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CHEMISTRY
PAPER:2, PHYSICAL CHEMISTRY-I
MODULE: 35 , Introduction to Extended Hückel Theory (EHT)

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CHEMISTRY

PAPER:2, PHYSICAL CHEMISTRY-I

MODULE: 35 , Introduction to Extended Hückel Theory (EHT)

1. Learning Outcomes

After studying this module, you shall be able to

- Understand the basis of Extended Hückel Theory (EHT)
- Appreciate the extension of HMO theory for studying other chemical systems.

2. Introduction

Hückel Molecular Orbital (HMO) theory was one of the first semi-empirical methods developed in early 1930s for deducing the electronic structure of molecules containing conjugated double bonds.

HMO theory applies to planar conjugated π -systems only. This theory treats the π electrons separately from σ electrons. It is the simplest of all theories and is built upon the following approximations:

1. Only considers π electrons.
2. The σ skeleton of the molecule is assumed frozen.
3. Ignores electron-electron repulsions.
4. The basis set for molecular orbital (MO) approximation consists of one $p\pi$ -orbital on each atom.
5. The coulomb integrals (α) for all the carbon atoms in a molecule are assumed to be similar as all the carbon atoms in the π system are similar, though not identical.

$$\alpha = H_{ii} = \int \psi_i^* \hat{H} \psi_i d\tau$$

6. All the resonance integrals (β) between directly linked atoms are assumed to be same while those between atoms that are not directly bonded are neglected (Nearest neighbor interaction considered).

$$\beta = H_{ij} = \int \psi_i^* \hat{H} \psi_j d\tau$$

7. All overlap integrals representing overlap of atomic orbitals centered on different atoms are neglected.

$$S_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases}$$

With all the above mentioned assumptions, HMO theory gives a good qualitative picture of the electronic structures of π -conjugated molecules. The major advantage of HMO theory is that the calculations can be performed manually with no need of computers.

3. Extension of Hückel Molecular Orbital Theory

HMO theory has been extensively used for studying π -conjugated molecules. However, one can extend this qualitative MO theory in a number of ways to treat a variety of other chemical systems.

- **Neighboring interactions:** HMO theory assumes nearest neighbor interactions only. However, non-nearest neighbor interactions do influence the MO picture of the system. Non-nearest neighbor interactions do alter the energies of the MO's in significant ways leading to better quantitative accuracy of the results.
- **Bond length alternation:** Bond length alternation refers to the difference in the bond lengths of two adjacent bonds of π -conjugated system. Bond lengths influence

β (resonance integral) value, i.e., if two bonds have different bond lengths, they should have different β values. Shorter bond length indicates strong orbital overlap with large (negative) β value. This means that the parameter β is a function of bond length.

All the β parameters for benzene are the same which means that all the bonds are of equal or nearly equal length.

- **Hetero-atoms and other substituents:** Often, the molecules of interest consist of hetero-atoms such as nitrogen or oxygen and other substituents. Within Hückel framework, these chemically distinct atoms and bonds have different values of α and β parameters. The α values are primarily influenced by the nature of atoms. This means that different atoms have different α values. For example, the electronegativity of oxygen atom is very much different than that of carbon atom. This difference is reflected in the α value of the respective atom. Further, the β values change in accordance with bond length alternation (as explained above).
- **σ and π bonded molecules:** Hückel treatment can be extended to describe molecules considering both σ and π bonds. Over here, one can simply include s , p_x , p_y atomic orbitals (σ bond) along with p_z atomic orbitals (π bond). The major difficulty is that there are so many orbitals involved with a correspondingly large number of parameters (α 's and β 's) to be determined.

There is no one set of parameters here, on the basis of which the extension of HMO theory yields good quantitative and qualitative results. Generally, all sorts of such techniques are termed as Extended Hückel Theory.

4. Extended Hückel Theory (EHT)

The basic methods of Extended Hückel calculations have been proposed by several people. Here, we will consider the method of Hoffmann because of its systematic development and application.

The Extended Hückel Theory (EHT) is a semi-empirical quantum chemistry method. This method was developed by Roald Hoffmann in 1963 and is based on Hückel's method. While the original HMO theory considers only π electrons, the EHT treats σ electrons along with the π electrons.

Extended Hückel Theory was first used by Roald Hoffmann, who along with Robert Burns Woodward developed rules for explaining reaction mechanisms (Woodward-Hoffmann rules). He used the pictures of the MO's from EHT to work out the orbital interactions in the cyclo-addition reactions.

EHT is similar to HMO theory but is no longer restricted to planar conjugated molecules. EHT takes into account both σ and π orbitals and can be used for both planar and non-planar molecules. Like HMO theory, EHT too ignores electron-electron repulsions. However, EHT does not ignore overlap but calculates all the overlap integrals explicitly. The distinctive feature of EHT is that it treats only the valence electrons of the atoms present in a molecule and considers the core electrons frozen.

