

# Huckel Molecular Orbital Theory of Conjugated Systems

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The carbon compounds containing alternate double and single bonds are called conjugated molecules. The carbon atoms of these molecules are  $sp^2$  hybridized to form three hybrid orbitals which are directed towards three adjacent atoms and form  $\sigma$  bonds. The unhybridized  $2p_z$  orbitals are parallel to each other and perpendicular to the molecular plane. Since  $\sigma$  and  $\pi$  electrons are in the planes perpendicular to each other, the interaction between them may be neglected in the planar conjugated molecule. Therefore, the MOs for  $\pi$  electrons in a conjugated system may be considered independently of  $\sigma$ -electrons. These orbitals are set up according to linear combination of  $2p_z$  AOs of each C-atom in a conjugated molecule. This concept was first introduced by Huckel (1931) and later developed by Coulson and Higgins (1947).

Let us consider a conjugated system of double and single bonds containing  $n$  carbon atoms. Each C atom contributes one  $2p_z$  AO with one  $\pi$  electron. According to LCAO, the MO may be written as:

$$\Psi_i = \sum_{j=1}^n C_{ij} \phi_j$$

Where  $i = 1, 2, 3, \dots, n$  and  $j = 2p_z$  orbital on C atom  $j$ .

The  $n\pi$  MOs are formed by the overlap of  $n$   $2p_z$  AOs.

Huckel MO theory is similar to the MOT of homonuclear diatomic molecules. Huckel made the following postulates:

- i. All overlap integrals are zero i.e.  $S_{ij} = 0$
- ii. Coulomb integral  $H_{ij}$  shows that energy of an electron in  $2p_z$  orbital on  $i^{\text{th}}$  C atom. All such integrals are equal and denoted by  $\alpha$ .
- iii. The exchange integrals indicated the energy of interaction of the AOs. For atoms  $i$  and  $j$  not bonded directly,  $H_{ij} = H_{ji} = 0$  unless the  $i^{\text{th}}$  and  $j^{\text{th}}$  orbitals are on adjacent C atoms in which they are represented by  $\beta$ .
- iv. The resonance integrals ( $\beta$ ) between non-neighbours are set equal to zero.

The Huckel secular equation may now be written as:

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

Defining a dimensionless parameter  $x$  as  $x = \frac{\alpha - E}{\beta}$ , the above equation may be written as

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

The conjugated system thus has  $n$  energy levels and  $n$  MOs. The energy of  $k^{\text{th}}$  MO is given by

$$E_k = \alpha + x_k \beta$$

Where  $x_k$  is the  $k^{\text{th}}$  root of the polynomial. Since Coulomb integral  $\alpha$  and resonance integral  $\beta$  are negative, a positive value of  $x_k$  represents an energy level which is more negative and more stable. Such an energy level is called bonding molecular orbital (BMO). A negative value of  $x_k$  represents an energy level which has higher energy and hence less stability than an electron in a carbon 2pz orbital. Such level is called antibonding molecular orbital (ABMO). The energy level corresponding on  $x_k$  being zero is called non-bonding molecular orbital (NBMO).