

# Molecular Orbitals in Inorganic Chemistry

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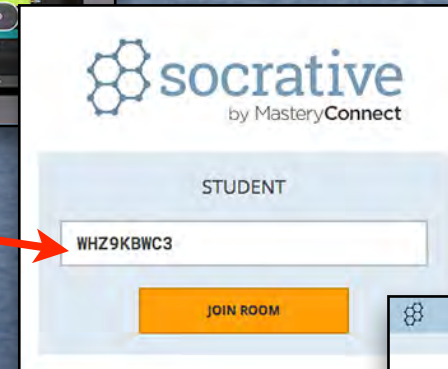
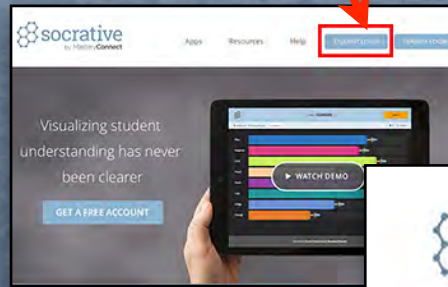
# Resources

## Use Socrative

- ◆ [www.socrative.com](http://www.socrative.com)
- ◆ student login!!
- ◆ join

**WHZ9KBWC3**

- ◆ wait for me to start the test quiz
- ◆ complete the quiz!!



quiz will appear  
on your device



# Resources

## Web

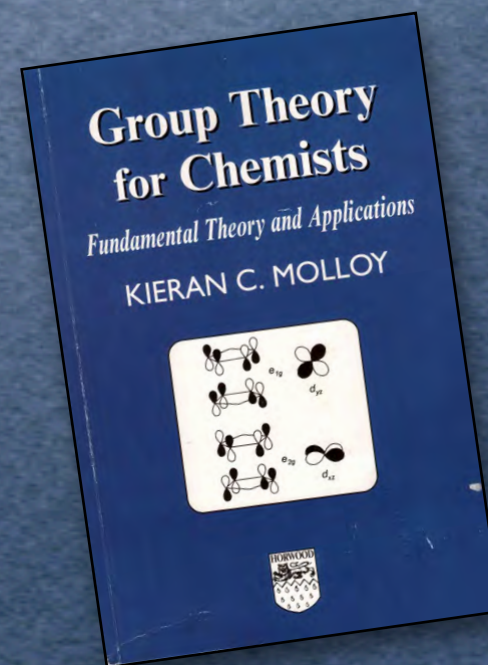
- ◆ notes AND slides
- ◆ link to panopto when it becomes available
- ◆ model answers to “in class activity” questions
- ◆ model answers to self-study problems / exam prep
- ◆ optional background support for beginners
- ◆ questions answered section (from student queries)
- ◆ files for visualising MOs
- ◆ optional material to for experts
- ◆ links to interesting people and web-sites
- ◆ links to relevant research papers on MOs

## Reading

- ◆ **OPTIONAL** background material, supports lectures adds more details and explanation
- ◆ some elective reading is advisable
- ◆ if you are interested in a wider perspective and more complex problems see me!

## Recommended Text

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



# Resources

## Find my web page

- ◆ type “Hunt theoretical chemistry” into search engine
- ◆ top hit should be my website

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

- ◆ click on teaching
- ◆ under Year Two
- ◆ find Molecular Orbitals in Inorganic Chemistry
- ◆ goto Lecture 1
- ◆ click on “slides as presented in the lecture”

your website is a god send when you miss out one little part or need something clarified

I really like that model answers to the tutorial problems are online. This was very helpful because I could look through them myself

Hunt Research Group

Home Contacts Profile Papers Talks Research Group Openings **Teaching** Links

**Hunt Research Group**

The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modelling.

Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to **ionic-liquids** and **deep eutectic solvents**.

We study the making and breaking of molecules. This includes **catalytic mechanisms** (for group II and frustrated lewis acid-base pairs) and chemical **decomposition** (for green fuels, bio-fuels and ionic-liquids).

