiene we can use linear variation theory to obtain a set of linear homogeneous equations

$$\sum_{k=1}^{k=n} C_k \left| H_{ik} - WS_{ik} \right| = 0$$

$$i = 1,4 \quad \text{and} \quad n = 1,4$$

The Hückel method

Butadiene

Non - trivial solutions
are only possible if
the secular determinant
is zero

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{21} - ES_{21} & H_{22} - E & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - E & H_{34} - ES_{34} \\ H_{41} - ES_{41} & H_{42} - ES_{42} & H_{43} - ES_{43} & H_{44} - E \end{vmatrix} = 0$$

Each of the two roots $W = E_i$
$i = 1, 4$ can be substituted
into the set of linear equations
to obtain orbital coefficients

$$\psi^i = \sum_{k=1}^{k=n} C_i^k p_\pi^k$$

$k = 1, 4 \; ; \; i = 1, 4$

The Hückel method

The Hückel approximation

1. all overlaps are set to zero $S_{ij} = 0$

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{11} - E \end{vmatrix} = 0 \qquad \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{11} - E \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{21} - ES_{21} & H_{22} - E & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - E & H_{34} - ES_{34} \\ H_{41} - ES_{41} & H_{42} - ES_{42} & H_{43} - ES_{43} & H_{44} - E \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} - E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} - E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{vmatrix} = 0$$

The Hückel method

The Hückel approximation

1. All overlaps are set to zero $S_{ij} = 0$

2. All diagonal terms are set equal to Coulomb integral α

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{11}-E \end{vmatrix} = 0 \qquad \begin{vmatrix} \alpha-E & H_{12} \\ H_{21} & \alpha-E \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22}-E & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33}-E & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha-E & H_{12} & H_{13} & H_{14} \\ H_{21} & \alpha-E & H_{23} & H_{24} \\ H_{31} & H_{32} & \alpha-E & H_{34} \\ H_{41} & H_{42} & H_{43} & \alpha-E \end{vmatrix} = 0$$

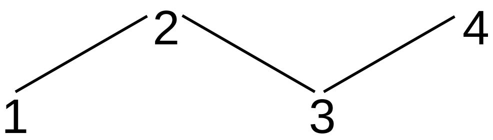
The Hückel method

The Hückel approximation

1. All overlaps are set to zero $S_{ij} = 0$

2. All diagonal terms are set equal to Coulomb integral α

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



$$\begin{vmatrix} \alpha - E & H_{12} \\ H_{21} & \alpha - E \end{vmatrix} = 0$$

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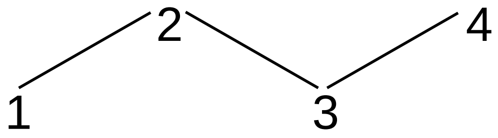
$$\begin{vmatrix} \alpha - E & H_{12} & 0 & 0 \\ H_{21} & \alpha - E & H_{23} & 0 \\ 0 & H_{32} & \alpha - E & H_{34} \\ 0 & 0 & H_{43} & \alpha - E \end{vmatrix} = 0$$

The Hückel method

The Hückel approximation



1. All overlaps are set to zero $S_{ij} = 0$

2. All diagonal terms are set equal to Coulomb integral α

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

4. All remaining resonance integrals are set to β

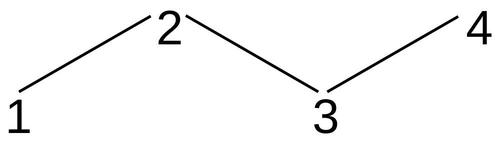
$$\begin{vmatrix} \alpha - E & H_{12} \\ H_{21} & \alpha - E \end{vmatrix} = 0 \qquad \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha - E & H_{12} & 0 & 0 \\ H_{21} & \alpha - E & H_{23} & 0 \\ 0 & H_{32} & \alpha - E & H_{34} \\ 0 & 0 & H_{43} & \alpha - E \end{vmatrix} = 0$$

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

The Hückel method

The Hückel approximation



1. All overlaps are set to zero $S_{ij} = 0$

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

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

The Hückel method

Solutions for ethylene

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

$$(\alpha-E)^2=\beta^2;(\alpha-E)=\pm\beta$$

$$E_1=\alpha+\beta\ \ (\alpha \text{ and } \beta \text{ negative})$$

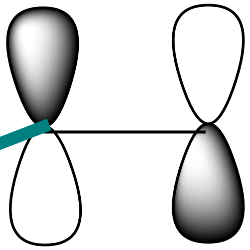
$$E_2=\alpha-\beta\ \ (\alpha \text{ and } \beta \text{ negative})$$

