Inorganic Chemistry - II

Subject code :. MCH0201

Semester :- IInd

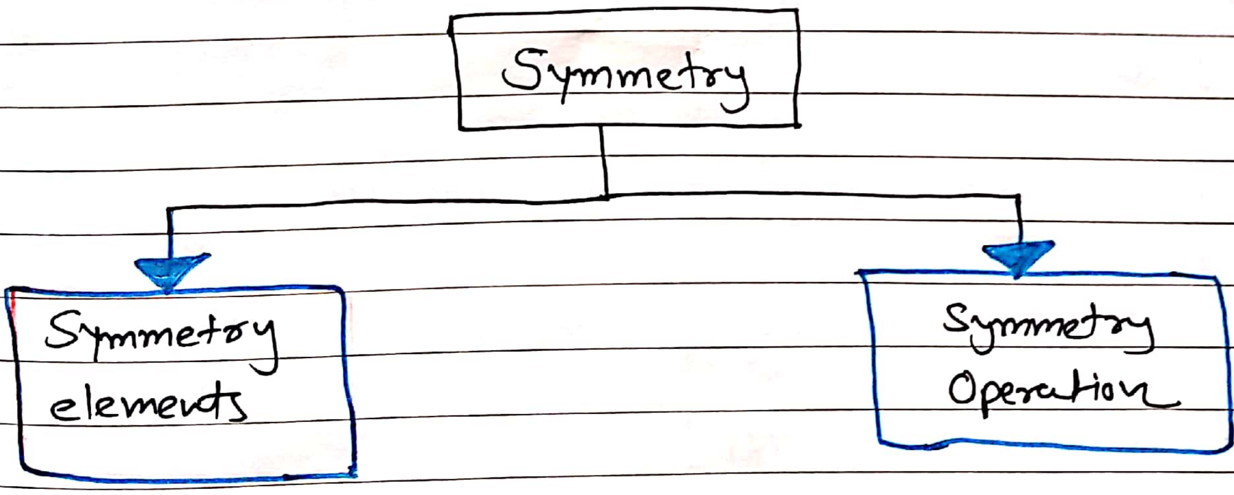
Unit - 2 - Symmetry & group theory

* Introduction :-

- Group theory is a mathematical method by which aspects of a molecule give the information about its property, like spectra, structure, polarity, symmetry.

- Most of molecules are symmetrical molecule.

→



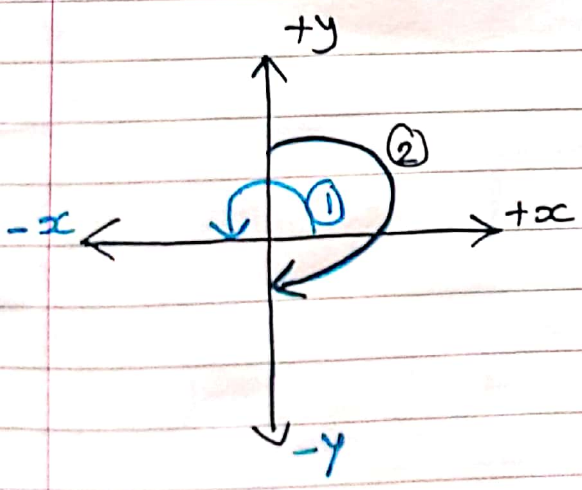
Symmetry Elements

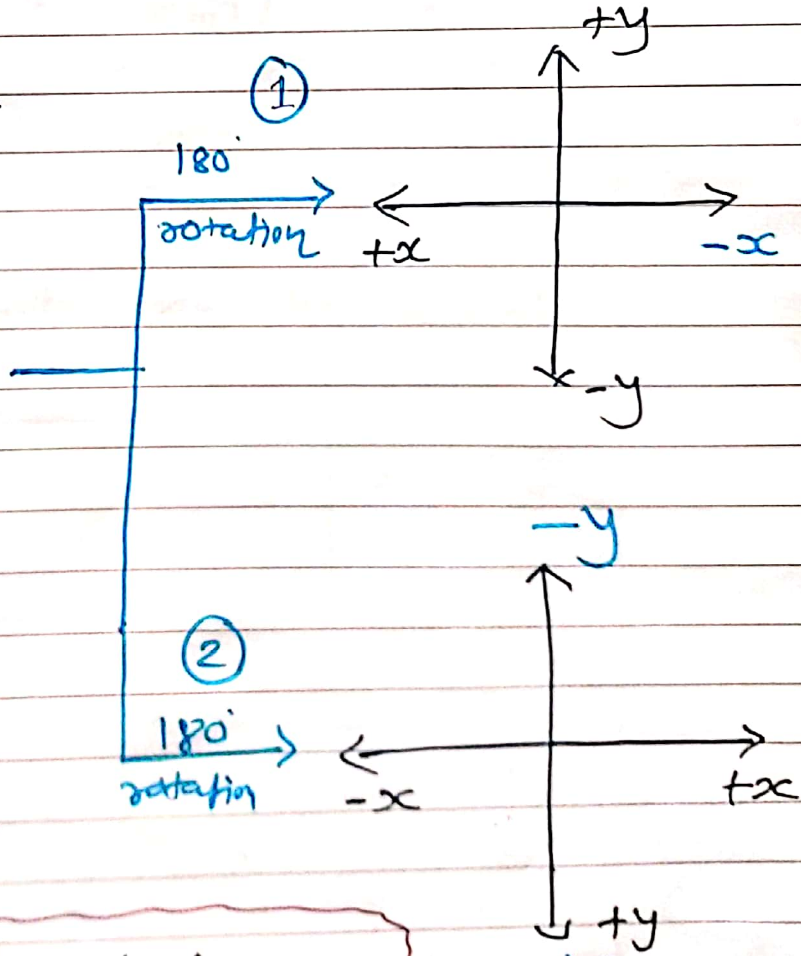
"A line, plane or a point in or through a molecule about which a symmetry operation is performed is called **symmetry element**."

OR

"These are the geometrical elements like line, plane with respect to which one or more symmetric operations are carried out."

→ 2-D Rotation

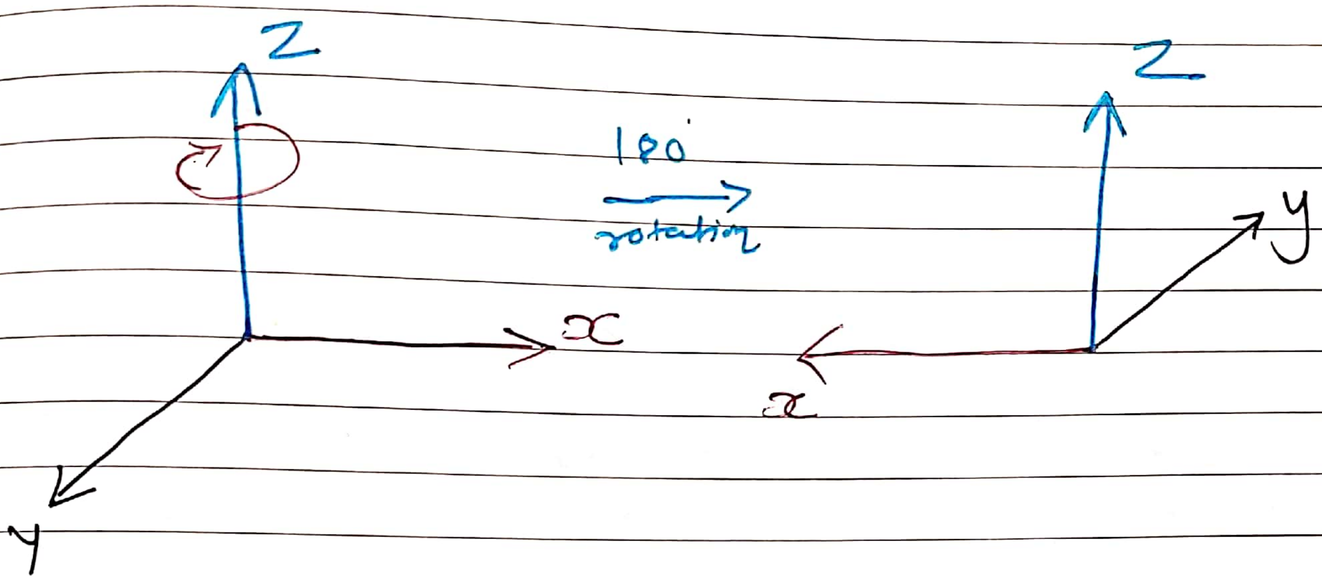




Horizontal axis → Vertical axis

Vertical axis → Horizontal axis

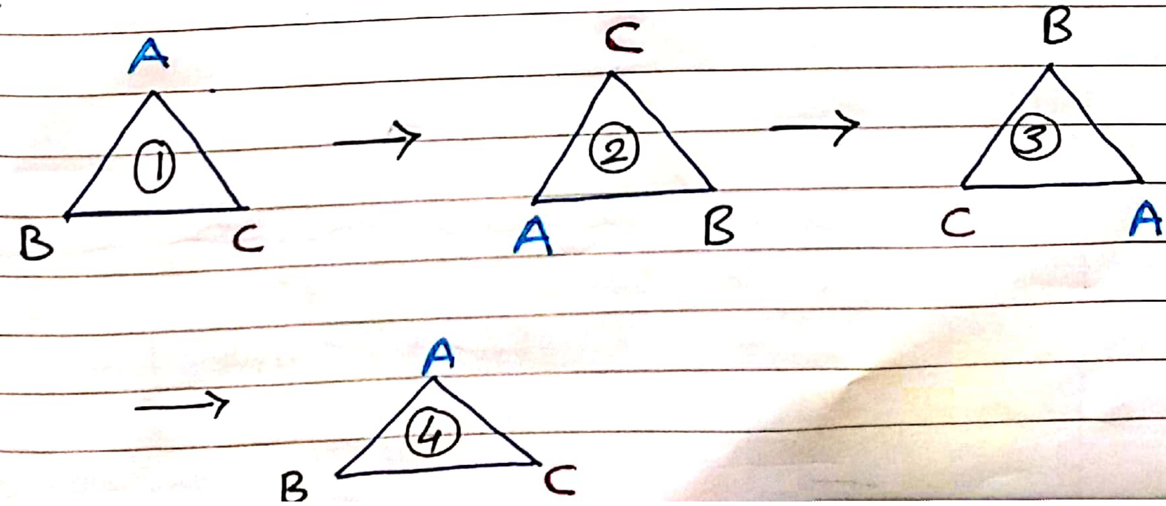
3-D Rotation :-



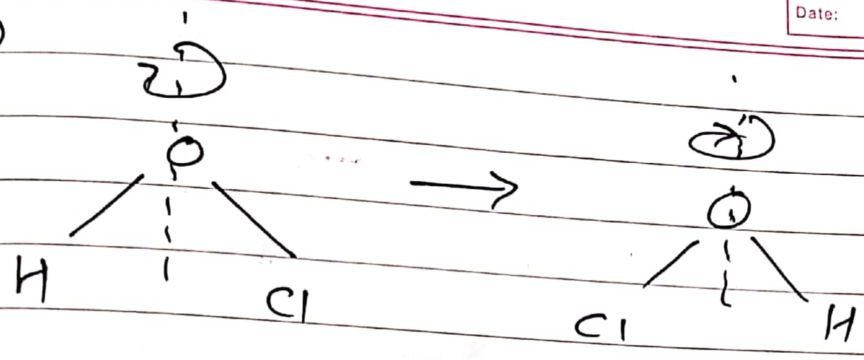
Left axis → Right axis
Front axis → Back axis

- Symmetry elements can be described by following terms.

