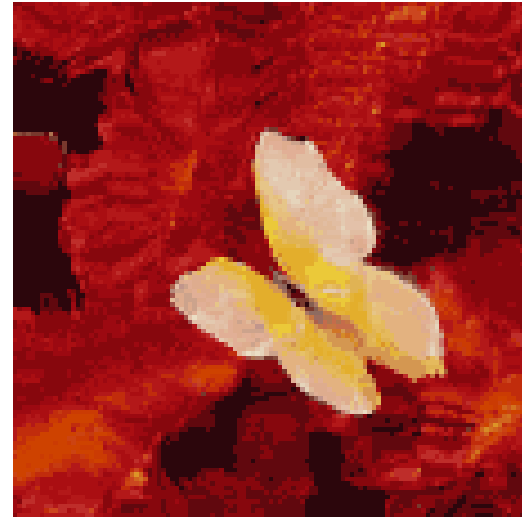


# What is Symmetry ?



# What is Symmetry and why is it important?

An action which leaves an object looking the same after a transformation is called a **symmetry operation**. Typical symmetry operations include **rotations**, **reflections**, and **inversions**. There is a corresponding **symmetry element** for each symmetry operation, which is a **point**, **line**, or **plane** with respect to which the symmetry operation is performed. For instance, a **rotation is carried out around an axis**, **a reflection is carried out in a plane**, while **an inversion is carried out in a point**.

Some objects are "more symmetrical" than others. A sphere is more symmetrical than a cube because it looks the same after rotation through any angle about the diameter. A cube looks the same only if it is rotated through certain angles about specific axes, such as **90°**, **180°**, or **270°** about an axis passing through the centers of any of its opposite faces, or by **120°** or **240°** about an axis passing through any of the opposite corners. Here are also examples of different molecules which remain the same after certain symmetry operations: **NH<sub>3</sub>**, **H<sub>2</sub>O**, **C<sub>6</sub>H<sub>6</sub>**, **CBrClF**.

We will classify molecules that possess the same set of symmetry elements. **This classification is very important**, because it allows to make some general conclusions about molecular properties without calculation. Particularly, we will be able to decide **if a molecule has a dipole moment, or not** and to know in advance the **degeneracy of molecular states**. We also will be able to **identify overlap, or dipole moment integrals which necessarily vanish** and obtain **selection rules for transitions in diatomic and polyatomic molecules**.

# Symmetry and Conservation Laws

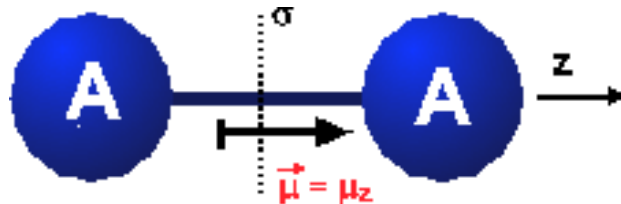
- Homogeneity of time  $\rightarrow$   
*conservation of energy*  
( $t \rightarrow t_0+t$  does not affect equations in dynamics)
- Homogeneity of space  $\rightarrow$   
*conservation of linear momentum*
- Isotropy of space  $\rightarrow$   
*conservation of angular momentum*

# Symmetry and properties

Symmetry accounts for *properties* of matter,  
e.g. the *electric dipole moment* of homonuclear diatomic molecules:

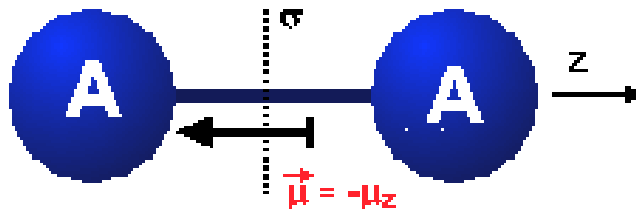
## Assumption:

molecule A-A displays a dipole moment  $\mu$  parallel to the positive z-axis:



## Symmetry conclusion:

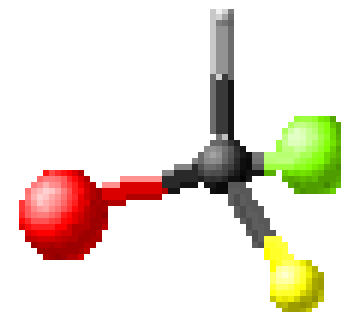
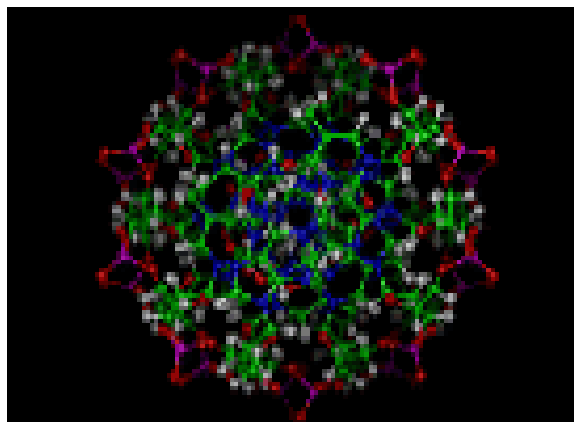
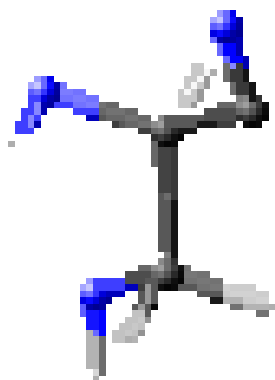
A-A must display the same dipole moment in the opposite direction:



## Conclusion:

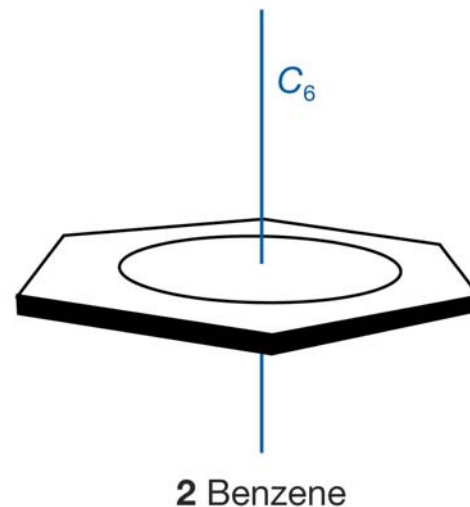
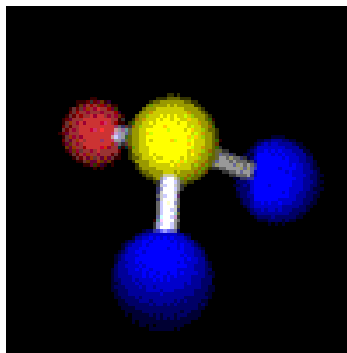
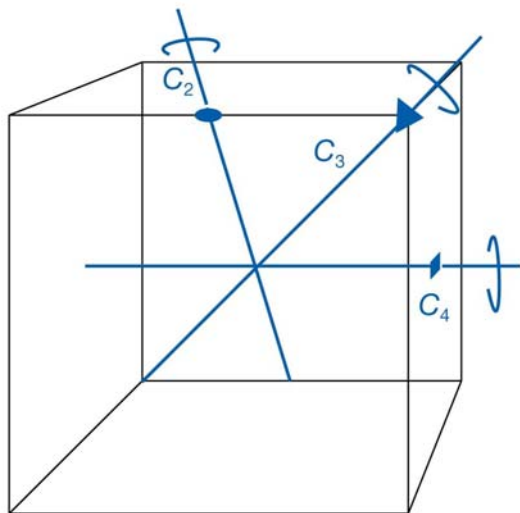
The molecule displays *no dipole moment* in direction  $z$ , i.e.  $\mu_z = 0$ !

# I. Symmetry Operations and Symmetry Elements: Identity, E



The identity, **E**, consists of doing nothing: the corresponding symmetry element is an entire object. In general, any object undergo this symmetry operation.

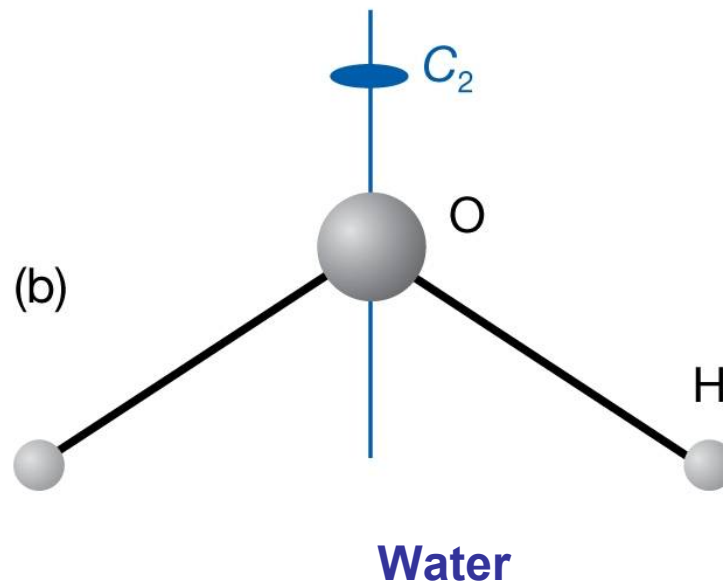
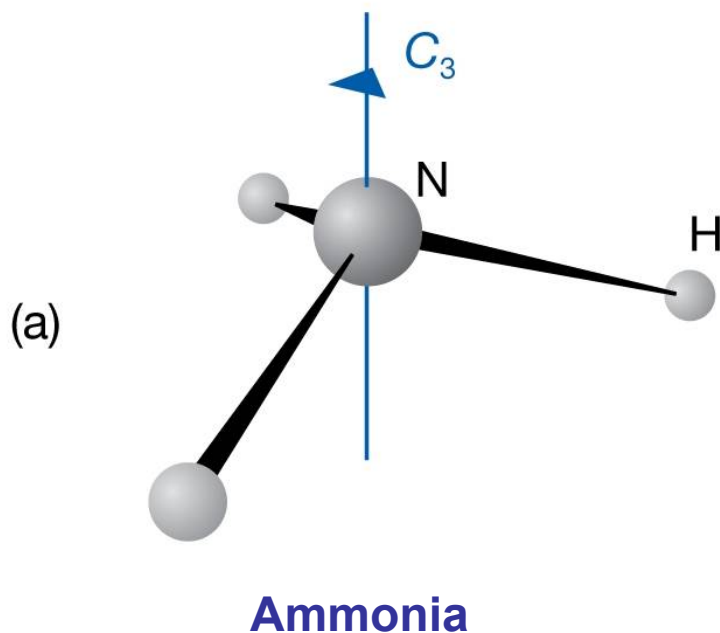
## II. Symmetry Operations and Symmetry Elements: n-fold Rotation, $C_n$



The n-fold rotation about an n-fold axis of symmetry,  $C_n$  is rotation through the angle  $360^\circ/n$ . Particularly, the operation  $C_1$  is a rotation through  $360^\circ$  which is equivalent to the identity  $E$ .

$C_6H_6$  molecule has one six-fold axis  $C_6$  and six twofold axes  $C_2$ . If a molecule possess several rotational axes, then the one of them with the greatest value of  $n$  is called **the principal axis**.

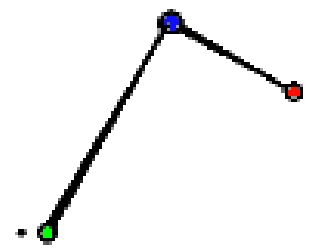
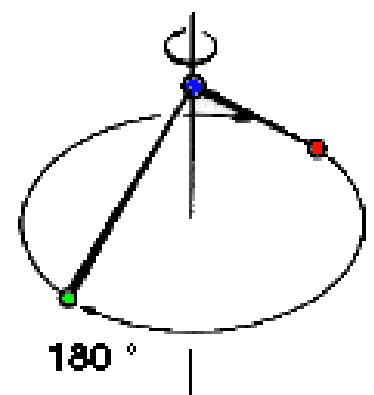
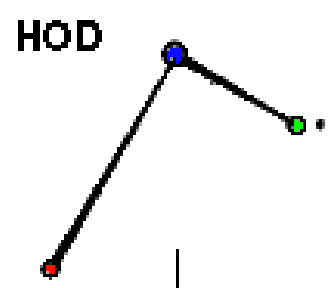
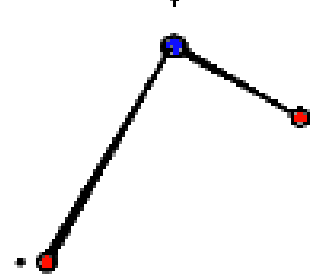
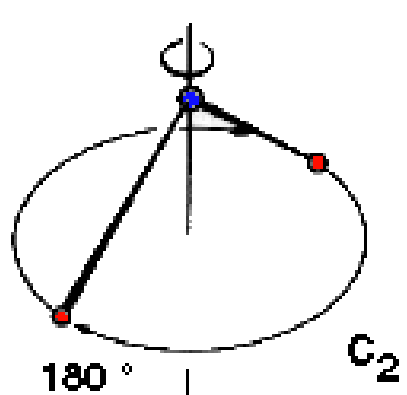
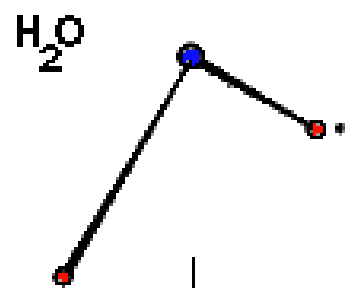
## II. Symmetry Operations and Symmetry Elements: n-fold Rotation, $C_n$



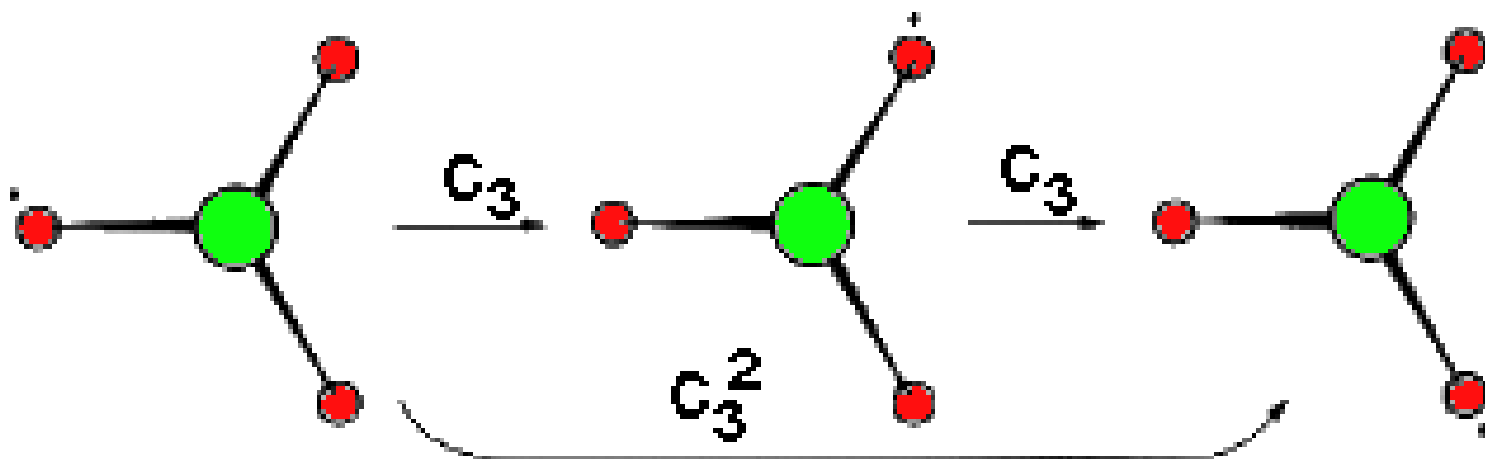
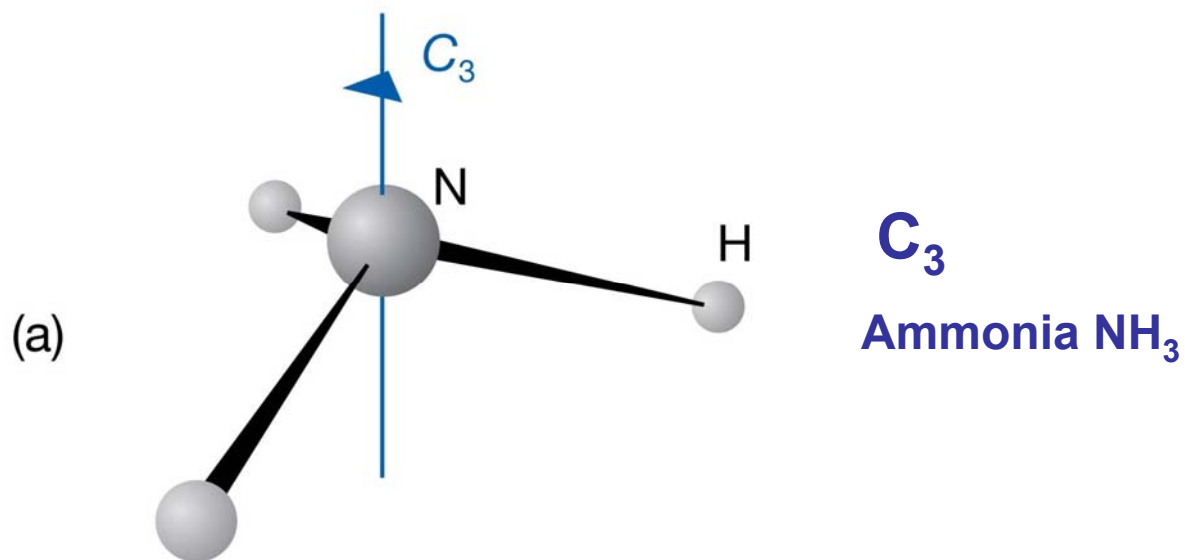
$H_2O$  molecule has one twofold axis,  $C_2$ .  $NH_3$  molecule has one threefold axis,  $C_3$  which is associated with two symmetry operations:  $120^\circ$  rotation  $C_3$  and  $240^\circ$  (or  $-120^\circ$ ) rotation  $C_3^2$ .

