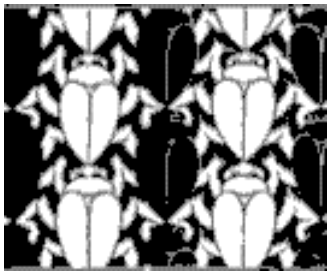
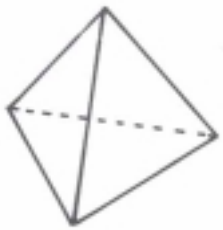
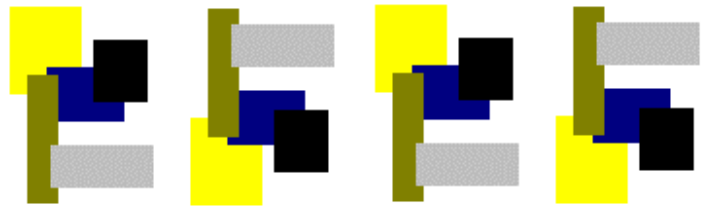
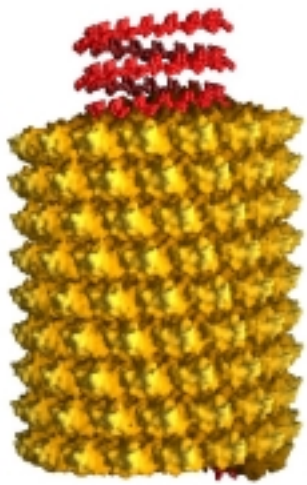
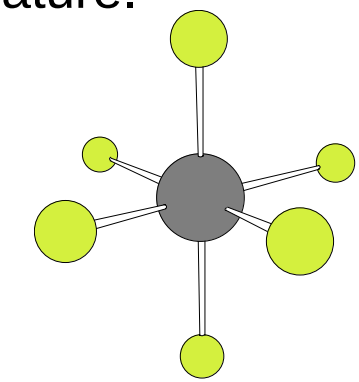
Symmetry and Introduction to Group Theory

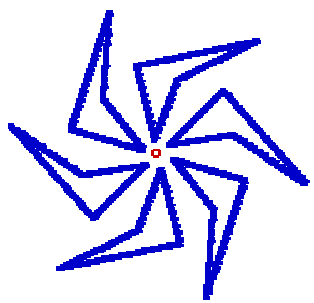





Symmetry is all around us and is a fundamental property of nature.






Symmetry and Introduction to Group Theory

The term *symmetry* is derived from the Greek word “symmetria” which means “measured together”. An object is symmetric if one part (e.g. one side) of it is the same* as all of the other parts. You know intuitively if something is symmetric but we require a precise method to describe how an object or molecule is symmetric.

Group theory is a very powerful mathematical tool that allows us to rationalize and simplify many problems in Chemistry. A group consists of a set of symmetry elements (and associated symmetry operations) that completely describe the symmetry of an object.

We will use some aspects of group theory to help us understand the bonding and spectroscopic features of molecules.

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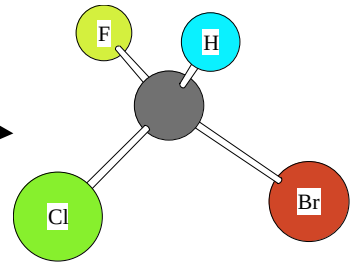
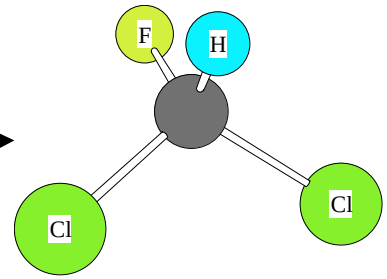
We need to be able to specify the symmetry of molecules clearly.

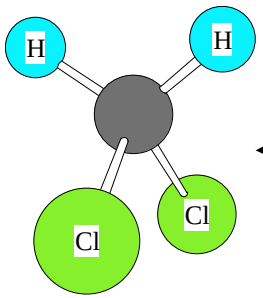
No symmetry – CHFClBr →



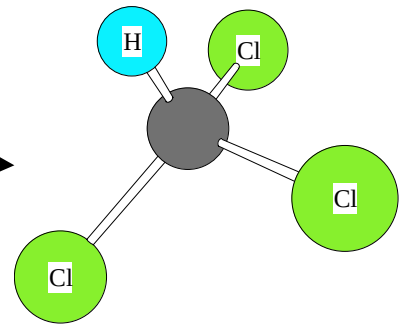
Some symmetry – $CHFCl_2$ →



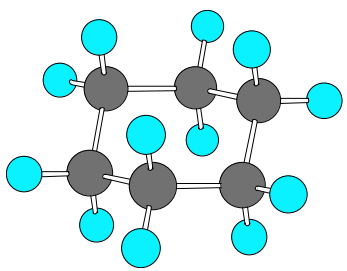
← More symmetry – CH_2Cl_2

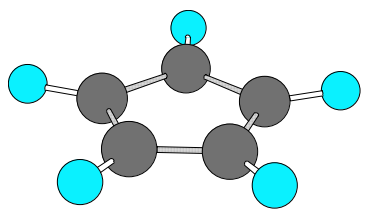


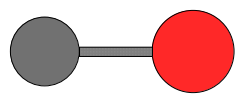
More symmetry ? – $CHCl_3$ →



What about ?







Point groups provide us with a way to indicate the symmetry unambiguously.

Symmetry and Point Groups

Point groups have symmetry about a single point at the center of mass of the system.

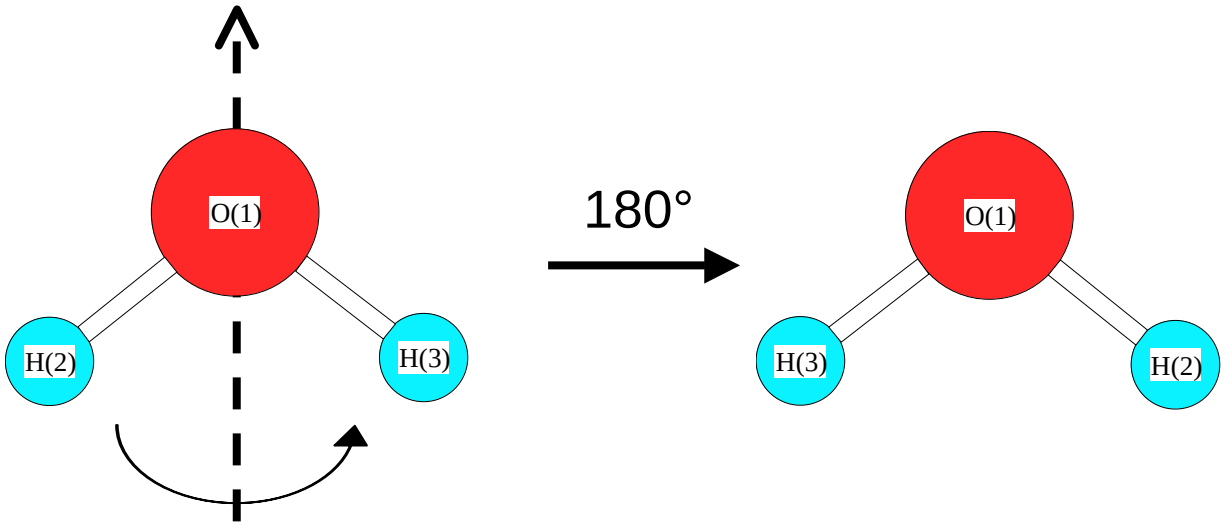
Symmetry elements are geometric entities about which a *symmetry operation* can be performed. In a point group, all symmetry elements must pass through the center of mass (the point). A symmetry operation is the action that produces an object identical to the initial object.

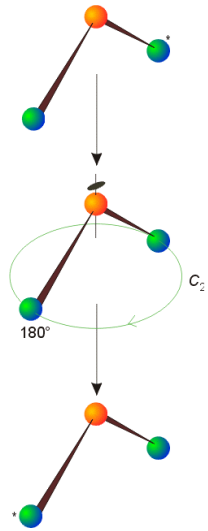
The symmetry elements and related operations that we will find in molecules are:

Element	Operation
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Center of symmetry, i	Inversion
	Identity, E

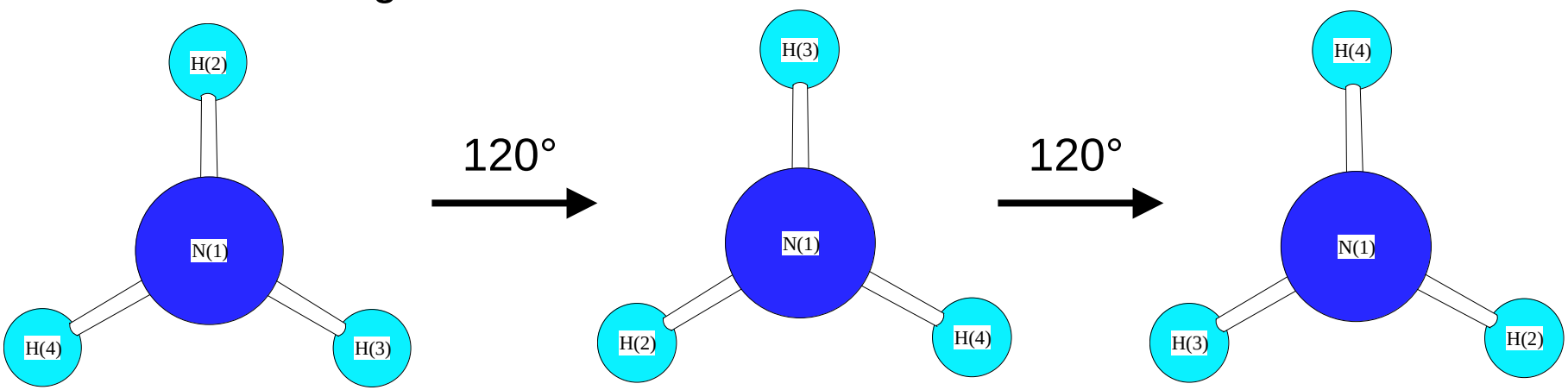
The Identity operation does nothing to the object – it is necessary for mathematical completeness, as we will see later.

n-fold rotation - a rotation of 360°/n about the C_n axis (n = 1 to ∞)





In water there is a C_2 axis so we can perform a 2-fold (180°) rotation to get the identical arrangement of atoms.



In ammonia there is a C_3 axis so we can perform 3-fold (120°) rotations to get identical arrangement of atoms.

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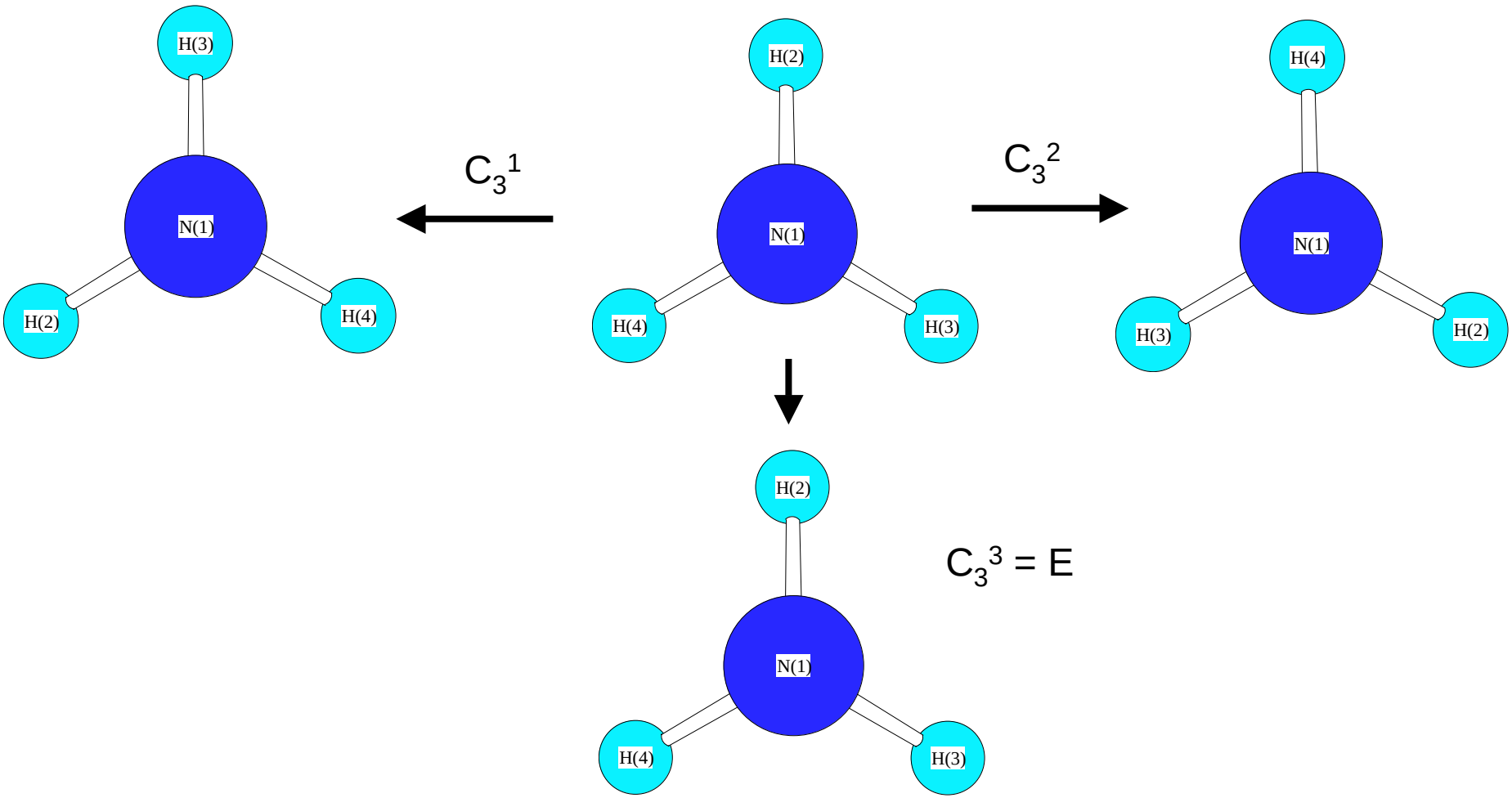
Notes about rotation operations:

- Rotations are considered positive in the counter-clockwise direction.
- Each possible rotation operation is assigned using a superscript integer m of the form C_n^m.
- The rotation C_n^n is equivalent to the identity operation (nothing is moved).



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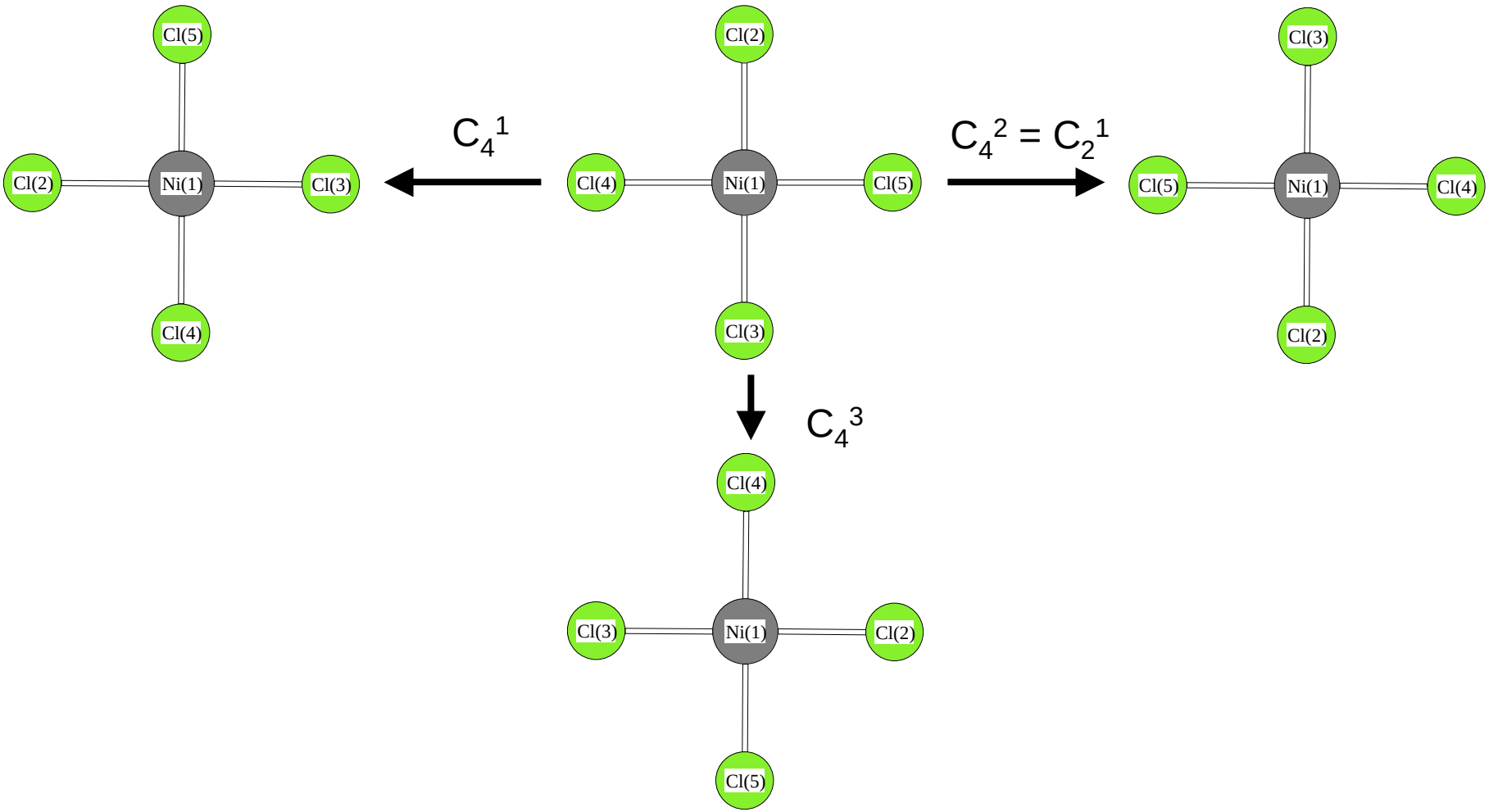
Notes about rotation operations, C_n^m:

- If n/m is an integer, then that rotation operation is equivalent to an n/m - fold rotation.

e.g. $C_4^2 = C_2^1$, $C_6^2 = C_3^1$, $C_6^3 = C_2^1$, etc. (identical to simplifying fractions)



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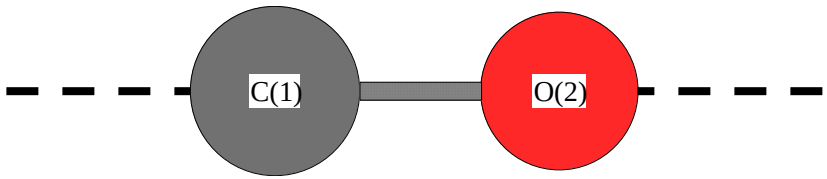
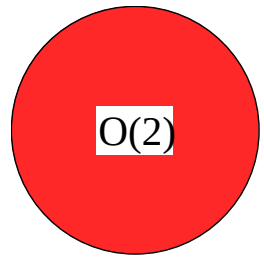
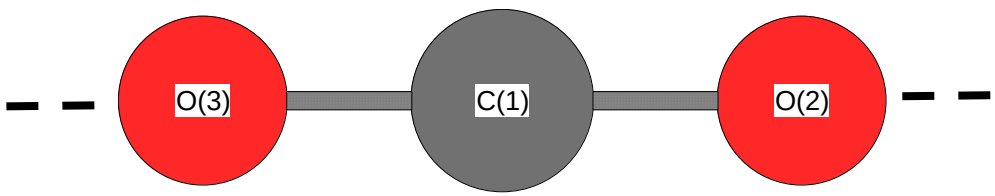
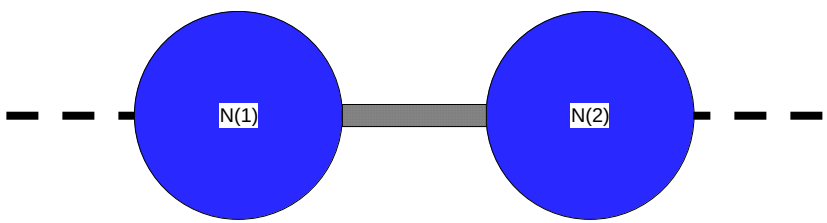
Notes about rotation operations, C_n^m:

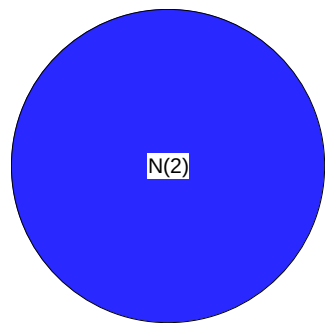
- Linear molecules have an infinite number of rotation axes C_∞ because any rotation on the molecular axis will give the same arrangement.





