Physical Chemistry III (728342)

Chapter 5: Molecular Symmetry

Piti Treesukol
Kasetsart University
Kamphaeng Saen Campus

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Molecular Symmetry

- **Molecular symmetry:**
  The classification of any molecule according to its symmetry, correlating to its molecular properties
- Importance of molecular symmetry

2

Group Theory

- The systematic discussion of symmetry is called **Group Theory.**
- The symmetry elements of objects
  - **Symmetry operation:** an action that leaves an object looking the same after it has been carried out
  - **Symmetry element:** an element (plane, line, point) that correlates to the specific symmetry operator (unchanged)

Symmetry Operation	Symmetry Elements
Rotation	Line (axis of rotation)
Reflection	Plane
Inversion	Point

3

Point Group

- **Point Group**: the classification of objects according to symmetry elements corresponding to operations that leave at least one common point unchanged.
- The more extensive classification, including the translation through space, is called **Space Group**.

4

Operations and Symmetry Elements

- Five kinds of symmetry operations in Point Group
  - The identity, E
  - An n-fold rotation, C_n
  - A reflection, σ
  - An inversion, i
  - An n-fold improper rotation, S_n

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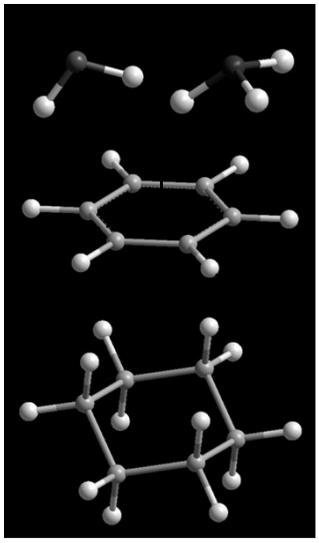
The Identity, E

- The identity operation is doing nothing!
  - Every molecule is indistinguishable from it self thus they have the identity element.

6

An n-fold Rotation, C_n

- An n-fold rotation about an n-fold axis of rotation, C_n, is a rotation through 360°/n
  - C_1 = E
  - C_2 = 180° rotation
  - C_3 = 120° rotation (C_3' and C_3")
  - C_6 = 60° rotation (C_1^1, C_1^2 ... C_1^5)
- If a molecule possesses several rotational axis, the one with the greatest value of n is called **the principal axis (Z)**.



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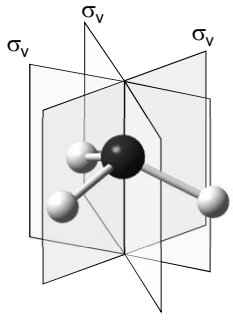
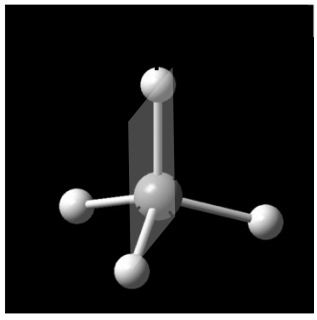
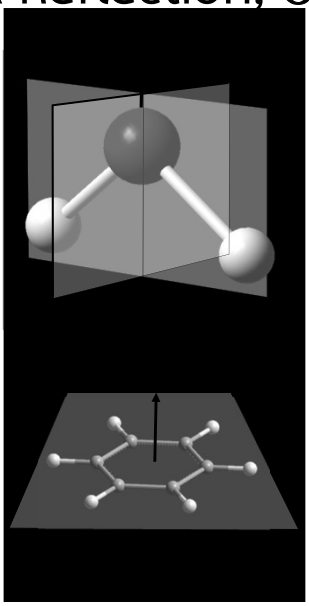
A Reflection, σ

- A reflection is a mirror plane.
  - **σ_v –** parallel to the principle axis
  - **σ_d –** parallel to the principle axis and bisect the angle between two C_2 axes
  - **σ_h –** perpendicular to the principle axis







