

M.Sc. Semester-II
Compulsory Paper-7 (CP-7)
Group Theory and Spectroscopy



I. Symmetry and Group Theory in Chemistry
Lecture 2 : Point group, Classification and Representation of Groups



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Symmetry and Group Theory in Chemistry : 25 Hrs

Symmetry elements and symmetry operation, Group and Subgroup, Point group, Classification and representation of groups, The defining property of a group, Sub group and Class, Group multiplication table for C_{2v} , C_{2h} and C_{3v} point group, Generators and Cyclic groups. Similarity Transformation, Table of conjugates for C_{2v} , C_{2h} and C_{3v} point group, Schonflies symbols.

Matrix notation for symmetry operation, Representations of groups by matrices (representation for the C_n , C_{nv} , C_{nh} and D_{nh} groups to be worked out explicitly). Character of a representation, Mulliken symbols for irreducible representations, Direct product relationship, Applications of group theory to quantum mechanics-identifying non-zero matrix elements.

The great orthogonal theorem (without proof) and rules derived from this theorem. Derivation of the orthonormalization condition. Character table. Construction of character table: C_{2v} and C_{3v} (only). Reducible representations and their reduction. Total character and their calculation. Application of character table in determination of IR and Raman active vibrations: H_2O , BF_3 and N_2F_2

Coverage:

1. Point group
2. Classification and representation of groups

Lecture 2 : Point group, Classification and representation of groups

Point Group :

Molecules with the same symmetry elements are placed into *point groups*.

In general, you will not need to assign a molecule to its point group.

Recognition of the features of some common point groups is useful.

Water and ammonia both belong to the C_{nv} class of molecules. These have vertical planes of reflection, but no horizontal planes.

The D_{nh} groups have a horizontal plane in addition to vertical planes.

Many inorganic complexes belong to these symmetry groups.

In assigning a point group, we typically ignore the fine detail, such as conformation isomers, of the ligands.

In working problems using group theory, the point group of the molecule will usually be provided to you.

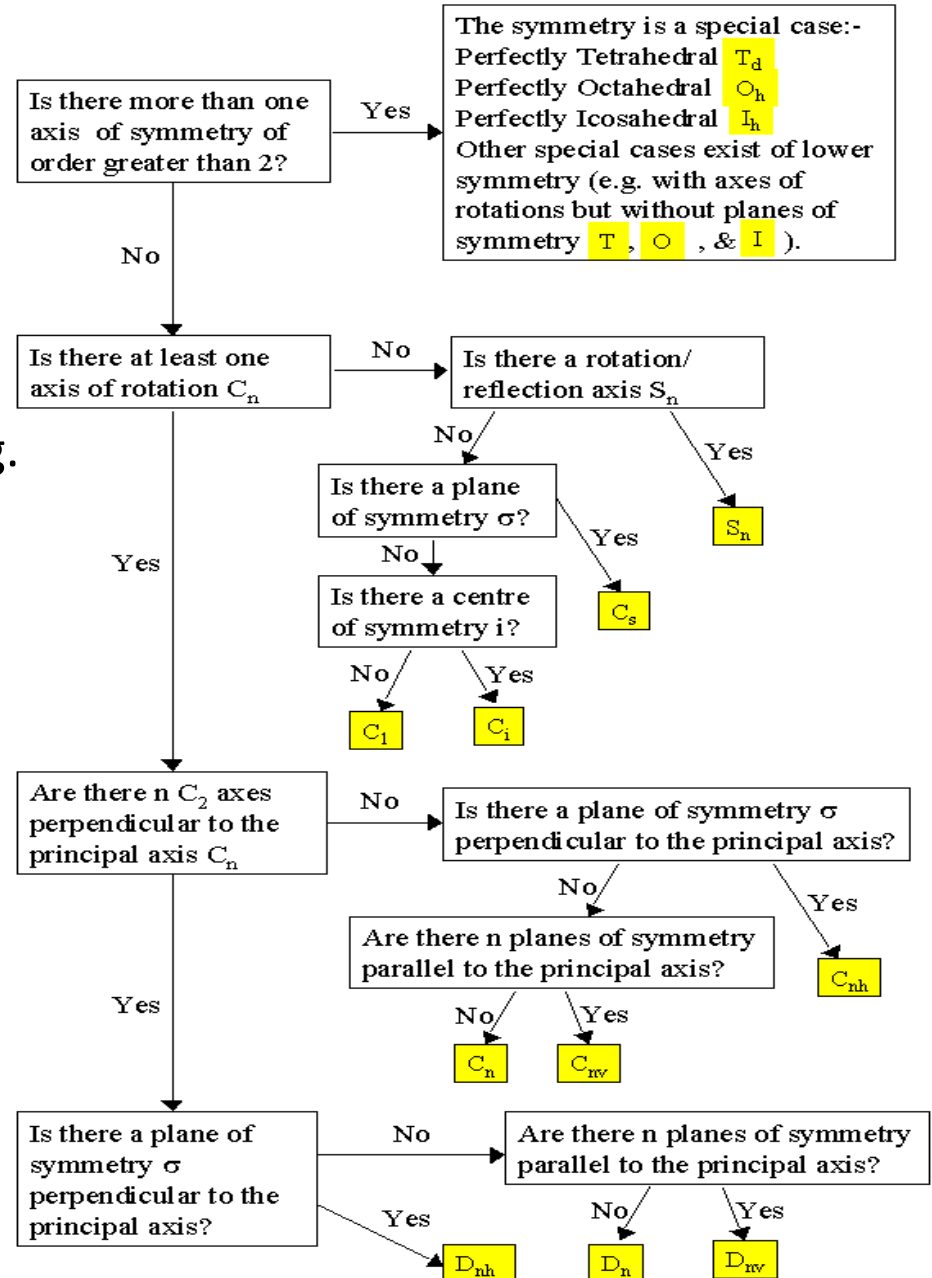
Highly symmetrical molecules, such as identically substituted tetrahedrons or octahedrons belong to their own point groups (T_d or O_h respectively).

Lecture 2 : Point group, Classification and representation of groups

Identifying point groups:

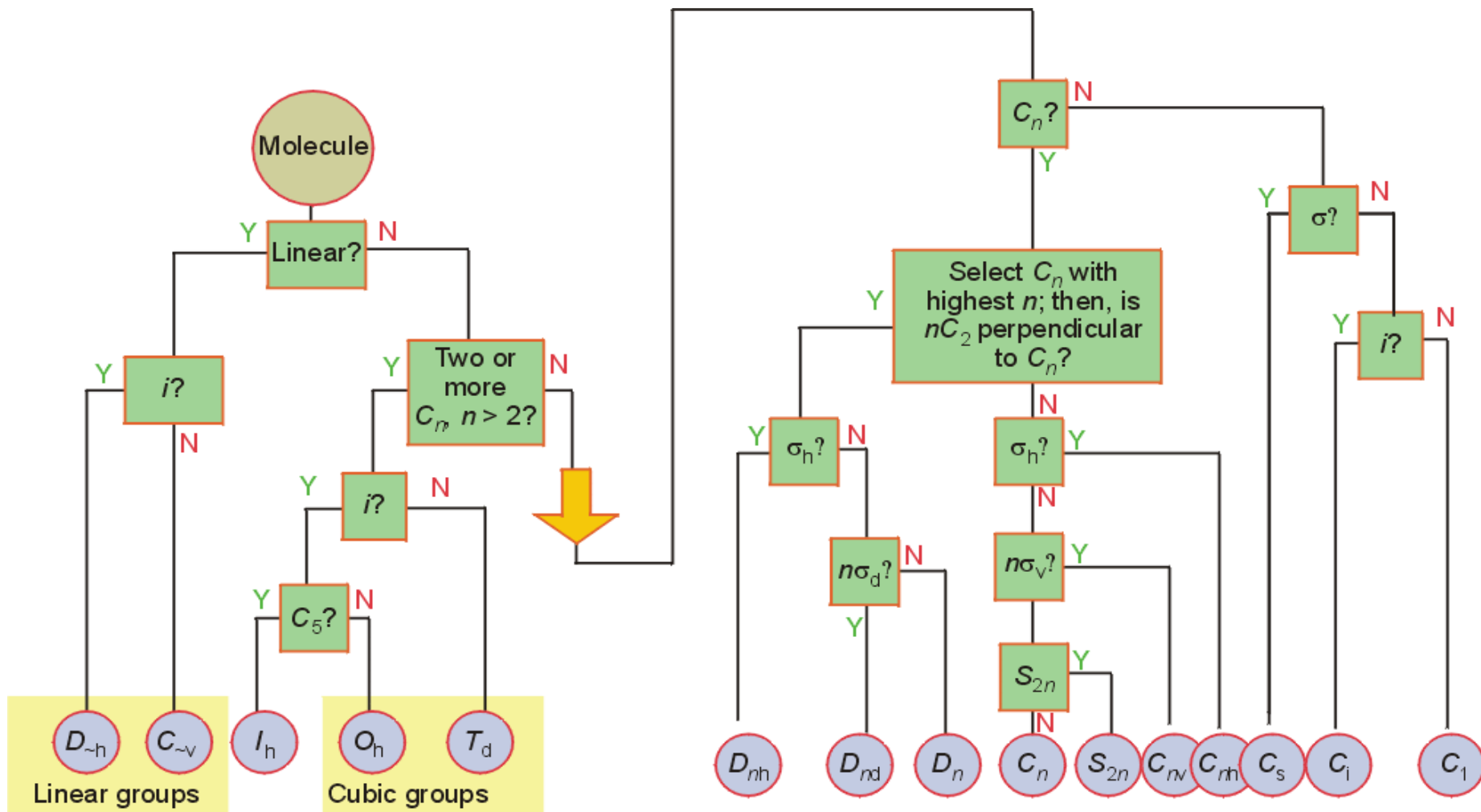
We can use a flow chart such as this one to determine the point group of any object. The steps in this process are:

1. Determine the symmetry is special (e.g. octahedral).
2. Determine if there is a principal rotation axis.
3. Determine if there are rotation axes perpendicular to the principal axis.
4. Determine if there are mirror planes.
5. Assign point group.



