

# Huckel Molecular Orbital Theory

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# Introduction to Hückel Molecular Orbital Theory

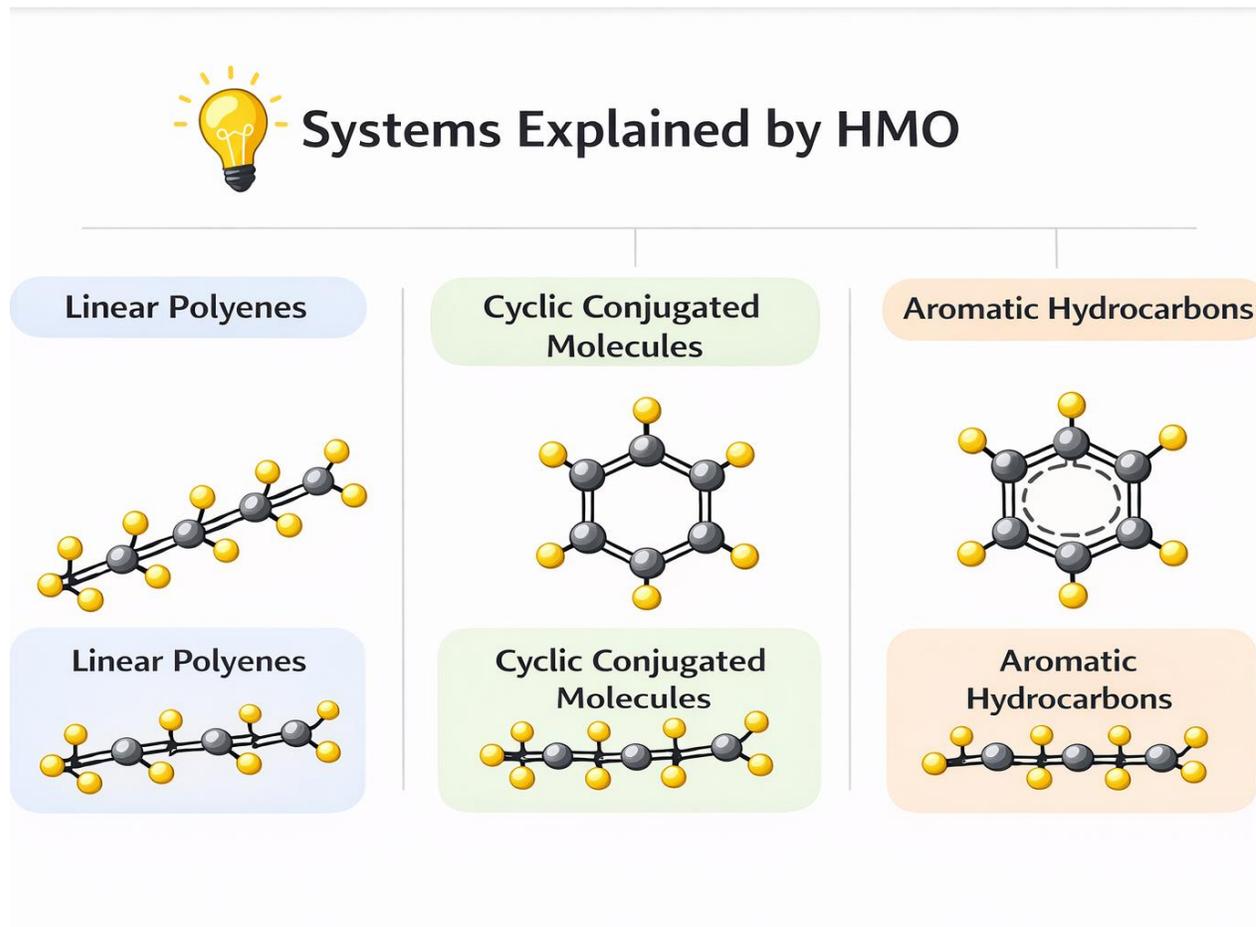
Hückel Molecular Orbital (HMO) theory is a **simple quantum mechanical method** used to study:

- Electronic structure of **conjugated  $\pi$ -electron systems**
- Molecular orbital energies
- Charge distribution
- Bond order
- Aromaticity and stability
- It applies only to  **$\pi$ -electrons**, while  $\sigma$ -framework is treated as fixed.

# Systems Explained by

## HMO

- Linear polyenes
- Cyclic conjugated molecules
- Aromatic hydrocarbons



# Basic Assumptions of HMO Theory

1. Only  $\pi$ -electrons are considered.
2. Each carbon contributes one  $p_z$  orbital.
3. Overlap between non-neighbouring atoms is neglected.
4. All Coulomb integrals are equal ( $\alpha$ ).
5. All resonance integrals between adjacent atoms are equal ( $\beta$ ).
6. Molecular orbitals are linear combinations of atomic orbitals (LCAO).

# Hückel theory of conjugated systems

- The conjugated linear polyenes such as 1,3 butadiene and 1,3, 5-hexatriene and cyclic polyenes such as benzene, naphthalene were studied by E. **Hückel** in 1931.
- In a conjugated unsaturated hydrocarbon with alternate single and double bonds, molecules are generally planar.
- In an n-carbon system each carbon atom is  $sp^2$  hybridized and has  $2p_z$  orbitals centered on it.
- The electrons in  $sp^2$  orbitals are called  $\sigma$  electrons are caught in molecular orbital plane.
- Each  $2p_z$  orbital which is perpendicular to the molecular plane contains one  $\pi$  electron.

- According to LCAO-MO approximation this can be written as following for MO:

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

- $\phi_j$  is the  $2p_z$  orbital center in carbon atom  $j$ .
- $\phi$ s are also known as basis sets.
- $n$   $\pi$ -molecular orbitals are formed from  $n$   $2p_z$  atomic orbitals.
- HMO theory is similar to MO theory of homonuclear diatomic molecules.
- Difference: HMO theory uses  $2p_z$  orbitals as basis functions.  $H_2$  molecule uses  $1s$  orbitals as basis functions.

# Hückel Assumptions

- **Overlap Integrals**

- All overlap integrals are neglected:

$$S_{ij}=0$$

- **Coulomb Integral**

- $H_{ii}$  represents the energy of an electron in a  $2p_z$  orbital on the  $i^{\text{th}}$  carbon atom.
- Denoted by  **$\alpha$  (alpha)**.

- **Exchange (Resonance) Integral**

- $H_{ij}=H_{ji}=0$  for non-adjacent carbon atoms.
- For **adjacent carbon atoms**, the integral is denoted by  **$\beta$  (beta)**.

# Limitation of HMO Theory

- Neglect of overlap between adjacent carbon atoms is the **most severe and unrealistic assumption**.
- Despite this, HMO theory:
  - Provides a **good qualitative description of  $\pi$ -bonding**.
  - Shows **reasonable agreement with experimental results**.