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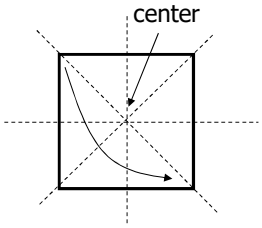
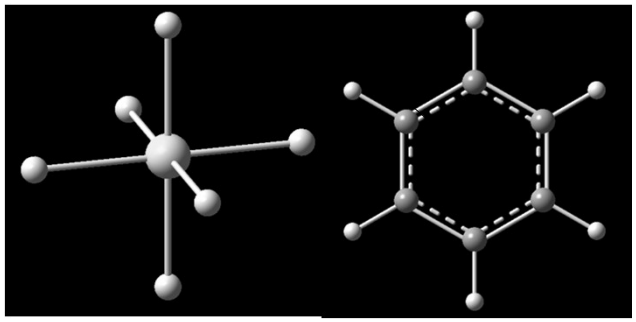
An Inversion, i

- An inversion through a center of symmetry
  - If the origin point is the center of symmetry

$$\hat{i}(x, y, z) = (-x, -y, -z)$$





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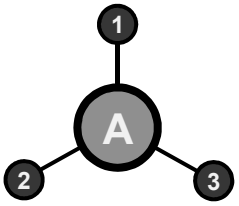
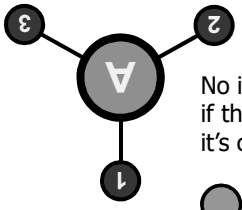
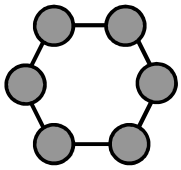
More examples about inversion

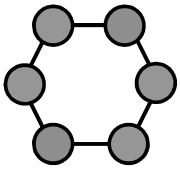




No inversion
if the inversion point is on atom A,
it's changed upon the inversion



the inversion point is
at the center



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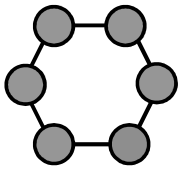
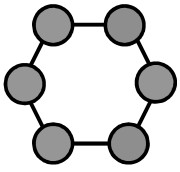


No inversion



No inversion

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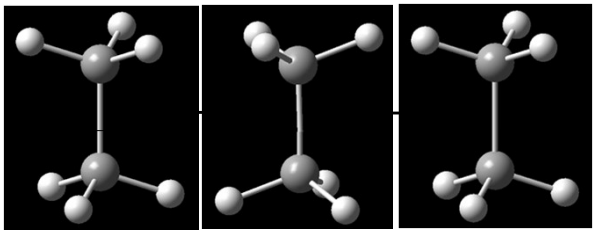
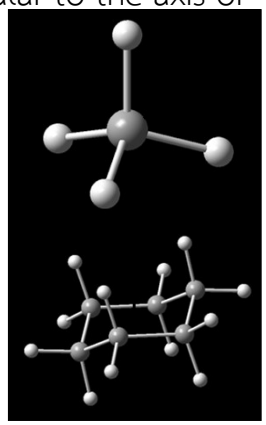
An n-fold Improper Rotation, S_n

- An n-fold improper rotation is composed of two successive transformation:
  - Rotation through 360°/n
  - Reflection through a plane perpendicular to the axis of that rotation.





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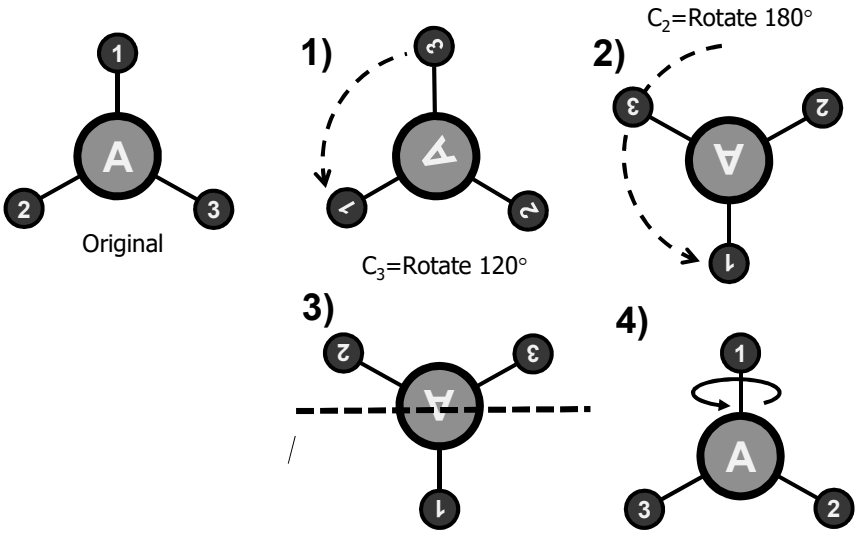
Example of Acceptable Operator



