Molecular Orbital Theory

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LB405

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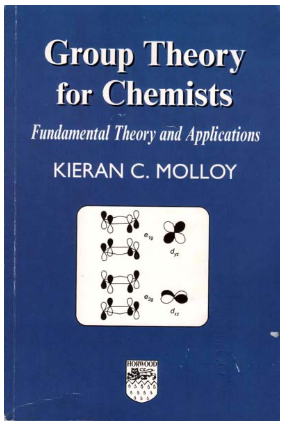
Resources

Web and Social Media Resources:

- information on my web-site under "Teaching"
- copies of notes and slides
- model answers to in-class activities, self-study/test preparation questions
- optional background support for beginners, optional extras for experts
- files for visualising MOs
- links to interesting people, web-sites, and research papers



Reading Resources:

- Kieran C. Molloy, Group Theory for Chemists, Harwood Publishing
- Another useful text is: Alan Vincent, Molecular Symmetry and Group Theory, Second edition, 2001, John Wiley & Sons Ltd, Chichester.
- If you want to know more contact me and I will be happy to recommend more advanced texts for you to look at.

What is this Course About?

- Symmetry is a key part of chemistry
  - underpins the shapes and structures of molecule
  - underpins bonding
  - underpins reactivity
  - underpins most spectroscopies
- You will learn how to describe and use symmetry
- You will learn how to construct Molecular Orbital (MO) diagrams
- You will learn how to use and interpret MO diagrams
- For the future: we use MO theory to understand and predict the bonding, structure and reactivity of molecules

Introducing Symmetry

Introduction

- we will describe what symmetry is
- develop a notation for being able to describe the symmetry of molecules
- we will learn about the symmetry operations, elements and operators
- focus on rotation, reflection and inversion
- we expand on a number of concepts related to rotations and improper rotations including coincident elements and equivalent operations
- we will learn about the point group of a molecule, a notation which summarises the symmetry of a molecule, and how to work out the point group of any specific molecule

Symmetry is Important!

- in determining the equivalent H or C atoms in an NMR spectrum
- in deciding if a molecule is chiral
- in the labelling of atomic orbitals
- in distinguishing between σ and π orbitals in organic chemistry
- in octahedral transition-metal complexes
- in determining isomers: cis/trans, fac/mer, staggered/eclipsed, chair/boat
- in organic stereo-electronic effects
- for the MO diagram and the photoelectron spectrum
- in determining the HOMO and LUMO and reactivity of a species
- in labelling electronic excitations and nuclear vibrations
- in determining the IR and Raman spectrum
- in determining features like the dipole moment and UV spectrum.

What is Symmetry? (starting description)

- symmetry occurs when you can move/rotate/reflect an object and the *initial and final states are indistinguishable*, ie they can be superimposed on each other, they map onto each other
- symmetry occurs all around us in the everyday world, **Figure 1**. As humans we are very good at finding symmetry, and we tend to find things that exhibit symmetry beautiful
- often in nature the symmetry is not exact, but using mathematics we can treat exact symmetry

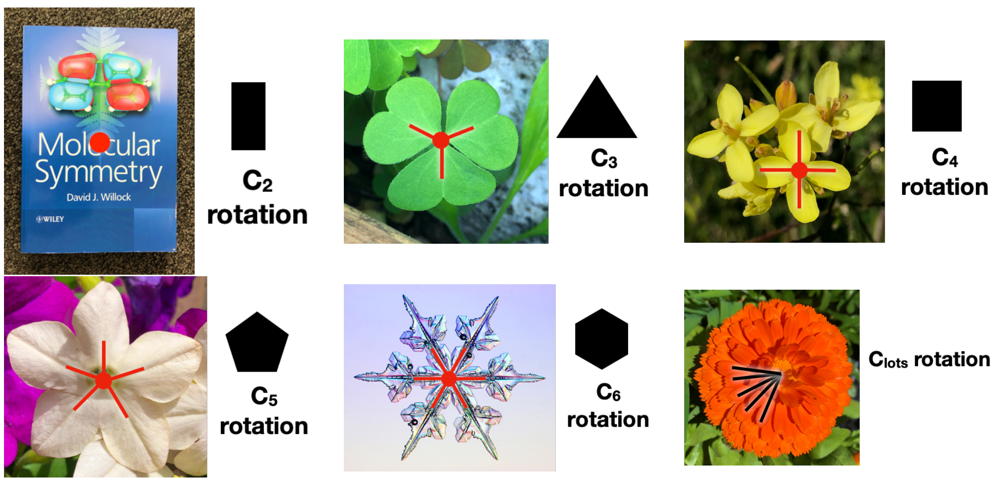


Figure 1 rotational symmetry in the natural world[1]

- **symmetry operations** involve the *physical act or action* of moving a molecule, they leave the initial and final states of the molecule indistinguishable with respect to the type of nuclei.
- each symmetry operation has an associated **symmetry element**, symmetry elements are the *geometric object* about which the operation is executed, they are an axis, plane or point
- every molecule (and actually every object) has a special operation called E, think of E for "existing"