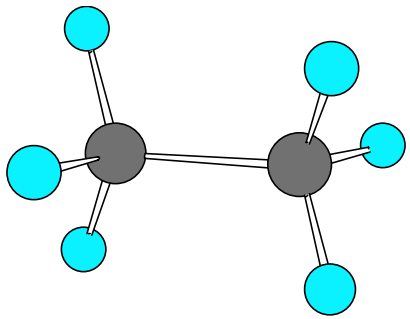






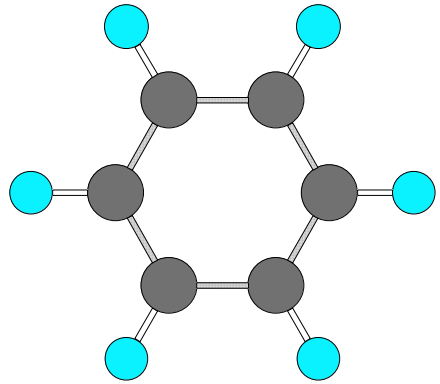
The *Principal axis* in an object is the highest order rotation axis. It is usually easy to identify the principle axis and this is typically assigned to the z-axis if we are using Cartesian coordinates.

Ethane, C_2H_6

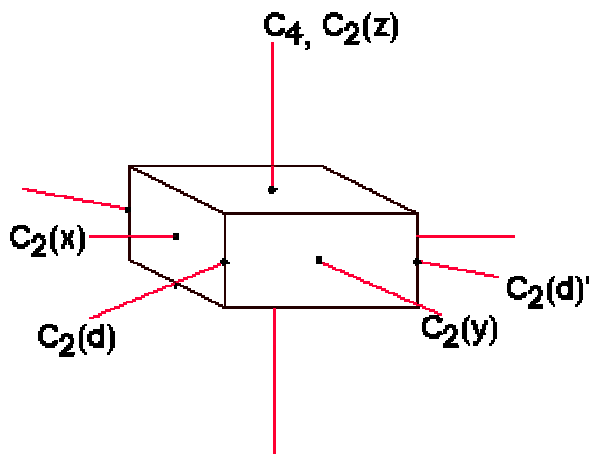


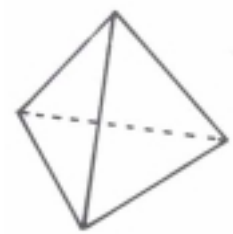
The principal axis is the three-fold axis containing the C-C bond.

Benzene, C_6H_6



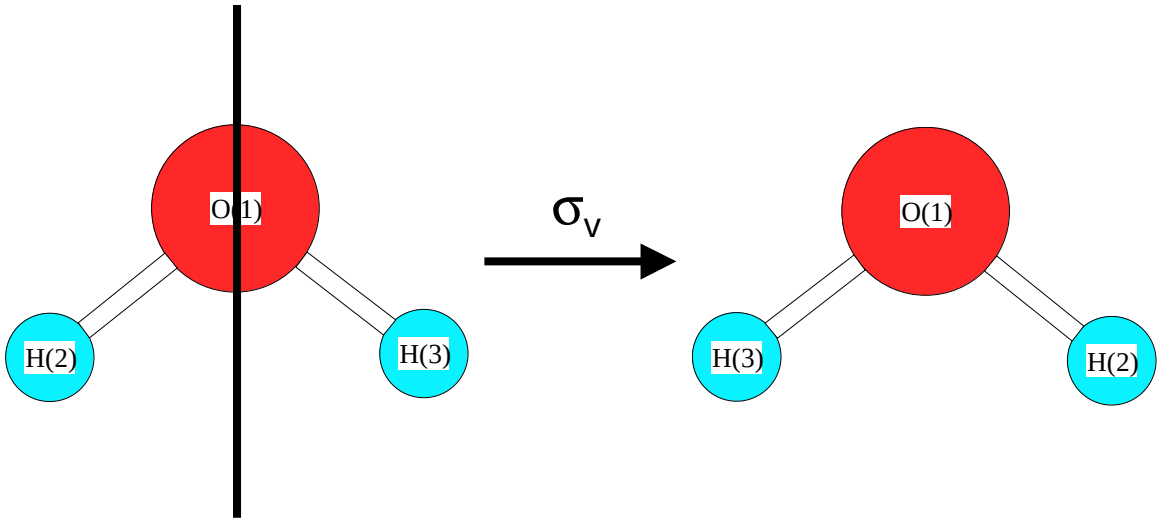
The principal axis is the six-fold axis through the center of the ring.

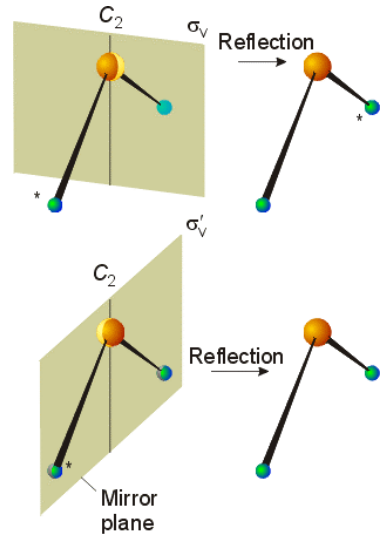


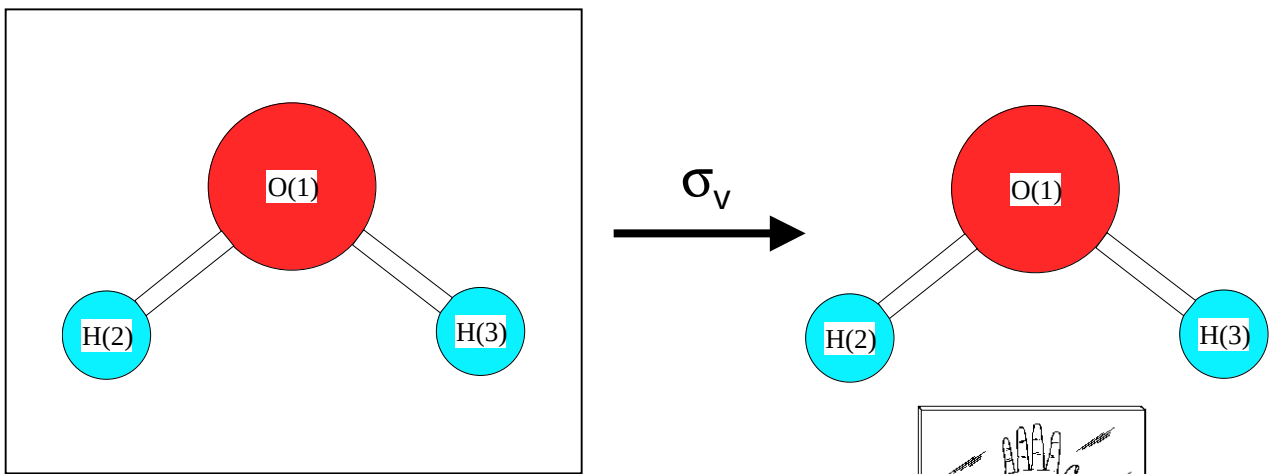


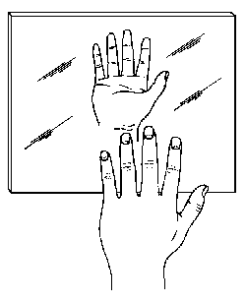
The principal axis in a tetrahedron is a three-fold axis going through one vertex and the center of the object.

Reflection across a plane of symmetry, σ (mirror plane)







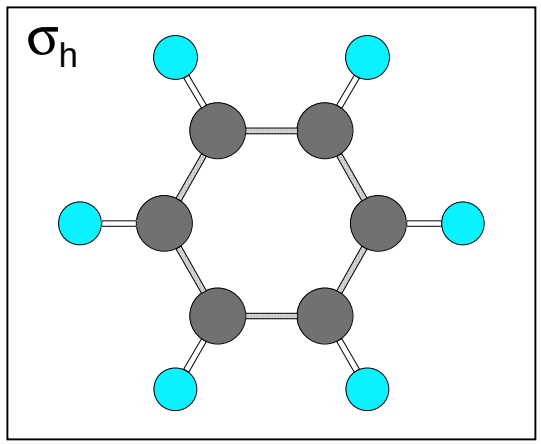


Handedness is changed by reflection!

These mirror planes are called “vertical” mirror planes, σ_v, because they contain the principal axis. The reflection illustrated in the top diagram is through a mirror plane perpendicular to the plane of the water molecule. The plane shown on the bottom is in the same plane as the water molecule.

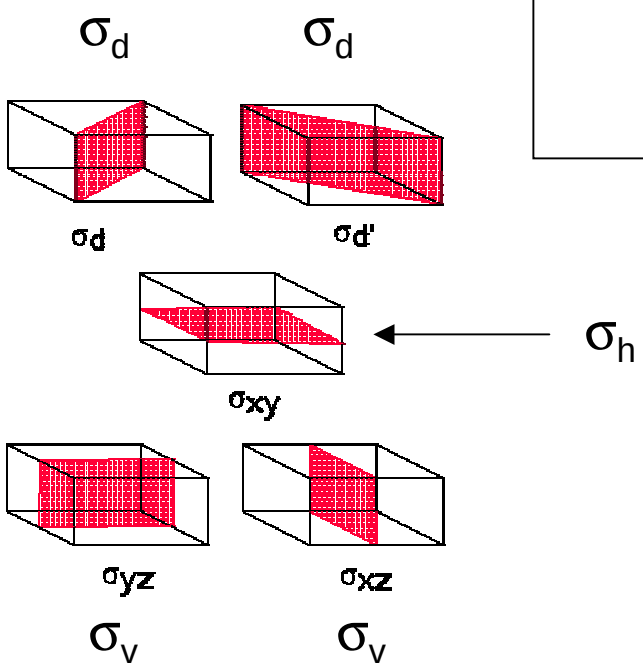
Notes about reflection operations:

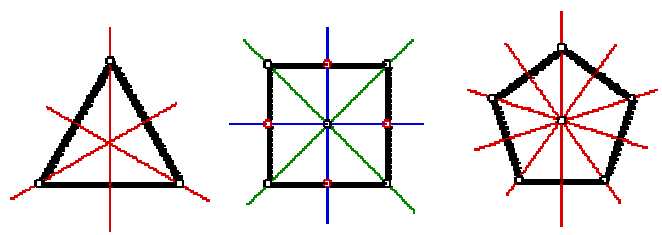
- A reflection operation exchanges one half of the object with the reflection of the other half.
- Reflection planes may be vertical, horizontal or dihedral (more on σ_d later).
- Two successive reflections are equivalent to the identity operation (nothing is moved).



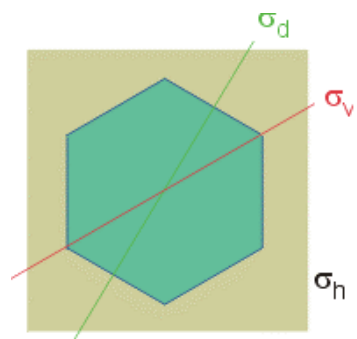
A "horizontal" mirror plane, σ_h, is perpendicular to the principal axis. This must be the xy-plane if the z-axis is the principal axis.

In benzene, the σ_h is in the plane of the molecule – it "reflects" each atom onto itself.



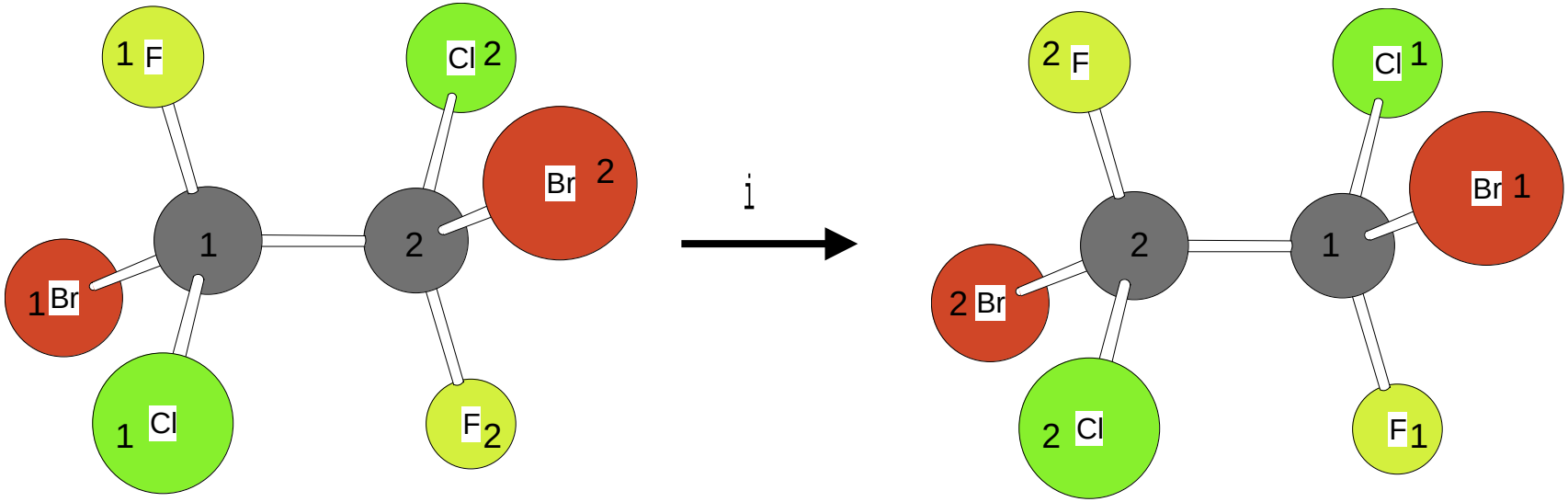


Vertical and dihedral mirror planes of geometric shapes.

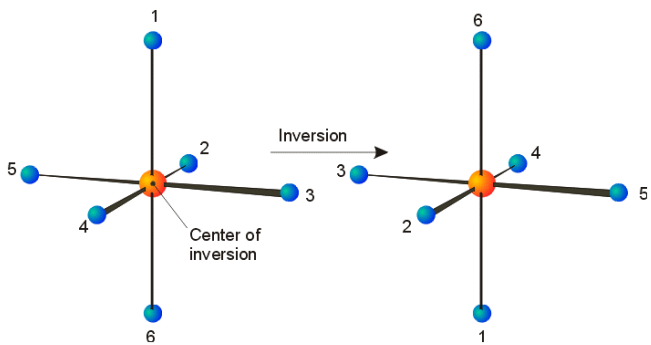


Inversion and centers of symmetry, i (inversion centers)

In this operation, every part of the object is reflected through the inversion center, which must be at the center of mass of the object.



[x, y, z] $\xrightarrow{i}$ [-x, -y, -z]



We will not consider the matrix approach to each of the symmetry operations in this course but it is particularly helpful for understanding what the inversion operation does. The inversion operation takes a point or object at [x, y, z] to [-x, -y, -z].