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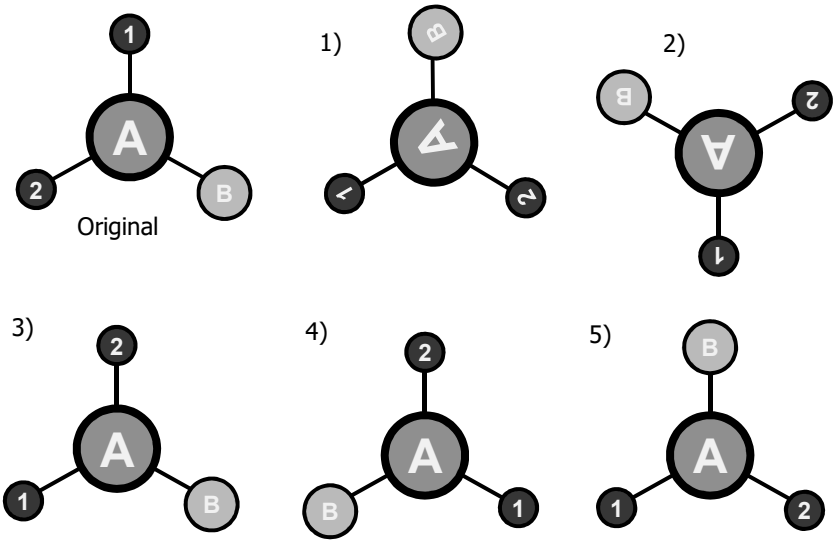
What operator is applied?



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The Symmetry Classification of Molecules

- Molecules with the same list of elements are classified to the same group.
  - The groups C_1, C_i and C_s (no rotational axis)
  - The groups C_n, C_{nv} and C_{nh} (n-fold axis)
  - The groups D_n, D_{nh}, D_{nd} (n-fold axis and n perpendicular C_2s)
  - The groups S_n (n-fold improper axis)
  - The cubic groups
    - Tetrahedral groups (T, T_d, T_h)
    - Octahedral groups (O, O_h)
    - Icosahedral groups (I)

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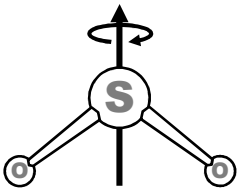
Example of Character Table

- The characters of all representations are tabulated in a character table.



C_{2v}	E	C_2	σ_v	σ_v'	h=4	
A_1	1	1	1	1	Z	z^2, y^2, x^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	X	xz
B_2	1	-1	-1	1	y	yx

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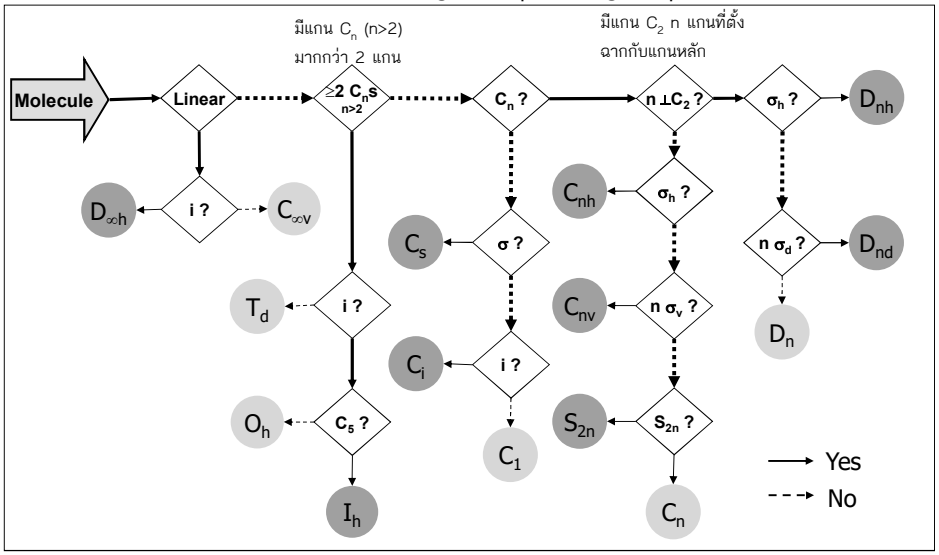
Determining the Point Group

