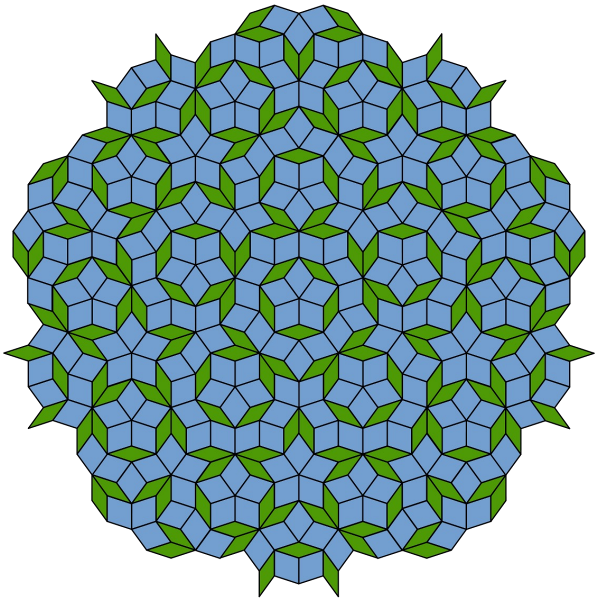
MSE 423 Fall 2025 – Week 8

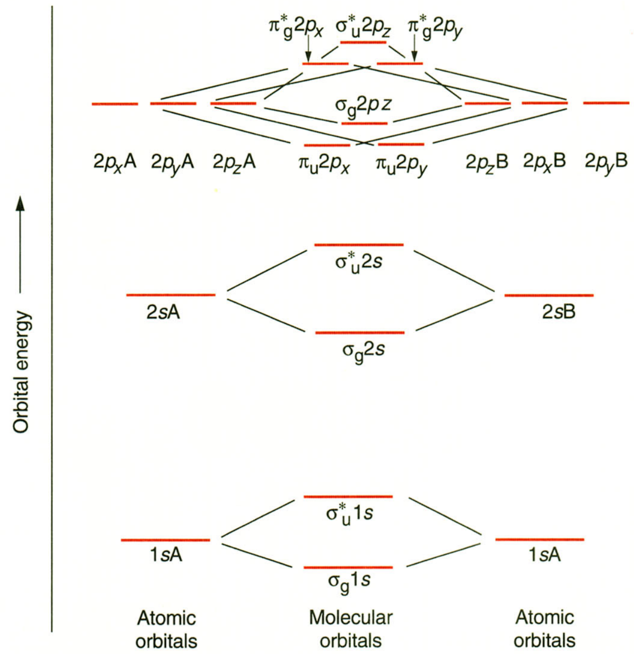
Symmetry



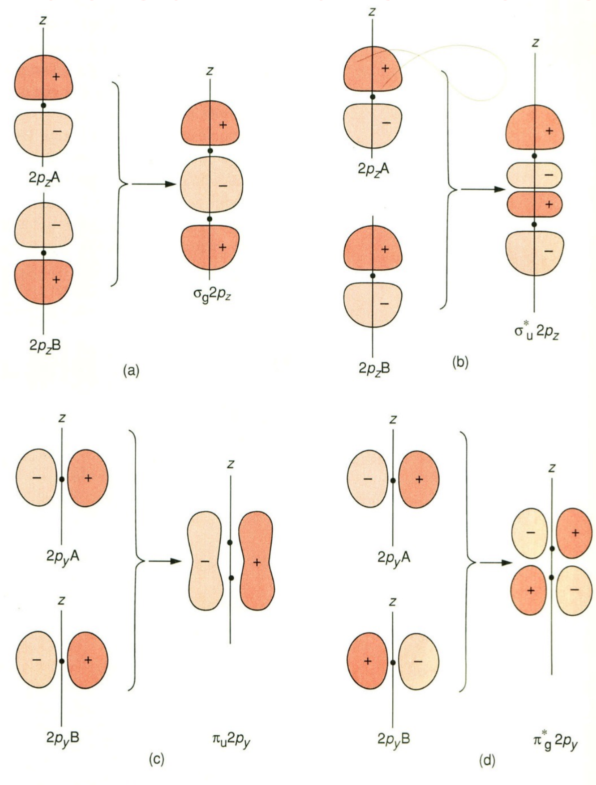
Last week

- Date/location of the exam
- Auf-bau and spin oribtals
- XPS and composition analysis
- Hydrogen molecular ion H_2^+
- LCAO: linear combination of atomic (HF is good) orbitals
