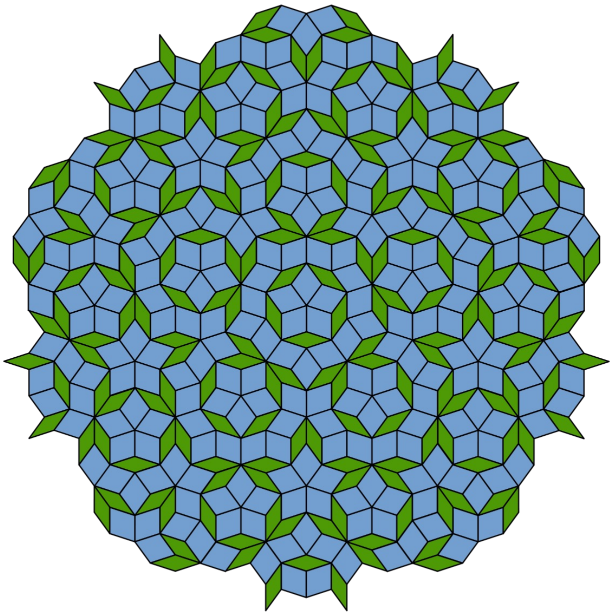
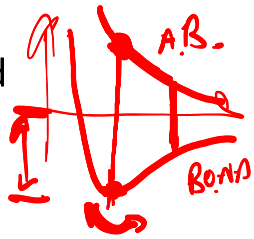
MSE 423 Fall 2025 – Week 8

