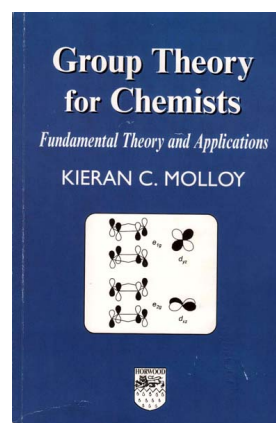


Resources

Web and Social Media Resources:

- information on my web-site under "Teaching"
 - copies of notes and slides
 - model answers to in-class activities
 - model answers to the self-study problems, and exam preparation questions
 - optional background support for beginners, optional extra material for experts
 - files for visualising MOs
 - links to interesting people and web-sites
 - links to research papers related to MO theory



- Socrative
 - interactive quiz app used in lectures
 - www.socrativ.com
 - classroom: WHZ9KBWC3

Reading Resources:

Recommended text:

- Kieran C. Molloy, Group Theory for Chemists, Harwood Publishing Limited, Chichester.
- IMPORTANT! Use only the following selections:
 - Part 1 Chapter 1: Symmetry
 - all of Part III: Application of Group Theory to Structure and Bonding
- the other parts of this text are used for my course next year "Spectroscopy and Characterisation" (feel free to have a peek!)
- Other books and reading will be listed on the web-site over the duration of the course, this is background reading and it will support the lectures. Some **elective reading is advisable** but this is entirely OPTIONAL, do not try to read everything I recommend!
- 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.

Why study Molecular Orbital Theory?

- molecular Orbital (MO) theory supersedes valence bond theory (main group elements), crystal field theory (transition metal and organometallic chemistry) and ad-hoc bonding arguments that have been employed to explain the stability of clusters. MO theory is one way to think about bonding in solids.
- For example the VSEPR picture of O₂ has no unpaired electrons, yet experimentally (liquid) O₂ is found to be paramagnetic (**Figure 1**) indicating that there are unpaired electrons! One of the early successes of MO theory was to explain why liquid oxygen is paramagnetic.
- For example Crystal Field Theory explains the splitting of the d orbitals into t_{2g} and e_g orbitals however the magnitude of this splitting is based on the electrostatic effect of the ligands, and predicts that the splitting for charged ligands should be larger than that for a neutral ligand. However, experimental evidence is that F⁻ a charged ligand has a smaller Δ_{oct} than a neutral ligand, water! [TiF₆]³⁻ Δ_{oct} = 19 000 cm⁻¹ but [Ti(H₂O)₆]³⁺ Δ_{oct} = 20 300 cm⁻¹, **Figure 2**. MO theory is able to neatly and easily explain why water ligands generate a larger Δ_{oct} than fluorine ligands. During this course you will also find out why these energy levels are labelled t_{2g} and e_g and what the labels mean.
- For example we all know the structure of ethane (C₂H₆), **Figure 3**, why then does diborane which has a similar chemical formula (B₂H₆) form such an outlandish structure? MO theory explains this structure simply and easily.

What is course about?

Learning how to describe and use symmetry

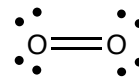
Learning how to construct Molecular Orbital (MO) diagrams

Learning how to interpret MO diagrams

Learning how MO theory can be used to understand and predict the bonding, structure and reactivity of molecules

Where will I use the material covered in this course?

- Theoretical Methods, Quantum Chemistry, Electronic Properties of Solids
- Main Group Elements, Organometallic Chemistry, Crystal and Molecular Architecture
- MO diagrams form a part of experiments in the "Computational Chemistry Lab"



6 valence electrons each
2 into the double bond
2 lone pairs

removed due to
copyright

Figure 1 (a) VSEPR for O₂ and (b) Liquid Oxygen¹

removed due to
copyright

Figure 2 (a) Visible spectra of [TiF₆]³⁻ and [Ti(H₂O)₆]³⁺.²

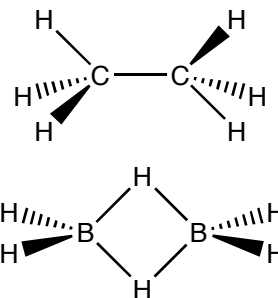


Figure 3 The odd structure of B₂H₆

¹ (Source: Web Elements [<http://www.webelements.com/>] where the image is obtained from Prof James Marshall's (U. North Texas, USA) Walking Tour of the elements).