$$\sum_{k=1}^{k=n} C_k\left|H_{ik}-WS_{ik}\right|=0$$

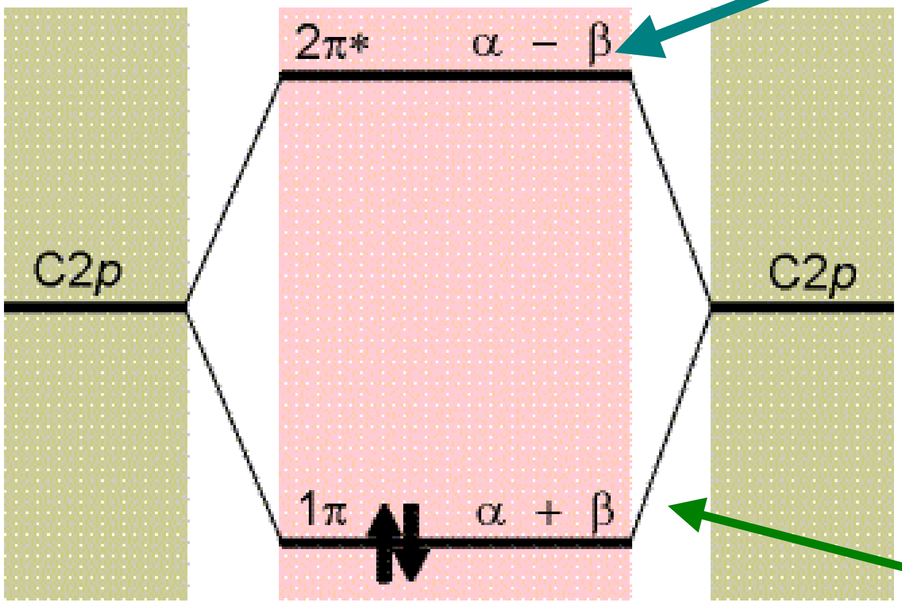
$$i=1,2 \ \text{ and } n=1,2$$

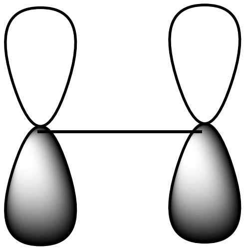
$$\psi^i=\sum_{k=1}^{k=n} c_i^k p_\pi^k$$

$$k=1,2\ ;\ i=1,2$$



$$\psi_2=-\frac{1}{\sqrt{2}}p_\pi^1+\frac{1}{\sqrt{2}}p_\pi^2$$





$$\psi_1=\frac{1}{\sqrt{2}}p_\pi^1+\frac{1}{\sqrt{2}}p_\pi^2$$

The Hückel method

Solutions for butadiene

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

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

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

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

$$(\alpha - E)^4 - (\alpha - E)^2\beta^2 \quad -(\alpha - E)^2\beta^2 \quad -(\alpha - E)^2\beta^2 \quad +\beta^4$$

$$(\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + \beta^4 = 0$$

The Hückel method

Solutions for butadiene

$$(\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + \beta^4 = 0$$

Dividing by β^2 : $\dfrac{(\alpha - E)^4}{\beta^4} - 3\dfrac{(\alpha - E)^2}{\beta^2} + 1 = 0$

