Lecture 12: Analytically Solvable HMO Problems

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Chem 150/250 Fall 2023

11/01/2023

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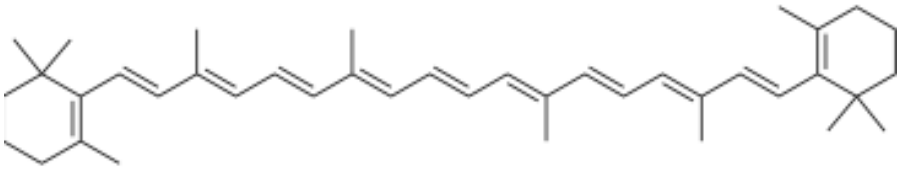
Linear Polyenes and Polymethines

- C_nH_{n+2}
- Example: β-carotene



- Topological matrix:

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

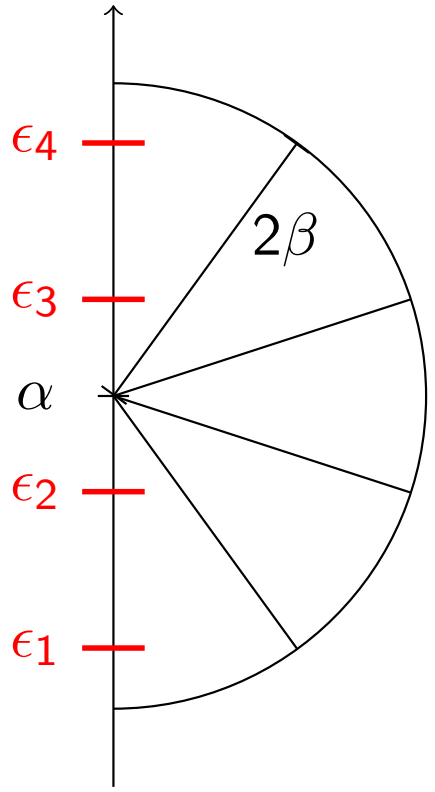
- $\mathbf{M}$ is tridiagonal and Toeplitz. General solution for any n?

HMO Energy Eigenvalues

- HMO eigenvalue spectrum:

$$\epsilon_j = \alpha + 2\beta \cos \frac{j\pi}{n+1}, \quad j = 1, \ldots, n$$

- Graphical construction: Frost semicircle, e.g. $n = 4$:

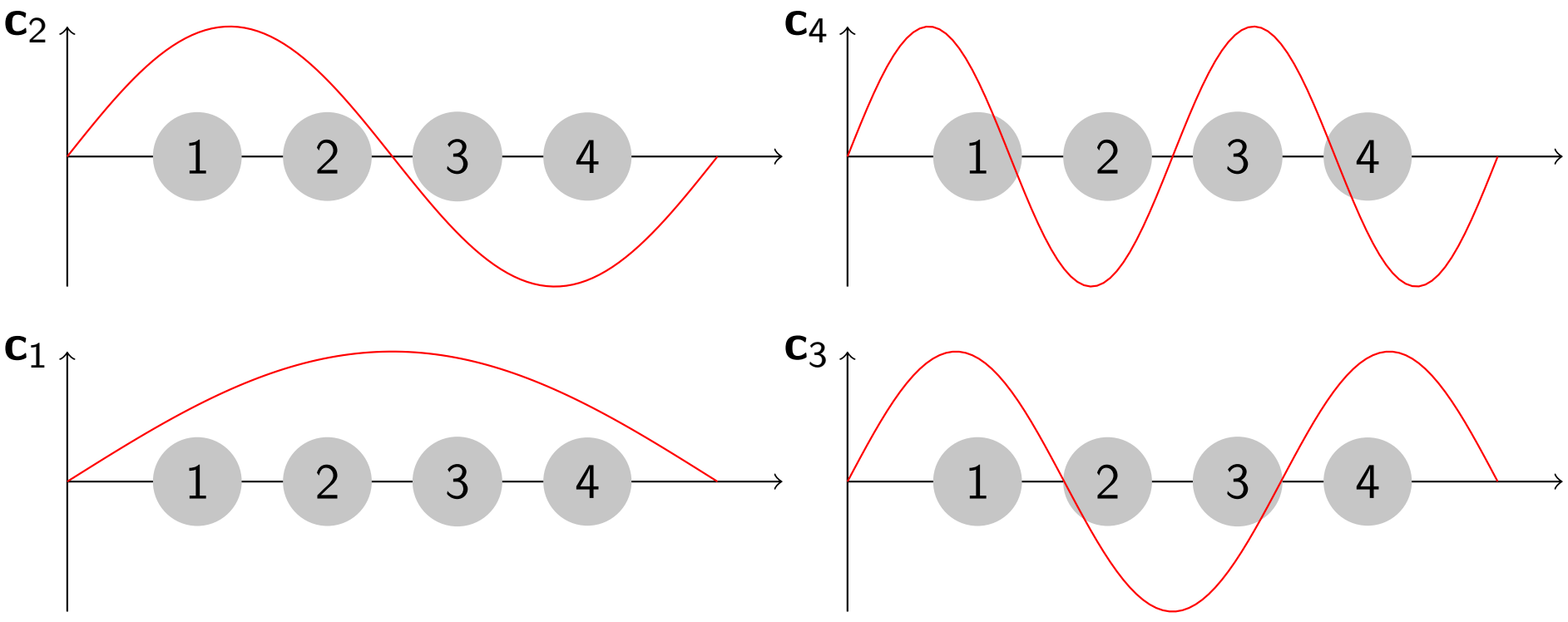


HMO Eigenvectors

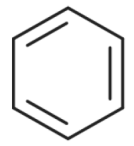
- MO coefficients:

$$c_{\mu j} = \sqrt{\frac{2}{n+1}} \sin \frac{j\mu\pi}{n+1}$$

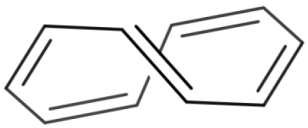
- Graphical construction: Standing waves, e.g., $n = 4$:



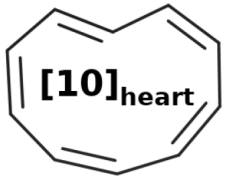
Hückel Annulenes

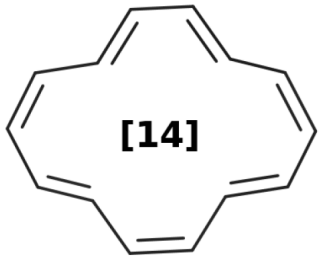


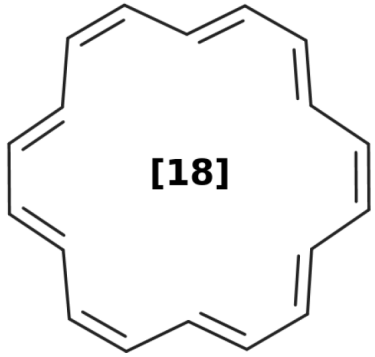
benzene



$[10]_{twist}$







- C_nH_n, cyclic
- Topological matrix of Hückel annulenes:

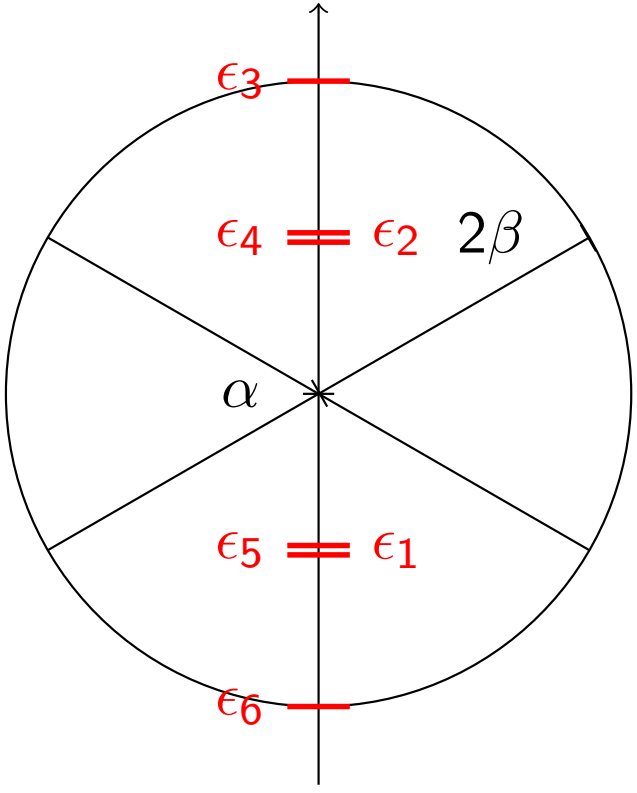
$$\mathbf{M} = \begin{pmatrix} 0 & 1 & 0 & \dots & 1 \\ 1 & 0 & 0 & \dots & 0 \\ & & \ddots & & \\ 0 & 0 & \dots & 0 & 1 \\ 1 & 0 & \dots & 1 & 0 \end{pmatrix}$$