² Source: "Metal-Ligand Bonding by Rob Janes and Elaine More, 2004, The Open University, Milton Keynes, p14-15

MO theory is important for understanding structure and chemical reactivity

- In **1981** Kenichi Fukui (Japan) and Roald Hoffmann (USA) shared the Nobel prize in chemistry for their independent investigations in the "orbital symmetry interpretation of chemical reactions"
- In **1998** Walter Kohn (USA) and John Pople (USA) shared the Nobel prize in chemistry for the development of computational methods, these are the modern methods used to determine "real" molecular orbitals.

removed due to
copyright

Figure 4 Kenichi Fukui³, Roald Hoffmann⁴, Walter Kohn⁵, and John Pople⁵

- In **2009** Prof. Eisenstein a theoretical chemist received the American Chemical Society award for Organometallic Chemistry
- In **2013** the Nobel Prize in chemistry went to three theoretical chemists: Martin Karplus, Michael Levitt and Arieh Warshel for "the development of multiscale models for complex chemical systems"



Figure 5 Odile Eisenstein receiving her award

removed due to
copyright

Figure 6 Martin Karplus⁶, Michael Levitt⁷ and Arieh Warshel⁷

³ source:http://www.britannica.com/nobel/micro/222_39.html

⁴ source:http://nobelprize.org/nobel_prizes/chemistry/laureates/1981/

⁵ source:http://nobelprize.org/nobel_prizes/chemistry/laureates/1998/index.html

⁶ http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2013/

Symmetry

Why is symmetry important?

- places you have already meet symmetry:
 - 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
- the symmetry of a molecule is crucially important to its behaviour
 - it determines the MO diagram and thus the photoelectron spectrum
 - it determines the HOMO and LUMO and thus the reactivity of the species
 - it determines when symmetry breaking interactions occur
 - it determines the vibrations that the molecule can undergo and thus the IR and Raman spectrum
 - it determines the electronic interactions the molecule can undergo, thus determining features like the dipole moment, and UV spectrum.

treated in my course
"Spectroscopy &
Characterisation"

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
 - a few examples are C_{2v} , $D_{\infty h}$ and T_d
 - last year you had a flow chart to help you identify the point group of a molecule **you will have this flow chart in the exam!**

Symmetry Operations and Elements

- **symmetry operations** involve the "physical act" of moving a molecule however they leave the initial and final states of the molecule indistinguishable with respect to the type of nuclei.
- For example, in **Figure 7a** under a C_2 rotation the H-atoms move (H_a and H_b are exchanged) however unless they have been specifically labelled the final and initial structures look identical, **Figure 7b**

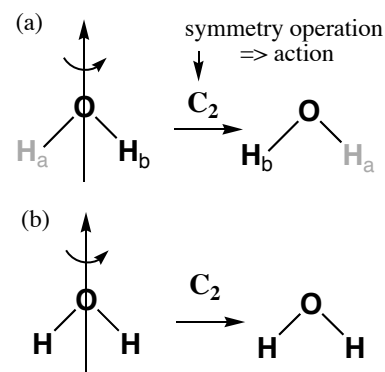


Figure 7 Symmetry operations

- each symmetry operation has an associated **symmetry element**, symmetry elements are the geometric object about which the operation is executed, thus they are: the axis, plane or point
- when drawing out symmetry operations/elements make sure your diagrams are neat. Clearly indicate the symmetry element on the molecule. When showing the effect of an operation draw an arrow with the symmetry operator above it and the final structure after the operation.

IMPORTANT!

- Include axial information.
 - The principle or highest n-axis is always the z-axis.
 - beware of diatomics which have the z-axis along the bond
 - symmetry elements are generally associated with a particular Cartesian axis (z) or plane (yz, xz).
- **Figure 8** shows symmetry operations and elements
 - identity (E) every object has this, think of it as E for "existing"
 - n-fold rotation (C_n) rotation of $(360/n)^\circ$ around an n-fold rotation *axis*
 - reflection (σ_v , σ_d or σ_h) in a mirror *plane*
 - inversion (i) takes a point at (x, y, z) to (-x, -y, -z) through the inversion *point* (i)
 - improper rotation (S_n) a rotation around an n-fold improper rotation *axis* (S_n) followed by reflection in a *plane* (σ_h) perpendicular to the rotation axis.