Lecture 2 : Point group, Classification and representation of groups

Identifying point groups

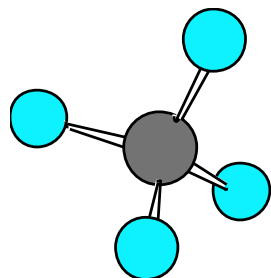
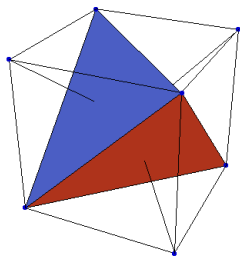


Lecture 2 : Point group, Classification and representation of groups

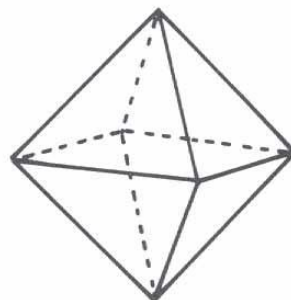
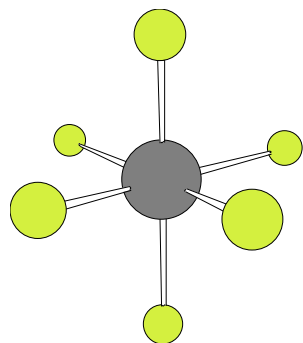
Identifying point groups

Special cases:

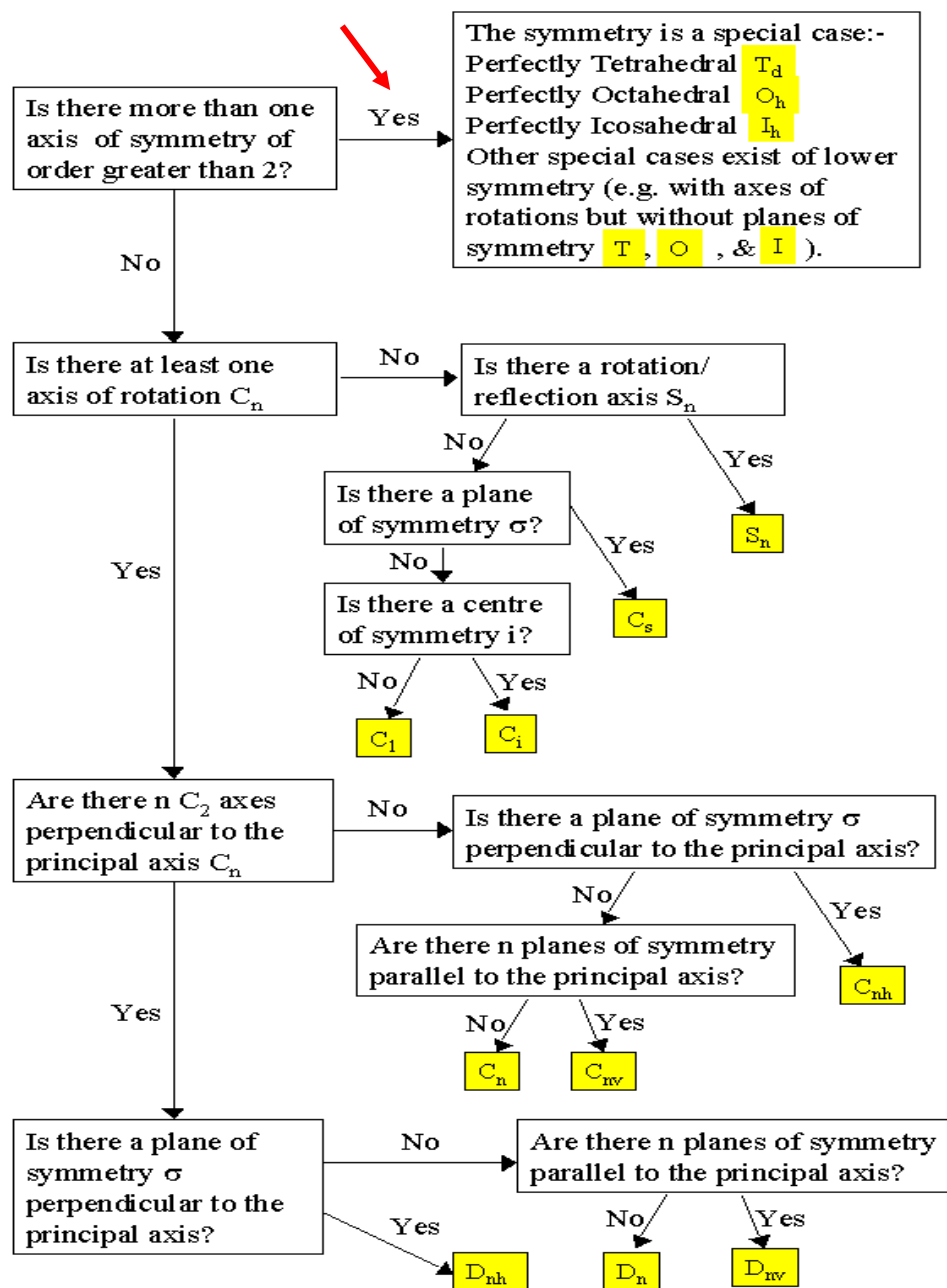
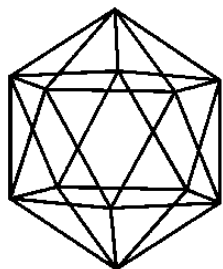
Perfect tetrahedral (T_d) e.g. P_4 , CH_4



Perfect octahedral (O_h) e.g. SF_6 , $[B_6H_6]^{-2}$



Perfect icosahedral (I_h) e.g. $[B_{12}H_{12}]^{-2}$, C_{60}



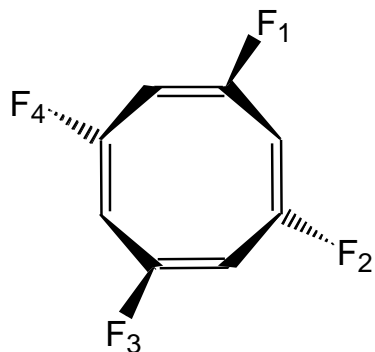
Lecture 2 : Point group, Classification and representation of groups

Identifying point groups

Low symmetry groups:

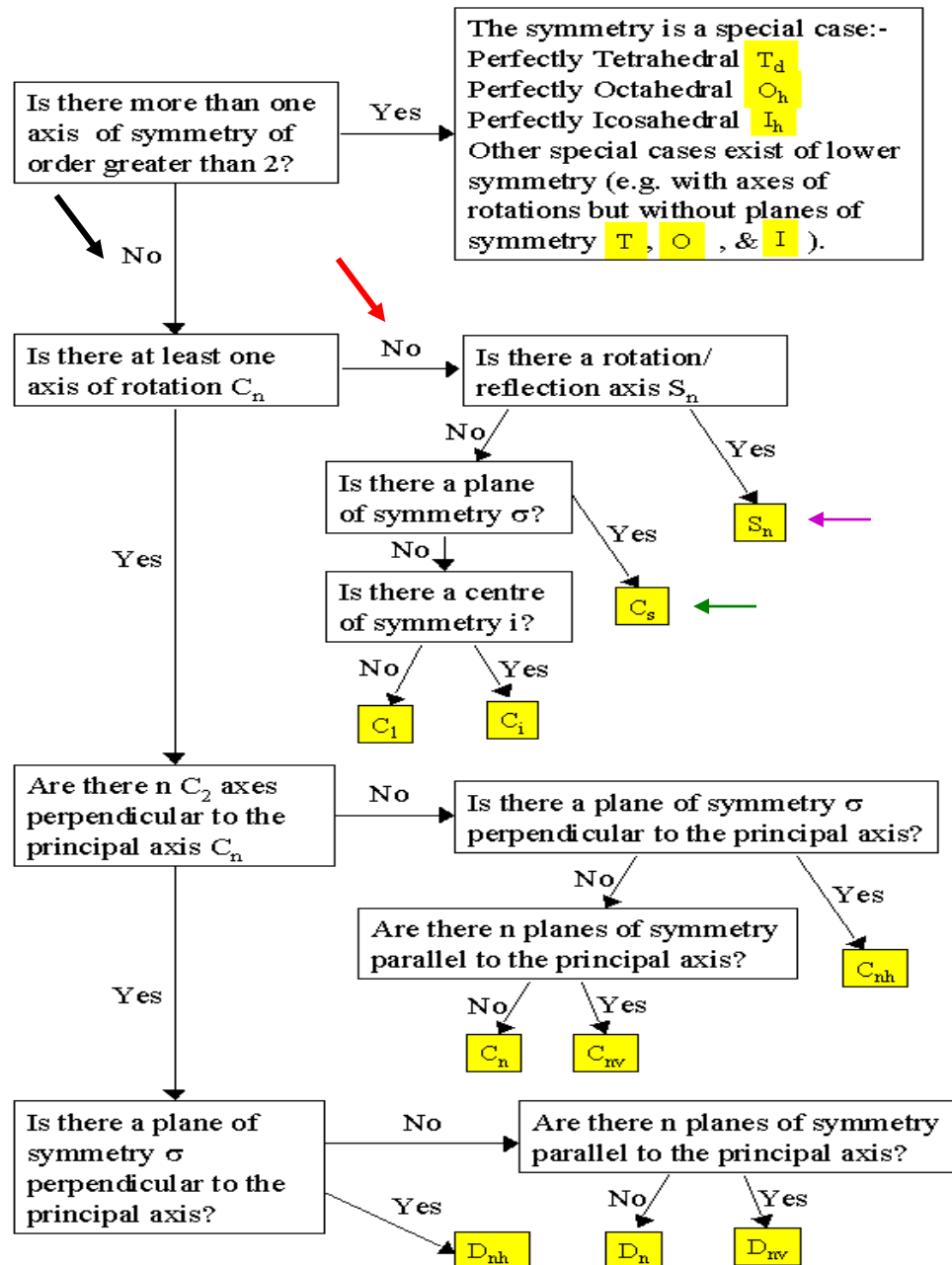
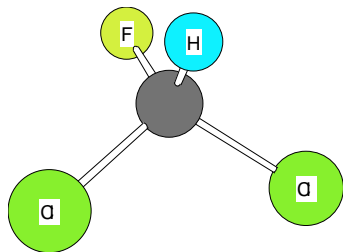
Only* an improper axis (S_n)

