Symmetry :- Symmetry means that a certain portion of an object looks exactly like another portion of the same object. Ideas about symmetry are of great importance in connection with both theoretical & experimental studies of molecular structure. The basic principle of symmetry are applied in quantum mechanics, spectroscopy & structural determination by X-Ray, neutron & electron diffraction. Aspects of symmetry also determine whether a molecule can be optically active or whether it may have dipole moment.

It also helps in understanding the stereochemistry of molecules. A thorough knowledge of structure shape & symmetry of molecules & an overall understanding of symmetry & mechanisms of reactions leads to efficient designing of asymmetric synthesis which are vital in chemical, pharmaceutical & polymer Industry.

The systematic discussion of symmetry is called group theory. This theory gives a simple & direct method for arriving at useful conclusions with minimum calculations about the geometry & electronic structure of molecules.

Symmetry operations & Symmetry elements :-

Symmetry elements :- are defined as (Imaginary) geometrical entities such as points, lines or planes that are present in a molecule about which when symmetry operations are performed, the molecule presents an Indistinguishable configuration. The nature of symmetry elements present in any molecule depends on its geometry.

Symmetry operations :- These are simple geometrical operations such as reflection, rotation or Inversion which when performed on the molecule, give rise to an Indistinguishable configuration of the same molecule. Thus, the presence of symmetry elements in a molecule can be Identified by performing the appropriate symmetry operation

Table: Symmetry elements & Associated Operation:

Symmetry element	Operation
Identity element (E) or (I)	The operator that leave the system unchanged or doing nothing (360° rotation)
Plane of symmetry (σ)	Reflection across the plane of symmetry.
Center of symmetry (or Inversion center) (i)	Projection through the center of symmetry to an equal distance on the other side form the center or Inversion of all coordinates

Symmetry element	Operation
Proper axis of symmetry or Proper rotation axis (C_n)	Counterclockwise rotation about the C_n axis by $2\pi/n$ (or $360°/n$) where 'n' is an integer & is called order of the axis
Improper axis of symmetry (S_n) or Improper rotation axis (also known as rotation-reflection axis or alternating axis)	Counterclockwise rotation about the S_n axis by $2\pi/n$ followed by reflection in a plane perpendicular to the axis (viz. the combined operation of a C_n rotation followed by reflection across a σ_h mirror plane)

Identity element (E) :- Identity element is present in all molecules. Identity is the operation of not doing anything. When a molecule is not operated upon by any symmetry element, the system is left unchanged & the configuration of the molecule is identical with the original configuration. Though it may appear that this element does not have any significance, but it has its own mathematical relevance.

~~Plane of symmetry (σ)~~ :-

The Inversion operation & the center of symmetry (i) :- A molecule has a center of symmetry (i) if there is a point such that a straight line from any nucleus projected through the point encounters an equivalent nucleus equidistant from the center. The center of symmetry (or Inversion center) is the symmetry element, & the operation is inversion through the center by which one-half of the molecule can be generated from the other half. The action of inversion operation is to transform the coordinates (x, y, z) into their respective negatives (−x, −y, −z). For example a cube, a sphere & an octahedron possess a center of symmetry whereas a triangle & a pyramid does not. The inversion operation may be represented in matrix notation by

$$i \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

If the inversion operator is applied twice we obtain the original configuration as

$$i \cdot i \begin{bmatrix} x \\ y \\ z \end{bmatrix} = i \cdot \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Thus the successive application of i an even number of times produces the Identity operator E.