- A flowchart for determining the point group of a molecule



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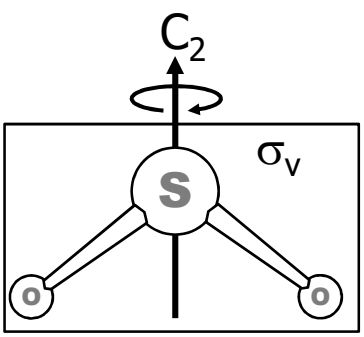
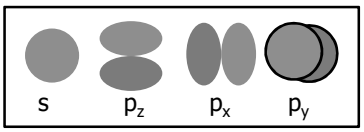
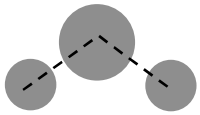
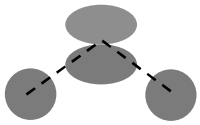
LCAO-MO of SO_2



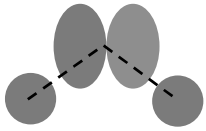




c_1 3s(S) - c_2 2s(O1) - c_2 2s(O2)

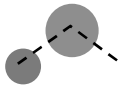
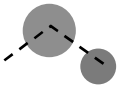
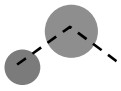
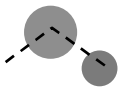
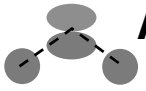
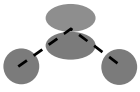
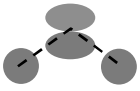
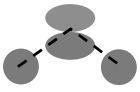
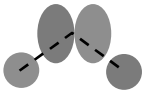
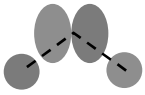
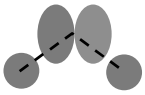
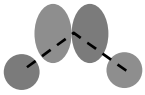


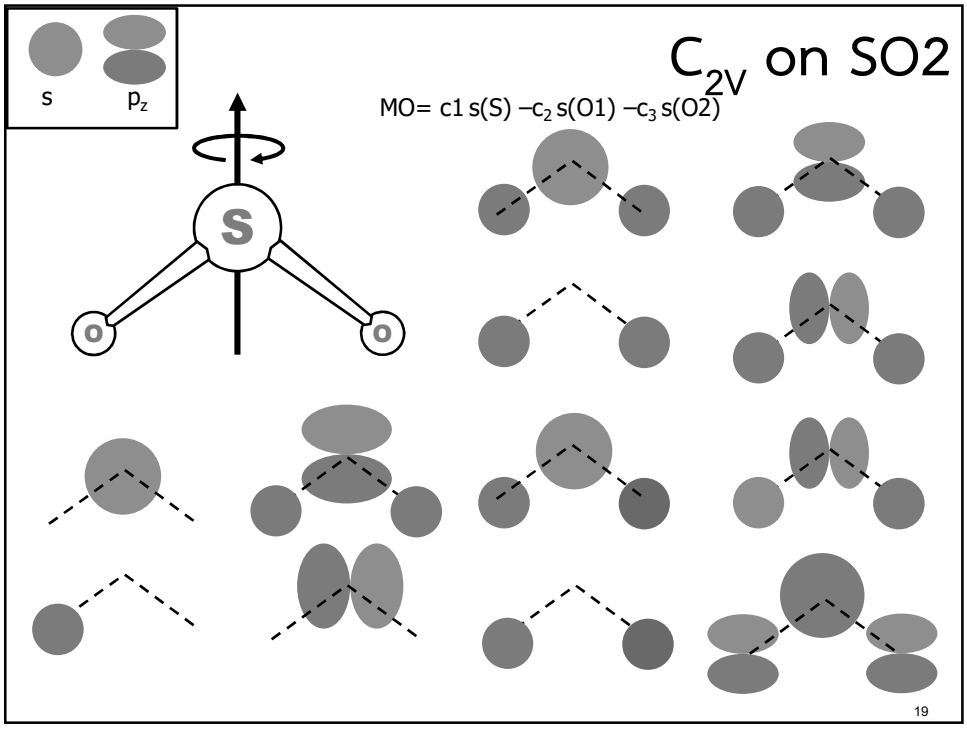
c_1 3p_z(S) + c_2 2s(O1) + c_2 2s(O2)