Symmetry

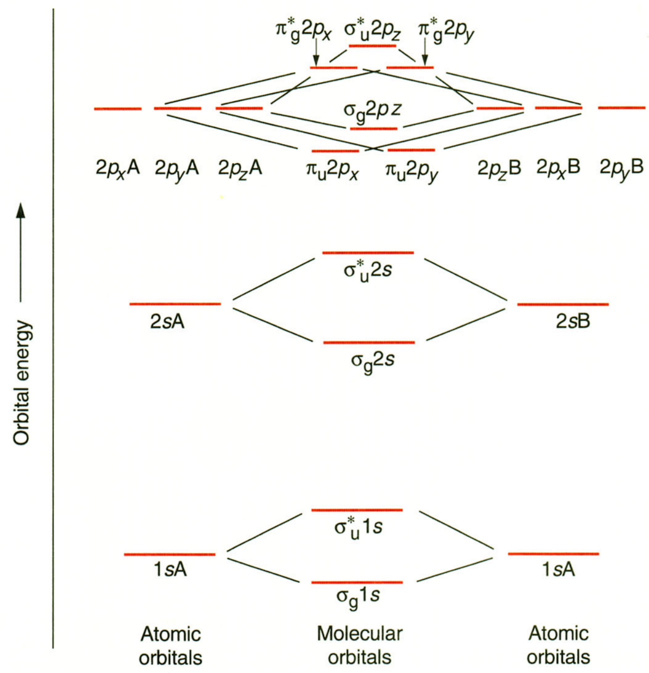


Last week

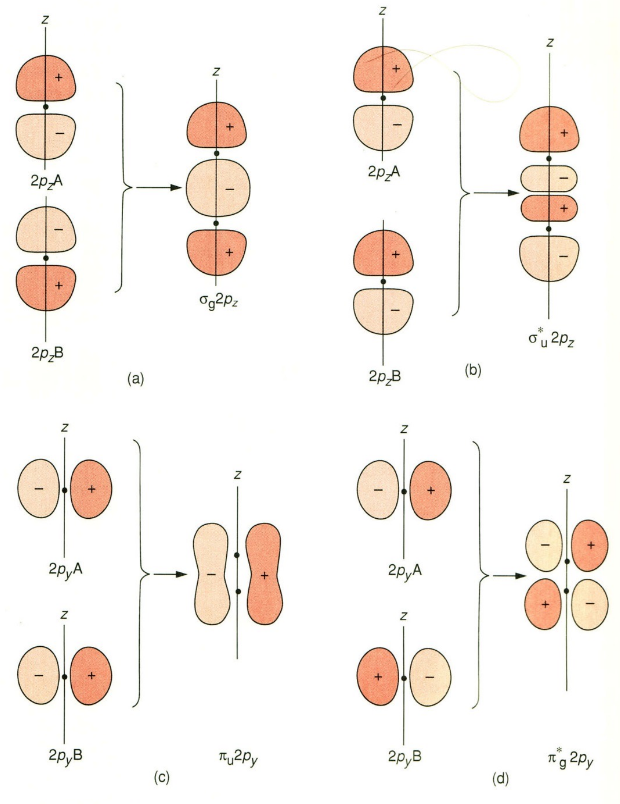
- Date/location of the exam
- Auf-bau and spin orbitals
- XPS and composition analysis
- Hydrogen molecular ion H_2^+
- LCAO: linear combination of atomic (HF is good) orbitals
- Bonding and antibonding solutions for H_2^+
- Potential energy surfaces in the bonding and antibonding state
- More complex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



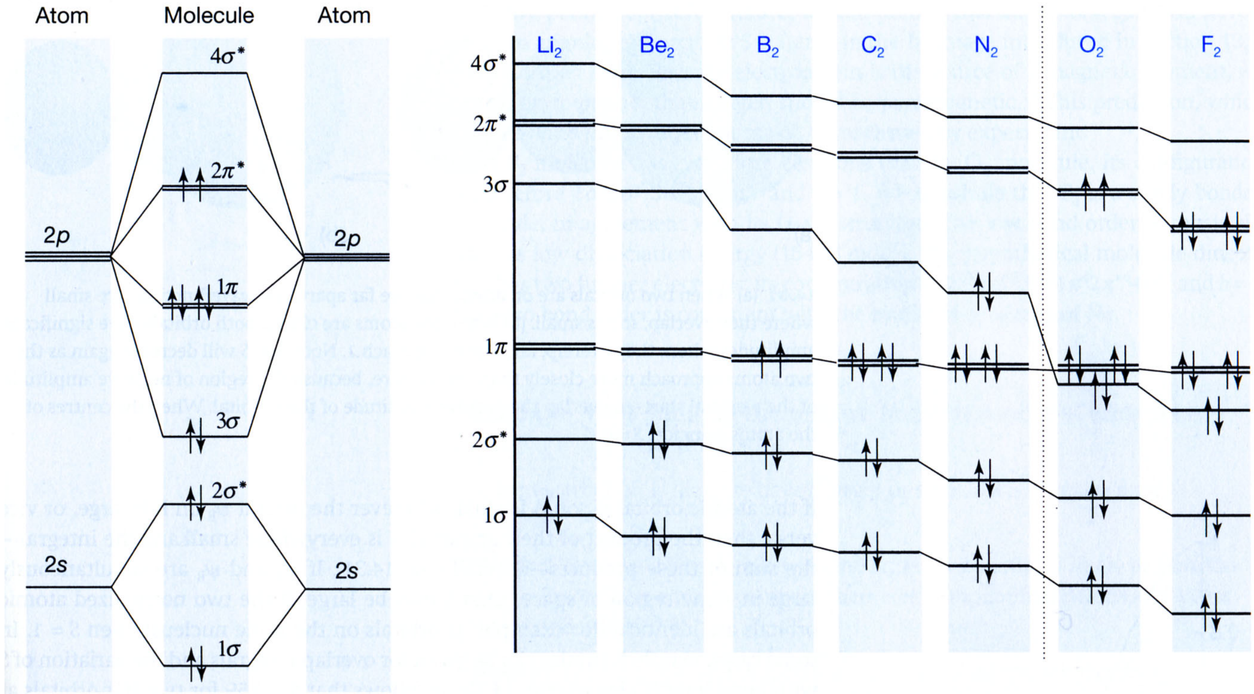
Homonuclear Diatomic Levels (I)



Homonuclear Diatomic Levels (II)