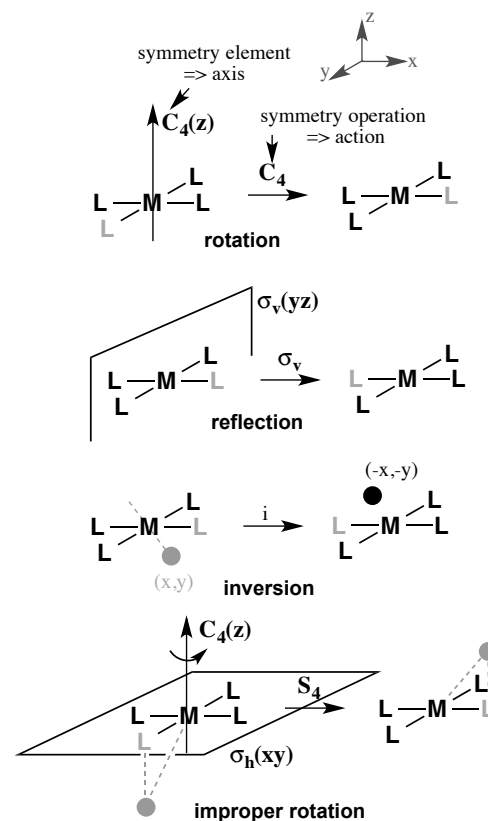


Figure 8 Examples of different symmetry operations

Symmetry Operators

- each physical operation has an associated mathematical **operator**, which represents the physical act, eg a C_2 operator represents the physical action of carrying out a 180° rotation
- the operator is normally represented as a matrix which allows us to write a mathematical equation for the action of the operation on a wavefunction or molecule, **Figure 9**
- you will study operators in more detail in your Theoretical Methods course, we won't discuss them any further here

treated in my course
"Spectroscopy &
Characterisation"

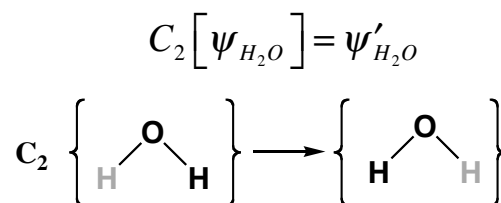


Figure 9 An operator acts on a wavefunction

Notation

- 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).

An Example: H₂O

- for H₂O the symmetry elements (**Figure 10**) are:

- the identity E
- one rotation about a C₂(z) axis
- one reflection in a $\sigma_v(yz)$ plane
- one reflection in the $\sigma_v(xz)$ plane

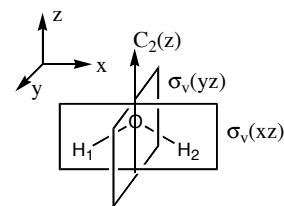


Figure 10 Symmetry elements for H₂O

- determine the point group for H₂O (use flow chart)
 - is the molecule linear? NO
 - are there two or more C_n n>2? NO
 - is there a C_n? YES C₂
 - are there nC₂ perpendicular to C_n? NO
 - is there a σ_h ? NO
 - is there a σ_v ? YES
 - therefore the point group of H₂O is C_{2v}

In-Class Activity

- A **socrative quiz** will start, it is related to this image which is part of an answer to a question from an old exam

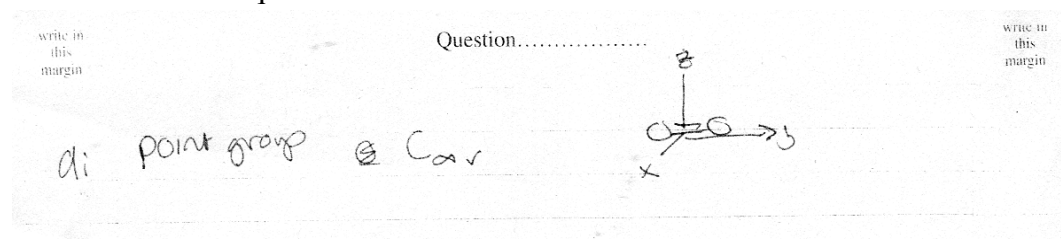


Figure 11

- What is wrong with this answer? The question "Given this molecule of cis-H₄ clearly indicate all of the symmetry elements on a diagram. (4 marks)"