-c_1 3p_x(S) - c_2 2s(O1) + c_2 2s(O2)

Operation on MO's of SO_2

	C_2	σ_v	σ'_v
 c_1 3s(S) + c_2 2s(O1)	 x	 =1	 x
A1  c_1 3p_z(S) - c_2 2s(O1) - c_3 2s(O2)	 =1	 =1	 =1
B1  -c_1 3p_x(S) + c_2 2s(O1) - c_3 2s(O2)	 =-1	 =1	 =-1



Character Table

- **Character Table** is a table that characterizes the different symmetry types possible in the point group.
- The entries in a complete character table are derived by using the formal techniques of group theory.

C_{2v}	E	C_2	σ_v	σ_v'	h=4	
A_1	1	1	1	1	Z	z^2,y^2,x^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	X	xz
B_2	1	-1	-1	1	y	yx

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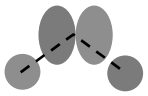
Operation & Matrix

$-c_1\ 3p_x(S) + c_2\ 2s(O1) - c_3\ 2s(O2)$



B1

$$\hat{C}_2(3p_S,2s_{O1},2s_{O2}) = (3p_S,2s_{O1},2s_{O2})\begin{bmatrix}-1 & 0 & 0\\ 0 & 0 & -1\\ 0 & -1 & 0\end{bmatrix} = (-3p_S,-2s_{O2},-2s_{O1})$$

$$\hat{\sigma}_v(3p_S,2s_{O1},2s_{O2}) = (3p_S,2s_{O1},2s_{O2})\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} = (3p_S,2s_{O1},2s_{O2})$$

$$\hat{\sigma}'_v(3p_S,2s_{O1},2s_{O2}) = (3p_S,2s_{O1},2s_{O2})\begin{bmatrix}-1 & 0 & 0\\ 0 & 0 & -1\\ 0 & -1 & 0\end{bmatrix} = (-3p_S,-2s_{O2},-2s_{O1})$$

Representations and Characters

- All the operators can be written in the matrix form.
- The matrix is called a representation of an operator.
  - C_{2v}

$$\mathbf{D}(E) = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} \qquad \mathbf{D}(\sigma_v) = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$\mathbf{D}(C_2) = \begin{bmatrix}-1 & 0 & 0\\ 0 & 0 & -1\\ 0 & -1 & 0\end{bmatrix} \qquad \mathbf{D}(\sigma_v') = \begin{bmatrix}-1 & 0 & 0\\ 0 & 0 & -1\\ 0 & -1 & 0\end{bmatrix}$$

- The Matrix representative is called $\Gamma^{(n)}$, where n is the dimention of the matrix
- The character of the representation matrix is the sum of diagonal elements.

$$\Gamma(E) = 3 \quad \Gamma(\sigma_v) = 3 \quad \Gamma(C_2) = -1 \quad \Gamma(\sigma_v') = -1$$

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Reduce- and Inreducible Representation

- Inspection of the representatives reveals that they are all of block-diagonal form.
- This shows that the p_s is never mixed with the rest.

$$\mathbf{D}(E)=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\ \mathbf{D}(\sigma_v)=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\ \mathbf{D}(C_2)=\begin{bmatrix}-1&0&0\\0&0&-1\\0&-1&0\end{bmatrix}\ \mathbf{D}(\sigma_v')=\begin{bmatrix}-1&0&0\\0&0&-1\\0&-1&0\end{bmatrix}$$

