Part II: Symmetry Operations and Point Groups

C734b

Definitions

1.- symmetry operations: leave a set of objects in **indistinguishable** configurations said to be equivalent

-The identity operator, E is the "do nothing" operator. Therefore, its final configuration is not distinguishable from the initial one, but **identical** with it.

2.- symmetry element: a geometrical entity (line, plane or point) with respect to which one or more symmetry operations may be carried out.

Four kinds of symmetry elements for molecular symmetry

1.) Plane operation = reflection in the plane

2.) Centre of symmetry or inversion centre:
operation = inversion of all atoms through the centre

3.) Proper axis operation = one or more rotations about the axis

4.) Improper axis operation = one or more of the sequence rotation about the axis followed by reflection in a plane perpendicular ($\perp$) to the rotation axis.

1. Symmetry Plane and Reflection

A plane must pass through a body, not be outside.

Symbol = σ. The same symbol is used for the operation of reflecting through a plane

σ_m as an operation means "carry out the reflection in a plane normal to m".

$\therefore$ Take a point $\{e_1, e_2, e_3\}$ along $(\hat{x}, \hat{y}, \hat{z})$

$\sigma_x\{e_1, e_2, e_3\} = \{-e_1, e_2, e_3\} \equiv \{\bar{e}_1, e_2, e_3\}$

Often the plane itself is specified rather than the normal.

$\Longrightarrow$ $\sigma_x = \sigma_{yz}$ means "reflect in a plane containing the y- and z-, usually called the yz olane

-atoms lying in a plane is a special case since reflection through a plane doesn't move the atoms.
Consequently all planar molecules have at least one plane of symmetry $\equiv$ molecular plane

Note: σ produces an equivalent configuration.

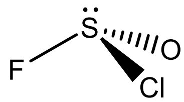
$\sigma^2 = \sigma\sigma$ produces an identical configuration with the original.

$\therefore$ $\sigma^2 = E$

$\therefore$ $\sigma^n = E$ for n even; n = 2, 4, 6,…

$\sigma^n = \sigma$ for n odd; n = 3, 5, 7,…

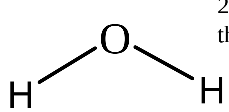
Some molecules have no σ-planes:



Linear molecules have an infinite number of planes containing the bond axis.

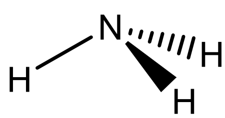
Many molecules have a number of planes which lie somewhere between these two extremes:

Example: H_2O



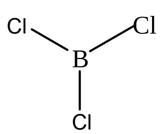
2 planes; 1 molecular plane + the other bisecting the H-O-H group

Example: NH_3



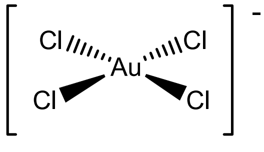
3 planes containing on N-H bond and bisecting opposite HNH group

Example: BCl_3



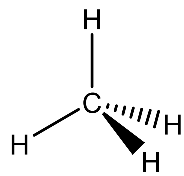
4 planes; I molecular plane + 3 containing a B-Cl bond and bisecting the opposite Cl-B-Cl group

Example: $[AuCl_4]^-$ square planar

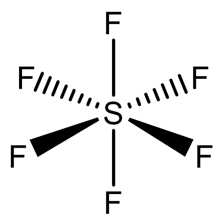


5 planes; 1 molecular plane + 4 planes; 2 containing Cl-Au-Cl + 2 bisecting the Cl-Au-Cl groups.

Tetrahedral molecules like CH_4 have 6 planes.



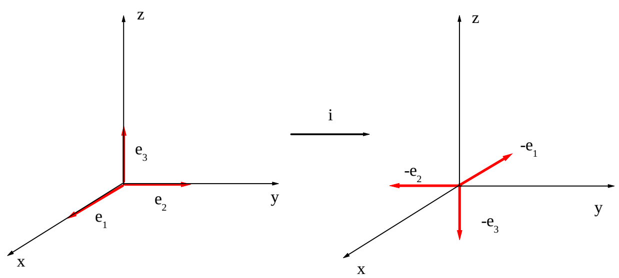
Octahedral molecules like SF_6 have 9 planes in total



2.) Inversion Centre

-Symbol = i

- operation on a point $\{e_1, e_2, e_3\}$ $i\{e_1, e_2, e_3\} = \{-e_1, -e_2, -e_3\}$



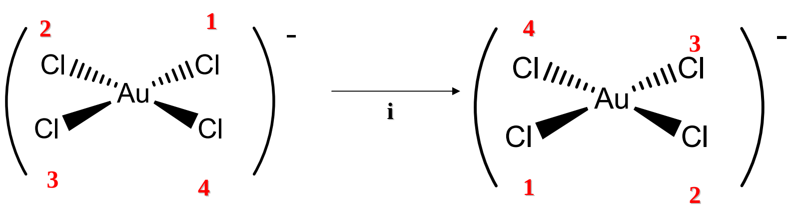
-If an atom exists at the inversion centre it is the only atom which will not move upon inversion.

