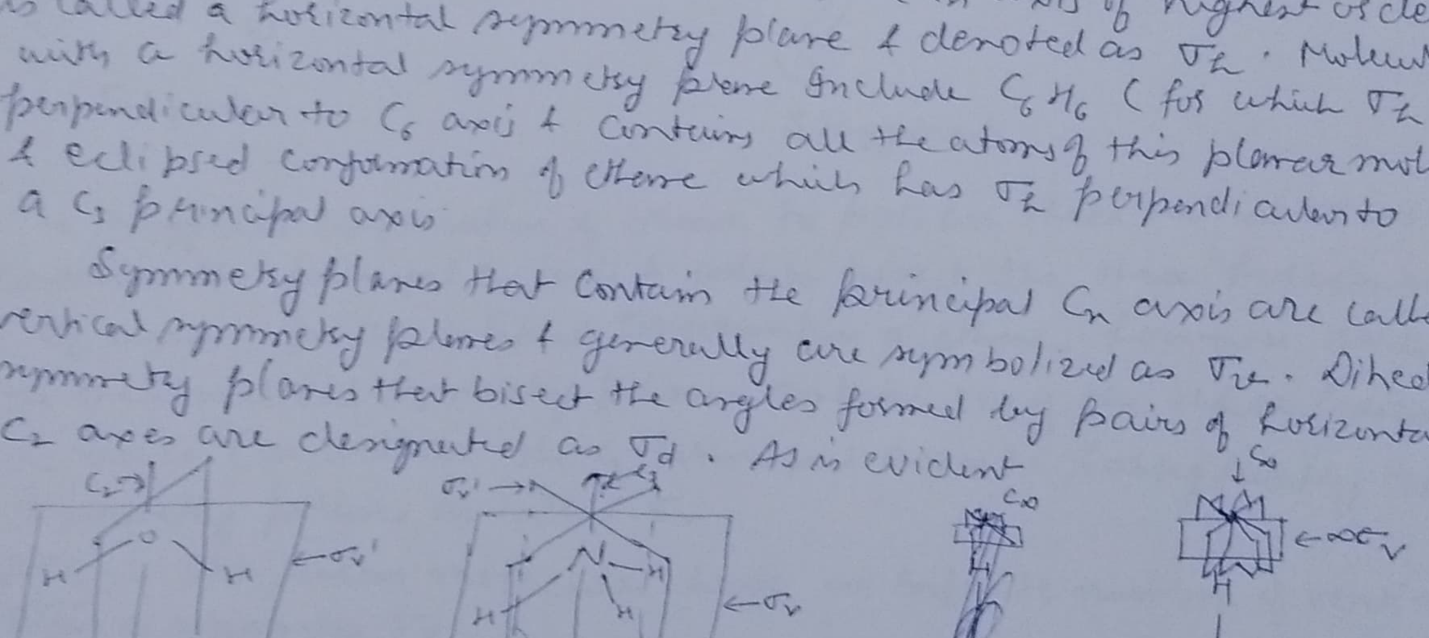
**The reflection operation & the symmetry plane (σ)**:- If reflection of all of the nuclei through a plane in a molecule gives a configuration physically indistinguishable from the original one, the molecule is said to have a symmetry plane. The symmetry plane is represented by σ & the reflection operator is represented by σ. Since operator σ gives a configuration equivalent to the original & since application of the same σ twice to a molecule produces its original configuration, it follows that a symmetry plane generates only one distinct operation in that $\sigma^k = \sigma$ when k is odd & $\sigma^k = E$ when k is even.

If the xz plane is a symmetry plane the reflection operation σ may be represented by $\sigma \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$

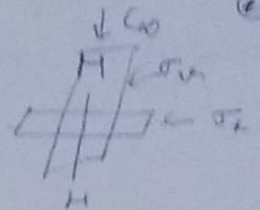
A symmetry plane (& corresponding operation of reflection) perpendicular to the direction of the principal $C_n$ axis (i.e. the normal of symmetry plane is coincident with the $C_n$ axis of highest order n) is called a horizontal symmetry plane & denoted as $\sigma_h$. Molecules with a horizontal symmetry plane include $C_6H_6$ (for which $\sigma_h$ is perpendicular to $C_6$ axis & contains all the atoms of this planar molecule) & eclipsed conformation of ethane which has $\sigma_h$ perpendicular to a $C_3$ principal axis.