① **Identity (E)**



e.g. (2)



- This is not Equivalent configuration because Cl atom take place the position of H atom.

(2) Axis of Symmetry (C_n)

→ An axis around which a rotation by $360/n$ results in a molecule indistinguishable from the original molecule.

→ This is also called n fold rotational axis & denoted as "C_n".

$$n = \frac{360^\circ}{\theta}$$

n = order of axis
θ = Angel of rotation

→ The imaginary axis will be passed by symmetrically.

→ Examples are C_2 in H_2O & C_3 in NH_3.

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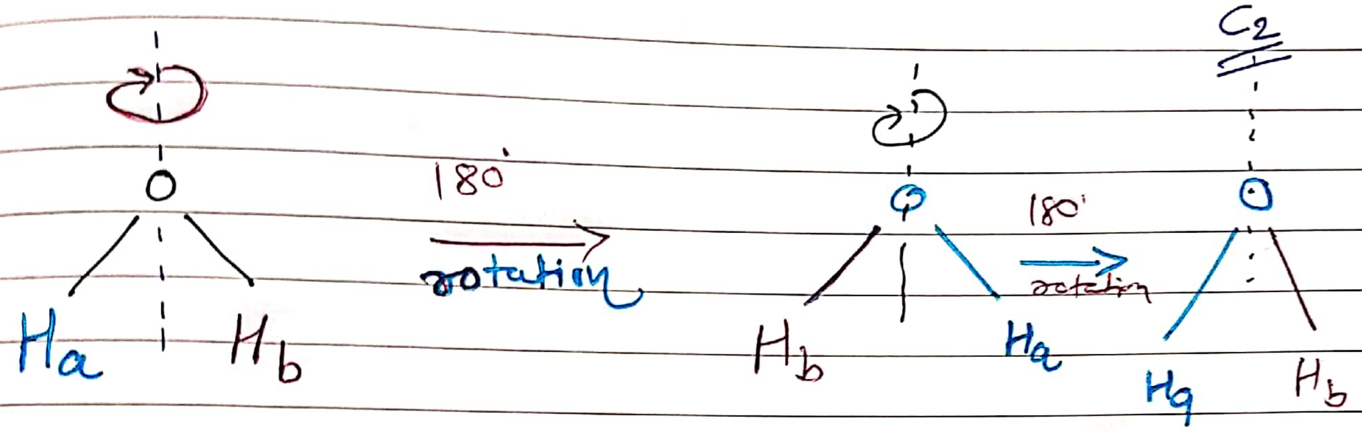
- A molecule can have more than one symmetry, the one with $\boxed{\text{highest } n}$ is called principal axis.

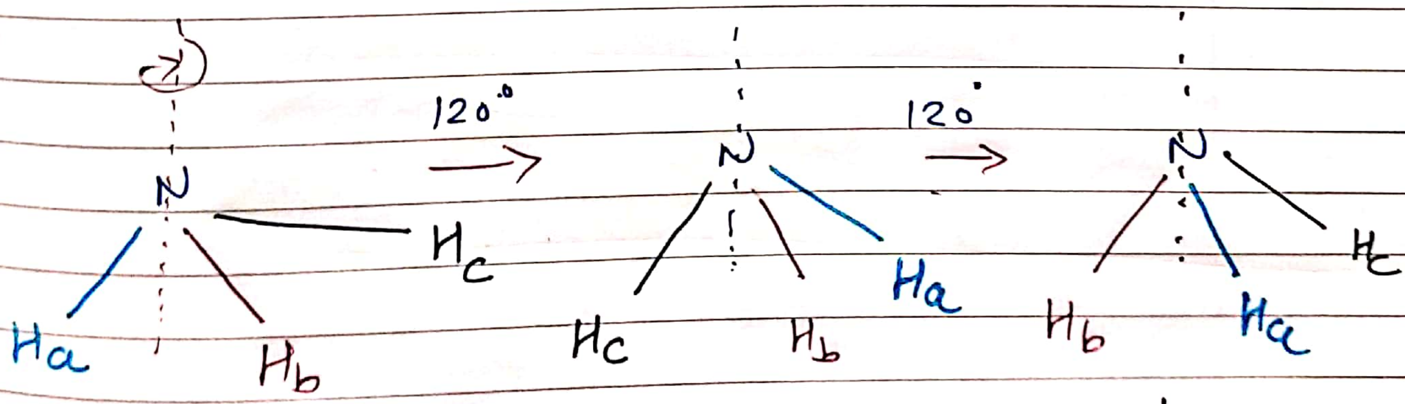
- E.g. ① H_2O molecule:



$$\therefore n = \frac{360}{\theta} = \frac{360}{180} = 2$$

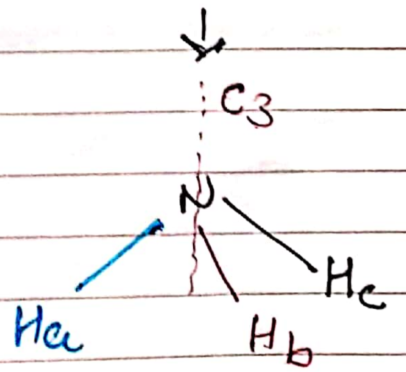
$\therefore C_n = C_2$ axis symmetry.

② NH_3 molecule



$$\therefore n = \frac{360}{\theta} = \frac{360}{120} = 3$$

$\boxed{\therefore C_3 \text{ axis symmetry}}$



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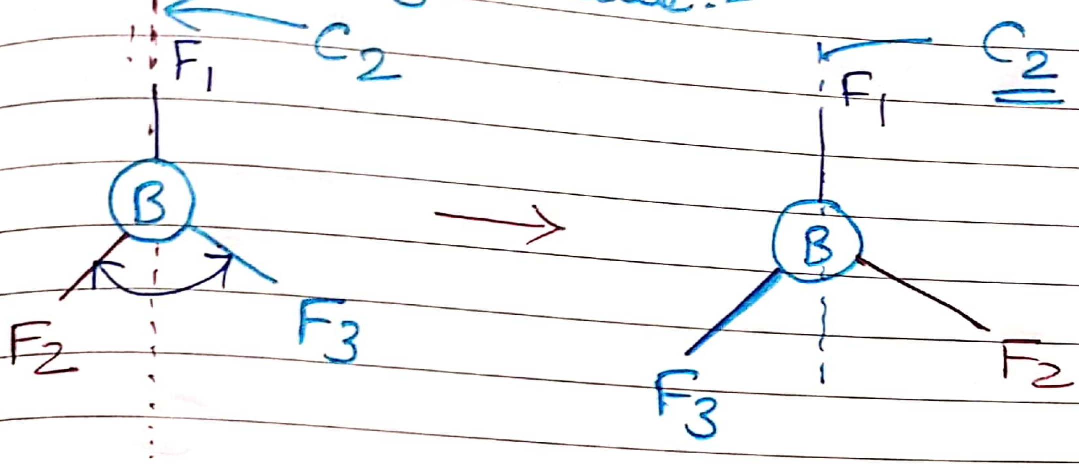
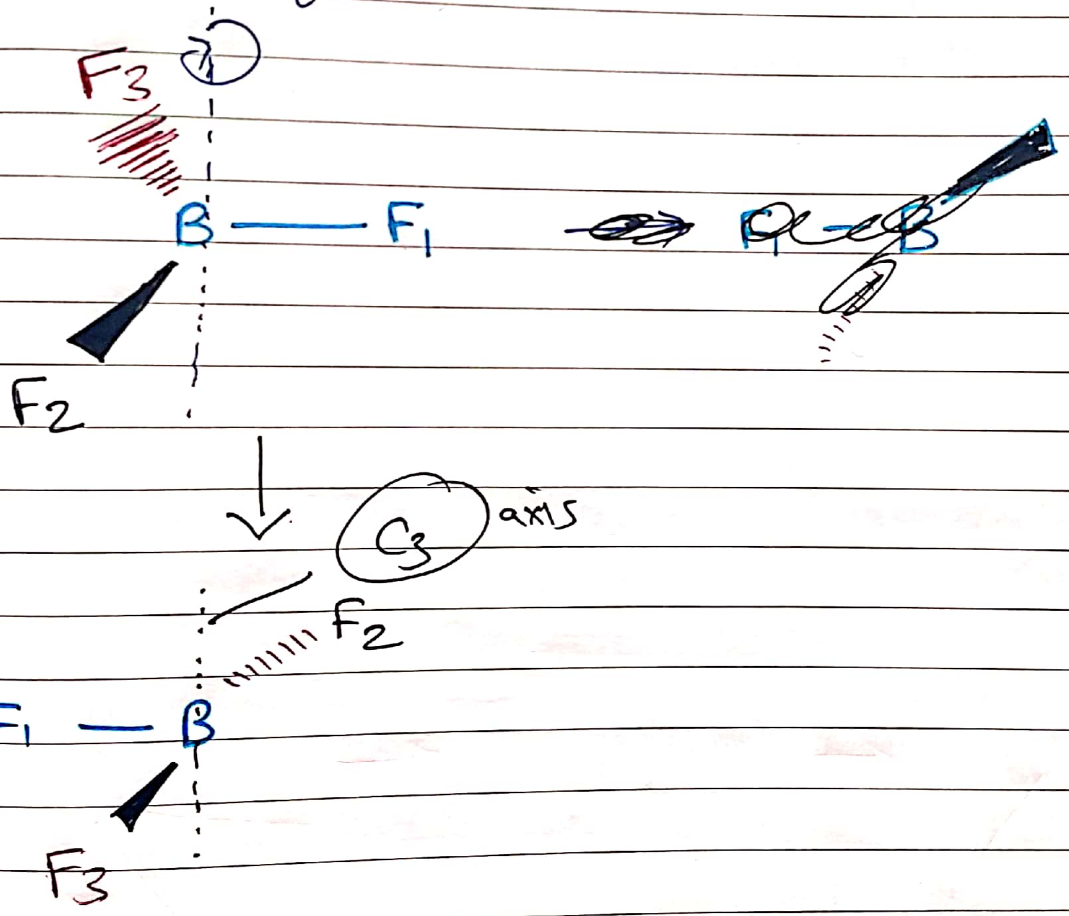
③ In BF_3 molecule:-



- If we assume a molecule in 3 dimension.



- In short, no of atoms rotate around the axis is term as n.

- In H_2O molecule, two atoms (H_a & H_b) are rotate around the axis i.e. C_2 Symmetry.

- In NH_3 molecule, three hydrogen atoms are rotate around the axis i.e. C_3 symmetry.

- In BF_3, molecule, there are two symmetry possible. In C_2 symmetry, F_1 molecule is fixed and F_2, F_3 is rotate around the axis.

- In BF_3, the axis is passed through Boron atom; therefore three florine atom will rotate around the axis. i.e. C_3 symmetry.

- C_3 is the principal axis & C_2 is the subsidiary axis.

Symbol of the proper rotation axis	Order of rotation axis	$360^\circ/n$
C_2	2	180°
C_3	3	120°
C_4	4	90°
C_5	5	72°
C_6	6	60°

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3. Plane of symmetry (σ)

→ Imaginary plane which bisects the molecule in two equal halves, in such a way that each half of the molecule is a mirror image of other half.