Rotations

- introducing rotations
  - a C_2 rotation rotates a molecule (or any other object) by 180º, **Figure 2**
  - in **Figure 2** the water molecule *A is mapped onto B*, both A and B look the same, A and B are related by symmetry
  - it is only when we label a particular H atom in the water molecule we realise that it has moved
  - the C_2 rotation operation occurs around the C_2 rotation axis

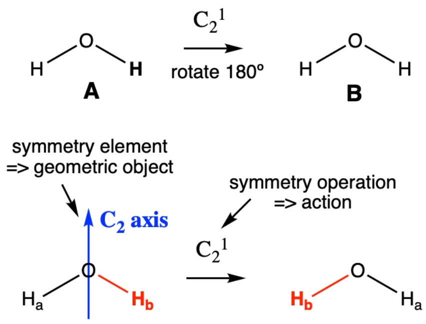
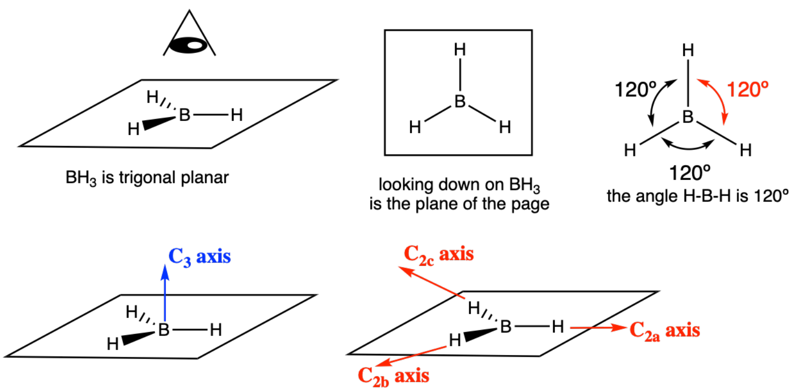


Figure 2 a simple (C_2) rotation

- there are many possible rotation operations
  - C_2 rotation rotates a molecule (or any other object) by 180º
  - C_3 rotation rotates a molecule by 120º
  - C_4 rotation rotates a molecule by 90º
  - and C_5, C_6, C_7 .... all the way up to C_∞
  - C_∞ is a special operation, we will come back to this a little further on
  - definition: an n-fold rotation (C_n) is a rotation of (360/n)º around an n-fold rotation axis
- molecules can have multiple different rotation axes
  - molecules can have more than one rotation axis, **Figure 3**
  - for example planar BH_3 has 4 rotation axes, 1 C_3 axis and $3C_2$ axes
  - different axes of the same type have subscripts a, b, c and so on



[1] snowflake image used with permission from Prof. Libbrech, Caltech
https://www.its.caltech.edu/~atomic/

Figure 3 BH_3 has more than one rotation axis

important

- the highest rotation axis is always the **principle** rotation axis
  - thus for H_2O the principle axis is the C_2 axis (the only axis!)
  - for BH_3 the principle axis is the C_3 axis (3 is larger than 2)

In-Class Activity P1

- What is the principle axis for PCl_5?

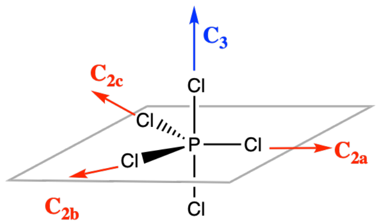


Figure 4 PCl_5 rotation axes

Cartesian Coordinate System

- when defining the symmetry elements of a molecule we always use a cartesian coordinate system, **Figure 5**
  - normally the origin of the cartesian coordinates is taken as the central atom or the center of the molecule
  - however often this is too messy and we place the unit vector definition off to the side, the origin is still understood to be at the center of the molecule
  - the *z-axis is always along the principle axis*
  - always *label the axes* that lie on a cartesian axis with the axis definition

important

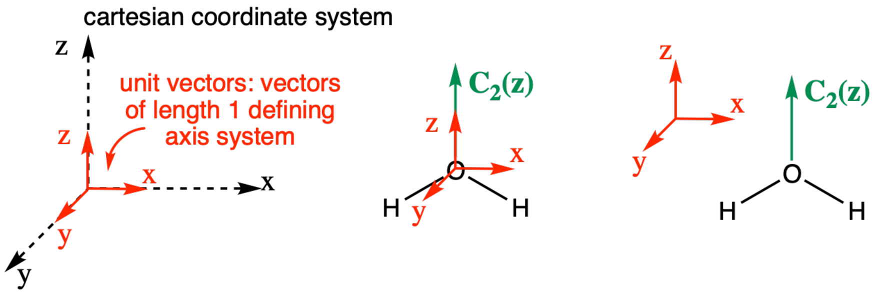


Figure 5 labelling rotation axes using cartesian coordinate system

  - the orientation of the axial system will depend on how you draw the molecule, **Figure 6**, make sure you orient the axis definition properly!
  - if an axis does not lie on a cartesian axis then there is no additional label (for example C_{2b} and C_{2c} have no axis label in **Figure 6**)
  - if the cartesian axes label does not differentiate the symmetry elements then use another notation (primes or a, b etc) to identify different axes.