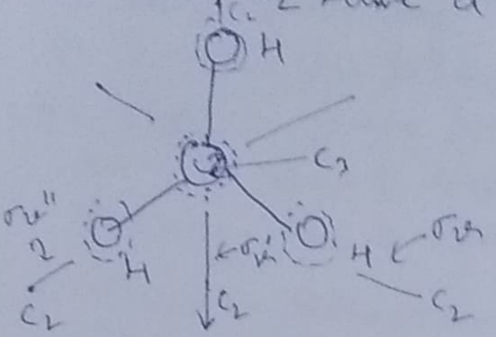
Symmetry planes that contain the principal $C_n$ axis are called vertical symmetry planes & generally are symbolized as $\sigma_v$. Dihedral symmetry planes that bisect the angles formed by pairs of horizontal $C_2$ axes are designated as $\sigma_d$. As is evident

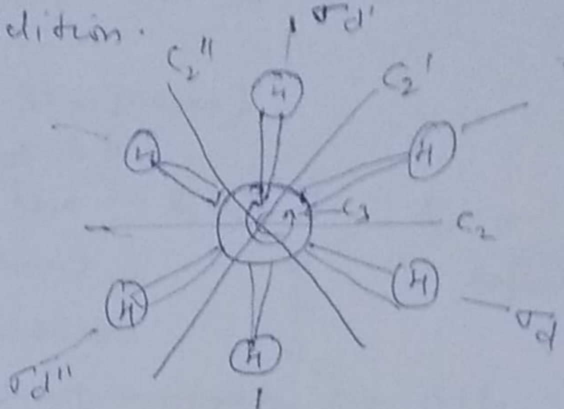


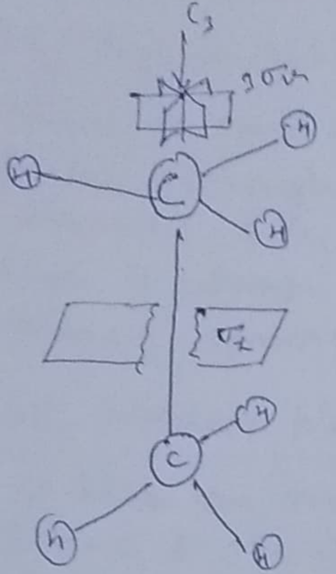

From figure, a $H_2O$ molecule has two vertical symmetry planes $\sigma_v$ & $\sigma_v'$ which are perpendicular to each other. One of these symmetry planes ($\sigma_v$) comprises the plane of molecule, & the other ($\sigma_v'$) is perpendicular to it. The two fold axis ($C_2$) lies in the intersection of two symmetry planes. Ammonia has three $\sigma_v$ containing the $C_3$ axis & benzene has six $\sigma_v$ containing the $C_6$ principal axis. The linear molecule HCl has an infinite number of vertical symmetry planes of type $\sigma_v$, all of which include the $C_\infty$

rotational axis. Homonuclear diatomic molecules such as $H_2$ or $Cl_2$ have a $\sigma_h$ in addition.

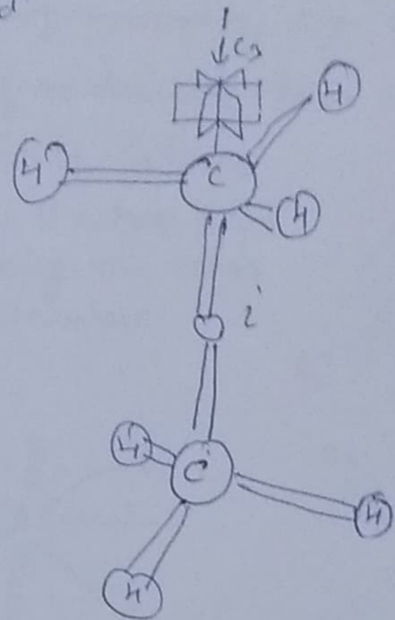



Eclipsed




Staggered.