→ This is given the symbol "σ"

→ The elements generate only one operation that of reflection in the plane.

→ $\sigma^2 = E$; the identity, because reflection in a plane followed by reflection back again, returns all point to the position from which they started. i.e. Identical.

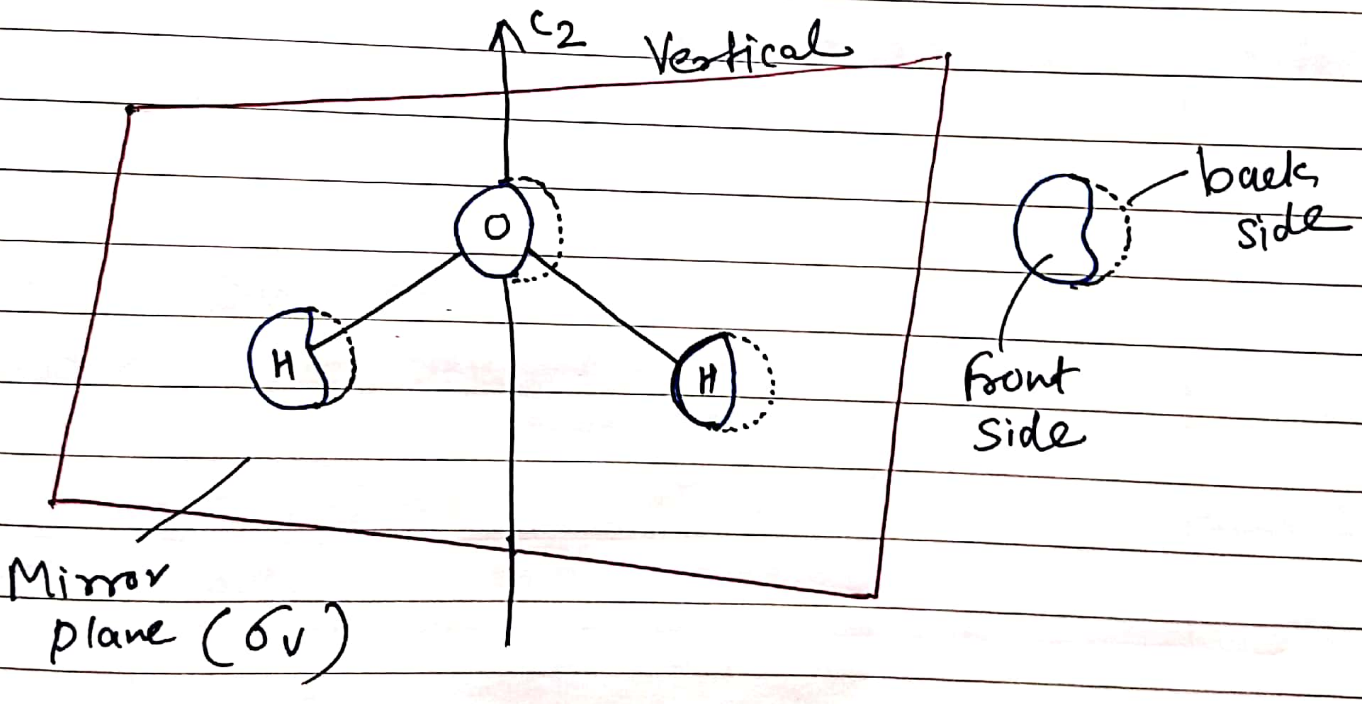
→ Water has two of them; one in the plane of molecule itself and one perpendicular to it.

→ A symmetry plane parallel with the principal axis is dubbed vertical (σ_v). and one perpendicular to it horizontal (σ_h) or (σ_v').

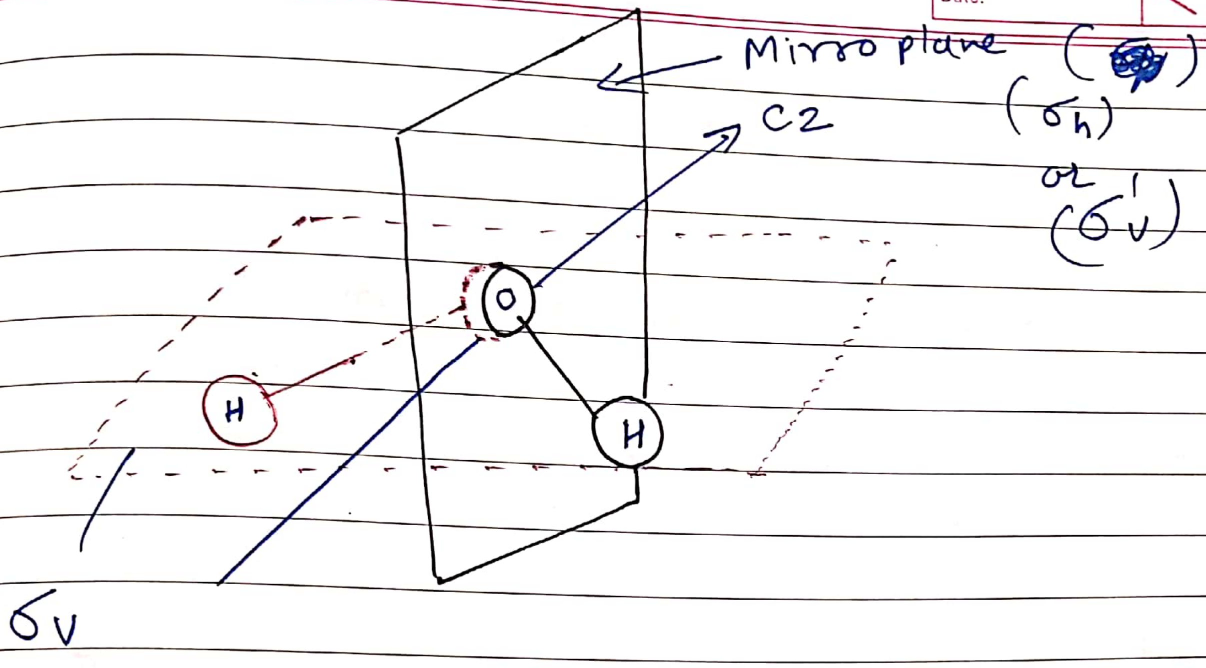
→ A third type of symmetry plane exists: if a vertical symmetry plane additionally bisects the angle between two fold rotation axes perpendicular to the principle axis, the plane is dubbed dihedral (σ_d).

→ A symmetry plane can also be identified by Cartesian orientation, e.g. (xz) or (yz).

→ Eg. <u>H_2O molecule</u>



[The mirror plane of symmetry in the molecular plane ~~should~~ of H_2O molecule. The plane should be thought of as infinitely thin & serving to reflect one 'side' of the molecule into the other.]

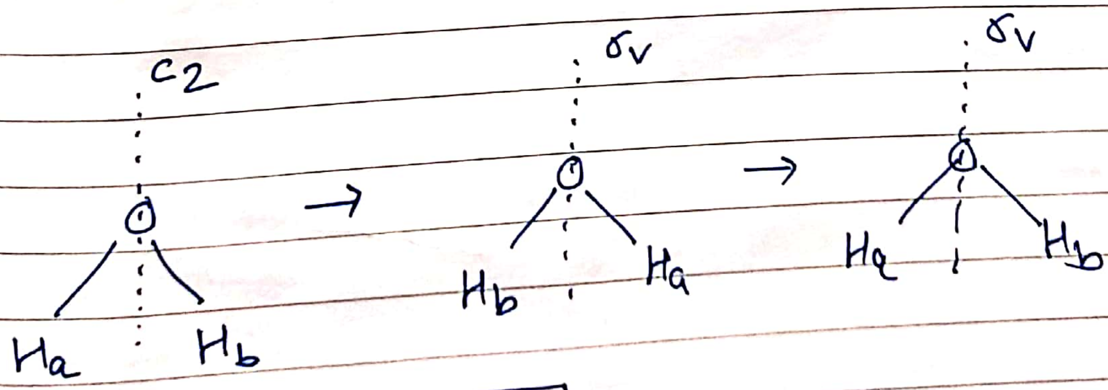


[A second mirror plane of symmetry, perpendicular to the first, in the H_2O molecule. The line of intersection of the two mirror planes is the twofold rotation axis.]

Here σv can be calculated by using symmetry of axis (C_n).

In H_2O molecule, C_2 is present, therefore $2\sigma_v$ will be present.

e.g.



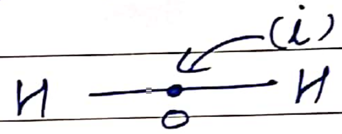
$\therefore$ $\boxed{C_2 = 2\sigma_v}$

4. Center of symmetry or Inversion Centre (i)

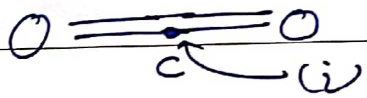
- A molecule has a center of symmetry when, for any atom in the molecule, an imaginary point exists, diametrically opposite this centre an equal distance from it.

- It is denoted as "i".

- e.g. H_2O :-

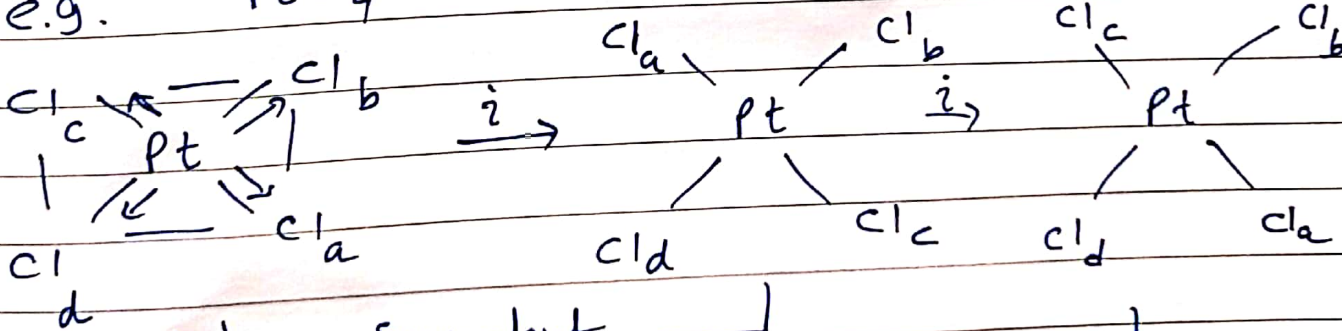


CO_2 :-



- The atom must be same in opposite direction.

