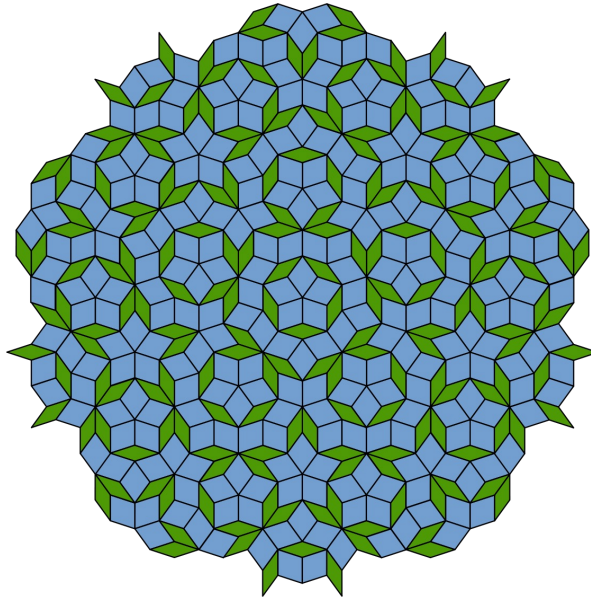


Symmetry



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Last week

- 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 Lengths and Bond Energies

TABLE 11.2 Some Average Bond Lengths^a

Bond	Bond Length, pm	Bond	Bond Length, pm	Bond	Bond Length, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—Cl	127.4	C=O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

^aMost values (C—H, N—H, C—H, ...) are averaged over a number of species containing the indicated bond and may vary by a few picometers. Where a diatomic molecule exists, the value given is the actual bond length in that molecule (H₂, N₂, HF, ...) and is known more precisely.

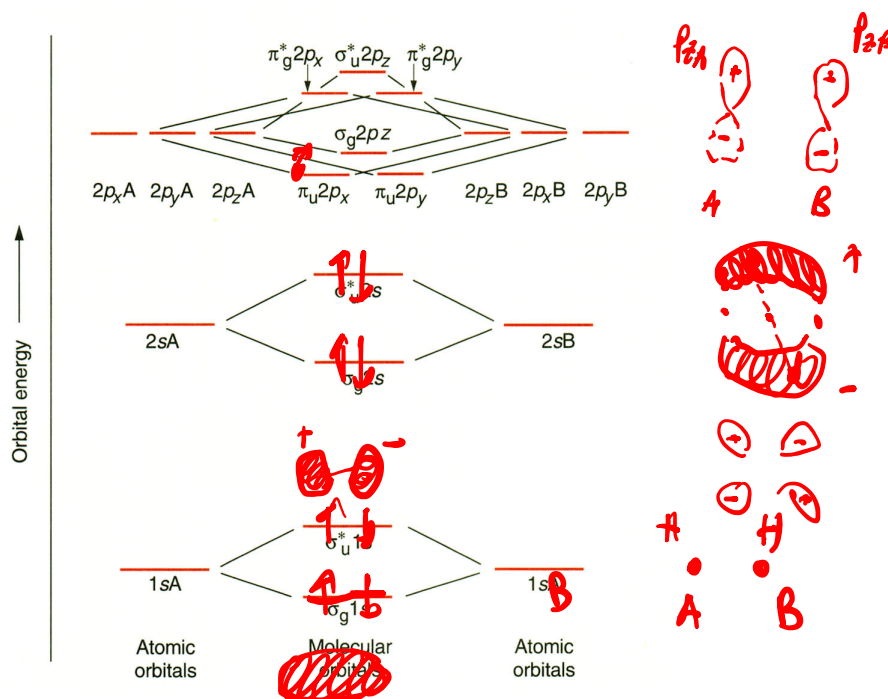
TABLE 11.3 Some Average Bond Energies^a

Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C=O	360	O=O	498
H—Br	364	C=O	736 ^b	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
				Br—Br	193
				I—I	151

^aAlthough all data are listed with about the same precision (three significant figures), some values are actually known more precisely. Specifically, the values for the diatomic molecules; H₂, HF, HCl, HBr, HI, N₂ (N≡N), O₂ (O=O), F₂, Cl₂, Br₂, and I₂ are actually bond-dissociation energies, rather than average bond energies. ^bThe value for the C=O bonds in CO₂ is 799 kJ/mol.