-All other atoms occur in pairs which are "twins". This means no inversion centre for molecules containing an odd number of more than one species of atoms.

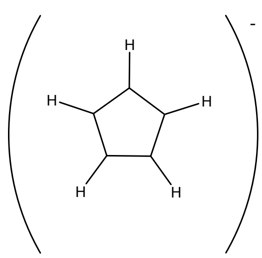
$$i^2 = ii = E$$

$$\Rightarrow \quad i^n = E \quad n \text{ even}$$
$$i^n = i \quad n \text{ odd}$$

Example:



but



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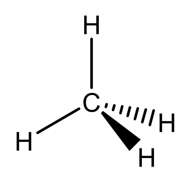
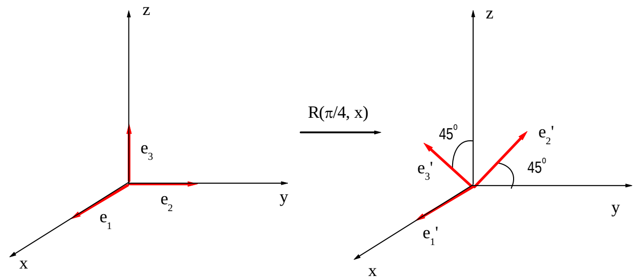


have no inversion centre even though in the methane case the number of Hs is even

3. Proper Axes and Proper Rotations

- A proper rotation or simply rotation is effected by an operator R(Φ,n) which means "carry out a rotation with respect to a fixed axis through an angle Φ described by some unit vector n".

For example: $R(\pi/4, x)\{e_1, e_2, e_3\} = \{e_1', e_2', e_3'\}$



Take the following as the convention:
a rotation is positive if looking down axis of rotation the rotation appears to be counterclockwise.

More common symbol for rotation operator is C_n where n is the order of the axis.

$\Longrightarrow$ C_n means "carry out a rotation through an angle of $\Phi = 2\pi/n$"

$\therefore$ $R(\pi/4) \equiv C_8$ $\quad$ $R(\pi/2) = C_4$ $\quad$ $R(\pi) = C_2$ $\quad$ etc.

C_2 is also called a binary rotation.

Product of symmetry operators means: “carry out the operation successively beginning with the one on the right”.

$\therefore$ $C_4C_4 = C_4^2 = C_2 = R(\pi, n)$

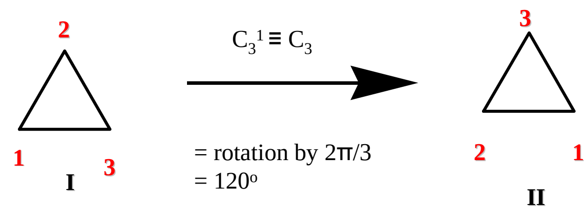
$(C_n)^k = C_n^{\,k} = R(\Phi, n)$; $\Phi = 2\pi k/n$

$\therefore$ $C_n^{-k} = R(-\Phi, n)$; $\Phi = -2\pi k/n$

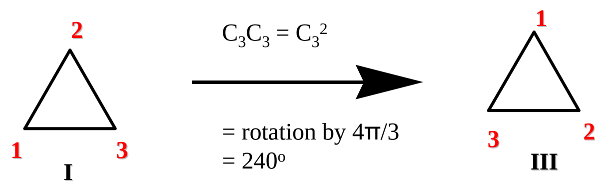
$C_n^{\,k}C_n^{-k} = C_n^{\,k+(-k)} = C_n^{\,0} \equiv E$

$\Rightarrow$ C_n^{-k} is the inverse of $C_n^{\,k}$

Example:



C_3 axis is perpendicular to the plane of the equilateral triangle.



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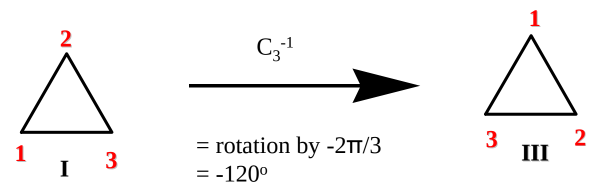
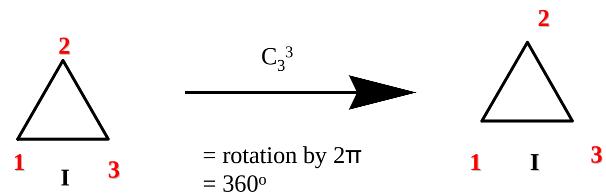
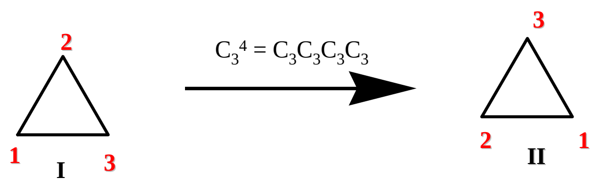


∴ $C_3^2 = C_3^{-1}$



∴ $C_3^3 = E$

What about C_3^4?