- e.g. $PtCl_4$



Equivalent

Identical (E)

$\therefore$ $\boxed{2i = E}$

5. Improper rotation axis (S_n)

"

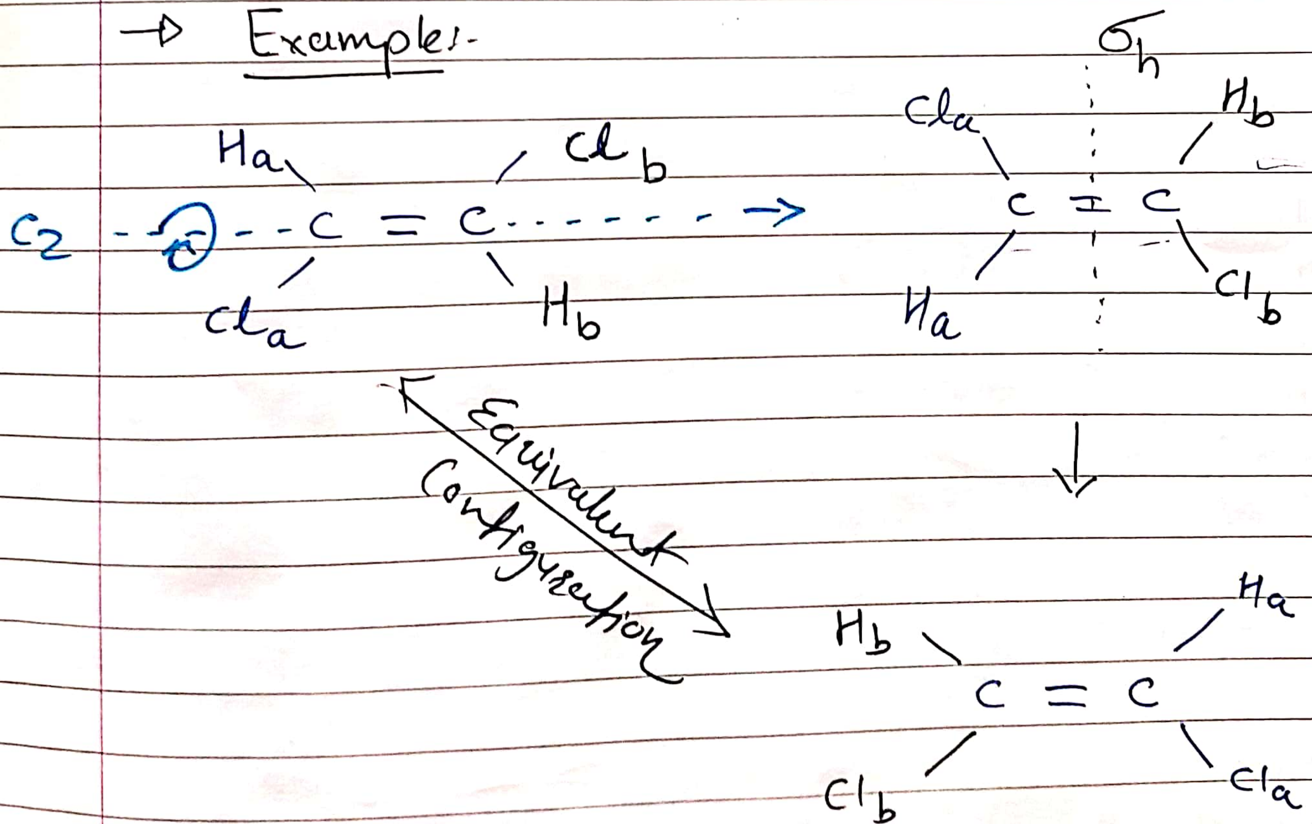
- An axis around which a rotation by a reflection in a plane perpendicular to it, leave the molecule unchanged.

- It is also called as an n-fold improper rotation axis.

- ~~Example~~: It is denoted as S_n.

- $\boxed{\therefore \quad S_n = \sigma_h \cdot C_n}$

- Example:-



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* Symmetry Operations :-

① ⟹ "A molecule or object is said to posses a particular operation if that operation when applied leaves the molecule unchanged.

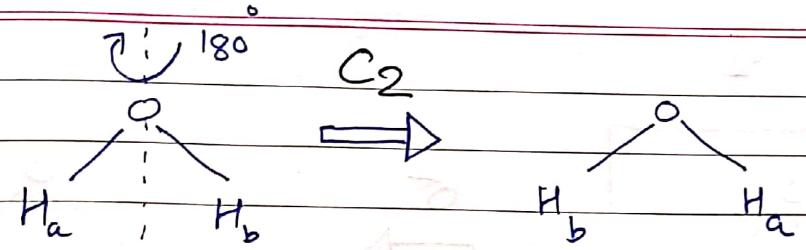
⟹ There are 5 kinds of operations :-

① Identity (E)

- Does nothing, has no effect.
- i.e. this operation brings back the molecule to the original orientation.
- All molecule posses the identity operation.

② n - Fold Rotations :- (C_n)

- C_n, where n is an integer, rotation by $360°/n$ about a particular axis defined as the n- fold rotation axis.
- $C_2 = 180°$, $C_3 = 120°$, $C_4 = 90°$ rotations.
- Rotation of H_2O about the axis shown by $180°$ (C_2) gives the same molecule back.
- Therefore, H_2O posses the C_2 symmetry element.



③ Reflection : (σ)

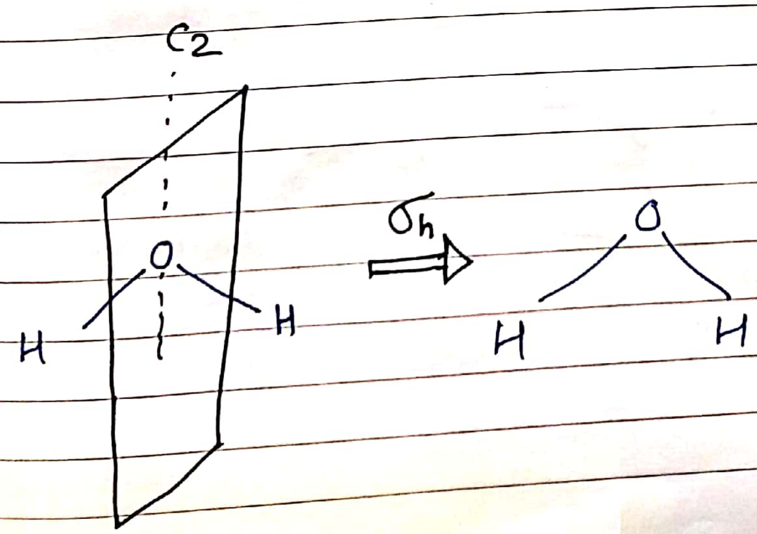
- If reflection about a mirror plane gives the same molecule / object back than there is a plane of symmetry. (σ)

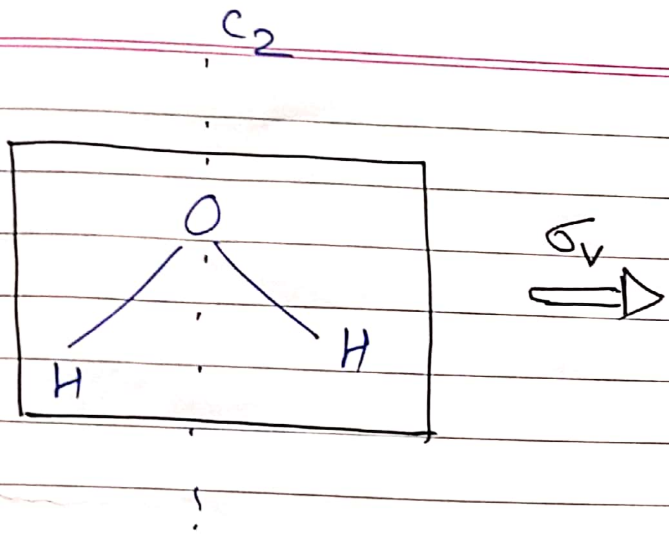
- If plane contains the principle rotation axis (i.e. parallel); it is a vertical plane (σ_v).

- If plane is $\boxed{\text{perpendicular}}$ to the principle rotation axis, it is a horizontal plane (σ_h).

- If plane is parallel to the principle rotation axis, but $\boxed{\text{bisects}}$ angle between $2C_2$ axes, it is a diagonal plane. (σ_d)

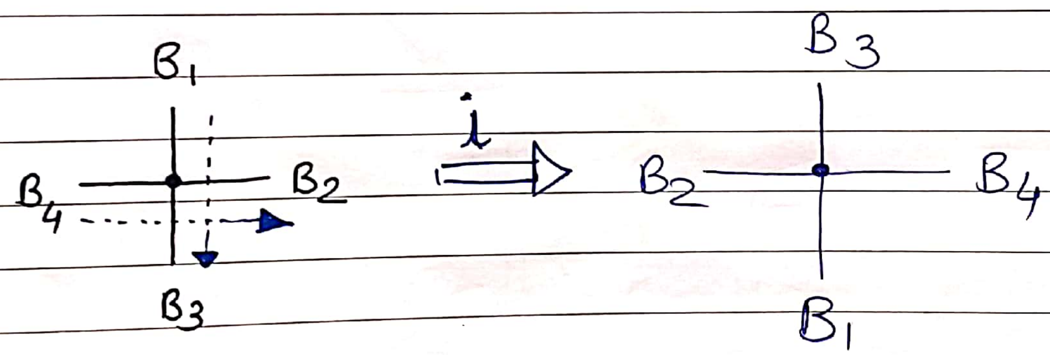
- H_2O posses 2 σ_v mirror plane of symmetry because they are both parallel to the principal rotation axis. (C_2)





[4] Inversion (i)

- The operation is to move every atom in the molecule in a straight line through the inversion centre to the opposite side of the molecule.

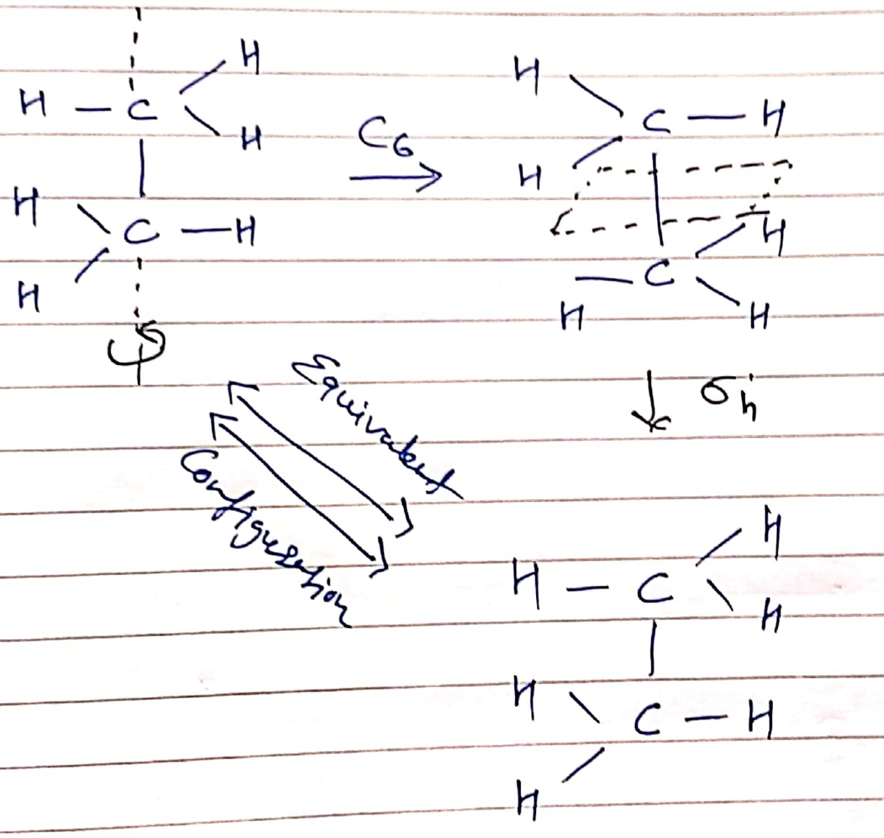


[5] Improper Rotation (S_n)

- n fold rotation followed by reflection through mirror plane perpendicular to the rotation axis also known as the Rotation Reflection axis.