The staggered conformation of ethane to possess three vertical $\sigma_d$ which contain the principal $C_3$ axis & which bisect the three horizontal $C_2$ axes. In the eclipsed conformation of ethane, however, each of the three vertical symmetry planes contains one of the three horizontal $C_2$ axes (as well as the $C_3$ principal axis). Consequently these symmetry planes are called $\sigma_v$.

NOTE:- All linear molecules have an infinite number of vertical plane of symmetry $\sigma_v$

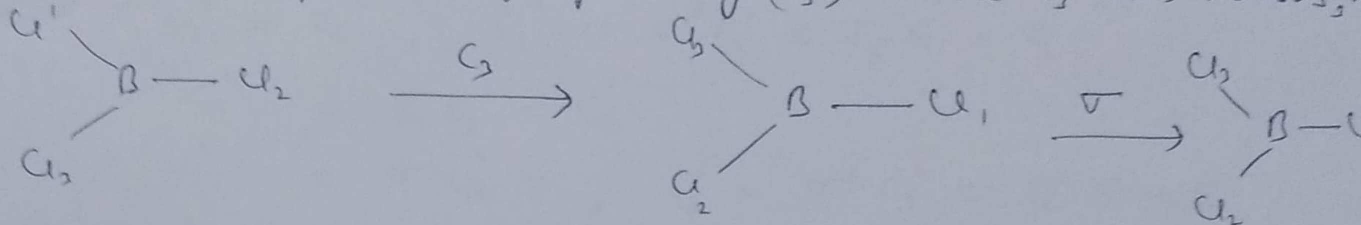
## The operation of Improper Rotation & the Improper Axis ($S_n$):

The operation of Improper rotation consists of a rotation by $2\pi/n$ radians about an axis followed by reflection in a plane perpendicular to the axis. Thus Improper rotation operator $S_n$ is the product of two operators

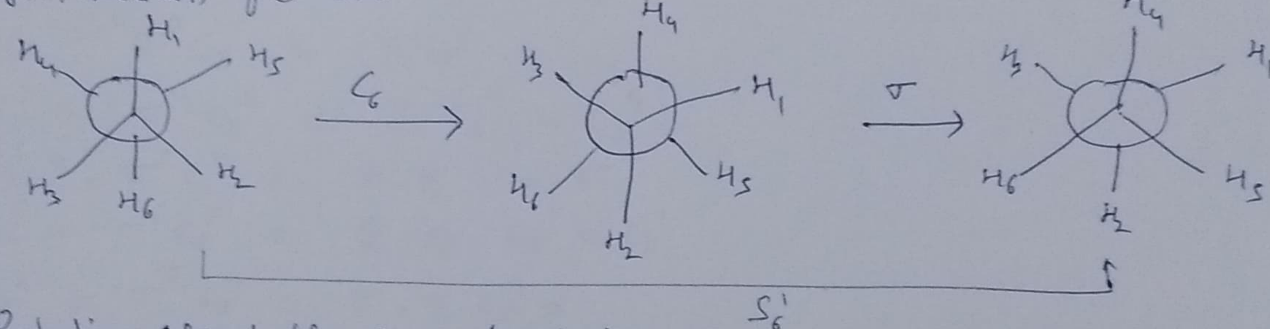
$$S_n = \sigma C_n .$$

This means that the operators $C_n$ & $\sigma$ are applied successively. As we will see, a molecule need not possess the symmetry element $\sigma$ or $C_n$ to have the symmetry element $S_n$.

In $BCl_3$ the $C_3$ axis is perpendicular to the molecular plane. Rotation $120^\circ$ ($C_3$) followed by reflection about the molecular plane gives an Indistinguishable configuration. Hence the molecule is said to possess an Improper axis of symmetry ($S_3$). Hence $C_3$ axis is also $S_3$ axis.




Consider the end-on-view (Newmann Projection) of staggered confirmation of ethane.




Rotation about the C–C bond through an angle of $60^\circ$ followed by reflection about the perpendicular plane at the center of symmetry gives an Indistinguishable configuration. Hence C–C bond axis is the $S_6$ axis

<u>NOTE</u>: No $C_6$ axis exists in the molecule, only $S_6$ axis is present.

The eclipsed confirmation of ethane has an $S_3$ axis