e.g. 1,3,5,7-tetrafluorocyclooctatetraene, S_4



Only a mirror plane (C_s)

e.g. CHCl_2

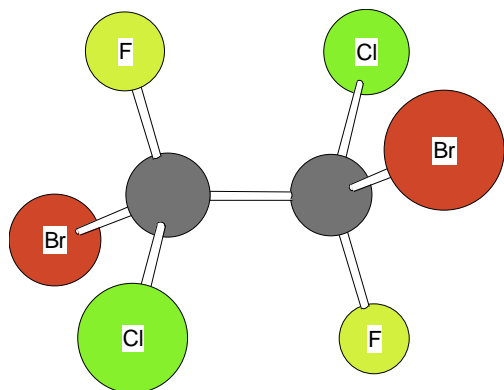


Lecture 2 : Point group, Classification and representation of groups

Identifying point groups

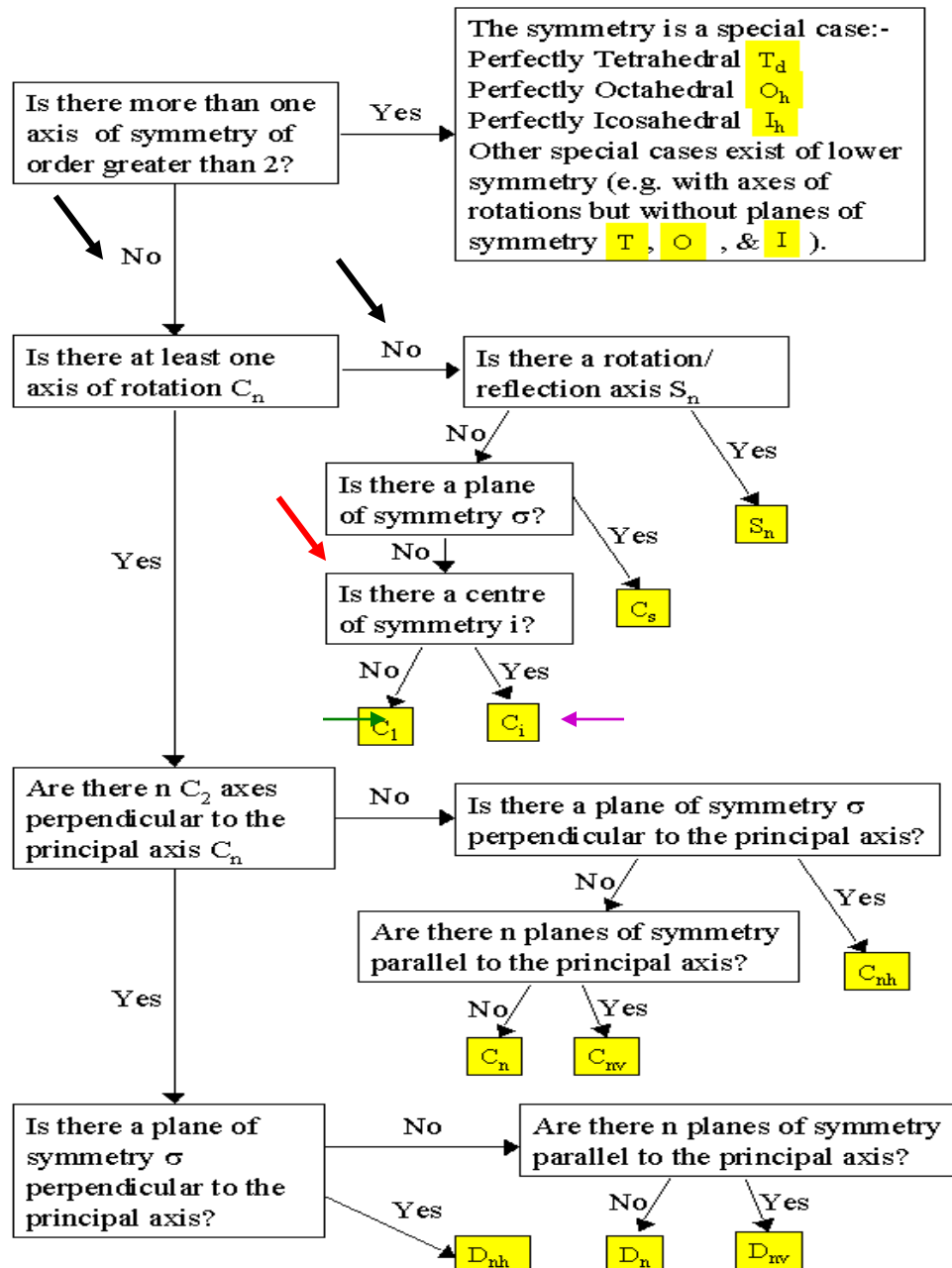
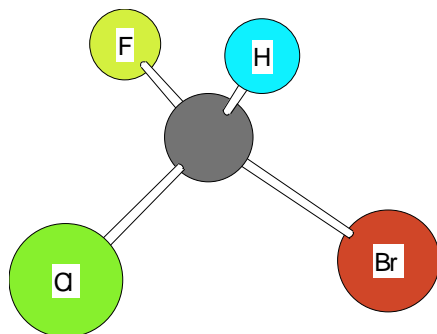
Low symmetry groups:

Only an inversion center (C_i)
e.g. (conformation is important !)



No symmetry (C_1)

e.g. CHFCIBr

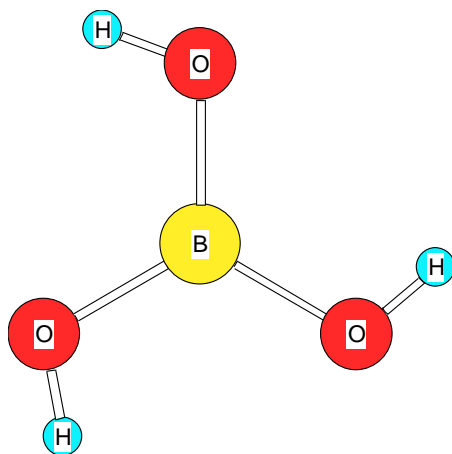


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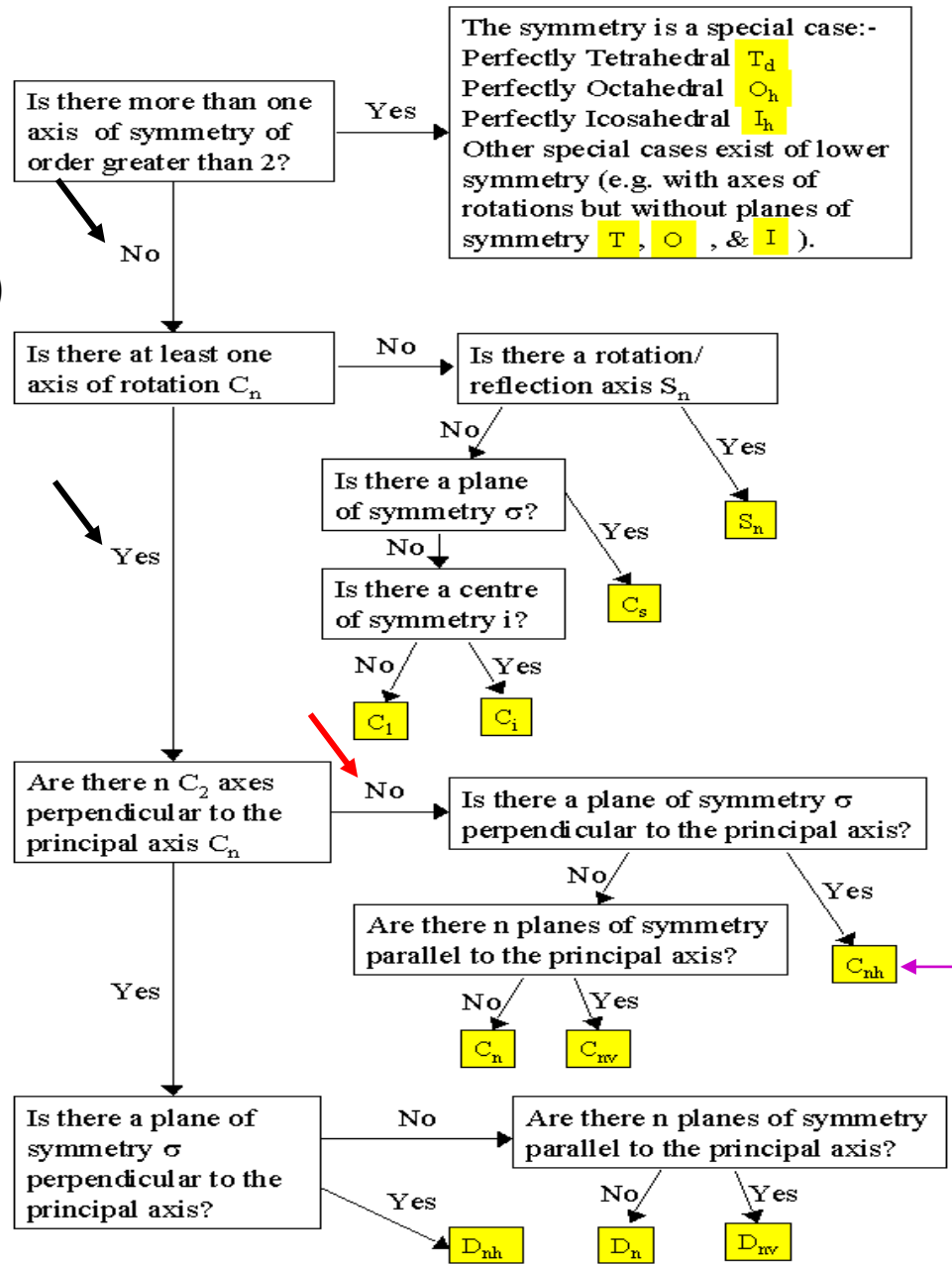
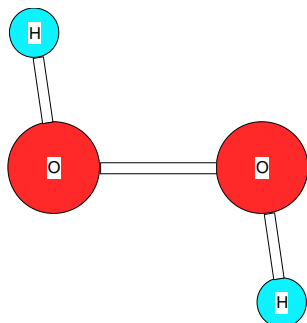
Identifying point groups

C_n type groups:

A C_n axis and a σ_h (C_{nh})
 e.g. $B(OH)_3$ (C_{3h} , conformation is important !)



e.g. H_2O_2 (C_{2h} , conformation is important !)