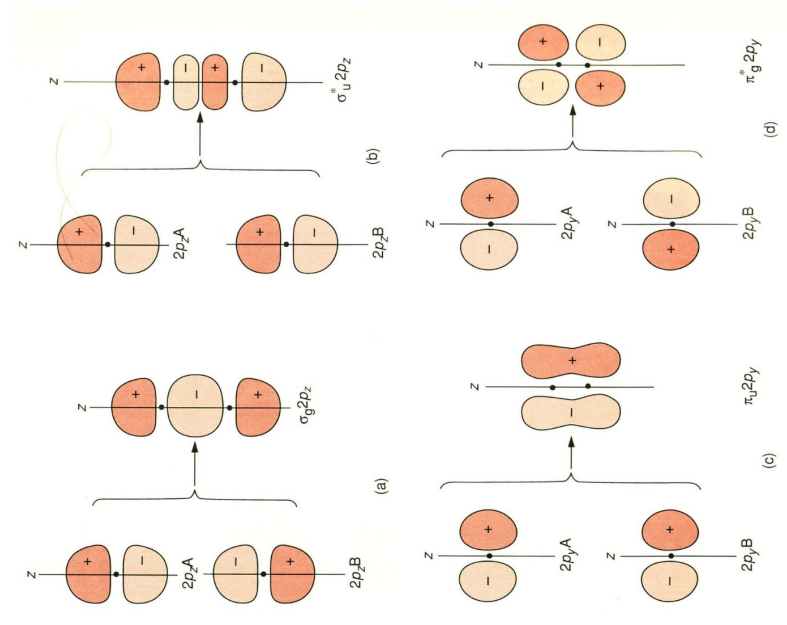
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Homonuclear Diatomic Levels (I)



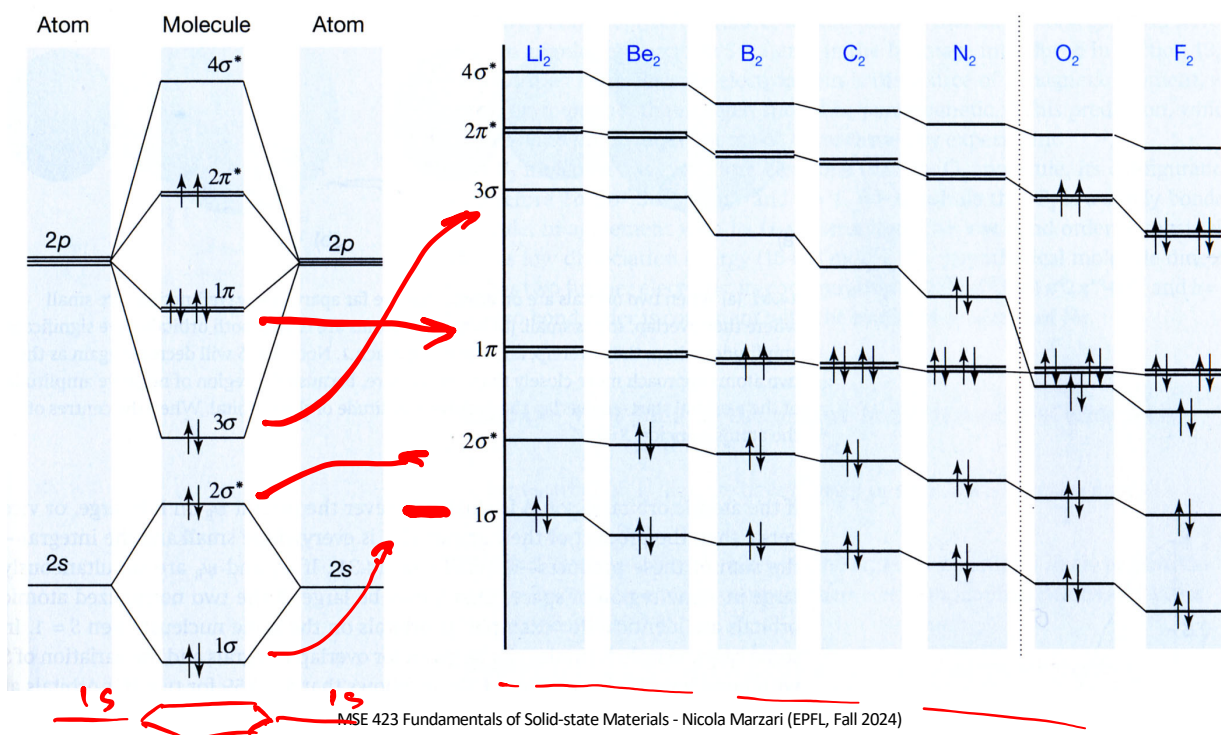
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Homonuclear Diatomic Levels (II)



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Homonuclear Diatomic Levels (III)



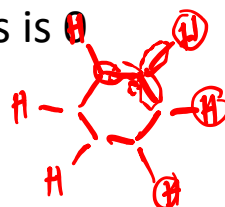
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Even simpler than LCAO: Empirical tight binding and Hückel approach

