

# Lecture 37 — MOs for Polyatomic Molecules & Hückel Theory

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

## Learning Objectives

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- Construct MOs for polyatomic molecules using symmetry-adapted linear combinations (SALCs)
  - Apply the Hückel approximation to conjugated  $\pi$  systems
  - Solve the Hückel secular determinant for small molecules
  - Calculate  $\pi$ -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

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### 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: $\text{H}_2\text{O}$ ( $C_{2v}$ )

O contributes:  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$  H<sub>1</sub> and H<sub>2</sub> 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  $\sigma$  and  $\pi$  electrons and focus only on the  $\pi$  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

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#### Ethylene ( $C_2H_4$ ) — 2 $\pi$ electrons

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

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

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

#### Butadiene ( $C_4H_6$ ) — 4 $\pi$ electrons

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

Solutions:  $x = \pm 0.618, \pm 1.618$

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

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

#### Delocalization Energy

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

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

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

#### Benzene — 6 $\pi$ electrons

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

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

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

This large stabilization is **aromaticity**.

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### 4. Hückel Rules

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## 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	$\pi$ 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  $\pi$  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  $\pi$  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 $4n + 2 \pi$ 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  $\pi$ -orbital diagrams — provides the foundation for modern data-driven electronic structure predictions.

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## Practice Problems

1. **Allyl system.** Solve the Hückel secular determinant for the allyl radical ( $C_3H_5$ ,  $3 \pi$  electrons). Find the three MO energies and calculate  $E_\pi$ .
2. **Naphthalene.** Naphthalene ( $C_{10}H_8$ ) has  $10 \pi$  electrons. Without solving the  $10 \times 10$  determinant, use Hückel's rule to predict whether it is aromatic.
3. **H<sub>2</sub>O 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  $B_2$ .

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Next lecture: Electronic Transitions & the Franck-Condon Principle