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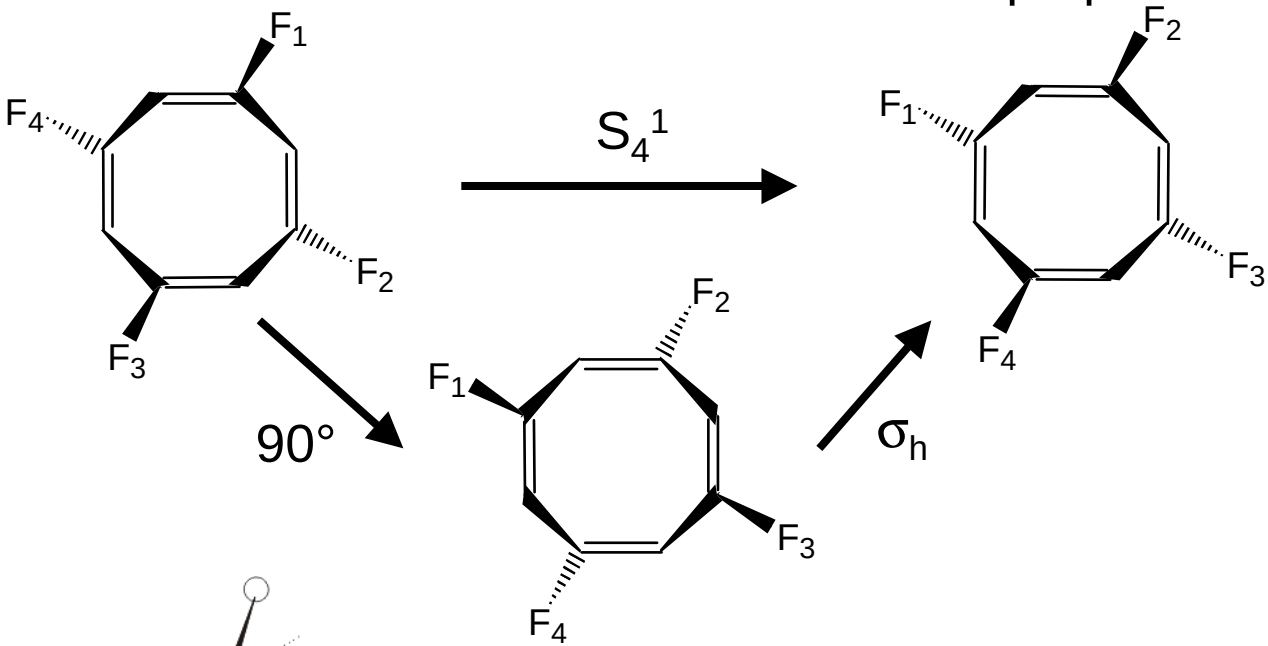
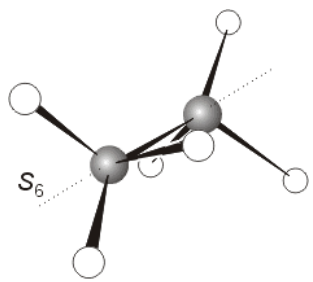
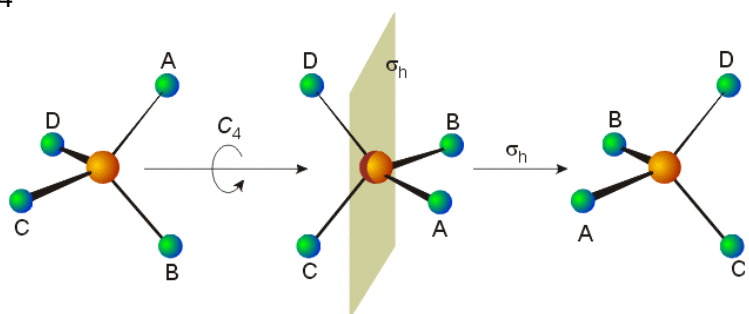
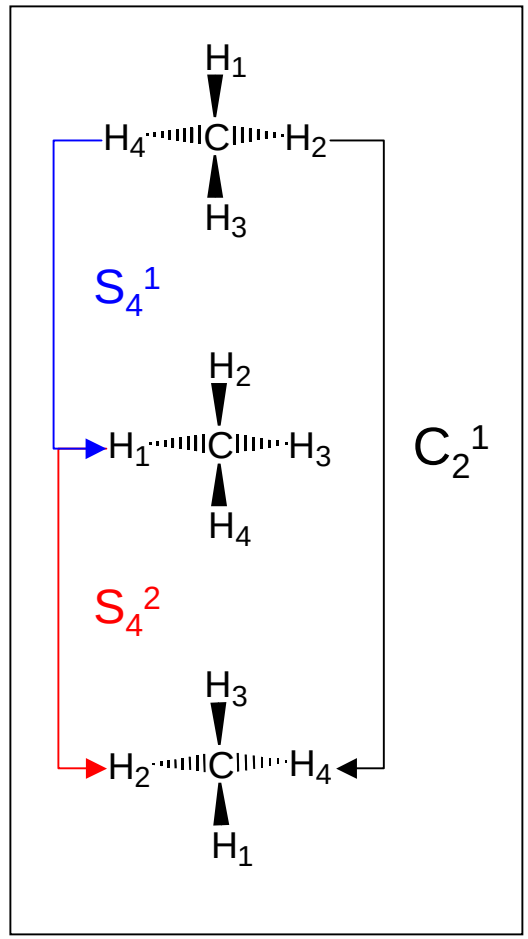
n-fold improper rotation, S_n^m (associated with an improper rotation axis or a rotation-reflection axis) This operation involves a rotation of 360°/n followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as "proper" rotations.





1 S_6 axis





Note that: $S_1 = \sigma$, $S_2 = i$, and sometimes $S_{2n} = C_n$ (e.g. in box) this makes more sense when you examine the matrices that describe the operations.

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:

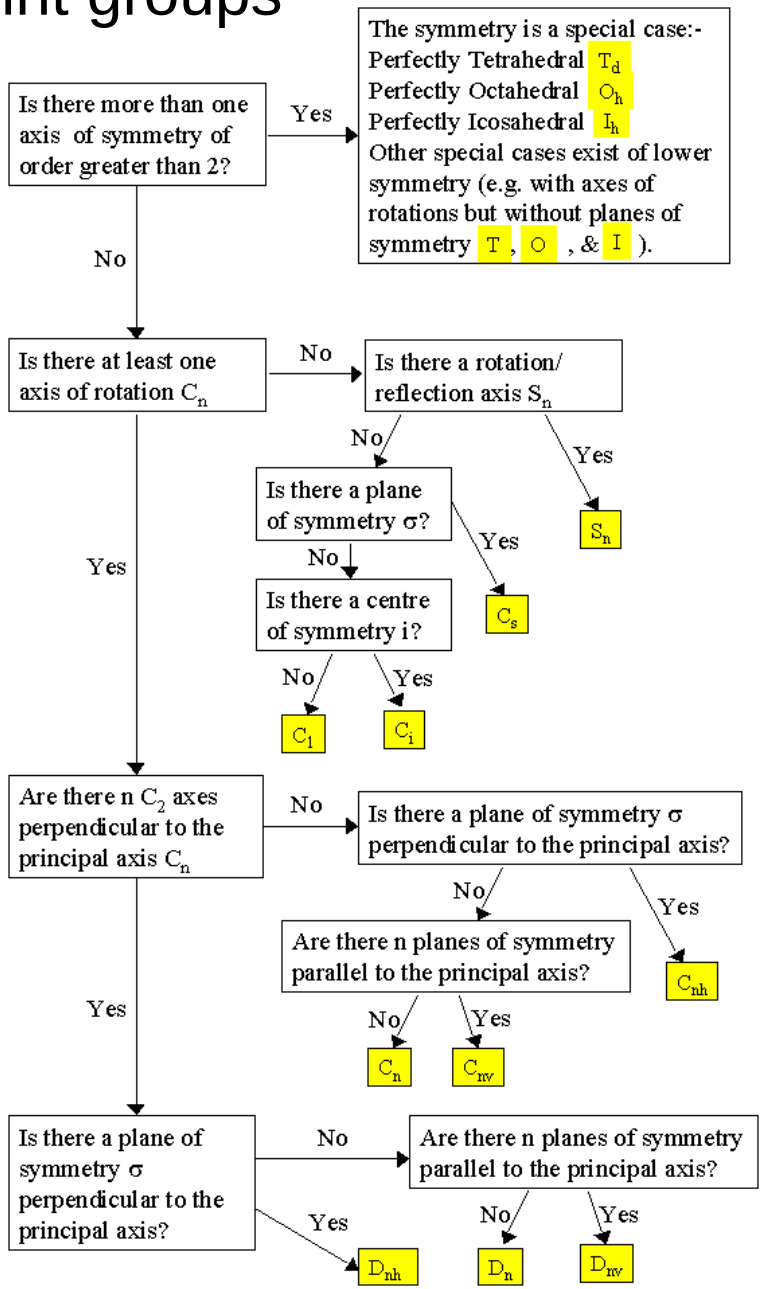
1. Determine the symmetry is special (e.g. octahedral).

2. Determine if there is a principal rotation axis.

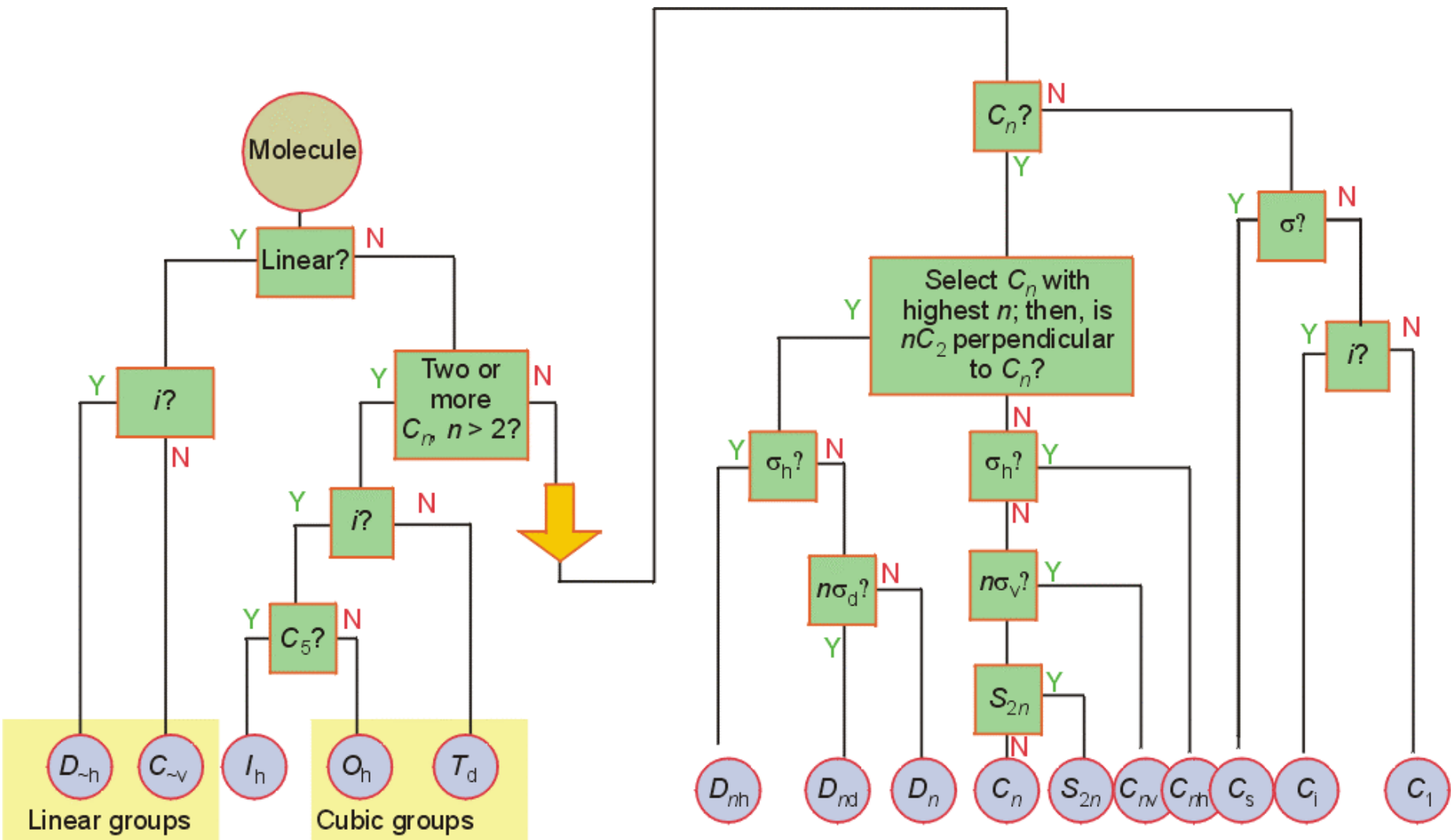
3. Determine if there are rotation axes perpendicular to the principal axis.

4. Determine if there are mirror planes.

5. Assign point group.



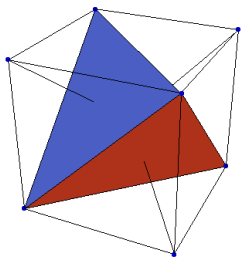
Identifying point groups

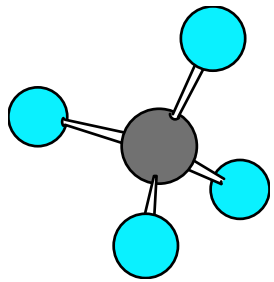


Identifying point groups

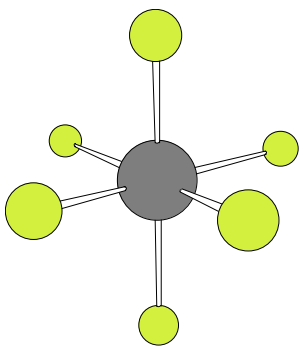
Special cases:

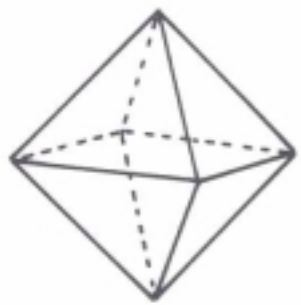
Perfect tetrahedral (T_d) e.g. P_4, CH_4



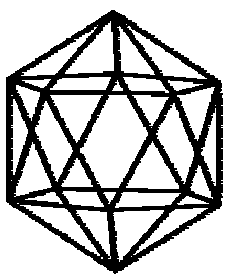


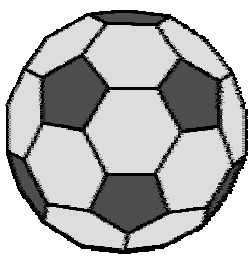
Perfect octahedral (O_h) e.g. SF_6, $[B_6H_6]^{-2}$

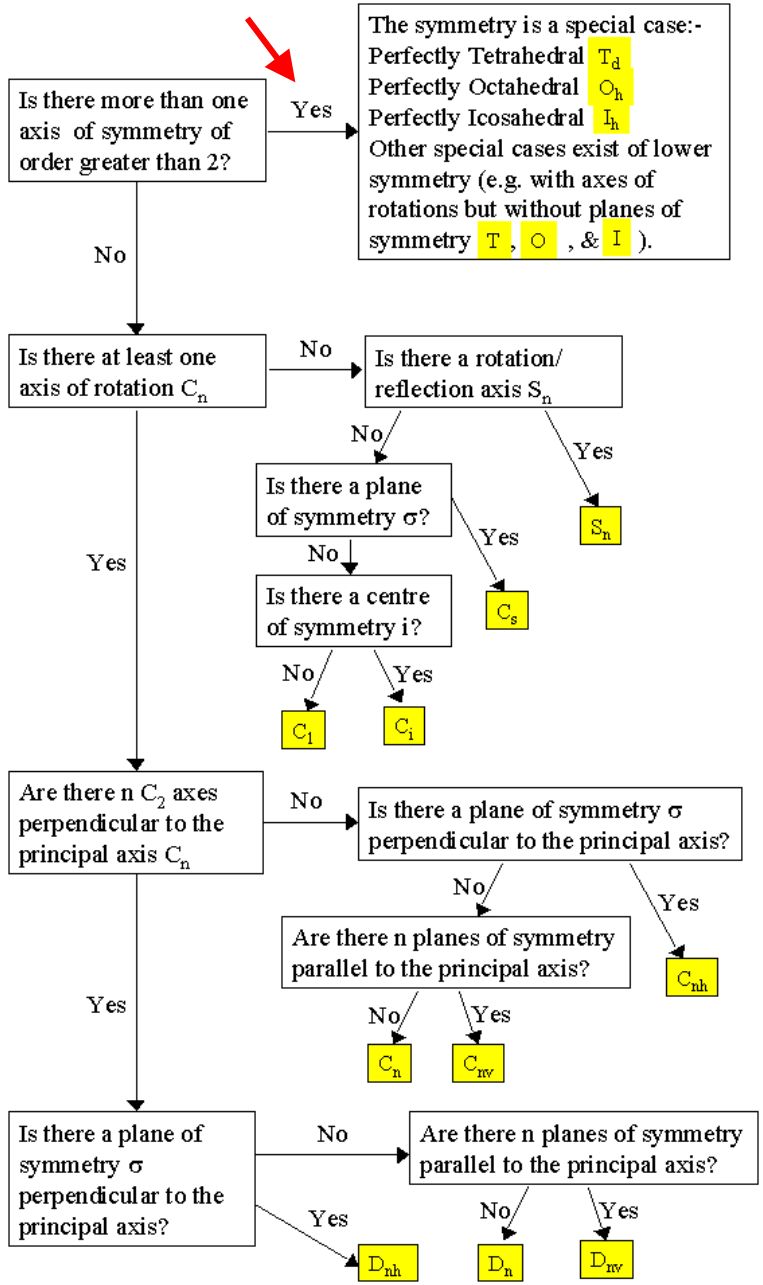




Perfect icosahedral (I_h) e.g. $[B_{12}H_{12}]^{-2}$, C_{60}





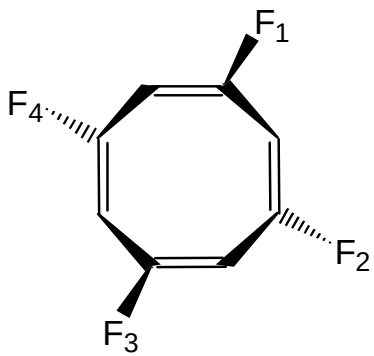


Identifying point groups

Low symmetry groups:

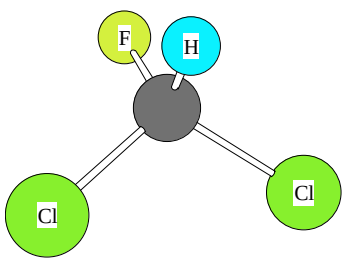
Only* an improper axis (S_n) ←

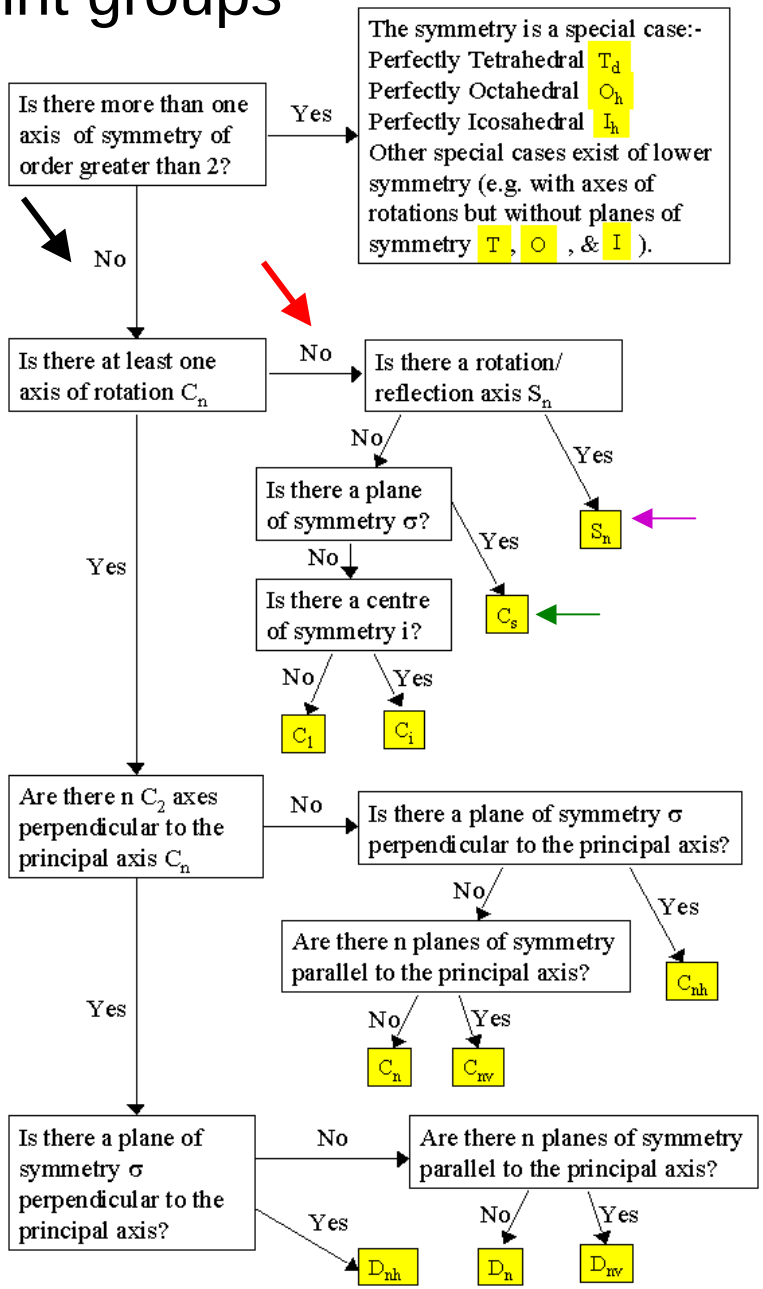
e.g. 1,3,5,7-tetrafluoroCOT, S_4



Only a mirror plane (C_s) ←

e.g. $CHFCl_2$



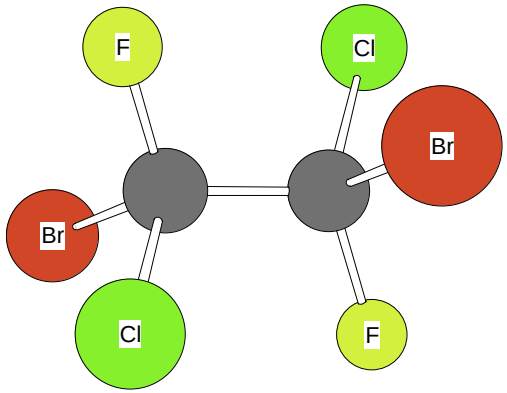


Identifying point groups

Low symmetry groups:

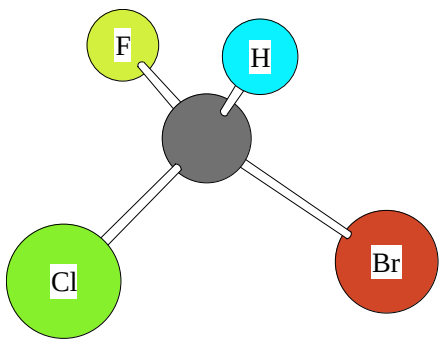
Only an inversion center (C_i)

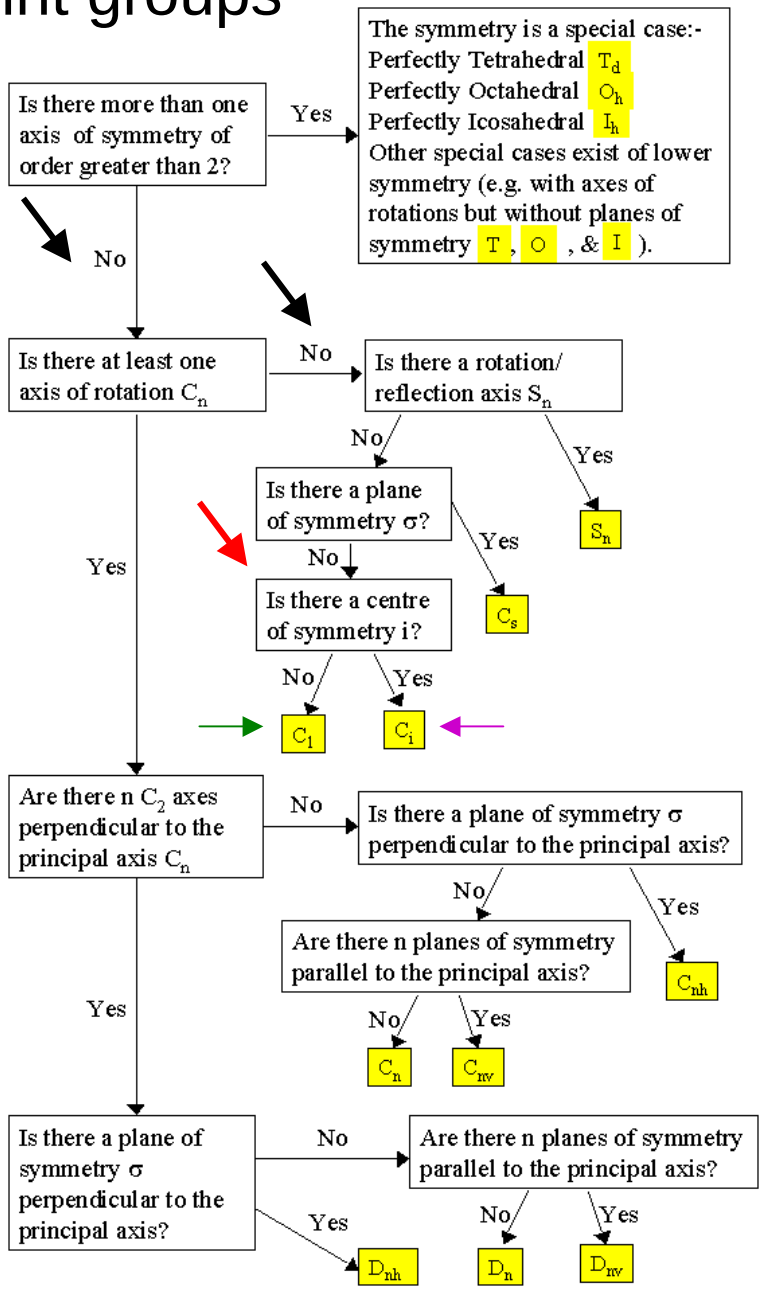
e.g. (conformation is important !)



No symmetry (C_1)

e.g. CHFClBr



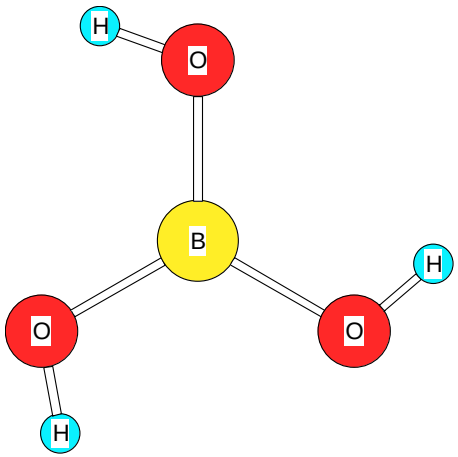


Identifying point groups

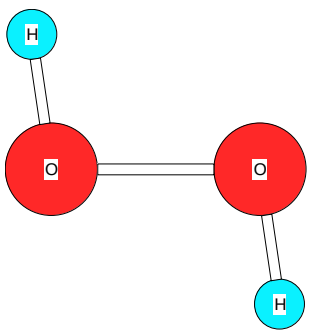
C_n type groups:

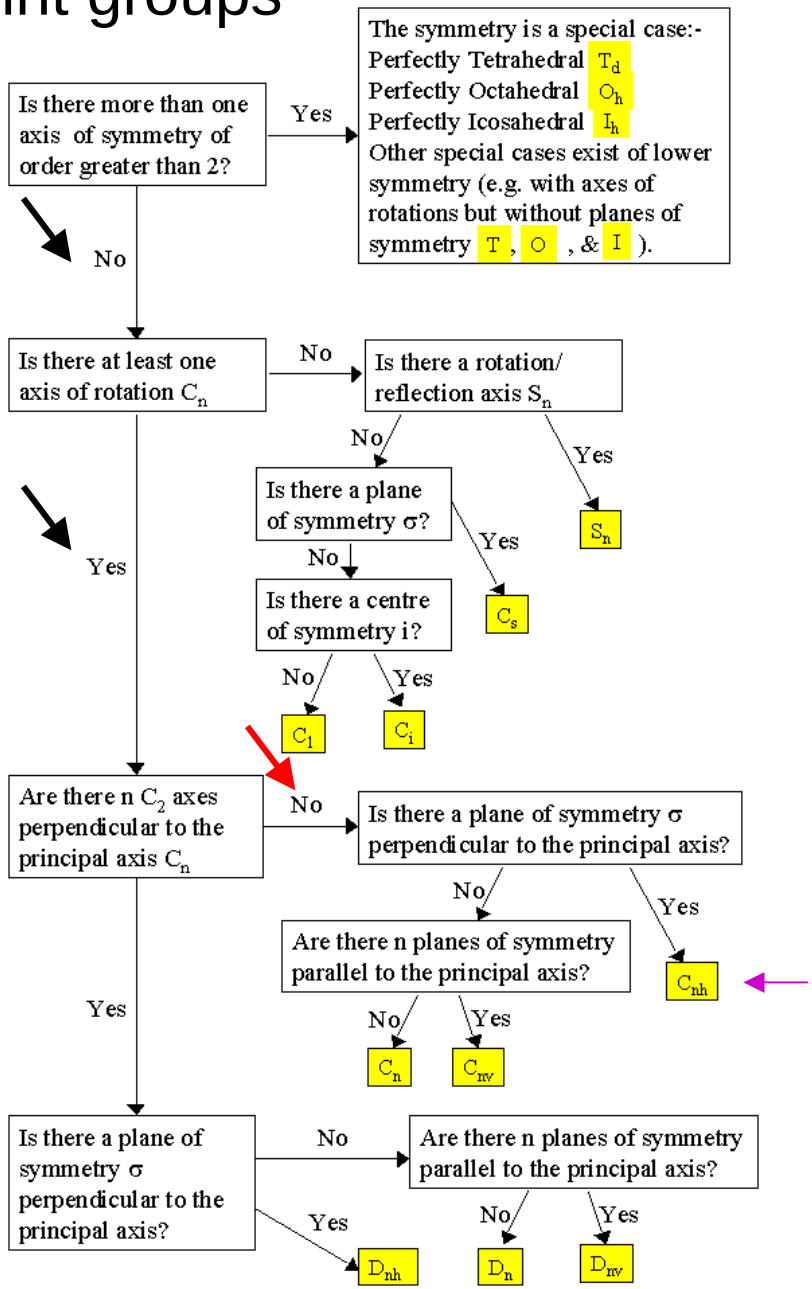
A C_n axis and a σ_h (C_{nh})

e.g. $B(OH)_3$ (C_{3h}, conformation is important !)



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





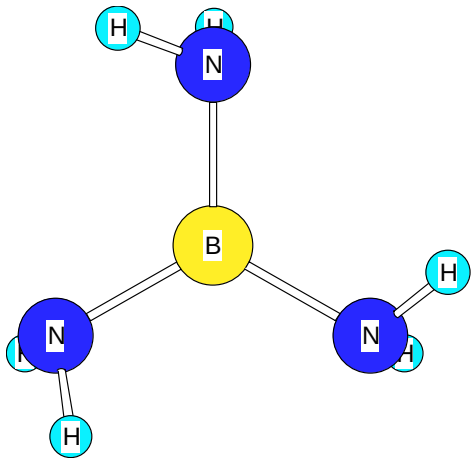
Note: molecule does not have to be planar e.g. $B(NH_2)_3$ (C_{3h}, conformation is important !)

Identifying point groups

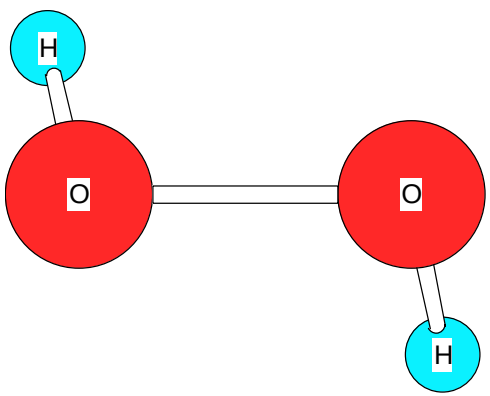
C_n type groups:

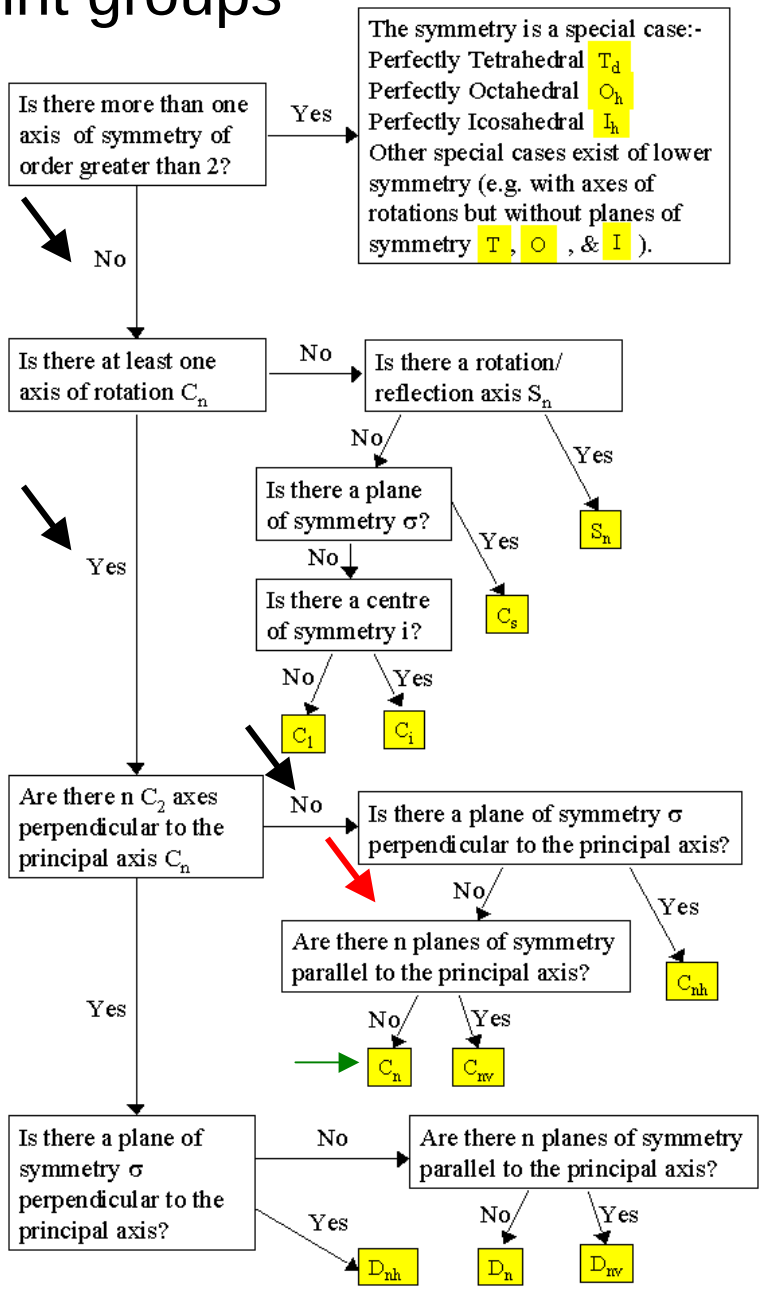
Only a C_n axis (C_n) ←

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



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



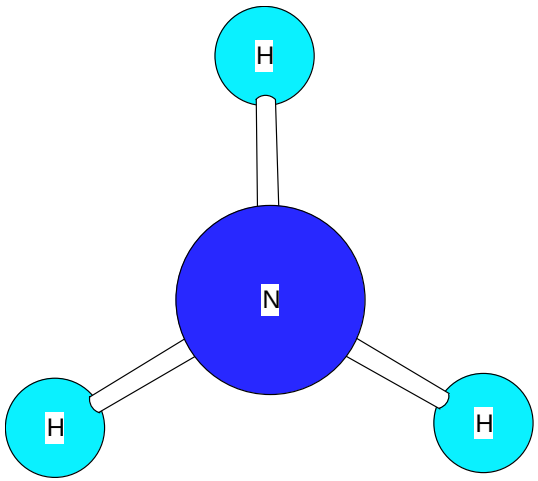


Identifying point groups

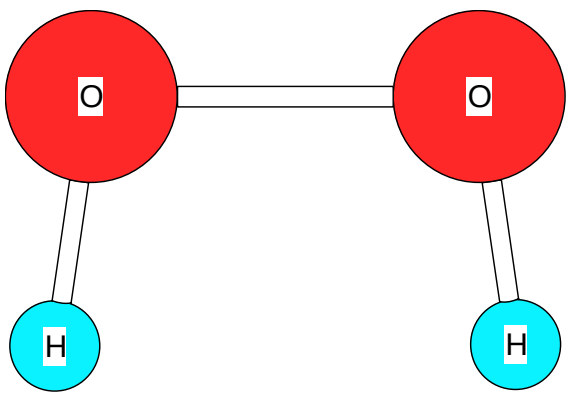
C_n type groups:

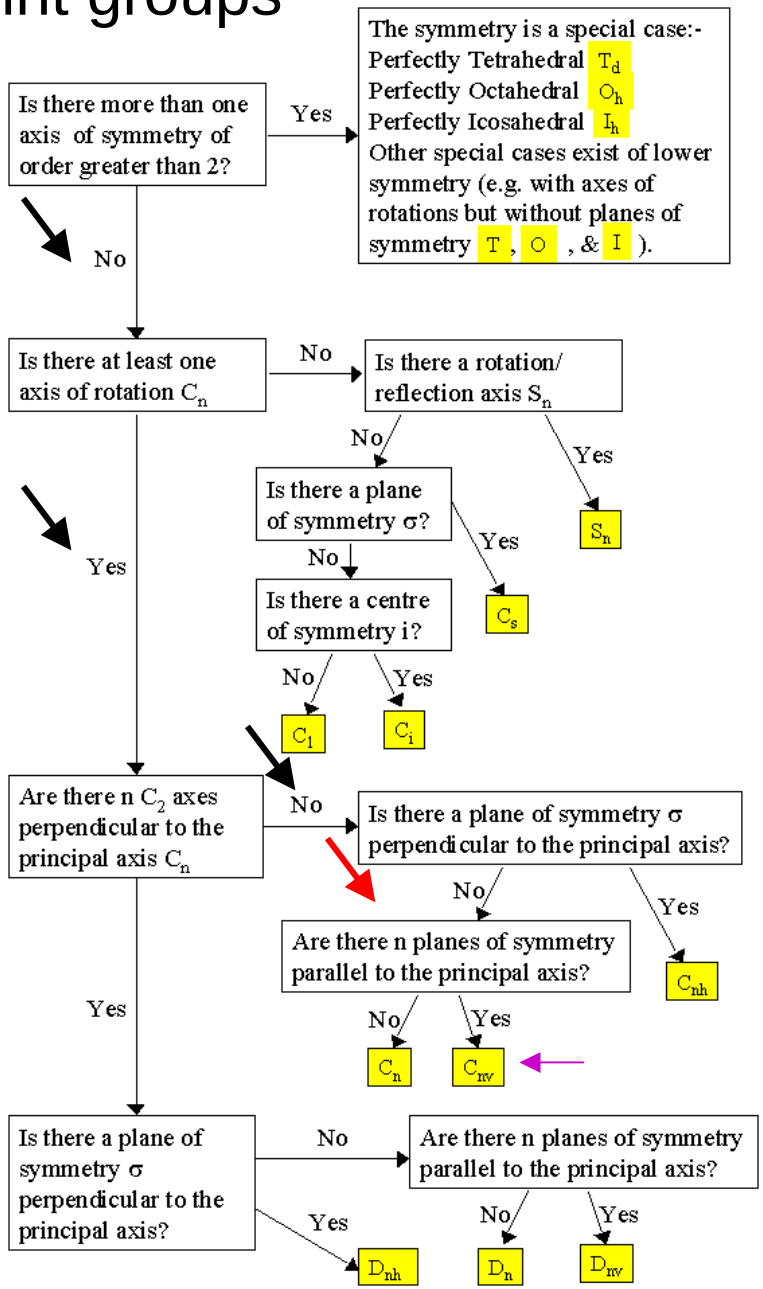
A C_n axis and a σ_v (C_{nv}) ←

e.g. NH_3 (C_{3v})



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



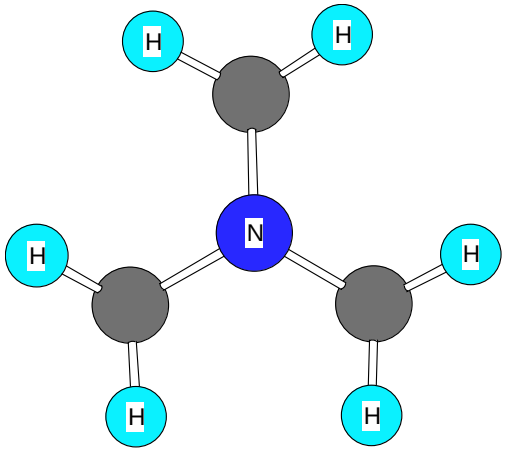


Identifying point groups

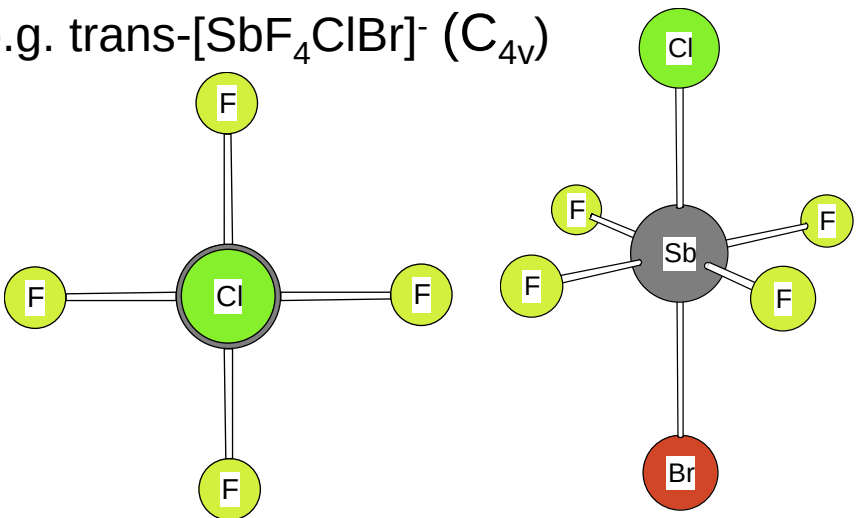
C_n type groups:

A C_n axis and a σ_v (C_{nv})

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

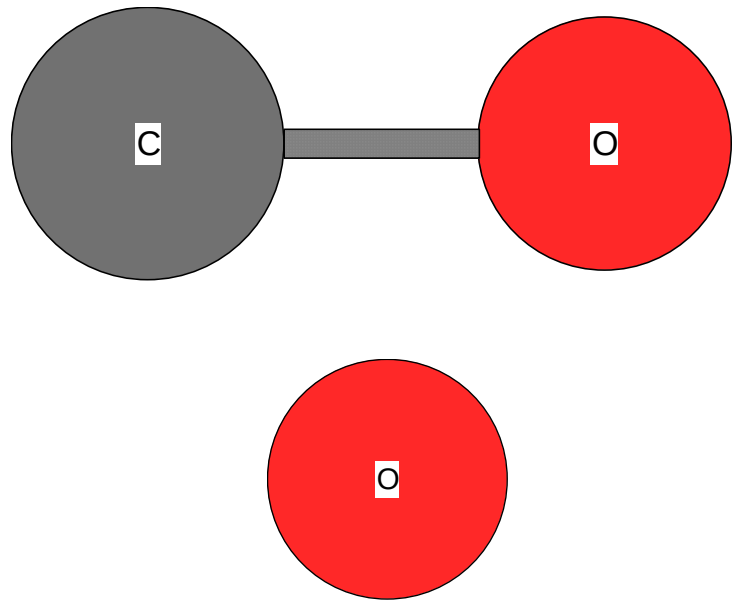


e.g. trans-$[SbF_4ClBr]^-$ (C_{4v})



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

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

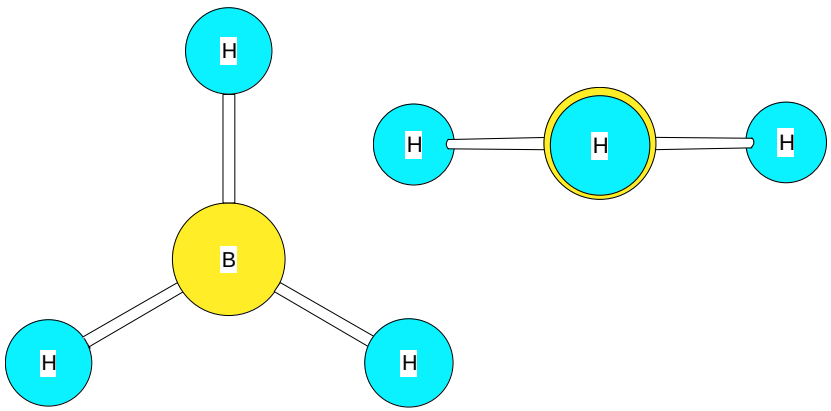


Identifying point groups

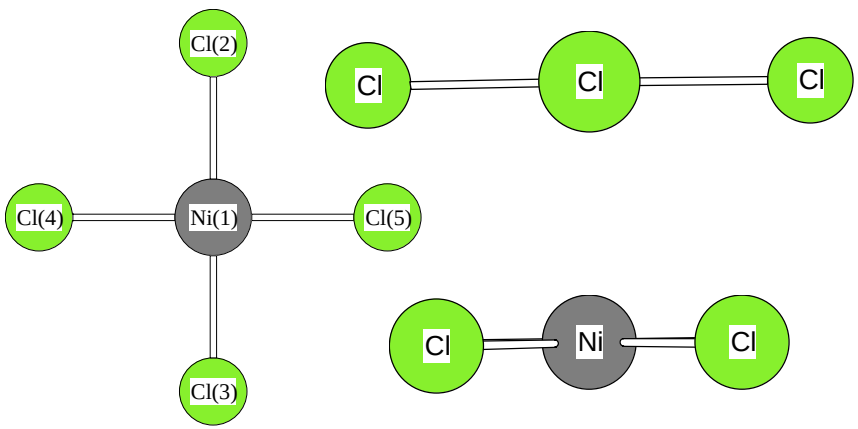
D_n type groups:

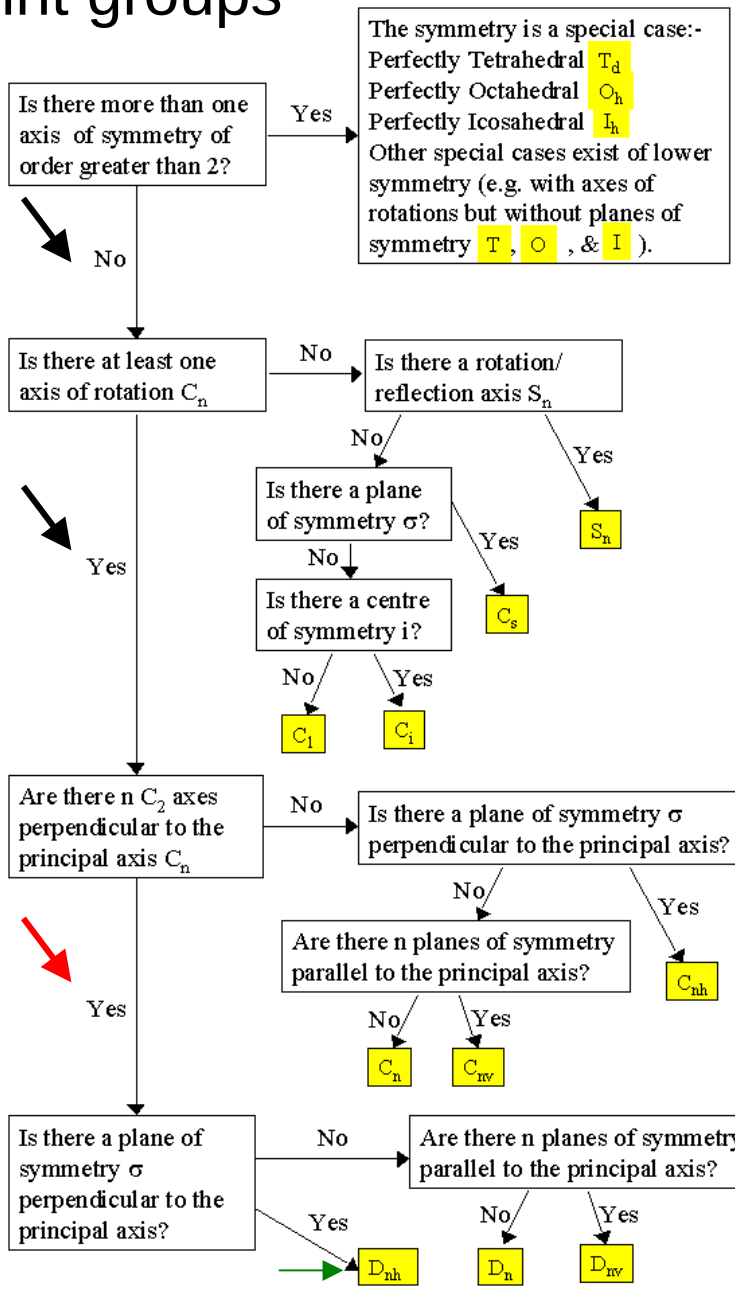
A C_n axis, n perpendicular C_2 axes and a σ_h (D_{nh}) ←

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



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



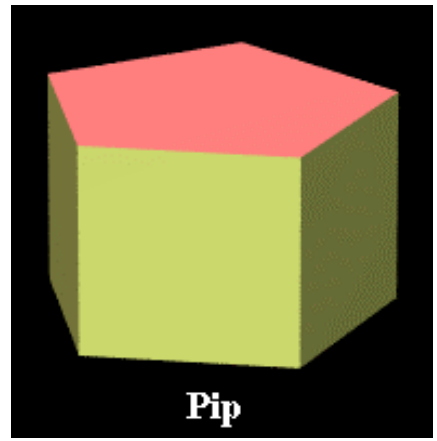


Identifying point groups

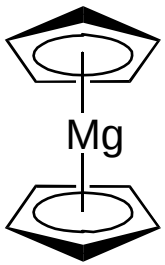
D_n type groups:

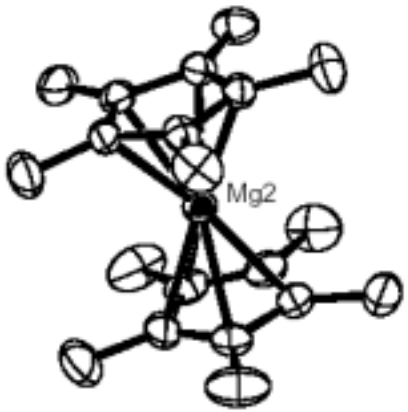
A C_n axis, n perpendicular C_2 axes and a σ_h (D_{nh})

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



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

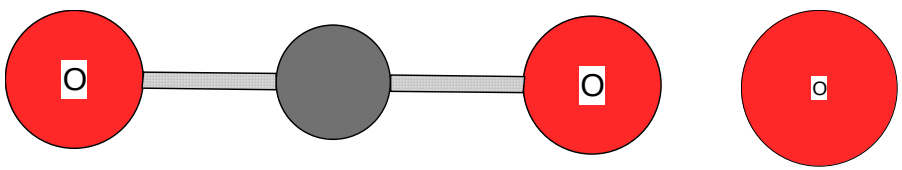




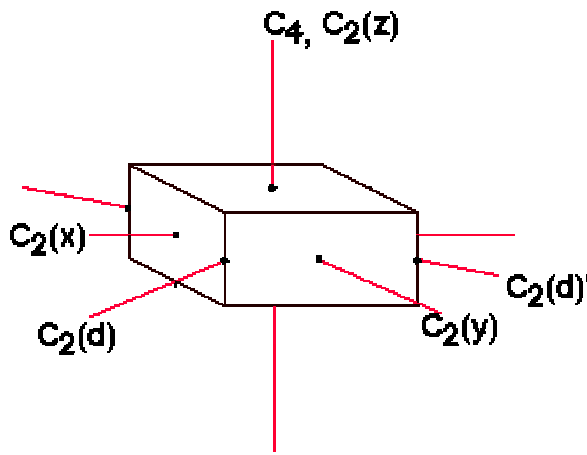
View down the C_5 axis

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})

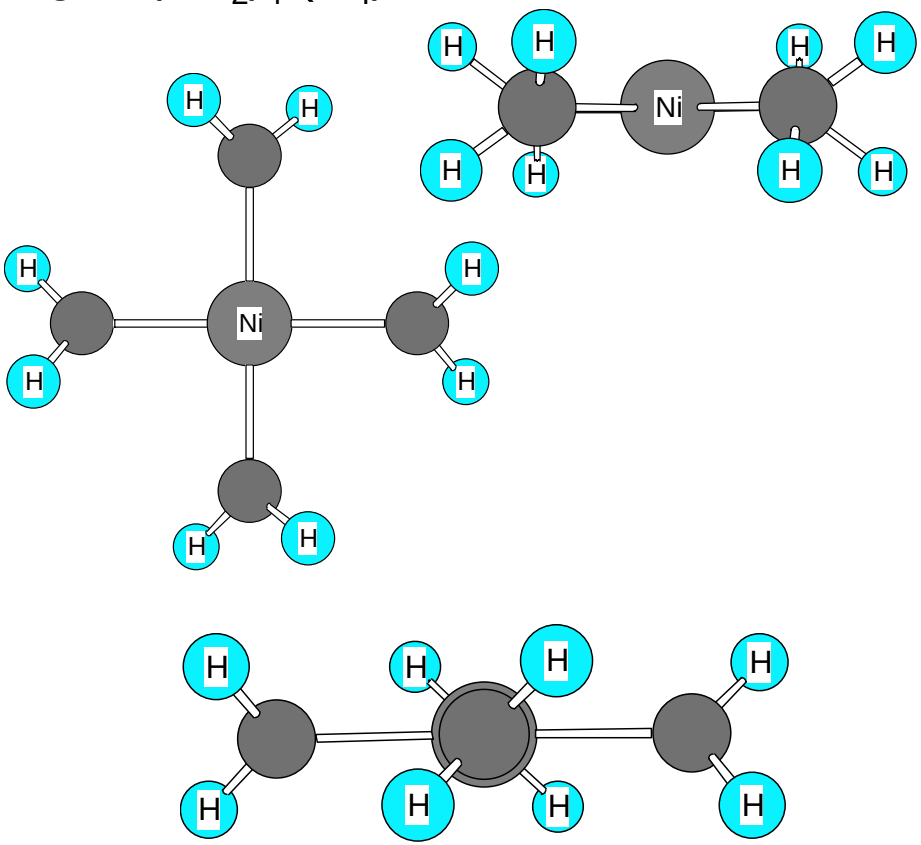


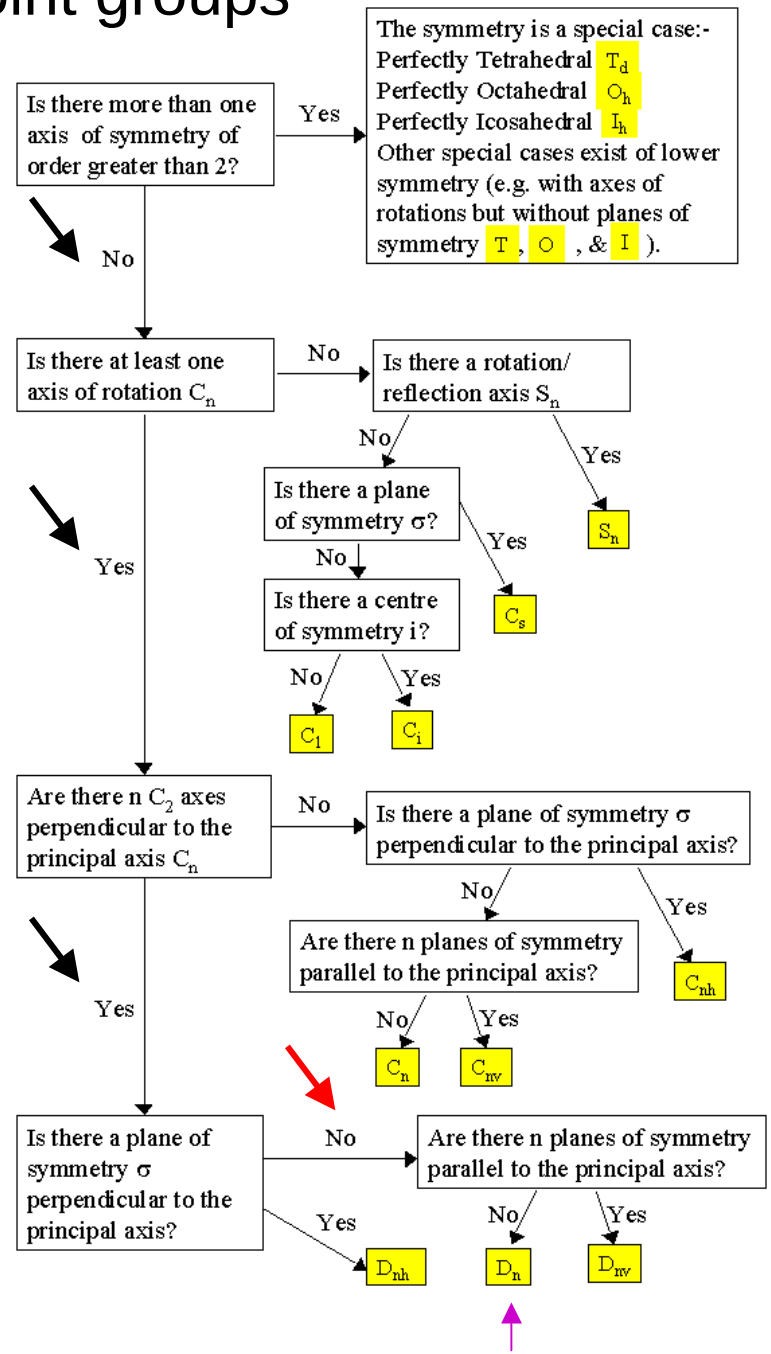
Identifying point groups

D_n type groups:

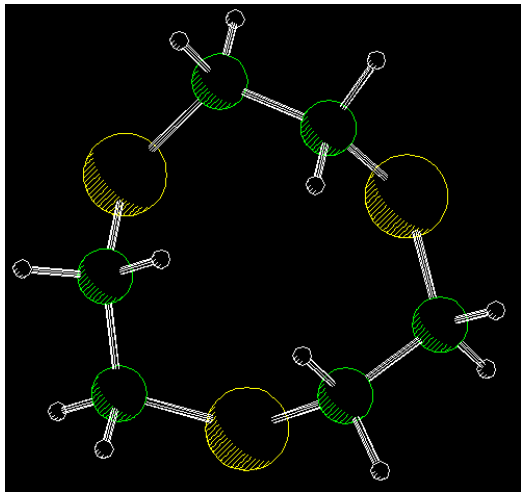
A C_n axis, n perpendicular C_2 axes and **no mirror planes** (D_n) ←
-propellor shapes

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



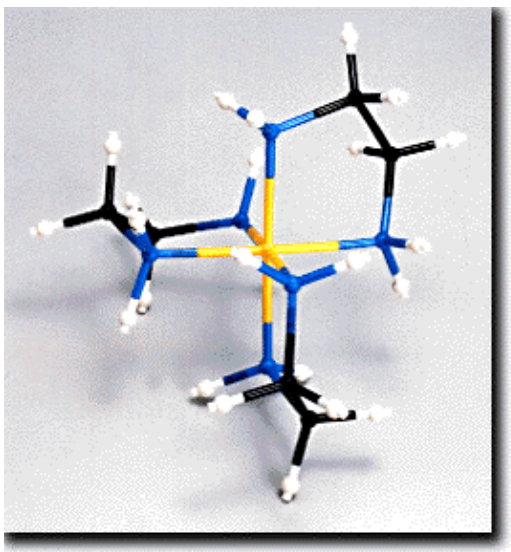


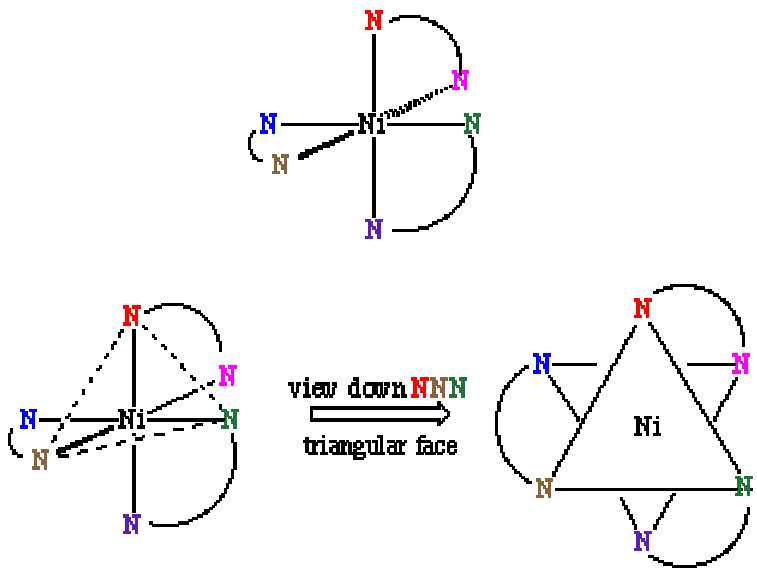
e.g. $(SCH_2CH_2)_3$ (D_3 conformation is important!)



e.g. propellor (D_3)

e.g. $Ni(en)_3$ (D_3 conformation is important!) en = $H_2NCH_2CH_2NH_2$



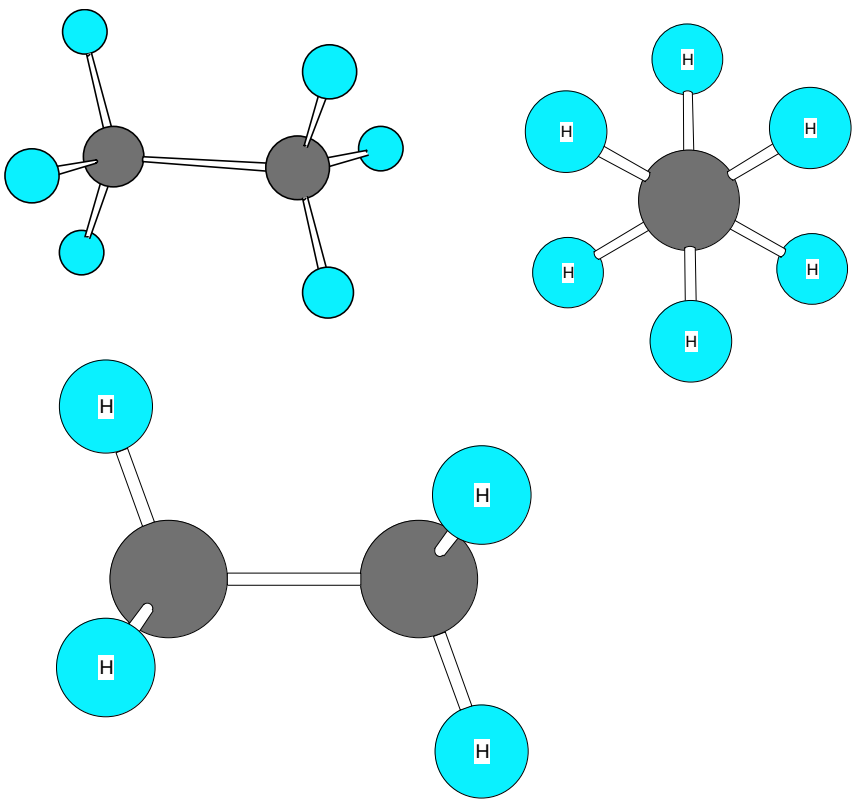


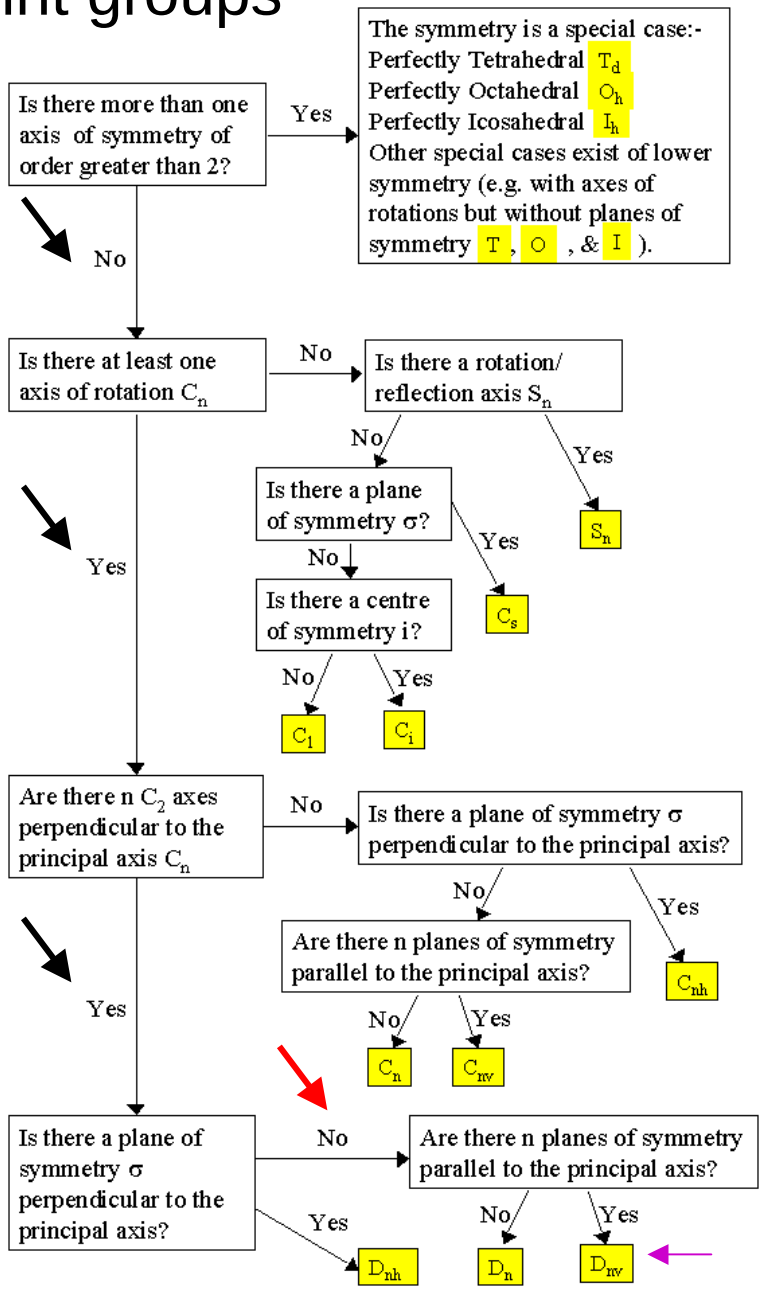
Identifying point groups

D_n type groups:

A C_n axis, n perpendicular C_2 axes and a σ_d (D_{nd}) ←

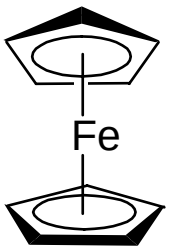
e.g. ethane, $H_3C\text{-}CH_3$
(D_{3d} in the staggered conformation)

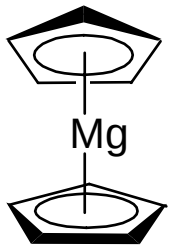


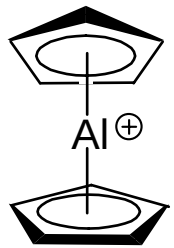


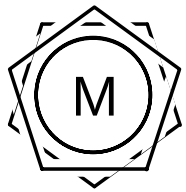
dihedral means between sides or planes – this is where you find the C_2 axes

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

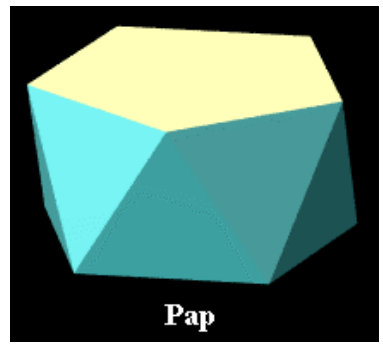




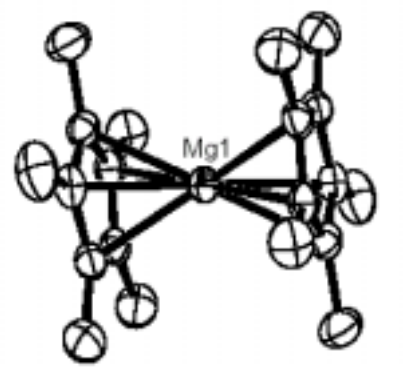




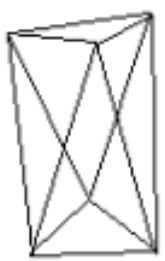
View down the C_5 axis



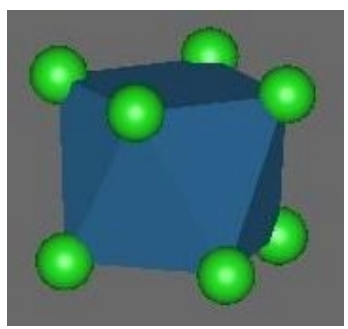
These are pentagonal antiprisms



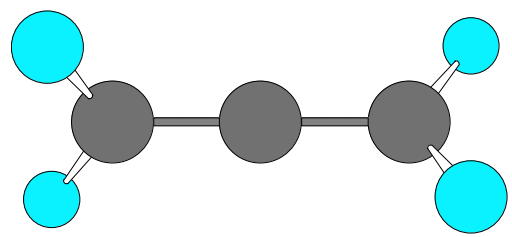
e.g. triagular antiprism (D_{3d})



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



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



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:

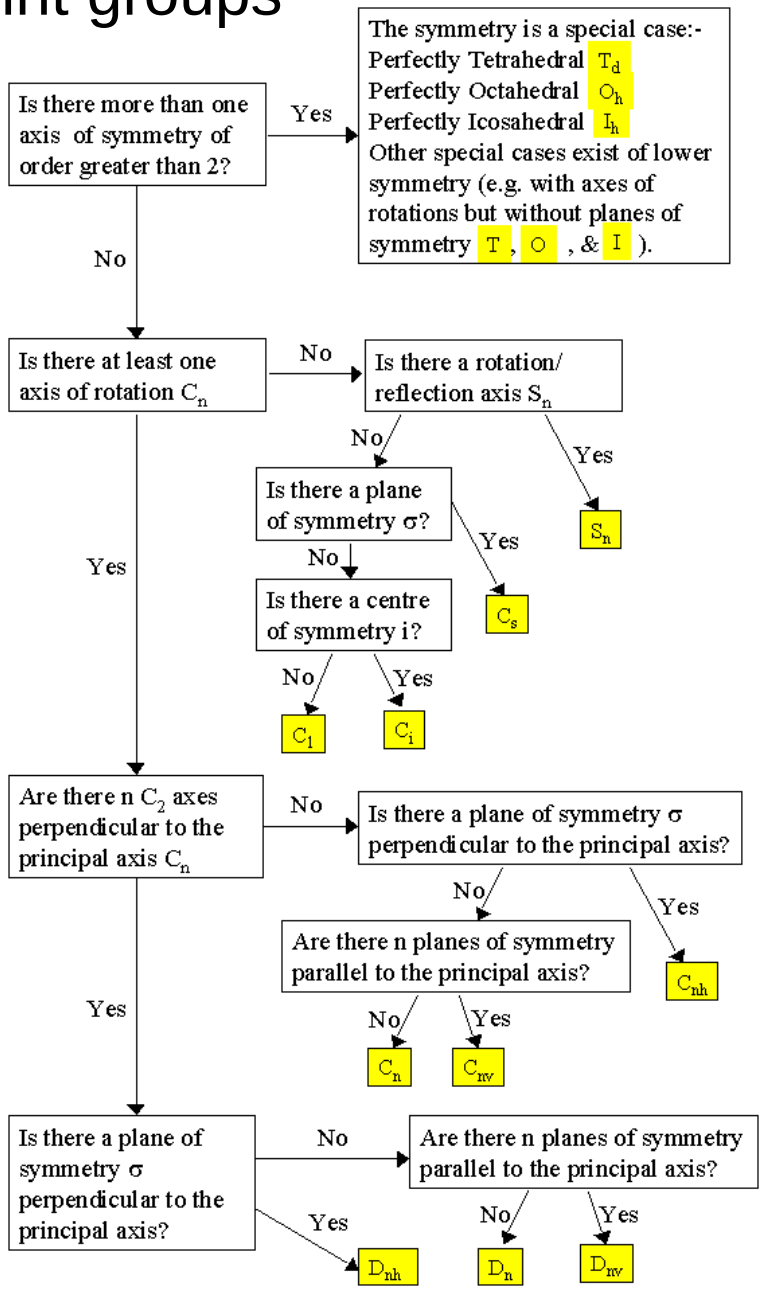
1. Determine the symmetry is special (e.g. tetrahedral).

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.



Character Tables for Point Groups

Each point group has a complete set of possible symmetry operations that are conveniently listed as a matrix known as a *Character Table*. As an example, we will look at the character table for the C_{2v} point group.

Point Group Label

Symmetry Operations – The *Order* is the total number of operations

C_{2V}	E	C_2	σ_v (xz)	σ'_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 C_{2v} the order is 4:
1 E, 1 C_2, 1 σ_v and 1 σ'_v

Character

Representation of B_2

Symmetry Representation Labels

Representations are subsets of the complete point group – they indicate the effect of the symmetry operations on different kinds of mathematical functions. Representations are orthogonal to one another. The *Character* is an integer that indicates the effect of an operation in a given representation.

Character Tables for Point Groups

The effect of symmetry elements on mathematical functions is useful to us because orbitals are mathematical functions! Analysis of the symmetry of a molecule will provide us with insight into the orbitals used in bonding.