- The 3-D representative matrix ($\Gamma^{(3)}$) can be separated into $\Gamma^{(1)}+\Gamma^{(2)}$)

$$\Gamma^{(1)} \Rightarrow \mathbf{D}(E)=1\ \mathbf{D}(\sigma_v)=1\quad \mathbf{D}(C_2)=1\ \mathbf{D}(\sigma_v')=-1$$

$$\Gamma^{(2)} \Rightarrow \mathbf{D}(E)=\begin{bmatrix}1&0\\0&1\end{bmatrix}\ \mathbf{D}(\sigma_v)=\begin{bmatrix}1&0\\0&1\end{bmatrix}\ \mathbf{D}(C_2)=\begin{bmatrix}0&-1\\-1&0\end{bmatrix}\ \mathbf{D}(\sigma_v')=\begin{bmatrix}0&-1\\-1&0\end{bmatrix}$$

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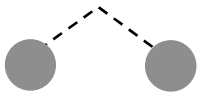
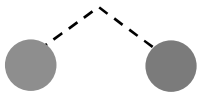
- According to the matrix representation, 2s(O1) and 2s(O2) are mixed together.
- Using the LC, we can write the new basis as s_A=2s(O1)+2s(O2) and s_B=2s(O1)-2s(O2)



$$\Gamma^{(1)} \Rightarrow \mathbf{D}(E)=1\ \mathbf{D}(\sigma_v)=1\quad \mathbf{D}(C_2)=1\ \mathbf{D}(\sigma_v')=1$$



$$\Gamma^{(1)} \Rightarrow \mathbf{D}(E)=1\ \mathbf{D}(\sigma_v)=1\quad \mathbf{D}(C_2)=-1\ \mathbf{D}(\sigma_v')=-1$$

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The Structure of Character Tables

Group — *Symmetry Operations Class* — *Order (# operations)*

C_{3v}	E	$2C_3$	$3\sigma_v$	h=6	
A_1	1	1	1	Z	z^2, $x^2 + y^2$
A_2	1	1	-1		
E	2	-1	0	(x,y)	(xy, x^2-y^2),(xz,yz)

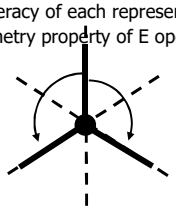
Irreducible Representations — *Symmetry Properties (χ)*

# of degerneracy of each representative is specified by the symmetry property of E operation or χ(E).

Labels A, B: 1-D E: 2-D T: 3-D

$A \rightarrow \chi(C_n) = 1$ $B \rightarrow \chi(C_n) = -1$

$1 \rightarrow \chi(\sigma_v) = 1$ $2 \rightarrow \chi(\sigma_v) = -1$



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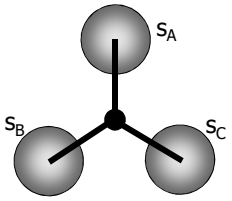
The Classification of LC of Orbitals

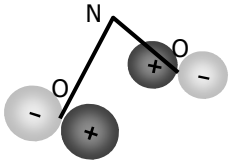
- NH_3
  - LCAO: $\psi_1 = \psi_A + \psi_B + \psi_C$

    $\chi(E) = 1 \quad \chi(C_3) = 1 \quad \chi(\sigma_v) = 1$



  this orbital is of symmetry species A1 and it contributes to a_1 MO in NH_3.

- NO_2 $\psi_1 = \psi_A - \psi_B$
  - LCAO: $\chi(E) = ? \quad \chi(C_2) = ? \quad \chi(\sigma_v) = ? \quad \chi(\sigma_v') = ?$



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Orbitals with nonzero overalp

- Only orbitals of the same symmetry species may have nonzero overlap, so only orbitalsof the same symmetry species form bonding and antibonding combinations.

