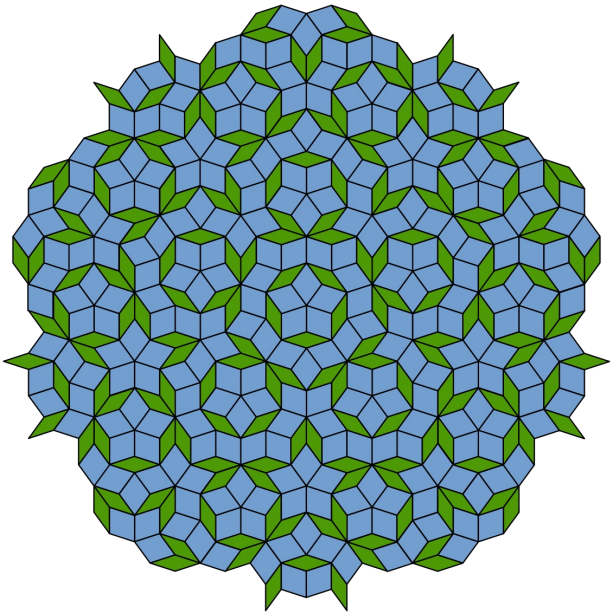
MSE 423 Fall 2024 – Week 8

Symmetry



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

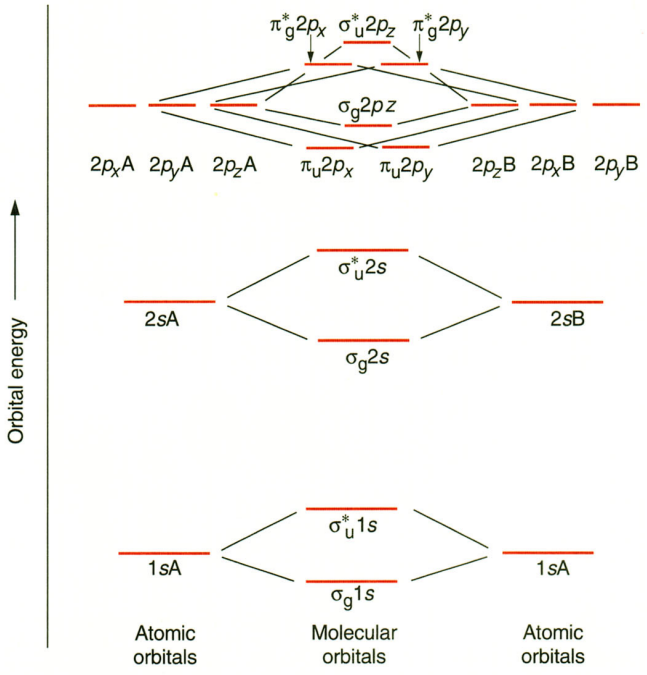
[a] Most values (C—H, N—H, C—H, ...) are averaged over a number of species containing the indicated bond and may vary by a few picometers. Where a diatomic molecule exists, the value given is the actual bond length in that molecule (H_2, N_2, HF, ...) and is known more precisely.

TABLE 11.3 Some Average Bond Energies[a]

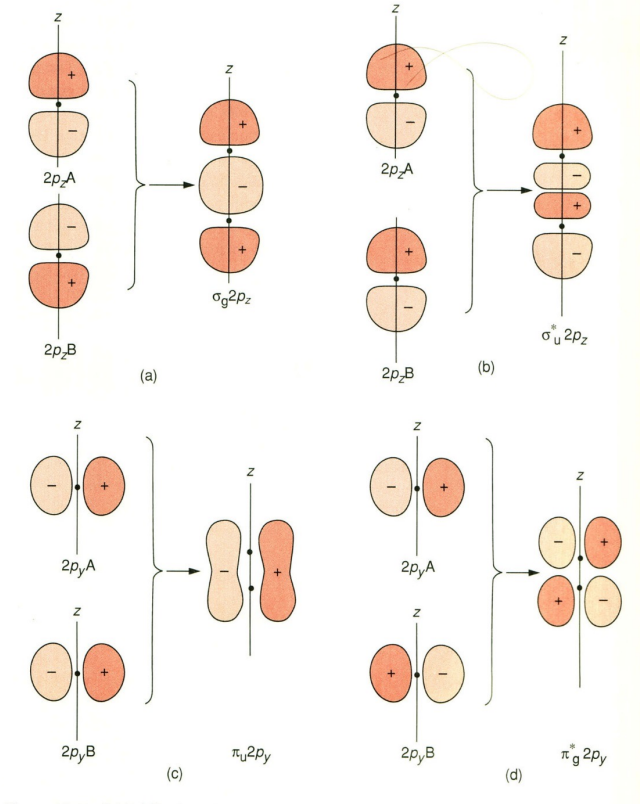
Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol	Bond	Bond Energy, kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736[b]	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
	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