Introducing: $x = \dfrac{(\alpha - E)^2}{\beta^2}$

$$x^2 - 3x + 1 = 0$$

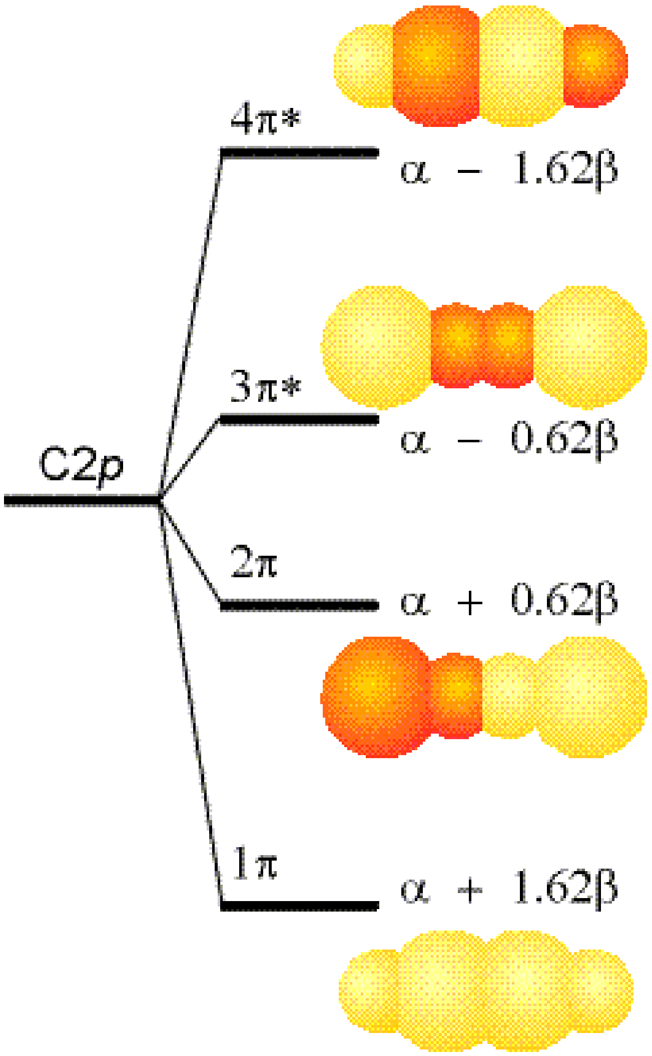
$x = 2.62$; $x = 0.38$

Thus

$E = \alpha \pm 1.62\beta$ and $\alpha \pm 0.62\beta$

The Hückel method

Solutions for butadiene



$$\sum_{k=1}^{k=n} C_k \left| H_{ik} - WS_{ik} \right| = 0$$

$i = 1, 4$ and $n = 1, 4$

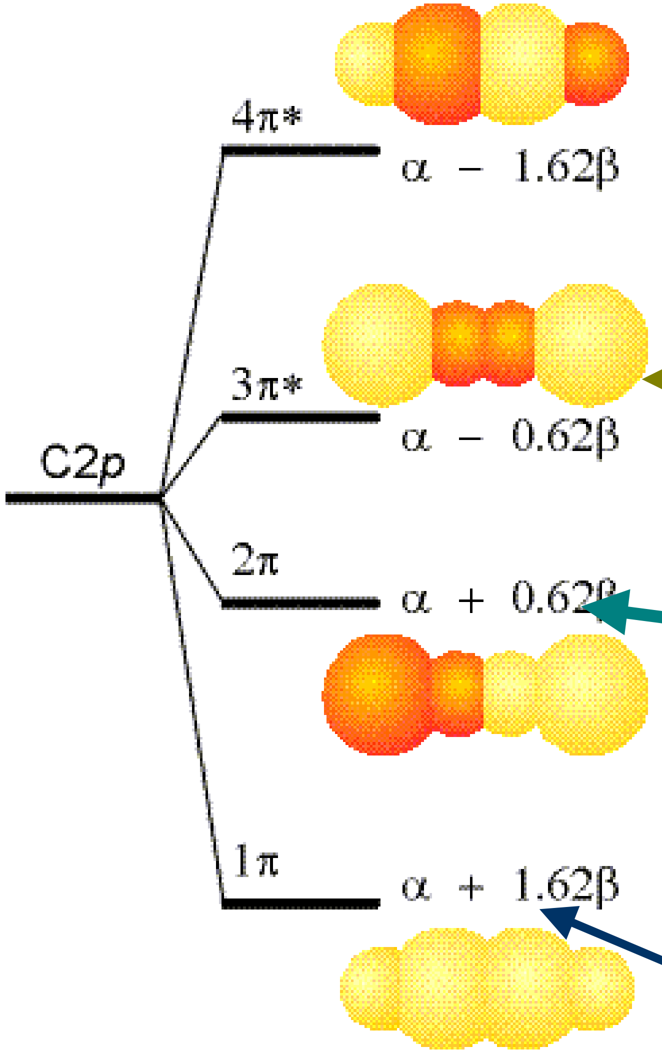
$$\psi^i = \sum_{k=1}^{k=n} C_i^k p_\pi^k$$