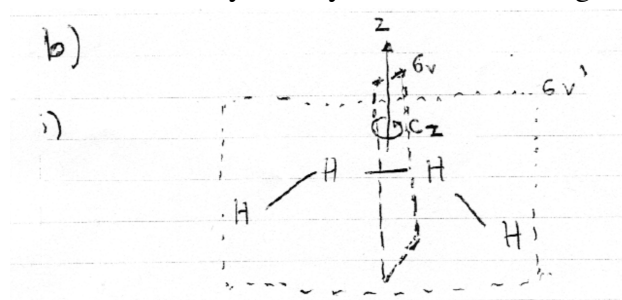


Figure 12

Character Tables

Introducing the Character Table

IMPORTANT!
bring these
tables to lectures

- a key part of this course is learning how to use character tables, character tables tell us how the molecular orbitals of a molecule transform under the point group of the molecule ... more on this later.
- I have given you a separate handout containing the main symmetry group character tables, **you will have character tables in the exam!**
- below, **Figure 13**, is the character table for the C_{2v} symmetry group:

point group		symmetry operations				characters
C_{2v}		E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
symmetry labels	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

irreducible representation

identifies the symmetry label of cartesian axes

Figure 13 Character table for C_{2v} point group

Using a Character Table: The first MO of water

- the best way to become familiar with a character table is to use it, we will cover two examples now.
- let us consider an s atomic orbital placed on each of the atoms of water (**Figure 14**), this is in-fact the lowest energy MO for water, it consists of a positive combination of the H 1s AOs and the O 2s AO.
- water has C_{2v} symmetry or belongs to the C_{2v} point group, so we use the C_{2v} character table (**Figure 13**)
- then we ask ourselves how does this MO transform under C_{2v} symmetry?
- One way to work this out is to set up a **representation table** as shown below (**Figure 15**)
 - a representation table shows the effect of each symmetry operation on an object (this can be a molecule, a molecular orbital or anything else) with the symmetry of the point group.
 - capital gamma (Γ) is used when the representation of something is unknown.

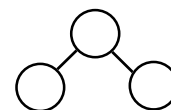


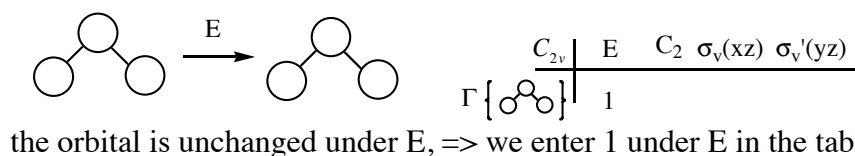
Figure 14 Lowest energy MO of water

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \{ \text{MO} \}$				

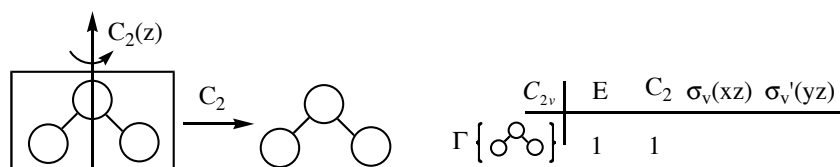
Figure 15 Representation table

- now apply each of the symmetry operations of the group to the molecular orbital (**Figure 16**)

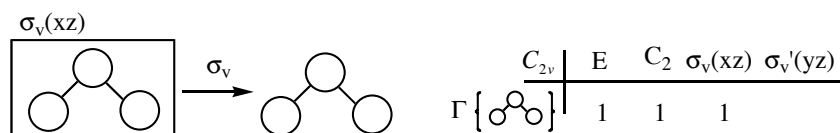
- if the **phase remains unchanged** under a symmetry operation enter **1**
- if the **phase is reversed** under a symmetry operation enter **-1**
- "under" is a strange word to use, but it is standard terminology. When we say "under C_2 " we mean "what happens when we perform the C_2 operation"



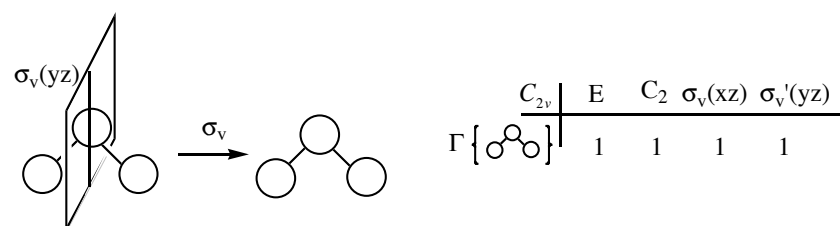
the orbital is unchanged under E, => we enter 1 under E in the table.



the orbital is unchanged under C_2 , that is on applying the rotation of 180° to the molecule it looks exactly the same => we enter 1 under C_2 in the table.



the orbital is unchanged under $\sigma_v(xz)$ => we enter 1 under $\sigma_v(xz)$



the orbital is unchanged under $\sigma_v(yz)$ => we enter 1 under $\sigma_v(yz)$

Figure 16 Determining an irreducible representation

- then we then compare the generated representation to the list of irreducible representations on the C_{2v} character table, and we determine which one it matches, **Figure 17**

