CHAPTER 1: Nature of Bonding in Organic Molecules

❖ **Huckel’s Rule: Energy Level of \( \pi \)-Molecular Orbitals**

Huckel’s rule states that all the planar and conjugated systems with \( 4n + 2 \) \( \pi \)-electrons will be aromatic, and therefore, will be more stable than their acyclic conjugates.

The theoretical basis for Hückel's rule is the Hückel molecular orbital theory (HMO), which was proposed by Erich Hückel in 1930. This theory considers a very simple linear combination of atomic orbitals molecular orbitals method for the determination of energies of molecular orbitals of \( \pi \)-electrons in \( \pi \)-delocalized molecules, such as ethylene, benzene, butadiene, and pyridine.

![Diagram of aromatc and antiaromatic structures](image)

\( 4n+2 \) \( \pi \)-electrons
(aromatic)

\( 4n \) \( \pi \)-electrons
(antiaromatic)

❖ **Main Features of Hückel Molecular Orbital Theory**

1. It is limited to conjugated hydrocarbons only.
2. Only \( \pi \)-electron density of MOs is included because these determine much of the spectral and chemical properties of these compounds. The \( \sigma \)-electron density is thought to form the framework of the molecule and \( \sigma \)-connectivity is employed to find whether two \( \pi \)-orbitals interact or not. Nevertheless, the orbitals generated by \( \sigma \)-orbitals are overlooked and presumed not to interact with \( \pi \)-electrons, which is called as \( \sigma \)-\( \pi \) separability. It is defensible by the orthogonality of \( \pi \) and \( \sigma \) orbitals in planar molecular geometries. That’s why the Hückel method is only limited to systems that are nearly or completely planar.
3. The theory is based on the variational method to the linear combination of atomic orbitals and makes simple assumptions about the resonance, overlap, and Coulomb integrals of these atomic orbitals. Also, it doesn’t try to solve the Schrödinger equation, and neither the functional form of the atomic basis nor particulars of the Hamiltonian involved.
4. For different hydrocarbons, the theory takes atomic connectivity as the only input value; empirical parameters are only required after the incorporation of heteroatoms.
5. The theory successfully predicts the number of energy levels for a given molecule, their degeneracy and it expresses the energies molecular orbital in terms of two parameters, called \( \alpha \), the energy of an electron in an atomic \( 2p \) orbital, and \( \beta \) which represents the energy of interaction between two \( 2p \) orbitals. The typical convention makes both \( \alpha \) and \( \beta \) be as negative quantities. In order to fully understand and equate systems in a qualitative or semi-quantitative manner, clear numerical values for these parameters are typically not needed.
6. This theory also enables the calculation of charge density for each atom in the \( \pi \) framework, the fractional bond order between any two carbon atoms, and the overall dipole moment of the molecule.
**Energy Level of Some Typical \( \pi \)-Molecular Orbitals**

The exact procedure to determine the energy levels of conjugated \( \pi \)-bonded systems is beyond the scope of this book. However, the results from theory can be concluded in some simple mathematical expressions which can be used to yield the required energy levels. For linear and cyclic systems (with \( N \) atoms), general solutions are given below.

1. **Linear system (polyene/polyenyl):** The energy of different molecular orbitals for these types of systems can be obtained from the expression given below.

\[
E_k = \alpha + 2\beta \cos \left( \frac{(k + 1)\pi}{N + 1} \right)
\]

Where \( k = 0, 1, 2, 3 \ldots N - 1 \) and \( N \) is the number conjugated carbons. Once the energies of different molecular orbitals are obtained, they should be arranged in accenting order on the energy level diagram.

*i) Ethylene:* In case of ethylene, \( N = 2 \), we get

For \( k = 0 \)

\[
E_0 = \alpha + 2\beta \cos \left( \frac{(0 + 1)\pi}{2 + 1} \right) = \alpha + \beta
\]

For \( k = 1 \)

\[
E_1 = \alpha + 2\beta \cos \left( \frac{(1 + 1)\pi}{2 + 1} \right) = \alpha - \beta
\]

The corresponding energy level diagram is given below.

![Energy Level Diagram of Ethylene](image)

Figure 13. The \( \pi \)-molecular orbital energy level diagram of ethylene.
ii) Allyl: In case of allyl, $N = 3$, we get

for $k = 0$

$$E_0 = \alpha + 2\beta \cos\left(\frac{(0 + 1)\pi}{(3 + 1)}\right) = \alpha + \sqrt{2}\beta$$ \hspace{1cm} (4)

for $k = 1$

$$E_1 = \alpha + 2\beta \cos\left(\frac{(1 + 1)\pi}{(3 + 1)}\right) = \alpha$$ \hspace{1cm} (5)

for $k = 2$

$$E_2 = \alpha + 2\beta \cos\left(\frac{(2 + 1)\pi}{(3 + 1)}\right) = \alpha - \sqrt{2}\beta$$ \hspace{1cm} (6)

The corresponding energy level diagram is given below.

![Energy Level Diagram](image)

Figure 14. The $\pi$-molecular orbital energy level diagram of allyl.

iii) Butadiene: In case of butadiene, $N = 4$, we get

for $k = 0$

$$E_0 = \alpha + 2\beta \cos\left(\frac{(0 + 1)\pi}{(4 + 1)}\right) = \alpha + 1.618 \beta$$ \hspace{1cm} (7)

for $k = 1$

$$E_1 = \alpha + 2\beta \cos\left(\frac{(1 + 1)\pi}{(4 + 1)}\right) = \alpha + 0.618 \beta$$ \hspace{1cm} (8)

for $k = 2$

$$E_2 = \alpha + 2\beta \cos\left(\frac{(2 + 1)\pi}{(4 + 1)}\right) = \alpha - 0.618 \beta$$ \hspace{1cm} (9)

for $k = 3$

$$E_3 = \alpha + 2\beta \cos\left(\frac{(3 + 1)\pi}{(4 + 1)}\right) = \alpha - 1.618 \beta$$ \hspace{1cm} (10)
The corresponding energy level diagram is given below.