- It is an imaginary axes passing through the molecule, on which when the molecule is rotated by $2\pi/n$ angle & then reflected on a plane perpendicular to the rotation axis then an equivalent orientation is observed.

- ~~Note~~:- example:- straggered ethane



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* Representation of Matrices of point group.

→ It is the arrangement of elements represented as U_{ij};

i.e. i → Row
j → Column

$$U = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \cdots & a_{3n} \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{bmatrix}_{m \times n}$$

← Row

Column —

⇒ Types of Matrix :-

① Raw Matrix

- "A matrix which has only one row. called the row matrix."

- Example :- $\begin{bmatrix} 1 & 2 & 3 \end{bmatrix}_{1 \times 3}$

② Column Matrix

- "A matrix which has only one column called column matrix."

- Example :- $\begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}_{3 \times 1}$

[3] <u>Square Matrix</u>

→ "If the number of column and number of row are same is called square matrix."

→ <u>Example:-</u>

$$\begin{bmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{bmatrix}_{3\times3}.$$

[4] <u>Null Matrix</u>

→ "If the all the elements are zero is called null matrix."

→ Example :-

$$\begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}_{2\times2}$$

[5] <u>Unit Matrix</u>

→ " ~~The diagonal element Uij are all equal to 1 and all other numbers~~

→ "The diagonal elements are equal to 1 and off diagonal elements are zero is called Unit Matrix."

→ e.g.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}_{3\times3}$$

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[6] Scallar Matrix :-

→ " A diagonal matrix in which all the elements are main diagonal is same called scallar matrix."

→ Example :

$$\begin{bmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{bmatrix}_{3\times 3}$$

[7] Transpose Matrix :-

→ " A matrix obtained by interchanging the rows & column of a matrix is called "Transpose Matrix".

→ It is denoted by A^T.

→

$$\therefore A = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}_{3\times 3}$$

$$\therefore A^T = \begin{bmatrix} 1 & 4 & 7 \\ 2 & 5 & 8 \\ 3 & 6 & 9 \end{bmatrix}_{3\times 3}.$$

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☆ Multiplication of Matrix :-

→ "Mutiplication of matrices A_{ij} & B_{ij} is possible when no. of column of A is equal to no. of row of B."

→ e.g.

$$A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}, \quad B = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}$$

$$A \times B = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \times \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}$$

$$= \begin{bmatrix} a_{11} \cdot b_{11} + a_{12} \cdot b_{21} & a_{11} \cdot b_{12} + a_{12} \cdot b_{22} \\ a_{21} \cdot b_{11} + a_{22} \cdot b_{21} & a_{21} \cdot b_{12} + a_{22} \cdot b_{22} \end{bmatrix}$$

e.g. $A = \begin{bmatrix} -1 & 4 \\ 2 & 3 \end{bmatrix}, \quad B = \begin{bmatrix} 9 & -3 \\ 6 & 1 \end{bmatrix}$

$$\therefore A \times B = \begin{bmatrix} -1 & 4 \\ 2 & 3 \end{bmatrix} \times \begin{bmatrix} 9 & -3 \\ 6 & 1 \end{bmatrix}$$

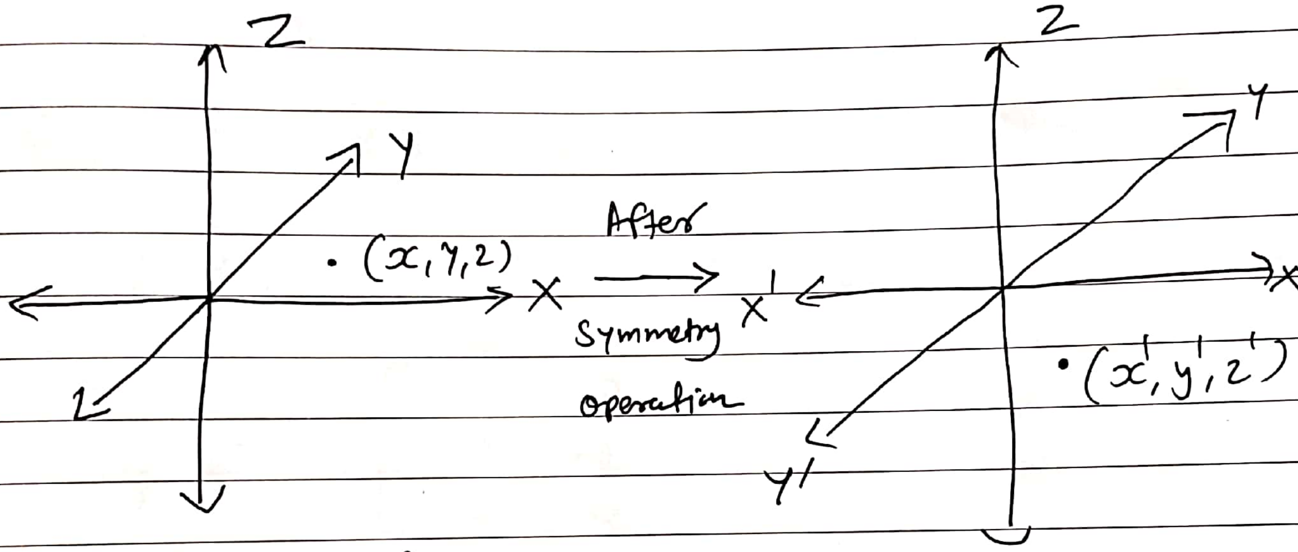
$$= \begin{bmatrix} (-1) \times 9 + 4(6) & (-1)(-3) + 4(1) \\ 2 \times 9 + 3(6) & 2(-3) + 3(1) \end{bmatrix}$$

$$= \begin{bmatrix} -9 + 24 & 3 + 4 \\ 18 + 18 & -6 + 3 \end{bmatrix} = \begin{bmatrix} 15 & 7 \\ 36 & -3 \end{bmatrix}$$

* Matrix representation of symmetry elements. *

[1] Identity (E)

- Represented as unit matrix



(old position)

Z'

(New position)

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

[2] Reflection through a plane.

- In XY plane
  (xyz ⟶ x y -z)

$$\sigma_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

→ In YZ plane

[XYZ → −X Y Z]

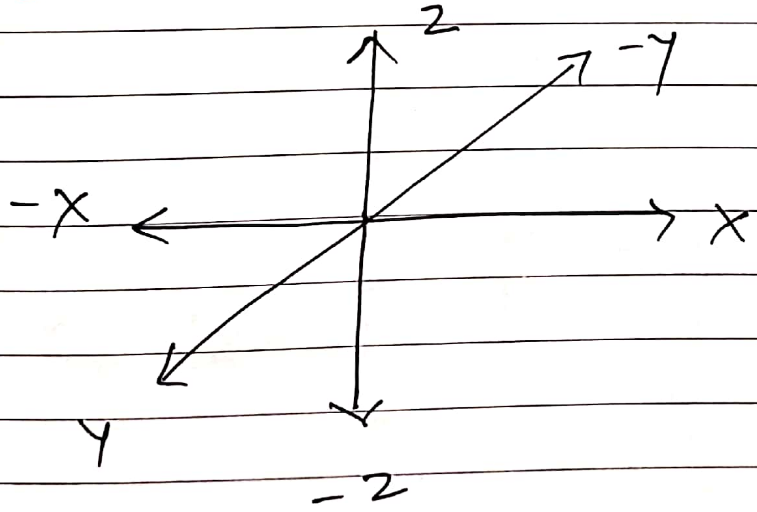
$$\sigma_x = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

→ In XZ plane

[XYZ → X −Y Z]

$$\sigma_y = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

[3] Inversion (i)

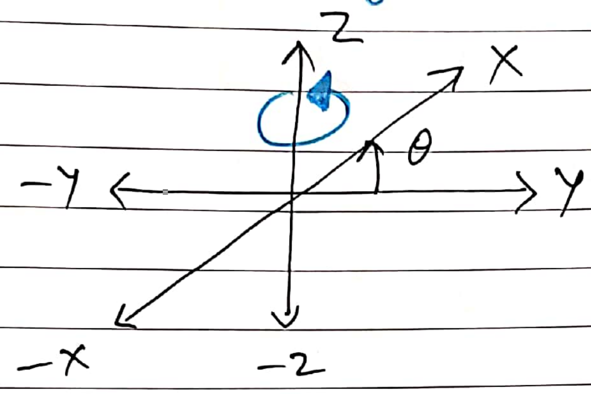


$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \xrightarrow{i} \begin{bmatrix} -X \\ -Y \\ -Z \end{bmatrix}$$

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

[4] Rotation through n-fold axis

→



$$\theta = \frac{2\pi}{n}$$

- Rotation along z-axis

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} \longrightarrow \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

- C_n (z-axis) $= \begin{bmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & 1 \end{bmatrix}$

For $C_{2_{(2)}}$ axis $\Rightarrow \theta = \frac{2\pi}{n} = \frac{2 \times 180}{2} = 180^\circ$

$$= \begin{bmatrix} \cos 180^\circ & \sin 180^\circ & 0 \\ -\sin 180^\circ & \cos 180^\circ & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_{2(z)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Similarly,

$$C_{2(x)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_{2(y)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

[Write positive integer through which rotation take place through axis]

[5] Rotation Reflection axis (S_n)

$$S_n(z) = \sigma_z \cdot C_n(z).$$

$$S_n(z) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

* Point Groups

→ Each point group is a collection of all the symmetry operations that can be carried out on a molecule belonging to that group.

→ • Identity (E) :- Found in all molecule

• Inversion (i) :- Centre of symmetry

• Rotation (C_n) :- Axis of symmetry

• Reflection (σ) :- Plane of symmetry

• Improper axis of rotation ( ) :- (S_n)

:- Rotation followed by reflection in a plane perpendicular to that axis.

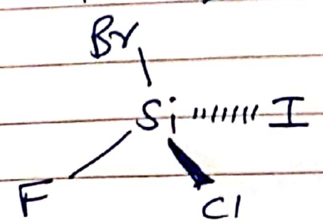
⇒ Various point groups :-

[1] Very low Symmetry point group :-

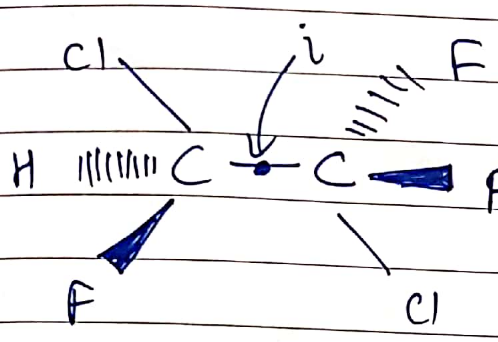
{ C_1, C_i, C_s }

→ "Does not passes axis of symmetry."

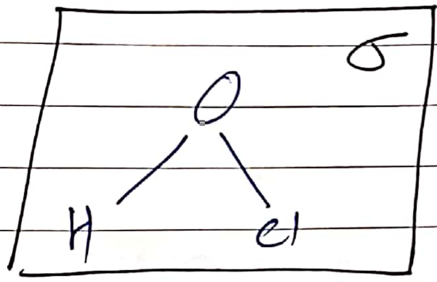
→ e.g. C_1 → Only E



→ C_i → Only E, i



→ C_s → Only E & σ.