Note: molecule does not have to be planar e.g. $B(NH_2)_3$ (C_{3h} , conformation is important !)

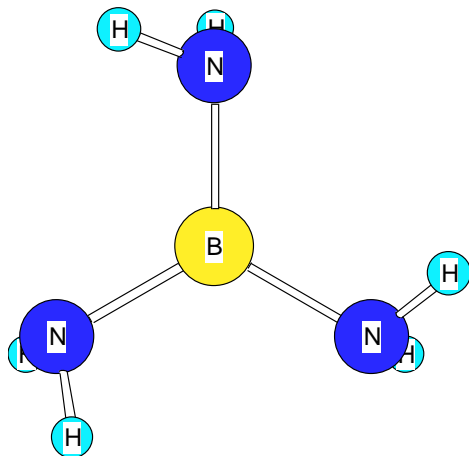
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Identifying point groups

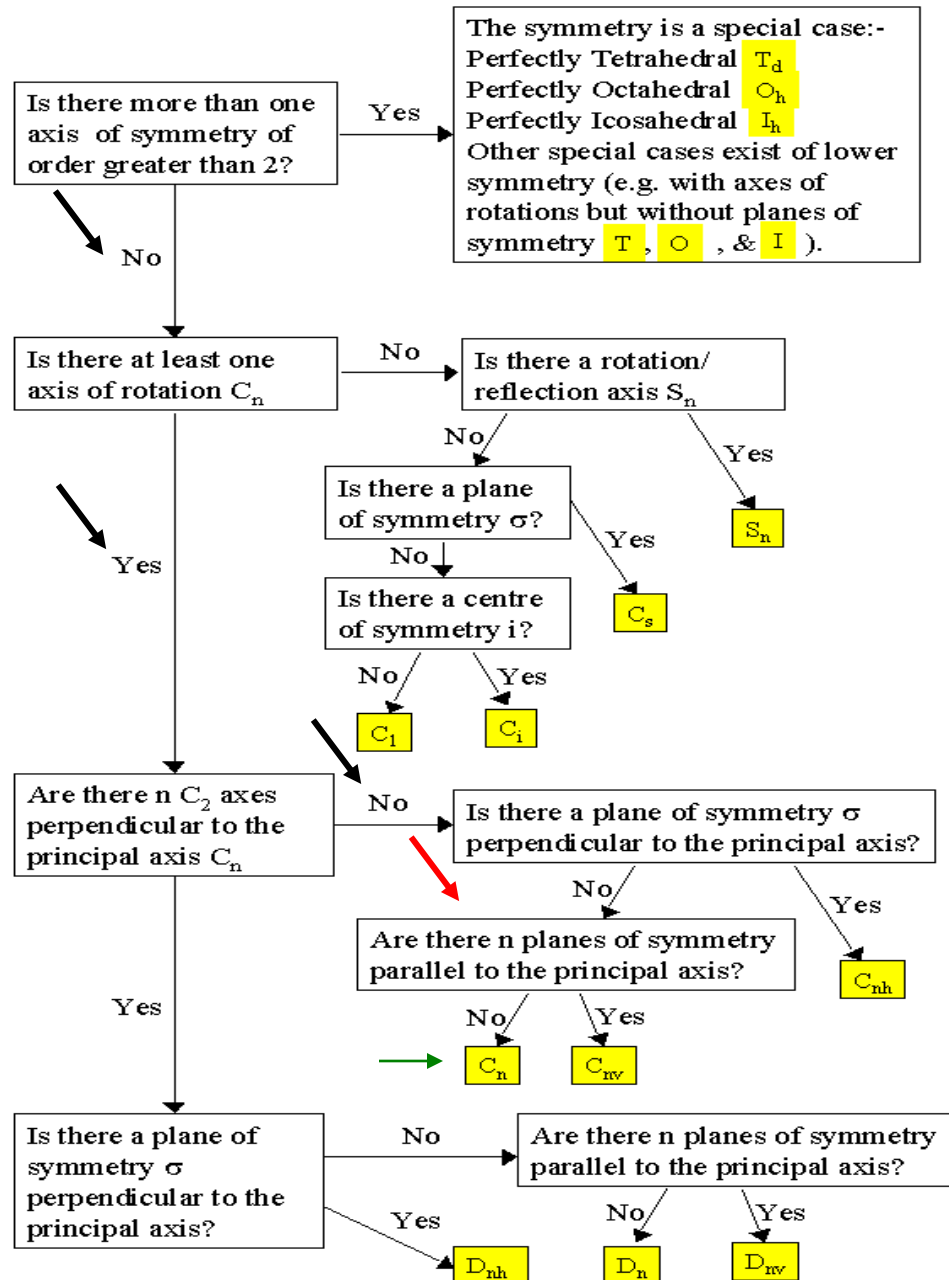
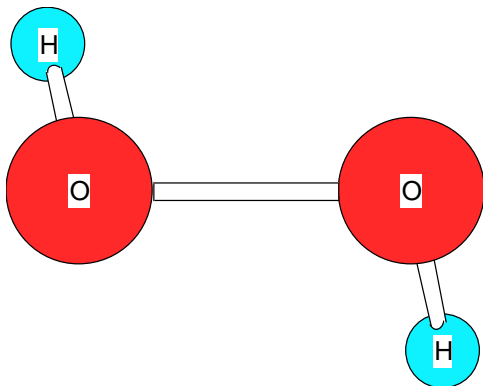
C_n type groups:

Only a C_n axis (C_n) ←

e.g. $B(NH_2)_3$ (C_3 , conformation is important !)



e.g. H_2O_2 (C_2 , conformation is important !)