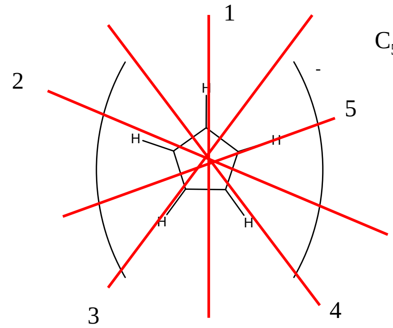
∴ $C_3^4 = C_3$

⟹ only C_3, C_3^2, E are separate and distinct operations

Similar arguments can be applied to any proper axis of order n

Example: **C_6:** C_6;
$C_6^{2} \equiv C_3$
$C_6^{3} \equiv C_2$
$C_6^{4} \equiv C_6^{-2} \equiv C_3^{-1}$
$C_6^{5} \equiv C_6^{-1}$
$C_6^{6} \equiv E$

Note: for C_n n odd the existence of one C_2 axis perpendicular to or σ containing C_n implies n-1 more separate (that is, distinct) C_2 axes or σ planes

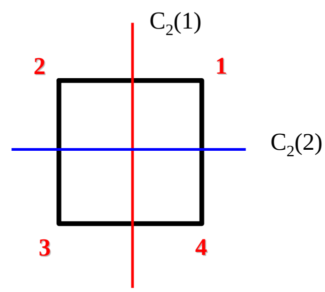


C_5 axis coming out of the page

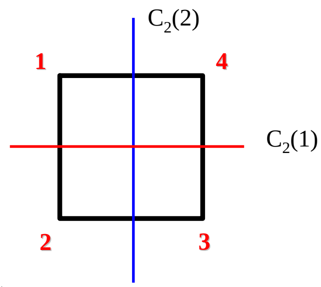
* When > one symmetry axis exist, the one with the largest value of n
≡ PRINCIPLE AXIS

Things are a bit more subtle for C_n, n even

Take for example C_4 axis:



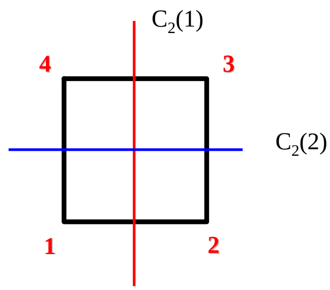
C_4 →



i.e.; $C_2(1) \rightarrow C_2(2)$; $C_2(2) \rightarrow C_2(1)$

C_4 →

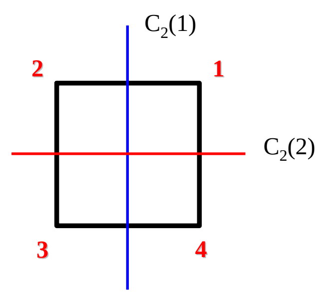
Total = $C_4^2 = C_2$



i.e.; $C_2(1) \rightarrow C_2(1)$; $C_2(2) \rightarrow C_2(2)$

C_4 →

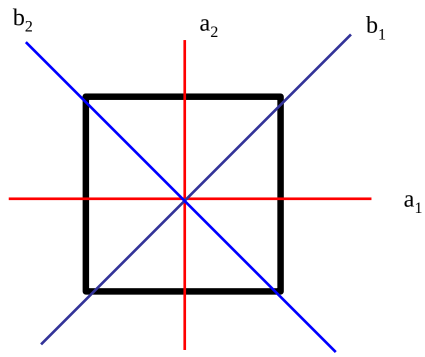
Total $C_4^3 = C_4^{-1}$



i.e.; $C_2(1) \rightarrow C_2(2)$; $C_2(2) \rightarrow C_2(1)$

Conclusion: $C_2(1)$ and $C_2(2)$ are not distinct

Conclusion: a C_n axis, n even, may be accompanied by n/2 sets of 2 C_2 axes



4 C_2 axes: (a_1, a_2) and (b_1, b_2).

C_n rotational groups are Abelian

4. Improper Axes and Improper Rotations

Accurate definitions:

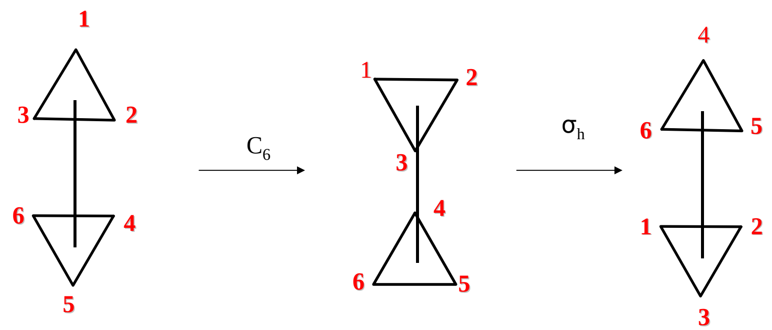
Improper rotation is a proper rotation $R(\Phi, n)$ followed by inversion $\equiv iR(\Phi, n)$

Rotoreflection is a proper reflection $R(\Phi, n)$ followed by reflection
in a plane normal to the axis of rotation, σ_h

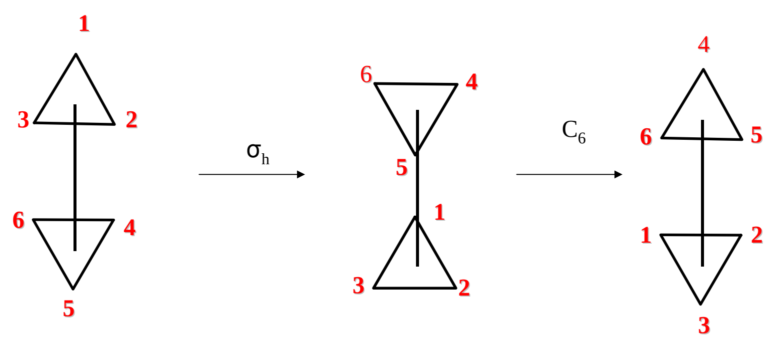
Called $S_n = \sigma_h R(\Phi, n)$ $\Phi = 2\pi/n$

Cotton and many other books for chemists call S_n an improper rotation, and we will too.

Example: staggered ethane (C_3 axis but no C_6 axis)



Note:



$\Rightarrow$ $S_n = \sigma_h C_n$ or $C_n \sigma_h$ The order is irrelevant.

Clear if C_n exists and σ_h exists S_n must exist.
HOWEVER: S_n can exist if C_n and σ_h do not.
The example above for staggered ethane is such a case.

The element S_n generates operations $S_n, S_n^2, S_n^3, \ldots$

However the set of operations generated are different depending if n is even or odd.

n even

$\{S_n, S_n^2, S_n^3, \ldots, S_n^n\} \equiv \{\sigma_h C_n, \sigma_h^2 C_n^2, \sigma_h^3 C_n^3, \ldots, \sigma_h^n C_n^n\}$

But $\sigma_h^n = E$ and $C_n^n = E$ $\Longrightarrow$ $S_n^n = E$

and therefore: $S_n^{n+1} = S_n$, $S_n^{n+2} = S_n^2$, etc, and $S_n^m = C_n^m$ if m is even.

Therefore for S_6, operations are:

S_6
$S_6^2 \equiv C_6^2 \equiv C_3$
$S_6^3 \equiv S_2 \equiv i$
$S_6^4 \equiv C_6^4 \equiv C_3^2$
$S_6^5 \equiv S_6^{-1}$
$S_6^6 \equiv E$

Conclusion: the existence of an S_n axis requires the existence of a $C_{n/2}$ axis.

S_n groups, n even, are Abelian.

n odd

Consider $S_n^n = \sigma_h^n C_n^n = \sigma_h E = \sigma_h$

$\Rightarrow$ σ_h must exist as an element in its own right, as must C_n.

Consider as an example an S_5 axis. This generates the following operations:

$S_5^1 = \sigma_h C_5$

$S_5^2 = \sigma_h^2 C_5^2 \equiv C_5^2$

$S_5^3 = \sigma_h^3 C_5^3 \equiv \sigma_h C_5^3$

$S_5^4 = \sigma_h^4 C_5^4 \equiv C_5^4$

$S_5^5 = \sigma_h^5 C_5^5 \equiv \sigma_h$

$S_5^6 = \sigma_h^6 C_5^6 \equiv C_5$

$S_5^7 = \sigma_h^7 C_5^7 \equiv \sigma_h C_5^2$

$S_5^8 = \sigma_h^8 C_5^8 \equiv C_5^3$

$S_5^9 = \sigma_h^9 C_5^9 \equiv \sigma_h C_5^4$

$S_5^{10} = \sigma_h^{10} C_5^{10} \equiv E$

It's easy to show that $S_5^{11} = S_5$ $\therefore$ The element S_n, n odd, generates 2n distinct operations