[a] Although 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: H_2, HF, HCl, HBr, HI, N_2 (N≡N), O_2 (O=O), F_2, Cl_2, Br_2, and I_2 are actually bond-dissociation energies, rather that average bond energies.
[b] The value for the C=O bonds in CO_2 is 799 kJ/mol.

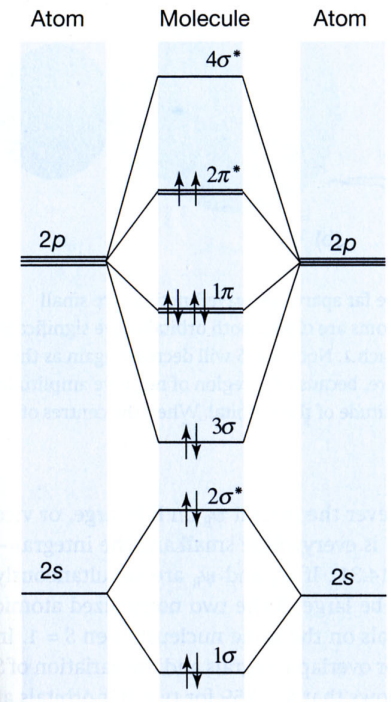
Homonuclear Diatomic Levels (I)

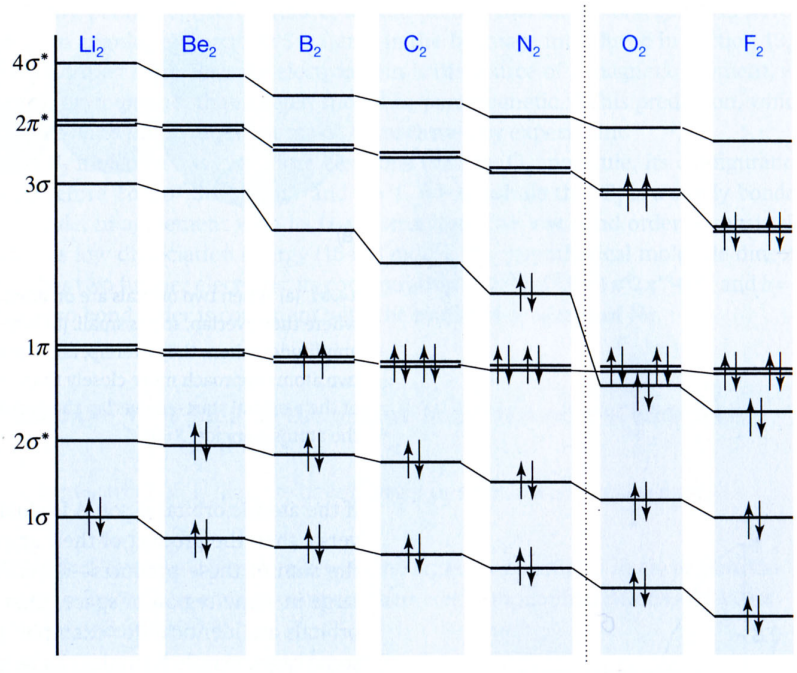


Homonuclear Diatomic Levels (II)



Homonuclear Diatomic Levels (III)