Overarching all of these areas is a specialisation in **hydrogen-bonding**, acid-base interactions and an

5th October 2019

Hunt Research Group

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**Teaching**

Hunt Group main page

**Year One**

- Year 1 Computational Chemistry Lab

**Year Two**

- **Molecular Orbitals in Inorganic Chemistry**
- Spectroscopy and Characterisation II
- 3d rotatable orbitals of CH<sub>4</sub>
- Year 2 Computational Chemistry Lab

**Year Three**

- Year 3 Computational Chemistry Lab
- Chemistry wiki

**Links**

**General Chemistry**

- socratic
- web elements
- periodic table of videos from the University of Nottingham, short videos about each element of the periodic table.
- chemistry apples
- leeds chemistry experiments for demonstration, photos and some live as video clips
- Compound Interest a blog which explains the chemistry of or in everyday items, for example glow sticks, tomatoes, painkillers

## Lecture 1

(updated for 2016)

1. slides from the lecture for printing: [pdf](#)
2. slides as presented in the lecture: [high resolution pdf 19.1 MB](#)
3. slides as presented in the lecture: [low resolution pdf 1.4 MB good for mobile devices](#)
4. notes from the lecture: [pdf](#)
5. flow chart and character tables handouts (bring to class every week!):
  - [flow-chart](#)
  - [character tables](#)
6. resources related to this lecture [optional](#)
  - a bit more detail on how to find the characters for degenerate representations [pdf](#)
  - how to find the improper rotations for the D<sub>3h</sub> point group [pdf](#)
  - extra for [experts](#), improper rotations for the O<sub>h</sub> point group [pdf](#)
  - Part 1: Symmetry from [Group Theory for Chemists](#)
  - if you like doing things in a problem based format the following is very good, Programme 1: Symmetry Elements and Operations from [Molecular Symmetry and Group Theory](#) (2nd Edition), Alan Vincent, John Wiley & Sons Ltd, Chichester, 2001.
  - imperial chemistry department [symmetry web-site](#) has 3D movable examples of symmetry elements for water [good](#)
7. famous theoreticians: [optional](#)
  - in 2009 Prof. Eisenstein a theoretical chemist recieved the American Chemical Society award for organometallic chemistry [Interview with Prof Eisenstein](#)
  - [Emily Carter](#) Professor in Energy and the Environment Princeton University and elected as a Fellow of the American Chemical Society in 2012
  - [Sharon Hammes-Schiffer](#) elected as a Member of the National Academy of Sciences, 2013
  - the nobel prize in chemistry 1981 went to [Fukui and Hoffmann](#)
  - the nobel prize in chemistry 1998 went to [Kohn and Pople](#)
  - the nobel prize in physics 2008 went to [Yoichiro Nambu, Makoto Kobayashi, Toshihide Maskawa](#)
  - the nobel prize in chemistry 2013 went to [Martin Karplus, Michael Levitt, Arieh Warshel](#)
  - Who was [Christopher Longuet-Higgins?](#)

# Lecture 1 Outline

## ● introduction

- ◆ why study MO theory
- ◆ what this course is about

## ● revision: symmetry

- ◆ symmetry operations, elements and operators
- ◆ point groups and flow chart

## ● character tables

- ◆ what is a character table?
- ◆ using a character table
- ◆ multiple symmetry operations
- ◆ degenerate symmetry labels
- ◆ improper rotations
- ◆ equivalent symmetry operations

# Why Study MO Theory?

## Supersedes VSEPR theory

- ◆ valence shell electron pair repulsion theory
- ◆ VSEPR predicts  $O_2$  diamagnetic (paired electrons) the experimental evidence is that  $O_2$  is paramagnetic (unpaired electrons)

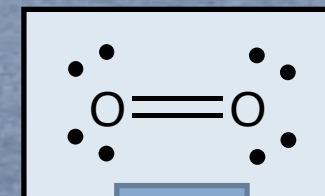


Fig. 1

## Supersedes Crystal Field Theory

- ◆ dAOs are split by the field of the ligands
- ◆ negative ligands should produce a larger  $\Delta_{oct}$
- ◆ but experimentally it is found that F- ligands have a smaller  $\Delta_{oct}$  than  $H_2O$

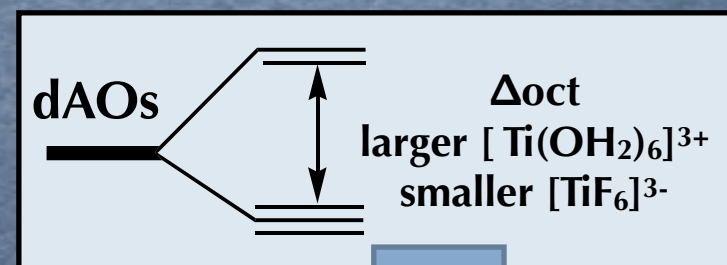


Fig. 2

## Required for "odd" bonding situations

- ◆ structure of ethane is well known, diborane  $B_2H_6$  was assumed to be similar!
- ◆ while a 2nd year undergraduate, H. Christopher Longuet-Higgins proposed the structure of diborane together with his tutor R. Bell