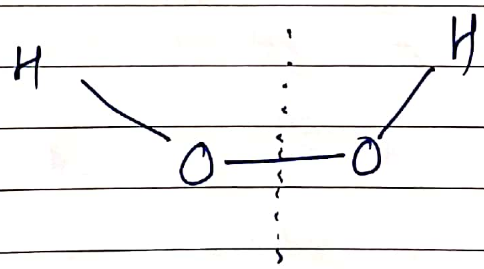


[2] Cyclic Group (C_n)

→ "Having one n-fold axis of symmetry"

→ $C_n \Rightarrow E, C_n$

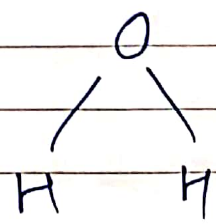
C_2 →



⇒ * C_{nv} group. ($E, C_n, n\sigma_v$)

" n. vertical plane through axis "

C_{2v} → ex. SO_2Cl_2 →



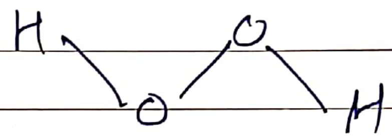
$C_{3v} \rightarrow NH_3, PCl_3, POCl_3, CH_3Cl.$

$C_{4v} \rightarrow IF_5.$

$\Rightarrow$ C_{nh} group. $[E, C_n, \sigma_h]$

[One horizontal plane perpendicular to C_n axis]

$C_{2h} \Rightarrow$

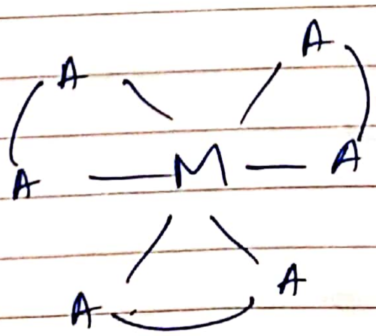


[3] Dihedral Groups (D) (E, C_n, nC_2)

- If there is one n-fold axis and n-2 fold axis perpendicular to C_n at equal angle to each other.

- * $D_n \longrightarrow E, C_n, nC_2$

- e.g. $D_3 \rightarrow M(AA)_3$

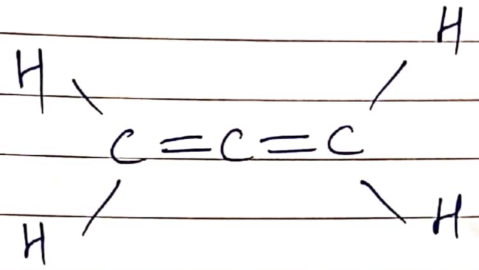


- * **Dnd** : (E, C_n, nC_2, $n\sigma_v$)

n - vertical plane.

e.g. D_{5d} → Ferrocene

D_{2d} →



- * D_{nh} (E, C_n, nC_2, $n\sigma_v$, σ_h, S_n)

e.g.

D_{2h} → N_2O_4

D_{3h} → BCl_3, PCl_5

D_{4h} → $[PtCl_4]^{-2}$

[4] Linear Group:

→ * $C_{\infty v}$ → [Unsymmetrical linear molecule]

[E, C_∞, ∞C_v]

e.g. I - Cl , ----C = O---- C_∞

→ * $D_{\infty h}$ → [Symmetrical linear molecules]

$[E, C_\infty, \infty C_v, \infty C_2, \sigma_h, S_\infty]$

e.g. $N \equiv N$, $H-H$, $O=C=O$ C_∞

C_2 axis

[5] Very High Symmetry Groups :-

(I_h, O_h, T_d)

- "When molecule passes two or more n fold axis $(n > 2)$"

→ * T_d (Tetrahedral)

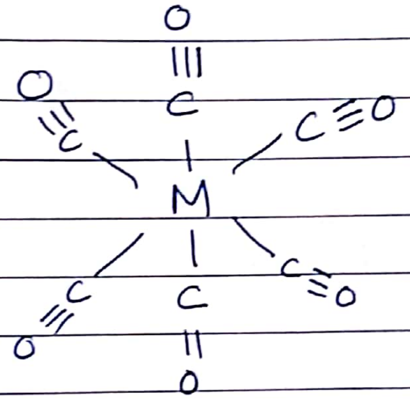
" Three C_2 axis perpendicular to each other $(3C_2)$, four 3-fold axis $(4C_3)$, six σ_d, three S_4

e.g. CH_4 , $SiCl_4$, NH_4^+

→ * Octahedral (O_h)

" 3 C_4 axis perpendicular to each other and four 3-fold axis ($4C_3$) and one point of inversion (i) "

e.g. $M(CO)_6$



→ * Icosahedral (I_h)

" Besides this, it also passes a C_5 axis "

ex :- C_{60} (fullerene).

* Group Postulates :-

- A complete set of operation is called group.

- For H_2O molecule, C_{2v} → $E, C_2, \sigma_{xz}, \sigma_{yz}$ are present

⇒ Crieteria for group

[1] Identity operation must be member of group which commutes with all the elements and leave them unchanged.

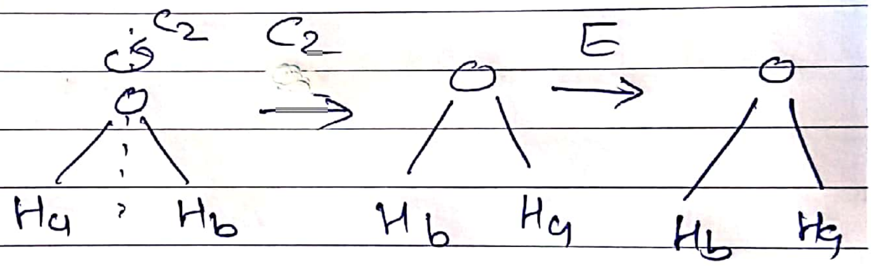
$$\therefore \boxed{E \cdot A = A \cdot E = A.}$$

E : Identity, A : Other operation

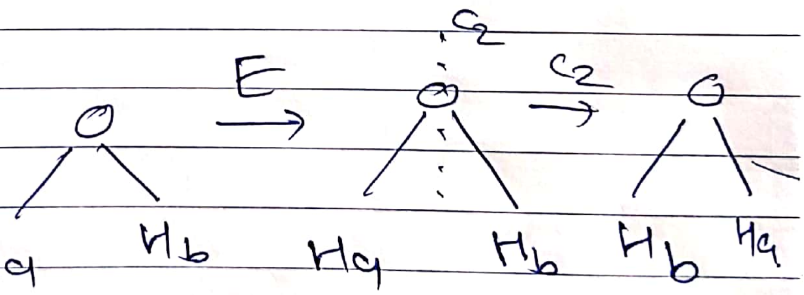
$\therefore$ e.g. $E \cdot C_2 = C_2 \cdot E = C_2$

⇒ For H_2O molecule

• $C_2 \cdot E$:



• $E \cdot C_2$:



$$\therefore \boxed{E \cdot C_2 = C_2 \cdot E = C_2}$$

[2] The inverse of each operation is also a member of group.

$$\boxed{\therefore A \cdot A^{-1} = A^{-1} \cdot A = E}$$

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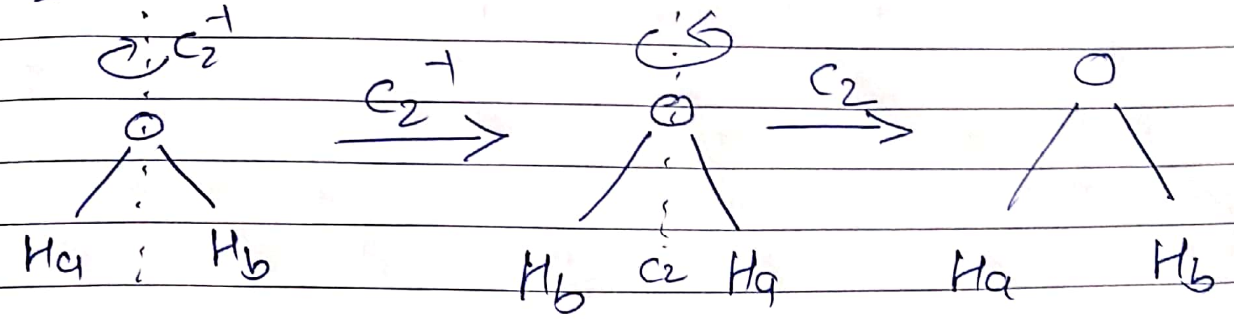
e.g. $C_2^{-1} \cdot C_2 = E.$

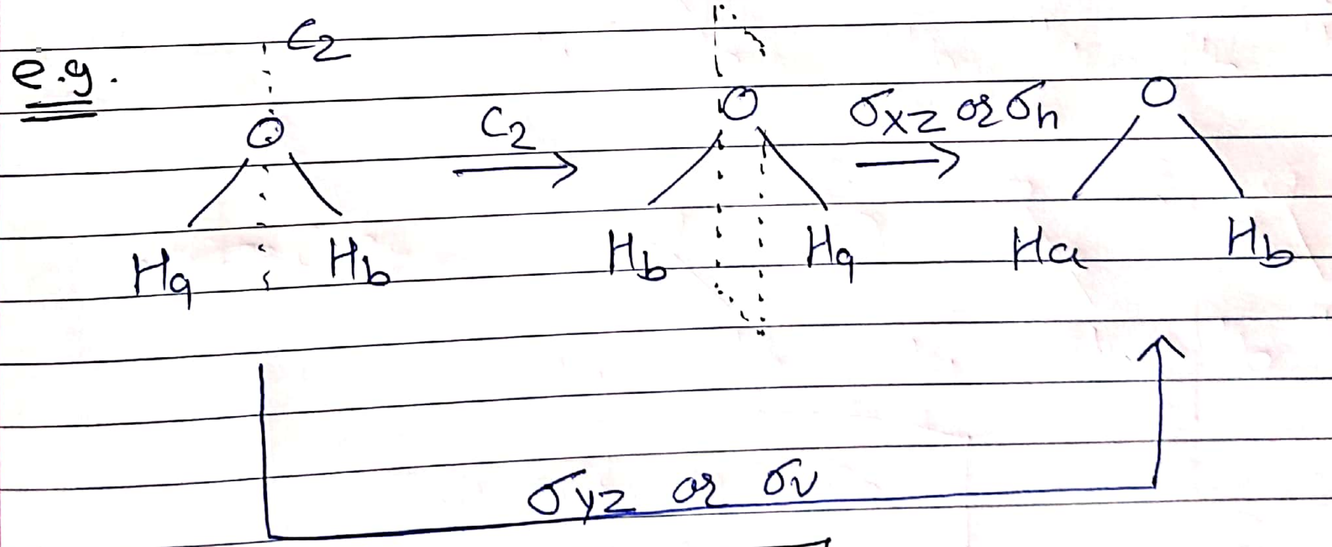


Anti clockwise   clockwise   E

[3] Two elements A & B of a group combines to give a third element C, which is also an element of the group.

$\therefore \boxed{AB = C}$ (if $AB = BA$ (Commutative))

e.g.