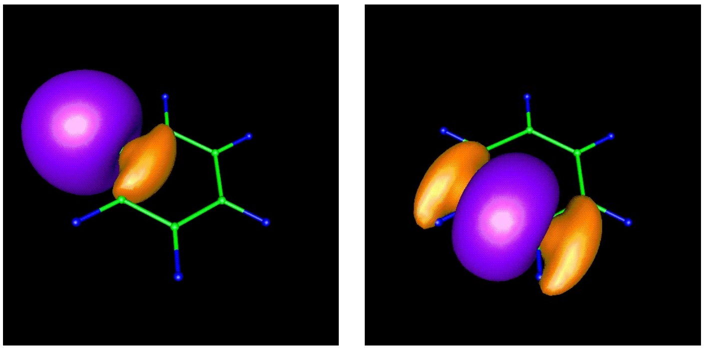
Homonuclear Diatomic Levels (III)

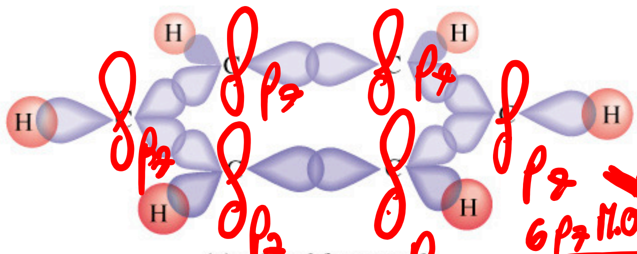


Even simpler than LCAO: Empirical tight binding and Hückel approach

- 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)





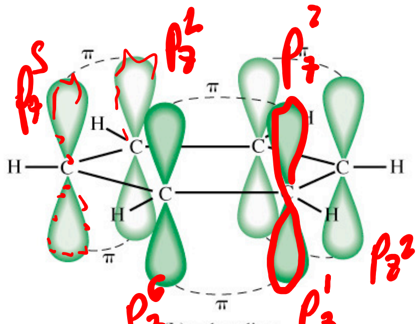
(a) σ bond framework

$(6 \times 4\ C + 6 \times 1\ H)$

$30\ e^-$

24 M.O. ⇒ 12 BONDING, 12 ANTIBONDING

6 p_z M.O.



