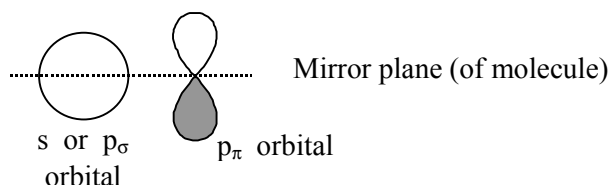


6 Hückel Theory

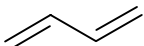
This theory was originally introduced to permit qualitative study of the π -electron systems in planar, conjugated hydrocarbon molecules (i.e. in "flat" hydrocarbon molecules which possess a mirror plane of symmetry containing all the carbon atoms, and in which the atoms of the carbon skeleton are linked 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.

$$\begin{aligned} \text{i.e.} \quad \int \phi_i \hat{H} \phi_j . d\tau &= \beta && : \text{if atoms } i \text{ and } j \text{ are directly } \sigma\text{-bonded.} \\ &= 0 && : \text{if atoms } i \text{ and } j \text{ are non-bonded.} \end{aligned}$$

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

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

(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.

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

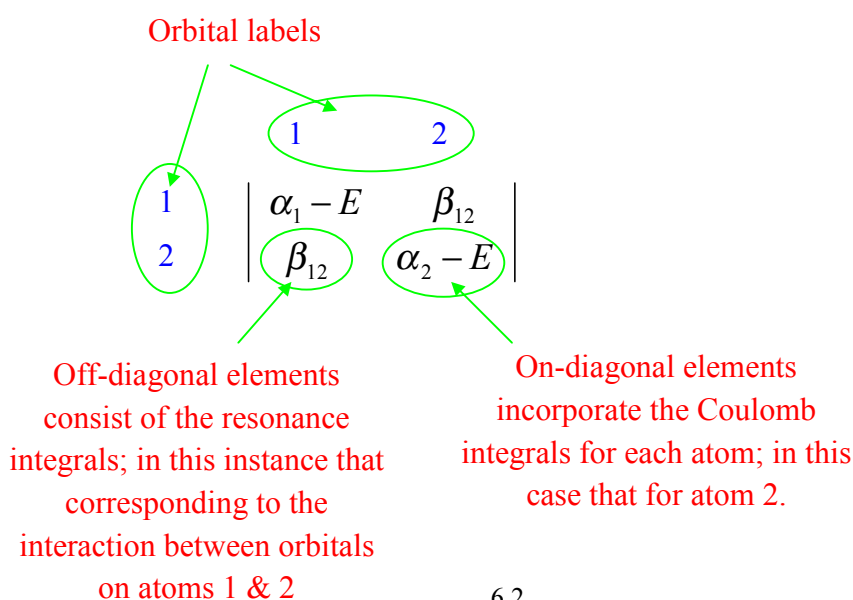
For three overlapping orbitals the approach outlined in Chapter 4 leads to a secular determinant of the form:

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

From a comparison of the two secular determinants given above, it is becoming clear that all such secular determinants have a characteristic structure:

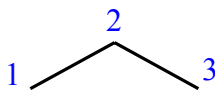
1. each row and column may be associated with one of the atomic orbitals; thus the first row and first column contain information about the nature of orbital 1 and its interactions with the other orbitals, the second row and second column contain information about the nature of orbital 2 and its interactions 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:



Linear Conjugated Hydrocarbons

C_3 Molecules (3-atom chain)



Secular Determinant / Equation

$$\begin{array}{c} 1 \\ 2 \\ 3 \end{array} \begin{array}{|c|c|c|} \hline 1 & 2 & 3 \\ \hline \alpha - E & \beta & 0 \\ \hline \beta & \alpha - E & \beta \\ \hline 0 & \beta & \alpha - E \\ \hline \end{array} = 0$$

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

$$\Rightarrow x(x \cdot x - 1 \cdot 1) - 1(1 \cdot x - 1 \cdot 0) + 0(1 \cdot 1 - x \cdot 0) = 0$$