## II. Symmetry Operations and Symmetry Elements: n-fold Rotation, $C_n$

$C_2$

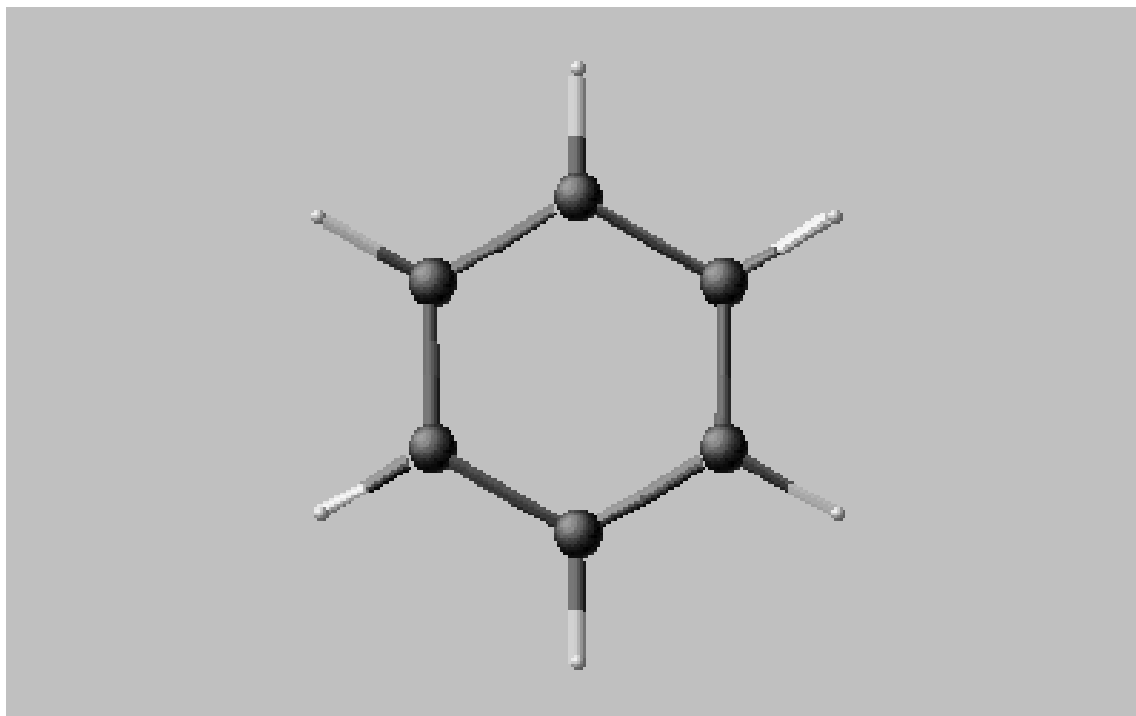


## II. Symmetry Operations and Symmetry Elements: n-fold Rotation, $C_n$



## II. Symmetry Operations and Symmetry Elements: n-fold Rotation, $C_n$

$C_6$



**Benzene: one  $C_6$  axis and six  $C_2$  axes**

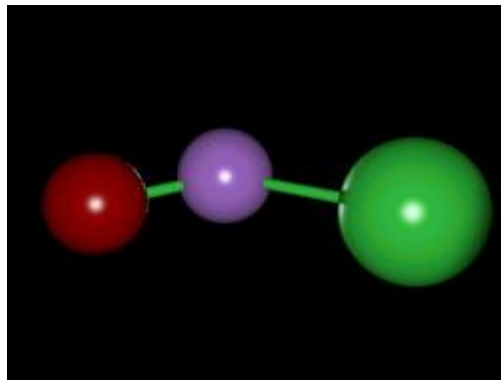
## II. Symmetry Operations and Symmetry Elements: n-fold Rotation, $C_\infty$



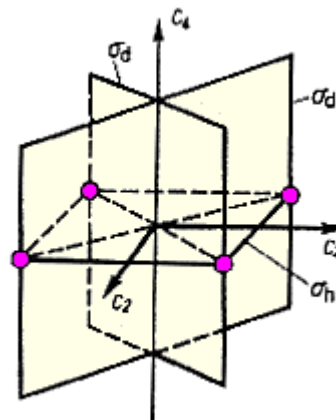
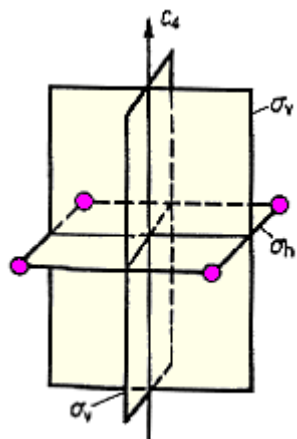
HCN

**All linear molecules including all diatomics have a  $C_\infty$  axis, because rotation on any angle remains the molecule the same.**

### III. Symmetry Operations and Symmetry Elements: Reflection, $\sigma$

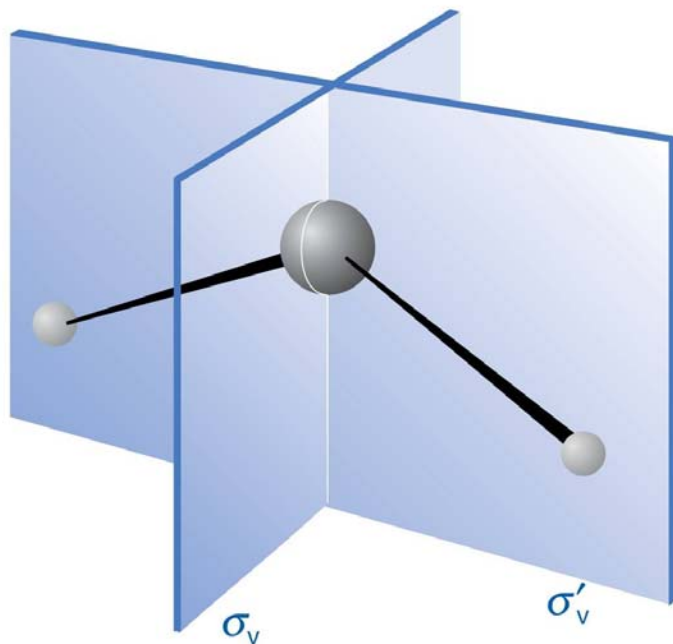


The reflection in a mirror plane is described by  $\sigma$ .

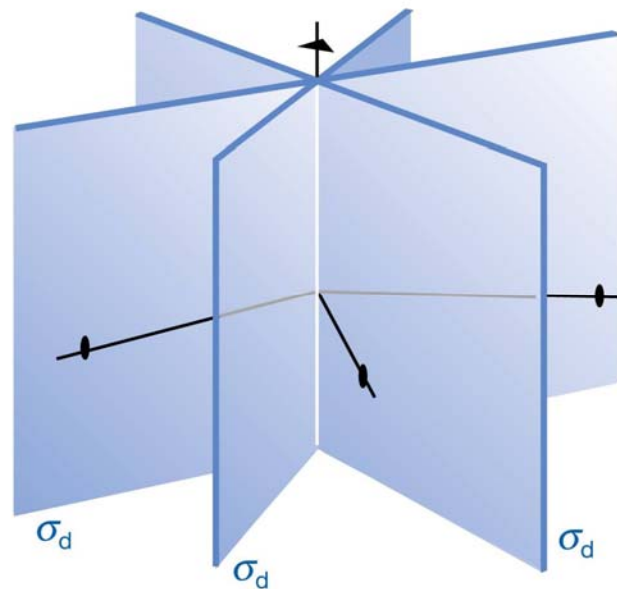


The orientation of a mirror plane relative to the molecule's main axis is indicated by a subscript.  $\sigma_h$  indicates a plane which is perpendicular to this axis or **h**orizontal, whereas  $\sigma_v$  is the symbol for **v**ertical mirror planes containing the main axis. If such a plane bisects the angle between a pair of rotational axis  $C_2$ , we have a **d**iagonal mirror plane  $\sigma_d$ .

### III. Symmetry Operations and Symmetry Elements: Reflection, $\sigma_v$



H<sub>2</sub>O



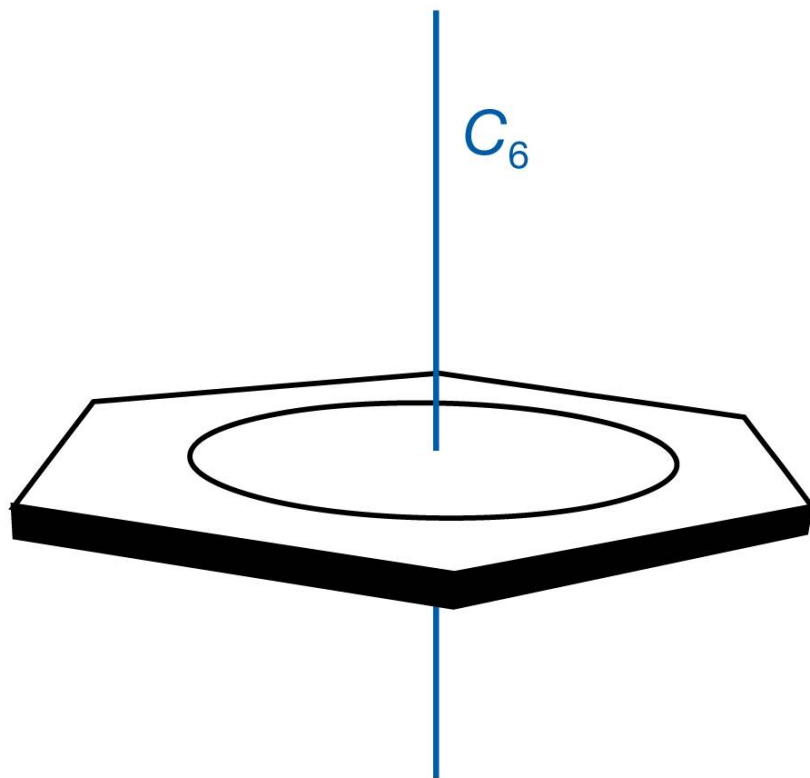
BF<sub>3</sub>

The reflection in a mirror plane is described by  $\sigma$ .

If the plane contains the principal axis, it is called **vertical** and denoted  $\sigma_v$ . For instance, the **H<sub>2</sub>O** molecule has two vertical planes of symmetry and the **NH<sub>3</sub>** molecule has three.

A vertical mirror plane which bisects the angle between two **C<sub>2</sub>** axes is called a dihedral plane and is denoted by  $\sigma_d$ .

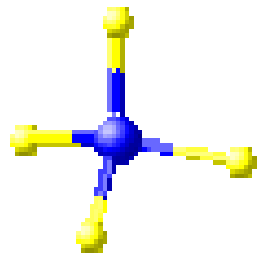
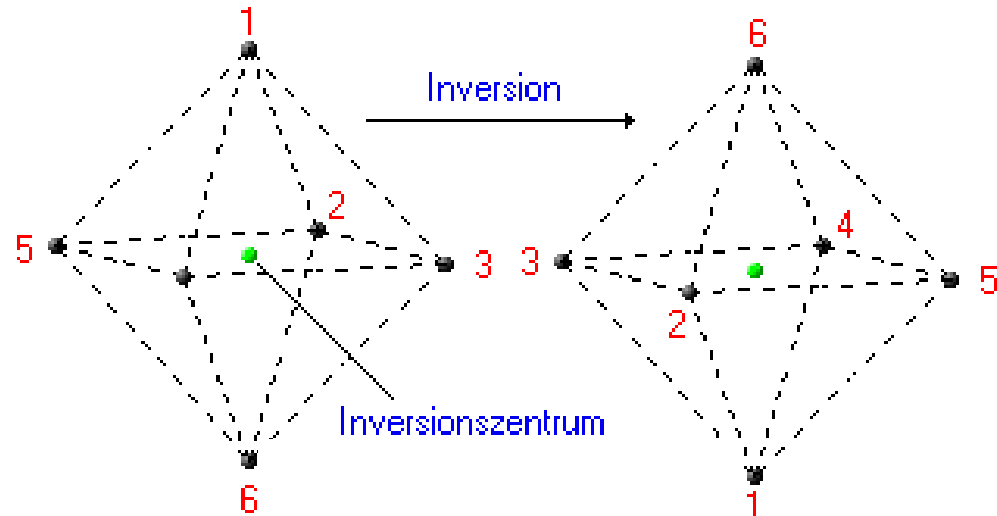
### III. Symmetry Operations and Symmetry Elements: Reflection, $\sigma_h$



2 Benzene

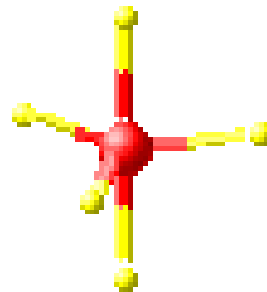
If the plane of symmetry is *perpendicular* to the principal axis, it is called **horizontal** and denoted  $\sigma_h$ . For instance,  $C_6H_6$  molecule has a  $C_6$  principal axis and a horizontal mirror plane.

# IV. Symmetry Operations and Symmetry Elements: Inversion, $i$



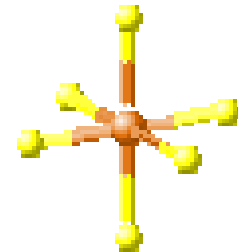
?

$\text{SF}_4$



?

$\text{PF}_5$

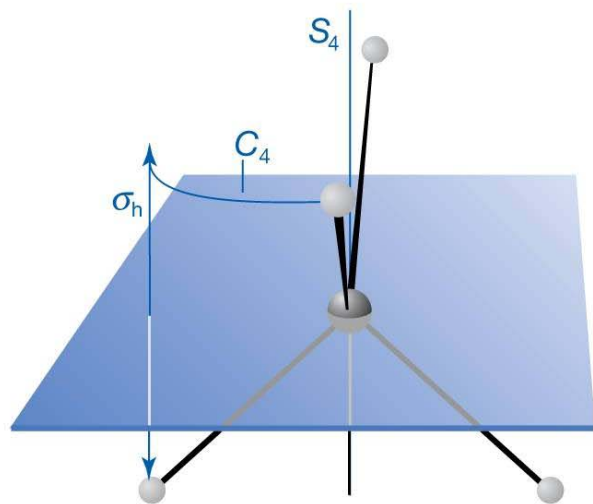


?