(b) π bonding

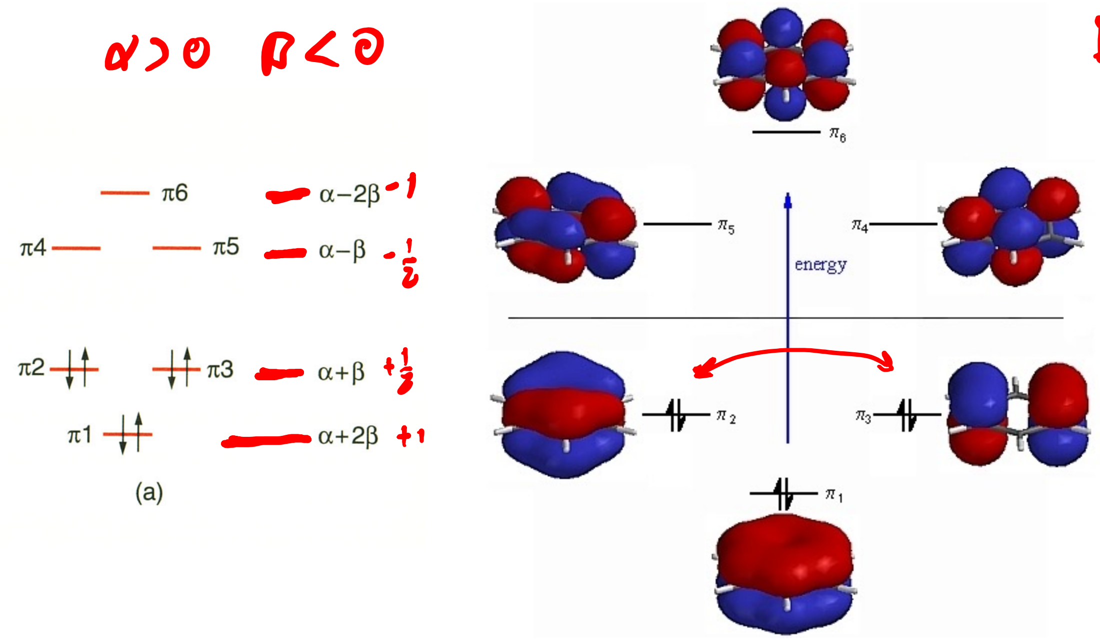
Benzene energy levels

$$\hat{H}_{HUCKEL} = \begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ 0 & \beta & \alpha & \beta & & \\ 0 & 0 & \beta & \alpha & \beta & \\ 0 & 0 & & \beta & \alpha & \beta \\ \beta & 0 & & & \beta & \alpha \end{pmatrix}$$