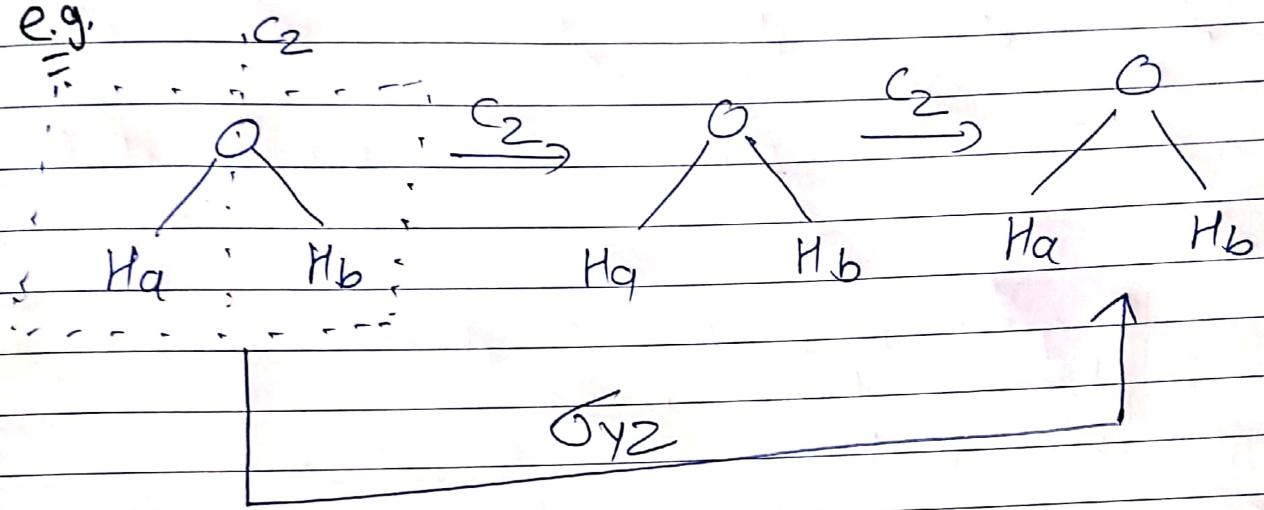


$\therefore \boxed{C_2 \cdot \sigma_{xz} = \sigma_{yz}}$

[4] An element combine with itself to form another element of the group.

$$\boxed{\therefore\ A \cdot A \rightarrow \text{Another Element}}$$

e.g.



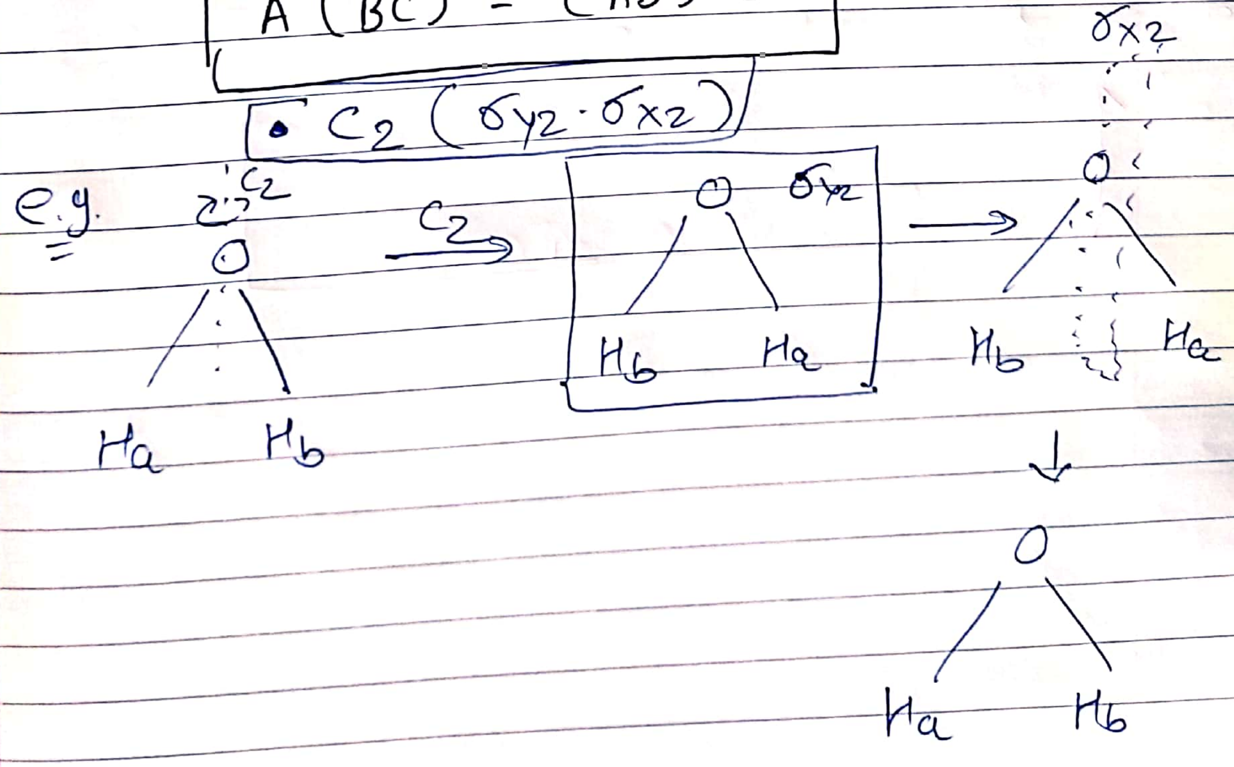
$$\boxed{\therefore\ C_2 \cdot C_2 = \sigma_{y2}}$$

[5] Every member of group obeys associative law of combination.

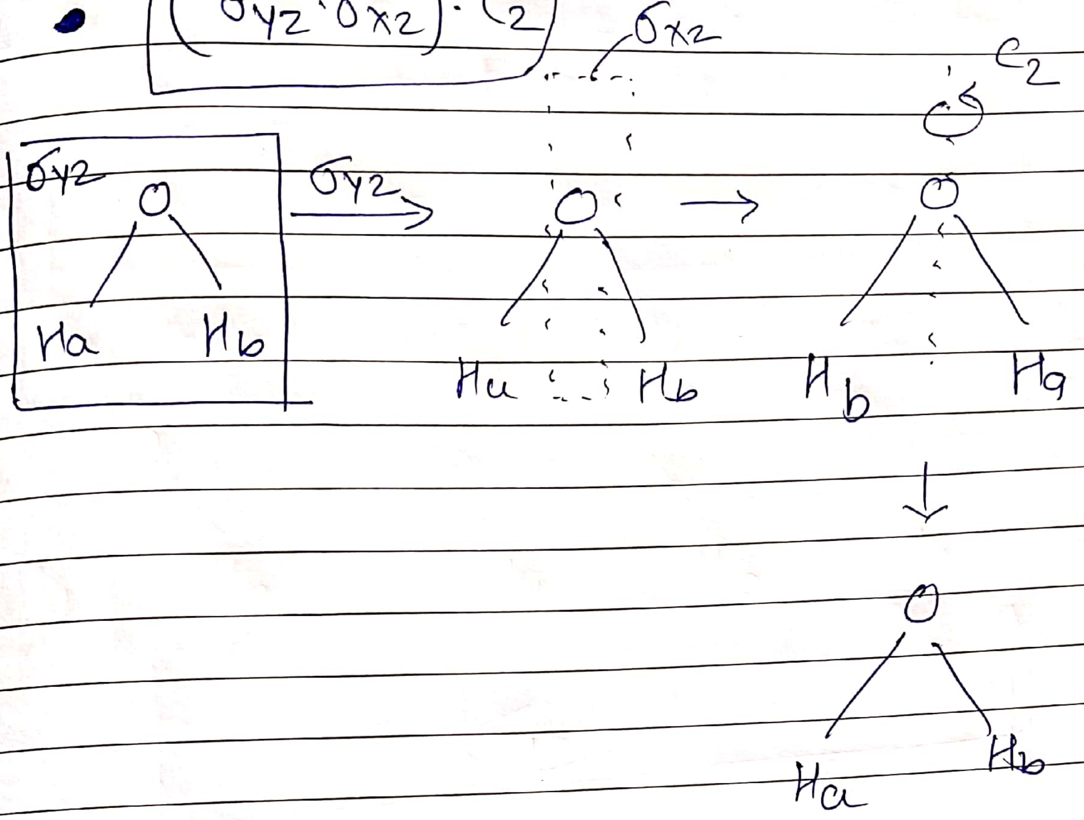
$$\boxed{A(BC) = (AB) \cdot C}$$

• $C_2(\sigma_{y2} \cdot \sigma_{x2})$

e.g.



• $\boxed{(\sigma_{yz} \cdot \sigma_{xz}) \cdot C_2}$



* <u>Representation</u>

→ "Representation is a set of matrices which represents the operation of a point group."

→ It can be classified in to two types.

1. Reducible Representation
2. Irreducible Representation

→ (1) <u>Reducible Representation</u>

→ A representation of higher dimension

which can be reduced to representation of lower dimensions is called reducible representation.

→ The reducible representation & its reduction can be understood by carrying out a similarity transformation.

→ Suppose A, B, C, D is a representation of a group in which [B] [C] = [D]. If only diagonal elements of the matrix is shown & similarity transformation is done

$$X^{-1} A X = A'$$
$$X^{-1} B X = B'$$
$$X^{-1} C X = C'$$
$$X^{-1} D X = D'$$

⇒ [2] Irreducible representation

→ Those representation which cannot be further reduced to representations of lower dimensitions are called irreducible representation.

→ "Irreducible represention is depends on the number of class present in particular point group."

→ e.g. In H_2O molecule, C_{2V} point group is present. In C_{2v}, four class (E, C_2, σ_{xz}, σ_{yz}) are present.

→ ∴ Therefore, In H_2O molecule four irreducible representation are possible.

Character (χ)-

→ Character is defined as the summation of upper left element to lower right element is called character.

→ It is denoted as χ.

→ e.g.

Upper left

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Lower right

$$\chi = 1 + 1 + 1 = 3.$$

⊛ Great Orthogonality Theorem [GOT]

→ This theorem is concerned with the elements of matrices constituting irreducible representation of a point group.

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The mathematical representation of GOT is

$$\sum_R \left[\Gamma_i(R)_{mn}\right]\left[\Gamma_j(R)_{m'n'}\right] = \frac{h}{\sqrt{L_i L_j}}\,\delta_{ij}\,\delta_{mm'}\,\delta_{nn'}$$

where,

h = Order of the group or class

i & j = Irreducible representation of group.

$L_i L_j$ = Dimensions of these two irreducible representation.

Γ_i = (Lamda i) i^{th} irreducible representation

R = Generic element of the group. It represents particular operation in the group.

$\Gamma_i(R)_{mn}$ = Matrix element at the intersection of the m^{th} row with n^{th} column of the matrix representing R in the i^{th} irreducible representation.

δ = Kornecker delta symbol.

i.e. $\delta_{ij} = 0$ for $i \neq j$,

$\delta_{ij} = 1$ for $i = j$.

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Rules for the irreducible representation & character table formation [GOT]

- **Rule :- 1**

→ The number of irreducible representation in a group is equal to no. of class present in the group.

e.g. For C_{2V} point group.