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$\Gamma \left\{ \text{orbital} \right\}$	1	1	1	1	
↓					
$\Gamma \left\{ \text{orbital} \right\} \Rightarrow a_1$					

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	h=4 z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

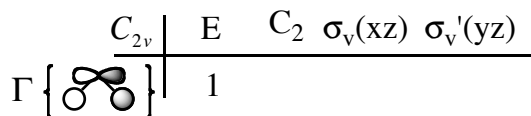
Figure 17 Matching a unknown representation to an irreducible representation

- this MO transforms as the irreducible representation labelled A_1
- by convention we label orbital symmetries we use small letters, therefore the first molecular orbital water has a_1 symmetry.

IMPORTANT

In-Class Activity

- Now determine the symmetry label for the second lowest energy MO of water, **Figure 18**. This is composed of H 1s AOs and the O 2p_x AO.



- Symmetry label:

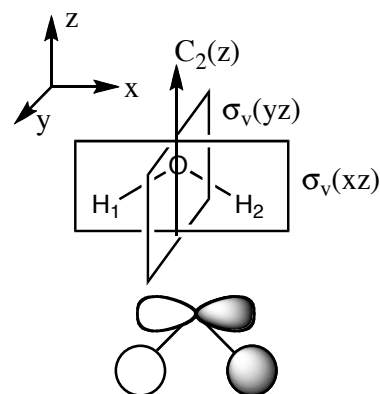


Figure 18 Second lowest energy MO of water

Using a Character Table: More Complex Point Groups

- There are several more features of character tables that are important. We will use as an example the D_{3h} point group character table (**Figure 19**).

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	

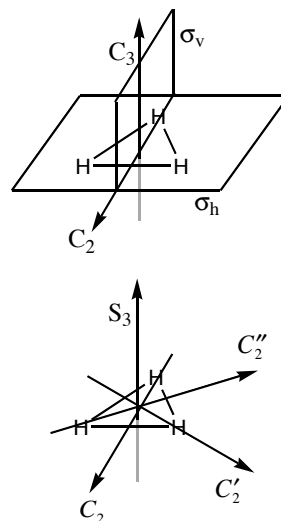


Figure 19 D_{3h} character table and selected symmetry elements

Multiple Symmetry Operations

- 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 $3\sigma_v$?
- the number in front indicates the **number of operations**
 - $2C_3$ indicates that there are 2 distinct C_3 operations
 - $3C_2$ indicates that there are 3 distinct C_2 operations
- the best way to illustrate this is via some examples, so let us start by considering three H atoms arranged in a planar equilateral triangle, **Figure 20**
 - this is an important example because H₃ is a common molecular fragment (as in BH₃)
 - H₃⁺ is very important in interstellar chemistry; it is the most abundant molecular ion in the universe. A good website about H₃⁺ is <http://h3plus.uiuc.edu/>

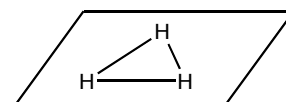


Figure 20 H₃ example

- there are $2C_3$ operations in D_{3h} (**Figure 19**)
 - C_n = rotate by $(360^\circ)/n$
 - so C_3 = rotate by 120°
 - on the diagram ① to the left I have located the C_3 axis and circled one H atom
 - under one C_3 operation, denoted C_3^1 where the 1 indicates one rotation by 120° the circled H atom shifts, ②
 - under a second C_3 operation, denoted C_3^2 the circled H atom shifts again, ③
 - under a third C_3 operation, denoted C_3^3 the circled H atom shifts a third time, ④
 - on the third time (under C_3^3) the circled H atom has returned to its starting point, and diagram ④ is exactly the same as diagram ①, thus C_3^3 is equivalent to E
 - C_3^3 has already been counted as E
 - thus there are 2 unique C_3 operations around a *single* C_3 axis and hence the header $2C_3$ in the character table