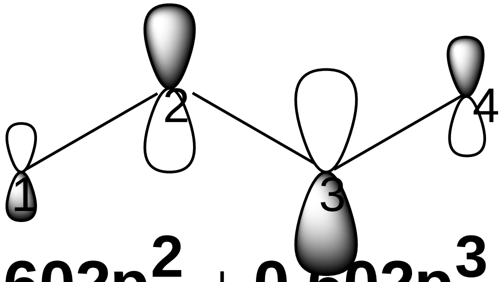
$k = 1, 4$; $i = 1, 4$

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

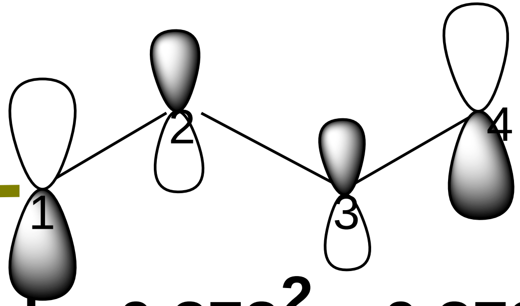
The Hückel method

Solutions for butadiene

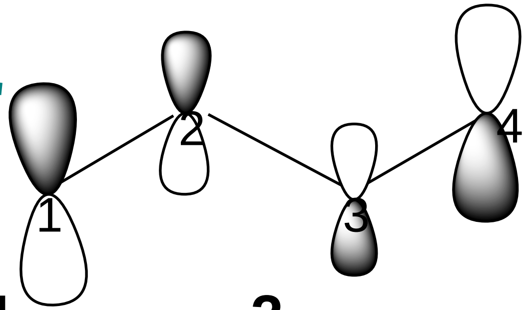




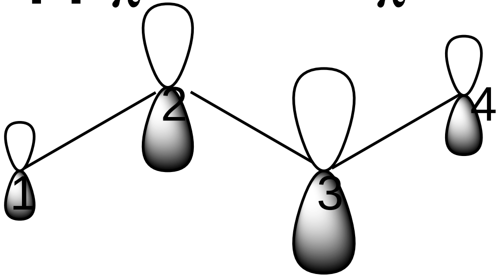
$0.372p_{\pi}^{1} - 0.602p_{\pi}^{2} + 0.602p_{\pi}^{3} - 0.372p_{\pi}^{4}$



$0.602pp_{\pi}^{1} - 0.372_{\pi}^{2} - 0.372p_{\pi}^{3} + 0.602p_{\pi}^{4}$



$-0.602pp_{\pi}^{1} - 0.372_{\pi}^{2} + 0.372p_{\pi}^{3} + 0.602p_{\pi}^{4}$



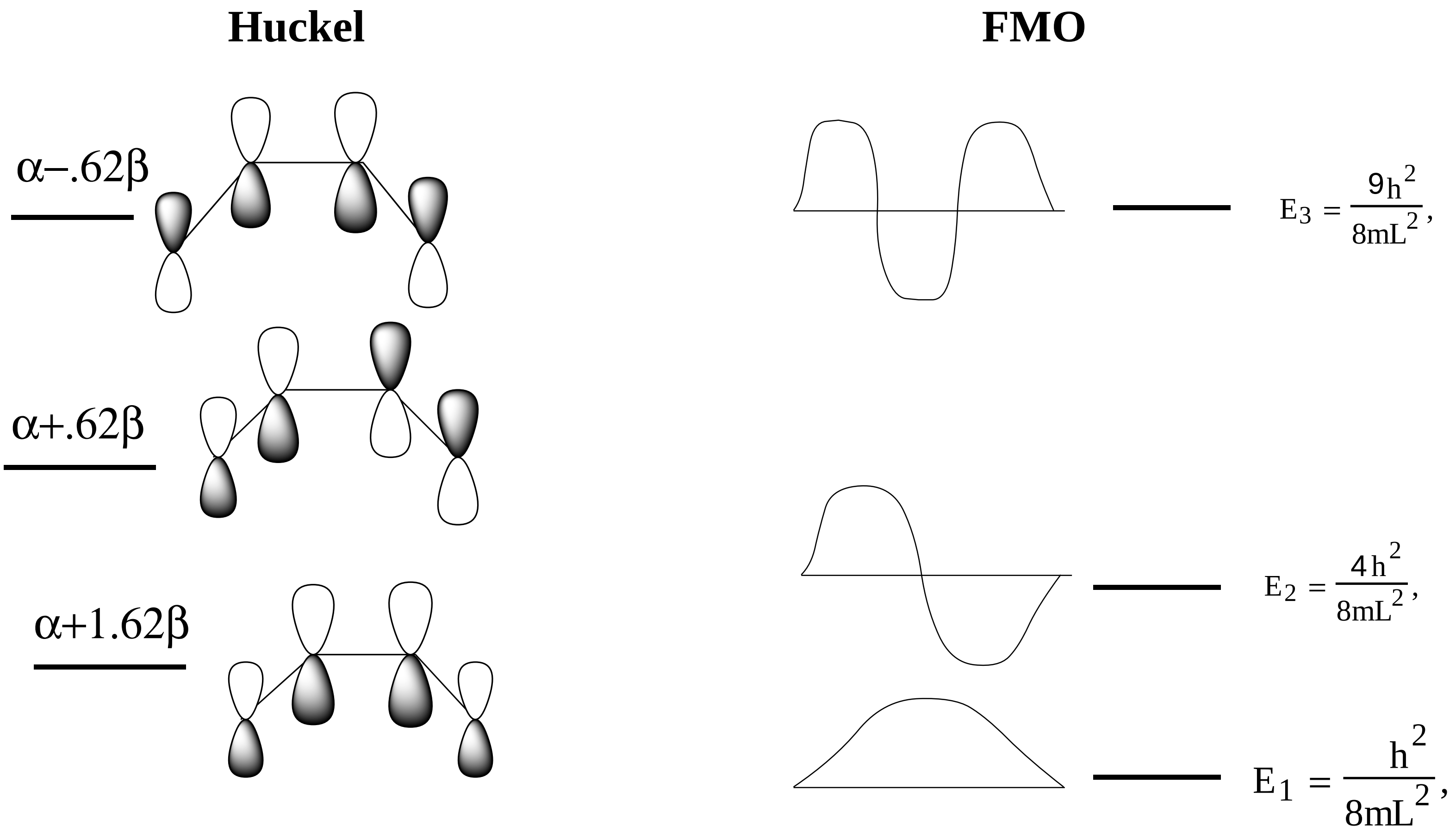
$0.372p_{\pi}^{1} + 0.602p_{\pi}^{2} + 0.602p_{\pi}^{3} + 0.372p_{\pi}^{4}$