- Bonding and antibonding solutions for H_2^+
- Potential energy surfaces in the bonding and antibonding state
- More complex molecules (and methane/ammonia/water)
- sp, sp^2 and sp^3 hybridization
- Bond length and bond energies

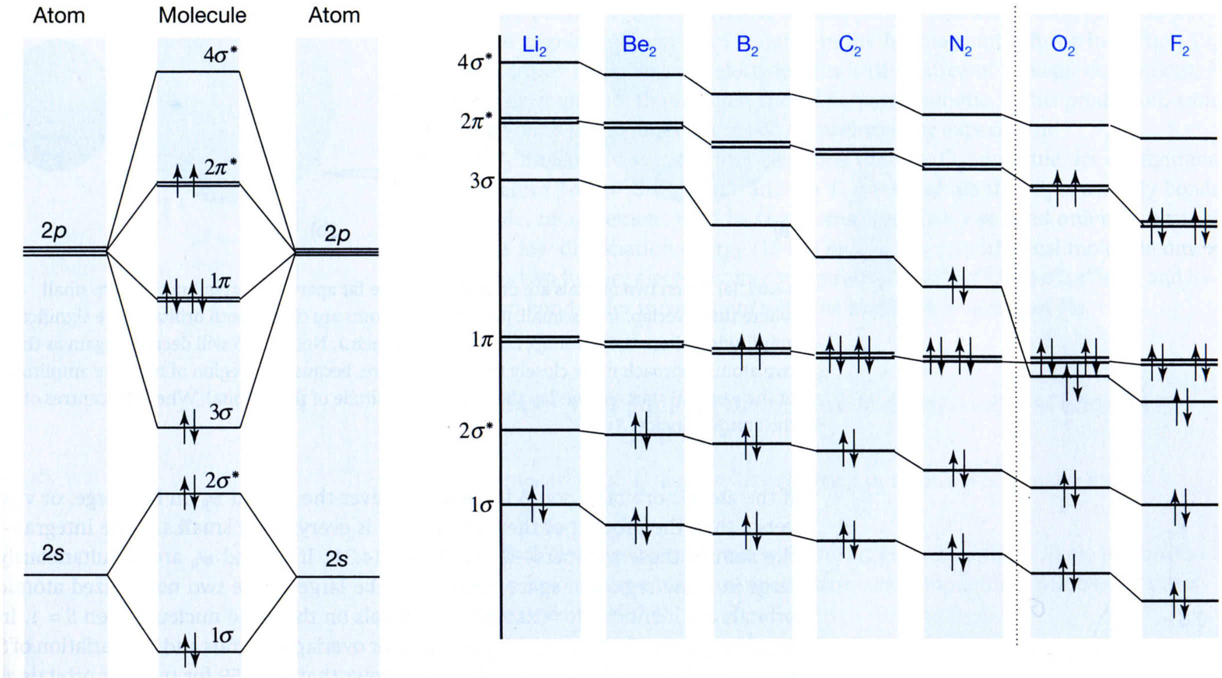
Homonuclear Diatomic Levels (I)



Homonuclear Diatomic Levels (II)