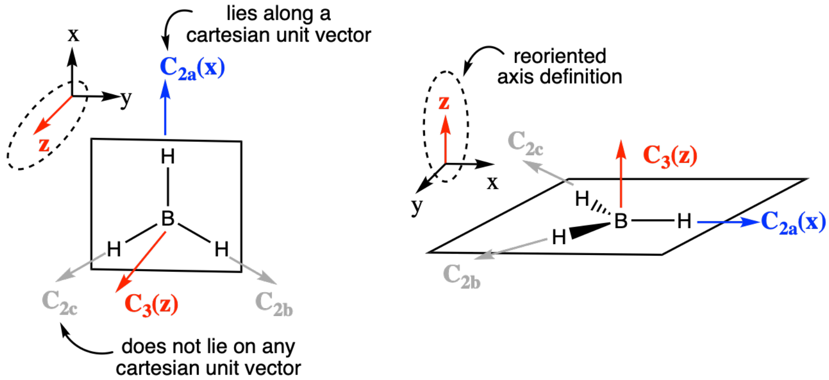


Figure 6 labelling different representations of the molecule

In-Class Activity P2

- Add the cartesian labels to the relevant axes shown on benzene in **Figure 7**.

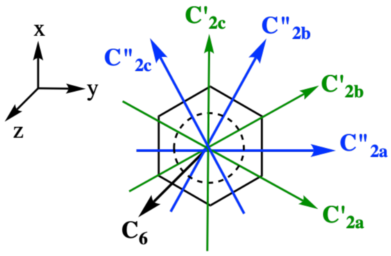


Figure 7 benzene rotation axes

Sequential Rotation Operations

- when we carry out sequential rotations around an axis, we denote each sequential rotation with a superscript
  - $C_3^1 \rightarrow C_3^2 \rightarrow C_3^3$
  - for example rotating 120º twice is a C_3^2 operation, **Figure 8**
  - the direction of rotation does not matter as long as we are consistent with all rotations, ie make all rotations clockwise or counter-clockwise

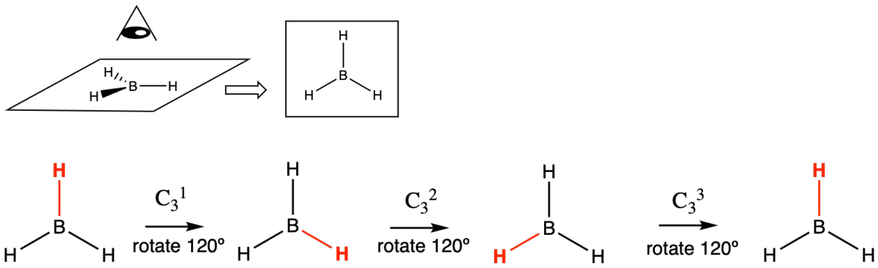


Figure 8 C_3 rotations

- rotation operations around an axis form a **group**
  - for example the C_3 group contains 3 operations C_3^1 , C_3^2 and C_3^3
  - the C_4 group contains 4 operations C_4^1, C_4^2, C_4^3 and C_4^4
  - <u>definition</u>: a C_n group has n members
  - notice that if we rotate a C_n axis n times we come back to the starting structure!
  - thus C_3^3=E and C_4^4=E and so on (where E is the existence operation)
  - there is a whole branch of important mathematics called **group theory** groups are very important for mathematics, philosophy, physics and chemistry and if you are interested there is a lot more to discover

In-Class Activity P3

- on a molecule of $[PtCl_4]^{2-}$ (**Figure 9**) draw a diagram like that in the bottom of **Figure 8** above for the sequential rotations

  $C_4^1 \rightarrow C_4^2 \rightarrow C_4^3 \rightarrow C_4^4$

  - the rotation angle is 360º/4=90º.

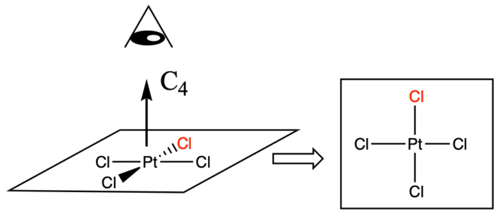


Figure 9 $[PtCl_4]^{2-}$

Reflections

- we can reflect an object in a mirror plane
  - the symmetry operation is **reflection**
  - the symmetry element is the **mirror plane**
- mirror planes are very common in the wider world
  - the alpaca has reflection symmetry, but it is not exact, in the way a geometric shape will reflect exactly onto itself
  - the leaf below has mirror symmetry for the overall shape, but the veins do not have mirror symmetry

Reflection mirror plane

Figure 10 reflection symmetry in the natural world

- in chemistry we define 3 different types of mirror plane:
  - σ_v is a *vertical* mirror plane
  - σ_h is a *horizontal* mirror plane
  - σ_d is a *bisecting* mirror plane
- σ_v and σ_d reflection planes often come in pairs and with C_2 axes
- identify when a mirror plane lies on a cartesian plane
- vertical mirror planes pass vertically through the rotation axis, **Figure 11**