Symmetry of Functions

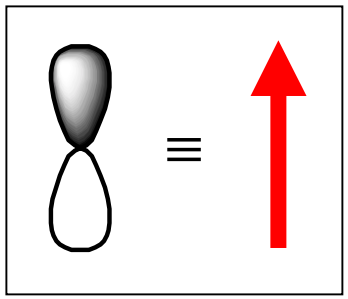
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

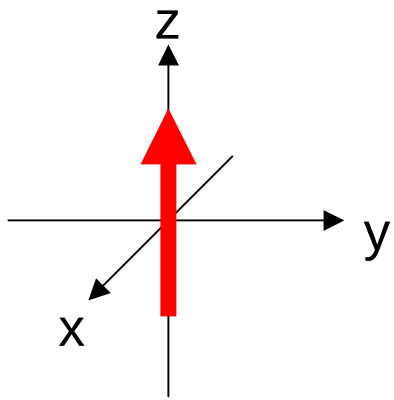
Notes about symmetry labels and characters:

"A" means symmetric with regard to rotation about the principle axis.
"B" means anti-symmetric with regard to rotation about the principle axis.
Subscript numbers are used to differentiate symmetry labels, if necessary.
"1" indicates that the operation leaves the function unchanged: it is called "symmetric".
"-1" indicates that the operation reverses the function: it is called "anti-symmetric".

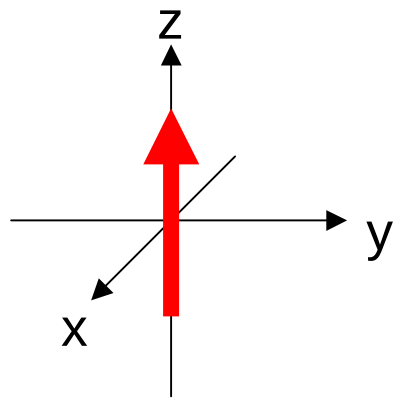
 Symmetry of orbitals and functions

A p_z orbital has the same symmetry as an arrow pointing along the z-axis.





E
C_2
σ_v (xz)
σ'_v (yz)

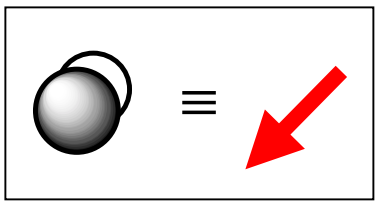


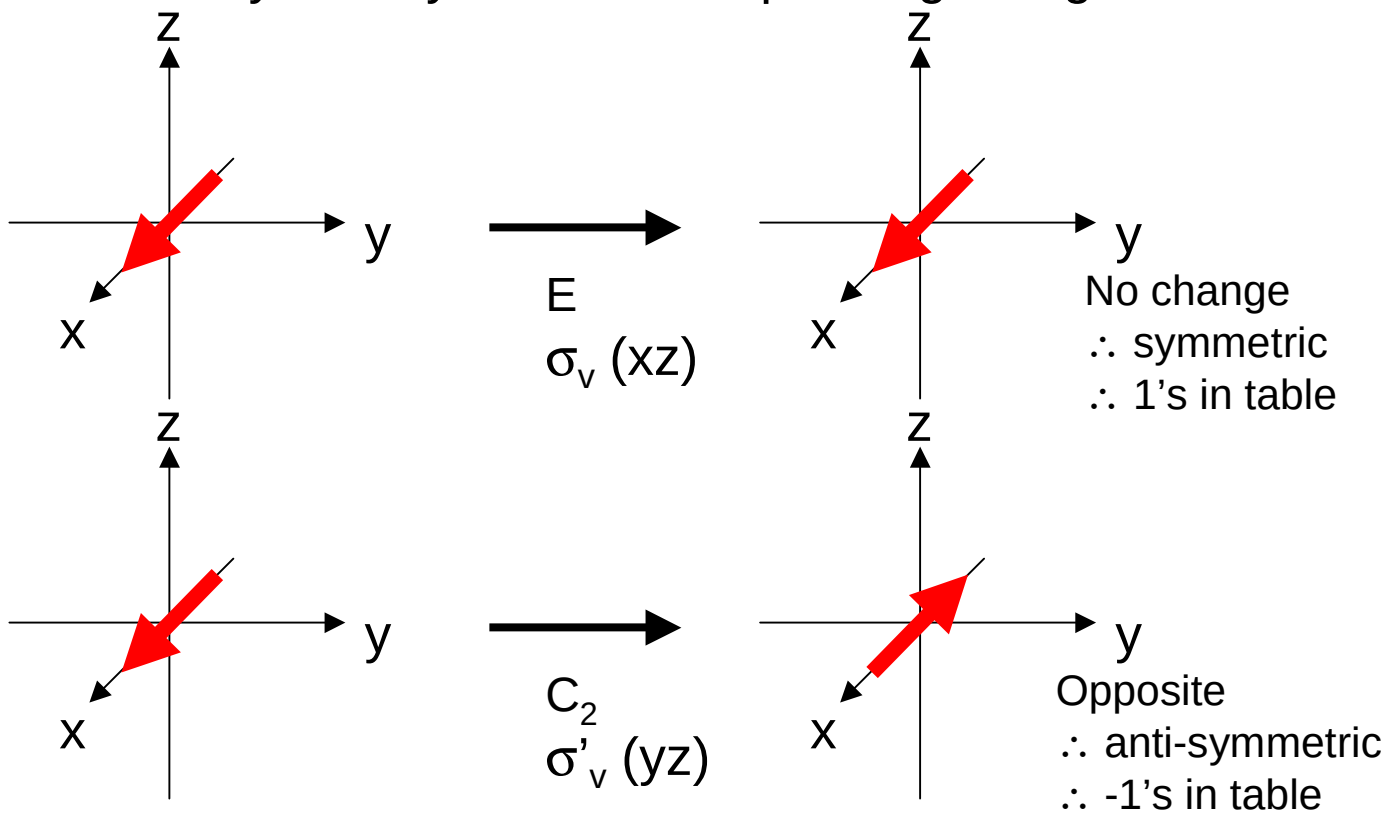
No change
$\therefore$ symmetric
$\therefore$ 1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

 Symmetry of orbitals and functions

A p_x orbital has the same symmetry as an arrow pointing along the x-axis.

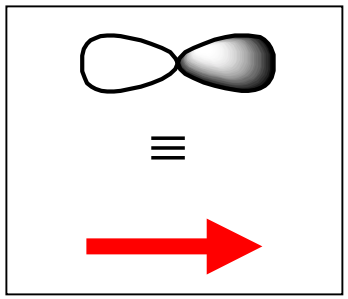




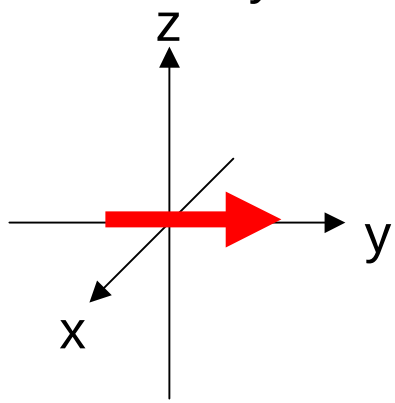
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

 Symmetry of orbitals and functions

A p_y orbital has the same symmetry as an arrow pointing along the y-axis.

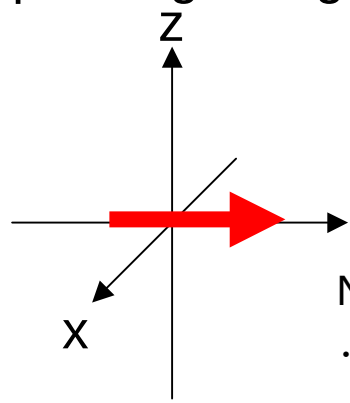


≡

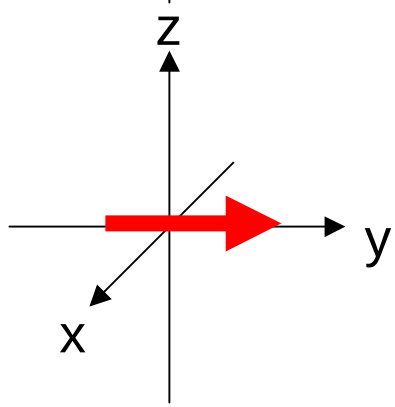


E

σ'_v (yz)

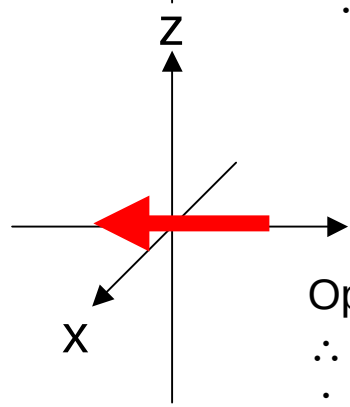


No change
∴ symmetric
∴ 1's in table



C_2

σ_v (xz)



Opposite
∴ anti-symmetric
∴ -1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

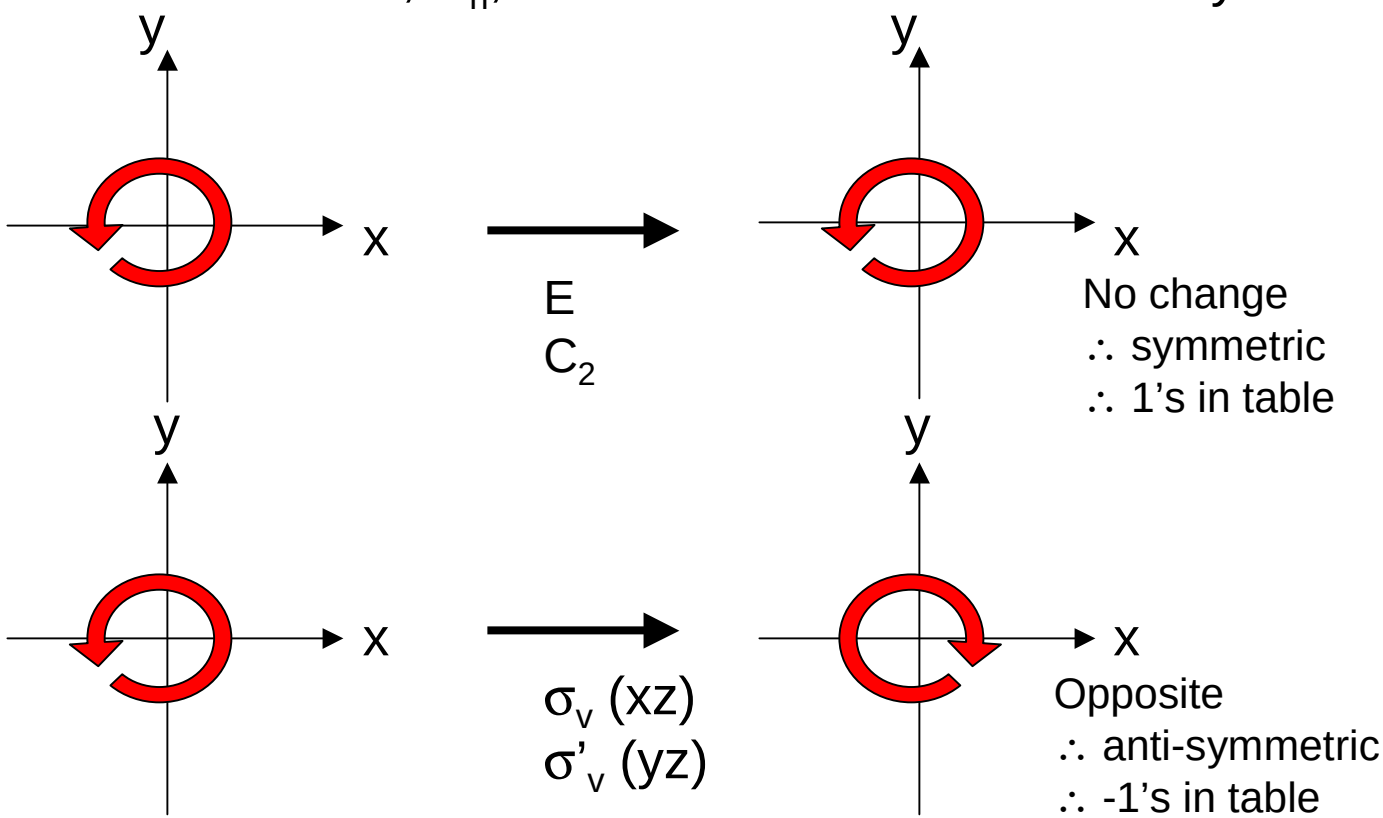
Symmetry of orbitals and functions

Rotation about the n axis, R_n, can be treated in a similar way.

The z axis is pointing out of the screen!

If the rotation is still in the same direction (e.g. counter clock-wise), then the result is considered symmetric.

If the rotation is in the opposite direction (i.e. clock-wise), then the result is considered anti-symmetric.

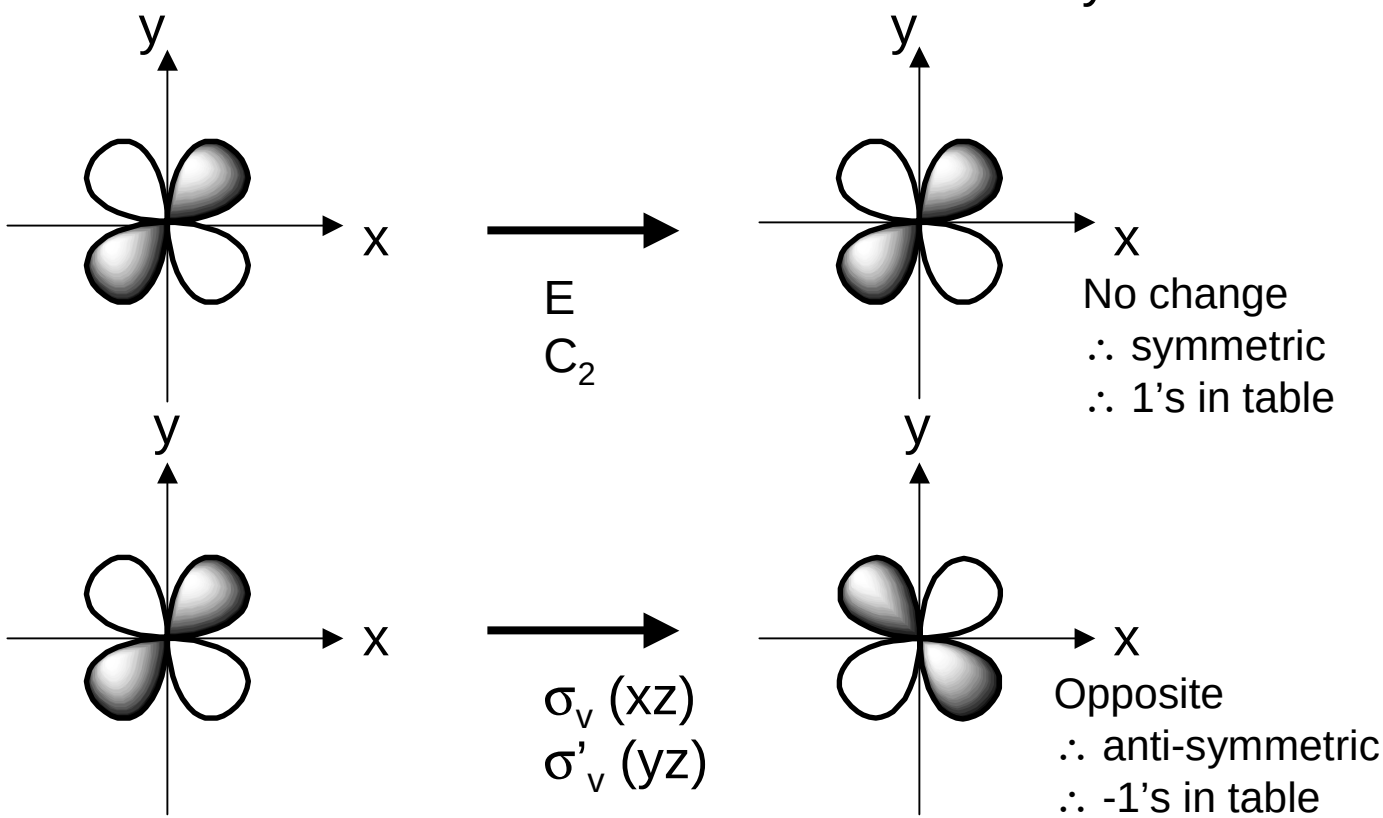


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Symmetry of orbitals and functions

d orbital functions can also be treated in a similar way

The z axis is pointing out of the screen!

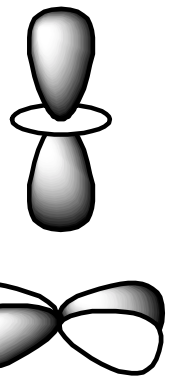


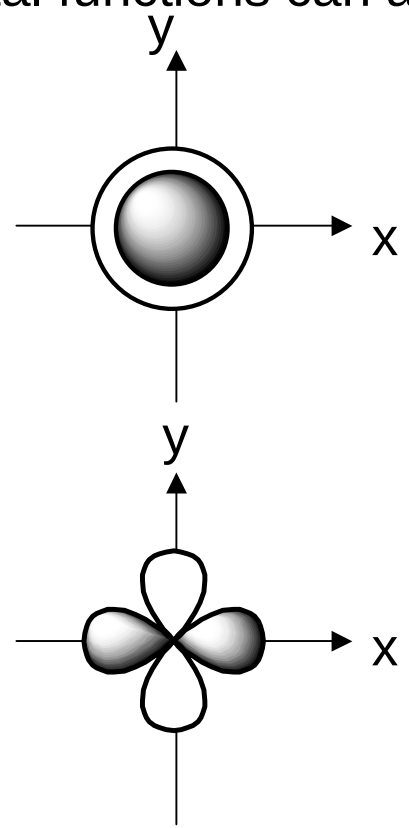
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Symmetry of orbitals and functions

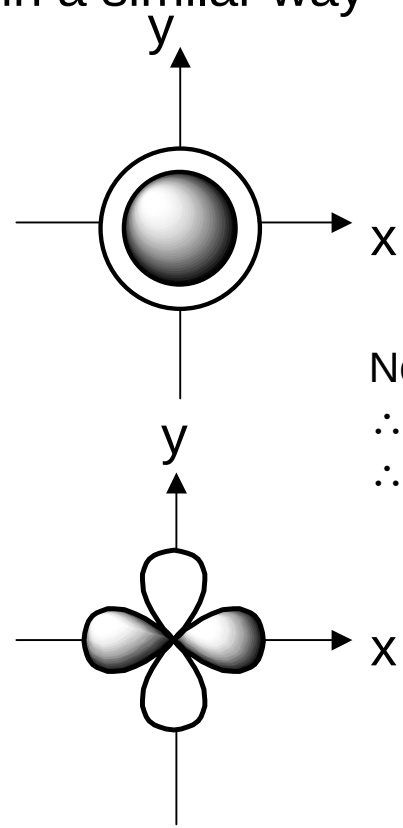
d orbital functions can also be treated in a similar way

The z axis is pointing out of the screen!
So these are representations of the view of the d_{z^2} orbital and $d_{x^2-y^2}$ orbital down the z-axis.