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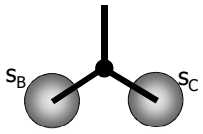
Vanishing Integrals & Orbital Overlap

- The value of integrals and orbital overlap is independent of the orientation of the molecule.

$$I = \int f_1 f_2 d\tau$$

  - I is invariant under any symmetry operation of the molecule, otherwise it must be zero.
  - For I not to be zero, the integrand $f_1 f_2$ must have symmetry species A_1.
- Example: f_1 = s_B and f_2 = s_C of NH_3



f_1:	1	1	1
f_2:	2	−1	1
$f_1 f_2$:	2	−1	1

⟶ not A_1 $\quad I = \int s_B s_C d\tau = 0$

- Problem: f_1 = s_N and f_2 = s_A +s_B +s_C of NH_3

$$I = \int f_1 f_2 d\tau = 0 \quad ?$$

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Vanishing Integrals and Selectrion Rules

- Integrals of the form $I = \int f_1 f_2 f_3 d\tau$ are common in quantum mechanics.
- For the integral to be nonzero, the product $f_1 f_2 f$ must span A_1 or contain a component that span A_1.
- The intensity of line spectra arises from a molecular transition between some initial state i and a final state f and depends on the electric transition dipole moment μ_{fi}.

$$\mu_{z,f_i} = -e\int \psi_f^* z \psi_i d\tau = \langle \mathrm{f} | \mu_z | i \rangle$$

C_{2v}	E	C_2	σ_v	σ_v'
B_1	1	-1	1	-1
z	1	1	1	1
A_1	1	1	1	1
$A_1 z B_1$	1	-1	1	1

C_{2v}	E	C_2	σ_v(xz)	σ_v(yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	−1	R_z	xy
B_1	1	-1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

$\longrightarrow \mu_{z,f_i} = 0$ if *fzi* does not span species A_1

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- In many cases, the product of functions f_1 and f_2 spans a sum of irreducible representations.
- In these cases, we have to decompose the reducible representation into irreducible representations

C_{2v}	E	C_2	σ_v	σ_v'
A_2	1	1	-1	-1
B_1	1	-1	1	-1
$A_2 + B_1$	2	0	0	-2

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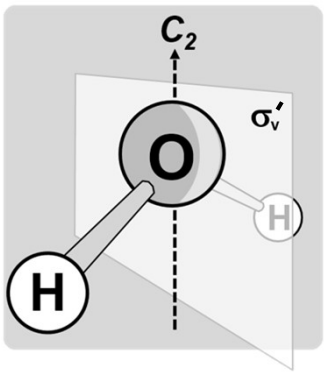
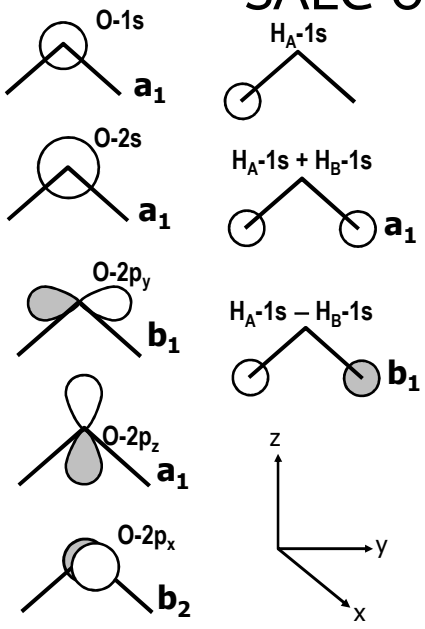
SALC of H_2O



C_{2V}	E	C_2 (z)	σ_v	σ'_v
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1



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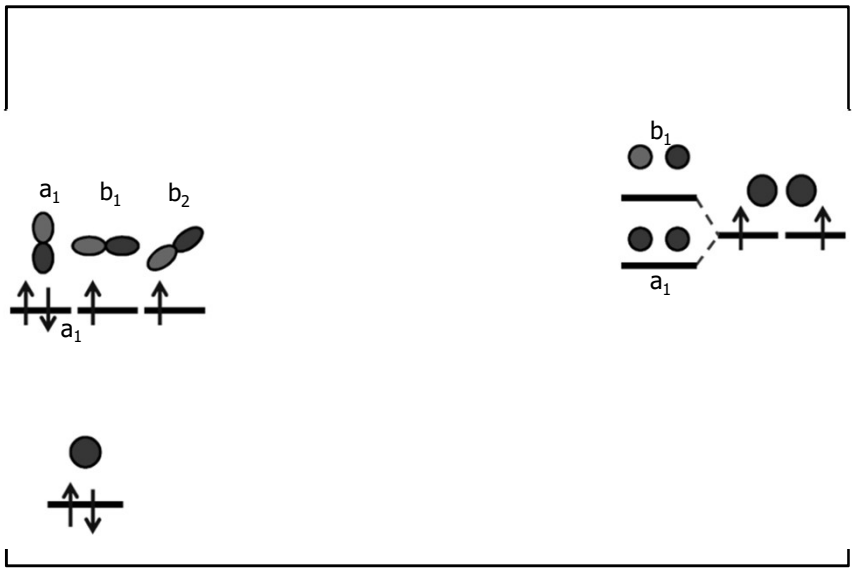
AO of H_2O