The Hückel method

Solutions for butadiene

Comparison between PIB and Huckel treatment of butadiene

Same nodal structure



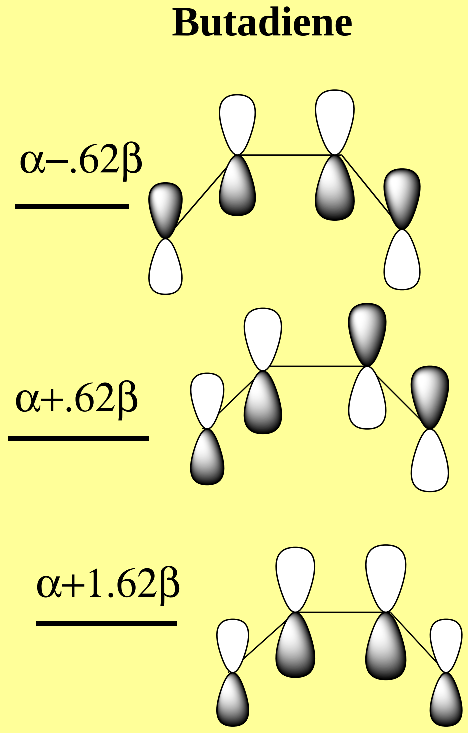
$$E_3 = \frac{9h^2}{8mL^2},$$

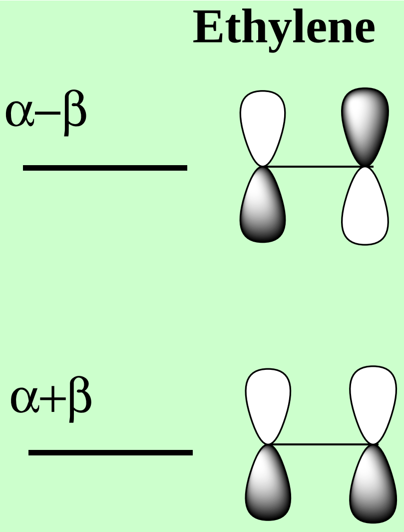
$$E_2 = \frac{4h^2}{8mL^2},$$

$$E_1 = \frac{h^2}{8mL^2},$$

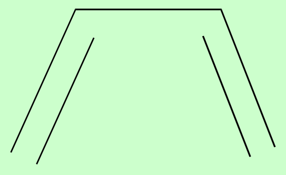
The Hückel method

Solutions for butadiene

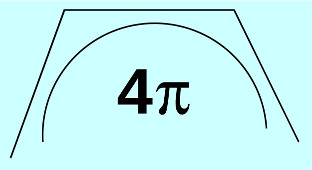




We can write butadiene as two localized π - bonds



Or two delocalized π - bonds



$E_\pi(\text{Bu}) - 2E_\pi(\text{Et})$ ∴ **delocalization energy**

$$E_\pi(\text{Bu}) = 2(\alpha + 1.62\beta) + 2(\alpha + .62\beta)$$

$$= 4\alpha + 4.48\beta$$

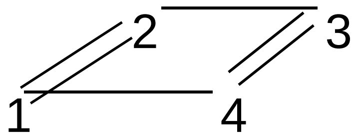
$$2E_\pi(\text{Et}) = 4(\alpha + \beta) = 4\alpha + 4\beta$$