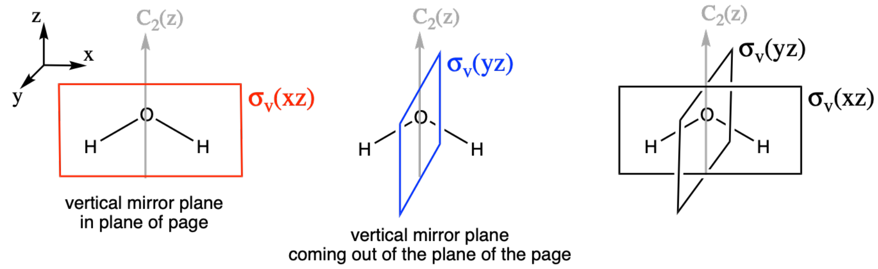


Figure 11 vertical mirror planes of water

- sometimes representing a mirror plane can be difficult and we use bold lines (solid or dashed) on a plan view, **Figure 12**

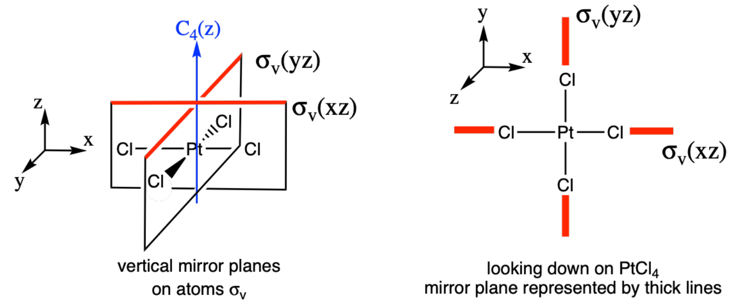


Figure 12 using bold lines to identify mirror planes

- bisecting mirror planes bisect bonds (or C_2 axes), **Figure 13**
  - you can think of "d" for disect to help remember this mirror plane

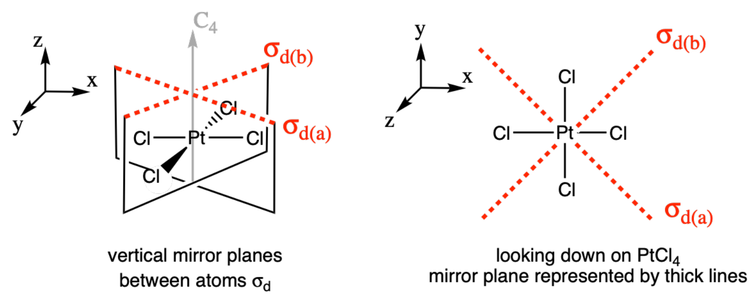


Figure 13 bisecting mirror planes

- horizontal mirror planes are *perpendicular to the principle rotation axis*, **Figure 14**

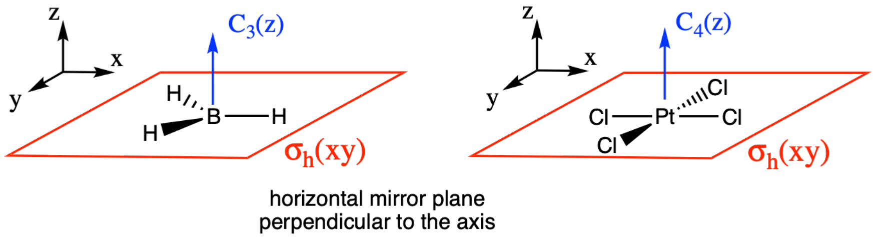


Figure 14 horizontal mirror planes

- molecules often have multiple symmetry operations, for example square planar $[PtCl_4]^{2-}$ exhibits all three types of mirror plane, **Figure 15**

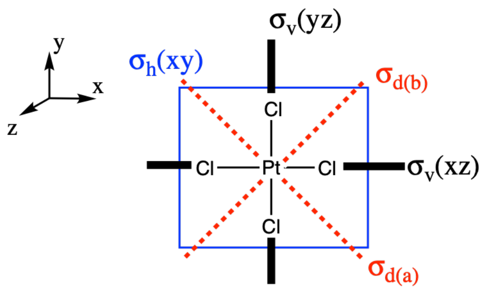


Figure 15 multiple mirror planes for one molecule

- molecules often also have **coincident symmetry operations**
  - for example every C_4 has a coincident C_2 axis (coincident=in the same place), **Figure 16**

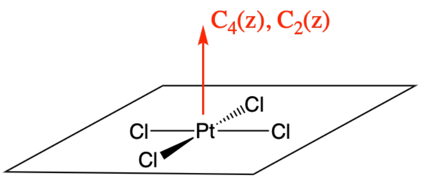


Figure 16 coincident C_4 and C_2

- molecules can have **equivalent symmetry operations**
  - **Figure 17** shows that rotating $[PtCl_4]^{2-}$ by 180º is the same is undertaking two 90º rotations, we say that the operations C_2^1 and C_4^2 are equivalent
  - from a given starting structure, equivalent operations generate the same final structure
  - for rotations the operation C_n^m with the *lower n* is preferred, hence we prefer C_2^1 over C_4^2
  - later in the workshop problems when you are asked to show (using a diagram) that two operations are equivalent, you should produce a diagram like that of **Figure 17**
  - these diagrams tell a story, make sure your story is complete by including the "conclusion" statement such as the A=B of **Figure 17**