E
C_2
σ_v (xz)
σ'_v (yz)



No change
∴ symmetric
∴ 1's in table

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Note that the representation of orbital functions changes depending on the point group – thus it is important to be able to identify the point group correctly.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

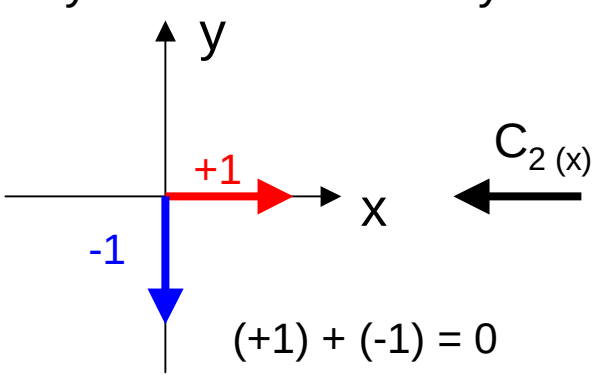
Symmetry of orbitals and functions

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

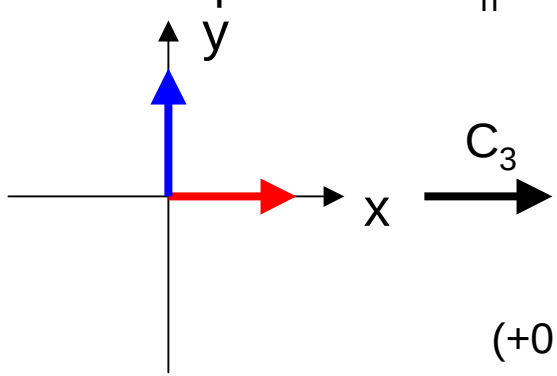
More notes about symmetry labels and characters:

-"E" indicates that the representation is doubly-degenerate – this means that the functions grouped in parentheses **must be treated as a pair** and can not be considered individually.

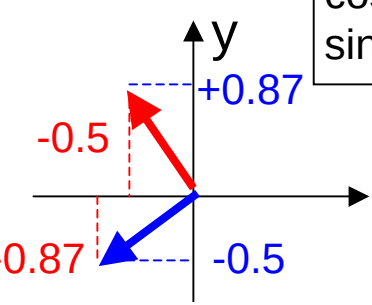
-The prime (') and (") double prime in the symmetry representation label indicates "symmetric" or "anti-symmetric" with respect to the σ_h.



(+1) + (-1) = 0



cos(120°) = -0.5
sin(120°) = 0.87



(+0.87) + (-0.87) + (-0.5) + (-0.5) = -1

Symmetry of orbitals and functions

O_h	E	8 C_3	6 C_2	6 C_4	3 C_2 (C_4^2)	i	6 S_4	8 S_6	3 σ_h	6 σ_d		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

More notes about symmetry labels and characters:

-“T” indicates that the representation is triply-degenerate – this means that the functions grouped in parentheses must be treated as a threesome and can not be considered individually.

-The subscripts g (gerade) and u (ungerade) in the symmetry representation label indicates “symmetric” or “anti-symmetric” with respect to the inversion center, i.

Chem 59-651 Character Tables and Bonding

We can use character tables to determine the orbitals involved in bonding in a molecule. This process is done a few easy steps.

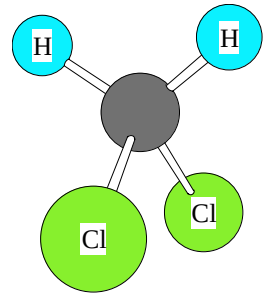
1. Determine the point group of the molecule.

2. Determine the *Reducible Representation*, Γ, for the type of bonding you wish to describe (e.g. σ, π, $\pi_{\perp}$, $\pi_{//}$). The Reducible Representation indicates how the bonds are affected by the symmetry elements present in the point group.

3. Identify the *Irreducible Representation* that provides the Reducible Representation; there is a simple equation to do this. The Irreducible Representation (e.g. $2A_1 + B_1 + B_2$) is the combination of symmetry representations in the point group that sum to give the Reducible Representation.

4. Identify which orbitals are involved from the Irreducible Representation and the character table.

Example, the σ bonding in dichloromethane, CH_2Cl_2.



The point group is C_{2v} so we must use the appropriate character table for the reducible representation of the sigma bonding, Γ_σ. To determine Γ_σ all we have to do is see how each symmetry operation affects the 4 σ bonds in the molecule – if the bond moves, it is given a value of 0, if it stays in the same place, the bond is given a value of 1. **Put the sum of the 1's and 0's into the box corresponding to the symmetry operation.**

The E operation leaves everything where it is so all four bonds stay in the same place and the character is 4 (1+1+1+1).

The C_2 operation moves all four bonds so the character is 0.

Each σ_v operation leaves two bonds where they were and moves two bonds so the character is 2 (1+1).

Overall, the reducible representation is thus:

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_σ	4	0	2	2

We now have to figure out what combination of symmetry representations will add up to give us this reducible representation. In this case, it can be done by inspection, but there is a simple equation that is useful for more complicated situations.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_σ	4	0	2	2

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Because the character under E is 4, there must be a total of 4 symmetry representations (sometimes called *basis functions*) that combine to make Γ_σ. Since the character under C_2 is 0, there must be two of A symmetry and two of B symmetry. The irreducible representation is $(2A_1 + B_1 + B_2)$, which corresponds to: s, p_z, p_x, and p_y orbitals – the same as in VBT. You can often use your understanding of VBT to help you in finding the correct basis functions for the irreducible representation.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_σ	4	0	2	2

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The formula to figure out the number of symmetry representations of a given type is:

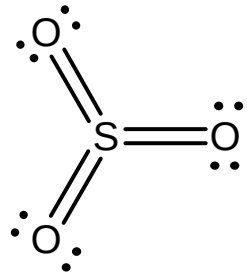
$$n_X = \frac{1}{\text{order}} \sum \left[(\#\text{ of operations in class}) \times (\text{character of RR}) \times (\text{character of X}) \right]$$

Thus, in our example:

$$n_{A_1} = \frac{1}{4}\left[(1)(4)(1)+(1)(0)(1)+(1)(2)(1)+(1)(2)(1)\right] \qquad n_{B_1} = \frac{1}{4}\left[(1)(4)(1)+(1)(0)(-1)+(1)(2)(1)+(1)(2)(-1)\right]$$

$$n_{A_2} = \frac{1}{4}\left[(1)(4)(1)+(1)(0)(1)+(1)(2)(-1)+(1)(2)(-1)\right] \qquad n_{B_2} = \frac{1}{4}\left[(1)(4)(1)+(1)(0)(-1)+(1)(2)(-1)+(1)(2)(1)\right]$$

Which gives: 2 A_1's, 0 A_2's, 1 B_1 and 1 B_2.



Example, the σ and π bonding in SO_3.

The point group is D_{3h} so we must use the appropriate character table to find the reducible representation of the sigma bonding, Γ_σ first, then we can go the representation of the π bonding, Γ_π. To determine Γ_σ all we have to do is see how each symmetry operation affects the 3 σ bonds in the molecule.

The E and the σ_h operations leave everything where it is so all three bonds stay in the same place and the character is 3 (1+1+1).

The C_3 and S_3 operations move all three bonds so their characters are 0.

The C_2 operation moves two of the bonds and leaves one where it was so the character is 1.

Each σ_v operation leaves one bond where it was and moves two bonds so the character is 1.

Overall, the reducible representation for the sigma bonding is:

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v
Γ_σ	3	0	1	3	0	1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$
Γ_σ	3	0	1	3	0	1

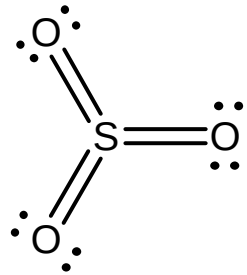
D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

$$n_{A'_1} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(1)(1)\right] \qquad n_{A'_1} = \frac{12}{12} = 1$$

$$n_{A'_2} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(1)(-1)\right] \qquad n_{A'_2} = \frac{0}{12} = 0$$

$$n_{E'} = \frac{1}{12}\left[(1)(3)(2) + (2)(0)(-1) + (3)(1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(1)(0)\right] \qquad n_{E'} = \frac{12}{12} = 1$$

We can stop here because the combination (A'_1 + E') produces the Γ_σ that we determined. None of the other representations can contribute to the σ bonding (i.e. $n_{A''1}$, $n_{A''1}$ and $n_{E''}$ are all 0). The irreducible representation (A'_1 + E') shows us that the orbitals involved in bonding are the s and the p_x and p_y pair; this corresponds to the sp^2 combination we find in VBT.



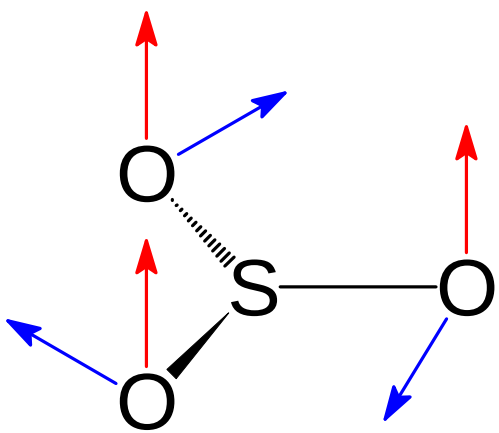
Now we have to determine Γ for the π bonding in SO_3.

To determine Γ_π we have to see how each symmetry operation affects the π systems in the molecule. The treatment is similar to what we did for sigma bonding but there are a few significant differences:

1) *Pi bonds change sign across the inter-nuclear axis*. We must consider the effect of the symmetry operation on the signs of the lobes in a π bond.

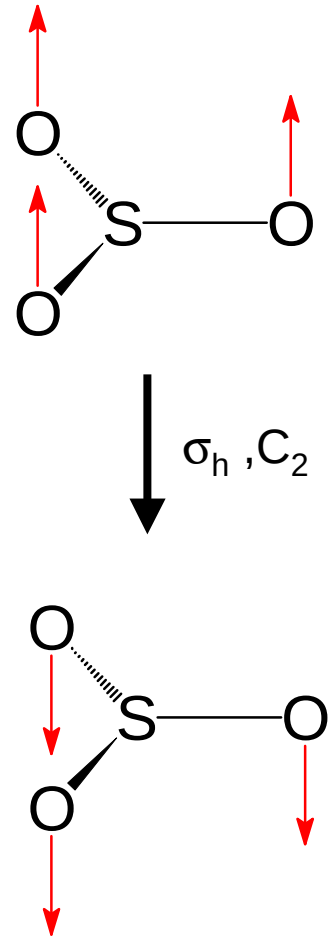
2) *There is the possibility of two different π type bonds for any given σ bond* (oriented 90° from each other). We must examine each of these.

This means that we have to find reducible representations for both the π system perpendicular to the molecular plane ($\pi_\perp$, vectors shown in red) and the pi system in the molecular plane ($\pi_{//}$, vectors shown in blue).



Note: These are just vectors that are associated with **each sigma bond** (not with any particular atom) – they could also be placed in the middle of each SO bond. The vectors should be placed to conform with the symmetry of the point group (e.g. the blue vectors conform to the C_3 axis).

Example, the σ and π bonding in SO_3.



First determine the reducible representation for the pi bonding perpendicular to the molecular plane, $\Gamma_{\pi\perp}$.

The E operation leaves everything where it is so all three vectors stay in the same place and the character is 3.

The C_3 and S_3 operations move all three vectors so their characters are 0.

The C_2 operation moves two of the vectors and reverses the sign of the other one so the character is -1.

The σ_h operation reverses the sign of all three vectors so the character is -3.

Each σ_v operation leaves one vector where it was and moves the two others so the character is 1.

Overall, the reducible representation for the perpendicular π bonding is:

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v
$\Gamma_{\pi\perp}$	3	0	-1	-3	0	1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$
$\Gamma_{\pi\perp}$	3	0	-1	-3	0	1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

$$n_{A'_1} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(1)\right] \qquad n_{A'_1} = \frac{0}{12} = 0$$

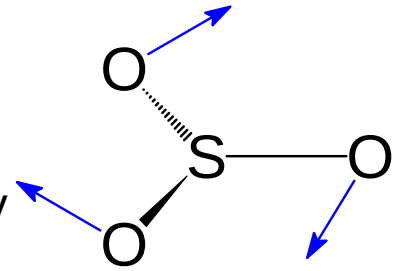
$$n_{A''_2} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(1)\right] \qquad n_{A''_2} = \frac{12}{12} = 1$$

$$n_{E''} = \frac{1}{12}\left[(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(-2) + (2)(0)(1) + (3)(1)(0)\right] \qquad n_{E''} = \frac{12}{12} = 1$$

Going through all the possibly symmetry representations, we find that the combination (A''_2 + E'') produces the $\Gamma_{\pi\perp}$ that we determined. The irreducible representation shows us that the possible orbitals involved in perpendicular π bonding are the p_z and the d_{xz} and d_{yz} pair. This is in agreement with the π bonding we would predict using VBT.

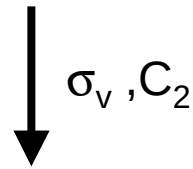
Example, the σ and π bonding in SO_3.

First determine the reducible representation for the π bonding in the molecular plane, $\Gamma_{\pi//}$.

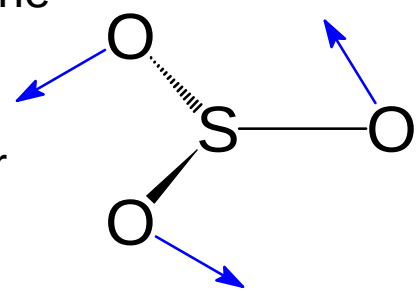


The E operation leaves everything where it is so all three vectors stay in the same place and the character is 3.

The C_3 and S_3 operations move all three vectors so their characters are 0.



The C_2 operation moves two of the vectors and reverses the sign of the other one so the character is -1.



The σ_h operation leaves all three vectors unchanged so the character is 3.

Each σ_v operation reverses the sign one vector where it was and moves the two others so the character is -1.

Overall, the reducible representation for the parallel π bonding is:

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v
$\Gamma_{\pi//}$	3	0	-1	3	0	-1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$
$\Gamma_{\pi//}$	3	0	-1	3	0	-1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

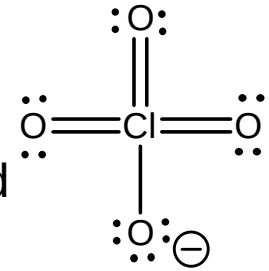
$$n_{A'_1} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(1)(-1)\right] \qquad n_{A'_1} = \frac{0}{12} = 0$$

$$n_{A'_2} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(-1)(-1)\right] \qquad n_{A'_2} = \frac{12}{12} = 1$$

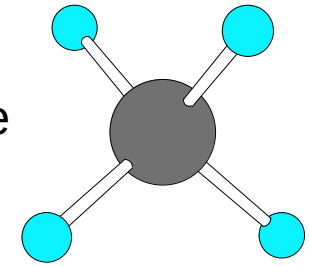
$$n_{E'} = \frac{1}{12}\left[(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(-1)(0)\right] \qquad n_{E'} = \frac{12}{12} = 1$$

Going through all the possibly symmetry representations, we find that the combination (A'_2 + E') produces the $\Gamma_{\pi//}$ that we determined. The possible orbitals involved in parallel π bonding are only the $d_{x^2-y^2}$ and d_{xy} pair. The A'_2 representation has no orbital equivalent. Note: **Such analyses do NOT mean that there is π bonding using these orbitals – it only means that it is possible based on the symmetry of the molecule.**

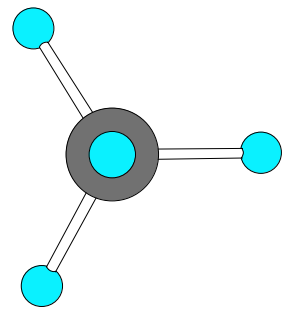
Example, the σ and π bonding in ClO_4^-.



The point group is T_d so we must use the appropriate character table to find the reducible representation of the sigma bonding, Γ_σ first, then we can go the representation of the π bonding, Γ_π.

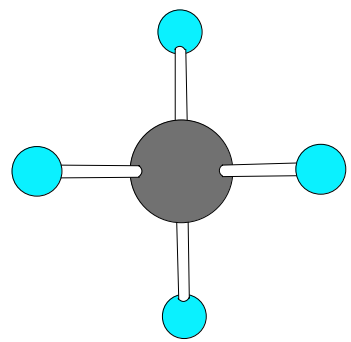


The E operation leaves everything where it is so all four bonds stay in the same place and the character is 4.



Each C_3 operation moves three bonds leaves one where it was so the character is 1.

The C_2 and S_4 operations move all four bonds so their characters are 0.



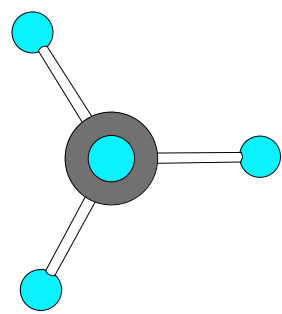
Each σ_d operation leaves two bonds where they were and moves two bonds so the character is 2.

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d
Γ_σ	4	1	0	0	2

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d
Γ_σ	4	1	0	0	2

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

The irreducible representation for the σ bonding is (A_1 + T_2), which corresponds to the s orbital and the (p_x, p_y, p_z) set that we would use in VBT to construct a the sp^3 hybrid orbitals suitable for a tetrahedral arrangement of atoms. To get the representation for the π bonding, we must do the same procedure that we did for SO_3, except that in the point group T_d, one can not separate the representations into parallel and perpendicular components. This is because the three-fold symmetry of the bond axis requires the orthogonal vectors to be treated as an inseparable pair.



Example, the σ and π bonding in ClO_4^-.

The analysis of how the 8 vectors are affected by the symmetry operations gives:

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d
Γ_π	8	-1	0	0	0

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

The irreducible representation for the π bonding is $(E + T_1 + T_2)$, which corresponds to the $d_{x^2-y^2}$ and d_{xy} pair for E and either the (p_x, p_y, p_z) set or the (d_{xy}, d_{xz}, d_{yz}) set for T_2, since T_1 does not correspond to any of the orbitals that might be involved in bonding. Because the (p_x, p_y, p_z) set has already been used in the σ bonding, only the (d_{xy}, d_{xz}, d_{yz}) set may be used for π bonding.