- Not tridiagonal, but still Toeplitz
- HMO energies (not ordered, *not* including degeneracy):

$$\epsilon_j = \alpha + 2\beta \cos \frac{2\pi j}{n}, \quad j = 1, \dots, n$$

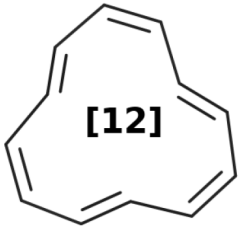
Frost Circle for Hückel Annulenes

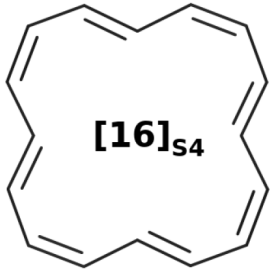
- Example: $n = 6$

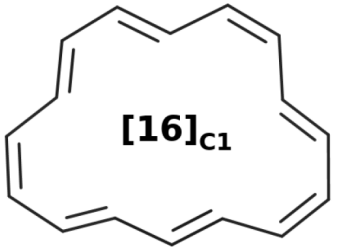


- Maximum resonance energy: Closed-shell ground state with $2, 6, 10, \ldots = 4n + 2\pi$ electrons (neutral case)
- Hückel aromaticity

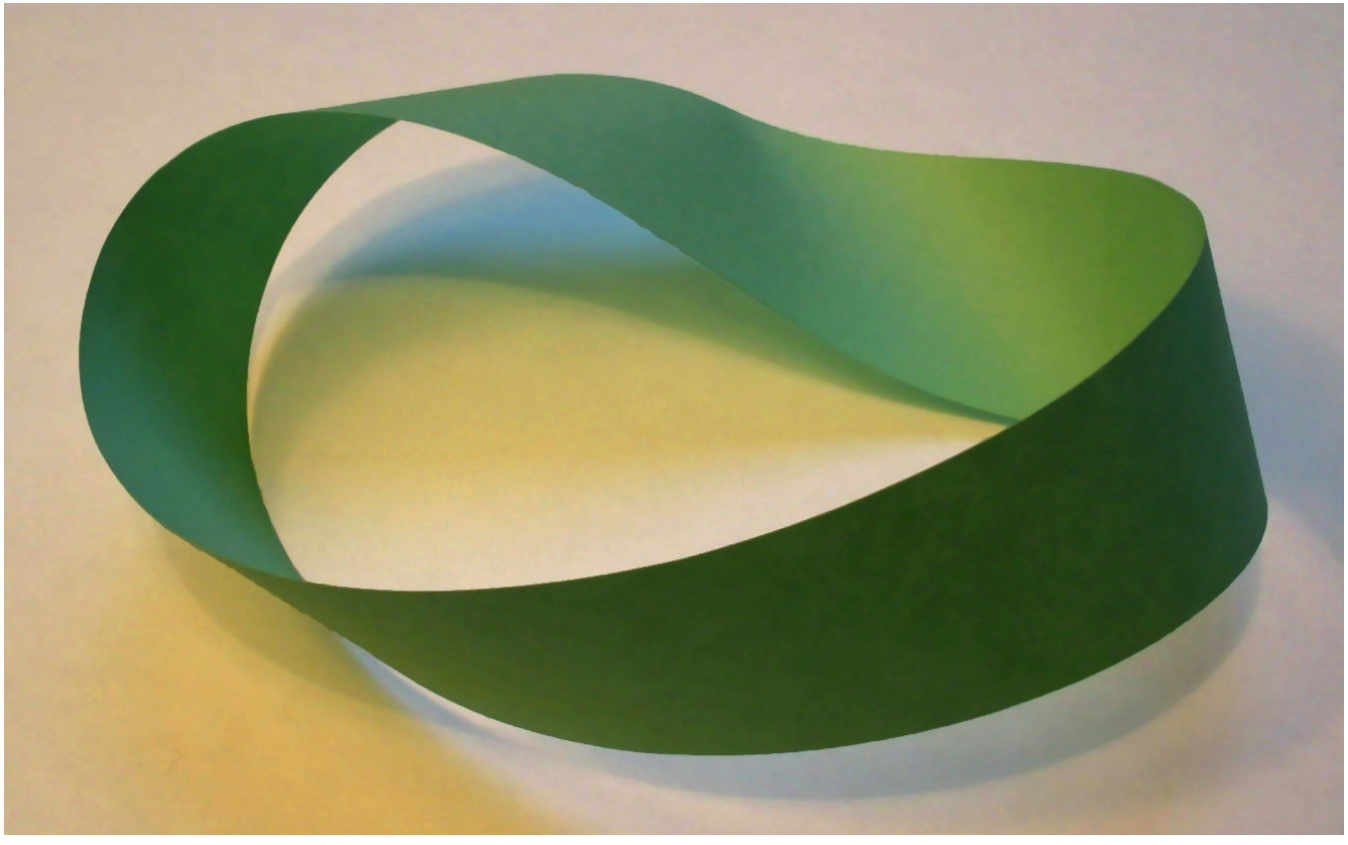
Möbius Annulenes







- C_nH_n, cyclic
- At least one node in all HMOs:



Wikipedia