$\text{SF}_6$

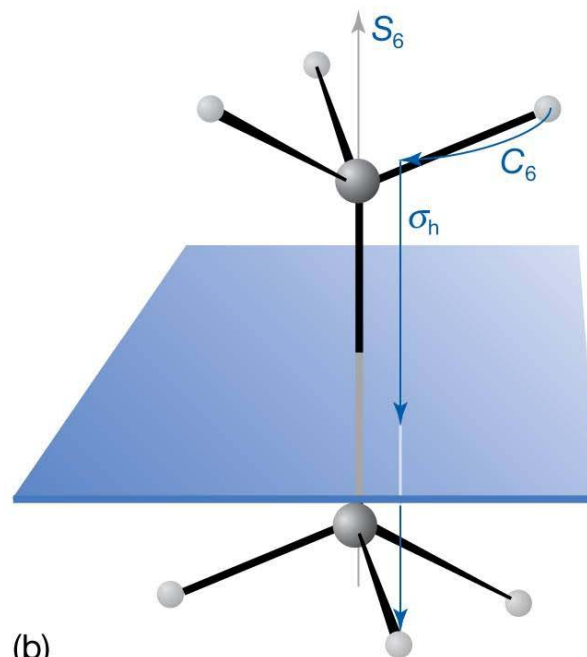
The **inversion** through **center of symmetry** is the operation which transforms all coordinates of the object according to the rule:  $(x,y,z) \rightarrow (-x,-y,-z)$ . For instance, a sphere, or a cube has a center of inversion, but  $\text{H}_2\text{O}$ , and  $\text{NH}_3$  have not.  $\text{C}_6\text{H}_6$  has a center of inversion.

# V. Symmetry Operations and Symmetry Elements: n-fold Improper Rotation, $S_n$



(a)

Methane  $\text{CH}_4$



(b)

Ethane  $\text{C}_2\text{H}_6$

The **n-fold improper** rotation about an **n-fold axis** of symmetry,  $S_n$  is a combination of two successive transformations. The first transformation is a rotation through  $360^\circ/n$  and the second transformation is a reflection through a plane perpendicular to the axis of the rotation. Note, that neither operation alone needs to be a symmetry operation. For instance,  $\text{CH}_4$  molecule has three  $S_4$  axes.

# Symmetry Classification of Molecules.

## Definition of the Group

In order to classify molecules according to symmetry one can list their symmetry elements and collect together the molecules with the same list of elements. More precisely, we can collect together the molecules which belong to the same **group**. According to the **group theory**, the symmetry operations are the members of a **group** if they satisfy the following **group axioms**:

- The successive application of two operations is equivalent to the application of a member of the group. In other words, if the operations **A** and **B** belong to the same group then  $\mathbf{A \cdot B = C}$ , where **C** is also the operation from the same group. Note, that in general  $\mathbf{A \cdot B \neq B \cdot A}$ .
- One of the operations in the group is the identity operation **E**. This means that  $\mathbf{A \cdot E = E \cdot A = A}$ .
- The reciprocal of each operation is a member of the group: if **A** belongs to a group, then  $\mathbf{A^{-1} = B}$ , where **B** is also the member of the group. Note, that  $\mathbf{A \cdot A^{-1} = A^{-1} \cdot A = E}$ .
- Multiplication of the operations is associative:  $\mathbf{A \cdot B \cdot C = (A \cdot B) \cdot C = A \cdot (B \cdot C)}$ .

# Classification of molecules according to symmetry



## Arthur Moritz Schönflies

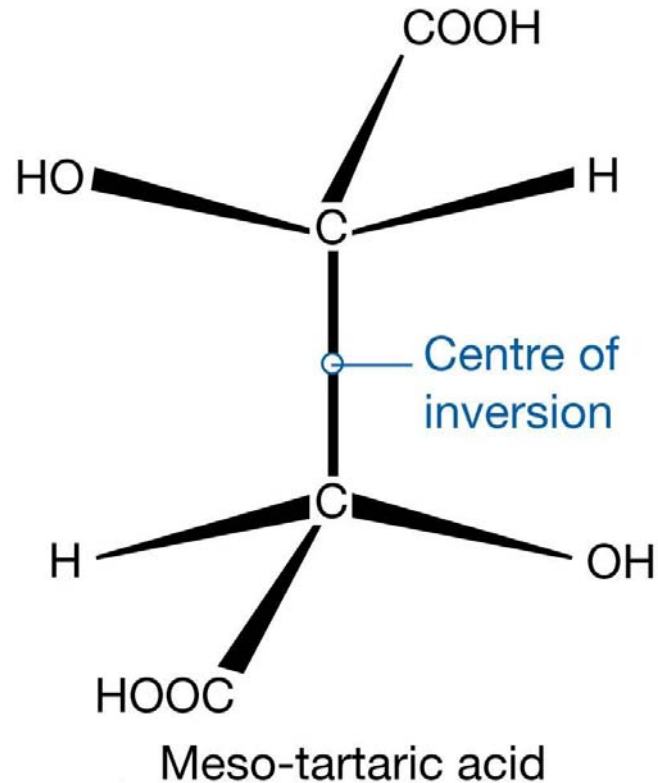
\*17 April 1853 in Landsberg an der Warthe,  
Germany (now Gorzów, Poland)

+ 27 May 1928 in Frankfurt am Main, Germany

### List of point groups:

$C_1$ ;  $C_i$ ;  $C_s$ ;  $C_n$ ;  $C_{nv}$ ;  $C_{nh}$ ;  $D_n$ ;  $D_{nh}$ ;  $D_d$ ;  $S_n$ ;  $T$  and  $O$

# Molecular symmetry point groups: Groups $C_1$ , $C_i$ , $C_s$



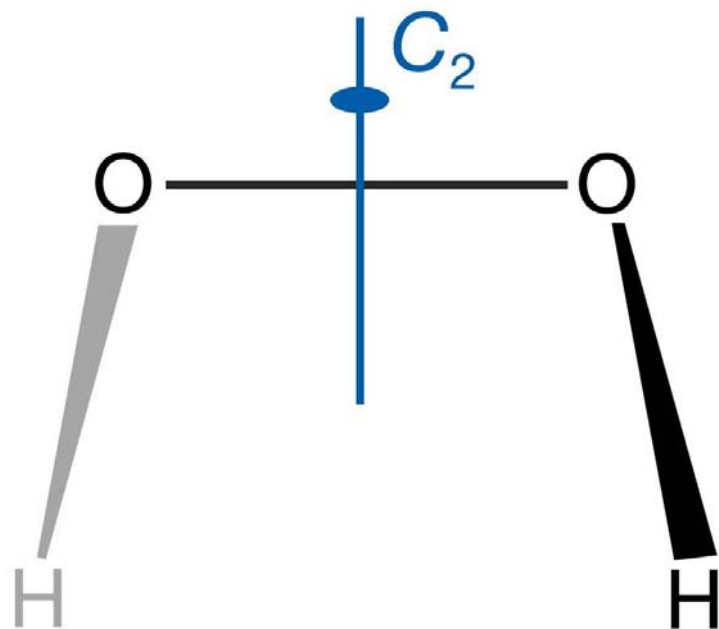
A molecule belongs to the group  $C_1$  if it has no elements other than identity  $E$ .  
Example: DNA.

A molecule belongs to the group  $C_i$ , if it consist of two operations: the identity  $E$  and the inversion  $i$ . Example: **meso-tartaric acid**.

A molecule belongs to the group  $C_s$ , if it consists of two elements: identity  $E$  and a mirror plane  $\sigma$ . Example: **HDO** or CINO

# Molecular symmetry groups: $C_n$

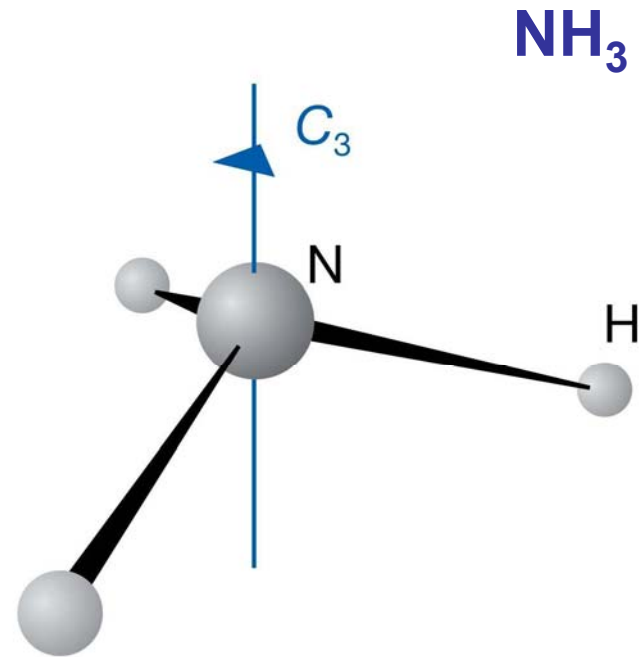
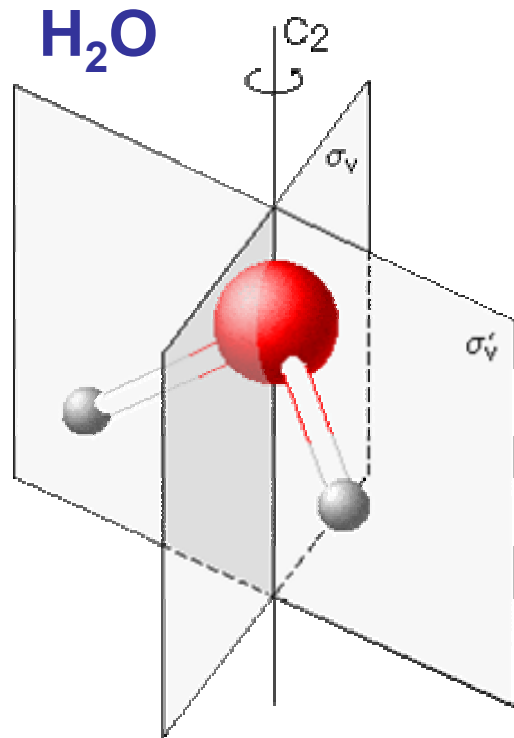
Group  $C_2$



A molecule belongs to the group  $C_n$  if it has a  $n$ -fold axis.

Example:  $H_2O_2$  belongs to the  $C_2$  group as it has the elements  $E$  and  $C_2$ .

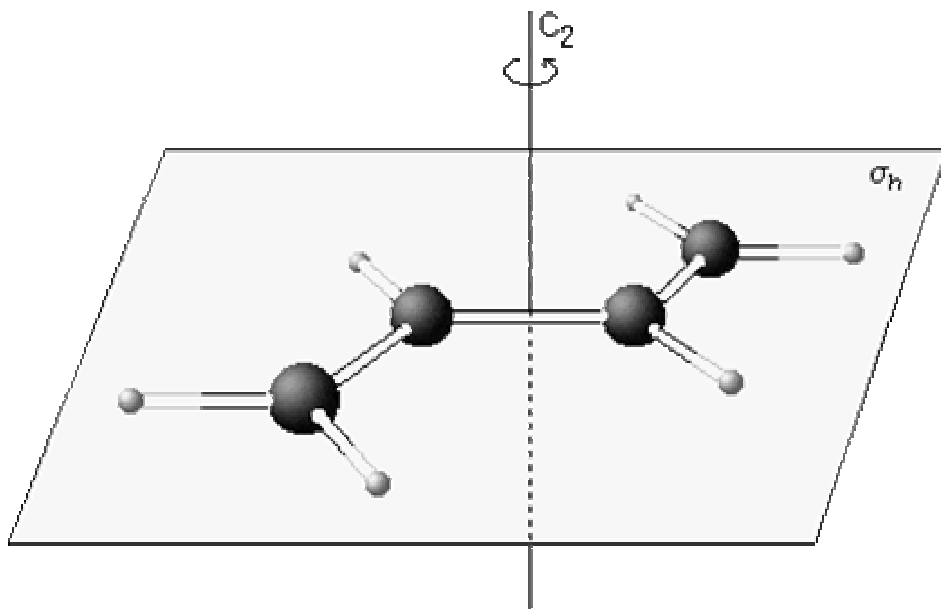
# Molecular symmetry groups: $C_{nv}$



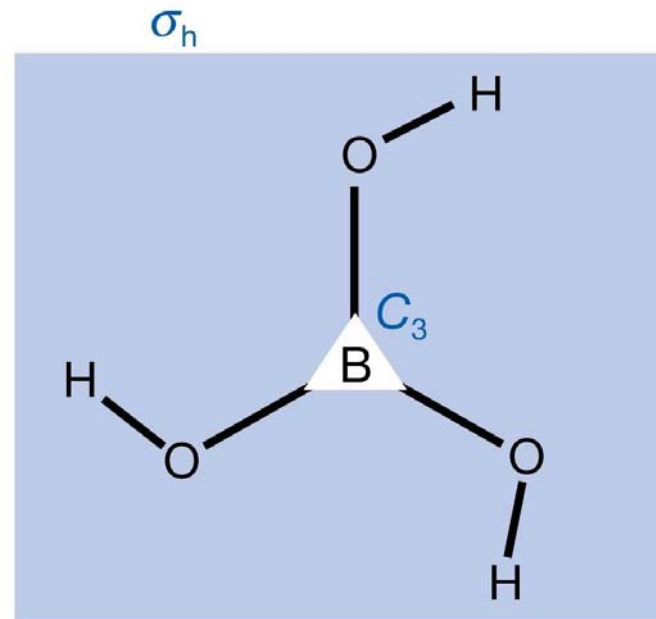
A molecule belongs to the group  $C_{nv}$ , if in addition to the identity  $E$  and a  $C_n$  axis, it has  $n$  vertical mirror planes  $\sigma_v$ .

Examples:  $H_2O$  belongs to the  $C_{2v}$  group as it has the symmetry elements  $E$ ,  $C_2$ , and two vertical mirror planes which are called  $\sigma_v$  and  $\sigma'_v$ .  $NH_3$  belongs to the  $C_{3v}$  group as it has the symmetry elements  $E$ ,  $C_3$ , and three  $\sigma_v$  planes. All heteroatomic diatomic molecules belong to the group  $C_{\infty v}$  because all rotations around the internuclear axis and all reflections across the axis are symmetry operations.

# Molecular symmetry groups: $C_{nh}$



Butadiene  $C_4H_6$ :  $C_{2h}$  group



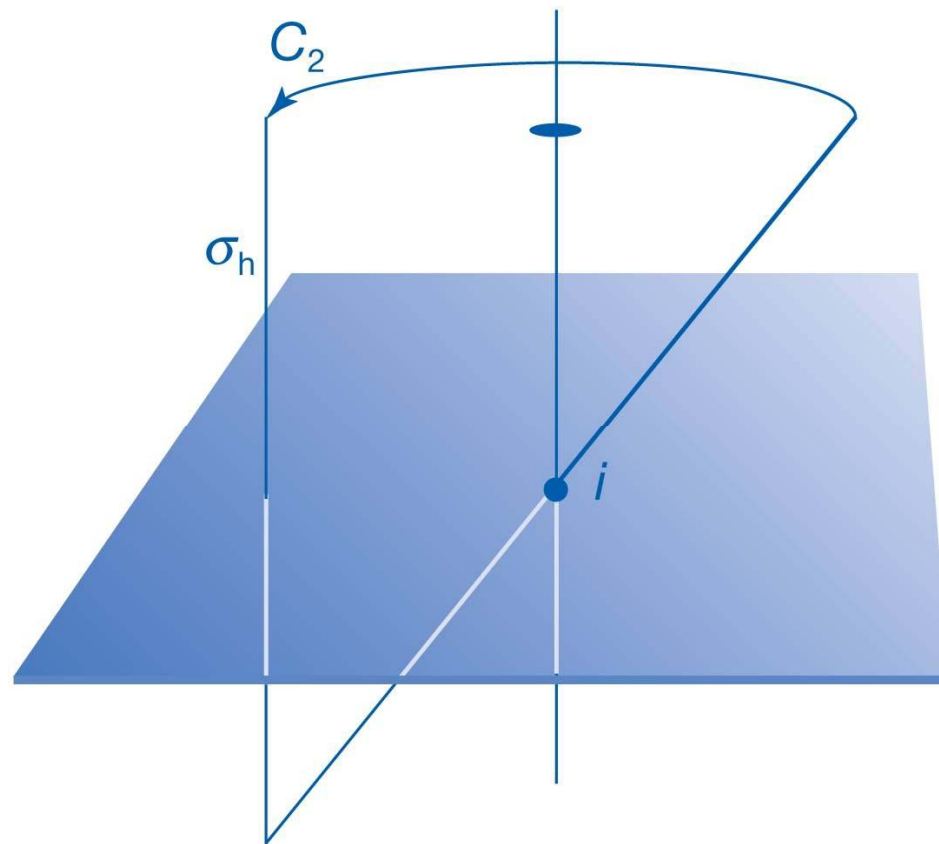
$B(OH)_3$

$C_{3h}$  group

A molecule belongs to the group  $C_{nh}$ , if in addition to the identity  $E$  and a  $C_n$  axis, it has a horizontal mirror plane  $\sigma_h$ .