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

Benzene – molecular orbitals

$\alpha > 0 \quad \beta < 0$



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

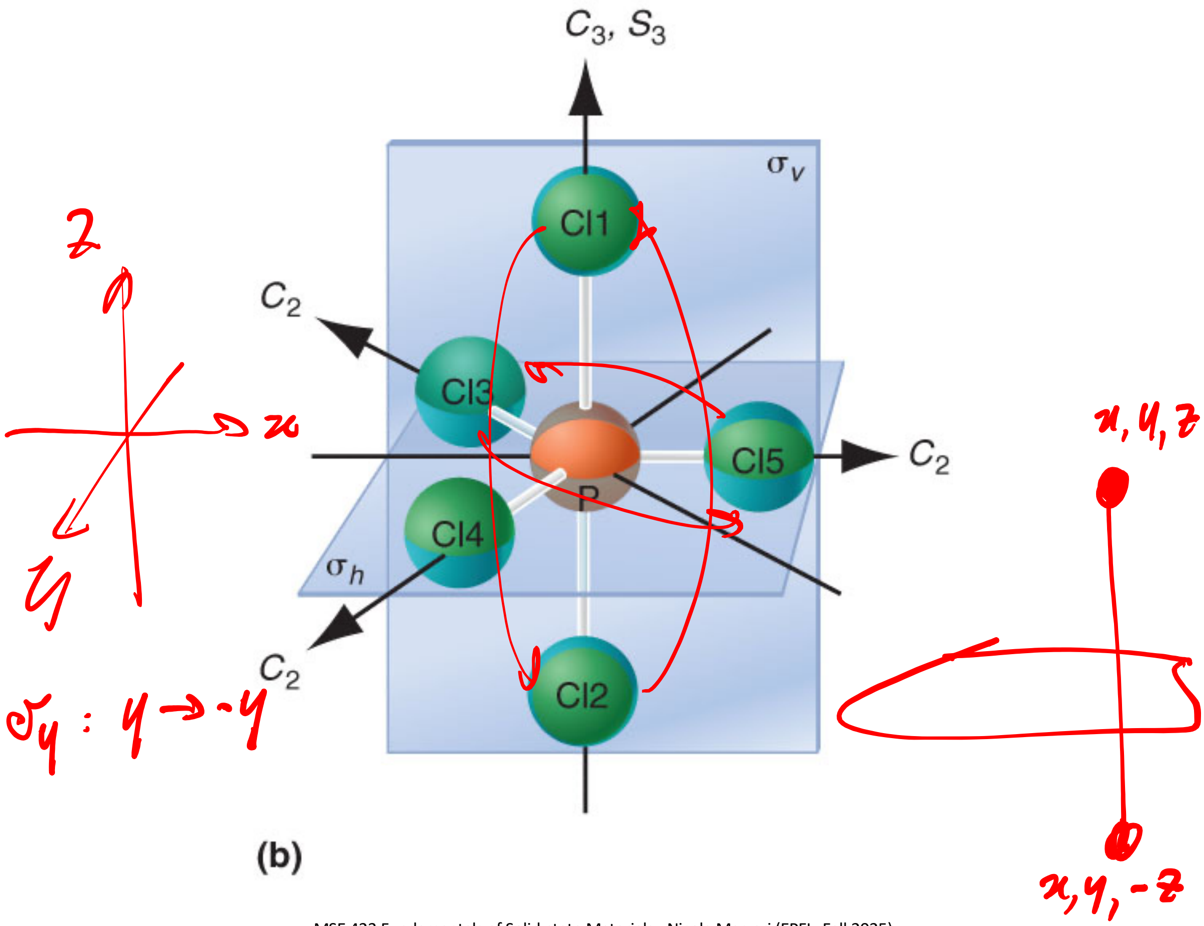


TABLE 17.1

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.

$(3+4)+27=$
$=3+(4+27)$

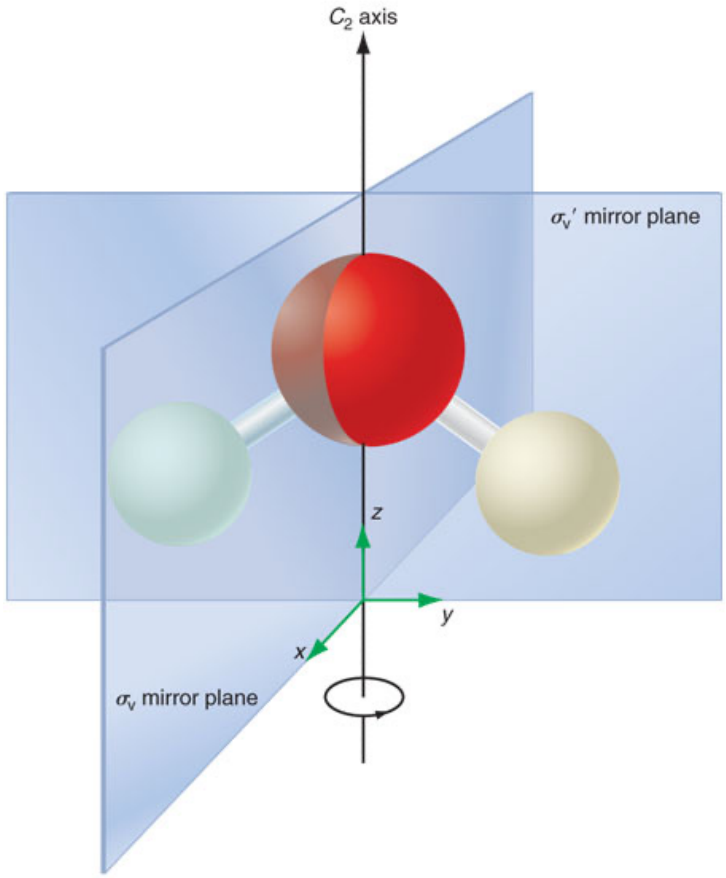
Examples

$-3\ -2\ -1,\ 0,\ 1,\ -$

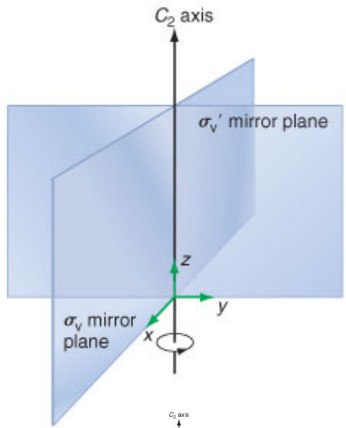
☼

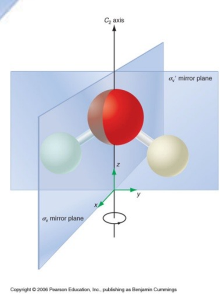
- Integer numbers, and addition
- ~~Integer numbers, and multiplication~~
- Real numbers, and multiplication ,
- Rotations around an axis by 360/n ,