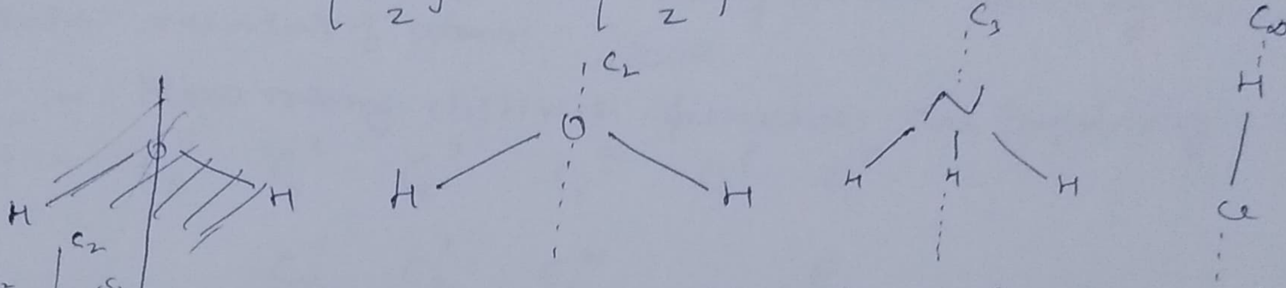
Since $i^k = i$ when k is odd. & $i^k = E$ when k is even, the center of symmetry generates only one distinct operation. In molecules with a center of symmetry, the nuclei may be thought of as occurring in centrosymmetric pairs with the exception of the nucleus (if any) lying at the center of symmetry. Centrosymmetric molecules include C_6H_6, SF_6, the staggered conformation of C_2H_6, CO_2 & C_2H_4.

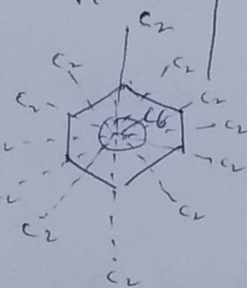
After Inversion, atoms generally shift to their exact diagonally opposite positions, so whenever diagonally opposite atoms are the same in a molecule, the molecules will have center of symmetry & vice-versa.

The Rotation operation & the symmetry axis or proper axis of symmetry:

A symmetry axis is a line about which rotation through an angle $2\pi/n$ radians brings a structure into coincidence with itself. The rotation operator is represented by C_n, where n is ~~...~~ referred to as the order of rotation (~~...~~ (where n is Integer). When $n=2$, the axis is referred to as the C_2 or diad axis, ~~...~~ or two fold, when $n=3$, the axis is referred to as C_3 or triad axis or three fold & so on. The rotation is conventionally taken as positive in counter clockwise direction. If the z axis is a two fold rotation axis, the action of the C_2 rotation operator is to transform the coordinates (x,y,z) to $(-x,-y,z)$. The C_2 rotation may be represented by

$$C_2 \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$





As shown, a water molecule has a C_2 axis passing through oxygen & bisecting the angle between the O–H bonds. The ammonia molecule has a C_3 axis passing through nitrogen. The benzene molecule has a C_6 axis perpendicular to the plane of ring & six C_2 axis lying in the plane of ring. Any linear molecule such as HCl, has C_∞ axis because the appearance of molecule is not changed by rotation of any angle (Infinity in number) about the Inter-nuclear axis.

If the C_2 operation is applied twice in succession, the Identity operator is obtained $C_2 C_2 = C_2^2 = E$

If the C_3 operator is applied twice in succession, a 240° rotation is obtained; If It is applied three times, the Identity operator is obtained

$$C_3 C_3 = C_3^2 \qquad C_3 C_3 C_3 = C_3^3 = E$$

The C_3^2 operator is a new operator; thus C_3 element of symmetry generates two operators, C_3 & C_3^2.

The operations generated by fourfold axis are

$$C_4^1 \quad C_4^2 \quad C_4^3 \quad C_4^4$$
$$C_2^1 \qquad\qquad E$$

where equivalent operations are listed below. Since C_2 axis ~~...~~ is always coincident with C_4 axis, only the operations ~~...~~ C_4^1 & C_4^3 are distinct operations of C_4 axis

In discussing symmetry operations, It is convenient to orient the molecules in right-hand Cartesian coordinate system. The thumb, Index & middle fingers of the right hand are pointed in three mutually perpendicular directions & these are taken as x, y & z directions respectively. The center of mass of the molecule under consideration is located at the origin of Cartesian coordinate system, & Its principal axis is ~~...~~ aligned with the z-axis. The principal axis is defined as the C_n axis with highest order n; If there are several rotational axes of the same highest symmetry (e.g. three two fold axes at right angle to one another) the z axis is taken along the one passing through greatest number of atom.