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

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

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

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

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

Now $E = \alpha - x\beta$

So the energies of the molecular orbitals are:

$$E = \alpha - \sqrt{2}\beta \quad \text{- Highest Energy}$$

$$E = \alpha$$

$$E = \alpha + \sqrt{2}\beta \quad \text{- Lowest Energy}$$

The secular equations are:

$$\begin{array}{rcccc} c_1(\alpha - E) & + & c_2\beta & + & 0 & = & 0 \\ c_1\beta & + & c_2(\alpha - E) & + & c_3\beta & = & 0 \\ 0 & + & c_2\beta & + & c_3(\alpha - E) & = & 0 \end{array}$$

or, in terms of x ,

$$c_1x \quad + \quad c_2 \quad + \quad 0 \quad = \quad 0 \quad [1]$$

$$c_1 \quad + \quad c_2x \quad + \quad c_3 \quad = \quad 0 \quad [2]$$

$$0 \quad + \quad c_2 \quad + \quad c_3x \quad = \quad 0 \quad [3]$$

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

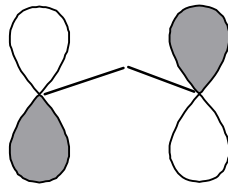
$$[1] \Rightarrow c_2 = 0$$

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

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

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

i.e.



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

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

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

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

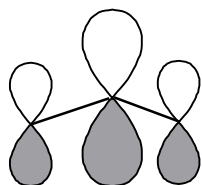
$$\sum c_i^2 = c_1^2 + c_2^2 + c_3^2 = c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 4c_1^2 = 1$$

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

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

$$\Rightarrow c_2 = \sqrt{2} \cdot \frac{1}{2} = \frac{1}{\sqrt{2}} \quad (= 0.707)$$

i.e.



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

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

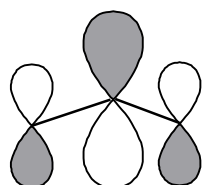
$$[1] \Rightarrow \sqrt{2}c_1 + c_2 = 0 \Rightarrow c_2 = -\sqrt{2}c_1$$

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

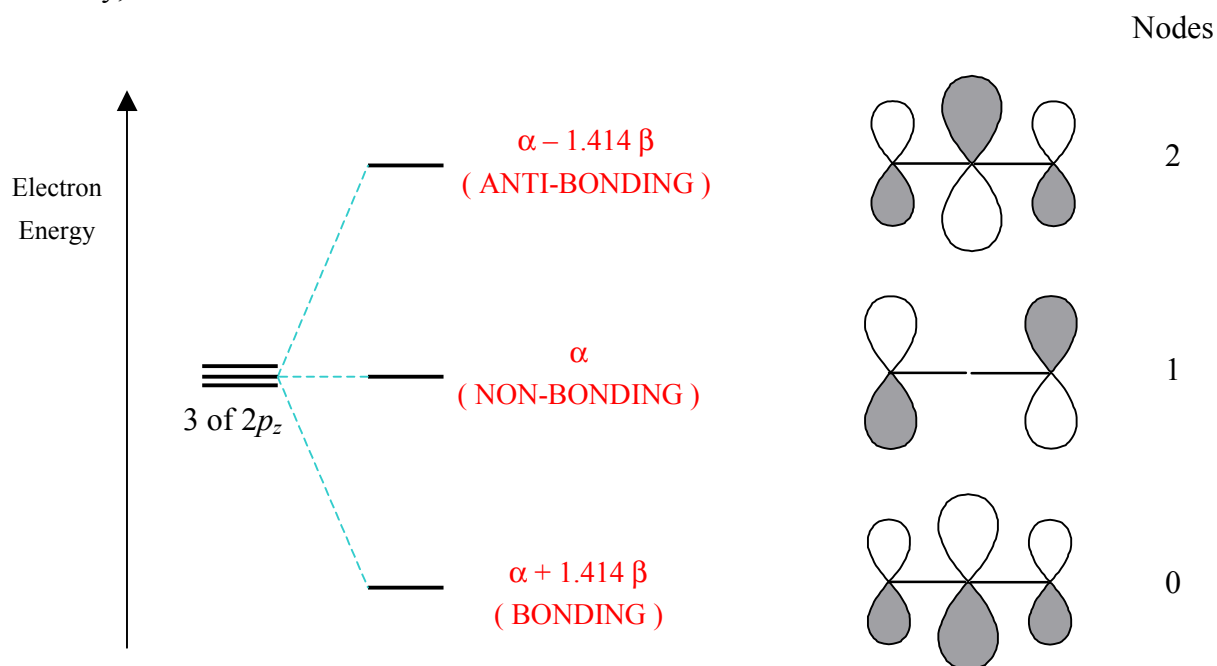
$$\Rightarrow c_1 = c_3 = \frac{1}{2} \quad (= 0.500)$$