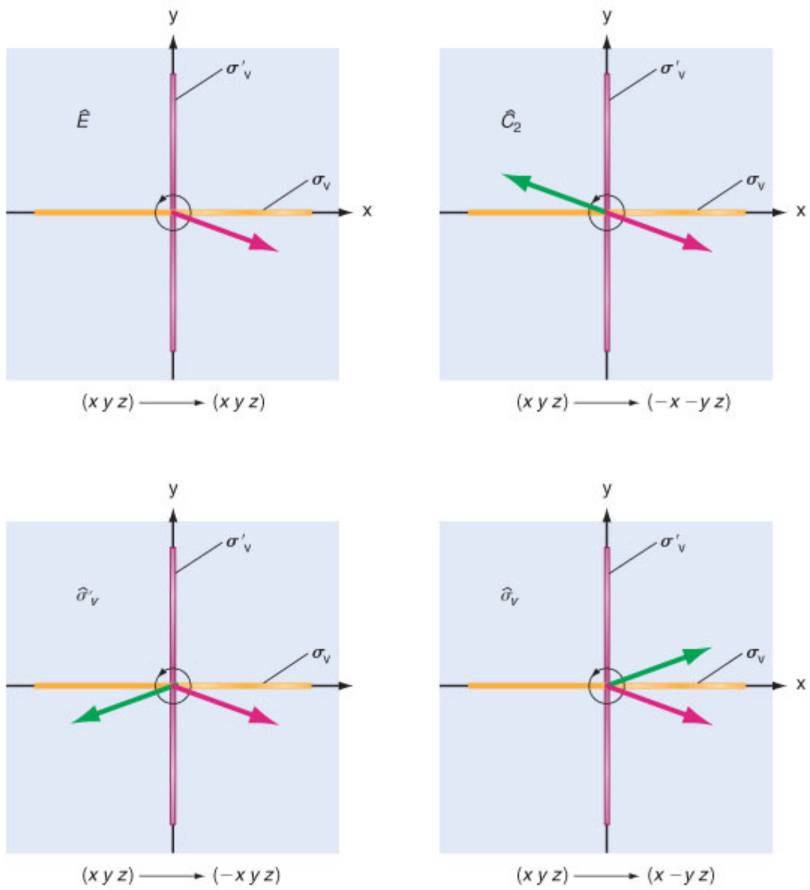
C_{2v}



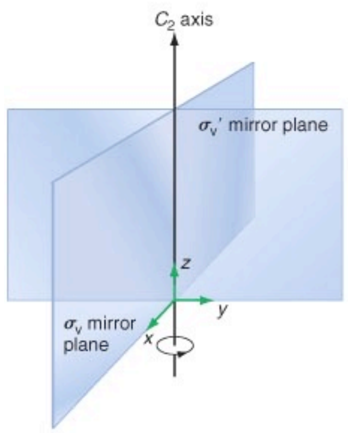
Symmetries of H_2O

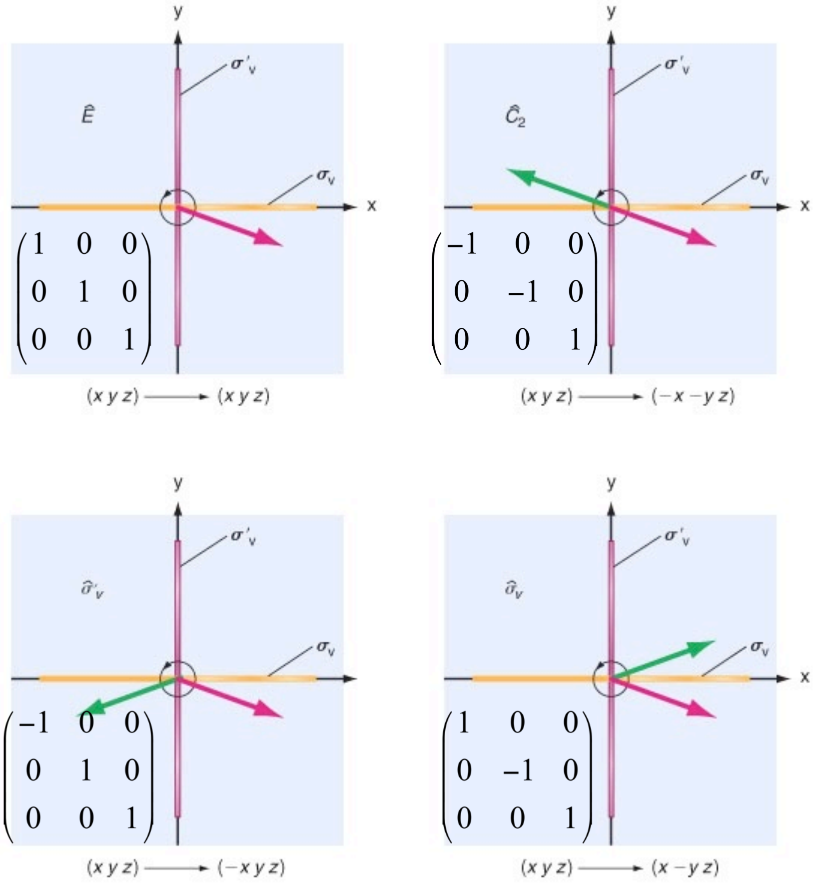






Symmetries of H_2O





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

	First Operation			
Second 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

$RR^{-1} = R^{-1}R = 1$

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

$$R\mathcal{H} = \mathcal{H}R \quad \cancel{\text{OR}} \Rightarrow \quad R\mathcal{H}R^{-1} = \mathcal{H}$$

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

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

$\mathcal{H}$ IS AN EIGENSTATES

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

- The symmetry operators identify groups of degenerate eigenstates of H

Common eigenstates in benzene of Hamiltonian and C_6

$$\phi_{A_{2u}} = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\phi_{B_{2g}} = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

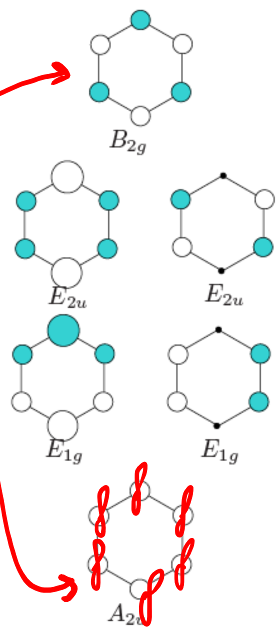
2 -1 -1 2 -1 -1