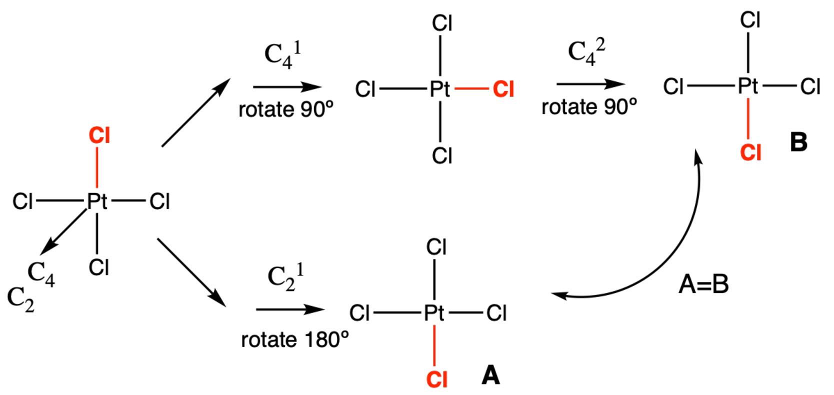


Figure 17 coincident rotation axes and equivalent operations

improper Rotation

- rotation around a n-fold *axis* (C_n) followed by reflection in a *plane* (σ_h) perpendicular to the rotation axis is an **improper rotation** (S_n).
- when evaluating the effects of improper rotations it is important (because of the reflection) to consider a point off the mirror plane, or a pAO on an atom, **Figure 18**

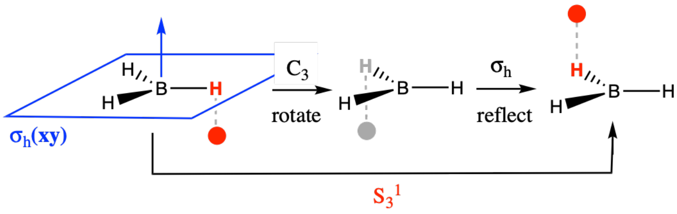


Figure 18 improper rotation

- improper rotations with an odd C_n rotation axis (ie n=3, 5) have to go around *twice* before the starting structure is regenerated, for n=odd $S_n^{2n}=E$
- for example in **Figure 19**, while it might appear that F in BF_3 maps back onto the starting configuration after S_3^3, when we consider a pAO on the F-atom we realise that the orbital is inverted after S_3^3 and in this case $S_3^3=\sigma_h$!

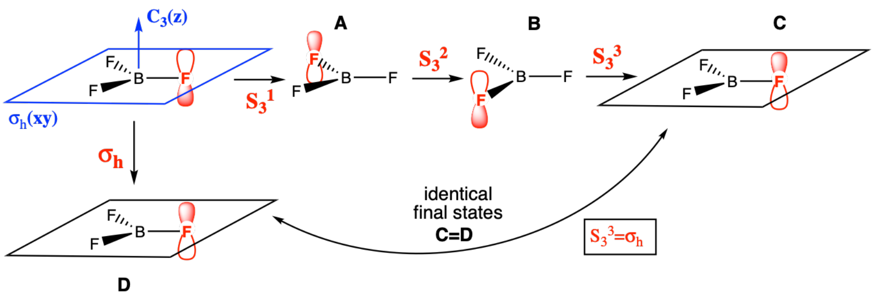


Figure 19 improper rotation

- many S_n operations are equivalent to other operations, which take priority

Inversion Operation

- inversion (i) takes a point at (x, y, z) to (-x,-y,-z) through the inversion *point* (i), **Figure 20**
- the inversion point or (inversion center) is generally in the center of a molecule, but does not need to sit "on" an atom.

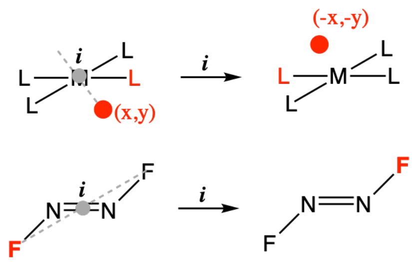
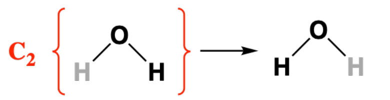


Figure 20 inversion

Symmetry Operators

$C_2[\psi(H_2O)]=\psi'(H_2O)$



$$D(C_2(z)) = \begin{pmatrix} cos(\pi) & -sin(\pi) & 0 \\ sin(\pi) & cos(\pi) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Figure 21 an operator acts on a wavefunction

- each physical symmetry operation also has an associated **mathematical operator**, which represents the physical act
- for example the C_2 operator represents the physical action of carrying out a 180º rotation
- use *brackets* when indicating an operator, these can be square or curly (your choice!) **Figure 21**
- the operator is normally represented mathematically as a matrix (for example $D(C_2)$) which allows us to write a mathematical equation for the action of the operation on a wavefunction or molecule. We will not be taking the matrix operator aspect of symmetry any further here!