- 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

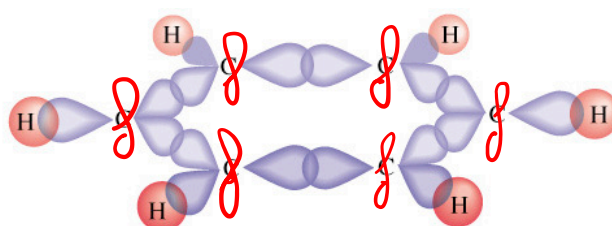
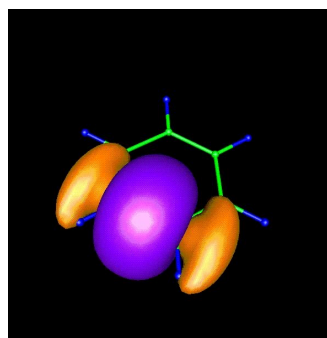
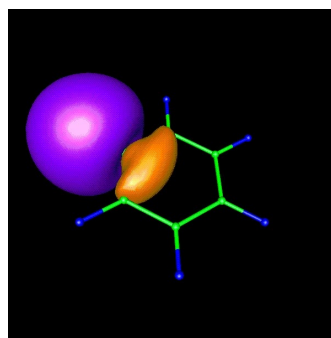
$$\langle p_z | \hat{H} | p_z \rangle = \alpha$$

$$\langle p_z | \hat{H} | p_z \text{ neighbor} \rangle = \beta$$



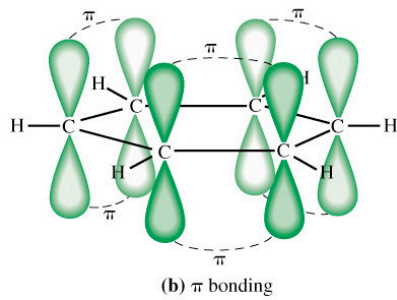
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Example: Benzene (C_6H_6)



(a) σ bond framework

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Benzene – energy levels

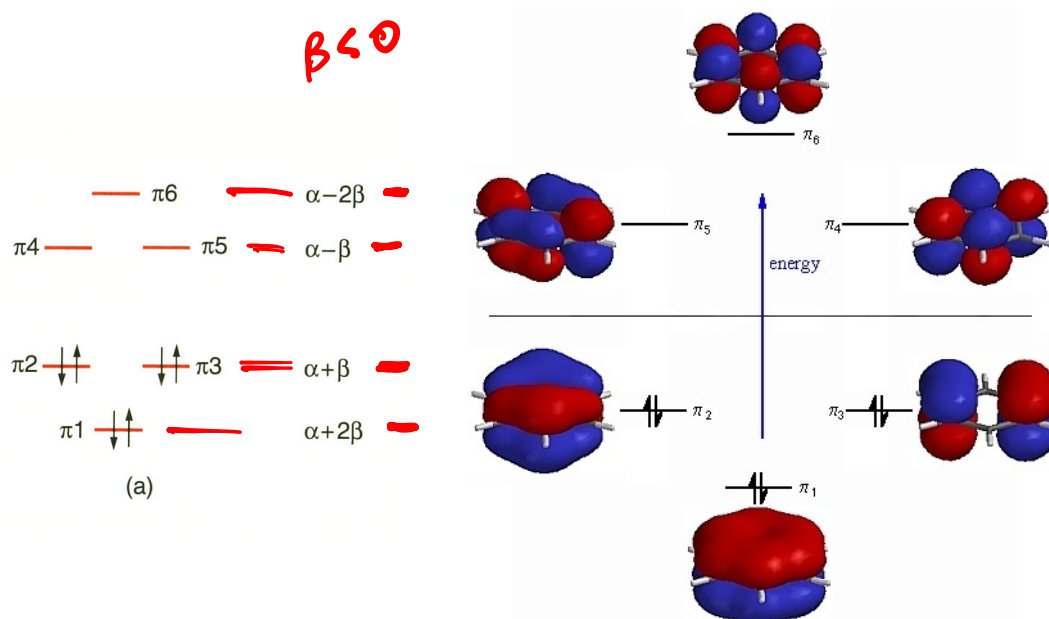
$$H_{\text{Hückel}} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

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

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Benzene – molecular orbitals

$$\beta < 0$$



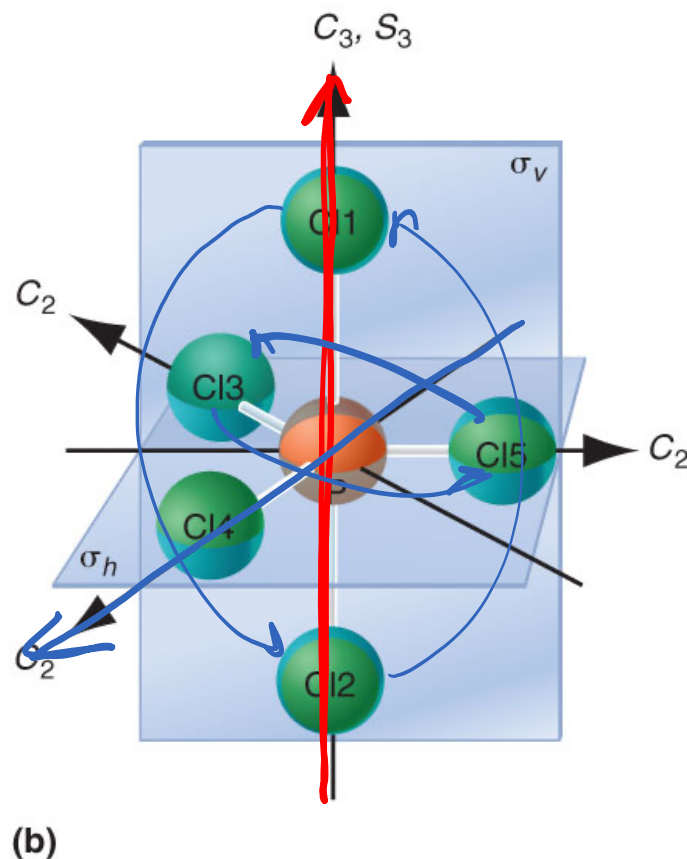
<http://www.chem.ucalgary.ca/SHMO/>

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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