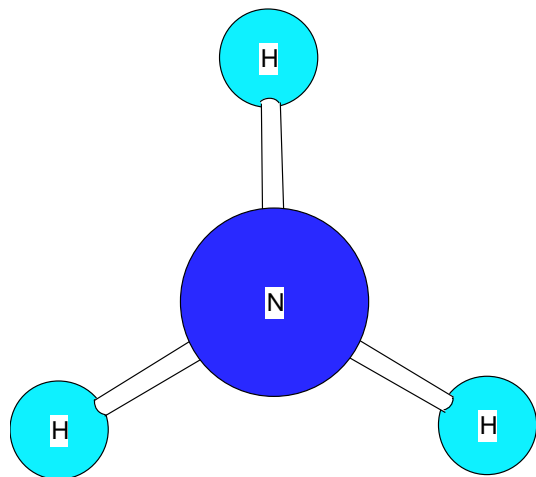


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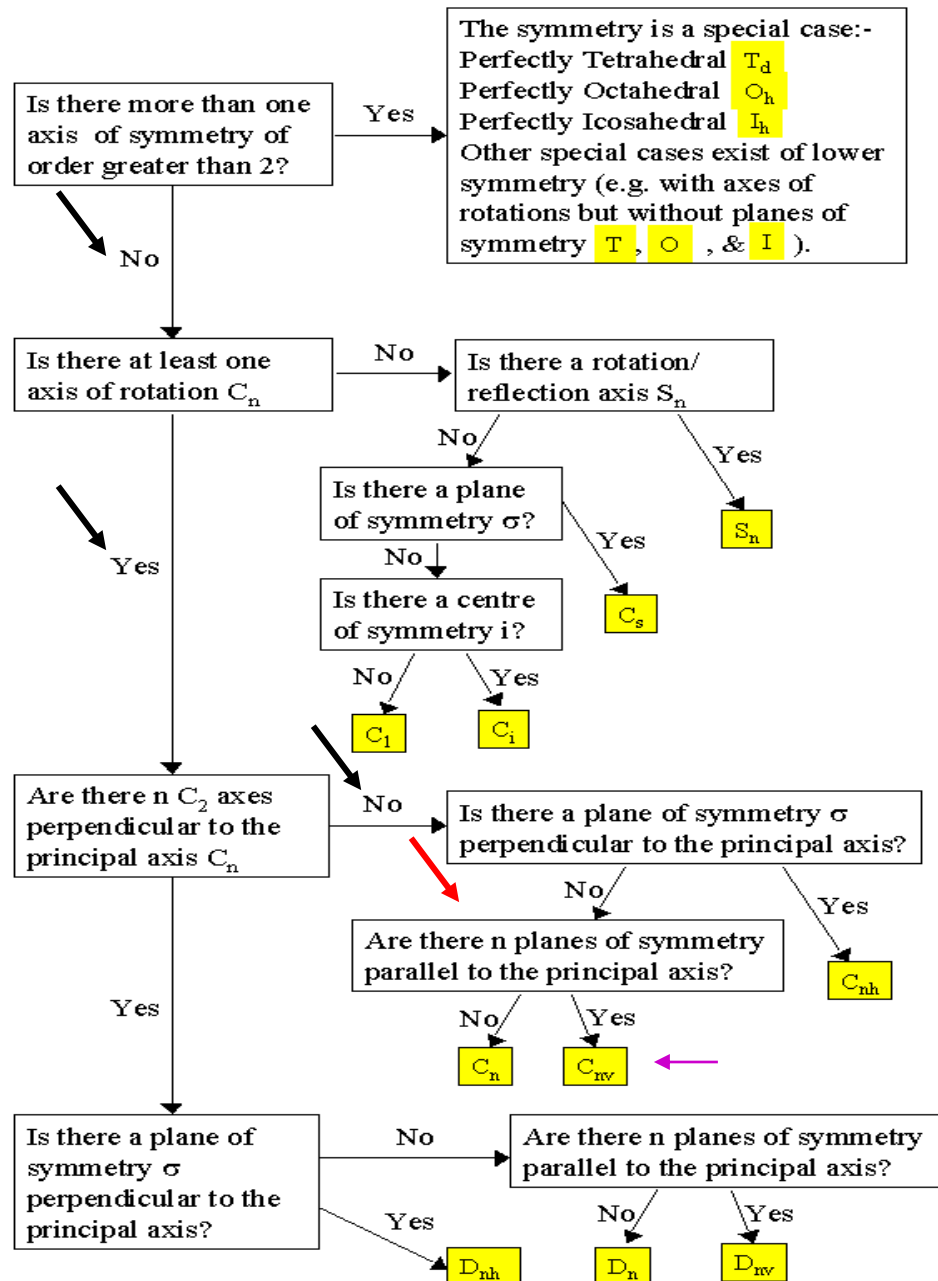
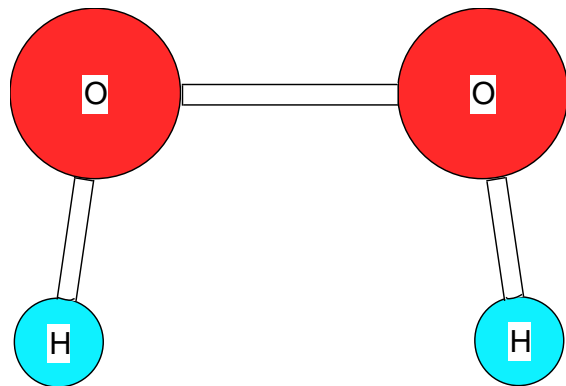
Identifying point groups

C_n type groups:

A C_n axis and a σ_v (C_{nv})
e.g. NH_3 (C_{3v})



e.g. H_2O_2 (C_{2v} conformation is important !)



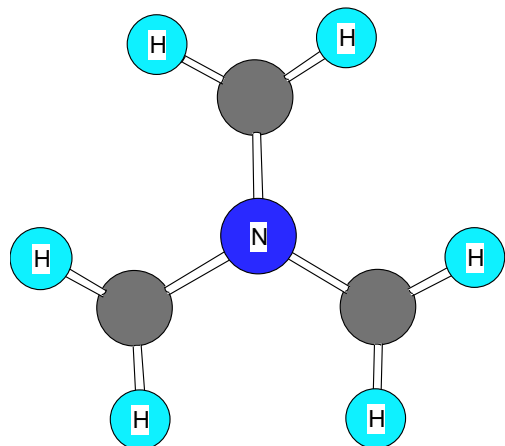
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C_n type groups:

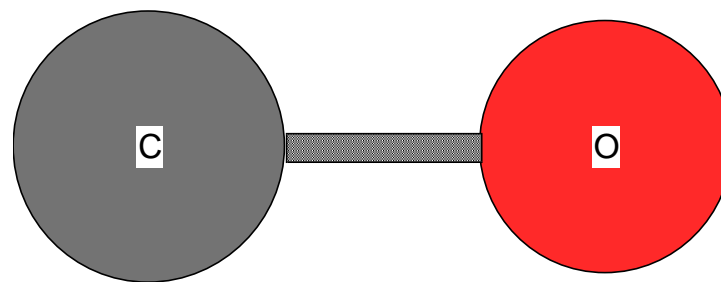
A C_n axis and a σ_v (C_{nv})

e.g. NH_3 (C_{3v} , conformation is important !)

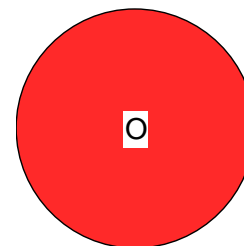
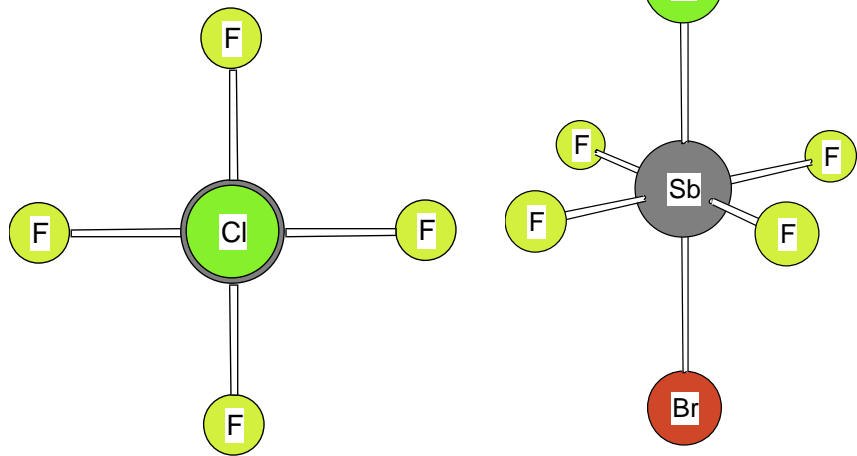


e.g. carbon monoxide, CO ($C_{\infty v}$)

There are an infinite number of possible C_n axes and σ_v mirror planes.



e.g. $\text{trans-}[\text{SbF}_4\text{ClBr}]^-$ (C_{4v})



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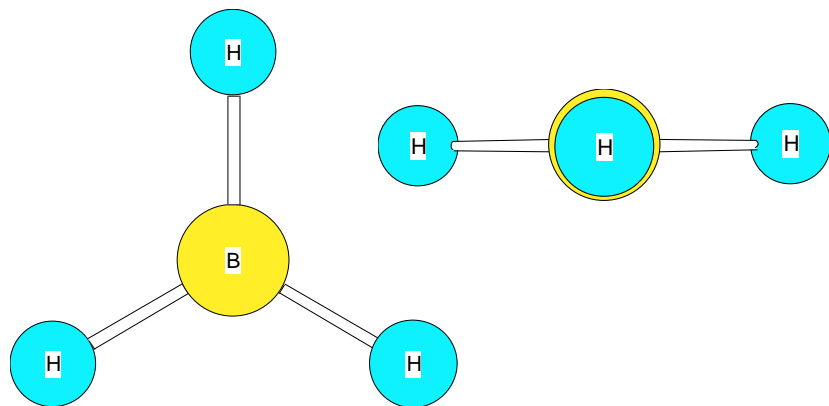
Identifying point groups

D_n type groups:

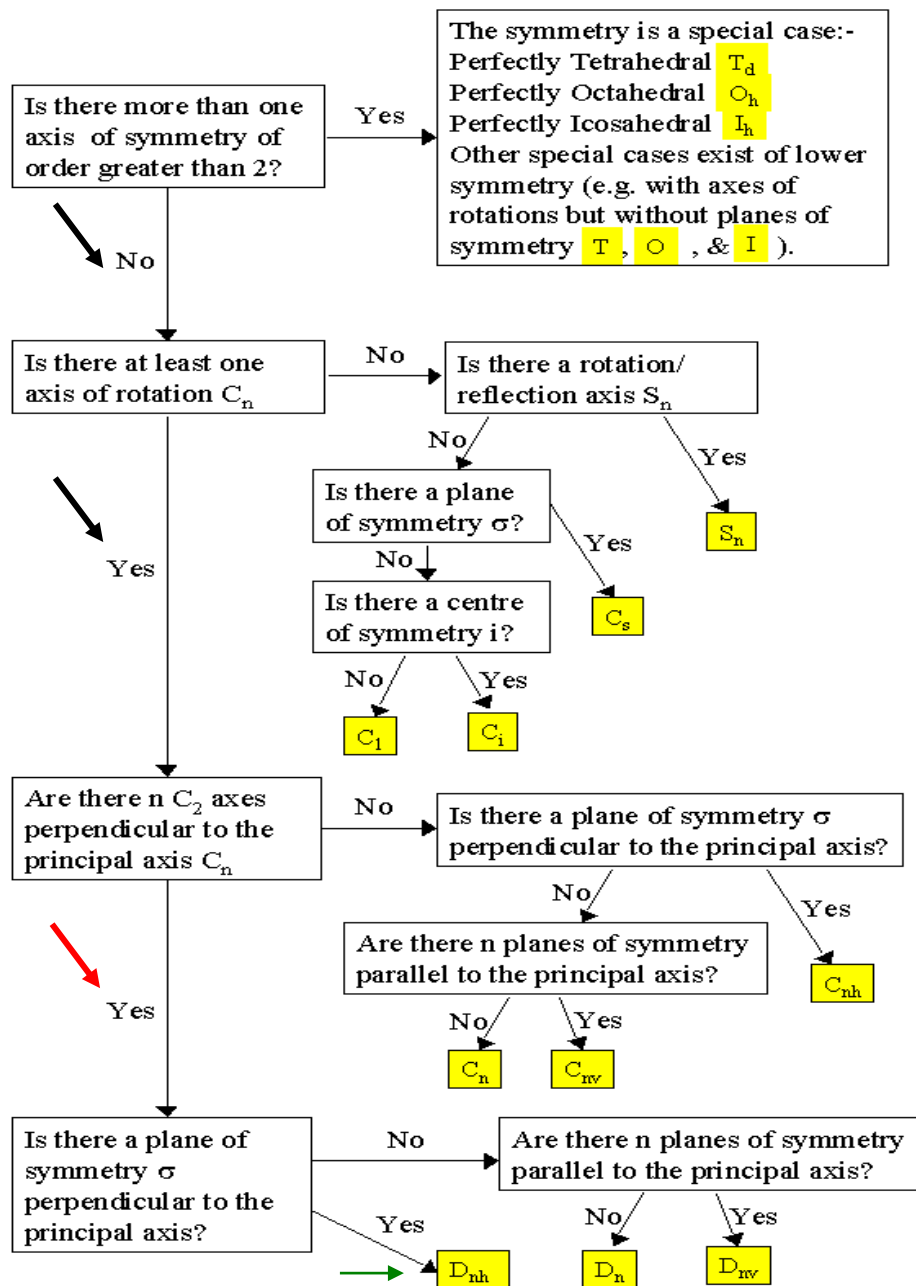
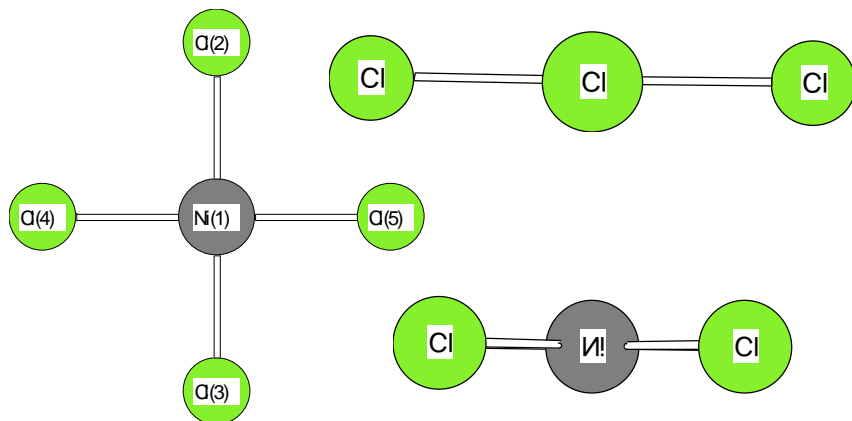
A C_n axis, n perpendicular C_2 axes