$$\Rightarrow c_2 = \frac{-1}{\sqrt{2}} \quad (= -0.707)$$

i.e.

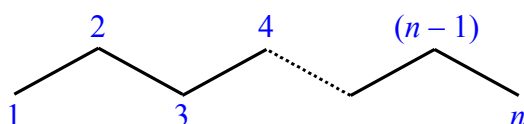


In summary,



< 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:

$$\begin{array}{c}
 1 \\
 2 \\
 3 \\
 \vdots \\
 n
 \end{array}
 \begin{array}{c}
 1 \quad 2 \quad 3 \quad \dots \quad n \\
 \begin{array}{|c|c|c|c|c|c|}
 \hline
 x & 1 & 0 & 0 & \dots & 0 \\
 \hline
 1 & x & 1 & & & \\
 \hline
 0 & 1 & x & & & \\
 \hline
 0 & & & & & \\
 \hline
 & & & & x & 1 \\
 \hline
 0 & \dots & \dots & \dots & 1 & x \\
 \hline
 \end{array}
 \end{array}
 = 0$$

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

Orbital coefficients: are given by

$$c_s \propto \sin\left(\frac{\pi ks}{n+1}\right) \quad [4]$$

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

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 ($n=3$).

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

i.e.

$$c_1 \propto \sin\left(\frac{3\pi}{4}\right) = \frac{1}{\sqrt{2}}, \quad c_2 \propto \sin\left(\frac{6\pi}{4}\right) = -1, \quad c_3 \propto \sin\left(\frac{9\pi}{4}\right) = \frac{1}{\sqrt{2}}$$

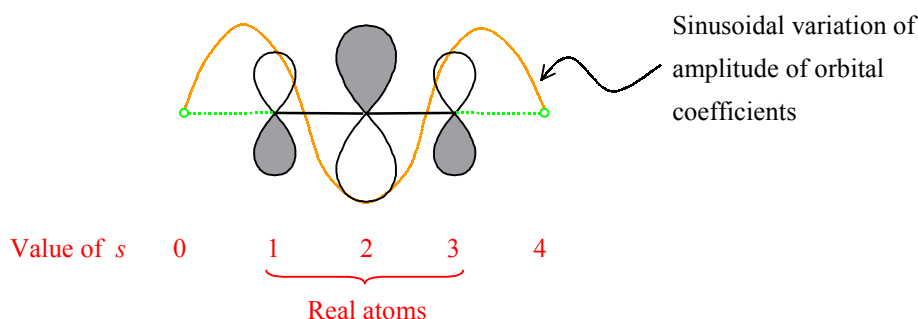
These coefficients are not normalized - to achieve this we need to multiply them all by the same constant value, chosen to ensure that the new values of the coefficients satisfy the condition that $\sum c_i^2 = 1$.

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 ($n = 3$).



Orbital energies: are given by

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

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 $+1$.

