

Lecture 11: Hückel Molecular Orbital Theory

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Assumptions

1. Applies to π electrons in planar hydrocarbons only.
2. Effective one-electron theory. Electrons are independent of each other. In the ground state, Hückel molecular orbitals (HMOs) are occupied according to the Aufbau principle; the N -electron wavefunction Φ_0 is an antisymmetrized product (Slater determinant) of all occupied HMOs.
3. The HMOs ϕ_i are linear combinations of atomic orbitals χ_μ (LCAO-MO ansatz),

$$\phi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \chi_{\mu}(\mathbf{r}).$$

4. The basis $\{\chi_{\mu}\}$ consists of one p orbital per C atom (minimal basis) for planar hydrocarbons. Differential overlap is neglected (CNDO, complete neglect of differential overlap):

$$S_{\mu\nu} = \int d^3r \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) = \delta_{\mu\nu}.$$

Assumptions

5. The Hamiltonian in the AO basis has the form

$$\mathbf{H} = \alpha \mathbf{1} + \beta \mathbf{M}.$$

The topological matrix \mathbf{M} depends on connectivity only:

$$M_{\mu\nu} = \begin{cases} 1 & \mu, \nu \text{ nearest neighbors} \\ 0 & \text{else} \end{cases}$$

α : Usually taken to be the negative p ionization energy of C. β : Sometimes related to spectroscopy or thermochemistry, but generally variable. *α and β are negative.*

6. The total energy is sum of all orbital energies $\{\epsilon_p\}$ times their occupation numbers $\{n_p\}$,

$$E_{\pi} = \sum_p n_p \epsilon_p.$$

Indexing Conventions

Indices	Indexed Quantity
i, j, k, \dots	Occupied orbitals
a, b, c, \dots	Virtual orbitals
p, q, r, \dots	General (occupied or unoccupied) orbitals
μ, ν, κ, \dots	Atomic orbitals/basis functions
σ, τ	Spin indices

- These are just aids for legibility, *not* definitions.

HMO Population Analysis

- Partitioning of total charge of

$$N_{\pi} = \sum_i n_i$$

π electrons into atomic contributions:

$$q_{\mu} = - \sum_i n_i c_{\mu i}^2$$

n_i : occupation number, q_{μ} : π charge of atom μ

- π bond order between atoms μ and ν :

$$p_{\mu\nu} = \sum_i n_i c_{\mu i} c_{\nu i}, \quad \mu \neq \nu,$$

- Also possible on per-orbital basis
- *Warning*: Populations and bond orders are not observable

HMO Resonance Energy

- Total π electron energy:

$$E_{\pi} = \sum_i n_i \epsilon_i$$

- Total π electron energy for $N_{\pi}/2$ (hypothetical) localized 2e2c bonds:

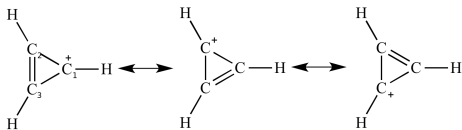
$$E_{2e2c} = \sum_i n_i (\alpha + \beta) = N_{\pi} (\alpha + \beta)$$

- Resonance energy: Energy gain due to delocalization,

$$E_{\text{res}} = E_{\pi} - E_{2e2c} = \sum_i n_i \beta (\lambda_i - 1),$$

where λ_i are eigenvalues of \mathbf{M} .

Example: Cyclopropenyl Cation



chem.ucla.edu (adapted)

- Topological matrix:

$$\mathbf{M} = \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

- \mathbf{H} and \mathbf{M} have the same eigenvectors \mathbf{c}_i . If λ_i is eigenvalue of \mathbf{M} for eigenvector \mathbf{c}_i , the corresponding HMO eigenvalue (orbital energy) is $\epsilon_i = \alpha + \beta\lambda_i$

Example: Cyclopropenyl Cation

- Eigenvalues and eigenvectors:

$$\lambda_1 = 2, \quad \epsilon_1 = \alpha + 2\beta, \quad \phi_1(\mathbf{r}) = \frac{1}{\sqrt{3}}(\chi_1(\mathbf{r}) + \chi_2(\mathbf{r}) + \chi_3(\mathbf{r}))$$

$$\lambda_2 = -1, \quad \epsilon_2 = \alpha - \beta, \quad \phi_2(\mathbf{r}) = \frac{1}{\sqrt{2}}(\chi_1(\mathbf{r}) - \chi_3(\mathbf{r}))$$

$$\lambda_3 = -1, \quad \epsilon_3 = \alpha - \beta, \quad \phi_3(\mathbf{r}) = \frac{1}{\sqrt{6}}(\chi_1(\mathbf{r}) - 2\chi_2(\mathbf{r}) + \chi_3(\mathbf{r}))$$

- ϕ_1 transforms according to A'_1 IRREP of D_{3h} , $\{\phi_2, \phi_3\}$ transform according to E' .

Example: Cyclopropenyl Cation

- π -populations and bond orders:

$$q_1 = q_2 = q_3 = -\frac{2}{3}, \quad p_{12} = p_{23} = p_{13} = \frac{2}{3}$$

- Total π electron energy (from orbital energies):

$$E_{\pi} = 2(\alpha + 2\beta)$$

- Resonance energy:

$$E_{\text{res}} = E_{\pi} - 2(\alpha + \beta) = 2\beta$$

Cyclopropenyl cation is aromatic.