

Molecular Orbital Theory

Lecture 1

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Outline

- resources
- what is this course about?
- introducing symmetry!
- rotations
- reflection,
- coincident and equivalent operations
- improper rotations
- inversion
- symmetry operators, notation
- character tables

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Resources

Main resource for information is my web-site

- notes AND slides, model answers
- optional material for beginners/experts
- links to interesting people, web-sites, research

<http://www.huntresearchgroup.org.uk>

Recommended Text

- Kieran Molloy, Group Theory for Chemists, Harwood Publishing, Chichester.
- only specific sections!!

The image shows a screenshot of the Hunt Research Group website. The website has a navigation menu with links for Home, Contacts, Profile, Papers, Talks, Research, Groups, Outreach, Teaching, and Links. The main content area features a profile picture of a woman and text describing the group's research in theoretical and computational chemistry, focusing on catalytic mechanisms, green fuels, bio-fuels, and solar-liquids. Below the website screenshot is the cover of the book 'Group Theory for Chemists: Fundamental Theory and Applications' by Kieran C. Molloy. Two handwritten-style text boxes are overlaid on the image: one says 'I like that model answers to the tutorial problems are online. This was very helpful because I could look through them myself' and the other says 'your website is a god send when you miss out one little part or need something clarified'.

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What is this Course About?

- 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

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Introducing Symmetry!

- describe what symmetry is
- develop a notation
- learn about symmetry operations, elements and operators
- focus on rotation, reflection and inversion
- learn about the point group of a molecule and how to find it

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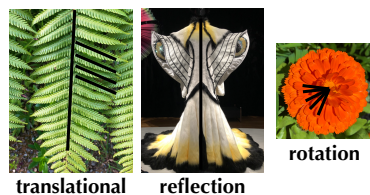
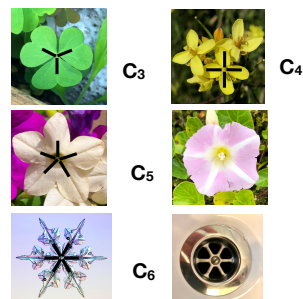
Symmetry

- Were have you met symmetry already?
 - equivalent H or C atoms in NMR
 - chirality
 - labelling of atomic orbitals
 - σ and π orbitals
 - octahedral transition metal complexes
 - isomerisation: cis/trans fac/mer staggered/eclipsed chair/boat
 - stereo-electronic effects => organic mechanisms
- Where understanding symmetry is crucial
 - MO diagrams => photoelectron spectrum
 - determines form of HOMO and LUMO => reactivity
 - in labelling electronic excitations and nuclear vibrations
 - determines allowed vibrations => IR and Raman spectrum
 - determines electronic interactions => UV-vis spectrum

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What is Symmetry?

- Symmetry occurs when you translate, rotate, reflect, or invert an object
- AND the initial and final states are indistinguishable
 - ie they can be superimposed onto each other
- Symmetry is all around us
 - in the everyday world
 - humans tend to find symmetrical things beautiful
 - humans are very good at identifying symmetry
- Symmetry
 - in the mathematical sense is exact
 - but real world symmetry is often not exact

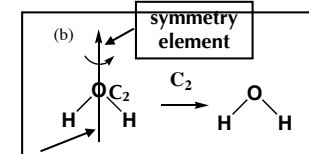
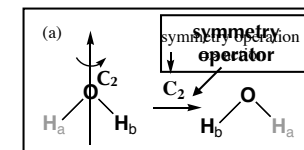


snowflake image used with permission from Prof. Libbrech, Caltech
<https://www.its.caltech.edu/~atomic/>

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Symmetry Operations

- Operation = physical action
 - Initial and final states are identical
- Element = geometric object
 - about which a symmetry operation occurs
 - rotation axis, reflection plane, inversion point
- Example
 - rotation of water around C_2 axis
 - initial and final states are identical
 - BUT if the nuclei are labeled H_a and H_b exchange places (O rotates in place)
- Every object has at least one symmetry operation, E (think E for existing)