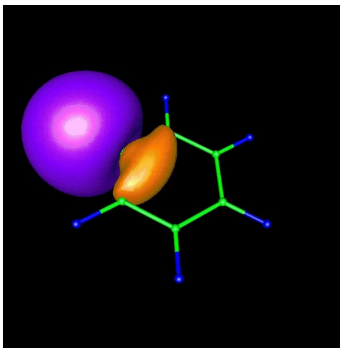


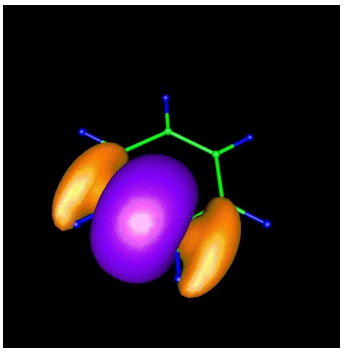


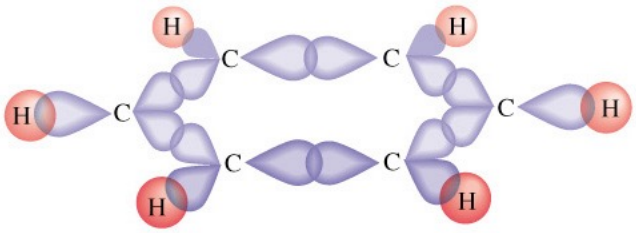
Even simpler than LCAO: Empirical tight binding and Hückel approach

- 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

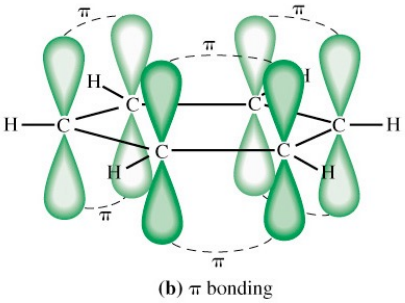
Example: Benzene (C_6H_6)