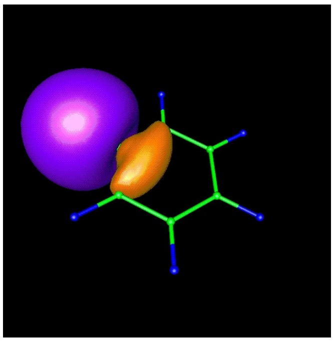
Homonuclear Diatomic Levels (III)

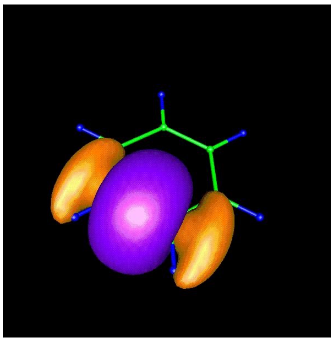


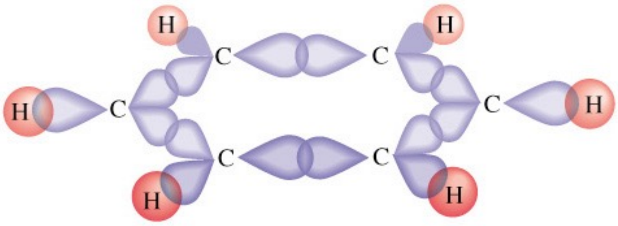
Even simpler than LCAO: Empirical tight binding and Hückel approach

- TB: The matrix elements of the Hamiltonian are "universal empirical parameters"
- Hückel: Planar / quasi-planar systems with delocalized π bonding: two parameters
  - α: matrix element between same orbital
  - β: matrix element between neighboring orbitals
  - Hamiltonian between further neighbors is 0

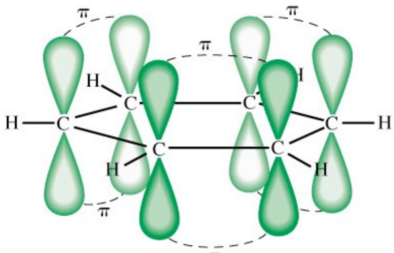
Example: Benzene (C_6H_6)







(a) σ bond framework

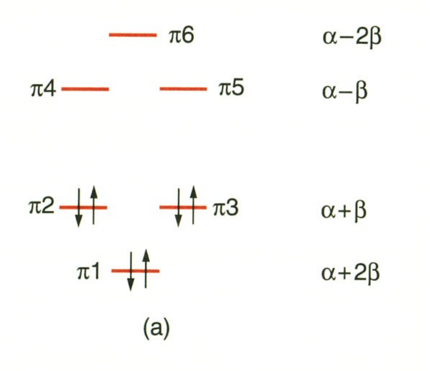


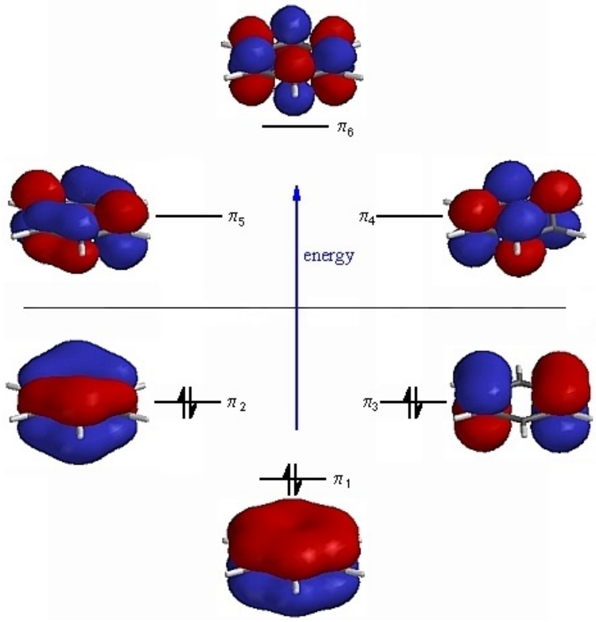
(b) π bonding

Benzene – energy levels

$$\det\begin{pmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{pmatrix} = 0$$