and a σ_h (D_{nh})

e.g. BH_3 (D_{3h})



e.g. $NiCl_4$ (D_{4h})



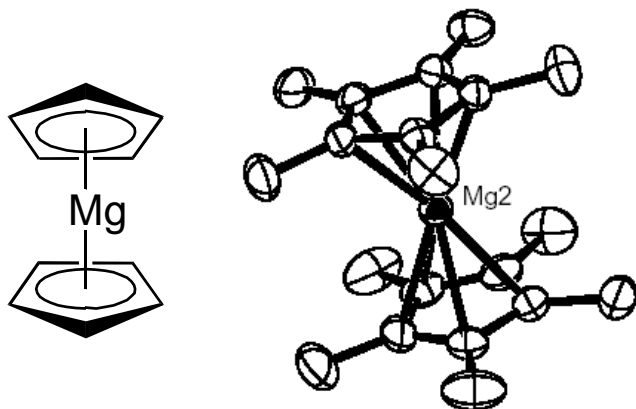
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Identifying point groups

D_n type groups:

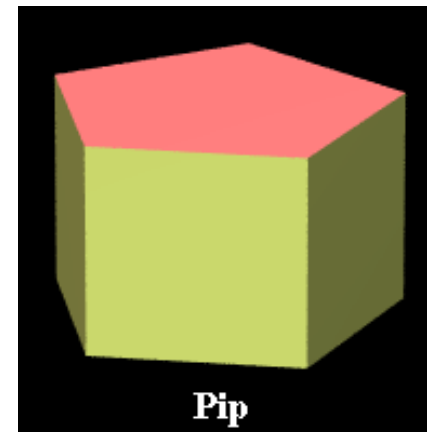
A C_n axis, n perpendicular C_2 axes
and a σ_h (D_{nh})

e.g. $Mg(\eta^5-Cp)_2$ (D_{5h} in the *eclipsed* conformation)



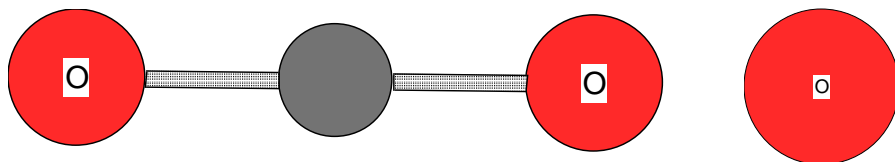
View down the C_5 axis

e.g. pentagonal prism (D_{5h})

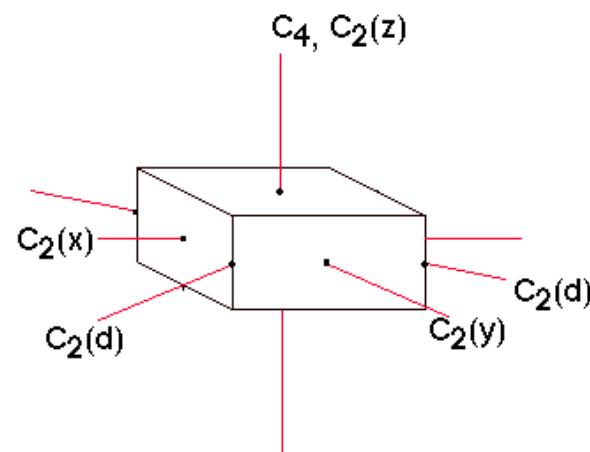


e.g. carbon dioxide, CO_2 or N_2 ($D_{\infty h}$)

There are an infinite number of possible C_n
axes and σ_v mirror planes in addition to
the σ_h .



e.g. square prism (D_{4h})



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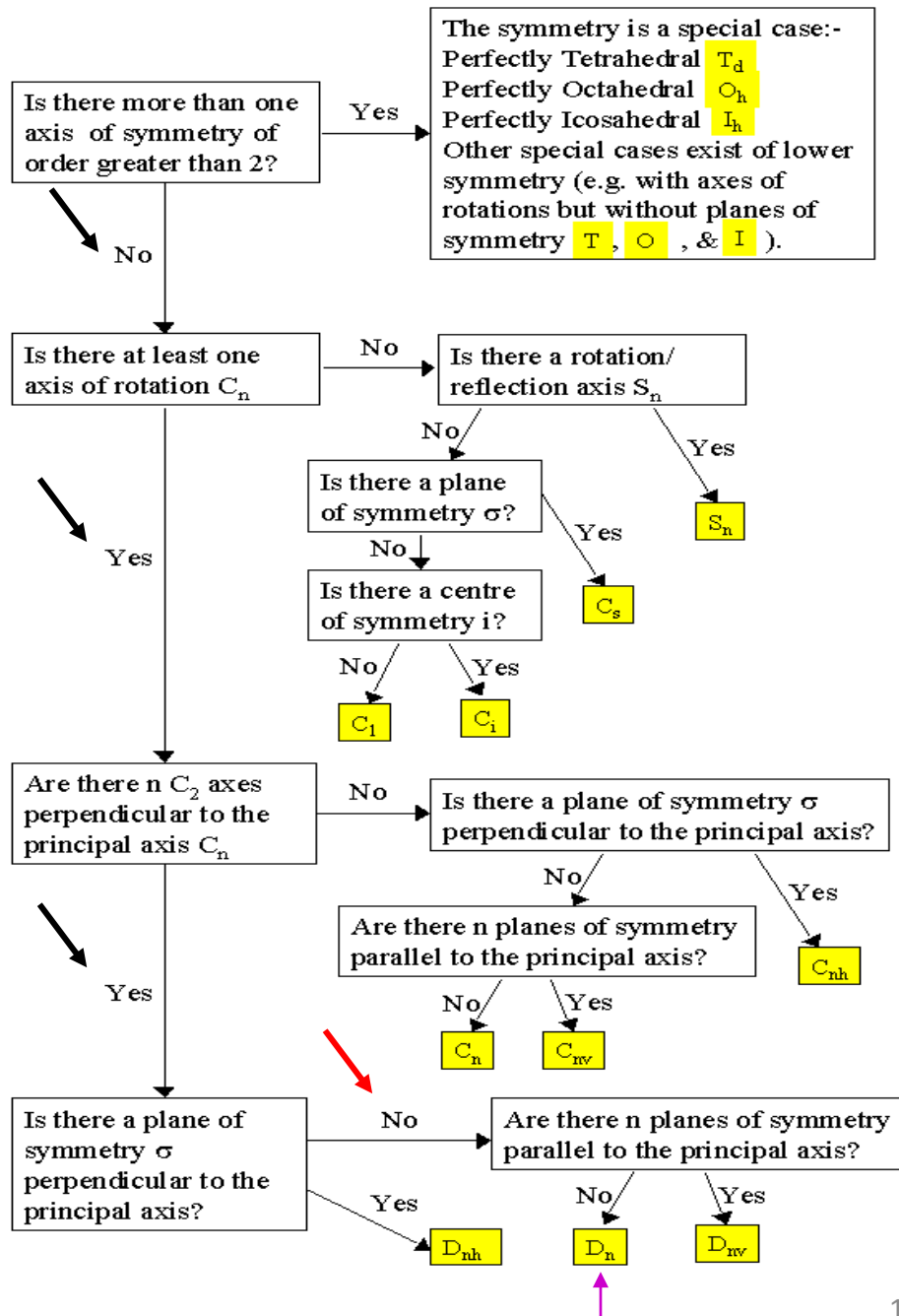
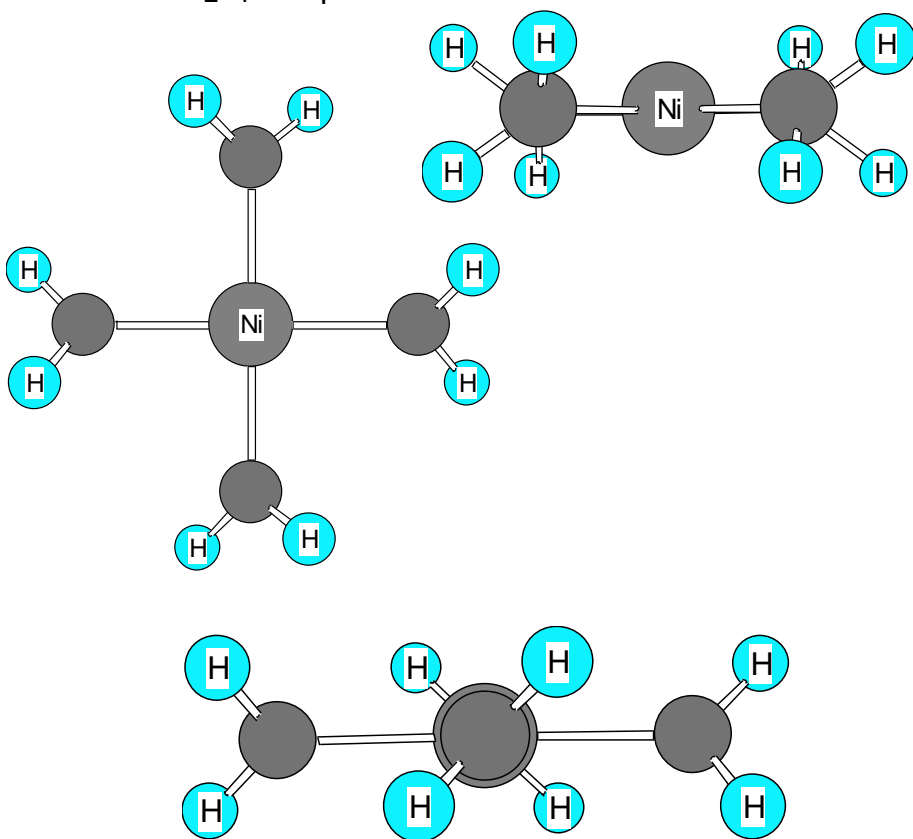
Identifying point groups