Notation

- you might have noticed the same notation is used for symmetry elements, operations and operators!
- to summarise:
  - symmetry operation (physical action)
  - symmetry element (geometric object)
  - symmetry operator (mathematical operator)
- you identify weather it is an operation, element or operator by the context

important

Symmetry Groups

- the symmetry group or **point group** of a molecule is the group of symmetry operations that leave the molecule unchanged
  - there are only a set number of symmetry groups in chemistry, a few examples are C_{2v}, $D_{\infty h}$ and T_d
- start by identifying the shape of the molecule (use VSEPR theory)
- find all of the symmetry elements on the molecule
- then use a symmetry flow chart to help identify the point group, **Figure 23**
- to make things easier we are going to specifically mention O_h and T_d otherwise the flow chart gets a bit confusing, **Figure 22**
  - methane is a tetrahedral molecule, a trigonal pyramidal shape, it can also be thought of as the two diagonals of a cube
  - 6-coordinate transition metals (with all the same ligands) are octahedral, atoms on all of ±x, ±y and ±z or if atoms were positioned in the centre of each face of a cube

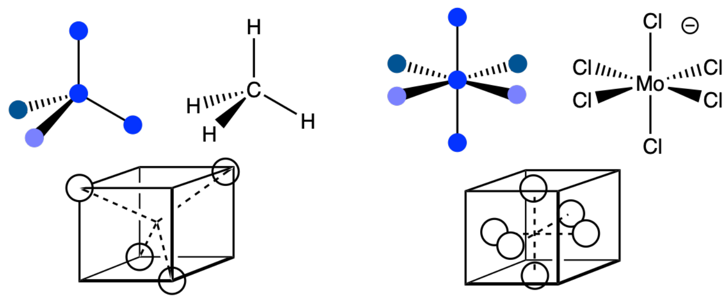


Figure 22 Tetrahedral and octahedral molecules

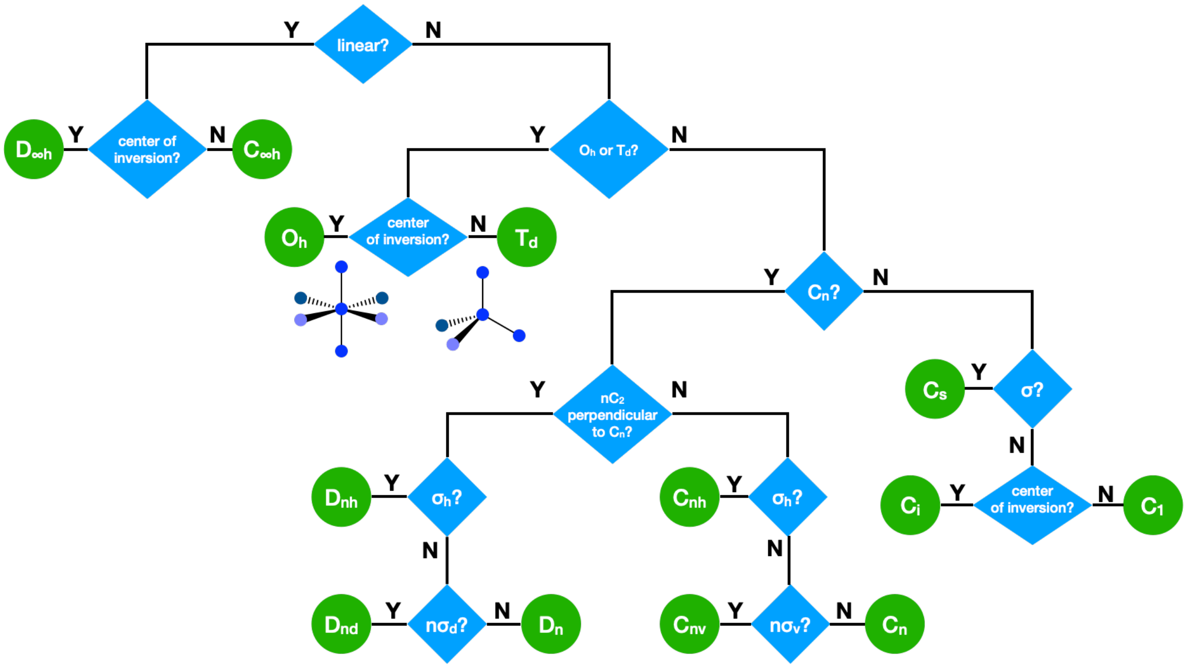


Figure 23 symmetry flow chart

see **Q4** and **Q5** for practice identifying the point group of molecules

- example: determine the point group for H_2O
  - molecular shape is planar
  - symmetry elements for water are E, C_2 and $2\sigma_v$ planes, **Figure 24**
  - then use the flow chart
    1. is the molecule linear? NO
    2. is the molecule T_d or O_h? NO
    3. is there a *principle* C_n axis? YES (n=2)
    4. are there nC_2 perpendicular to C_2? NO
    5. is there a σ_h? NO
    6. are there $n\sigma_v$? YES (n=2)
  - therefore the point group of **H_2O is C_{2v}**