C_2 operation

you should be able to draw neat diagrams showing symmetry operations

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Rotation Operations

Many rotations are possible

- ◆ C_2 rotation by 180°
- ◆ C_3 rotation by 120°
- ◆ C_4 rotation by 90°
- ◆ $C_5, C_6, C_7 \dots$ all the way up to C_∞

special

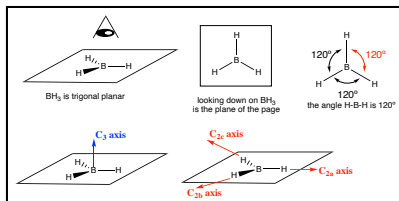
Definition: an n-fold rotation C_n is a rotation of $(360/n)^\circ$ around an n-fold rotation axis

A molecule can have multiple different rotation axes

- ◆ label different axes of the same type with subscript a, b, c ...

The principle axis is the highest C_n axis (with largest n)

- ◆ BH_3 principle axis is C_3



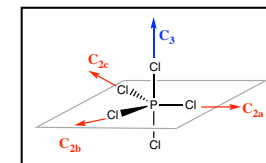
BH_3 (borane) has one C_3 axis three C_2 axes

Important!

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In-Class Activity P1

What is the principle axis for PCl_5 ? (phosphorus pentachloride)

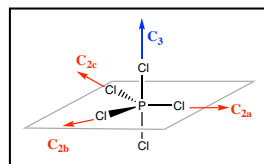


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In-Class Activity P1

What is the principle axis for PCl_5 ?

- ◆ the principle axis is the highest C_n axis
- ◆ there are C_3 and C_2 axes, the highest n=3
- ◆ C_3 is the principle axis

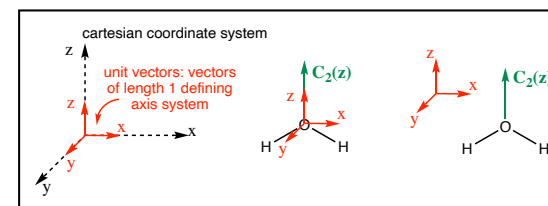


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Cartesian Coordinates

Define a cartesian coordinate system

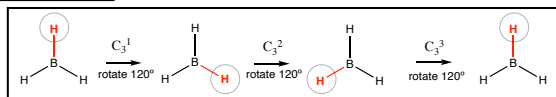
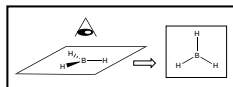
- ◆ use the center of the molecule as the origin
- ◆ but if your diagram is "messy" you can place it to the side



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Rotation Operations

rotation operations are sequential: $C_3^1 \rightarrow C_3^2 \rightarrow C_3^3$



rotation operations form a group

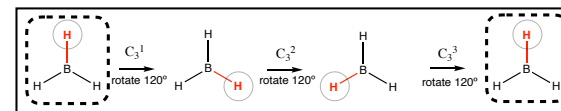
- the C_3 group has 3 members $\{C_3^1, C_3^2, C_3^3\}$
- definition: a C_n group has n members

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Rotation Operations

equivalent operations

- notice that $C_3^3 = E$
- we say that C_3^3 and E are equivalent operations
- for all rotation groups $C_n^n = E$



branch of mathematics called Group Theory

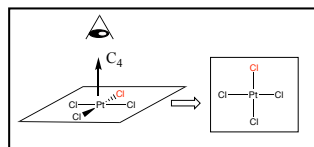
- about groups and how the elements/groups relate to each other
- groups are VERY important area in mathematics, philosophy, physics and chemistry
- we will not take this any further here

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In-Class Activity P3

on a molecule of $[PtCl_4]^{2-}$ draw a diagram showing sequential rotation operations

- like that shown in Figure 8

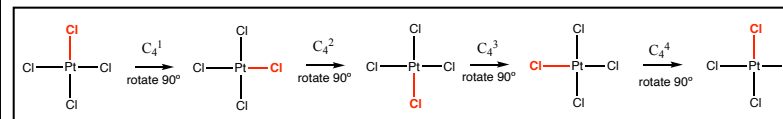
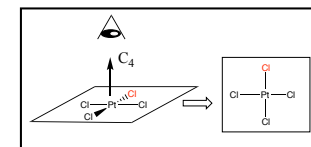