Examples: butadiene  $C_4H_6$ , which belongs to the  $C_{2h}$  group, while  $B(OH)_3$  belongs to the  $C_{3h}$  group.

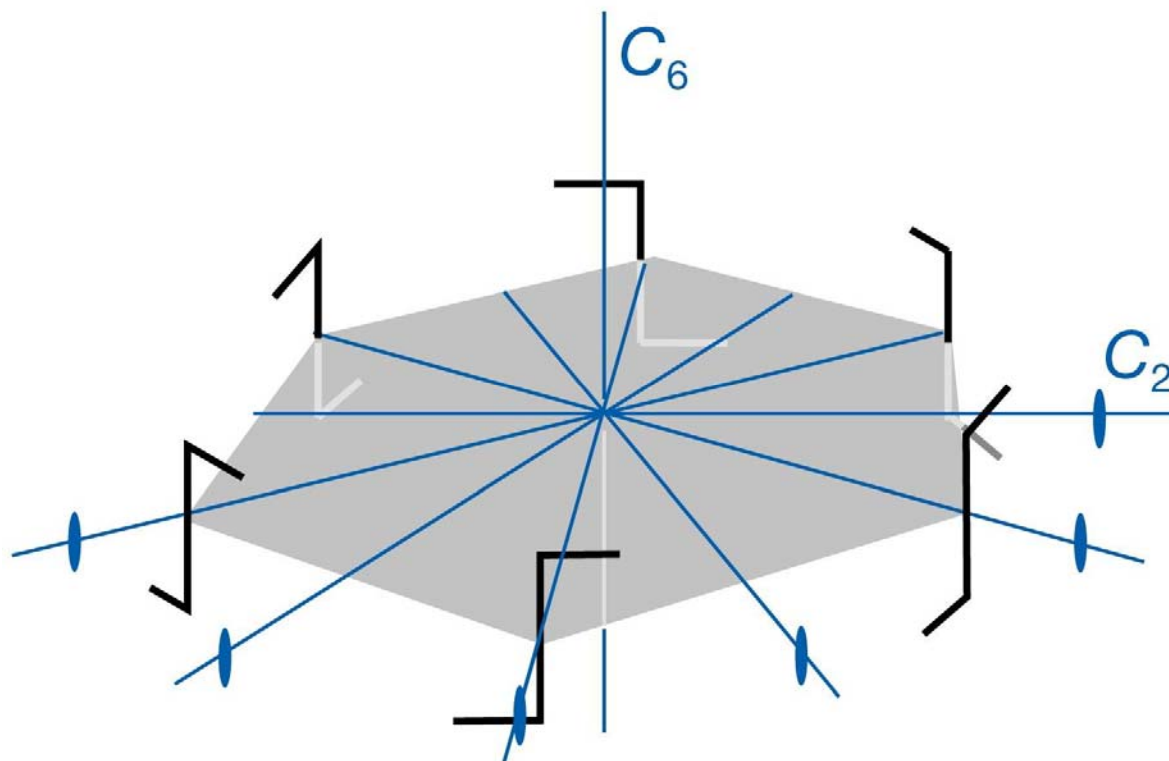
## Relation Between $C_2 + \sigma_h$ and the Inversion



$$C_2 \sigma_h = i$$

Note, that presence of  $C_2$  and  $\sigma_h$  operations imply the presence of a center of inversion. Thus, the group  $C_{2h}$  consists of a  $C_2$  axis, a horizontal mirror plane  $\sigma_h$ , and the inversion  $i$ .

# Molecular symmetry groups: $D_n$

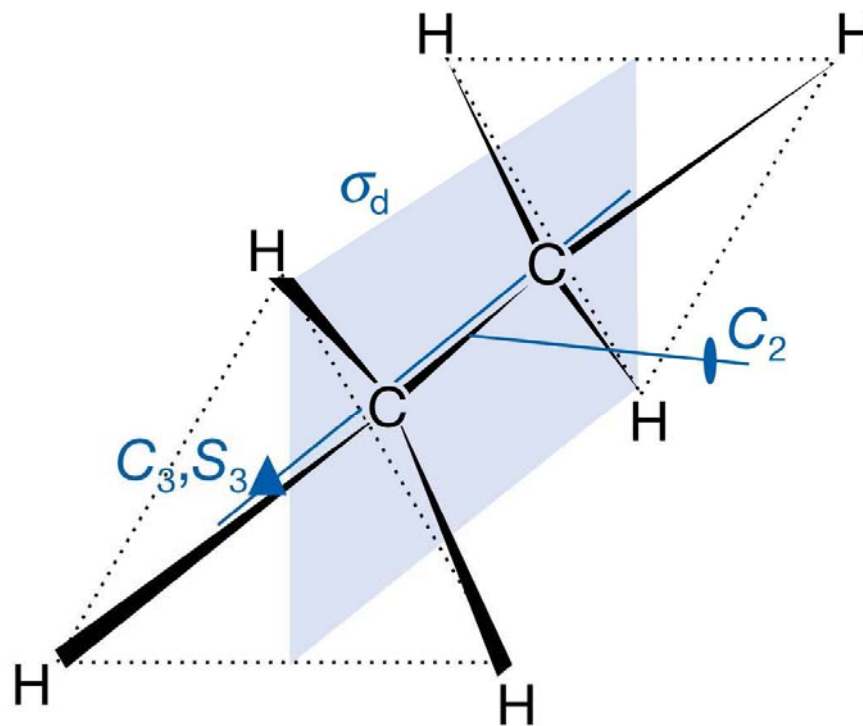


$D_6$  group

A molecule belongs to the group  $D_n$  if it has a  $n$ -fold principal axis  $C_n$  and  $n$  two-fold axes perpendicular to  $C_n$ .

$D_1$  is equivalent to  $C_2$  and the molecules of this symmetry group are usually classified as  $C_2$ .

# Molecular symmetry groups: $D_{nd}$

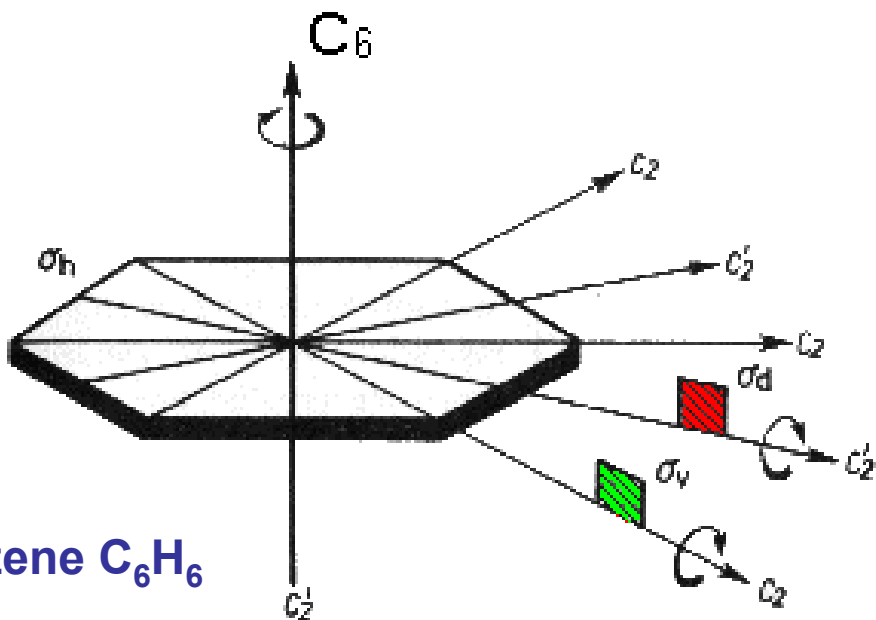


Ethane,  $\text{CH}_3\text{CH}_3$  ( $D_{3d}$ )

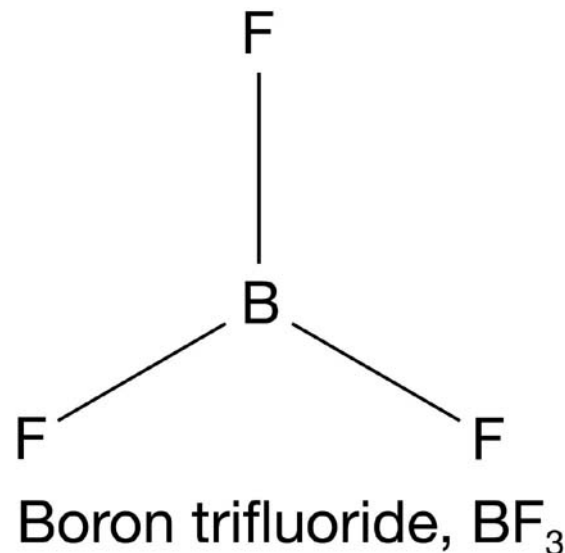
A molecule belongs to the group  $D_{nh}$ , if in addition to the  $D_n$  operations it possess  $n$  dihedral mirror planes  $\sigma_d$ .

Examples: the twisted,  $90^\circ$  allene,  $\text{C}_3\text{H}_4$  belongs to  $D_{2d}$  group, while the staggered confirmation of ethane belongs to  $D_{3d}$  group.

# Molecular symmetry groups: $D_{nh}$



Benzene  $C_6H_6$



A molecule belongs to the group  $D_{nh}$ , if in addition to the  $D_n$  operations it possess a horizontal mirror plane  $\sigma_h$ . As a consequence, these molecule have also necessarily  $n$  vertical planes of symmetry  $\sigma_v$  at angles  $360^\circ/2n$  to each other.

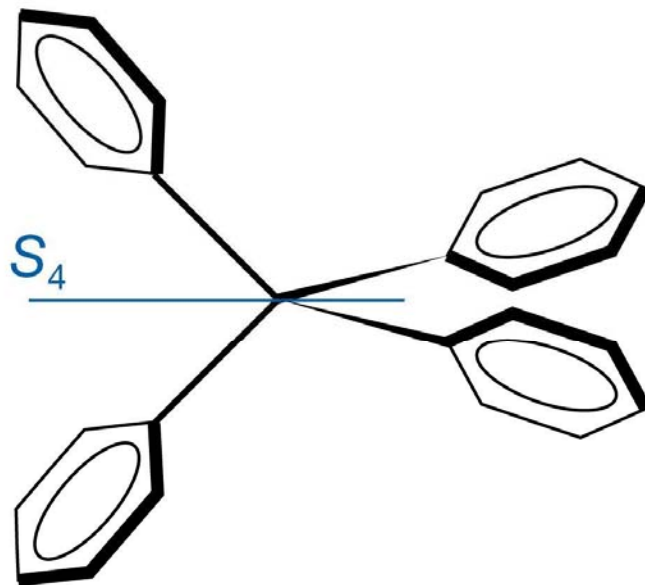
Examples:  $BF_3$  has the elements  $E$ ,  $C_3$ ,  $3 C_2$ , and  $\sigma_h$  and thus belongs to the  $D_{3h}$  group.

$C_6H_6$  has the elements  $E$ ,  $C_6$ ,  $3 C_2$ ,  $3 C_2'$  and  $\sigma_h$  and, thus, belongs to the  $D_{6h}$  group.

All homonuclear diatomic molecules, such as  $O_2$ ,  $N_2$ , and others belong to the  $D_{\infty h}$  group.

Other examples are ethene,  $C_2H_4$  ( $D_{2h}$ ),  $CO_2$  ( $D_{\infty h}$ ),  $C_2H_2$  ( $D_{\infty h}$ ).

## Molecular symmetry groups: $S_n$



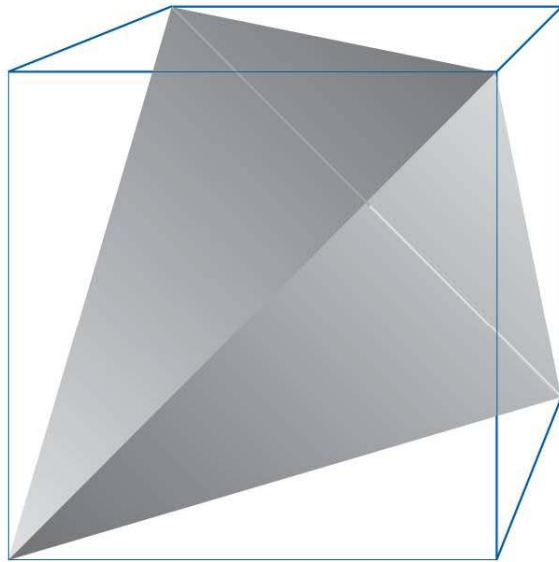
Tetraphenylmethane,  $C(C_6H_5)_4$  ( $S_4$ )

A molecule belongs to the group  $S_n$  if it possess one  $S_n$  axis.  
Example: **tetraphenylmethane** which belongs to the group  $S_4$ .

Note that the group  $S_2$  is the same as  $C_i$ , and such molecules are classified as  $C_i$ .

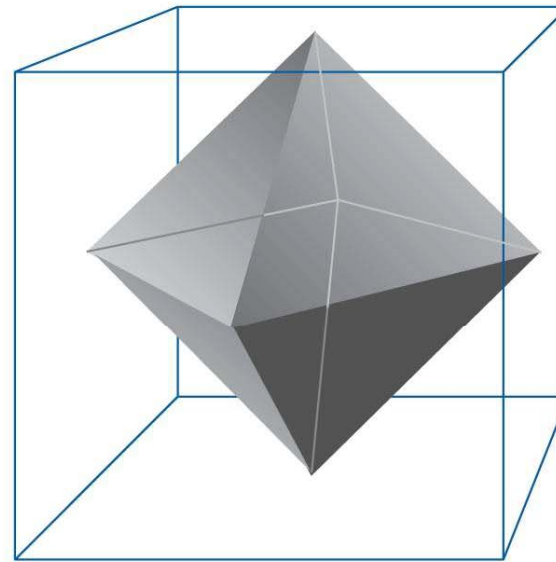
# The cubic groups: $T_d$ and $O_h$

Tetrahedral molecule



(a)  $\text{CH}_4$ :  $T_d$  group

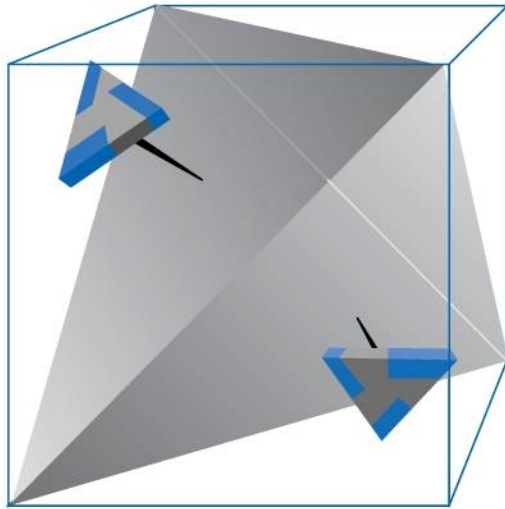
Octahedral molecule



(b)  $\text{SF}_6$ :  $O_h$  group

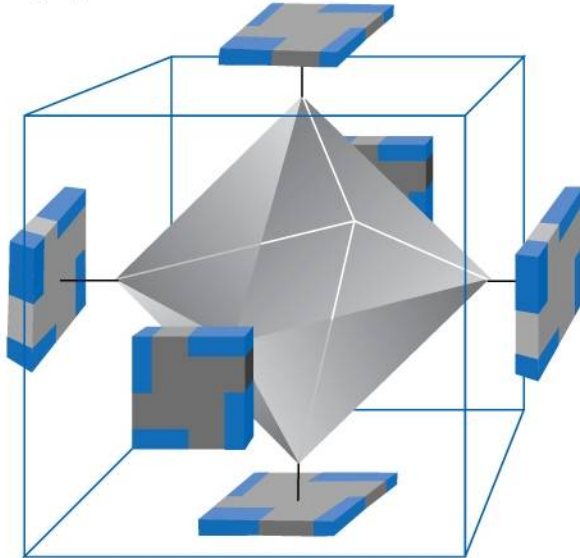
There are many important molecules with more than one principal axes, for instance,  $\text{CH}_4$  and  $\text{SF}_6$ . Most of them belong to the **cubic groups**, particularly to **tetrahedral groups**  $T$ ,  $T_d$ , and  $T_h$ , or to the **octahedral groups**  $O$  and  $O_h$ . If the object has the rotational symmetry of the **tetrahedron**, or **octahedron**, but has no planes of reflection, then it belongs to the simpler groups  $T$ , or  $O$ . The group  $T_h$  is based on  $T$ , but also has a center of inversion.