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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	$\hat{C}_n, \hat{C}_n^2, \dots, \hat{C}_n^n$ rotate about axis by $360^\circ/n$ 1, 2, $\dots$, 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 $360^\circ/n$, and reflect through a plane perpendicular to the axis.

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Group Theory

A group G is a finite or infinite set of elements $A, B, C, D, \dots$ together with an operation “ $\odot$ ” that satisfy the four properties of:

- Closure:** If A and B are two elements in G , then $A \odot B$ is also in G .
 $5 + 7 = 12$
- Associativity:** For all elements in G , $(A \odot B) \odot C = A \odot (B \odot C)$.
- Identity:** There is an identity element I such that $I \odot A = A \odot I = A$ for every element A in G .
- Inverse:** There is an inverse or reciprocal of each element. Therefore, the set must contain an element $B = \text{inv}(A)$ such that $A \odot \text{inv}(A) = \text{inv}(A) \odot A = I$ for each element of G .

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Examples

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

6

- Integer numbers, and addition

- Integer numbers, and multiplication

6

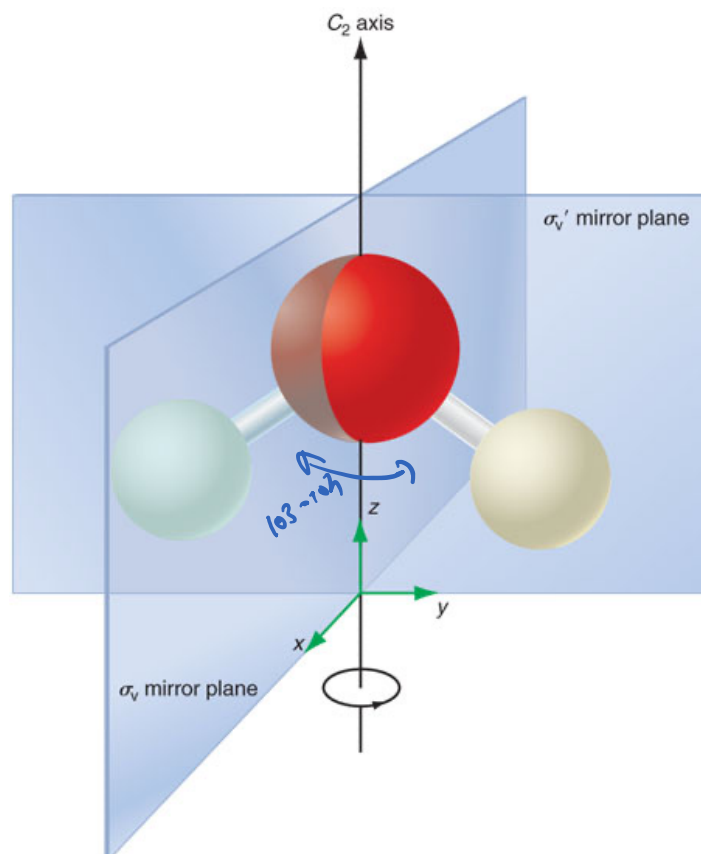
- Real numbers, and multiplication

6

- Rotations around an axis by $360/n$

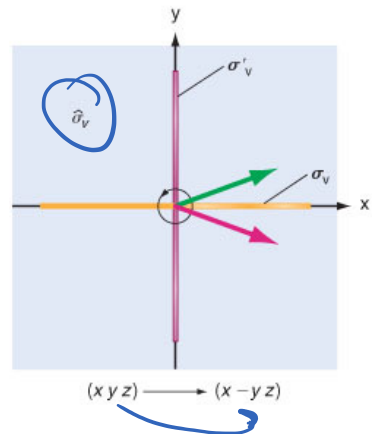
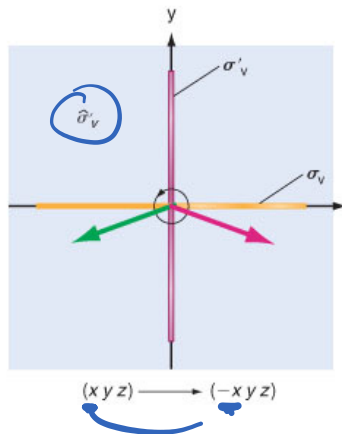
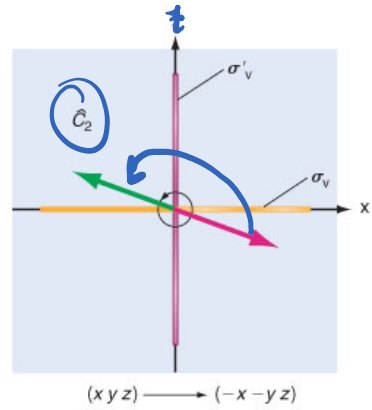
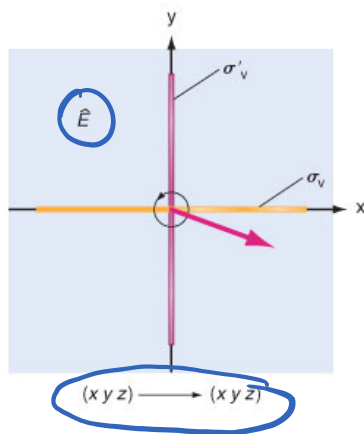
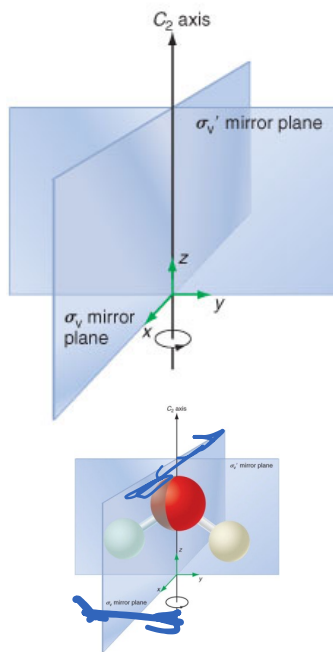
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C_{2v}



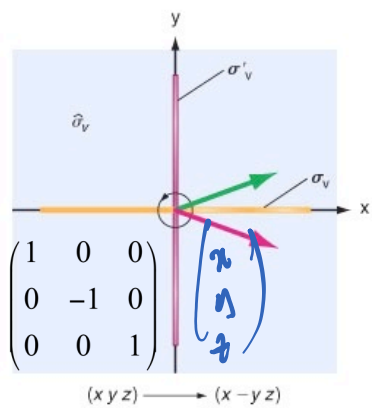
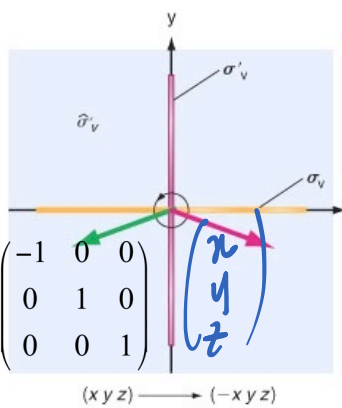
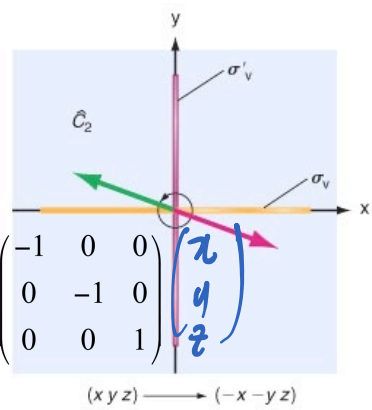
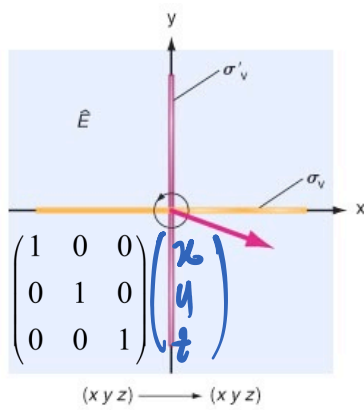
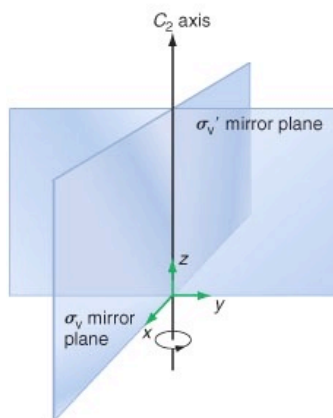
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Symmetries of H₂O



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Symmetries of H₂O



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The 4 symmetry operations of H₂O 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			
	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}'_v$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}'_v$	$\hat{\sigma}'_v$	$\hat{\sigma}_v$	$\hat{C}_2$	$\hat{E}$