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In-Class Activity P3

on a molecule of $[PtCl_4]^{2-}$ draw a diagram showing sequential rotation operations

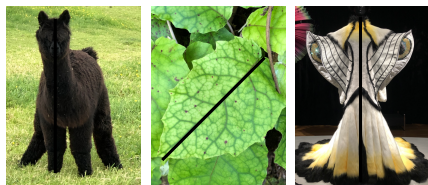
- like that shown in Figure 8



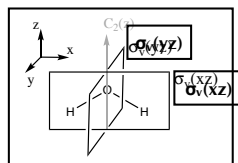
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Reflections

- operation=reflection
- element=mirror plane
- mirror planes are a common symmetry element in our everyday lives
- types of mirror plane
 - σ_v vertical
 - σ_h horizontal
 - σ_d bisecting (disecting)
- σ_v and σ_d often come in pairs and with C_2 axes
- always identify when a mirror plane lies on a cartesian plane



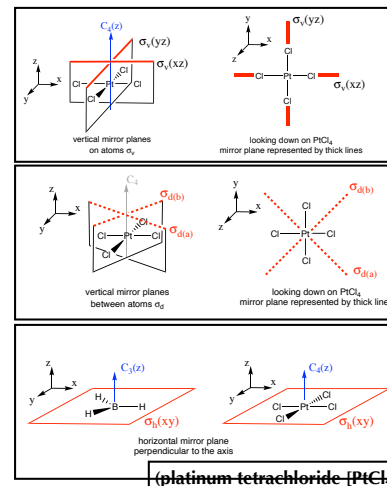
my photo from world wearable art exhibition



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Reflections

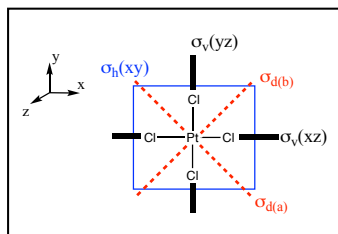
- drawing mirror planes
 - draw the plane, or
 - can be represented as a thick line on a plan view of a molecule
- mirror planes
 - σ_v pass vertically through a rotation axis
 - σ_d pass vertically through a rotation axis AND between bonds or C_2 axes
 - σ_h are perpendicular to the principle axis



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Multiple Symmetry Operations

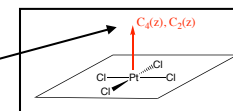
- Notice that molecules can have multiple symmetry operations
 - for example the many mirror plane of $[PtCl_4]^{2-}$



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Coincident Symmetry Elements

- Symmetry elements can be coincident
 - be in the same place
 - occurs for rotation axes
 - example: C_2 and C_4 coincident



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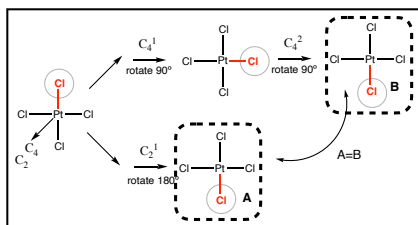
Equivalent Symmetry Operations

Symmetry operations can be equivalent

- generate the same final structure
- example: $C_2^1 = C_4^2$

We prefer "higher" symmetry

- for C_n^m prefer lower n operation
- "retain" C_2^1



if I ask you to show that two operations are equivalent this is the type of diagram you need to draw

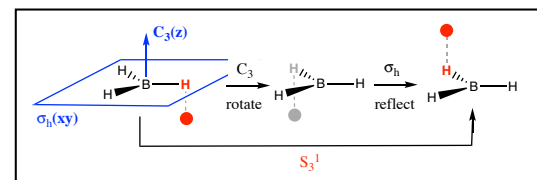
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Improper Rotation

rotation about an n-fold axis (C_n)

followed by reflection in a plane (σ_n) perpendicular to the rotation axis

- when evaluating make sure you pick a point off the mirror plane
- or a pAO on an atom