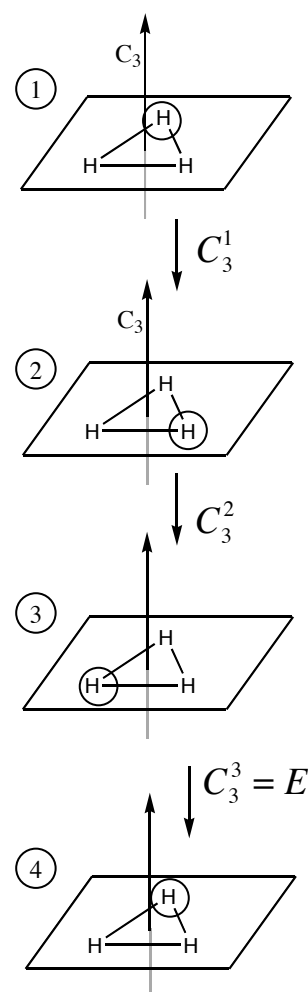


Figure 21 The $2C_3$ operations

- rotation operations in general
 - each rotation axis of order n , has n symmetry operations associated with it
 - C_3 axis has C_3^1 , C_3^2 and $C_3^3 = E$ = 3 operations
 - C_4 axis has C_4^1 , C_4^2 , C_4^3 and $C_4^4 = E$ = 4 operations
 - the final rotation returns the system to the starting position, thus it is a rule that $C_n^n = E$
 - for C_2 which has C_2^1 and $C_2^2 = E$ and since only one unique operation exists the superscript is often implicitly assumed.
 - these are called rotation groups, "groups" are mathematical entities, and there is a whole branch of mathematics devoted to studying groups called "group theory"
- There are $3C_2$ operations
 - the three C_2 axes are shown **Figure 22**
 - the axes are labelled C_2 , C_2' , C_2'' to indicate they are different symmetry elements
 - one short cut to finding symmetry elements is to realise that symmetry elements act on each other
 - once you have found one C_2 axis, you can use the C_3 axis to find the other two!

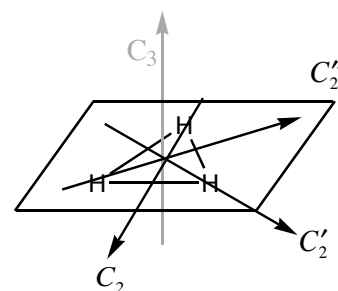


Figure 22 The $3C_2$ axes

IMPORTANT

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

Degenerate Symmetry Labels

- A and B (or a and b for MOs) are the symmetry labels for non-degenerate representations, they have only have characters ± 1
- E (or e) is the symbol used for a doubly degenerate irreducible representations (and should not be confused with the symmetry operation E or identity), under (the operation) E these always have characters of 2
- T (or t) is used to label triply degenerate irreducible representations, under E they always have a character of 3
 - T is important in the tetrahedral and octahedral point groups
 - where have you already seen e and t symmetry labels? *suggestions from the class*

How does Degeneracy Work?

- In a degenerate representation the individual components (orbitals) do NOT always map onto themselves, however they can map onto each other, so they must always be considered together
- p_x and p_y are components of the degenerate representation (E') under the D_{3h} point group
 - we start by taking a point on the tip of each orbital and define it's position in terms of the x and y axes, then we put these side by side forming a 2 by 2 matrix, **Figure 23**.

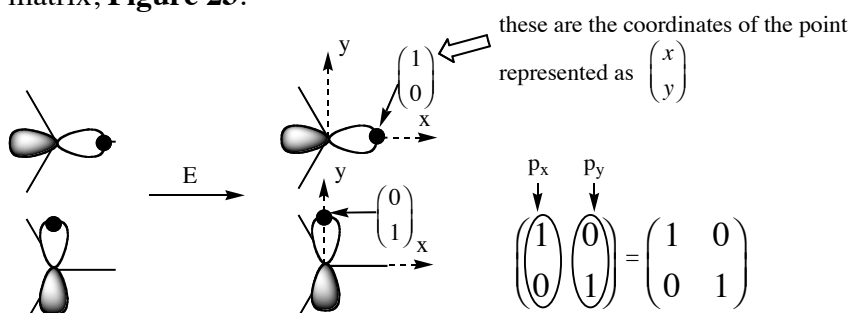


Figure 23 formation of the matrix from which we derive the characters

you will see
matrices in your
theoretical methods
courses

IMPORTANT

- The character is the **trace** which is the sum of the diagonal elements of this matrix (this is true of all characters they are the trace of matrices that represent the symmetry operations)
- to determine the irreducible representation we have to find the character of this matrix after each symmetry operation (of the D_{3h} point group)
 - we already know that under E p_x and p_y remain the same, thus the character is the trace of the matrix in **Figure 23**: $1+1=2$.
 - another example: under σ_v (**Figure 24**) the character is $1+(-1)=0$