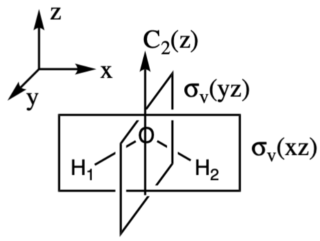


Figure 24 symmetry elements H_2O

In Class Activity P4

model answers on-line

- Determine the point group of NH_3
  - NH_3 is trigonal pyramidal
  - symmetry elements for NH_3 are E, C_3, and $3\sigma_v$ planes, **Figure 25**

USE THE FLOW CHART

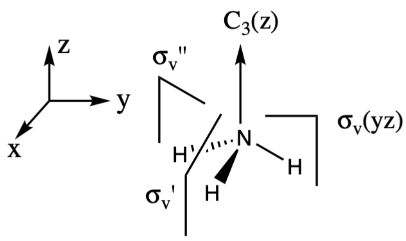
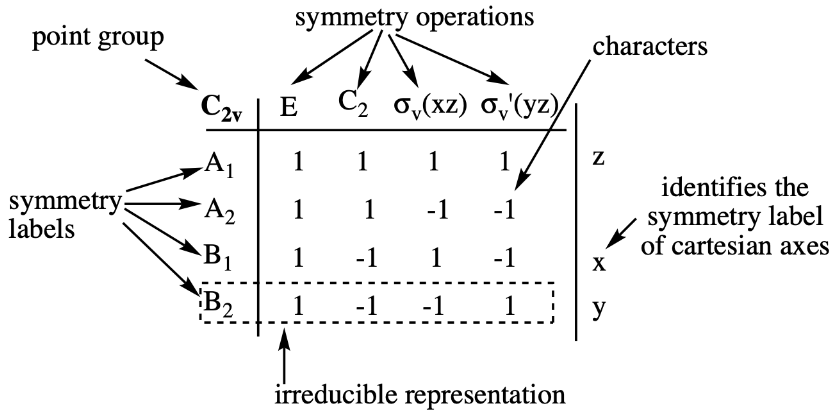


Figure 25 symmetry elements NH_3

Introducing Character Tables

- once we know the point group we can look at the "character table" for the point group, **Figure 26** is the character table for C_{2v}
- find the separate handout containing the main symmetry group character tables, take a minute to look over the character tables
- one advantage of character tables is that they allow us to evaluate if we have "found" all the symmetry operations of a group quickly



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

Figure 26 Character table for C_{2v} point group

- the primary use of character tables is to determine the symmetry labels of molecular orbitals, atomic orbitals, electronic states and vibrations.
- we reserve capital letters for vibrations and states (A_1, A_2, B_1, B_2) and use small letters for orbitals (a_1, a_2, b_1, b_2)
- the symmetry labels above are related to **irreducible representations (IR)**, which are the rows of the point group table, each IR tells us how an object behaves under each symmetry operation of the molecular point group

Using a Character Table: More Complex Point Groups

- have you noticed that some of the symmetry operations along the top of the character table have a number in front of them eg $2C_3$, $3C_2$, $2S_3$ and $3\sigma_v$?
- we will use as an example the D_{3h} point group,
- the number in front indicates the **number of operations**
  - o $2C_3$ indicates that there are 2 distinct C_3 operations
  - o $3C_2$ indicates that there are 3 distinct C_2 operations

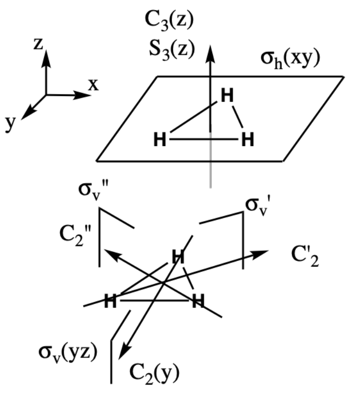


Figure 27 Symmetry elements of D_{3h} point group and H_3^+

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	h=12
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E"	2	-1	0	-2	1	0	

Figure 28 D_{3h} character table

- $2C_3$ operations in D_{3h}
  - **Figure 29** shows there are actually $3C_3$ operations: C_3^1, C_3^2 and C_3^3
  - but in character tables we *only keep the distinct operations*
  - $C_3^3$is equivalent to E, but E has already been included (operations to the left dominate)
  - thus there are only 2 distinct C_3 operations around the *single* C_3 axis
- there are $3C_2$ operations in D_{3h}
  - **Figure 30** illustrates the 3 C_2 axes: C_2, C_2', C_2''
  - the "dashes" are another way to indicate different symmetry elements
  - each C_2 axis has operations C_2^1 and C_2^2 however C_2^2 has already been counted as E
  - where there is a single symmetry operation the superscript 1 is often dropped $C_2^1 \rightarrow C_2$
  - each C_2 axis contributes one C_2^1 operation, thus there are 3 distinct C_2 operations
  - and 3 distinct C_2 axes

important!