Benzene – molecular orbitals

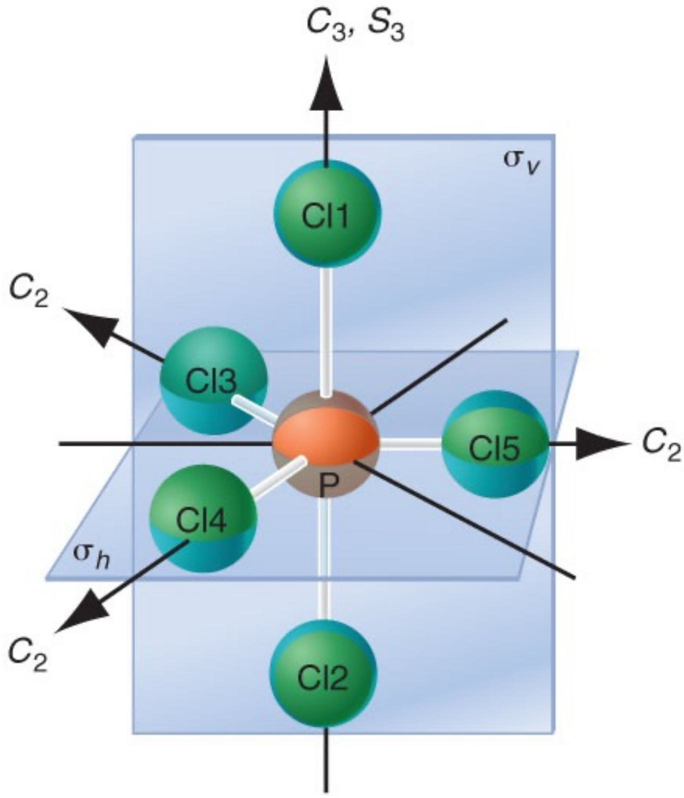




http://www.chem.ucalgary.ca/SHMO/

Symmetry

- Symmetry operations: actions that transform an object into a new but undistinguishable configuration
- Symmetry elements: geometric entities (axes, planes, points…) around which we carry out the symmetry operations



(b)

TABLE 17.1

Symmetry Elements and Their Corresponding Operations

Symmetry Elements		Symmetry Operations	
E	Identity	E	leave molecule unchanged
C_n	n-Fold rotation axis	$\hat{C}_n, \hat{C}_n^2, \ldots, \hat{C}_n^n$	rotate about axis by 360°/n 1, 2, … , n times (indicated by superscript)
σ	Mirror plane	$\hat{\sigma}$	reflect through the mirror plane
i	Inversion center	$\hat{i}$	$(x, y, z) \rightarrow (-x, -y, -z)$
S_n	n-Fold rotation-reflection axis	$\hat{S}_n$	rotate about axis by 360°/n, and reflect through a plane perpendicular to the axis.

Group Theory

A group G is a finite or infinite set of elements A, B, C, D…together with an operation "☼" that satisfy the four properties of:

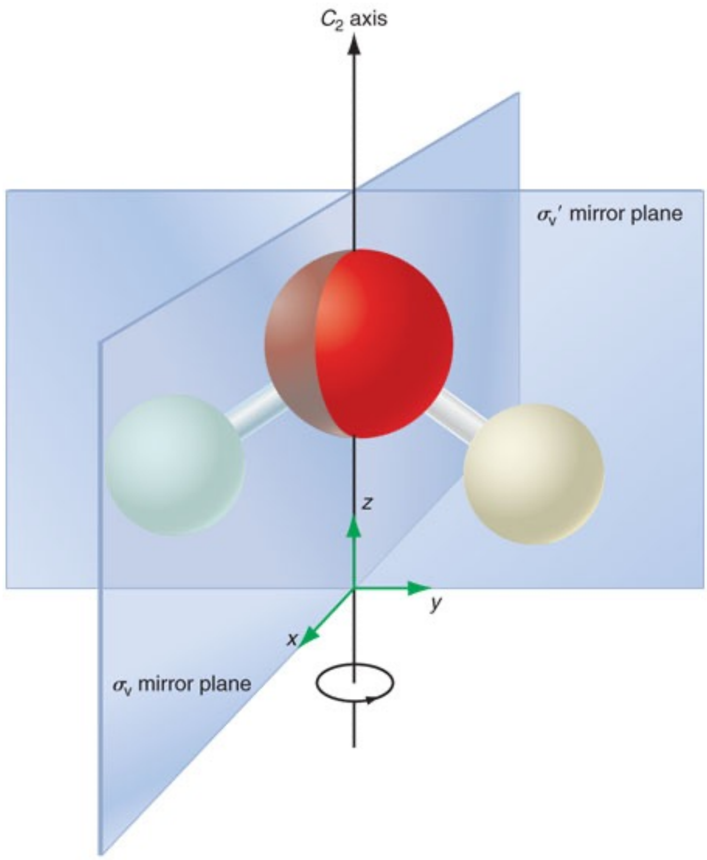
1. Closure: If A and B are two elements in G, then A☼B is also in G.
2. Associativity: For all elements in G, (A☼B) ☼C==A☼ (B☼C).
3. Identity: There is an identity element I such that I☼A=A☼I=A for every element A in G.
4. Inverse: There is an inverse or reciprocal of each element. Therefore, the set must contain an element B=inv(A) such that A☼inv(A)=inv(A) ☼A=I for each element of G.

Examples

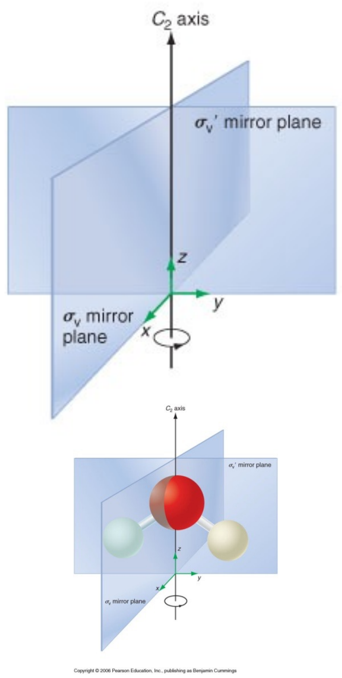
- Integer numbers, and addition
- Integer numbers, and multiplication
- Real numbers, and multiplication
- Rotations around an axis by 360/n

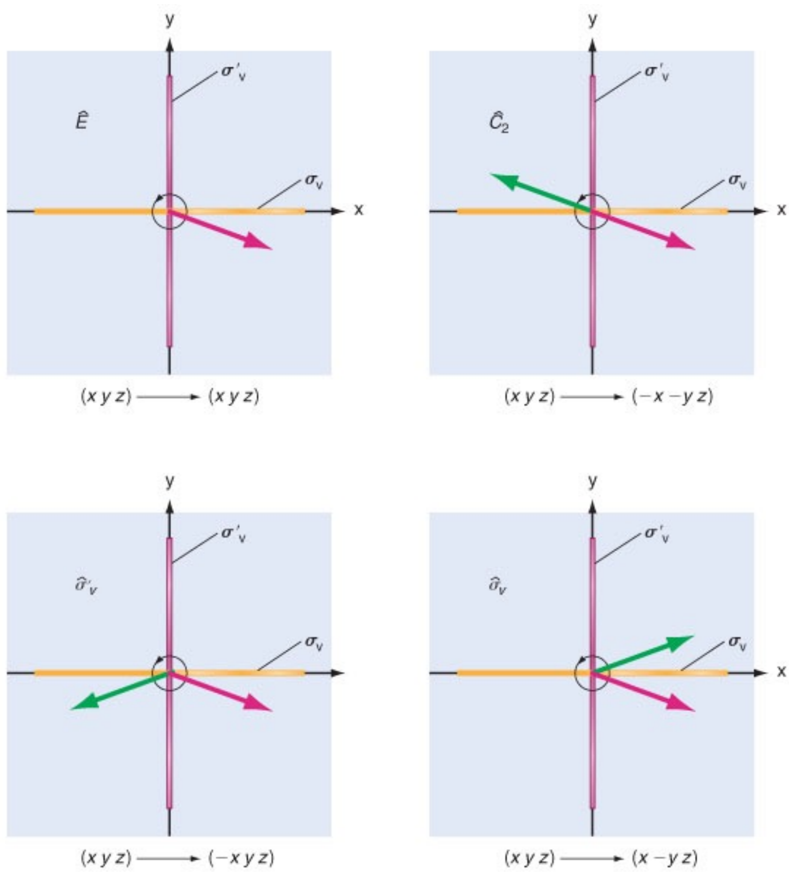
MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