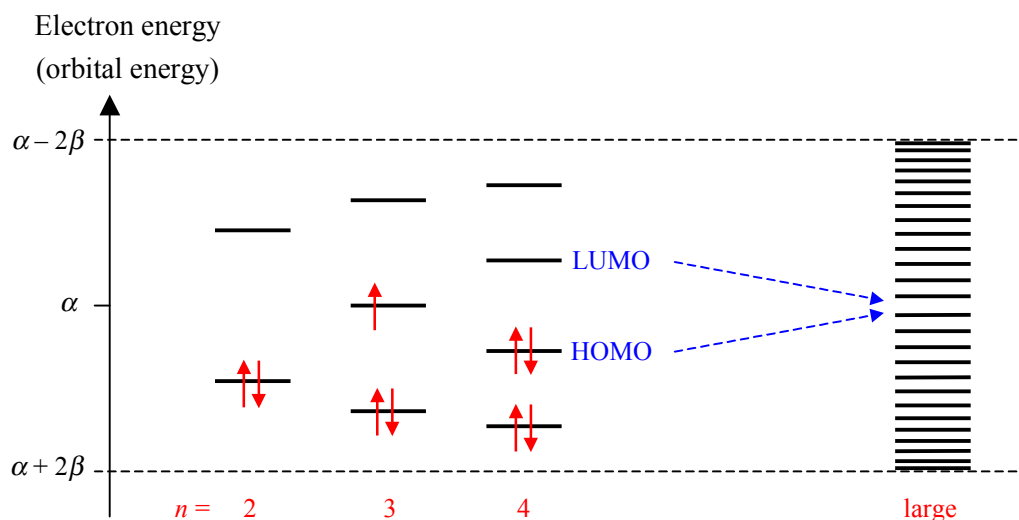
i.e.
$$-1 \leq \cos\left(\frac{\pi k}{n+1}\right) \leq +1$$

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

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.

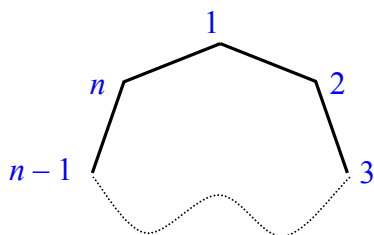
i.e. $h\nu = \Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ decreases as n increases.

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:

$$\begin{array}{c}
 \begin{array}{cccccc}
 & 1 & 2 & 3 & & n \\
 1 & x & 1 & 0 & 0 & \dots & 1 \\
 2 & 1 & x & 1 & & & \\
 3 & 0 & 1 & x & & & \\
 & 0 & & & & & \\
 & & & & & x & 1 \\
 n & 1 & \dots & \dots & \dots & 1 & x
 \end{array}
 \end{array} = 0$$

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

Orbital energies: are given by

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

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

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

$$\begin{array}{ll}
 k = 0, \pm 1, \pm 2, \dots, \left(\frac{n}{2}\right) & \text{for even } n . \\
 k = 0, \pm 1, \pm 2, \dots, \pm\left(\frac{n-1}{2}\right) & \text{for odd } n .
 \end{array}$$

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.
$$-1 \leq \cos\left(\frac{2\pi k}{n}\right) \leq +1$$

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

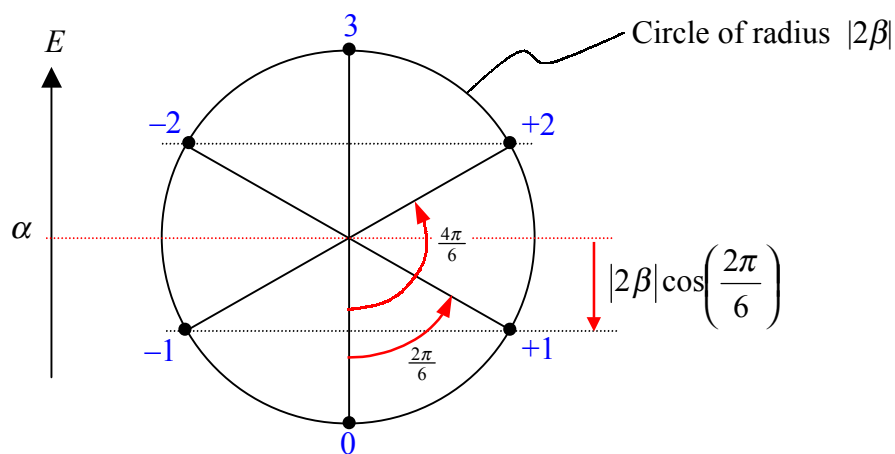
It is possible to represent equation [6] as a geometrical construction, and this is illustrated below.