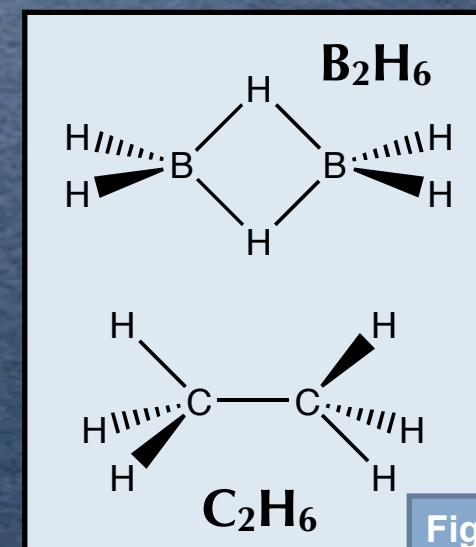


Fig. 3

# The Course

- **Learning how to describe and use symmetry**
- **Learning how to construct 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**
- **All relating back to other chemistry courses**
  - ◆ Main group chemistry, Organometallic and Coordination chemistry, Crystal and Molecular Architecture,
  - ◆ Theoretical Methods, Quantum Mechanics, Electronic Properties of Solids
- **Labs and workshops**
  - ◆ computational chemistry labs
  - ◆ your final year research project

# Why Study MO Theory?

## Nobel prize in 1981

- ◆ Kenichi Fukui
- ◆ Roald Hoffmann

“orbital symmetry interpretation of chemical reactions”

## Nobel prize in 1998

- ◆ Walter Kohn
- ◆ John Pople

for the development of modern computational methods





# Why Study MO Theory?

## ACS Organometallic Chemistry Award

◆ Odile Eisenstein

specialises in the use of quantum theoretical methods for the study of catalytic mechanisms

## Nobel prize in 2013

- ◆ Martin Karplus
- ◆ Michael Levitt
- ◆ Arieh Warshel



Fig. 5

Odile Eisenstein, reproduced with permission

“development of multiscale models for complex chemical systems”

Fig. 6 [http://nobelprize.org/nobel\\_prizes/chemistry/laureates](http://nobelprize.org/nobel_prizes/chemistry/laureates)

# Symmetry

## ● Were have you met symmetry already?

- ◆ equivalent H or C atoms in NMR
- ◆ chirality
- ◆ labelling of atomic orbitals
- ◆ s and p orbitals
- ◆ octahedral transition metal complexes
- ◆ isomerisation: cis/trans fac/mer staggered/eclipsed chair/boat

## ● Where understanding symmetry is crucial

- ◆ MO diagrams => photoelectron spectrum
- ◆ determines form of HOMO and LUMO => reactivity
- ◆ stereo-electronic effects => organic mechanisms
- ◆ symmetry breaking => Jahn-Teller distortions
- ◆ determines allowed vibrations => IR and Raman spectrum
- ◆ determines electronic interactions => dipole moment, UV-vis spectrum