# The cubic groups: T and O



**Tetrahedral molecule**

(a)  $T$



**Octahedral molecule**

(b)  $O$

**symmetry operations:** Identity  $E$   
n-fold rotation Rotation  $C_n$   
reflection  $\sigma$  ( $\sigma_v$ ,  $\sigma_d$ ,  $\sigma_h$ )  
inversion  $i$   
improper rotation  $S_n$

**point groups:**  
 $C_1$ ,  $C_i$ ,  $C_s$   
 $C_n$ ,  $C_{nv}$ ,  $C_{nh}$ ,  
 $D_n$ ,  $D_{nh}$ ,  $D_{nd}$ ,  
 $S_n$ ,  
 $T$ ,  $O$

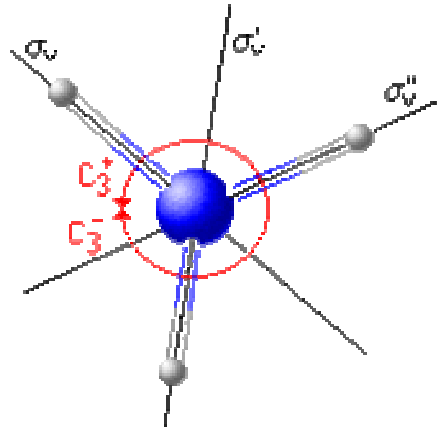
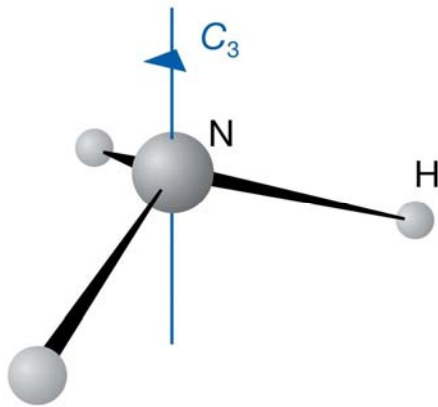
# Symmetry Classification of Molecules.

## Definition of the Group

In order to classify molecules according to symmetry one can list their symmetry elements and collect together the molecules with the same list of elements. More precisely, we can collect together the molecules which belong to the same **group**. According to the **group theory**, the symmetry operations are the members of a **group** if they satisfy the following **group axioms**:

- The successive application of two operations is equivalent to the application of a member of the group. In other words, if the operations **A** and **B** belong to the same group then  $\mathbf{A \cdot B = C}$ , where **C** is also the operation from the same group. Note, that in general  $\mathbf{A \cdot B \neq B \cdot A}$ .
- One of the operations in the group is the identity operation **E**. This means that  $\mathbf{A \cdot E = E \cdot A = A}$ .
- The reciprocal of each operation is a member of the group: if **A** belongs to a group, then  $\mathbf{A^{-1} = B}$ , where **B** is also the member of the group. Note, that  $\mathbf{A \cdot A^{-1} = A^{-1} \cdot A = E}$ .
- Multiplication of the operations is associative:  $\mathbf{A \cdot B \cdot C = (A \cdot B) \cdot C = A \cdot (B \cdot C)}$ .

# Group Multiplication Table: NH<sub>3</sub> molecule



These are all six symmetry operations of the molecule:

$E, C_3^+, C_3^-, \sigma_v, \sigma_v', \sigma_v''$

Let us show that these symmetry operations joint a group. It is easy to see that:

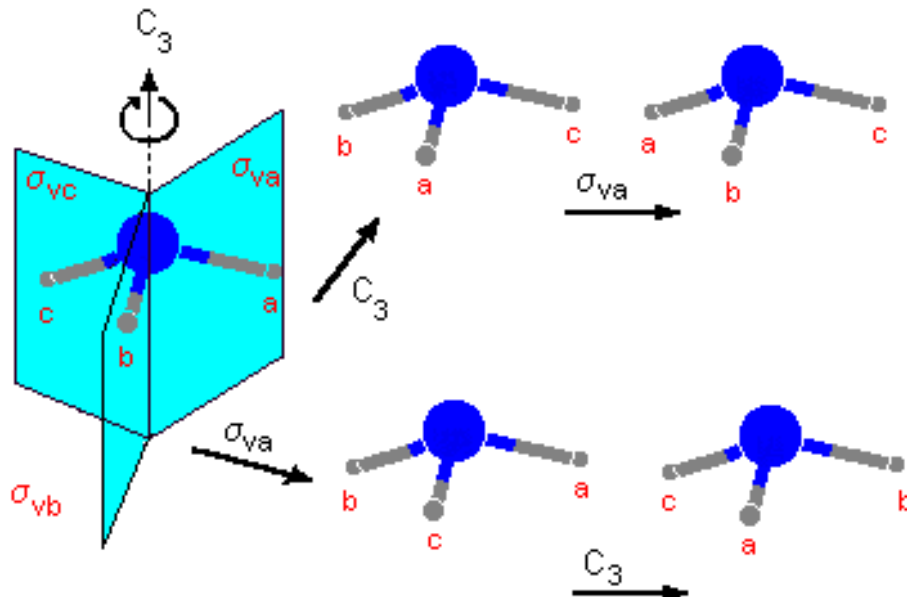
$$C_3^+ C_3^- = E$$

Also:

$$\sigma_{va} C_3 = \sigma_{vb}$$

and

$$C_3 \sigma_{va} = \sigma_{vc}$$



# Matrix representation of symmetry operations

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

$$\sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \begin{pmatrix} x \\ y \\ -z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

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

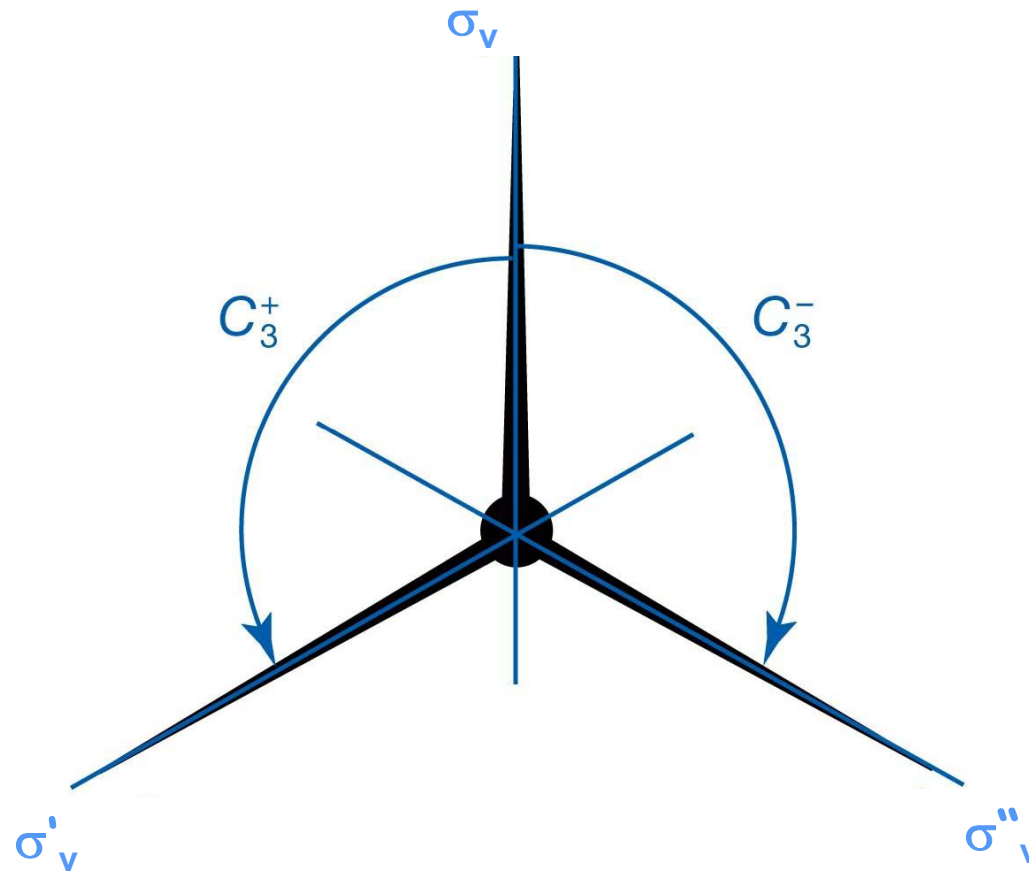
## Group Multiplication Table: $C_{3v}$ Group

	E	$C_3^+$	$C_3^-$	$\sigma_v$	$\sigma_v'$	$\sigma_v''$
E	E	$C_3^+$	$C_3^-$	$\sigma_v$	$\sigma_v'$	$\sigma_v''$
$C_3^+$	$C_3^+$	$C_3^-$	E	$\sigma_v'$	$\sigma_v''$	$\sigma_v$
$C_3^-$	$C_3^-$	E	$C_3^+$	$\sigma_v''$	$\sigma_v$	$\sigma_v'$
$\sigma_v$	$\sigma_v$	$\sigma_v''$	$\sigma_v'$	E	$C_3^-$	$C_3^+$
$\sigma_v'$	$\sigma_v'$	$\sigma_v$	$\sigma_v''$	$C_3^+$	E	$C_3^-$
$\sigma_v''$	$\sigma_v''$	$\sigma_v'$	$\sigma_v$	$C_3^-$	$C_3^+$	E

The total number of operations in a group is called the **group order**.  
Therefore, the order of  $C_{3v}$  is **6**.

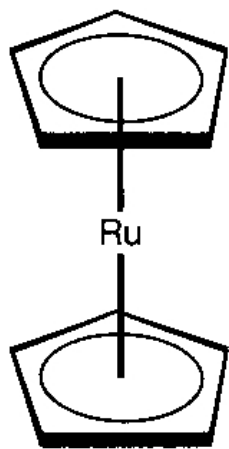
Each point group is characterized by its own multiplication table.

# Classes of Symmetry Operations: $C_{3v}$ group

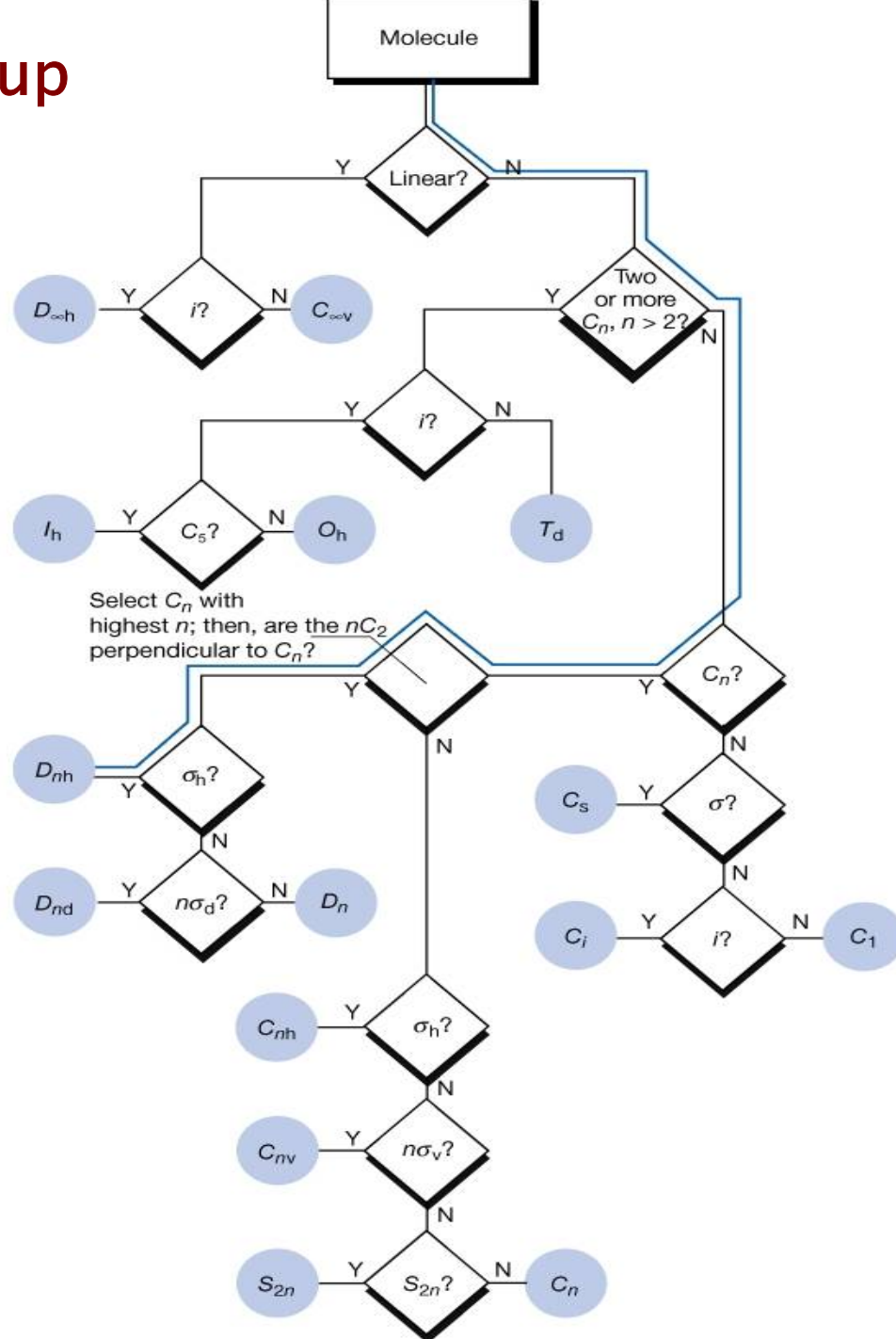


# Determine the Point Group of a Molecule

As an example just follow the blue line in the flow diagram to determine the point group of Ruthenocene ( $D_{5h}$ )



Ruthenocene,  $\text{Ru}(\text{C}_6\text{H}_5)_2$



# Some Consequences of Molecular Symmetry

As soon as the point group of a molecule is identified, some statements about its properties can be done.

## • Polarity

Polar molecules have a permanent electric dipole moment. For instance these are **NaCl**, **O<sub>3</sub>**, **NH<sub>3</sub>**, and many others. It is known that rotational absorption transitions can occur only in polar molecules. The group theory give important instructions, how the molecular symmetry is related to the molecular polarity. If a molecule belongs to the **C<sub>n</sub>** group, where **n>1**, then it cannot have a component of the dipole moment perpendicular to the symmetry axis. A dipole moment in these molecules can be only **parallel to the molecular axis**. The same is valid for any of the **C<sub>nv</sub>** group molecule. The molecules which belongs to **all other groups**, but **C<sub>s</sub>**, cannot have a permanent dipole moment, because they always have symmetry operations transforming one end of the molecule into another.

⇒ **Thus, only molecules which belong to the C<sub>n</sub>, C<sub>nv</sub>, or C<sub>s</sub> group can have a permanent dipole moment.**

## • Chirality

A **chiral molecule** cannot be transformed to itself with any **mirror transformation**. An **achiral molecule** can be transformed to itself with a **mirror transformation**. Chiral molecules are important because they are optically active in the sense that they can rotate the plane of polarized light passing through the molecular sample. A molecule may be **chiral** only if it **does not have an axis of improper rotation S<sub>n</sub>**. Note that the molecule with a center of inversion *i* belongs to **S<sub>2</sub>** group and, thus, it **cannot be chiral**. **Similarly, because S<sub>1</sub> = σ, any molecule with a mirror plane is achiral.**

## symmetry operations:

Identity  $E$

n-fold rotation Rotation  $C_n$

reflection  $\sigma$  ( $\sigma_v$ ,  $\sigma_d$ ,  $\sigma_h$ )

inversion  $i$

improper rotation  $S_n$

$\Rightarrow$  only molecules which belong to the  $C_n$ ,  $C_{nv}$ , or  $C_s$  group can have a **PERMANENT dipole moment**.

$\Rightarrow$  A molecule may be **CHIRAL** only if it **DOES NOT** have an axis of improper rotation  $S_n$ .

$\Rightarrow \Psi = \int \phi_1 \phi_2 \, d\tau = 0$  if  $\phi_1 \phi_2$  is not symmetric.