$$\phi^{(1)}_{E_{2u}} = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)$$

$$\phi^{(2)}_{E_{2u}} = \frac{1}{2}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

$$\phi^{(1)}_{E_{1g}} = \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\phi^{(2)}_{E_{1g}} = \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$



More general cases: rings and linear chains of arbitrary length

$C_n H_n$ $n=6$

As before, we use LCAO:

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

p_z on atom

$E = E(c_1, c_2, \ldots c_n)$

H_{rs}

ϕ: are not orthogonal S_{rs}

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

eigenvalue

$s = 1, 2, 3, 4, 5, 6$

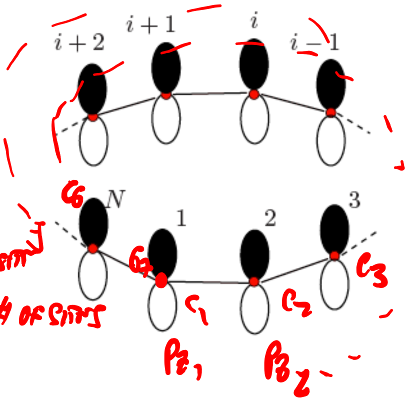
Only on-site and nearest-neighbor terms of the Hamiltonian are non-zero. rth Huckel equation:

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

Rings

Boundary condition (cycle of length N):

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



Trial wavefunction:

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

label eigen; label of the site; tot # of sites

Huckel equation:

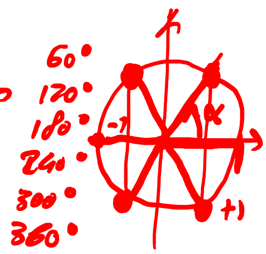
$$(\alpha - \epsilon_n)\overbrace{e^{i2\pi nr/N}}^{c_r} + \beta(\overbrace{e^{i2\pi n(r+1)/N}}^{c_{r+1}} + \overbrace{e^{i2\pi n(r-1)/N}}^{c_{r-1}}) = 0$$

$= \alpha - 2\beta$ $\quad -1 \ldots +1$ $\quad N=6$

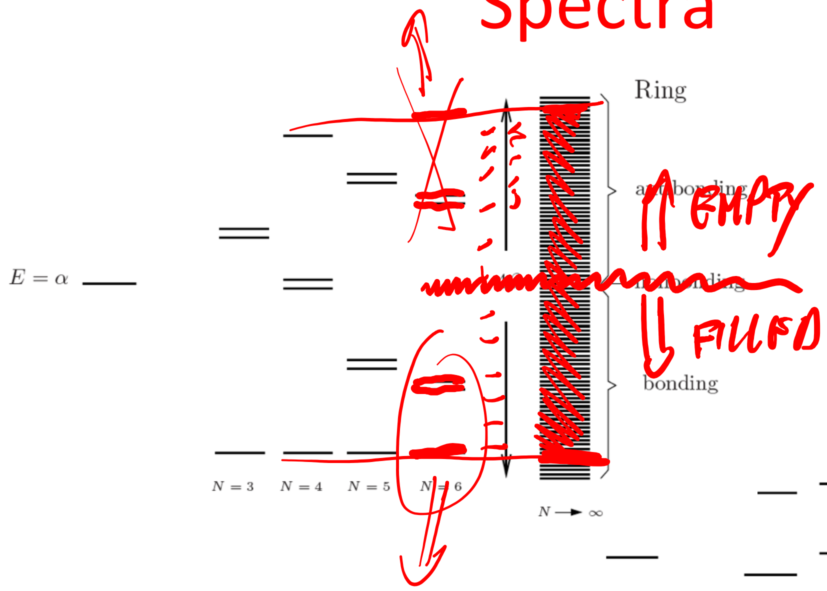
$= \alpha + 2\beta$

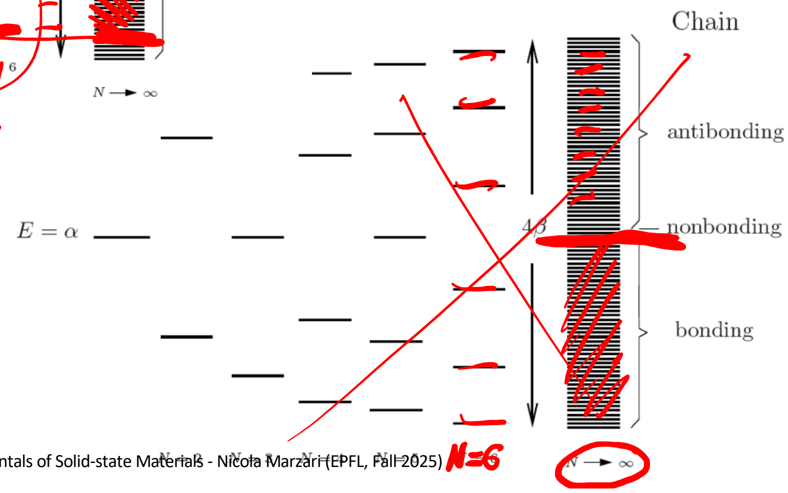
Solution (energy):

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



Spectra


Ring
antibonding
EMPTY
nonbonding
FILLED
bonding
$E = \alpha$
$N = 3$ $N = 4$ $N = 5$ $N = 6$
$N \longrightarrow \infty$


Chain
antibonding
nonbonding
bonding
$E = \alpha$
4β
N=6
$N \longrightarrow \infty$