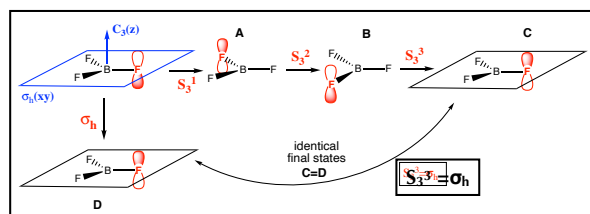


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Improper Rotations

S_n n=odd go around twice to generate E ie $S_n^{2n}=E$

- for example $S_3^3 = \sigma_h$



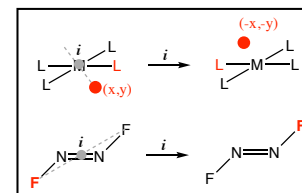
many of the S_n operations are equivalent to other operations which take priority

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Inversion

inversion

- operation: inversion
- element: inversion point
- takes a point (x,y,z) to $(-x,-y,-z)$
- the inversion point is generally in the center of the molecule, it does not need to be "on" an atom!



(dinitrogen difluoride N_2F_2)

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Symmetry Operators

Symmetry operator

- mathematical representation of the action (operation)
- operator "acts on" the wavefunction or molecule
- use square or curly brackets when writing an operator

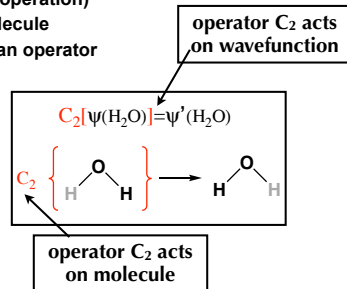
Example

- C_2 operator represent the C_2 rotation

Advanced (not required)

- the operator is represented as a matrix
- ie C_2 rotation matrix

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



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Same Notation!

Symmetry operation

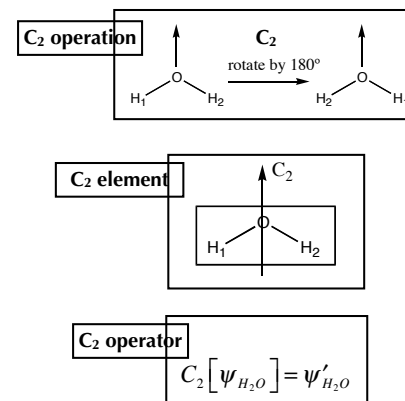
- the act of performing a motion

Symmetry elements

- objects about with symmetry operations occur

Symmetry operator

- mathematical representation of the action



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Symmetry Groups

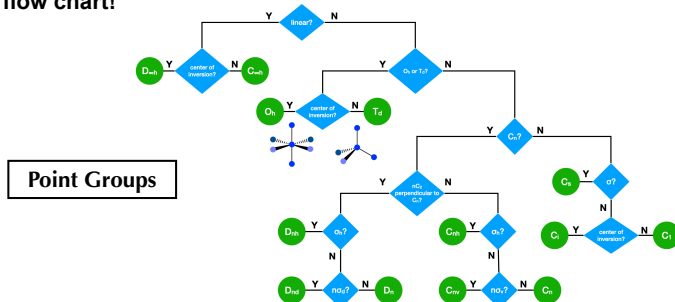
the group of symmetry operations that leave a molecule unchanged

examples: C_{2v} , $D_{\infty h}$ and T_d

start by identifying the shape of a molecule (VSEPR theory)

find all the symmetry operations

use the flow chart!