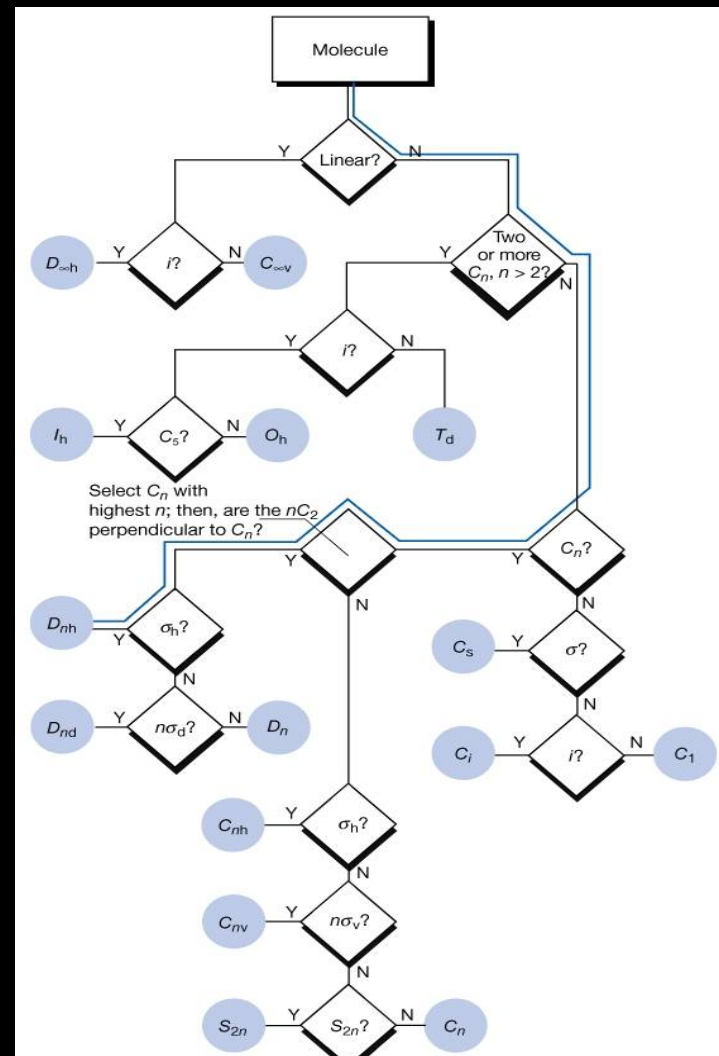
## point groups:

$C_1$ ,  $C_i$ ,  $C_s$ ,

$C_n$ ,  $C_{nv}$ ,  $C_{nh}$ ,

$D_n$ ,  $D_{nh}$ ,  $D_{nd}$ ,

$S_n$ ,  $T$ ,  $O$

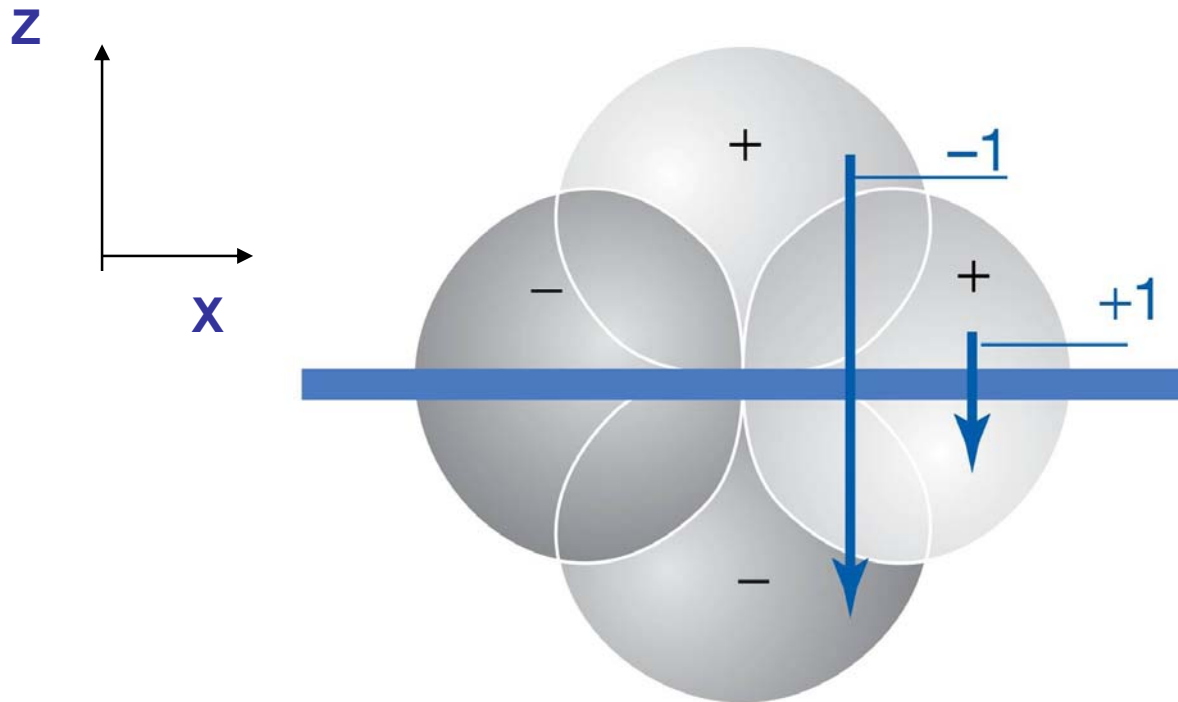


# Symmetry of Electronic Orbitals: Non-Degenerate Case

$$\text{Schrödinger Equation: } \mathbf{H} \Psi_k = \mathbf{E}_k \Psi_k$$

Each eigenfunction  $\Psi$  and energy level  $\mathbf{E}$  can be labelled with a symmetry index  $k$  which indicates the point symmetry group of the molecule!

Symmetry of two p orbitals under reflection through the mirror plane



$$\sigma p_x = p_x' = p_x$$

$$\sigma p_z = p_z' = -p_z$$

The quantitative characteristic of the labelling is a **Character Table** which shows the behavior of the molecular eigenfunctions under the symmetry operations of the molecular symmetry point group

# Character Table of a Symmetry Point Group

just a taste of it ...

$C_s$	E	$\sigma(xy)$	$h = 2$
A'	+1	+1	x,y
A''	+1	-1	z

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$	$h = 4$	
A <sub>1</sub>	1	1	1	1	z, z <sup>2</sup> , x <sup>2</sup> , y <sup>2</sup>	
A <sub>2</sub>	1	1	-1	-1	xy	R <sub>z</sub>
B <sub>1</sub>	1	-1	1	-1	x, xz	R <sub>y</sub>
B <sub>2</sub>	1	-1	-1	1	y, yz	R <sub>x</sub>

# Character Table of the Symmetry Point Group $C_{3v}$

Symmetry operation of this group form a class

Schönflies symbol

number of operations within a class

MULLIKEN symbols (species)

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

The character  $\chi$  of an element in a representation is the trace of the matrix for that element.

Transformation of cartesian coordinates  $x, y, z$  or functions of these coordinates and rotations  $R_i$  around these axis.

Here the number of symmetry operations  $h=6$  is now not equal to the number of possible species (3). That is because, some of the symmetry operations can be combined into classes, which means that they are of the same type (for example, rotations) and can be transferred into one another by a symmetry operation of the same group.

# Symmetry of Electronic Orbitals: Degenerate Case

Schrödinger Equation:  $H \Psi_k = E_k \Psi_k$

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

The symmetry species E is a **double degenerate** one. These species cannot be characterized simply by the character values  $\chi = \pm 1$ , as for non-degenerate case. The wavefunctions which belong to a degenerate state **are neither symmetric, nor antisymmetric** with respect to the symmetry operations of the group, but in general can be transformed as a **linear combination of each other**:

$$\begin{aligned} \Psi'_1 &= d_{11} \Psi_1 + d_{12} \Psi_2 \\ \Psi'_2 &= d_{21} \Psi_1 + d_{22} \Psi_2 \end{aligned} \quad \text{or} \quad \Psi'_k = \sum_j d_{kj} \Psi_j$$

The character  $\chi$  is the **sum of diagonal expansion coefficients**:  $\chi = d_{11} + d_{22}$   
 The character of the identity operator **E** is always equal to the degeneracy!

# Robert Sanderson Mulliken



**\* 7. June 1896 in Newburyport, MA (USA)  
+ 31. October 1986 in Arlington, VA (USA)**

**Nobel Prize for Chemistry 1966**

# MULLIKEN Symbols

1. The dimension of characters are denoted with one of the following capital letters:

In vibrational spectroscopy, F replaces T. The very common groups  $C_{nv}$ ,  $D_{nh}$  and  $D_{nd}$  have only characters of dimension 1 and 2.

2. If  $C_n$  represents rotation about the principal axis, the one-dimensional characters are A or B depending on the value of  $\chi(C_n)$ .

A and B thus indicate whether rotation of a wave function about an axis causes the sign to change (B) or to remain constant (A).

dimension	Mulliken symbol
1	A and B
2	E
3	T
4	G
5	H

$\chi(C_n)$	denoted as
+1	A
-1	B

# MULLIKEN Symbols (Indices)

Indices reflect an additional classification of symmetry.

3. If the molecule possesses an axis  $C_2$  or a plane of reflection  $\sigma$  or  $\sigma_d$  perpendicular to the principal axis  $C_n$ , the values for function  $\psi$  change or keep their sign and are therefore regarded as symmetric or antisymmetric, respectively. Analogous indices exist for E and T, but the underlying rules are more complicated.
4. Dependent on the effect of inversion  $i$ , Mulliken's symbols take the indices g for *gerade* and u for *ungerade*.
5. The way reflection on a horizontal plane affects a function is denoted by primed or doubly primed symbols.

function $\psi$	Index
sign unaffected	1
change of sign	2

$\chi(i)$	Index
+1	g
-1	u

$\chi(\sigma_h)$	Indicated by
+1	'
-1	"

# Character Table of the Symmetry Point Groups $C_2$ and $C_{2v}$

If  $C_n$  represents rotation about the principal axis, the one-dimensional characters are A or B depending on the value of  $\chi(C_n)$ .

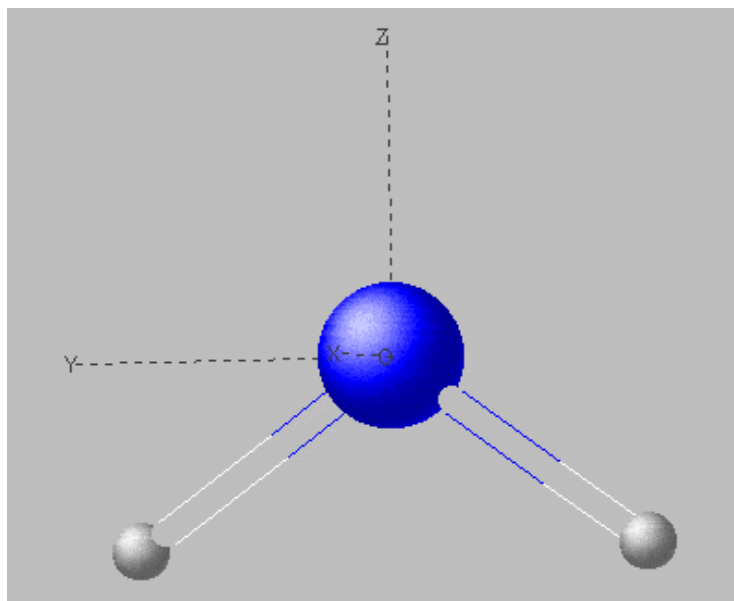
$C_2$	E	$C_2$		
A	1	1	$T_z; R_z$	$x^2; y^2; z^2; xy$
B	1	-1	$T_x; T_y; R_x; R_y$	$xz; yz$

function $\psi$	Index
sign unaffected	1
change of sign	2

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$	$h = 4$	
$A_1$	1	1	1	1	$z, z^2, x^2, y^2$	
$A_2$	1	1	-1	-1	$xy$	$R_z$
$B_1$	1	-1	1	-1	$x, xz$	$R_y$
$B_2$	1	-1	-1	1	$y, yz$	$R_x$

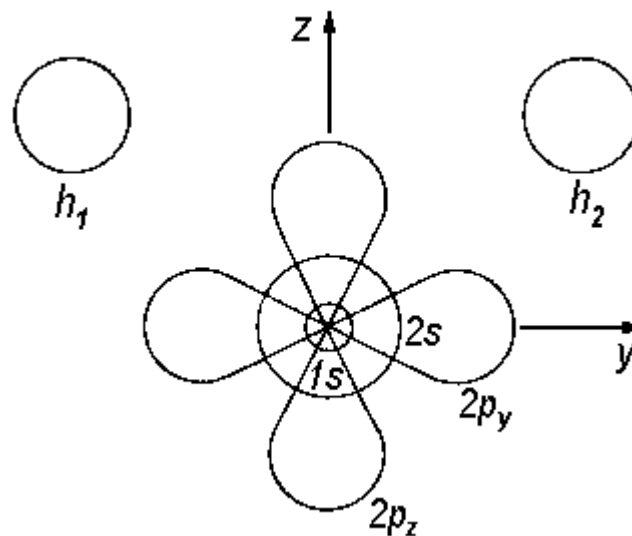
# Symmetry adopted orbitals (Example H<sub>2</sub>O)

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1



The 1s atomic orbitals  $h_1$  and  $h_2$  of both hydrogen atoms contribute to the bonding of the water molecule H<sub>2</sub>O. The oxygen atom has electrons in 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> states. We will proceed with the valence shell orbitals s, p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>.

The s orbital of the oxygen atom is totally symmetric to all symmetry operations. One says it is of  $a_1$  symmetry (lower case is used for a single orbital, while upper case is used for the total term value).



# Symmetry adopted orbitals: H<sub>2</sub>O, p<sub>x</sub>(O)

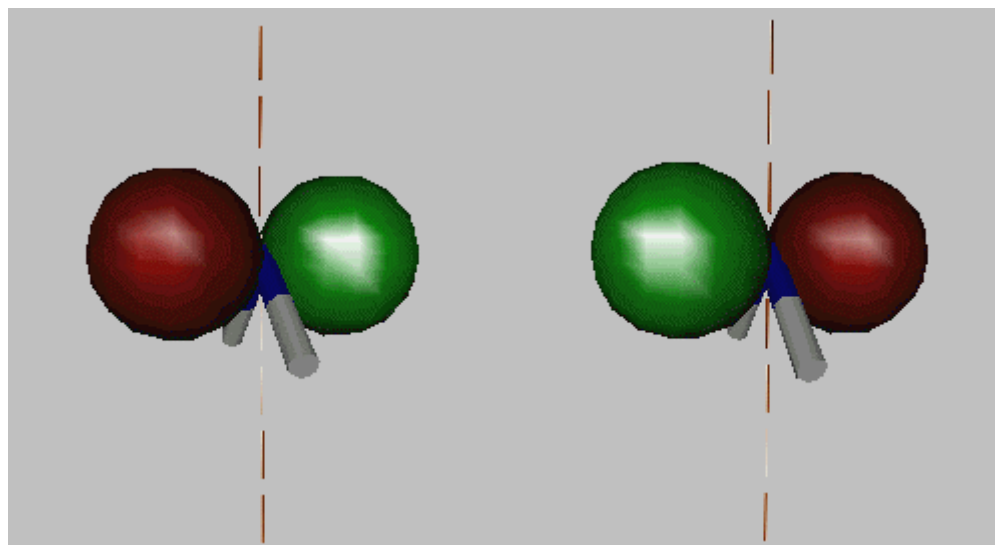
Identity gives 1

<b>E</b>	$C_2$	$\sigma_v$	$\sigma'_v$
1			

Rotation gives -1

<b>E</b>	$C_2$	$\sigma_v$	$\sigma'_v$
1	-1		

$C_2$  Rotation

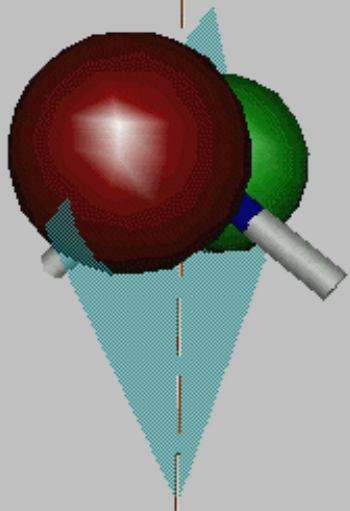


structure before rotation

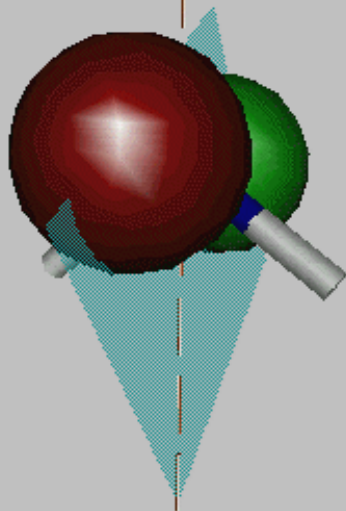
structure after rotation

around  $C_2$  axis

# Symmetry adopted orbitals: $\text{H}_2\text{O}$ , $p_x(\text{O})$



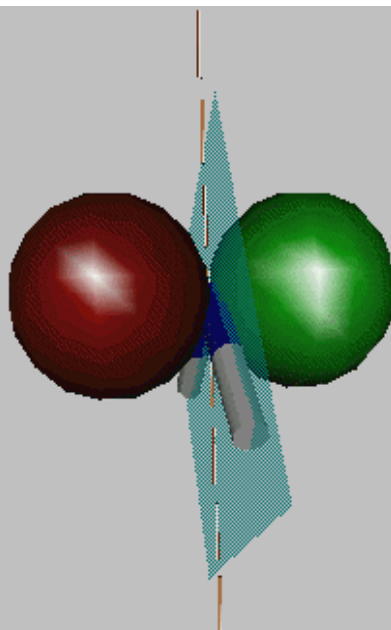
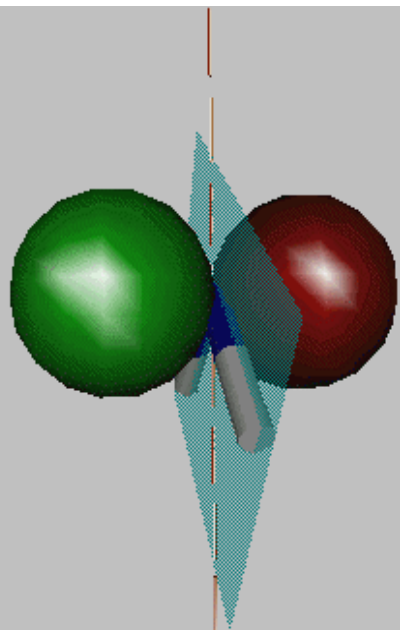
structure before reflection



