

Lecture 37 — MOs for Polyatomic Molecules & Hückel Theory

Reading: Engel 4th ed., Chapter 13 (Sections 13.1–13.4)

Learning Objectives

- Construct MOs for polyatomic molecules using symmetry-adapted linear combinations (SALCs)
 - Apply the Hückel approximation to conjugated π systems
 - Solve the Hückel secular determinant for small molecules
 - Calculate π -electron energies, delocalization energies, and bond orders
 - Classify MOs by their symmetry in the molecular point group
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1. MOs for Polyatomic Molecules

Strategy

1. **Identify the molecular point group**
2. **Choose a basis set** of AOs
3. **Construct SALCs** using projection operators (from Lecture 18)
4. **Combine SALCs** with AOs on the central atom of matching symmetry
5. **Fill with electrons** following aufbau, Pauli, and Hund

Example: H_2O (C_{2v})

O contributes: $2s$, $2p_x$, $2p_y$, $2p_z$ H₁ and H₂ contribute: $1s$ each

SALCs of H $1s$ orbitals:

- A_1 : $\phi_1 + \phi_2$ (symmetric)
- B_2 : $\phi_1 - \phi_2$ (antisymmetric)

These combine with O orbitals of matching symmetry:

Symmetry	O orbital	H SALC	MO formed
A_1	$2s, 2p_z$	$\phi_1 + \phi_2$	$1a_1$ (bonding), $2a_1$ (nb/bonding), $3a_1$ (nb)
B_2	$2p_y$	$\phi_1 - \phi_2$	$1b_2$ (bonding), $2b_2^*$ (antibonding)
B_1	$2p_x$	—	$1b_1$ (nonbonding lone pair)

This gives the MO diagram for water with 4 occupied MOs and 2 lone pairs ($1b_1$ and $3a_1$).

[!NOTE] **Concept Check 37.1** In the water molecule (C_{2v}), the oxygen $2p_x$ orbital is classified as nonbonding ($1b_1$). Why does it not combine with any of the hydrogen $1s$ orbitals?

2. Hückel Molecular Orbital Theory

The Approximations

For **conjugated planar** molecules, we separate σ and π electrons and focus only on the π system.

Hückel assumptions:

1. All overlap integrals $S_{ij} = \delta_{ij}$ (set to 0 for $i \neq j$, 1 for $i = j$)
2. All diagonal Hamiltonian elements: $H_{ii} = \alpha$ (Coulomb integral — same for all C atoms)
3. Off-diagonal elements: $H_{ij} = \beta$ if atoms i and j are bonded, 0 otherwise
4. $\alpha < 0$, $\beta < 0$ (both stabilizing)

The Secular Determinant

$$\det(H_{ij} - E\delta_{ij}) = 0$$

With the substitution $x = (\alpha - E)/\beta$:

$$\det(x\delta_{ij} + A_{ij}) = 0$$

where $A_{ij} = 1$ for bonded pairs, 0 otherwise.

3. Worked Examples

Ethylene (C₂H₄) — 2 π electrons

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \implies x^2 - 1 = 0 \implies x = \pm 1$$

$$E_1 = \alpha + \beta \text{ (bonding)}, E_2 = \alpha - \beta \text{ (antibonding)}$$

$$\pi\text{-electron energy: } E_\pi = 2(\alpha + \beta) = 2\alpha + 2\beta$$

Butadiene (C₄H₆) — 4 π electrons

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$\text{Solutions: } x = \pm 0.618, \pm 1.618$$

$$E_1 = \alpha + 1.618\beta, \quad E_2 = \alpha + 0.618\beta$$

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta$$

Delocalization Energy

$$E_{\text{deloc}} = E_\pi(\text{conjugated}) - E_\pi(\text{isolated double bonds})$$

$$\text{For butadiene: } 4\alpha + 4.472\beta - 2(2\alpha + 2\beta) = 0.472\beta$$

$$\text{Since } \beta < 0: \text{ delocalization stabilization} = 0.472|\beta| \approx 0.47 \times 75 = 35 \text{ kJ/mol}$$

Benzene — 6 π electrons

$$\text{Hückel energies: } E_k = \alpha + 2\beta \cos(2\pi k/6), \quad k = 0, \pm 1, \pm 2, 3$$

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

$$\text{Delocalization energy} = 8\beta - 6\beta = 2|\beta| \approx 150 \text{ kJ/mol}$$

This large stabilization is **aromaticity**.

4. Hückel Rules

Hückel's Rule for Aromaticity

A cyclic, planar, fully conjugated molecule is **aromatic** if it has $4n + 2 \pi$ electrons ($n = 0, 1, 2, \dots$):

$$4n + 2 = 2, 6, 10, 14, \dots$$

Anti-aromatic: $4n \pi$ electrons \rightarrow destabilized relative to open-chain analog

Species	π electrons	Aromatic?
Benzene	6	Yes
Cyclopentadienyl anion	6	Yes
Cycloheptatrienyl cation	6	Yes
Cyclobutadiene	4	Anti-aromatic
Cyclooctatetraene	8	Non-planar (avoids anti-aromaticity)

[!NOTE] **Concept Check 37.2** Applying Hückel's Rule ($4n + 2$), identify why the cycloheptatrienyl cation (7-membered ring, 6 π electrons) is considered aromatic, while the neutral cycloheptatriene molecule is not.

5. Symmetry Classification of MOs

Using group theory, we can directly determine the MO symmetry species rather than solving the secular determinant:

For benzene (D_{6h}):

- The 6 π MOs transform as: $a_{2u} + e_{1g} + e_{2u} + b_{2g}$
- Occupied: $a_{2u}^2 e_{1g}^4 \rightarrow$ ground state symmetry = $^1A_{1g}$

Key Equations Summary

Equation	Expression
Hückel approximation	$H_{ii} = \alpha, H_{ij} = \beta$ (bonded), $S_{ij} = \delta_{ij}$
Secular determinant	$\det(H - ES) = 0$
Cyclic energies	$E_k = \alpha + 2\beta \cos(2\pi k/N)$
Delocalization energy	$E_\pi(\text{conj}) - E_\pi(\text{isolated})$
Hückel's rule	Aromatic if $4n + 2$ π electrons

Recent Literature Spotlight

"Machine Learning for Electronically Excited States of Molecules" J. Westermayr, P. Marquetand, *Journal of Chemical Information and Modeling*, **2020**, 60, 3661–3673. [DOI](#)

This perspectives article reviews how machine learning can predict molecular orbital energies, electronic excitation energies, and spectral properties. The ML models are trained on quantum chemical data from Hückel-level through DFT calculations, demonstrating how the simple MO energy-level framework taught in this lecture — HOMO, LUMO, and π -orbital diagrams — provides the foundation for modern data-driven electronic structure predictions.

Practice Problems

- 1. Allyl system.** Solve the Hückel secular determinant for the allyl radical (C_3H_5 , 3 π electrons). Find the three MO energies and calculate E_π .
- 2. Naphthalene.** Naphthalene (C_{10}H_8) has 10 π electrons. Without solving the 10×10 determinant, use Hückel's rule to predict whether it is aromatic.
- 3. H_2O MOs.** Using the C_{2v} character table, verify that the SALC $\phi_1 + \phi_2$ belongs to A_1 and $\phi_1 - \phi_2$ belongs to B_2 .

Next lecture: *Electronic Transitions & the Franck-Condon Principle*