Point group

class

Irreducible Representation

C_{2V}	E	C_2	σ_{xz}	σ_{yz}
Γ_1				
Γ_2				
Γ_3				
Γ_4				

Character

- **Rule :- 2**

→ This rule is only applicable to identity (E) element. The sum of square of character (χ) in all the irreducible operations is equal to order (h).

$$\therefore \boxed{\sum_{i=1}^{K} [\chi_i(E)]^2 = h}$$

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- [illegible] : [illegible]

- The value of E should not be negative because there is no change in structure for identity operation.

- e.g

Γ_1	1
Γ_2	1
Γ_3	1
Γ_4	1

$$E = (1)^2 + (1)^2 + (1)^2 + (1)^2 = 4 = h$$

- **Rule - 3**

→ It is applied for particular character (Γ_1).

→ e.g.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1

→ The value of Γ_1 is calculated by addition of square of value of symmetry element and is equal to order (h).

→ $\therefore \Gamma_1 = (1)^2 + (1)^2 + (1)^2 + (1)^2$
$= 4$
$= h$

- Rule :- 4

→ "There are many number of character ($\Gamma_1, \Gamma_2, \Gamma_3 \dots$) are present in character table. Any two character are orthogonal with each other."

→ e.g. $\sum \chi_i(R) \cdot \chi_j(R) = 0$.

C_2

Γ_1 — χ_{1C_2} = ∴ $\chi_{1_{C_2}} \times \chi_{2_{C_2}} = 0$

Γ_2 — $\chi_2 C_2$

Γ_3

- Rule No. . 05

Addition of all irreducible representation are always equal to addition of all reducible representation.

$$\boxed{\therefore \sum(IR) = \sum(R)}$$

★ In short ; the GOT rules are . . . .

(IR = Irreducible representation)

① No. of IRs = No. of class
② Sum of square of character = Order (h)
③ Sum of square of character of all the IR = Order
④ All the IRs are orthogonal to each other.

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* C_{2v} character table formation using GOT theorem :

⇒ • Applying Rule No. 1. [No. of irreducible rep. = No. of class]

– C_{2v} point group has four class. i.e. $E, C_2, \sigma_{xz}, \sigma_{yz}$

∴ h = order = 4 = no. of class.

class

Point group → C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

Irreducible represent. (Γ_1 – Γ_4); character (table entries)

⇒ Applying Rule No. 2

$$E = \boxed{\sum_{i=1}^{K} \left[\chi_i(E)^2\right] = h}$$

∴ $E = (1)^2 + (1)^2 + (1)^2 + (1)^2 = 4$

⇒ Applying Rule No. 3. $\left[\sum_R \left[\chi_i(R)\right]^2 = h\right]$

For $\Gamma_1 = (1)^2 + (1)^2 + (1)^2 + (1)^2 = 4$

$\Rightarrow$ Applying Rule No. 4.

$\rightarrow$ Γ_2 is orthogonal to Γ_1.

$\therefore \sum \chi_i(R) \cdot \chi_j(R) = 0.$

$\therefore \chi_1(E) \cdot \chi_2(E) + \chi_1(C_2) \cdot \chi_2(C_2) +$

$\chi_1(\sigma_{xz}) \cdot \chi_2(\sigma_{xz}) + \chi_1(\sigma_{yz}) \cdot \chi_2(\sigma_{yz}) = 0$

$\therefore (1) \cdot (1) + (1) \cdot \chi_2(C_2) + (1) \cdot (\chi_2(\sigma_{xz})) +$
$(1) \cdot (\chi_2(\sigma_{yz}) = 1$

$\therefore (1) \cdot (1) + (1)(1) + 1(-1) + 1(-1) = 1$

$\rightarrow$ Now, Γ_3 is orthogonal to Γ_1 & Γ_2.

- For $\Gamma_3 \rightarrow \Gamma_1$.

$\chi_1(E) \cdot \chi_3(E) + \chi_1(C_2) \cdot \chi_3(C_2) + \chi_1(\sigma_{xz}) \cdot$

$\chi_3(\sigma_{xz}) + \chi_1(\sigma_{yz}) \cdot \chi_3(\sigma_{yz}) = 0$

$\therefore (1) \cdot (1) + (1) \chi_3 C_2 + (1) \chi_3 \sigma_{xz} + (1) \chi_3 \sigma_{yz} = 0$

$\llcorner$ (1)

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- For $\Gamma_3 \rightarrow \Gamma_2$.

$\therefore \chi_2(E)\cdot\chi_3(E) + \chi_2(C_2)\cdot\chi_3(C_2) +$

$\chi_2(\sigma_{xz})\cdot\chi_3(\sigma_{\cancel{xz}}) + \chi_2(\sigma_{yz})\cdot\chi_3(\sigma_{yz}) = 0$

$\therefore (1)\cdot(1) + (1)\cdot\chi_3(C_2) + (-1)(\chi_3\sigma_{xz})$

$+ (-1)\cdot\chi_3(\sigma_{yz}) = 0$ —— (2)

$\rightarrow$ Eq (1) = Eq (2)

$\therefore 1 + \chi_3 C_2 + \chi_3\sigma_{xz} + \chi_3\sigma_{yz} = 1 +$

$\chi_3 C_2 - \chi_3(\sigma_{xz}) - \chi_3(\sigma_{yz})$

$\therefore \chi_3(\sigma_{xz}) + \chi_3(\sigma_{yz}) = -\chi_3\sigma_{xz} - \chi_3\sigma_{yz}$

$\therefore 2(\chi_3(\sigma_{xz}) + \chi_3(\sigma_{yz})) = 0$

$\chi_3(\sigma_{xz}) + \chi_3(\sigma_{yz}) = 0$

$\therefore \chi_3(\sigma_{xz}) + (-1) = 0$ (Suppose the $\boxed{\chi_3(\sigma_{yz}) = -1}$)

$\therefore \boxed{\chi_3(\sigma_{xz}) = 1}$

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$\therefore$ Put the value of $\chi_3(\sigma_{xz})$ & $\chi_3(\sigma_{yz})$ in eq^n (2).

$\therefore 1 + \chi_3(C_2) + (-1)(1) + (-1)(-1) = 0$

$\therefore 1 + \chi_3(C_2) - 1 + 1 = 0$

$\therefore \boxed{\chi_3(C_2) = -1}$

→ For character - 4 (Γ_4).

$1 + \chi_4 C_2 + (1)(\chi_4 \sigma_{xz}) + (1)(\chi_4 \sigma_{yz}) = 0$

Here, put $\chi_4 \sigma_{xz} = -1$

$\chi_4 \sigma_{yz} = 1$

$\therefore \chi_4 C_2 = -1$

* Character Table *

→ It helps to understand the electronic, vibrational, Raman spectra of atomic orbitals, hybrid and molecular orbitals in polyatomic molecules.

→ The allowed transition can be known using character table of the particular group.

→ Character Table
- 4 coloumn
- 6 Parts.

1	2		
3	4	5	6

I.Rs :- Irreducible Representations

1 - Point Group

2 - Symmetric operation of the point group.

3 - Mulliken symbol of the IRs.

4 - Character of IRs

5 - Translation axis (x, y, z) + Rotational axis (R_x, R_y, R_z) } IR Active

6 - Quadratic function $(x^2, y^2, z^2, x^2-y^2, x^2+y^2, xy, yz, zx)$

RAMAN ACTIVE

✱ Mulliken Symbol

☆

→ One Dimension (1 D) — A (Symmetric) +1 / B (Antisymmetric) −1

with reference to principle axis.

→ Two Dimension (2D) → E

→ Three Dimension (3D) → T

☆ Subscript (1 & 2)

- Subsidiary axis
  - + → 1
  - − → 2
- Molecular plane
  - + → 1
  - − → 2
- Centre of inversion (i)
  - + → g
  - − → u
- (′) & (″)
  - (+) → ′
  - (−) → ″

e.g. C_{2v} - point group table

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_x	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

* Finding Reducible, Irreducible representation, Transitional, Rotational & Vibrational mode of C_{2V} character table for H_2O molecule

- Contributed of character per unshifted atom

Symmetry Operations.	Contribution of character per unshifted atom
E (Identity)	3
I (Inversion)	-3
Cn (Rotation along z-axis)	$2\cos\theta + 1$
Sn (Improper rotation)	$2\cos\theta - 1$
σ (Reflection)	1

$C_2 = 2\cos 180° + 1 = 2(-1)+1 = -1$
$C_3 = 2\cos 120° + 1 = 2(-1/2)+1 = 0$
$C_4 = 1$
$C_6 = 2$

C_2	-1
C_3	0
C_4	1
C_6	2

$S_3 = -2$	
$S_4 = -1$	
$S_6 = 0$	

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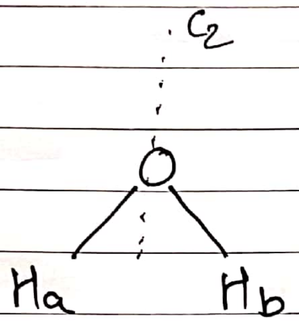
- Calculation for Reducible Representation for H_2O molecule (C_{2v} point group)



For : Unshifted atom

E - 3
C_2 - 1
σ_{xz} - 3
σ_{yz} - 1

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Unshifted atom	3	1	3	1
Contribution per atom	3	-1	1	1
$\Gamma_{red.}$ = Unshifted atom × Contribution	9	-1	3	1

- Calculation for Irreducible representation

Reduction Formula

$$N = \frac{1}{h} \sum \chi_{Red.} \cdot \chi_{irred.} \cdot \eta$$

N = Irreducible Representation
h = Order / or / No. of class
χ_{red} = Reducible rep. Value
χ_{irred} : Irreducible rep. Value
η = co-efficient for C_2 → 1
for 3 C_2 → 3

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For, C_{2v} character table

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_x	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

$$\Gamma_{A_1} = \frac{1}{4}\left[[9 \times 1 \times 1] + [(-1) \times 1 \times 1] + [3 \times 1 \times 1] + [1 \times 1 \times 1] \right]$$

$$= \frac{1}{4}[9 - 1 + 3 + 1]$$

$$\boxed{\Gamma_{A_1} = 3}$$

Similarly, $\Gamma_{A_2} = 1$, $\Gamma_{B_1} = 3$, $\Gamma_{B_2} = 2$.

$$\therefore \boxed{\Gamma_{\text{irreducible}} = 3A_1 + A_2 + 3B_1 + 2B_2}$$

→ For, See last column of character table

$$\Gamma_{\text{Transational mode}} = \underset{(z)}{A_1} + \underset{(x)}{B_1} + \underset{(y)}{B_2}$$

$$\Gamma_{\text{Rotational mode}} = \underset{(R_z)}{A_2} + \underset{(R_y)}{B_1} + \underset{(R_x)}{B_2}$$

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$$\Gamma_{\text{vibrational mode}} = \Gamma_{\text{irred.}} - [\Gamma_{\text{Trans}} + \Gamma_{\text{Rotational}}]$$

$$= \{3A_1 + A_2 + 3B_1 + 2B_2\} -$$

$$\{A_1 + B_1 + B_2 + A_2 + B_1 + B_2\}$$

$$= 2A_1 + B_1$$

$\therefore$ Total 3 vibration mode are present.

→ IR- Active :- x, y, z are present in character table

→ Raman Active :- If there is quadratic func^n $(x^2+y^2, z^2, xy, yz, zx, x^2-y^2)$

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