S_n groups, n odd, are not Abelian

Symmetry elements and point-symmetry operations

Symmetry element	Notation for symmetry element Schönflies	International	Corresponding operation	Symmetry operator
any arbitrary axis	C_1	1	identity [a]	$E = R(0\ \mathbf{n})$
centre	I	$\bar{1}$	inversion	I
proper axis	C_n	n	proper rotation	$R(\phi\ \mathbf{n}) = C_n$ or $C_{n\mathbf{n}}$ [b]
improper axis	$I C_n$	$\bar{n}$	rotation, then inversion	$I R(\phi\ \mathbf{n}) = I C_n$
plane	σ_m	m	reflection in a plane normal to **m**	σ_m
rotoreflection axis	S_n	$\tilde{n}$	rotation through $\phi = 2\pi/n$ followed by reflection in a plane normal to the axis of rotation	$S(\phi\ \mathbf{n}) = S_n$ or $S_{n\mathbf{n}}$

a) A body or molecule for which the only symmetry operator is E has no symmetry at all. However, E is equivalent to a rotation through an angle $\Phi = 0$ about an arbitrary axis. It is not customary to include C_1 in a list of symmetry elements except when the only symmetry operator is the identity E.

b) $\Phi = 2\pi/n$; n is a unit vector along the axis of rotation.

Products of Symmetry Operators

-Symmetry operators are conveniently represented by means of a **stereogram** or **stereographic projection**.

Start with a circle which is a projection of the unit sphere in configuration space (usually the xy plane). Take x to be parallel with the top of the page.

A point above the plane (+z-direction) is represented by a **small filled** circle.

A point below the plane (-z-direction) is represented by a **larger open** circle.

A general point transformed by a point symmetry operation is marked by an E.

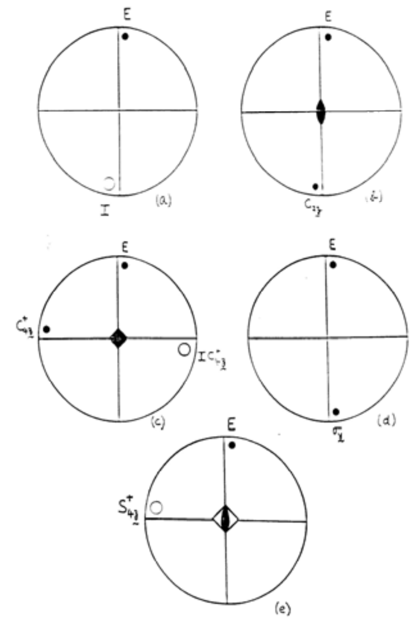
Symbols used to show an n-fold proper axis. For improper axes the same geometrical symbols are used but they are not filled in. Also shown are the corresponding rotation operator and angle of rotation ϕ .

n =	2	3	4	5	6	etc.

	digon	triangle	rhombus	pentagon	hexagon	......
operator :	C_2	C_3	C_4	C_5	C_6	......
$\phi = 2\pi/n$	π	$2\pi/3$	$\pi/2$	$2\pi/5$	$\pi/3$	......

For improper axes the same geometrical symbols are used but are not filled in.

Stereograms showing examples of the point symmetry operators listed in Table 2.1-1. (a) I (b) C_{2z} (c) $I C_{4z}^{+}$ (d) σ_y (e) S_{4z}^{+}.



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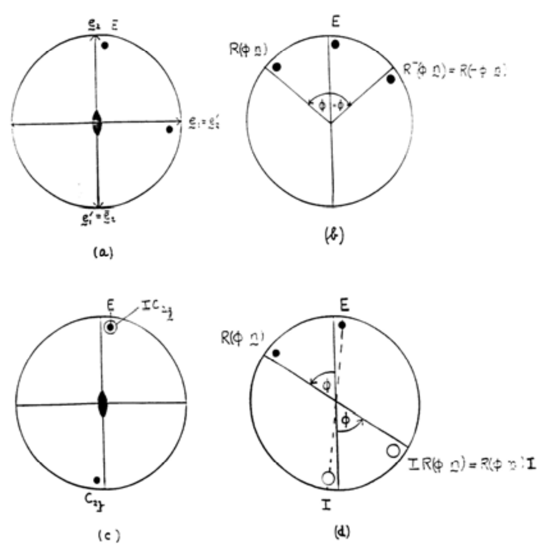
A few more stereograms

(a) The effect of $R^{-}(\pi/2\ \mathbf{z})$ on $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$. (b) A rotation $\mathbf{R}(-\phi\ \mathbf{n})$ means a *clockwise* rotation through an angle of magnitude ϕ about $\mathbf{n}$, that is $R^{-}(\phi\ \mathbf{n})$. (c) Proof that $I\,C_{2z} = \sigma_z$. (d) The location of the coordinate axes is arbitrary; here the plane of the stereogram is normal to $\mathbf{n}$.