C_{2v}

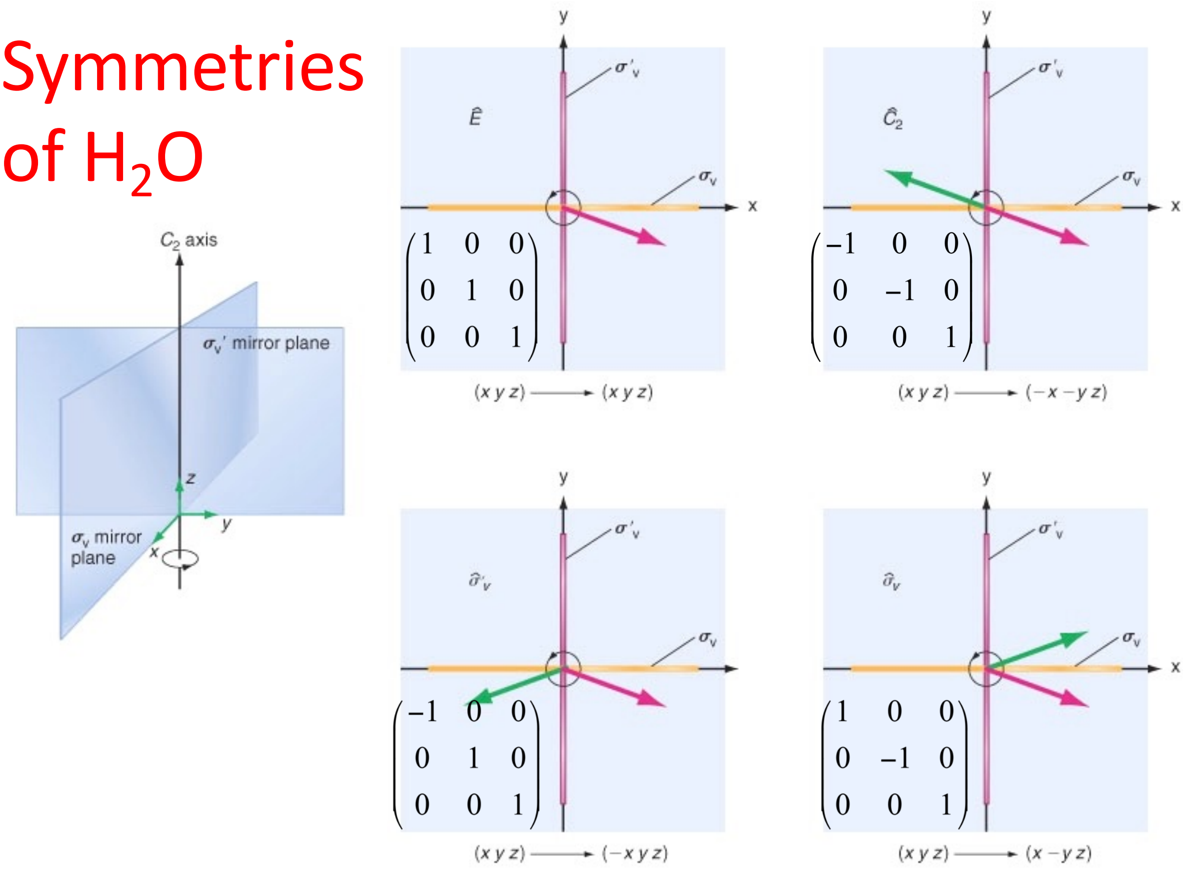


Symmetries of H_2O





Symmetries of H_2O



The 4 symmetry operations of H_2O form a group (called C_{2v})

1. Closure: A¤B is also in G.
- Associativity: (A¤B) ¤C=A¤ (B¤C)
- Identity: I¤A=A¤I
- Inverse: A¤inv(A)=inv(A) ¤A=I

Second Operation	First Operation $\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

Symmetry and Hamiltonians

- A system has a symmetry R if R has an inverse and commutes with the system Hamiltonian H:

$$R\mathcal{H} = \mathcal{H}R \qquad \text{OR} \qquad R\mathcal{H}R^{-1} = \mathcal{H}$$

- Suppose ψ is an eigenstate of the Hamiltonian. Then $R\psi$ is also an eigenstate associated with the same eigenvalue:

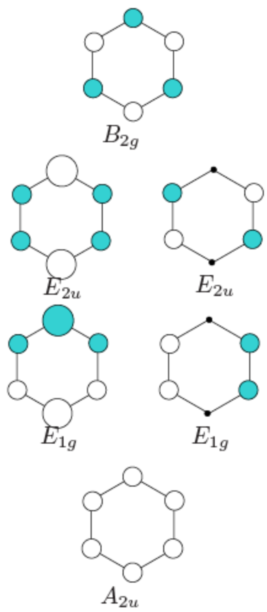
$$\mathcal{H}\psi = E\psi$$

$$\mathcal{H}(R\psi) = \mathcal{H}R\psi = R\mathcal{H}\psi = R(E\psi) = E(R\psi)$$

- The symmetry operators identify groups of degenerate eigenstates of H

Common eigenstates in benzene of Hamiltonian and C_6

$$\begin{aligned}
\phi_{A_{2u}} &= \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \\