Delocalization energy = .48β

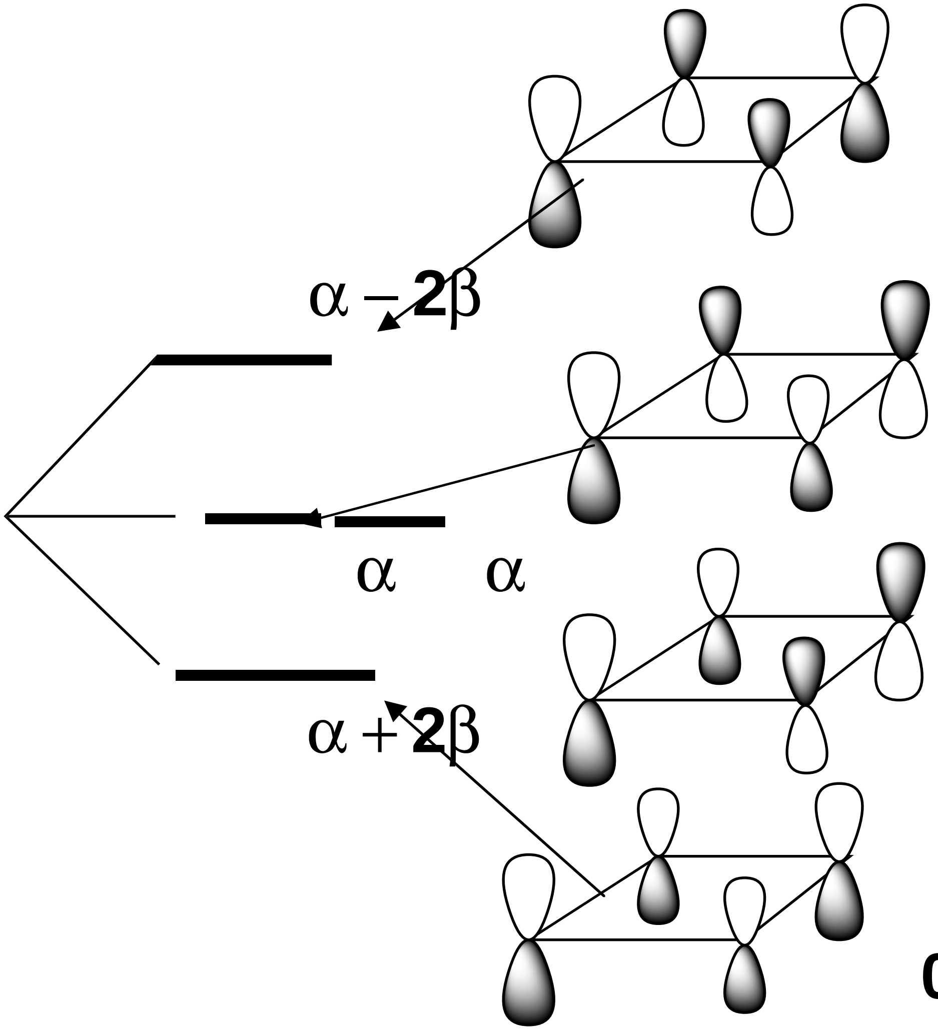
(–36 kJ mol^{-1})

The Hückel method

Cyclobutadiene



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



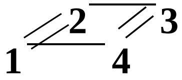
$$0.5p_\pi^1 - 0.5p_\pi^2 + 0.5p_\pi^3 - 0.5p_\pi^4$$

$$0.5p_\pi^1 - 0.5p_\pi^2 - 0.5p_\pi^3 + 0.5p_\pi^4$$

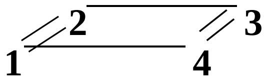
$$0.5p_\pi^1 + 0.5p_\pi^2 - 0.5p_\pi^3 - 0.5p_\pi^4$$