structure after reflection

on xz plane

E	$C_2$	$\sigma_v(xz)$	$\sigma'_v$
1	-1	1	



on yz plane

E	$C_2$	$\sigma_v$	$\sigma'_v(yz)$
1	-1	1	-1

# Classification of orbitals

For the  $p_x$  orbital we found

E	$C_2$	$\sigma_v$	$\sigma'_v(yz)$
1	-1	1	-1

Thus, it is of  $b_1$  symmetry.

atomic orbital	s	$p_x$	$p_y$	$p_z$
irreducible representation	$a_1$	$b_1$	$b_2$	$a_1$

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1

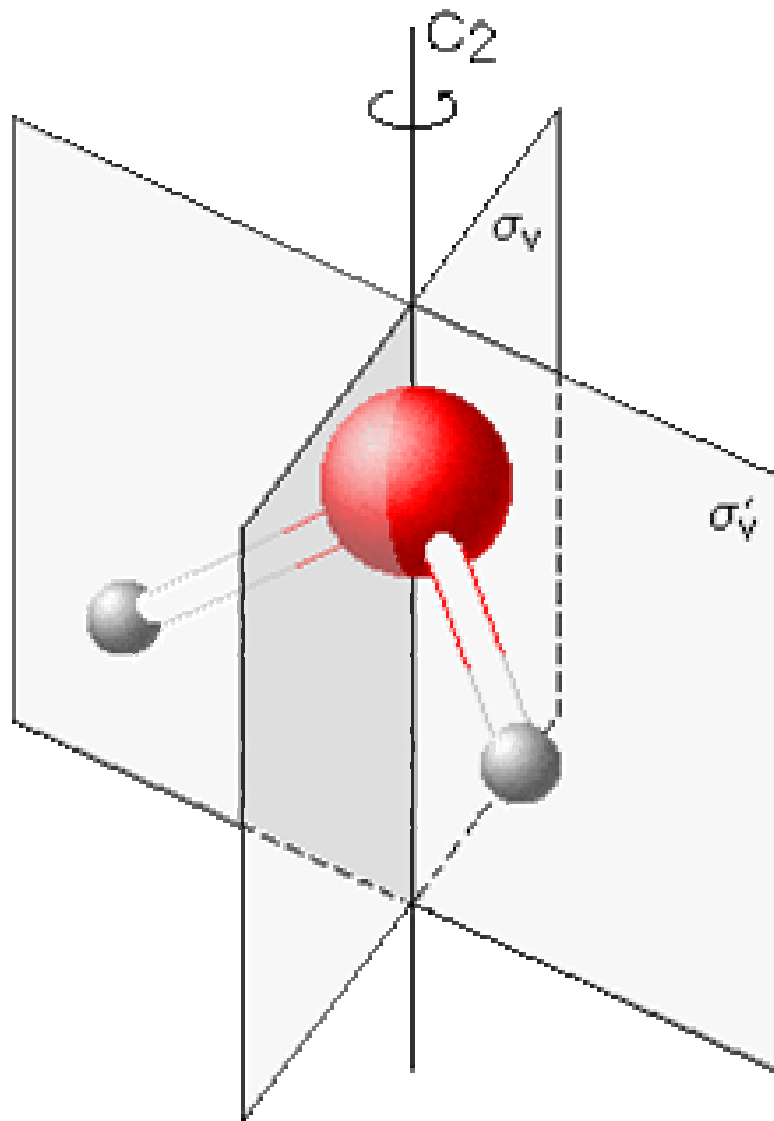
In contrast to the oxygen atom, the AOs  $h_1$  and  $h_2$  are **not** symmetry adapted as  $C_2$  or  $\sigma(xz)$  convert  $h_1$  in  $h_2$  and vice versa. However,  $h_s$  and  $h_a$  are symmetry adapted:

$$h_s = \frac{1}{\sqrt{2}} (h_1 + h_2)$$

$$h_a = \frac{1}{\sqrt{2}} (h_1 - h_2)$$

atomic orbital	$h_s$	$h_a$
irreducible representation	$a_1$	$b_2$

# Symmetry of Electronic Orbitals: H<sub>2</sub>O



$$O_2p_x = b_1$$

$$O_2p_y = b_2$$

$$O_2p_z = a_1$$

Molecular plane is YZ

# Construction of MO orbitals for H<sub>2</sub>O

Oxygen atomic orbitals	s	p <sub>x</sub>	p <sub>y</sub>	p <sub>z</sub>	h <sub>s</sub>	h <sub>a</sub>	Hydrogen adopted orbitals
irreducible representation	a <sub>1</sub>	b <sub>1</sub>	b <sub>2</sub>	a <sub>1</sub>	a <sub>1</sub>	b <sub>2</sub>	irreducible representation

Three AOs are of symmetry species a<sub>1</sub>. Therefore s, p<sub>z</sub> and h<sub>s</sub> are combined to yield *three* molecular orbitals.

$$1a_1 = c_{11}s + c_{12}p_z + c_{13}h_s$$

$$2a_1 = c_{21}s + c_{22}p_z + c_{23}h_s$$

$$3a_1 = c_{31}s + c_{32}p_z + c_{33}h_s$$

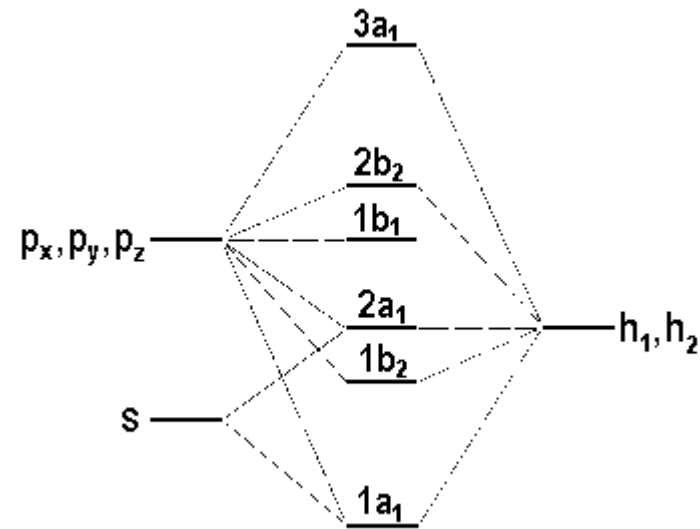
There is only one atomic orbital of b<sub>1</sub> symmetry. It cannot be introduced in any linear combination. It becomes a (neutral) molecular orbital of H<sub>2</sub>O.

$$1b_1 = p_x$$

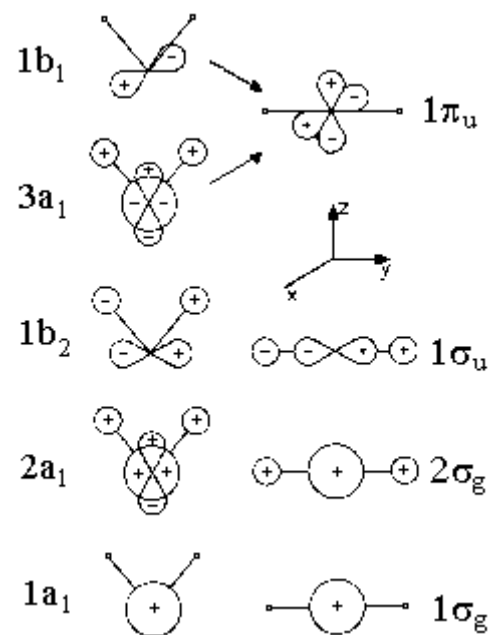
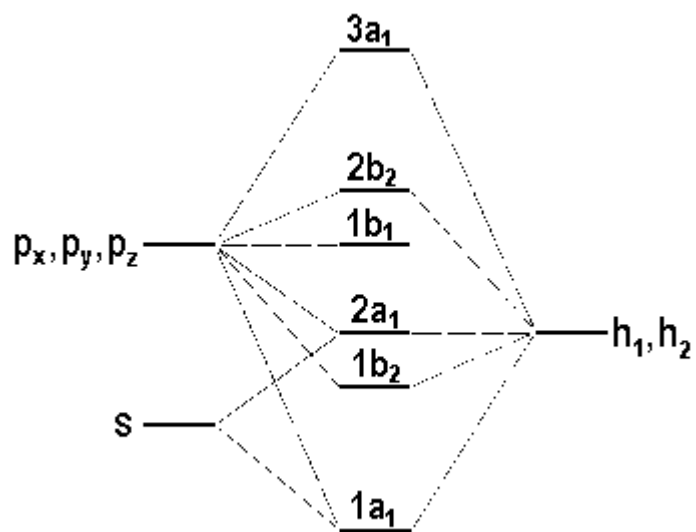
Finally, p<sub>y</sub> and h<sub>a</sub> belong to b<sub>2</sub> and are thus combined to yield two molecular orbitals

$$1b_2 = c_{44}p_y + c_{45}h_a$$

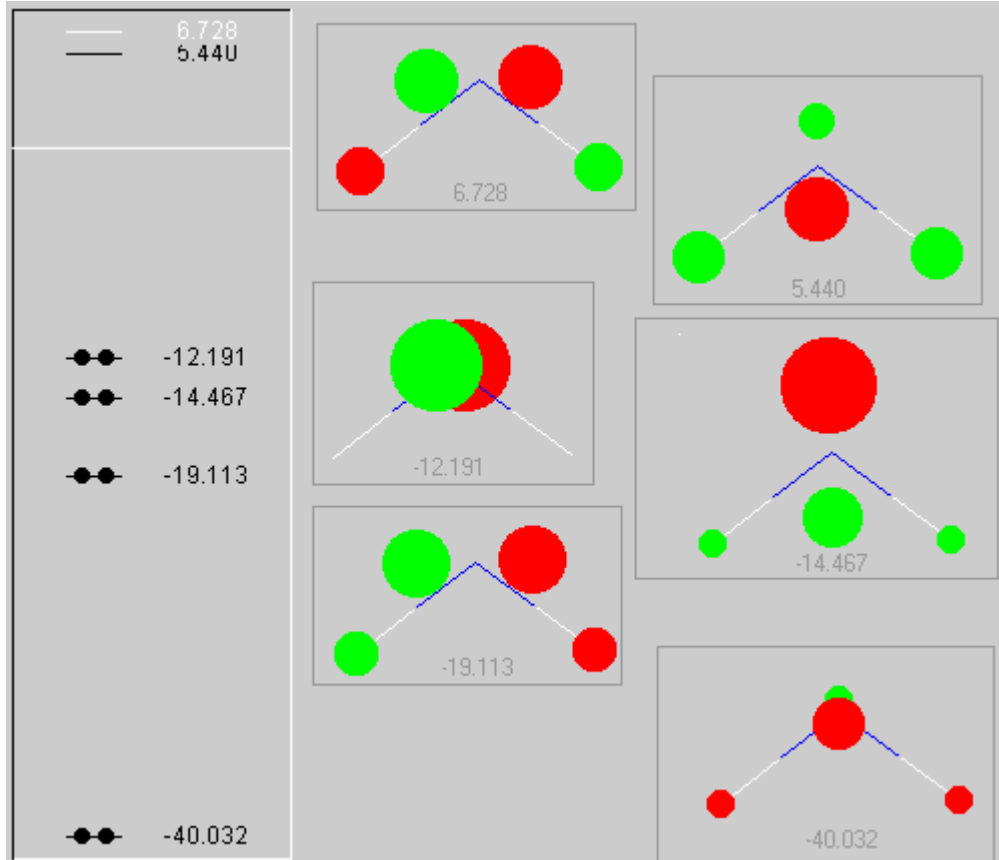
$$2b_2 = c_{54}p_y + c_{55}h_a$$



# Construction of MO orbitals for H<sub>2</sub>O



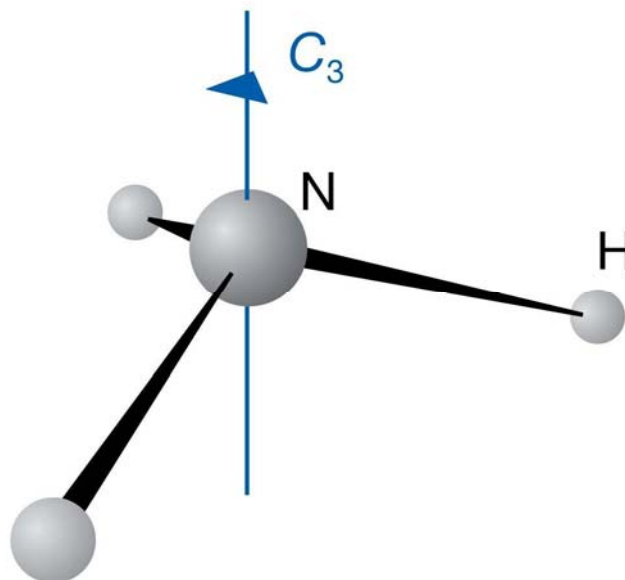
# MO orbitals for H<sub>2</sub>O: calculated



Energy	Symbol
6.728	2b <sub>2</sub>
5.440	3a <sub>1</sub>
-12.191	1b <sub>1</sub>
-14.467	2a <sub>1</sub>
-19.113	1b <sub>2</sub>
-40.032	1a <sub>1</sub>

E	s(H)	s(O)	p <sub>x</sub> (O)	p <sub>y</sub> (O)	p <sub>z</sub> (O)	s(H)	Symbol
6.728	0.525	0	0	-0.669	0	-0.525	2b <sub>2</sub>
5.440	-0.553	0.306	0	0	-0.544	0.553	3a <sub>1</sub>
-12.191	0	0	-1.000	0	0	0	1b <sub>1</sub>
-14.467	-0.309	0.354	0	0	0.827	-0.309	2a <sub>1</sub>
-19.113	-0.473	0	0	-0.743	0	0.473	1b <sub>2</sub>
-40.032	0.315	0.884	0	0	-0.143	0.315	1a <sub>1</sub>