\phi_{B_{2g}} &= \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) \\
\phi^{(1)}_{E_{2u}} &= \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) \\
\phi^{(2)}_{E_{2u}} &= \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6) \\
\phi^{(1)}_{E_{1g}} &= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) \\
\phi^{(2)}_{E_{1g}} &= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)
\end{aligned}$$



More general cases: rings and linear chains of arbitrary length

As before, we use LCAO:

$$\psi = \sum_r c_r \phi_r \qquad \epsilon = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_{rs} c_r^* c_s \langle \phi_r | H | \phi_s \rangle}{\sum_{rs} c_r^* c_s \langle \phi_r | \phi_s \rangle}$$

$$\frac{\partial \epsilon}{\partial c_r} = 0 \implies \sum_r (H_{sr} - \epsilon S_{sr}) c_r = 0$$

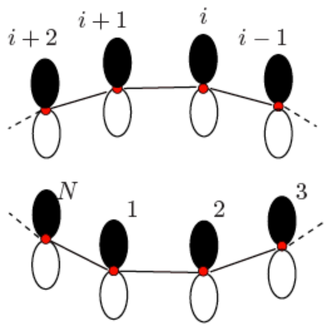
Only on-site and nearest-neighbor terms of the Hamiltonian are non-zero. rth Huckel equation:

$$(\alpha - \epsilon_n) c_r^{(n)} + \beta (c_{r+1}^{(n)} + c_{r-1}^{(n)}) = 0$$

Rings

Boundary condition (cycle of length N):

$$c_r^{(n)} = c_{N+r}^{(n)}$$



Trial wavefunction:

$$c_r^{(n)} = e^{i2\pi nr/N}$$

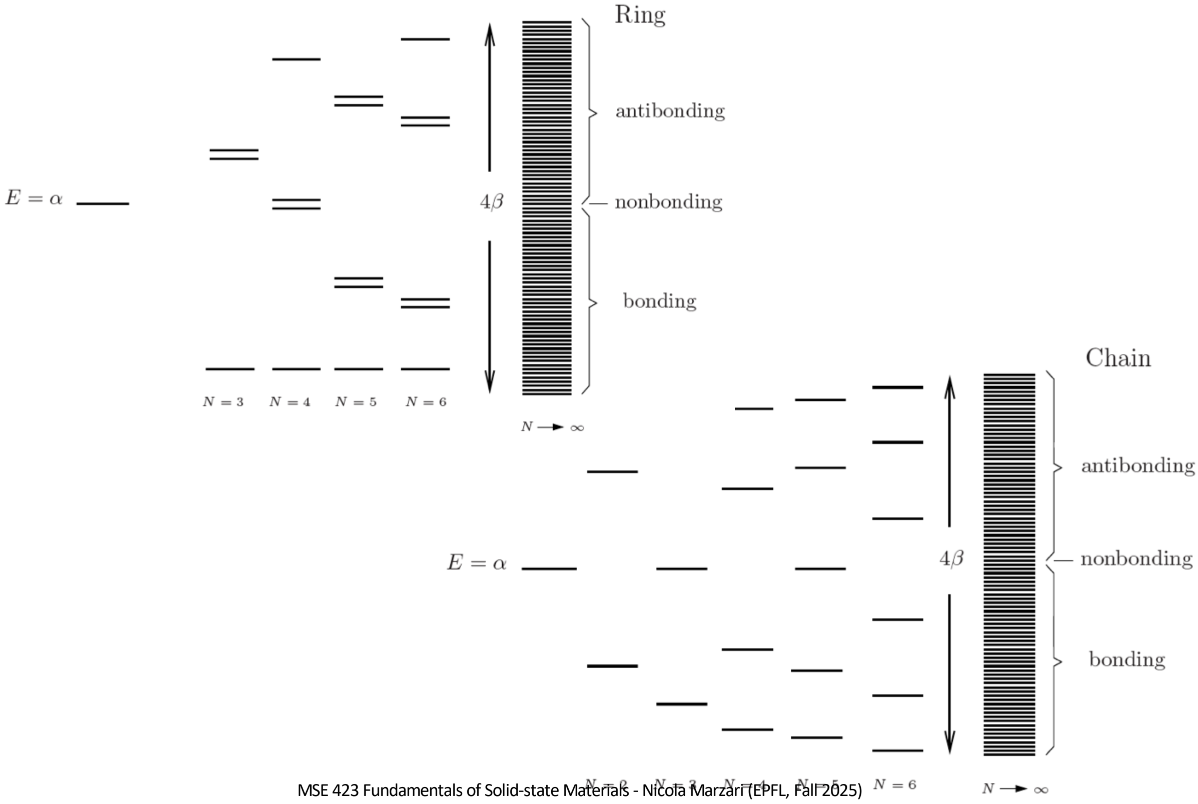
Huckel equation:

$$(\alpha - \epsilon_n) e^{i2\pi nr/N} + \beta (e^{i2\pi n(r+1)/N} + e^{i2\pi n(r-1)/N}) = 0$$

Solution (energy):

$$\epsilon_n = \alpha + 2\beta \cos(2\pi n/N)$$

Spectra



Ring
antibonding
nonbonding
bonding
$E = \alpha$
4β
$N = 3$
$N = 4$
$N = 5$
$N = 6$
$N \rightarrow \infty$
Chain
antibonding
nonbonding
bonding
$E = \alpha$
4β
$N = 6$
$N \rightarrow \infty$