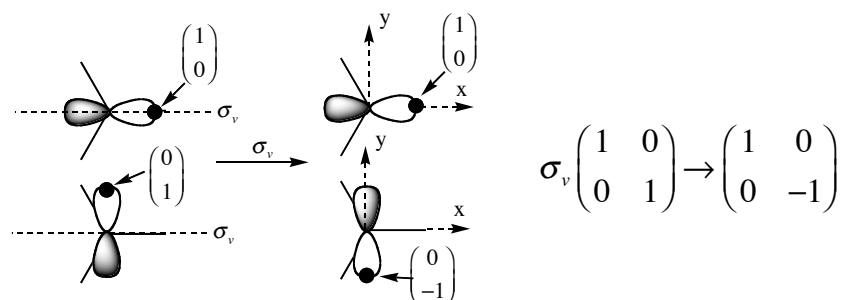


Figure 24 transformation of the p_x and p_y AOs under σ_v

In-Class Activity

- What is the character of the degenerate p_x and p_y AOs under the C_2 axis?
 - HINT: pick the easiest C_2 axis to work with, ie the one that is aligned with one of the orbitals
 - check your answer against the character table

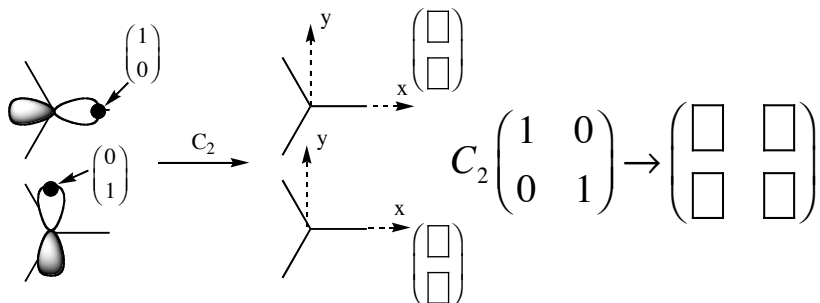


Figure 25 transformation of the p_x and p_y AOs under C_2

- If you want a more detailed explanation on degeneracy there is **supporting information** in the document "Degenerate representations" on my web-site.

Improper Rotations

- improper rotations are a rotation followed by a reflection in the plane perpendicular to the rotation axis.
- for D_{3h} the S_3 axis is the C_3 axis, and the reflection plane is the σ_h plane (Figure 26)

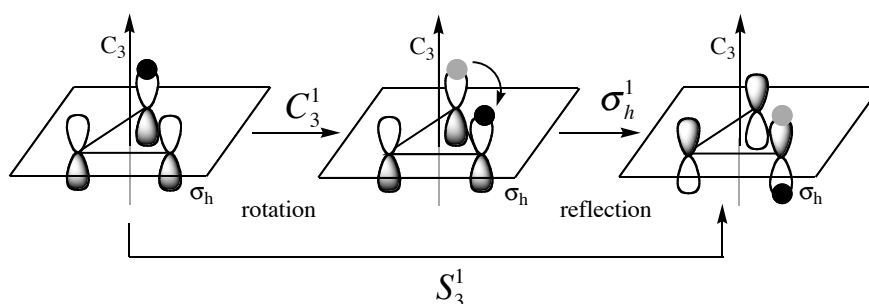


Figure 26 Components of S_3^1 improper rotation

IMPORTANT

- phase changes are very important for improper rotations, one of the best ways to visualise improper rotations is to use pAOs as shown above.
- When n is odd it takes improper rotations two full rotations about the principle axis to return the system to its starting point, ie $S_3^6 = E$.

Equivalent Operations

- if any operations are identical only one is included in the character table
- normally the operation that is "kept" is the one furthest to the left along the list of operations, however if it is axes, then the operation around the axis with the lowest n is retained.
- for example there are six possible S_3 operations under D_{3h} , but in the header row listing the symmetry operations for D_{3h} , only $2S_3$ operations are listed. S_3^1 is unique, but $S_3^2 = C_3^2$ and $S_3^3 = \sigma_h^1$ (Figure 27), C_3 and σ_h are further to the left than S_3 and so S_3^2 and S_3^3 are not included in the count of S_n operations

- if you work out all of the S_3^n operations up to S_3^6 you will find that there are only 2 unique operations (tutorial/homework problem!) and so we have $2S_3$ in the header row of the D_{3h} character table.