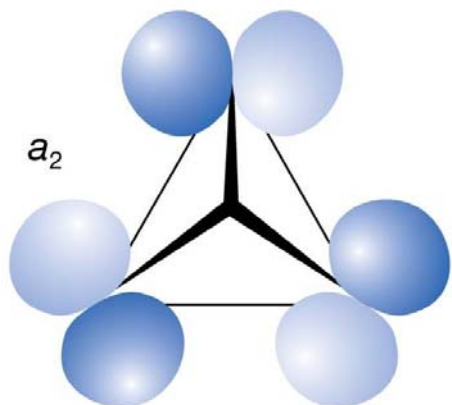
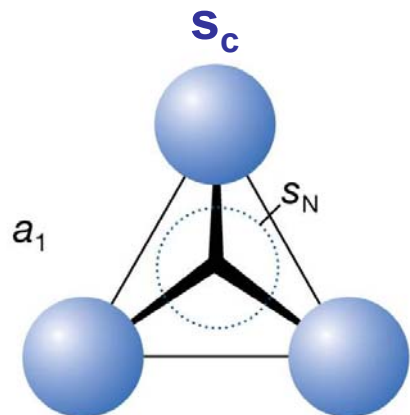
# Linear Combinations of Atomic Orbitals: $C_{3v}$ group



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

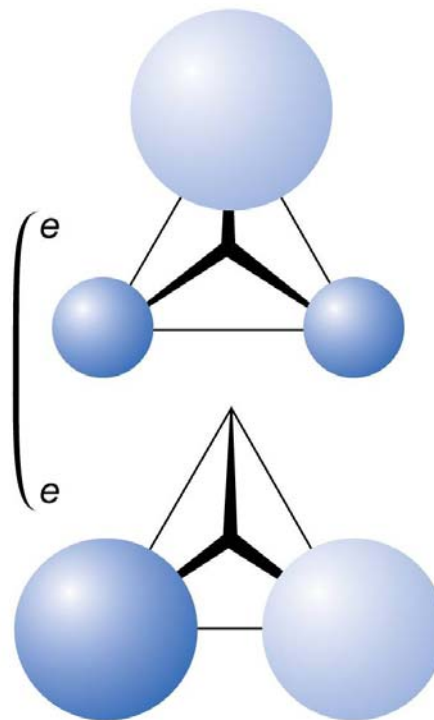
# Linear Combinations of Atomic Orbitals: $C_{3v}$ group

$$\text{NH}_3: s_1 = s_a + s_b +$$



$$\text{H}_3\text{C} - \text{CCl}_3: \psi = p_a + p_b + p_c$$

$$\text{NH}_3: s_2 = -s_a + \frac{1}{2}(s_b + s_c)$$

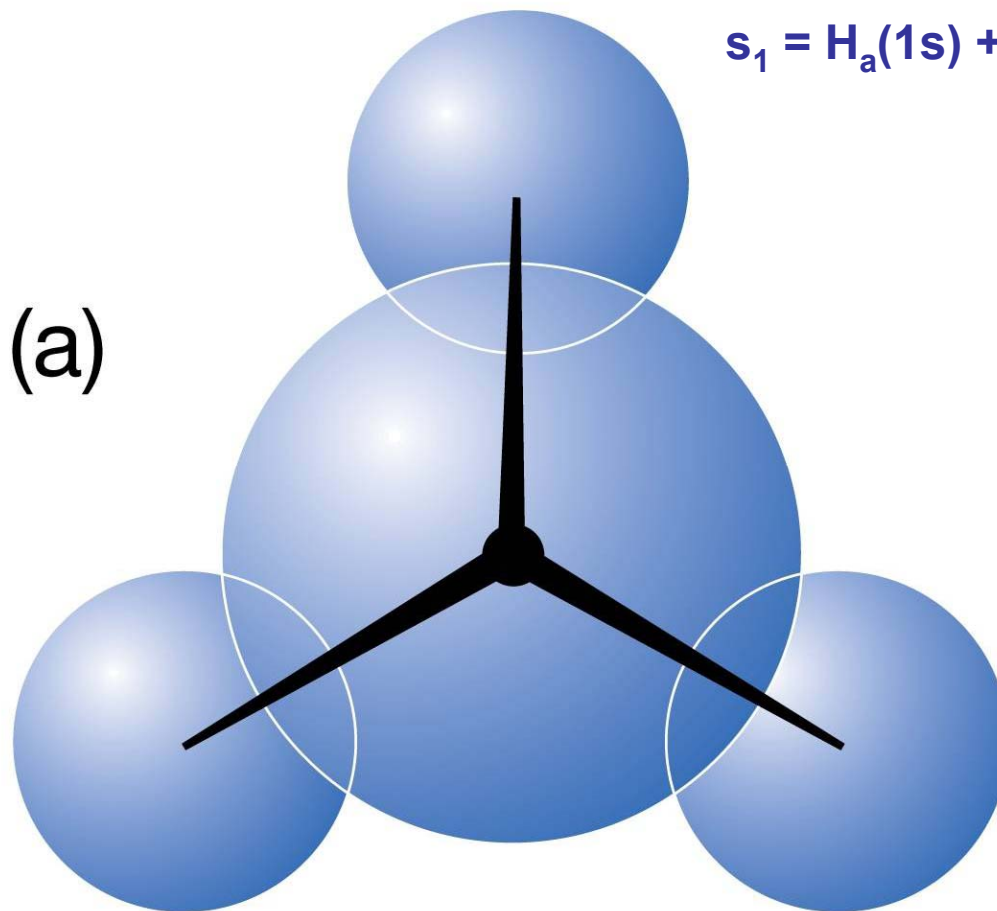


$$\text{NH}_3: s_3 = s_b - s_c$$

# Building of Bonding and Antibonding Orbitals

$a_1$  molecular orbital

$$s_1 = H_a(1s) + H_b(1s) + H_c(1s)$$



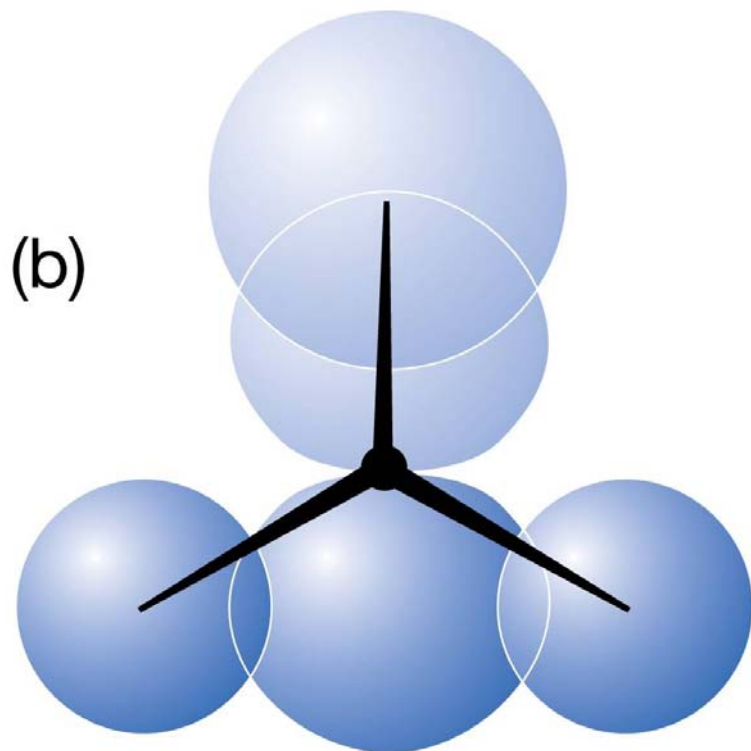
$$N(2s) + s_1$$

# Building of Bonding and Antibonding Orbitals

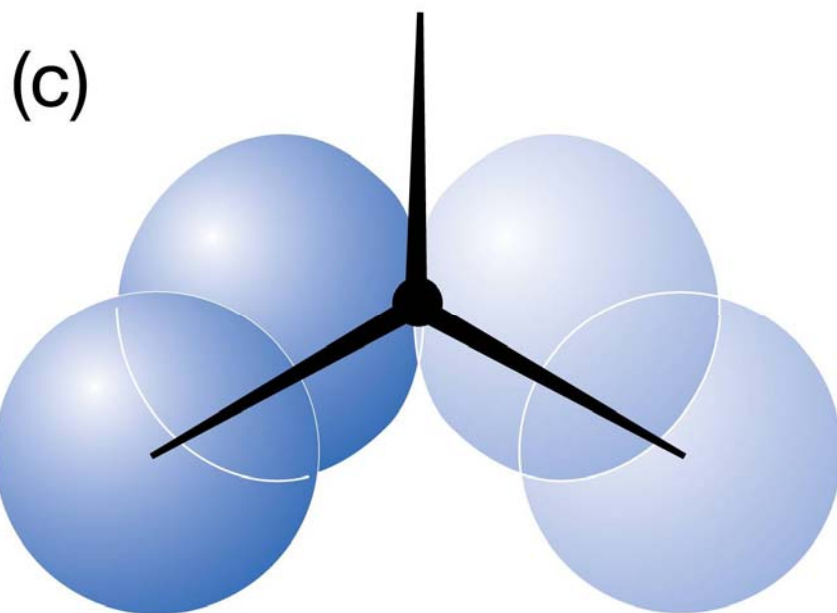
## e molecular orbitals

$$s_2 = -H_a(1s) + \frac{1}{2}H_b(1s) + \frac{1}{2}H_c(1s)$$

$$s_3 = H_b(1s) - H_c(1s)$$



$$N(2p_x) + s_2$$



$$N(2p_y) + s_3$$

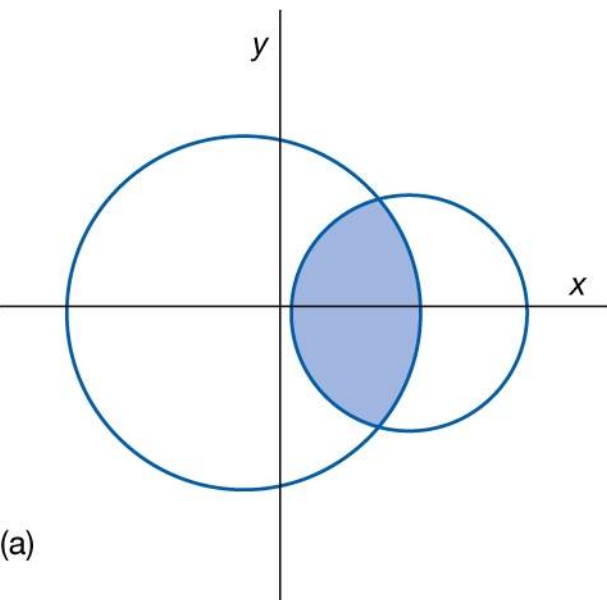
# Vanishing Integrals

The character tables provide a quick and convenient way of judging whether an overlap, or transition integral is necessary zero.

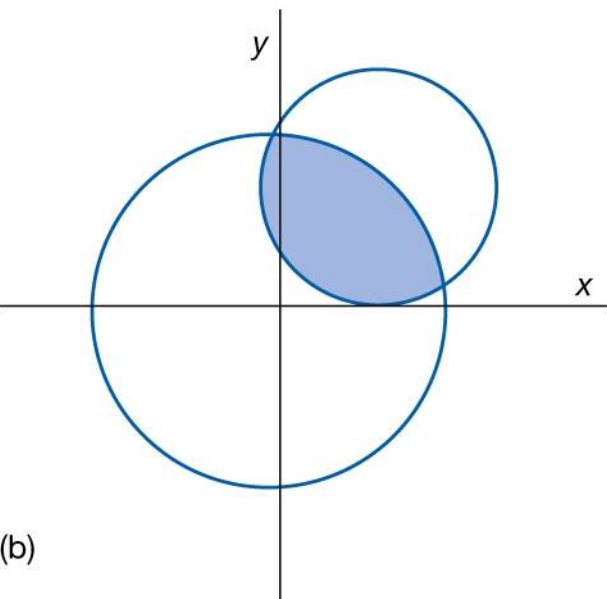
$$I = \int f_1 f_2 d\tau$$

The integral  $I$  is always a **scalar value**. The volume element  $d\tau$  is also a **scalar** as it is invariant under any coordinate transformations.

Thus, the product  $f_1 f_2$  must also remain unchanged by any symmetry operations of the molecular point group. If the integrand changes its sign under a symmetry operation the integral  $I$  is necessarily zero, because its positive part will cancel its positive part. Therefore, the integral can differ from zero if the product  $f_1 f_2$  spans the symmetry species  $A_1$ .



(a)



(b)

# Vanishing Integrals

If the symmetry species of the functions  $f_1$  and  $f_2$  are known, the group theory provides a formal procedure which can be used for determination of the symmetry species of the product  $f_1 f_2$ . **Particularly, the character table of the product  $f_1 f_2$  can be obtained just by multiplication of the characters from the character tables of the functions  $f_1$  and  $f_2$  corresponding to a certain symmetry operator.**

Let us consider the product of the  $f_1 = s_N$  orbital of the N atom and the linear combination of three hydrogen atom orbitals,  $f_2 = s_1 = s_a + s_b + s_c$  in  $\text{NH}_3$  molecule, each of the orbitals spans  $A_1$  species:

$$\begin{array}{l} f_1: \\ f_2: \\ f_1 f_2: \end{array} \quad \begin{array}{ccc} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{array}$$

**Symbolic notation**

$$A_1 \times A_1 = A_1$$

Therefore, the product  $f_1 f_2$  also spans  $A_1$  and therefore, the integral  $I$  in this case is **not necessary equal to zero**. Therefore, bonding and antibonding molecular orbitals can be formed from linear combinations of  $s_N$  and  $s_1$ .

# Vanishing Integrals

Let us consider the product of the  $f_1 = s_N$  orbital of the N atom in  $\text{NH}_3$  and  $f_2 = s_3 = s_B - s_C$  is the linear combination of the hydrogen atom wavefunctions. Now one function spans the  $A_1$  species and another the E species in  $C_{3v}$ . The product table of characters is

$$\begin{array}{l} f_1: \quad 1 \quad 1 \quad 1 \\ f_2: \quad 2 \quad -1 \quad 0 \\ f_1 f_2: \quad 2 \quad -1 \quad 0 \end{array}$$

**Symbolic notation**

$$A_1 \times E = E$$

The product characters 2, -1, 0 are those of the E species alone and therefore, the Integral must be zero. **Therefore, bonding and antibonding molecular orbitals cannot be formed from linear combinations of  $s_N$  and  $s_3$ .**

However, the  $N2p_x$  and  $N2p_y$  atomic orbitals also belong to the E species in  $C_{3v}$  and thus are suitable because they may have a nonzero overlap with  $s_2$  and  $s_3$ .

This construction can be verified by multiplying the characters as

$$\begin{array}{l} f_1: \quad 2 \quad -1 \quad 0 \\ f_2: \quad 2 \quad -1 \quad 0 \\ f_1 f_2: \quad 4 \quad 1 \quad 0 \end{array}$$

**Symbolic notation**

$$E \times E = A_1 + A_2 + E$$

**Only the orbitals of the same symmetry species may have nonzero overlap and therefore, form bonding and antibonding combinations**

# Selection Rules for Electronic Transitions

The integrals of the form

$$I = \int f_1 f_2 f_3 d\tau$$

are very important in quantum mechanics as they include **transition matrix elements**.

For dipole transitions in molecules under influence of electromagnetic radiation,  $f_1$  and  $f_3$  are the molecular wavefunctions of the **initial** and the **final** quantum states and  $f_2$  is a component of the molecular dipole moment,  $\mu_x$ ,  $\mu_y$  or  $\mu_z$ .

The integral  $I$  can be nonzero only if the product  $f_1 f_2 f_3$  spans totally symmetric representation  $A_1$ , or its equivalent.

Let us investigate whether an electron in an  $a_1$  orbital in  $H_2O$  can make an electric dipole transition to a  $b_1$  orbital. Having in mind that  $H_2O$  molecule belongs to the  $C_{2v}$  group, we should examine all three  $x$ ,  $y$ , and  $z$  components of the transition dipole moment which transform as  $B_1$ ,  $B_2$ , and  $A_1$ , respectively.

# Selection Rules for Electronic Transitions

Optical transition for **x-component** of the transition dipole moment

	E	C <sub>2</sub>	σ <sub>v</sub>	σ <sub>v</sub> '
f <sub>1</sub> (B <sub>1</sub> )	1	-1	1	-1
f <sub>2</sub> = x	1	-1	1	-1
f <sub>3</sub> (A <sub>1</sub> )	1	1	1	1
f <sub>1</sub> f <sub>2</sub> f <sub>3</sub>	1	1	1	1

Thus, the product **f<sub>1</sub>f<sub>2</sub>f<sub>3</sub>** spans the species **A<sub>1</sub>** and the transition for **x-component of the transition moment is not forbidden**. This component is **perpendicular to the molecular plane**. Similar calculations show that the transitions for **y- and z-components of the dipole moment are both forbidden**.

# Selection Rules for Electronic Transitions

## $C_{2v}$ symmetry