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Symmetry and Hamiltonians

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

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

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

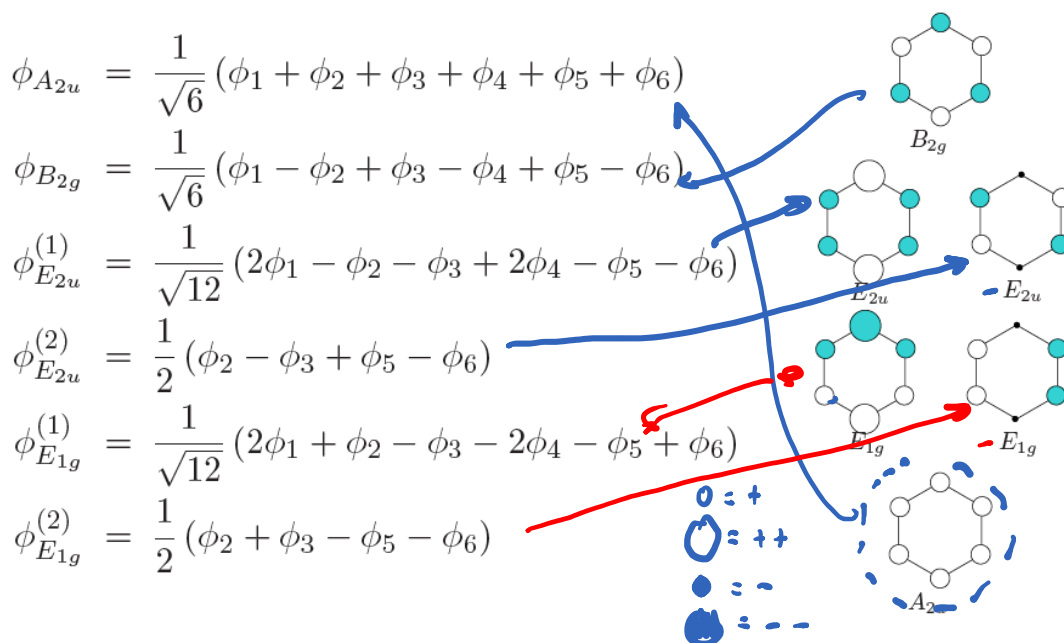
$$\mathcal{H}\psi = E\psi$$

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

- The symmetry operators identify groups of degenerate eigenstates of H

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Common eigenstates in benzene of Hamiltonian and C_6



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More general cases: rings and linear chains of arbitrary length

As before, we use LCAO:

$$\psi = \sum_{r=1}^N c_r \phi_r$$

N (number of carbon sites)

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

rs S ⇒ α, r N. of S ⇒ β

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

S_{rs} OVERLAP MATRIX

N EQUATIONS, S=1, ..., N

⟨φ_r | φ_s⟩ NOT ORTHOGONAL

Only on-site and nearest-neighbor terms of the Hamiltonian are non-zero. r^{th} Huckel equation:

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

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Rings

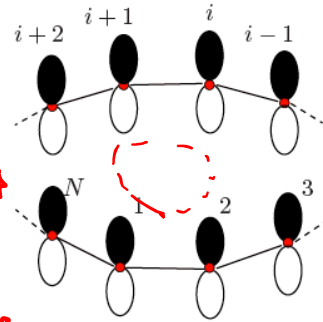
Boundary condition (cycle of length N):

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

Trial wavefunction:

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

STP NR AT LOOKING AT FOF STP S EIGENVALUE INDEX -



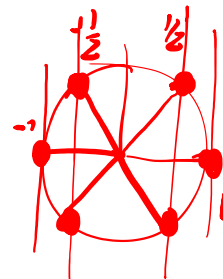
Huckel equation:

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

Solution (energy):

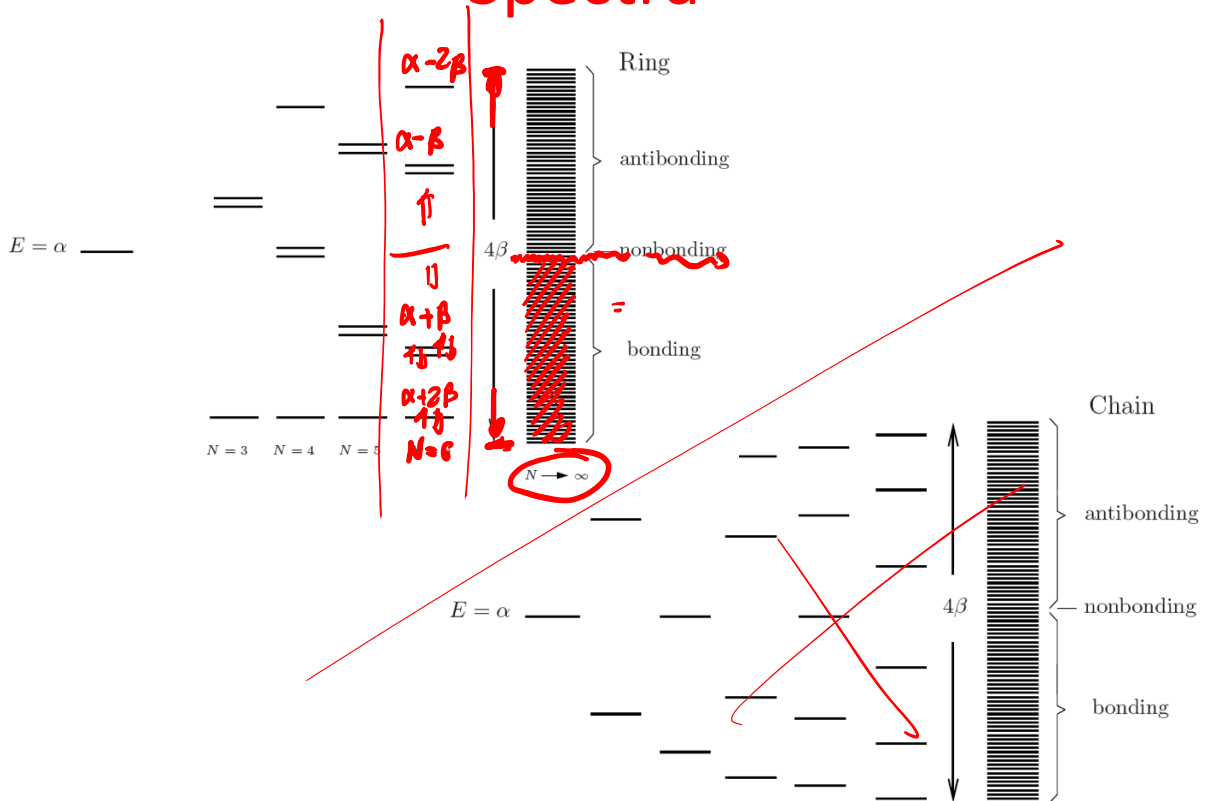
$$\epsilon_n = \alpha + 2\beta \cos(2\pi n/N)$$

