

Physical Chemistry

Lecture 32

Hueckel Molecular Orbital Theory

Molecular orbitals

- ◆ Describe the electronic structure
 - Span the entire molecule
 - Eigenfunctions of the Hamiltonian operator
- ◆ Approximated in various ways
 - Hartree-Fock calculation
 - LCAO-MOs
 - Valence-bond orbitals

Matrix formulation

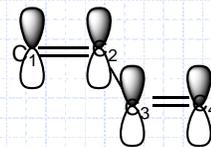
- ◆ Expand the wave function in a **basis**
- ◆ Form the Hamiltonian matrix in this basis
 - Results in a matrix equation
- ◆ Diagonalization of the matrix leads to
 - Eigenvalues of the energies
 - Expression for eigenfunctions in terms of the basis functions

$$H \cdot c = E \cdot c$$

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots$$

Hueckel molecular orbitals

- ◆ Useful qualitative description of the π orbitals of conjugated systems
 - Description of only part of the molecular orbital structure
 - Easy to develop
- ◆ Semiempirical theory
 - Assumes only overlap between orbitals on adjacent atoms
- ◆ Example: butadiene



$$\psi_{\pi} = c_1 \psi_{p1} + c_2 \psi_{p2} + c_3 \psi_{p3} + c_4 \psi_{p4}$$

Matrix equation

- ◆ Series of simultaneous equations
 - Contains
 - ◆ Hamiltonian matrix elements, H_{ij}
 - ◆ Overlap integrals, S_{ij}
 - Must solve to find energies and coefficients

$$\begin{aligned} c_1(H_{11} - \epsilon S_{11}) + c_2(H_{12} - \epsilon S_{12}) + c_3(H_{13} - \epsilon S_{13}) + c_4(H_{14} - \epsilon S_{14}) &= 0 \\ c_1(H_{21} - \epsilon S_{21}) + c_2(H_{22} - \epsilon S_{22}) + c_3(H_{23} - \epsilon S_{23}) + c_4(H_{24} - \epsilon S_{24}) &= 0 \\ c_1(H_{31} - \epsilon S_{31}) + c_2(H_{32} - \epsilon S_{32}) + c_3(H_{33} - \epsilon S_{33}) + c_4(H_{34} - \epsilon S_{34}) &= 0 \\ c_1(H_{41} - \epsilon S_{41}) + c_2(H_{42} - \epsilon S_{42}) + c_3(H_{43} - \epsilon S_{43}) + c_4(H_{44} - \epsilon S_{44}) &= 0 \end{aligned}$$

Matrix equation

- ◆ Approximations
 - S_{ij} only nonzero for same orbital
 - ◆ $S_{ii} = 1$
 - H_{ij} only nonzero for adjacent atoms and the same for all connected pairs
 - H_{ii} same for all atoms and nonzero

$$\begin{aligned} c_1(H_{11} - \epsilon) + c_2(H_{12}) &= 0 \\ c_1(H_{21}) + c_2(H_{22} - \epsilon) + c_3(H_{23}) &= 0 \\ c_2(H_{32}) + c_3(H_{33} - \epsilon) + c_4(H_{34}) &= 0 \\ c_3(H_{43}) + c_4(H_{44} - \epsilon) &= 0 \end{aligned}$$

Matrix equation

◆ Approximations

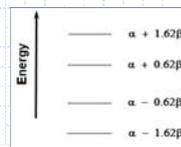
- $H_{ii} = \alpha$
- $H_{ij} = \beta$ for $i = j \pm 1$

$$\begin{aligned}c_1(\alpha - \varepsilon) + c_2\beta &= 0 \\c_1\beta + c_2(\alpha - \varepsilon) + c_3\beta &= 0 \\c_2\beta + c_3(\alpha - \varepsilon) + c_4\beta &= 0 \\c_3\beta + c_4(\alpha - \varepsilon) &= 0\end{aligned}$$

Solution of the matrix equation

- ◆ Equations can be written as a matrix equation
 - Diagonalization gives energies and associated sets of coefficients
- ◆ Equations can be solved simultaneously
 - Gives energies and associated sets of coefficients
- ◆ Solutions

$$(\alpha - \varepsilon)^2 = \frac{3 \pm \sqrt{5}}{2} \beta$$

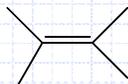
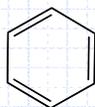


General use of Hückel theory

- ◆ Useful for understanding the various π orbitals in conjugated systems

◆ Examples

- Benzene
- Ethene
- Butadiene
- Cyclopentadiene



Summary

- ◆ Semiempirical approaches give approximate energy-level structure
- ◆ Hückel molecular orbital theory useful for describing π states of conjugated systems
 - Simple mathematics
 - Use of matrix equation
 - Easy to visualize the orbitals