(a) σ bond framework

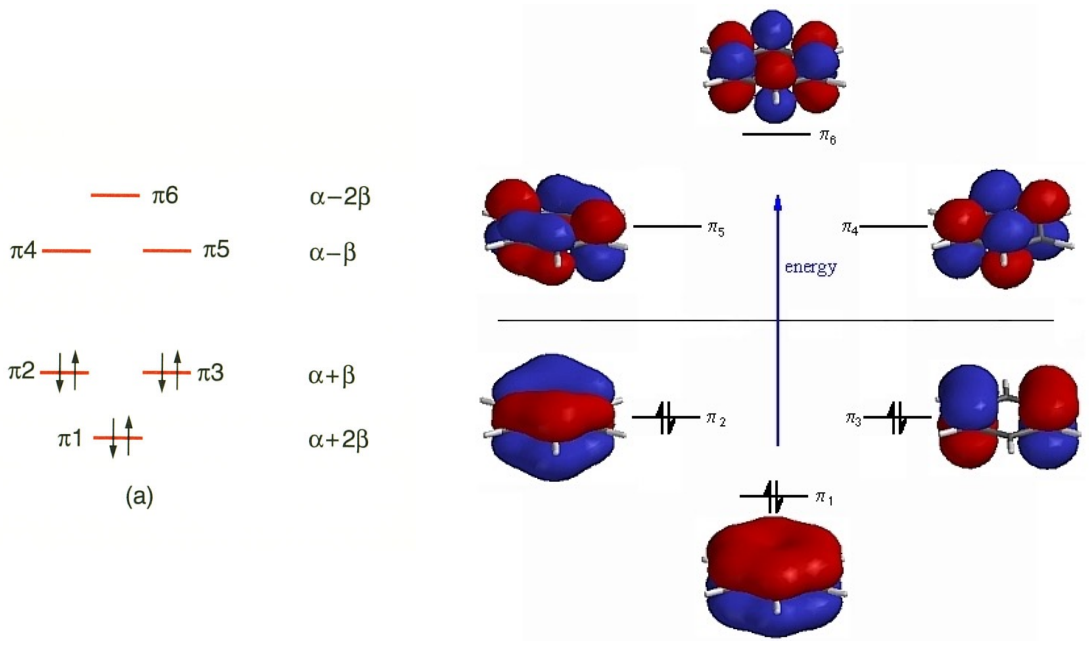


(b) π bonding

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

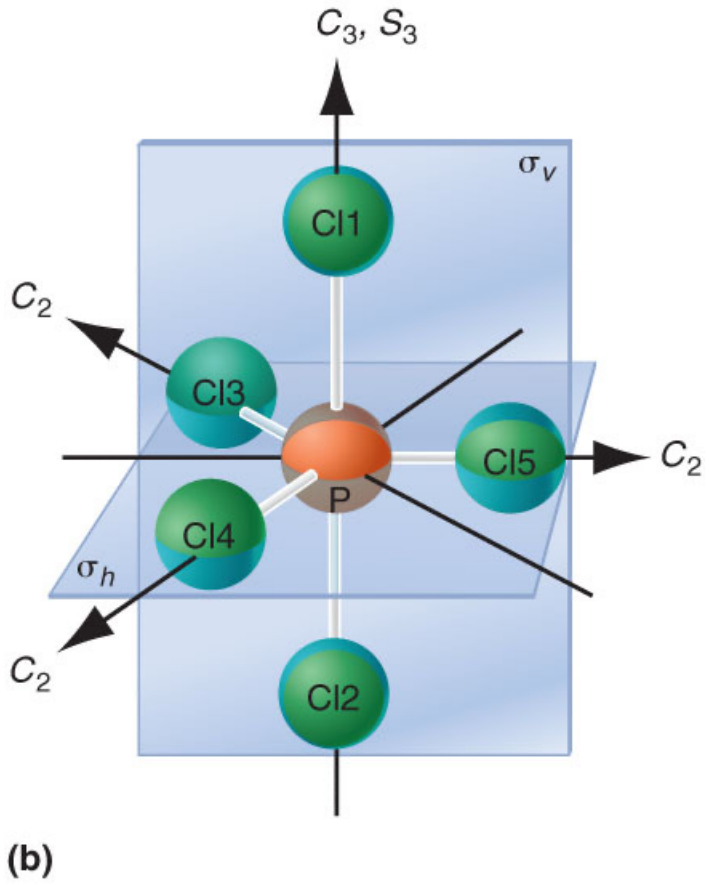


TABLE 17.1

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

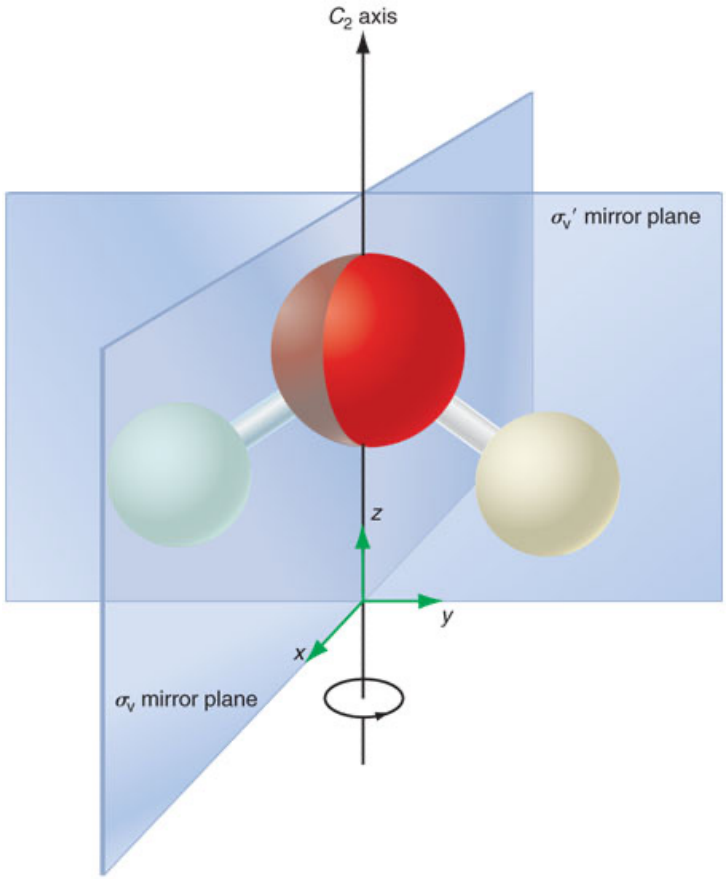
A group G is a finite or infinite set of elements A, B, C, D…together with an operation "☼" that satisfy the four properties of:

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.