![Energy Level Diagram](image)

Figure 15. The π-molecular orbital energy level diagram of butadiene.

2. Cyclic system, Hückel topology (annulene/annulenyl): The energy of different molecular orbitals for these types of systems can be obtained from the expression given below.

\[
E_k = \alpha + 2\beta \cos \frac{2k\pi}{N} \tag{11}
\]

Where \( k = 0, 1, 2, 3 \ldots N - 1 \) and \( N \) is the number conjugated carbons. Once the energies of different molecular orbitals are obtained, they should be arranged in accenting order on the energy level diagram.

i) Cyclopropenyl: In case of cyclopropenyl, \( N = 3 \), we get

For \( k = 0 \)

\[
E_0 = \alpha + 2\beta \cos \frac{2(0)\pi}{3} = \alpha + 2\beta \tag{12}
\]

For \( k = 1 \)

\[
E_1 = \alpha + 2\beta \cos \frac{2(1)\pi}{3} = \alpha - \beta \tag{13}
\]

For \( k = 1 \)

\[
E_2 = \alpha + 2\beta \cos \frac{2(2)\pi}{3} = \alpha - \beta \tag{14}
\]
The corresponding energy level diagram is given below.

\[
E_0 = \alpha + 2\beta \\
E_1 = E_2 = \alpha - \beta \\
E_3 = E_4 = \alpha \\
E_6 = \alpha + 2\beta
\]

Figure 16. The π-molecular orbital energy level diagram of cyclopropenyl.

ii) Cyclobutadiene: In case of cyclobutadiene, \( N = 4 \), we get

\[
\text{for } k = 0 \quad E_0 = \alpha + 2\beta \cos \frac{2(0)\pi}{4} = \alpha + 2\beta
\]

\[
\text{for } k = 1 \quad E_1 = \alpha + 2\beta \cos \frac{2(1)\pi}{4} = \alpha
\]

\[
\text{for } k = 2 \quad E_2 = \alpha + 2\beta \cos \frac{2(2)\pi}{4} = \alpha - 2\beta
\]

\[
\text{for } k = 3 \quad E_3 = \alpha + 2\beta \cos \frac{2(3)\pi}{4} = \alpha
\]

The corresponding energy level diagram is given below.

\[
E_0 = \alpha - 2\beta \\
E_1 = E_3 = \alpha \\
E_6 = \alpha + 2\beta
\]

Figure 17. The π-molecular orbital energy level diagram of cyclobutadiene.
iii) Benzene: In case of butadiene, $N = 6$, we get

\[
E_0 = \alpha + 2\beta \cos \left(\frac{2(0)\pi}{6}\right) = \alpha + 2\beta \quad \text{(16)}
\]

for $k = 0$

\[
E_1 = \alpha + 2\beta \cos \left(\frac{2(1)\pi}{6}\right) = \alpha + \beta \quad \text{(17)}
\]

for $k = 1$

\[
E_2 = \alpha + 2\beta \cos \left(\frac{2(2)\pi}{6}\right) = \alpha - \beta \quad \text{(18)}
\]

for $k = 2$

\[
E_3 = \alpha + 2\beta \cos \left(\frac{2(3)\pi}{6}\right) = \alpha - 2\beta \quad \text{(19)}
\]

for $k = 3$

\[
E_4 = \alpha + 2\beta \cos \left(\frac{2(4)\pi}{6}\right) = \alpha - \beta \quad \text{(20)}
\]

for $k = 4$

\[
E_5 = \alpha + 2\beta \cos \left(\frac{2(1)\pi}{6}\right) = \alpha + \beta \quad \text{(21)}
\]

for $k = 5$

The corresponding energy level diagram is given below.

Figure 18. The typical $\pi$-molecular orbital energy level diagram of the benzene molecule.
The corresponding Frost circle is given below.

The energy levels for cyclic systems can be obtained using the Frost circle method (named after the American chemist A. A. Frost). A circle with a center at \( \alpha \) with a radius of \( 2\beta \) is inscribed with a regular polygon with \( N \) sides with one vertex pointing downward; the \( y \)-coordinate of the vertices of the polygon then shows the energies of different orbital of the \([N]\)annulene/annulenyl system. Corresponding mnemonics exist for Möbius and linear systems. The energy level diagrams of different cyclic systems are assisted with the corresponding Frost cycle.

In the later period, it was extended to conjugated molecules with heteroatoms like pyrrole, pyridine, and furan. A more dramatic extension of the method (Hückel molecular orbital method) to include \( \sigma \)-electrons, known as the extended Hückel method (EHM), was developed by Roald Hoffmann.

The Hückel method’s extension provides some degree of quantitative accuracy for organic compounds in general and was employed to give computational justification for the famous Woodward-Hoffmann rules. In order to differentiate the original route from Hoffmann’s extension, the Hückel method is also well-known as the ‘simple Hückel method’ (SHM). Even though the method is quite simple, the Hückel route in its original form makes chemically useful and qualitatively accurate predictions for numerous common molecular geometries, and therefore, is a very powerful and widely popular educational toolkit. It is also included in textbooks of preliminary quantum chemistry and physical organic chemistry. Furthermore, many organic chemists, in specific, still apply Hückel theory routinely to find back-of-the-envelope, the very approximate profile of \( \pi \)-interactions.
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL
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