$$0.5p_\pi^1 + 0.5p_\pi^2 + 0.5p_\pi^3 + 0.5p_\pi^4$$

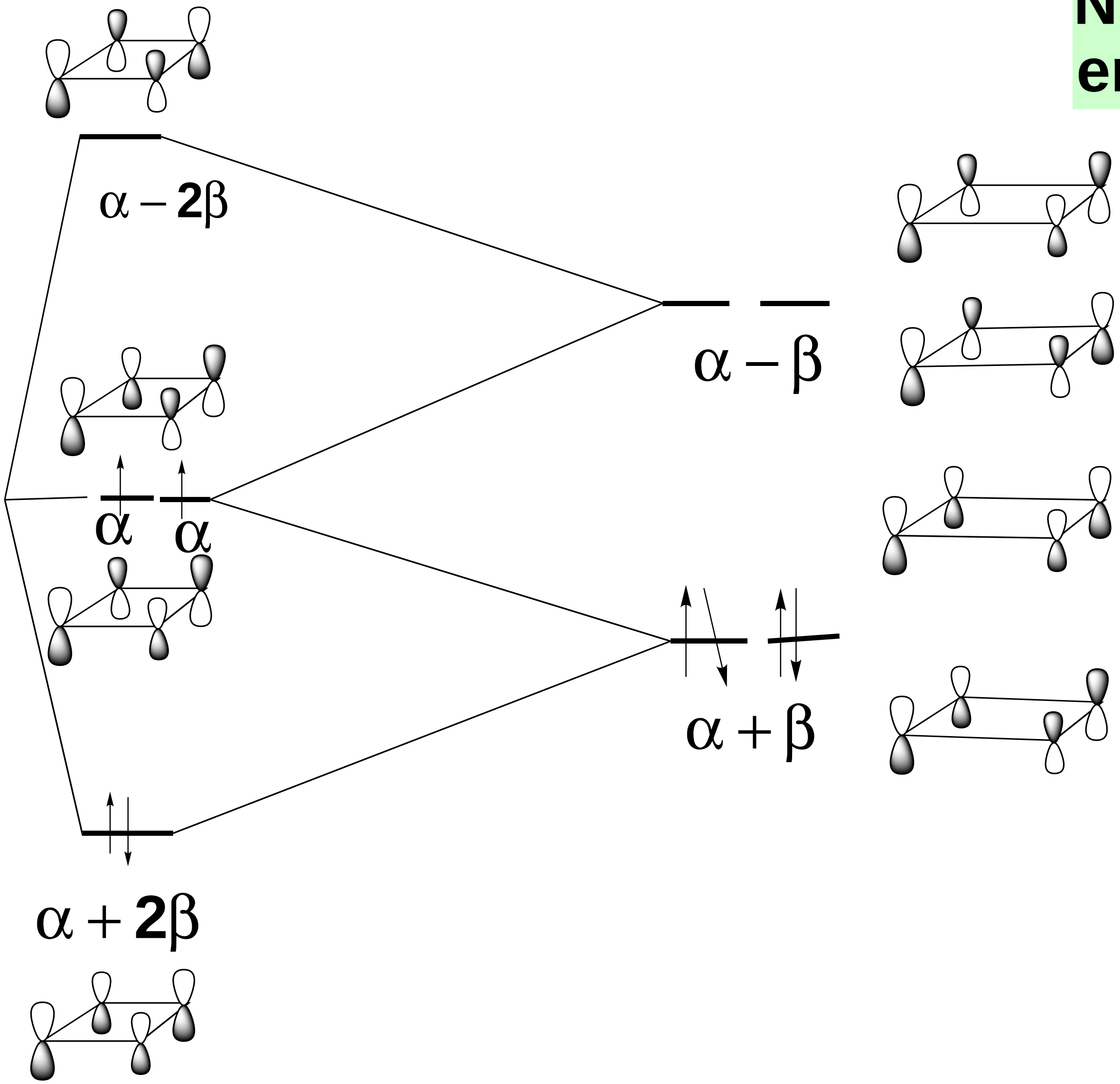
The Hückel method



Cyclobutadiene

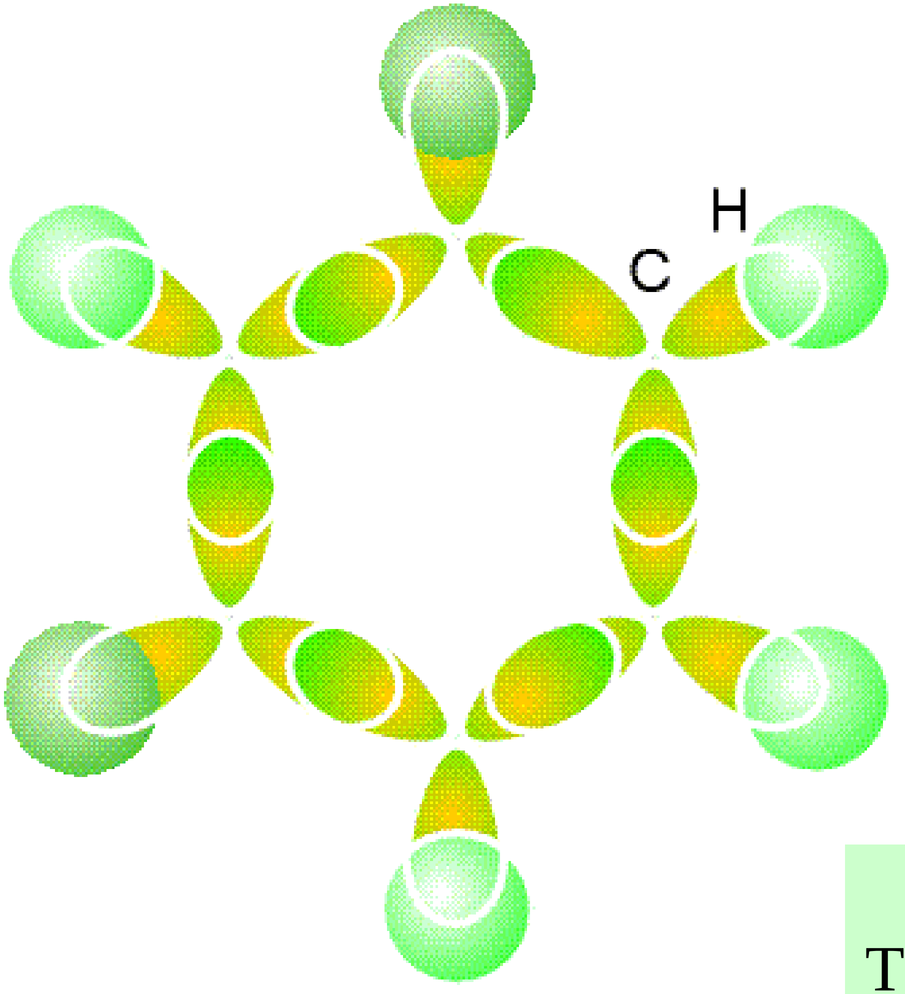


No delocalization energy

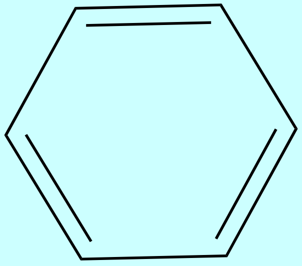


The Hückel method

Benzene



The C - C and C - H σ - orbitals



Benzene

The framework of benzene is formed by the overlap of Csp2 hybrids, which fit without strain into a hexagonal arrangement.