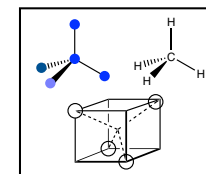
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T_d and O_h

The tetrahedral T_d and octahedral O_h point groups are special

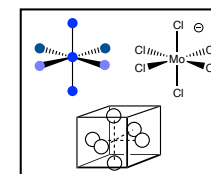
Tetrahedral

- have 4 identical ligands
- are arranged as a triangular based pyramid
- or as the opposite corners of a cube
- methane is an example



Octahedral

- have 6 identical ligands
- are arranged along the "axes"
- or as the centre of each face of a cube
- 6-coordinate TM complexes are octahedral

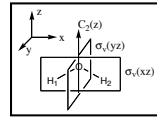


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Example: H₂O

Determine the point group of H₂O

- ◆ Shape: planar
- ◆ Symmetry elements for H₂O:
 - identity E
 - principle C₂ rotation axis
 - two reflection planes σ_v(yz) and σ_v(xz)



Flow chart for identifying the point group

- ◆ is the molecule linear? NO
- ◆ is the molecule T_d or O_h? NO
- ◆ is there a C_n? YES n=2
- ◆ are there 2C₂ perpendicular to C₂? NO
- ◆ is there a σ_h? NO
- ◆ are there 2σ_v? YES

difficult for me to put on a slide, you trace through the flow chart in your notes

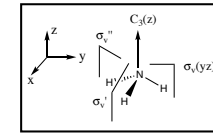
point group: C_{2v}

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In-Class Problem P4

Determine the point group of NH₃

- ◆ shape: trigonal pyramidal
- ◆ symmetry elements are: E, C₃ and 3σ_v

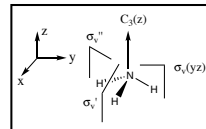


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In-Class Problem P4

Determine the point group of NH₃

- ◆ shape: trigonal pyramidal
- ◆ symmetry elements are: E, C₃ and 3σ_v



Flow chart for identifying the point group

- ◆ is the molecule linear? NO
- ◆ is the molecule T_d or O_h? NO
- ◆ is there a C_n? YES n=3
- ◆ are there 3C₂ perpendicular to C₃? NO
- ◆ is there a σ_h? NO
- ◆ are there 3σ_v? YES

point group: C_{3v}

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Character Tables

- find the sheet of character tables now, and take a look through the character tables for different point groups

Character tables for some chemically important symmetry groups			
C ₁	E	1	1
A ₁	1	1	1
A ₂	1	1	1
E ₁	2	1	1
E ₂	2	1	1

The C ₂ group			
C ₂	E	C ₂	1
A ₁	1	1	1
A ₂	1	1	1
E ₁	2	0	1
E ₂	2	0	1

Character Tables

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Character Tables

the parts of a character table

C_{2v} character table

symmetry operations: E, C₂, σ_v(xz), σ_v'(yz) (h=4)

symmetry labels: A₁, A₂, B₁, B₂

irreducible representation: A₁ → a₁ (lower case letters for orbitals)

1's and -1's are characters

symmetry of cartesian axes: z, x, y

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

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Multiple Symmetry Operations

Symmetry operations of D_{3h}

- ♦ 1 E identity
- ♦ 2 C₃ rotations
- ♦ 3 C₂ rotations
- ♦ 1 σ_h reflection
- ♦ 2 S₃ improper rotations
- ♦ 3 σ_v reflections

number of operations

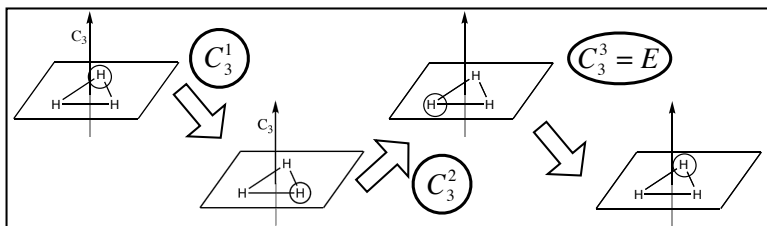
h = total number of operations

♦ = 1 + 2 + 3 + 1 + 2 + 3 = 12

D _{3h}	E	2C ₃	3C ₂	σ _h	2S ₃	3σ _v	h=12
A ₁ '	1	1	1	1	1	1	(T _x , T _y)
A ₂ '	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	T _z
A ₁ ''	1	1	1	-1	-1	-1	
A ₂ ''	1	1	-1	-1	-1	1	
E''	2	-1	0	-2	1	0	