n=1, ..., 1000



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Spectra

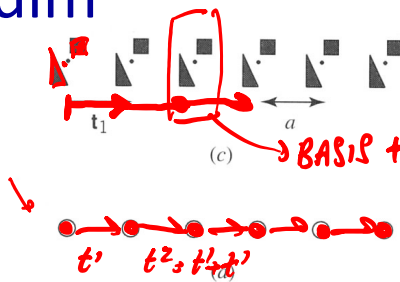


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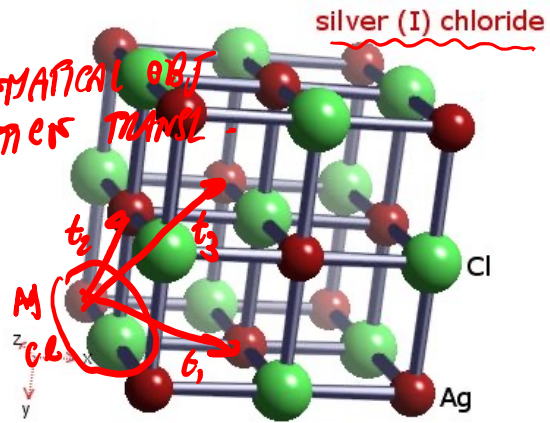
N=6 N->infinity

Translational Symmetry

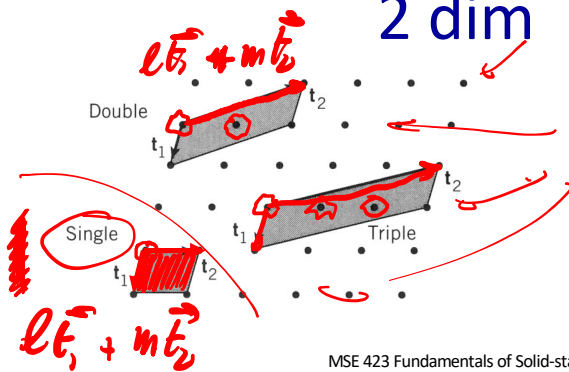
1 dim



3 dim



2 dim



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Bravais Lattices

- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

$$\{\vec{R}\} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad l, m \text{ and } n \text{ integers}$$

$\vec{a}_1, \vec{a}_2$ and $\vec{a}_3$ primitive lattice vectors

$\vec{a}_1, \vec{a}_2$ & $\vec{a}_3$ ARE LINEARLY INDEPENDENT

- 14 Bravais lattices exist in 3 dimensions (1848)
- M. L. Frankenheimer in 1842 thought they were 15. So, so naïve...