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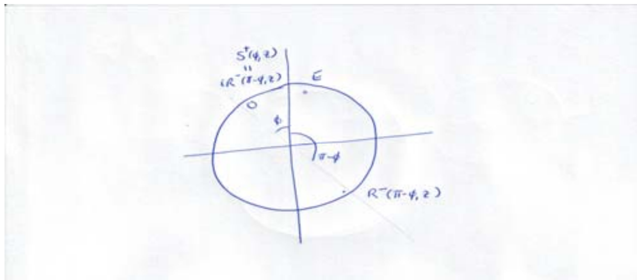
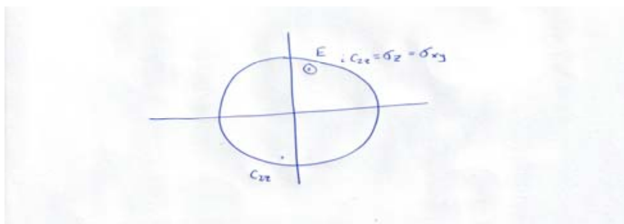
Example: Show that $S^{+}(\Phi,z) = iR^{-}(\pi-\Phi, z)$



Example: Prove $iC_{2z} = \sigma_z$



The complete set of point-symmetry operators including E that are generated from the operators $\{R_1, R_2, \ldots\}$ that are associated with the symmetry elements $\{C_1, i, C_n, S_n, \sigma\}$ by forming all possible products like R_2R_1 satisfy the necessary group properties:

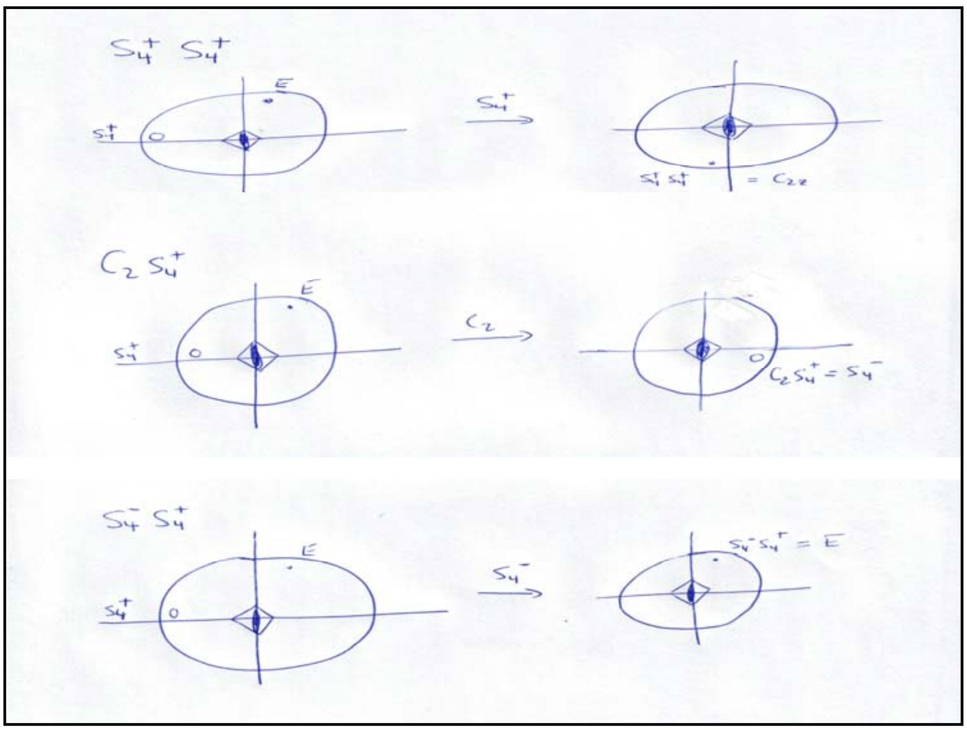
1) Closure
2) Contains E
3) Satisfies associativity
4) Each element has an inverse

Such groups of point symmetry operators are called **Point Groups**

Example: construct a multiplication table for the S_4 point group having the set of elements: $S_4 = \{E, S_4^+, S_4^2 = C_2, S_4^-\}$

S_4	E	S_4^+	C_2	S_4^-
E	E	S_4^+	C_2	S_4^-
S_4^+	S_4^+			
C_2	C_2			
S_4^-	S_4^-			

Complete row 2 using stereograms: $S_4^+S_4^+$, $C_2S_4^+$, $S_4^-S_4^+$ (column x row)