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2C₃ Rotations



only keep unique operations

- ♦ if already counted in a symmetry element to the left on the character table, or under a rotation of lower n it is not counted again

C₃¹ C₃² ~~C₃³~~

there are 2 unique C₃ operations

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3C₂ Rotations

three separate C₂ axes

- ♦ hint: if you find one C₂ axis and use C₃ to find the rest

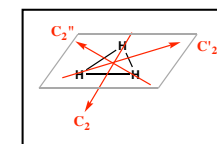
♦ each element is distinct:

♦ but C₂²=E

♦ only C₂¹ left, simply denoted as C₂ operation

thus each C₂ axis contributes one C₂ rotation

there are 3 unique C₂ operations



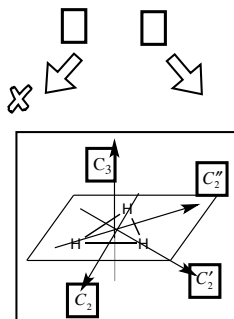
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Multiple Operations

☞ $2C_3$ and $3C_2$ appear in the character table of D_{3h}

- ◆ the table only “cares” about number of operations
- ◆ we have $2C_3$ operations about a SINGLE C_3 element
- ◆ we have $3C_2$ operations about THREE separate C_2 elements

one element
2 unique
operations



three elements
3 unique
operations

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Key Points

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

practice!!