- Thus we have seen how "$2C_3$, $3C_2$" appears in the character table header. It is important that you remember that this can be $2C_3$ operations around a **single** C_3 axis, or $3C_2$ operations around 3 **different** C_2 axes

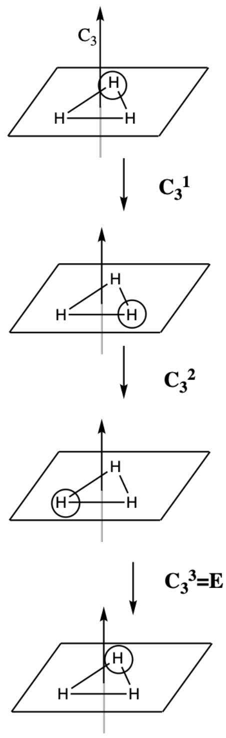


Figure 29 $2C_3$ operations

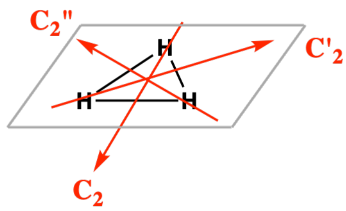


Figure 30 $3C_2$ axes

Key Points

- be able to write a definition for "symmetry element", "symmetry operation" and "symmetry operator"
- be able to identify the symmetry operations and elements for a molecule
- be able to draw clear diagrams showing the symmetry elements
- be able to draw clear diagrams showing the action of symmetry operations
- be able to use the flow chart and determine the molecular point group for any given molecule
- be able to identify and illustrate coincident symmetry elements
- be able to identify and illustrate equivalent symmetry operations
- be able to identify unique and non-unique symmetry operations
- be able to define all the components of a character table
- be able to identify when operations in the header row of the character table are due to multiple symmetry elements, or multiple symmetry operations

model answers on-line

Self-study Problems / Test Preparation

- **Q1** find, draw and label all the rotation axes for the square planar $[PtCl_4]^{2-}$ molecular ion
- **Q2** find, draw and label all the rotation axes and reflection planes for the trigonal planar BH_3 molecule
- **Q3** On a sketch of borazine illustrate and label the symmetry elements of the D_{3h} point group
- **Q4** Draw a diagram showing all the rotation operations for the C_5 group on the cyclopentadienyl anion
- **Q5** C_4^2 is equivalent to another operation in addition to $C_2(z)$ and $C'_2(x)$, which one is it?
    1. $\sigma_v(yz)$
    2. $C''_{2(b)}$
    3. $\sigma_v(xz)$
    4. $\sigma_{d(b)}$

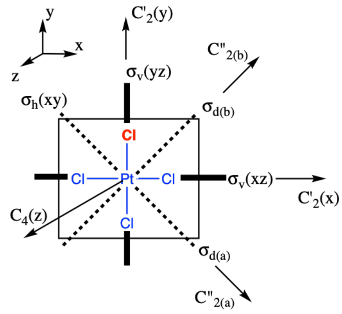


Figure 31 $[PtCl_4]^{2-}$ symmetry elements

- **Q6** What operation is S_3^2 equivalent to?
  Complete the diagram below and proving the equality.

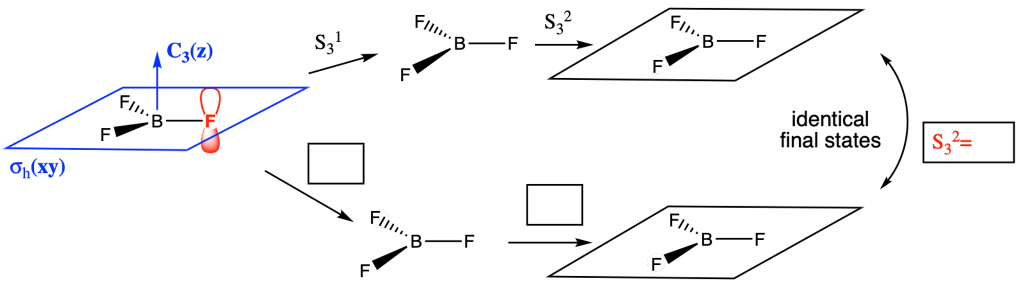


Figure 32 improper rotation

- **Q7** Which operation is S_3^4 equivalent to? Draw a diagram clearly proving this equality.
- **Q8** Work out all of the S_3^n operations up to S_3^6 for D_{3h} $[H_3]^+$ and determine the two unique S_3 operations.
- **Q9** identify the shape of the following molecules if they have a center of inversion, if the inversion point lies on an atom, identify that atom. (a) CO_2 (b)$SiCl_4$ (c) SF_6 (d) NH_3 (e) benzene
- **Q10** determine the point group of BH_3
- **Q11** determine the point group of the following molecules (* = more challenging)

a) SH_2
b) CO_2
c) $POCl_3$
d) trans-N_2F_2
e) CCl_4
f) $[PtCl_4]^{2-}$
g) CHFClBr
h) hydrazine N_2H_4
i) *cyclohexane (chair)
j) *cyclohexane (boat)
k) *benzene