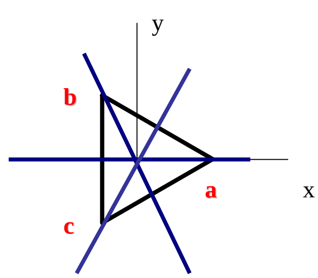
Complete Table

S_4	E	S_4^+	C_2	S_4^-
E	E	S_4^+	C_2	S_4^-
S_4^+	S_4^+	C_2	S_4^-	E
C_2	C_2	S_4^-	E	S_4^+
S_4^-	S_4^-	E	S_4^+	C_2

Another example: an equilateral triangle

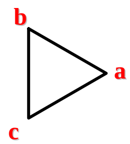
Choose C_3 axis along z

The set of distinct operators are G = (E, C_3^+, C_3^-, σ_A, σ_B, σ_C}



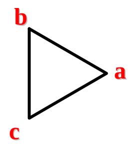
Blue lines denote symmetry planes.

Let Ψ_1 =



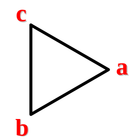
∴

$E\Psi_1$ =



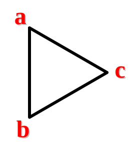
$= \Psi_1$

$\sigma_A\Psi_1$ =



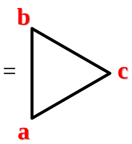
$= \Psi_4$

$C_3^+\Psi_1$ =



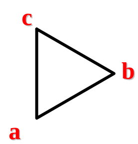
$= \Psi_2$

$\sigma_B\Psi_1$ =



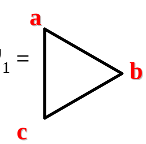
$= \Psi_5$

$C_3^-\Psi_1$=



$= \Psi_3$

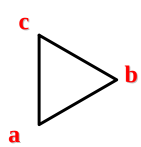
$\sigma_C\Psi_1$ =



$= \Psi_6$

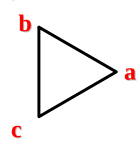
Typical binary products:

$C_3^+C_3^+\Psi_1 \;=\; C_3^+\Psi_2$



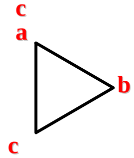
$\equiv C_3^-\Psi_1 \Rightarrow C_3^+C_3^+ = C_3^-$

$C_3^+C_3^-\Psi_1 \;= C_3^+\Psi_3$



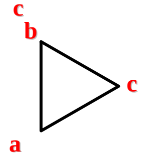
$\equiv E\Psi_1 \Rightarrow C_3^+C_3^- = E$

$C_3^+\sigma_A\Psi_1 \;= C_3^+\Psi_4$



$\equiv \sigma_C\Psi_1 \Rightarrow C_3^+\sigma_A = \sigma_C$

$\sigma_A C_3^+\Psi_1 \;=\; C_3^+\Psi_2$



$\equiv \sigma_B\Psi_1 \Rightarrow \sigma_A C_3^+ = \sigma_B$

etc.

Note: i) σ_A and C_3^+ do not commute   ii) Labels move, not the symmetry elements

Can complete these binary products to construct the multiplication table for G

Multiplication Table for the set G = {E, C_3^+, C_3^-, σ_A, σ_B, σ_C}

G	E	C_3^+	C_3^-	σ_A	σ_B	σ_C
E	E	C_3^+	C_3^-	σ_A	σ_B	σ_C
C_3^+	C_3^+	C_3^-	E	σ_C	σ_A	σ_B
C_3^-	C_3^-	E	C_3^+	σ_B	σ_C	σ_A
σ_A	σ_A	σ_B	σ_C	E	C_3^+	C_3^-
σ_B	σ_B	σ_C	σ_A	C_3^-	E	C_3^+
σ_C	σ_C	σ_A	σ_B	C_3^+	C_3^-	E

Symmetry Point Groups (Schönflies notation)

One symmetry element

1.) No symmetry: C_1 {E exists} order = 1

2.) sole element is a plane: C_s {σ, σ^2 = E} order = 2

3.) sole element is an inversion centre: C_i {i, i^2 = E} order = 2

4.) Only element is a proper axis of order n: C_n

{C_n^1, C_n^2, …, C_n^n = E} order = n These are Abelian cyclic groups.

5.) Only element is an improper axis of order n.

Two cases:

a) n even $\{E, S_n, C_{n/2}, S_n^3, \ldots, S_n^{n-1}$ order = n

Note: S_2 = i. $\Longrightarrow$ $S_2 = C_i$

Symbol: S_n

b) n odd order = 2n including σ_h and operations generated by C_n axis.

Symbol: C_{nh}

Two or more symmetry elements

Need to consider (1) the addition of different symmetry elements to a C_n axis and
(2) addition of symmetry planes to a C_n axis and nC_2' axes perpendicular to it.