D_n type groups:

A C_n axis, n perpendicular C_2 axes and **no mirror planes** (D_n)

-propellor shapes

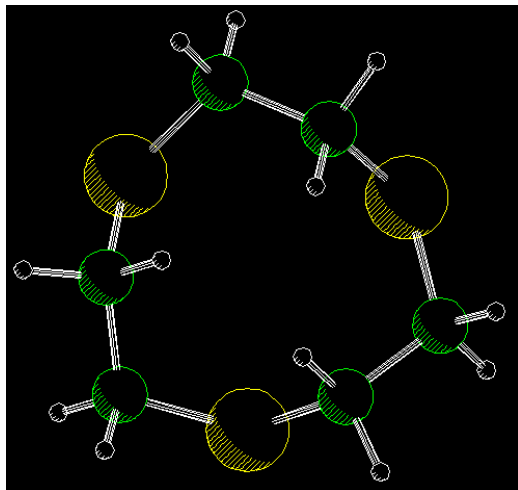
e.g. $Ni(CH_2)_4$ (D_4)



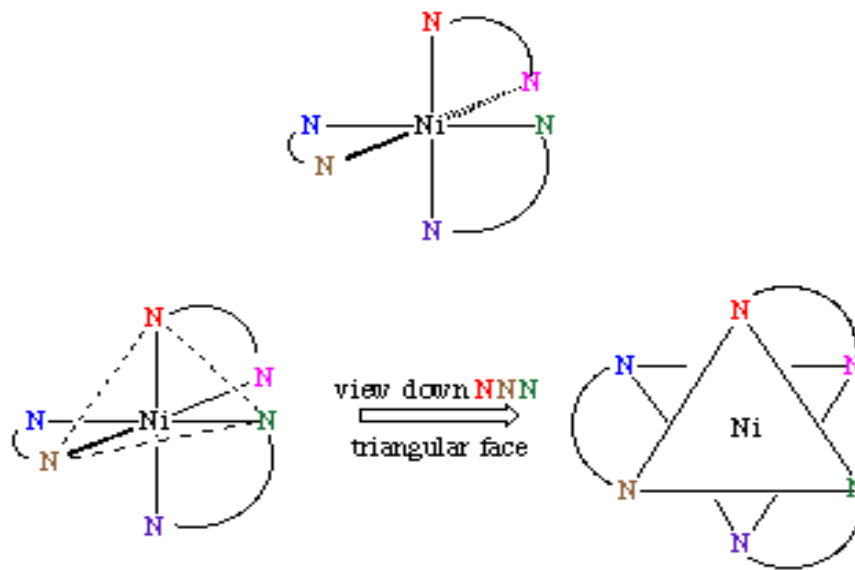
Lecture 2 : Point group, Classification and representation of groups

Examples:

$(\text{SCH}_2\text{CH}_2)_3$ (D_3 conformation is important!)



$\text{Ni}(\text{en})_3$ (D_3 conformation is important!) $\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

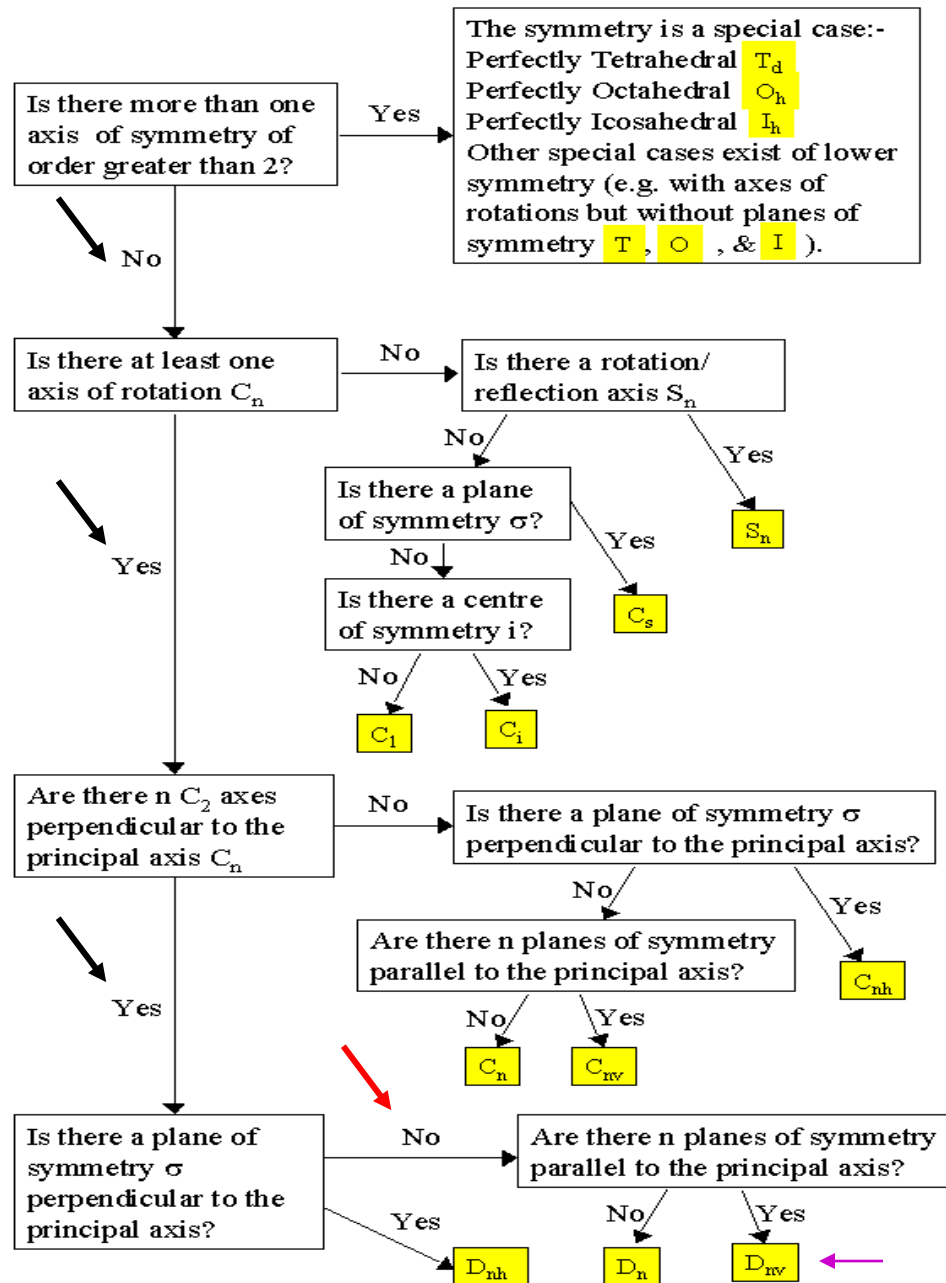
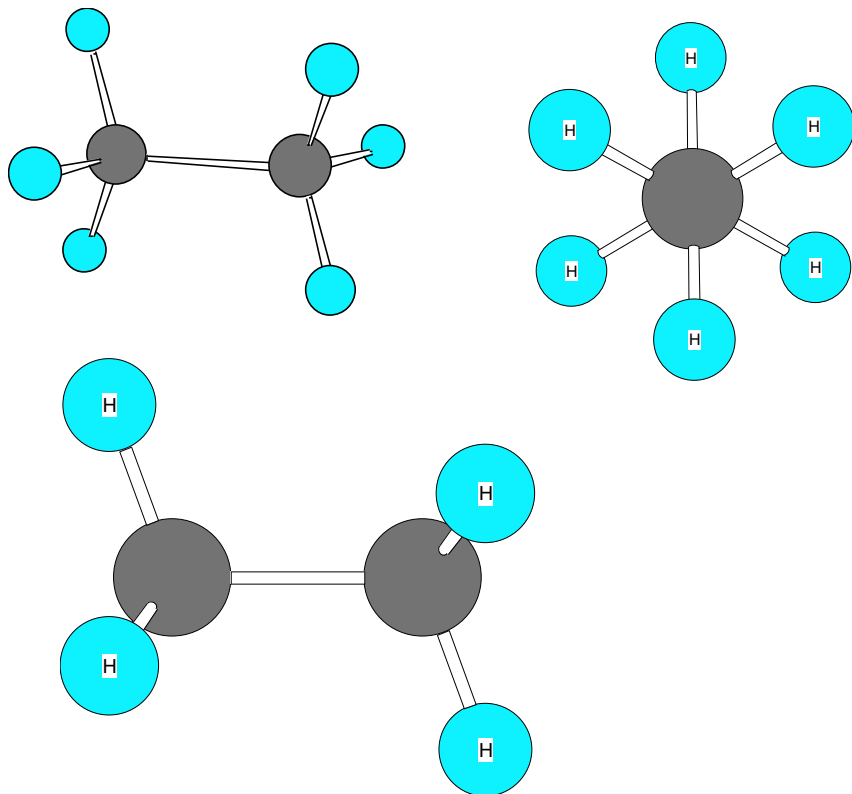