The Hückel method

Benzene

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

$$E = \alpha \pm 2\beta; \quad \alpha \pm \beta; \quad \alpha \pm \beta$$

$$\sum_{k=1}^{k=n} C_k \left| H_{ik} - WS_{ik} \right| = 0$$

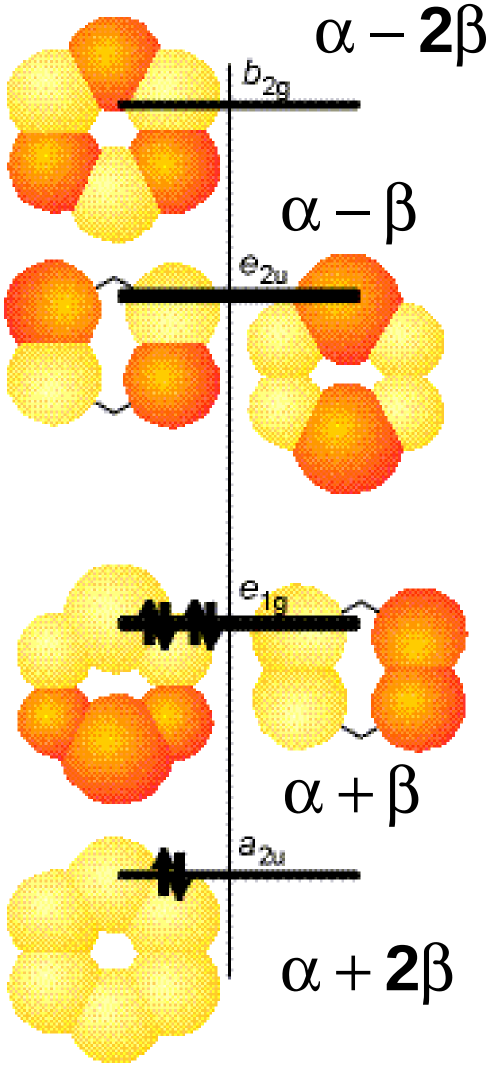
$i = 1, 6$ and $n = 1, 6$

$$\psi^i = \sum_{k=1}^{k=n} C_i^k p_\pi^k$$

$k = 1, 6$; $i = 1, 6$

The Hückel method

Benzene



$\alpha - 2\beta$

$\alpha - \beta$

$\alpha + \beta$

$\alpha + 2\beta$

Delocalization energy =

$$2(\alpha + 2\beta) + 4(\alpha + \beta) - 6(\alpha + \beta) = 2\beta$$

$-150\ \text{kJ mol}^{-1}$

What you should learn from this lecture

1. Be able to construct the secular determinant for a conjugated π-system within the Huckel approximation

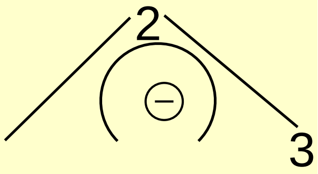
2. Be able to calculate orbital energies for simple systems

3. You will not be asked to find the molecular orbitals. However, you should be able to discuss provided orbitals in terms of bonding and anti-bonding interactions

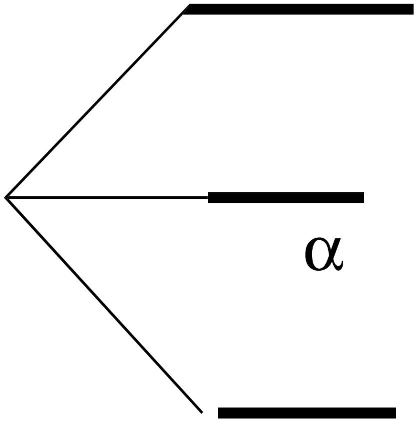
The Hückel method

The allyl system

allyl cation



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



$\alpha - 1.42\alpha$ $\quad 0.5p_\pi^1 - 0.707p_\pi^2 + 0.5p_\pi^3$

α $\quad 0.707p_\pi^1 - 0.707p_\pi^3$

$\alpha + 1.42\alpha$ $\quad 0.5p_\pi^1 + 0.707p_\pi^2 + 0.5p_\pi^3$