Application of Huckel Molecular Orbital Theory - Benzene Molecule

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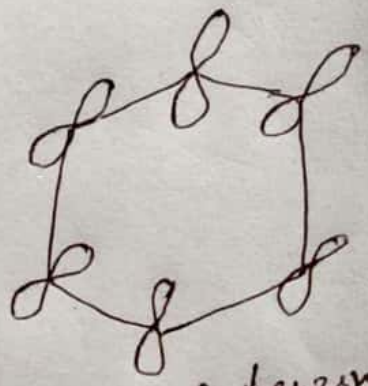
HUCKEL MOLECULAR THEORY TO BENZENE MOLECULE

From the study of both cyclic and open chain systems, it is apparent that for any planar systems of conjugated molecules, the order of the determinant is equal to the number of carbon atoms. Moreover, we can write x along the diagonal (of the first determinant), 1 for the off-diagonal terms for atoms which are nearest neighbours and zero anywhere else. Thus, we can write the secular determinant for any molecule by a simple inspection of that molecule. Illustrates the benzene molecule. The secular determinant for the benzene:-

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



A benzene molecule.

The energy levels of the benzene molecule are

$E_1 = \alpha + 2\beta$
$E_2 = \alpha + \beta$
$E_3 = \alpha + \beta$
$E_4 = \alpha - \beta$
$E_5 = \alpha - \beta$
$E_6 = \alpha - 2\beta$

of these E_1 E_2 and E_3 levels correspond to bonding MO's. Each of these bonding MO's can hold two π electrons with antiparallel spins. The six π electrons of benzene occupy

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these three bonding orbitals of low energy. On the other hand E_4, E_5 and E_6 levels correspond to antibonding MO's. However, two of the bonding energy levels (E_2 E_3) and two of the antibonding levels (E_4, E_5) are degenerate.

The total energy of the benzene molecule is $E = 2(\alpha+2\beta) + 4(\alpha+\beta) = 6\alpha+8\beta$.

If we assume that benzene consists of three localized single bonds and three localized double bonds, the energy of the molecule should be the sum of the energies of three-π bonds. The energy of the three ethene units is

$$3(2\alpha+2\beta) = 6\alpha+6\beta$$

Delocalization energy $= (6\alpha+8\beta)-(6\alpha+6\beta) = 2\beta$

The stabilization of benzene molecule is due to the lowering of energy by 2β units.

The molecular orbitals with bonding energies E_1, E_2 and E_3 are ψ_1, ψ_2 and ψ_3 respectively.

The ground state electronic configuration of the molecule is $\psi_1^2, \psi_2^2, \psi_3^2$.

The six secular equations corresponding to the secular determinant are solved using each energy value and normalization condition to obtain coefficients. The resulting six molecular orbitals of benzene are:-

$$\psi_1 = \frac{1}{\sqrt{6}}\left(\psi_2 p_{z(1)} + \psi_2 p_{z(2)} + \psi_2 p_{z(3)} + \psi_2 p_{z(4)} + \psi_2 p_z^{(5)} + \psi_2 p_{z(6)}\right); \quad E_1 = \alpha+2\beta$$

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$\psi_2 = \frac{1}{2}(\psi_{2p_z(2)} + \psi_{2p_z(3)} - \psi_{2p_z(5)} - \psi_{2p_z(6)})$; $E_2 = \alpha + B$

$\psi_3 = \frac{1}{2\sqrt{3}}(2\psi_{2p_z(1)} + \psi_{2p_z(2)} - \psi_{2p_z(3)} - 2\psi_{2p_z(4)} - \psi_{2p_z(5)} + \psi_{2p_z(6)})$;

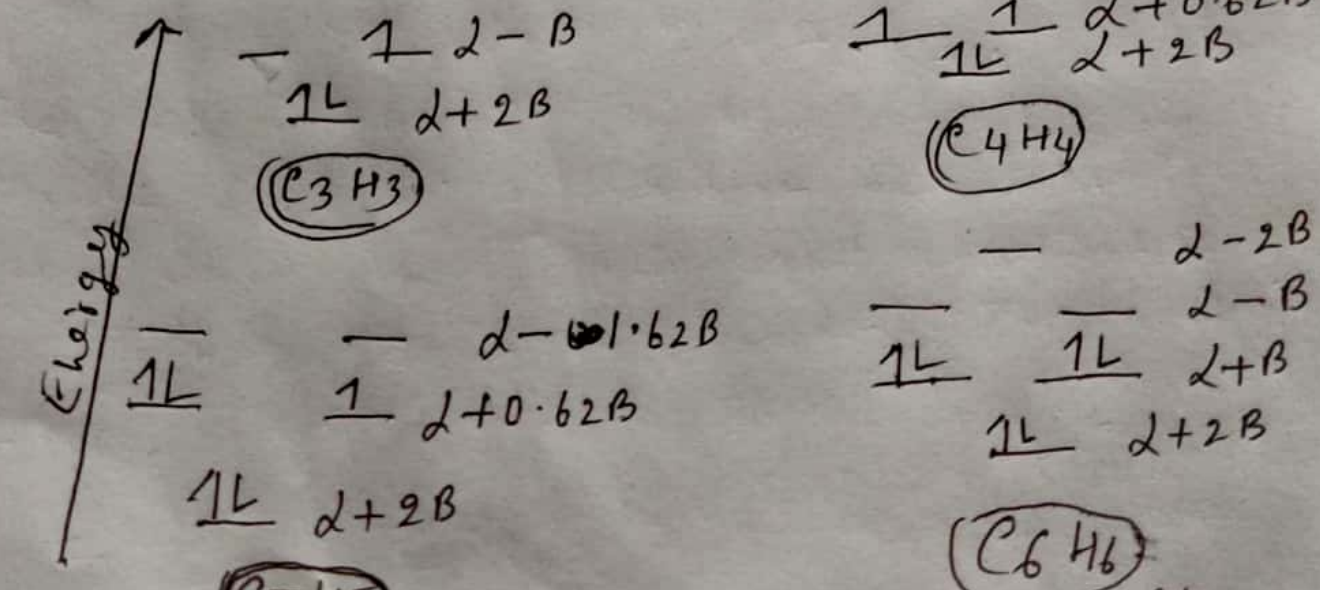
$E_3 = \alpha + B$

$\psi_4 = \frac{1}{2}(\psi_{2p_z(2)} - \psi_{2p_z(3)} + \psi_{2p_z(5)} - \psi_{2p_z(6)})$; $E_4 = \alpha - B$

$\psi_5 = \frac{1}{2\sqrt{3}}(2\psi_{2p_z(1)} - \psi_{2p_z(2)} - \psi_{2p_z(3)} + 2\psi_{2p_z(4)} - \psi_{2p_z(5)} - \psi_{2p_z(6)})$; $E_5 = \alpha - B$

$\psi_6 = \frac{1}{\sqrt{6}}(\psi_{2p_z(1)} - \psi_{2p_z(2)} + \psi_{2p_z(3)} - \psi_{2p_z(4)} + \psi_{2p_z(5)} - \psi_{2p_z(6)})$; $E_6 = \alpha - 2B$

For cyclic Polyenes with an odd number of π electrons, only the lowest level is non degerate, all other levels are doubly degenerate. The energy level diagrams, for monocyclic Polyenes with $N = 3, 4, 5$, and 6 are shown in fig. It is evident from the figure that cyclic Polyenes have filled bonding MO's if the number of π electrons is equal to $4n+2$, where $n = 0, 1, 2, \ldots$. this is the Huckel $(4n+2)$ rule.



Molecular energy level for Planar cyclic Polyenes.

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