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

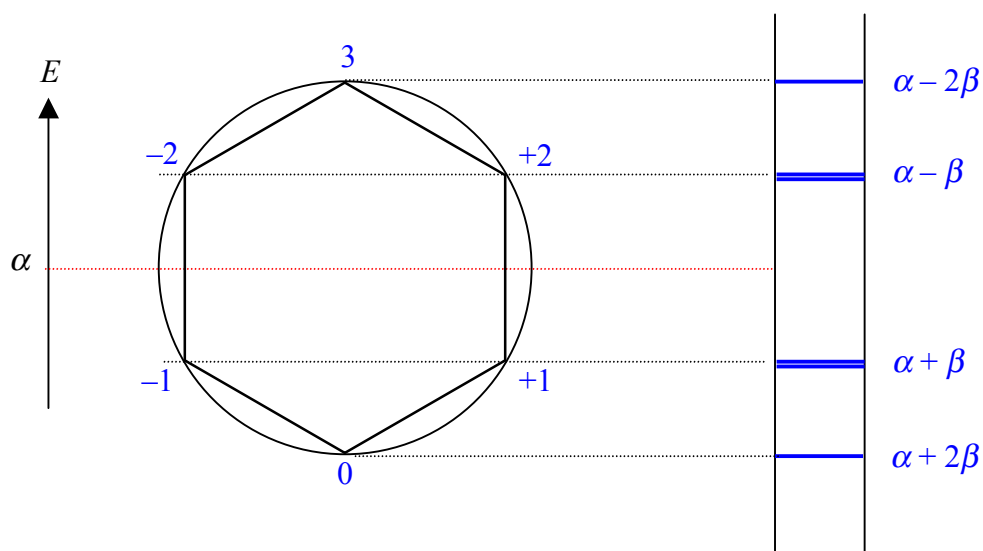
$$E = \alpha + 2\beta \cos\left(\frac{2\pi k}{6}\right)$$

where

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



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. $n = 3$, $n = 5$ >

Note : 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.

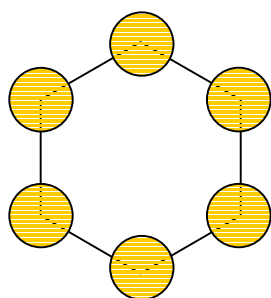
< Lecture - examples of stable cyclic systems >

What are the Wavefunctions ?

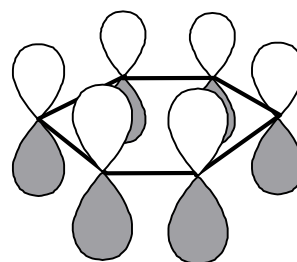
The wavefunctions are generally complex (i.e. contain imaginary parts), the exceptions being the non-degenerate solution(s).

- 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



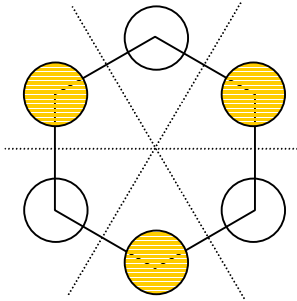
Side view

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).

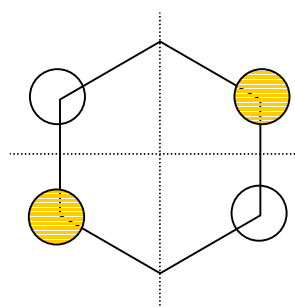
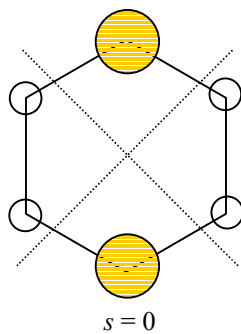
The coefficients for the real functions are:

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

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

e.g. for $n = 6$

$k = \pm 2$



$k = \pm 1$