To define symbols, consider the principle axis to be **vertical**.

$\Longrightarrow$ Symmetry plane perpendicular to C_n will be a horizontal plane σ_h

There are 2 types of vertical planes (containing C_n)

If all are equivalent $\Longrightarrow$ σ_v (v ≡ vertical)

There may be 2different sets (or classes)

one set = σ_v; the other set = σ_d (d = dihedral)

∴ adding σ_h to $C_n \rightarrow C_{nh}$ ($\equiv S_n$; n odd)

adding σ_v to C_n:
n odd $\rightarrow n\sigma_v$ planes
n even $\rightarrow n/2\ \sigma_v$ planes and $n/2\ \sigma_d$ planes

See previous discussion regarding C_4 axis.

Note: the σ_d set bisect the dihedral angle between members of the σ_v set.

Distinction is arbitrary: $\Rightarrow$ C_{nv} point group.

Next: add σ_h to C_n with n C_2' axes

$\Rightarrow$ D_{nh} point group (D for dihedral groups)

Note: $\sigma_h\sigma_v = C_2$. Therefore, need only find existence of C_n, σ_h, and σ_v's to establish D_{nh} group.

By convention however, simultaneous existence of C_n, n C_2's, and σ_h used as criterion.

Next: add σ_d's to C_n and n C_2' axes.

$\sigma_d \equiv$ vertical planes which bisect the angles between adjacent vertical planes

$\Rightarrow$ D_{nd} point group

Special Cases

1.) Linear molecules: each molecule is its own axis of symmetry. order = ∞

no $\sigma_{h:}$ $\Rightarrow$ $C_{\infty v}$ point group

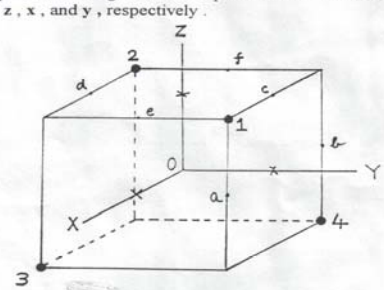
σ_h exists: $\Rightarrow$ $D_{\infty h}$ point group

2.) Symmetries with > 1 high-order axis

a) tetrahedron

Elements = $\{E, 8C_3, 3C_2, 6S_4, 6\sigma_d\}$ $\Rightarrow$ T_d point group

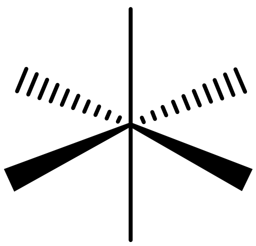
Alternate vertices of the cube (marked 1 , 2 , 3 , and 4) are the apices of a regular tetrahedron. Small crosses show where the X , Y , and Z axes intersect the cube faces. a , b ; c , d ; and e , f mark the mid-points of pairs of opposite cube edges that lie in planes that bisect the cube and are normal to z , x , and y , respectively .

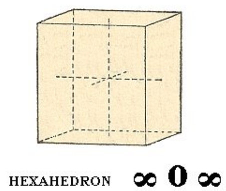


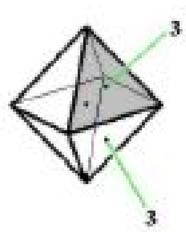
b) Octahedron (Cubic Group)

Group elements: $\{E, 8C_3, 6C_2, 6C_4, 3C_2\ (= C_4^2), i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d\}$

$\Rightarrow$ O_h point group



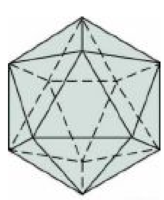




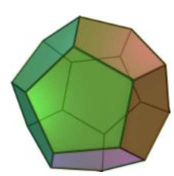
c) Dodecahedron and icosahedron

Group elements: $\{E, 12C_5, 12C_5^2, 20C_3, 15C_2, i, 12S_{10}, 12S_{10}^3, 20S_6, 15\sigma\}$

$\Rightarrow$ I_h point group (or Y point group)

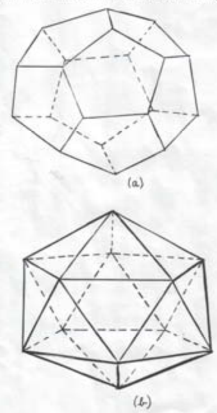


icosahedron



dodecahedron

The dodecahedron and the icosahedron are two of the five Platonic solids (regular polyhedra), the others being the tetrahedron, cube and octahedron. The dodecahedron (a) has twelve regular pentagonal faces with three pentagonal faces meeting at a point. The icosahedron (b) has twenty equilateral triangular faces, with five of these meeting at a point.



There are 4 other point groups: T, T_h, O, I which are not as important for molecules.

A systematic method for identifying point groups of any molecule