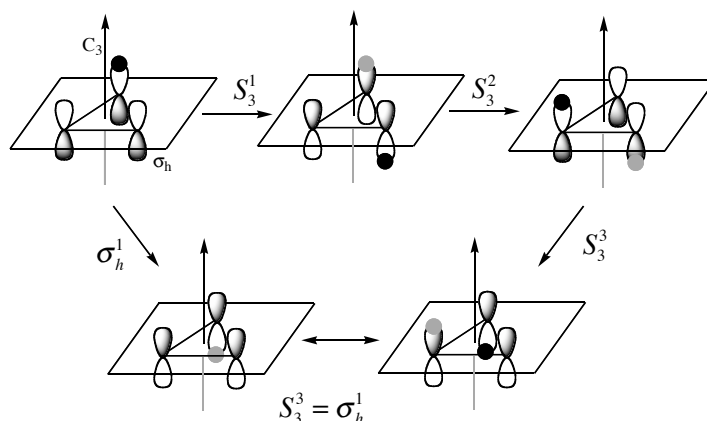


Figure 27 S_3^3 operation of the D_{3h} point group

- If you are finding improper rotations confusing there is **supporting information** in the document "Improper rotations of the D_{3h} point group" on my web-site.
- If you want something a bit **more challenging** there is the document "Improper rotations of the O_h point group" on my web-site.

Key Points

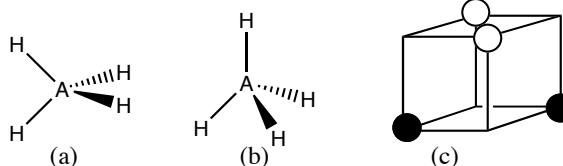
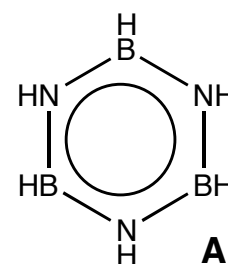
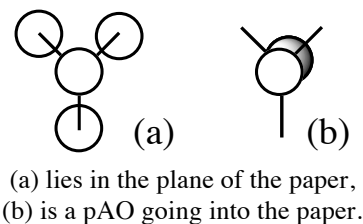
- be able to write a definition for "symmetry element", "symmetry operation" and "symmetry operator"
- be able to draw clear diagrams showing the symmetry elements of a molecule, and showing the action of symmetry operations on a molecule
- be able to define the components of a character table including: character, irreducible representation, and symmetry label
- be able to determine the symmetry label for a given MO
- be able to identify when operations in the header row of the character table are greater than one due to multiple symmetry elements, or multiple symmetry operations
- be able to identify the degeneracy of an irreducible representation from its symmetry label
- be able to determine the characters for degenerate representations
- be able to perform S_n operations
- be able to identify unique and non-unique symmetry operations

Online Resources

- Use my web-site it has lots of additional material
http://www.huntresearchgroup.org.uk/teaching/year2_mos.html
- copies of the slides (to print AND to watch)
- notes from the lecture
- the flow chart and character tables
- a link to the Panopto recordings (you will need to login)
- extra material (basics for beginners and more challenging material for the advanced)
- interesting links related to the lecture
- model answers to all the in-class problems
- model answers to the self-study problems and exam preparation

Self-study Problems / Exam Preparation

- The BH_3 molecule
 - determine the point group of BH_3 and on a molecule of BH_3 draw all of the symmetry elements
 - what is the correct axial orientation and why?
 - determine the symmetry label for the molecular orbitals shown above
 - construct a representation table for the "z-axis" and determine which irreducible representation it transforms as.
- What is the general procedure to determine the symmetry label of a molecular orbital? (*in your own words, use bullet points!*)
- What is the general procedure to determine the character of a degenerate set of orbitals? (*in your own words, use bullet points!*)
- Work out all of the S_3^n operations up to S_3^6 .
 - Show for the $\text{D}_{3h} \text{H}_3^+$ system that there are only two unique S_3 operations.
 - Which operation is S_3^4 equivalent to? Draw a diagram clearly illustrating this equality.
- Borazine (A) belongs to the D_{3h} point group. On a sketch of borazine illustrate and label the symmetry elements of the D_{3h} point group. (2007/8 exam question, worth 4 marks)
- More challenging: Discuss and illustrate the symmetry operations of the T_d point group.
 - **hint:** there are three useful ways of thinking about a tetrahedral molecule, each one emphasises a different aspect of symmetry:
 - (a) the C_2 axes
 - (b) the C_3 axes
 - (c) the cubic structure



Deeper Questions

- Here are some questions aimed to promote reflective thinking about today's material. Contact me if you want to discuss any of these points.
 - Swap the x and y axes and re-evaluate the symmetry of the H_2O MOs
 - Has changing the axial orientation changed the symmetry labels?
 - All of them, some of them, none of them?
 - Is this important?