Lecture 2 : Point group, Classification and representation of groups

Identifying point groups

D_n type groups:

A C_n axis, n perpendicular C_2 axes
and a σ_d (D_{nd})
e.g. ethane, H_3C-CH_3
(D_{3d} in the staggered conformation)

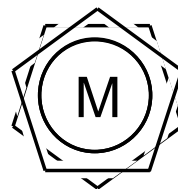
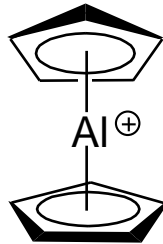
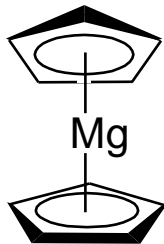
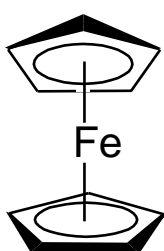


dihedral means between sides or planes – this is where you find the C_2 axes

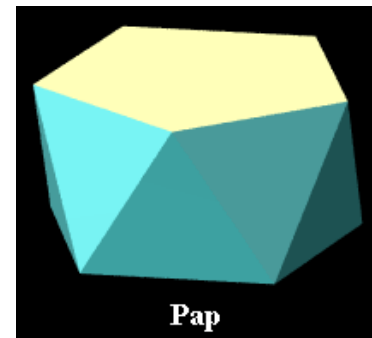
Lecture 2 : Point group, Classification and representation of groups

Examples:

e.g. $\text{Mg}(\eta^5\text{-Cp})_2$ and other metallocenes in the staggered conformation (D_{5d})

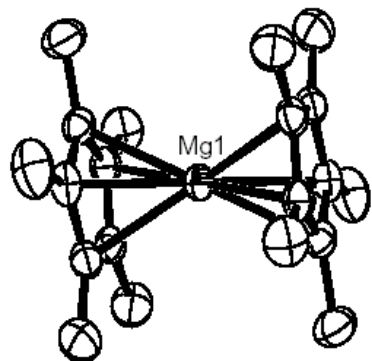


View down the C_5 axis

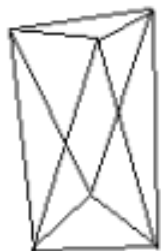


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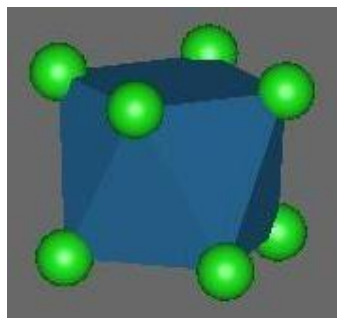
These are pentagonal antiprisms



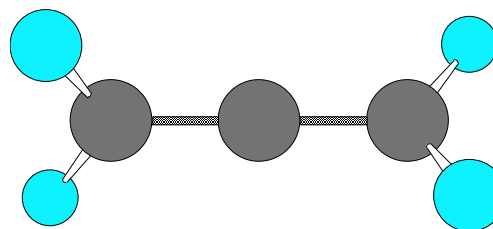
e.g. triangular antiprism (D_{3d})



e.g. square antiprism (D_{4d})



e.g. allene or a tennis ball (D_{2d})

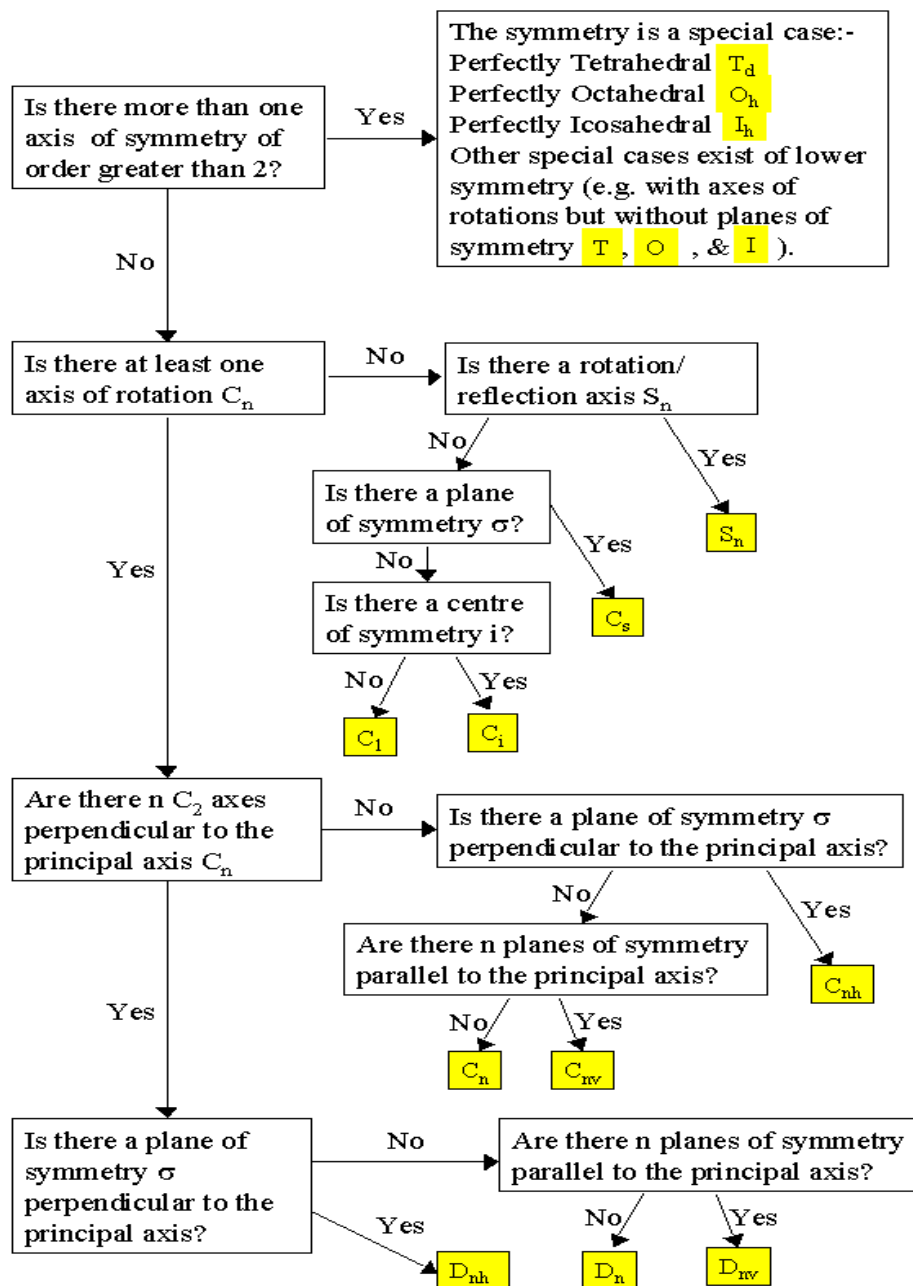


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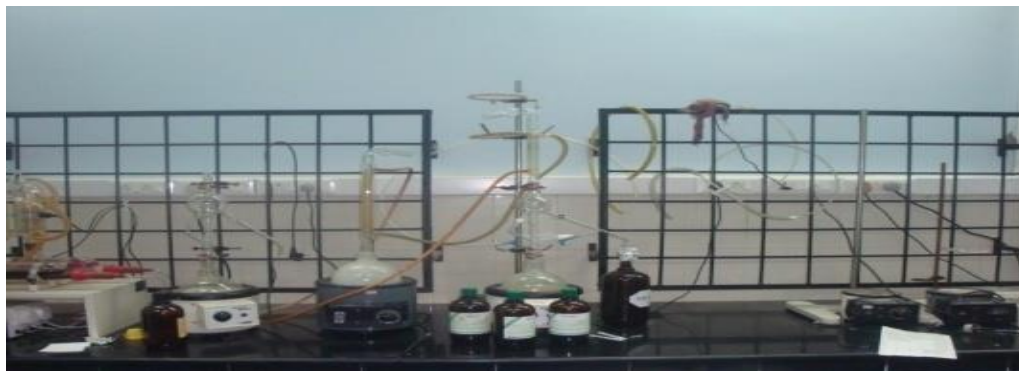
Identifying point groups

We can use a flow chart such as this one to determine the point group of any object. The steps in this process are:

1. Determine if the symmetry is special (e.g. tetrahedral).
2. Determine if there is a principal rotation axis.
3. Determine if there are rotation axes perpendicular to the principal axis.
4. Determine if there are mirror planes and where they are.
5. Assign point group.



Thank You



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