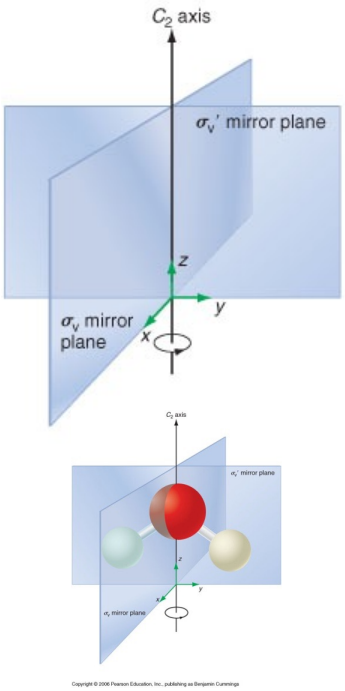
Examples

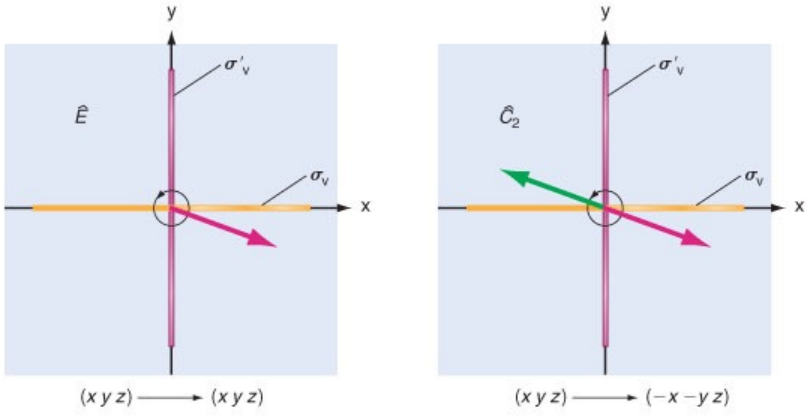
- Integer numbers, and addition
- Integer numbers, and multiplication
- Real numbers, and multiplication
- Rotations around an axis by 360/n