EHT begins with the approximation that the complete Hamiltonian is sum of one electron Hamiltonians,

$$\hat{H} = \sum_i H_i$$

, but the Hamiltonian is not specified. The complete electronic wave function ψ is taken as product of one electron wave functions (i.e., MO's ψ_i) and the total energy of the system E is taken as the sum of one electron MO energies (E_i).

$$\psi = \prod_i \psi_i$$

$$E = \sum_i E_i$$

Each molecular orbital is obtained by taking linear combination of atomic orbitals φ_j containing valence electrons only (core electrons are ignored).

$$\psi_i = \sum_j c_{ij} \varphi_j \quad , \varphi_j = \text{valence AO } 2s, 2p_x, 2p_y, 2p_z \text{ of C \& heteroatom and } 1s \text{ of H}$$

The set of orbitals defined above is called basis set.

Application of variation method leads to secular determinant,

$$\begin{vmatrix} H_{11} - \epsilon & H_{12} - \epsilon S_{12} & \dots \dots \dots \\ H_{21} - \epsilon S_{21} & H_{22} - \epsilon & \dots \dots \dots \\ \dots \dots \dots & \dots \dots \dots & H_{nn} - \epsilon \end{vmatrix} = 0$$

H_{ii} , the energy integral is given by the expression,

$$H_{ii} = \int \psi_i^* \hat{H} \psi_i d\tau$$

which looks like an integral representing the average energy of an electron in atomic orbital ψ_i centered on the atom i in the molecule. Hence, H_{ii} is set equal to the energy of an electron in i^{th} atomic orbital ψ_i of the isolated atom in the valence state.

The off-diagonal elements of Hamiltonian are evaluated using an approximate formula,

$$H_{ij} = \frac{1}{2} K [H_{ii} + H_{jj}] S_{ij}$$

where K is an adjustable parameter. The off-diagonal elements (which correspond to β and 0 in the HMO theory) in EHT are assumed proportional to overlap integral S_{ij} . The rationalization behind such an approximation is that the energy of interaction should be greater when the overlap between the atomic orbitals is greater and that an overlap interaction energy between low-energy atomic orbitals should be lower than that produced by an equal amount of overlap between higher-energy atomic orbitals. The contribution of these effects to the energy is scaled by a parameter K which is assigned a value of 1.75 by Hoffmann.

The total energy is calculated by summing the energies of the occupied MO's, taking into consideration their occupancy numbers. For example, for a closed shell, the total energy is given by

$$E_{EHT} = 2 \sum_i^{occ MO} \epsilon_i$$

Hoffmann suggested a value of 1.75 for K. Hoffmann assigned this value to K after studying the effect of this parameter on energies of occupied orbitals of ethane

4.2 Applications

EHT calculations can yield the following information:

- Determination of molecular structure.
- Computation of energy barriers for rotation about bonds.
- Determination of relative energies of different geometrical configurations of molecules
- Determination of energy and structure of transition state in a reaction. This also helps to choose reaction mechanism on the basis of calculated energy data.

- EHT is used as a preliminary step for determination of the approximate MO's in sophisticated quantum chemistry methods.

4.3 Drawbacks

The HMO and EHT methods are quite basic in that they use a very simplified Hamiltonian that ignores inter-electron interaction terms. The results obtained using EHT give good qualitative trends but are not very accurate because of the following reasons:

- H_{ij} is not exact
- H_{ij} increases with overlap causing system to show minimum energy when atoms collapse
- No core-core repulsions considered
- No electron –electron interactions considered

Several improved semi-empirical theories have been developed that include the above mentioned factors and give good results. Nonetheless, EHT does usually show qualitative correct trends in an easily explicable manner.

5. Summary

- HMO theory has been used for studying π -conjugated molecules.
- HMO theory can be extended in a number of ways to treat a variety of other chemical systems. These include:
 - ✓ Non-nearest neighbor interactions
 - ✓ Bond length alternation
 - ✓ Hetero-atoms and other substituents
 - ✓ σ and π bonded systems

All sorts of such techniques are termed as Extended Hückel Theory.

- In this module, Extended Hückel Theory developed by Hoffmann has been considered.
 - ❖ EHT takes into account both σ and π orbitals and can be used for both planar and non-planar molecules.
 - ❖ EHT too ignores electron-electron repulsions.
 - ❖ EHT does not ignore overlap but calculates all the overlap integrals explicitly.
 - ❖ The distinctive feature of EHT is that it treats only the valence electrons of the atoms present in a molecule and considers the core electrons frozen.
 - ❖ EHT begins with the approximation that the complete Hamiltonian is sum of one electron Hamiltonians
 - ❖ The EHT method is quite basic in that it uses a very simplified Hamiltonian.
 - ❖ Nonetheless, EHT does usually show qualitative correct trends in an easily explicable manner.

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