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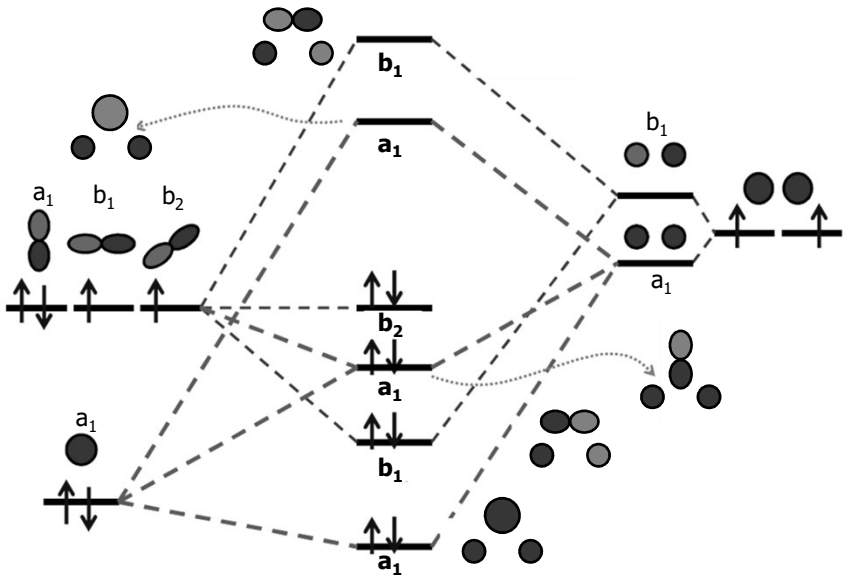
MO of H_2O



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Symmetry-adapted Linear Combinations

- Symmetry-adapted linear combination (SALC) are the building blocks of LCAO-MO
- To construct the SALC from basis:
  1. Construct a table showing the effect of each operation on each orbtial of the original basis.
  2. To generate the combination of a specified symmetry species, take each column in turn and:
     a) Multiply each member of the column by the character of the corresponding operation.
     b) Add together all the orbitals in each column with the factors as determined in a).
     c) Divide the sum by the order of the group.

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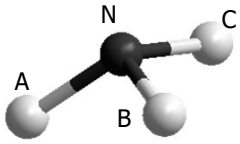
Example of building SALC

- s-orbitals of NH_3
  - Original basis are s_N, s_A, s_B, s_C

NH_3	Original basis			
	s_N	s_A	s_B	s_C
E	s_N	s_A	s_B	s_C
C_3^+	s_N	s_B	s_C	s_A
C_3^-	s_N	s_C	s_A	s_B
σ_v	s_N	s_A	s_C	s_B
σ_v'	s_N	s_B	s_A	s_C
σ_v''	s_N	s_C	s_B	s_A

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0



For A_1 combination (1,1,1,1,1,1)

$$\psi_1 = \tfrac{1}{6}\left(s_N + s_N + \ldots s_N\right) = s_N$$

$$\psi_2 = \psi_3 = \psi_4 = \tfrac{1}{6}\left(s_A + s_B + s_C + s_A + s_B + s_C\right) = \tfrac{1}{3}\left(s_A + s_B + s_C\right)$$

$$\Psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 = c_N s_N + c_H s_H$$

when $s_H = \left(s_A + s_B + s_C\right)$

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