7 Crystal classes

4 Lattice types

body

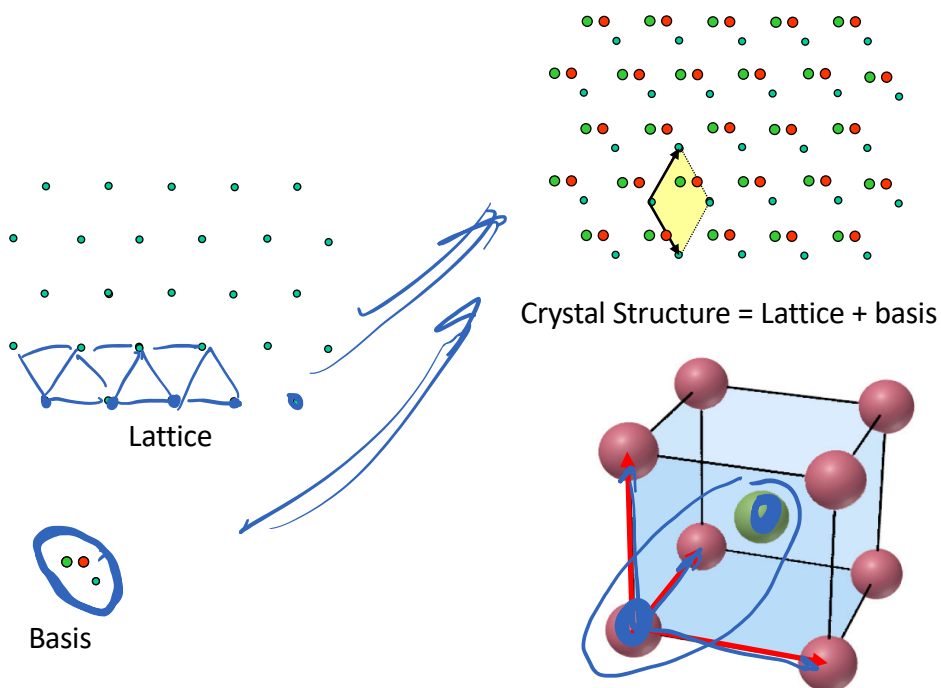
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

QUESTION FOR YOU:

HCP ≠ FCC
↳ Globus = FCC

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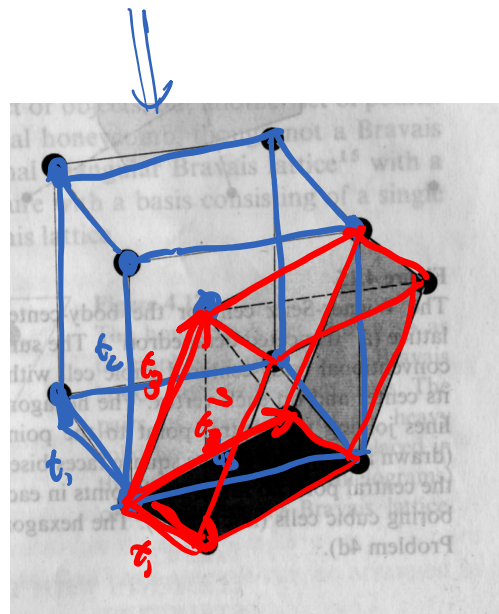
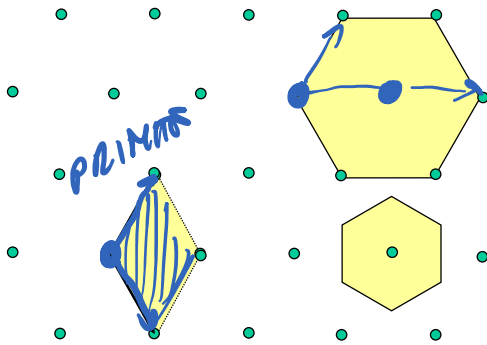
Crystal Structure = Lattice + Basis



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Primitive unit cell and conventional unit cell

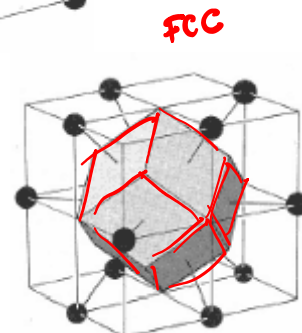
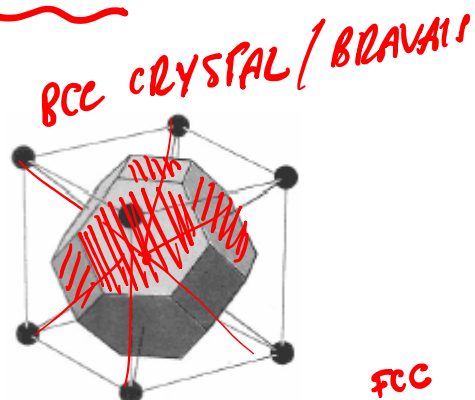
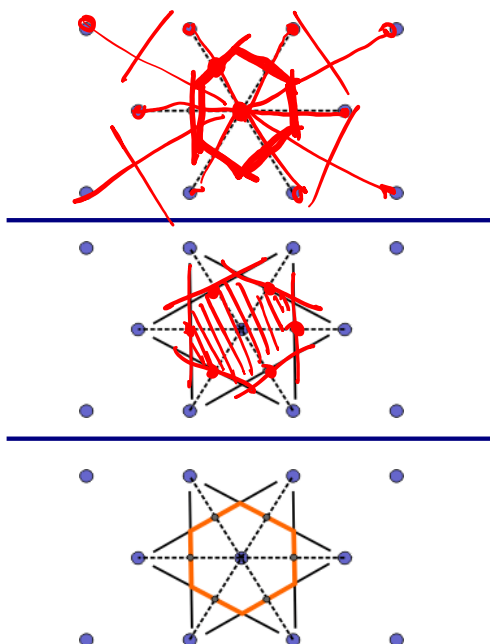
MINIMUM "VOLUME"



conventional $t_1 = (010)$ $t_2 = (100)$
 $t_3 = (001)$

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Wigner-Seitz cell



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