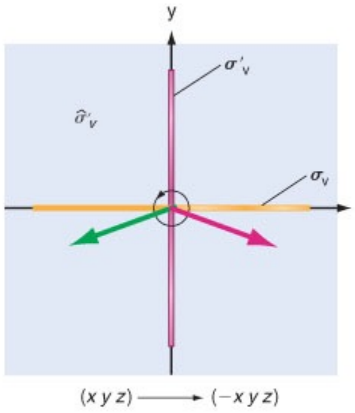
C_{2v}

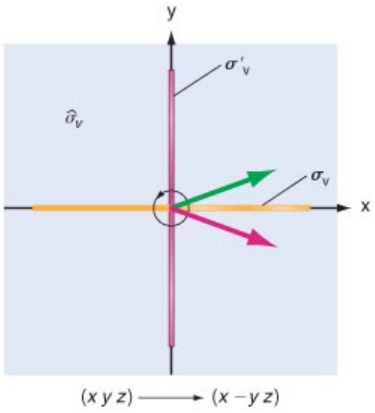


Symmetries of H_2O

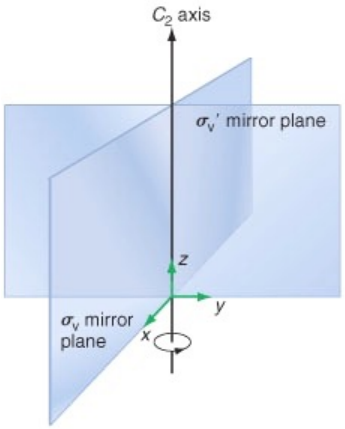


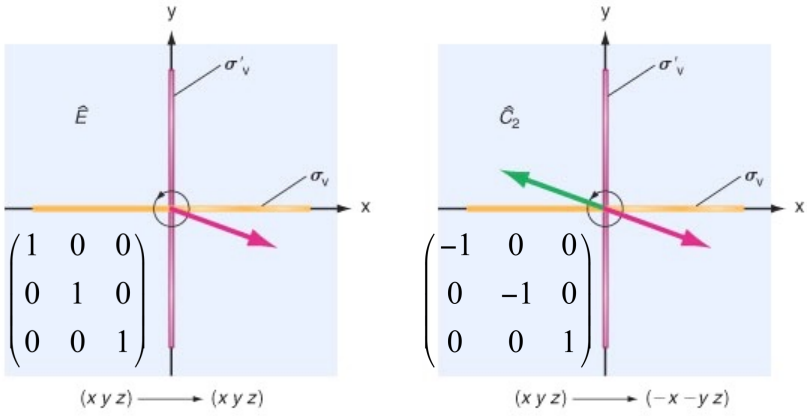


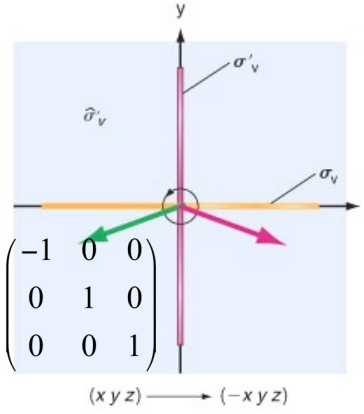


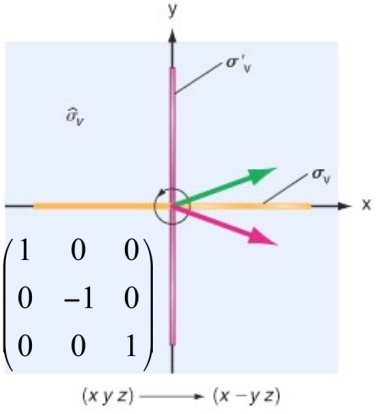


Symmetries of H_2O









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

- 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:

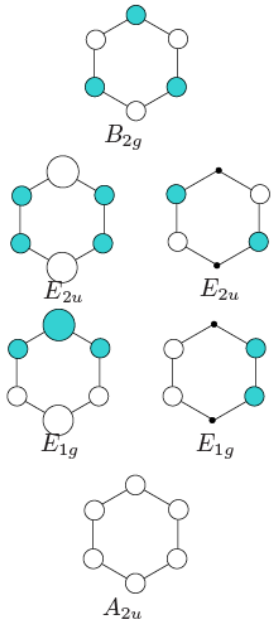
$$\mathcal{H}\psi = E\psi$$

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

- The symmetry operators identify groups of degenerate eigenstates of H

Common eigenstates in benzene of Hamiltonian and C_6

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



More general cases: rings and linear chains of arbitrary length

As before, we use LCAO:

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

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

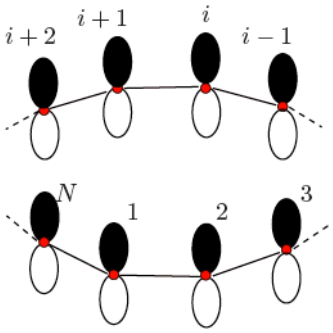
Only on-site and nearest-neighbor terms of the Hamiltonian are non-zero. r^{th} Huckel equation:

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

Rings

Boundary condition (cycle of length N):

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



Trial wavefunction:

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

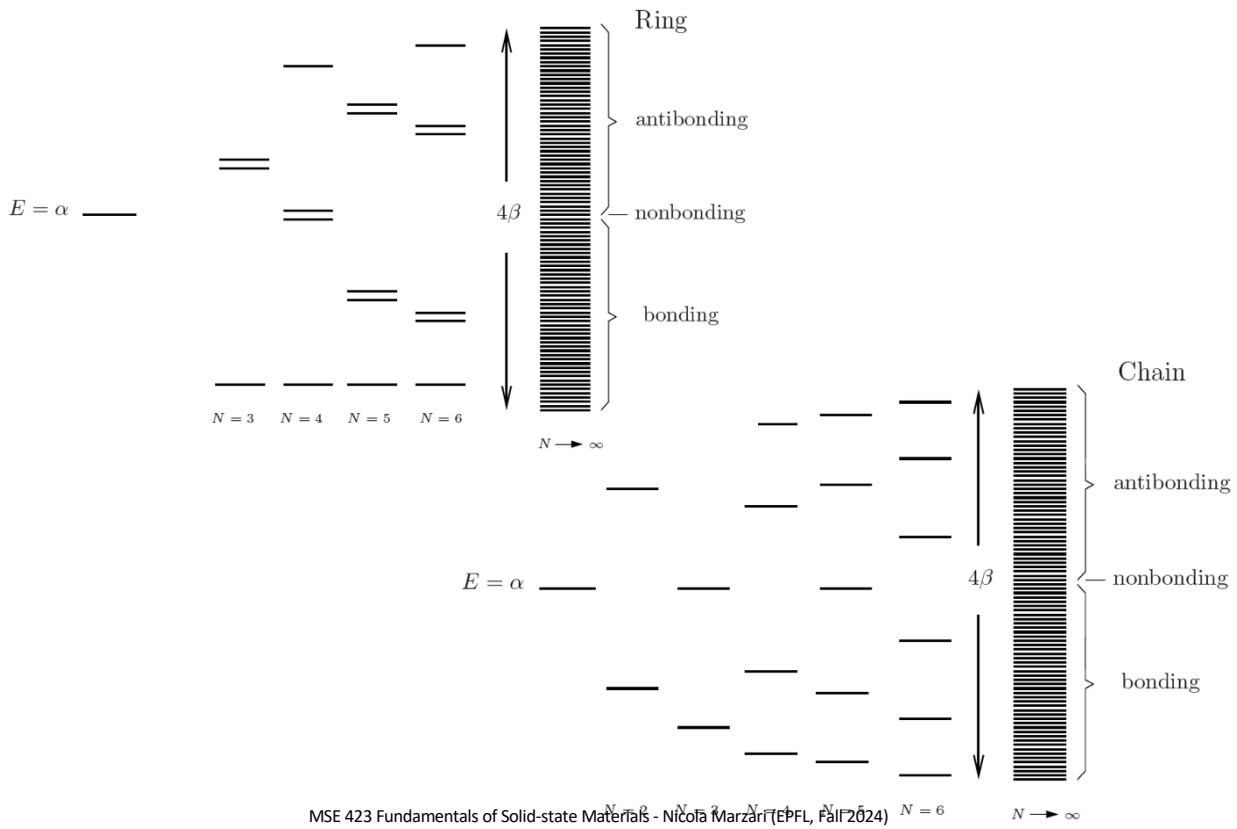
Huckel equation:

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

Solution (energy):

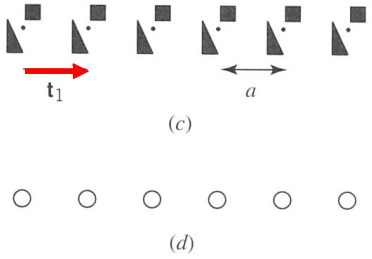
$$\epsilon_n = \alpha + 2\beta\cos(2\pi n/N)$$

Spectra

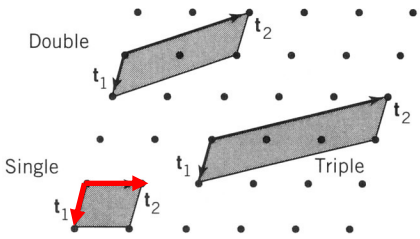


Translational Symmetry

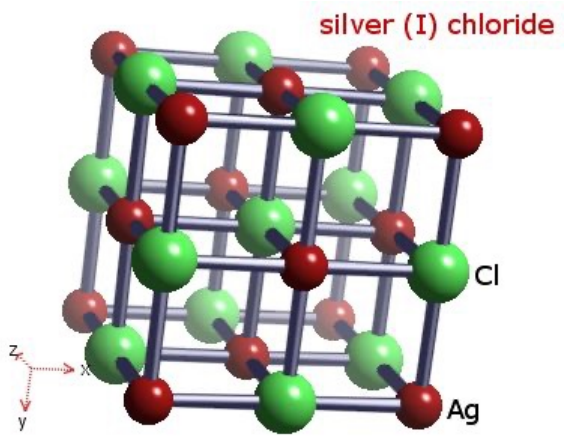
1 dim



2 dim



3 dim



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.