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QUESTION
 1. Identify the point group of the following molecules:
 (a) CH_4
 (b) BF_3
 (c) CH_2Cl_2
 (d) $CH_2=CH_2$
 (e) $CH_2=CHCN$
 (f) $CH_3CH=CH_2$
 (g) $CH_3C\equiv CH$
 (h) $CH_3C\equiv CCl$
 (i) $CH_3C\equiv CBr$
 (j) $CH_3C\equiv CBrCl$
 (k) $CH_3C\equiv CBrCl_2$
 (l) $CH_3C\equiv CBrCl_3$
 (m) $CH_3C\equiv CBrCl_4$
 (n) $CH_3C\equiv CBrCl_5$
 (o) $CH_3C\equiv CBrCl_6$
 (p) $CH_3C\equiv CBrCl_7$
 (q) $CH_3C\equiv CBrCl_8$
 (r) $CH_3C\equiv CBrCl_9$
 (s) $CH_3C\equiv CBrCl_{10}$
 (t) $CH_3C\equiv CBrCl_{11}$
 (u) $CH_3C\equiv CBrCl_{12}$
 (v) $CH_3C\equiv CBrCl_{13}$
 (w) $CH_3C\equiv CBrCl_{14}$
 (x) $CH_3C\equiv CBrCl_{15}$
 (y) $CH_3C\equiv CBrCl_{16}$
 (z) $CH_3C\equiv CBrCl_{17}$
 (aa) $CH_3C\equiv CBrCl_{18}$
 (ab) $CH_3C\equiv CBrCl_{19}$
 (ac) $CH_3C\equiv CBrCl_{20}$
 (ad) $CH_3C\equiv CBrCl_{21}$
 (ae) $CH_3C\equiv CBrCl_{22}$
 (af) $CH_3C\equiv CBrCl_{23}$
 (ag) $CH_3C\equiv CBrCl_{24}$
 (ah) $CH_3C\equiv CBrCl_{25}$
 (ai) $CH_3C\equiv CBrCl_{26}$
 (aj) $CH_3C\equiv CBrCl_{27}$
 (ak) $CH_3C\equiv CBrCl_{28}$
 (al) $CH_3C\equiv CBrCl_{29}$
 (am) $CH_3C\equiv CBrCl_{30}$
 (an) $CH_3C\equiv CBrCl_{31}$
 (ao) $CH_3C\equiv CBrCl_{32}$
 (ap) $CH_3C\equiv CBrCl_{33}$
 (aq) $CH_3C\equiv CBrCl_{34}$
 (ar) $CH_3C\equiv CBrCl_{35}$
 (as) $CH_3C\equiv CBrCl_{36}$
 (at) $CH_3C\equiv CBrCl_{37}$
 (au) $CH_3C\equiv CBrCl_{38}$
 (av) $CH_3C\equiv CBrCl_{39}$
 (aw) $CH_3C\equiv CBrCl_{40}$
 (ax) $CH_3C\equiv CBrCl_{41}$
 (ay) $CH_3C\equiv CBrCl_{42}$
 (az) $CH_3C\equiv CBrCl_{43}$
 (ba) $CH_3C\equiv CBrCl_{44}$
 (bb) $CH_3C\equiv CBrCl_{45}$
 (bc) $CH_3C\equiv CBrCl_{46}$
 (bd) $CH_3C\equiv CBrCl_{47}$
 (be) $CH_3C\equiv CBrCl_{48}$
 (bf) $CH_3C\equiv CBrCl_{49}$
 (bg) $CH_3C\equiv CBrCl_{50}$
 (bh) $CH_3C\equiv CBrCl_{51}$
 (bi) $CH_3C\equiv CBrCl_{52}$
 (bj) $CH_3C\equiv CBrCl_{53}$
 (bk) $CH_3C\equiv CBrCl_{54}$
 (bl) $CH_3C\equiv CBrCl_{55}$
 (bm) $CH_3C\equiv CBrCl_{56}$
 (bn) $CH_3C\equiv CBrCl_{57}$
 (bo) $CH_3C\equiv CBrCl_{58}$
 (bp) $CH_3C\equiv CBrCl_{59}$
 (bq) $CH_3C\equiv CBrCl_{60}$
 (br) $CH_3C\equiv CBrCl_{61}$
 (bs) $CH_3C\equiv CBrCl_{62}$
 (bt) $CH_3C\equiv CBrCl_{63}$
 (bu) $CH_3C\equiv CBrCl_{64}$
 (bv) $CH_3C\equiv CBrCl_{65}$
 (bv) $CH_3C\equiv CBrCl_{66}$
 (bv) $CH_3C\equiv CBrCl_{67}$
 (bv) $CH_3C\equiv CBrCl_{68}$
 (bv) $CH_3C\equiv CBrCl_{69}$
 (bv) $CH_3C\equiv CBrCl_{70}$
 (bv) $CH_3C\equiv CBrCl_{71}$
 (bv) $CH_3C\equiv CBrCl_{72}$
 (bv) $CH_3C\equiv CBrCl_{73}$
 (bv) $CH_3C\equiv CBrCl_{74}$
 (bv) $CH_3C\equiv CBrCl_{75}$
 (bv) $CH_3C\equiv CBrCl_{76}$
 (bv) $CH_3C\equiv CBrCl_{77}$
 (bv) $CH_3C\equiv CBrCl_{78}$
 (bv) $CH_3C\equiv CBrCl_{79}$
 (bv) $CH_3C\equiv CBrCl_{80}$
 (bv) $CH_3C\equiv CBrCl_{81}$
 (bv) $CH_3C\equiv CBrCl_{82}$
 (bv) $CH_3C\equiv CBrCl_{83}$
 (bv) $CH_3C\equiv CBrCl_{84}$
 (bv) $CH_3C\equiv CBrCl_{85}$
 (bv) $CH_3C\equiv CBrCl_{86}$
 (bv) $CH_3C\equiv CBrCl_{87}$
 (bv) $CH_3C\equiv CBrCl_{88}$
 (bv) $CH_3C\equiv CBrCl_{89}$
 (bv) $CH_3C\equiv CBrCl_{90}$
 (bv) $CH_3C\equiv CBrCl_{91}$
 (bv) $CH_3C\equiv CBrCl_{92}$
 (bv) $CH_3C\equiv CBrCl_{93}$
 (bv) $CH_3C\equiv CBrCl_{94}$
 (bv) $CH_3C\equiv CBrCl_{95}$
 (bv) $CH_3C\equiv CBrCl_{96}$
 (bv) $CH_3C\equiv CBrCl_{97}$
 (bv) $CH_3C\equiv CBrCl_{98}$
 (bv) $CH_3C\equiv CBrCl_{99}$
 (bv) $CH_3C\equiv CBrCl_{100}$