Möbius Annulenes

- Topological matrix of Möbius annulenes:

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

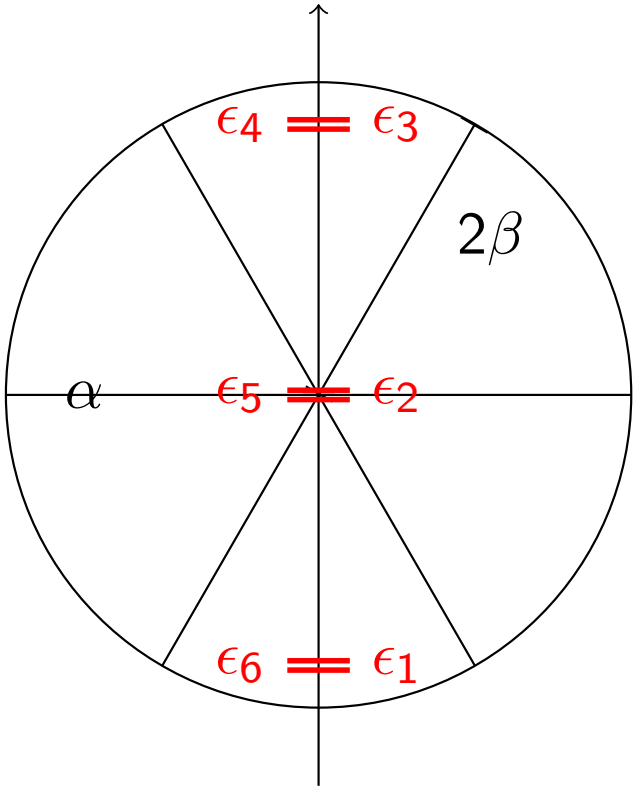
- Not tridiagonal, but still Toeplitz
- HMO energies (not ordered):

$$\epsilon_j = \alpha + 2\beta \cos \frac{(2j-1)\pi}{n}, \quad j = 1, \dots, n$$

- All eigenvalues doubly degenerate for even n

Frost Circle for Möbius Annulenes

- Example: $n = 6$



- Maximum resonance energy: Closed-shell ground state with $4, 8, 12, \ldots = 4n\pi$ electrons (neutral case)
- Möbius aromaticity[1]

[1] H. Fliegl et al., *J. Phys. Chem. A* **2009**, *113*, 8668–8676.