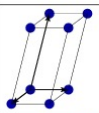
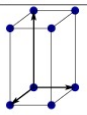
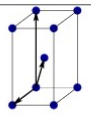
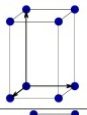
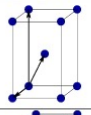
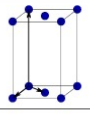
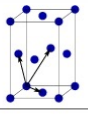
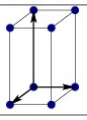
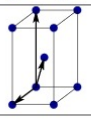
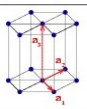
$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \qquad \text{l,m and n integers}$$

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

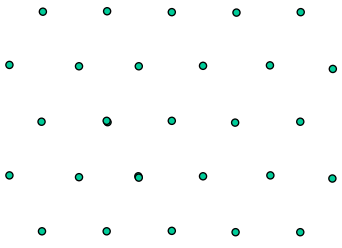
- 14 Bravais lattices exist in 3 dimensions (1848)
- M. L. Frankenheimer in 1842 thought they were 15. So, so naïve…

4 Lattice types

7 Crystal classes

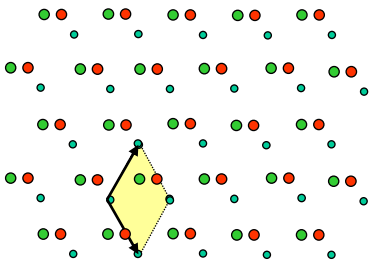
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2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

Crystal Structure = Lattice + Basis

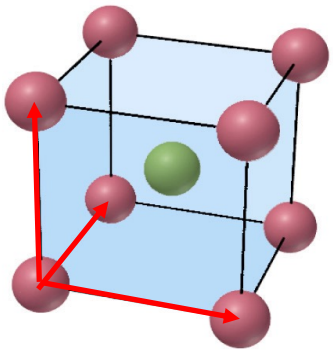


Lattice

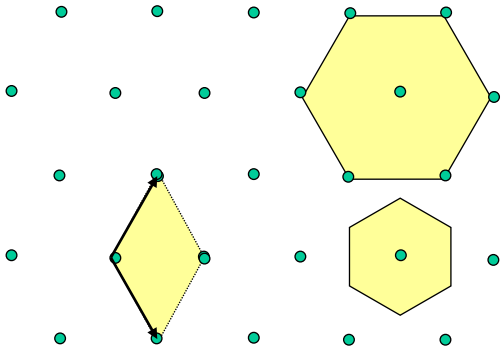
Basis

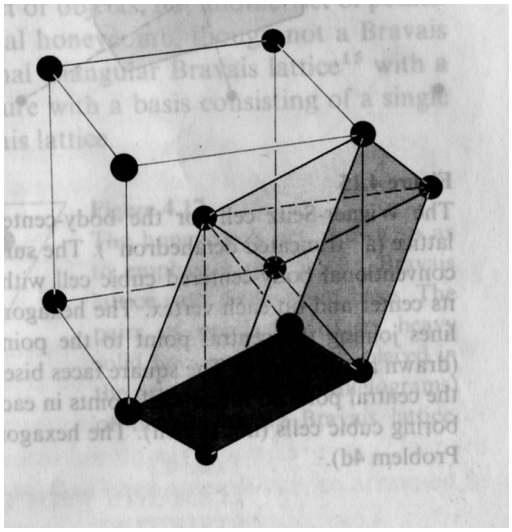


Crystal Structure = Lattice + basis



Primitive unit cell and conventional unit cell





Wigner-Seitz cell