# Point Group

## Examples

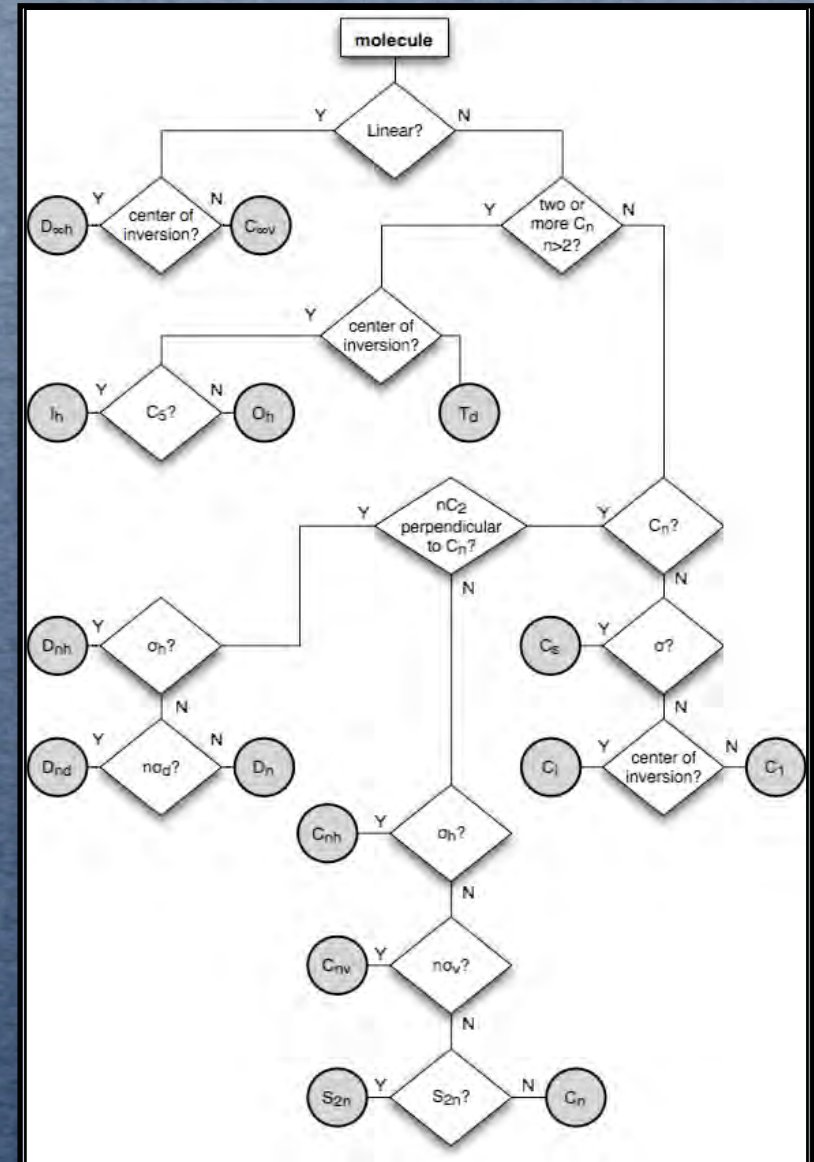
◆  $C_{2v}$   $D_{\infty h}$   $T_d$

## Use the flow chart from last year

◆ available in your exam

## Determined by the number and type of symmetry operations

Flow chart is on the web site



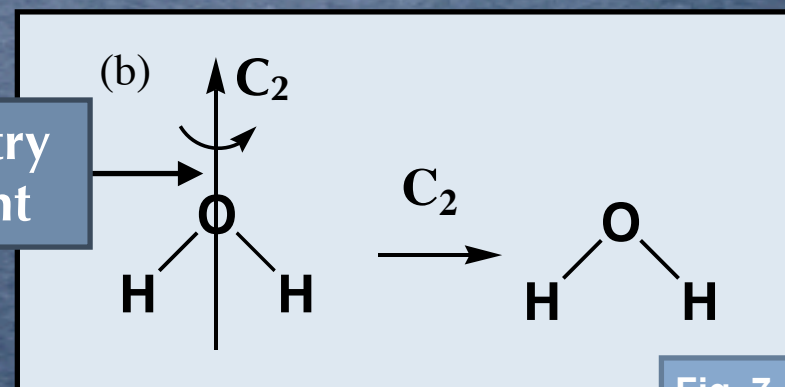
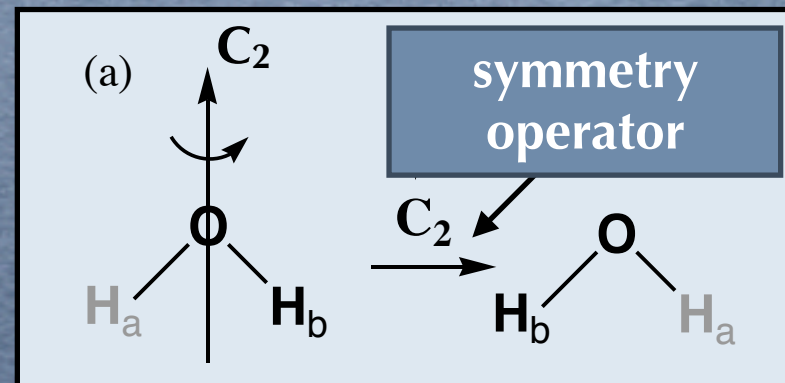
# Symmetry Operations

## Physical act of performing a motion

- ◆ example physical rotation of water around  $C_2$  axis
- ◆ if nuclei are labeled specific atoms move
- ◆  $H_a$  and  $H_b$  exchange places (O rotates in place)

## Initial and final states are identical with respect to nuclei

you should be able to draw neat diagrams showing symmetry operations



$C_2$  operation

Fig. 7

# Symmetry Elements

## Symmetry elements

- ◆ objects about which symmetry operations occur
- ◆ rotation axis
- ◆ reflection plane
- ◆ inversion point

see Figure 8 in your notes  
for revision of different  
symmetry elements

## Include axial information

- ◆ always put an axis definition on your diagram
- ◆ correctly orientate the axial system
- ◆ z-axis is aligned along the highest n-axis
- ◆ watch out for diatomics!
- ◆ z-axis is along the bond (why?)

**Important!**

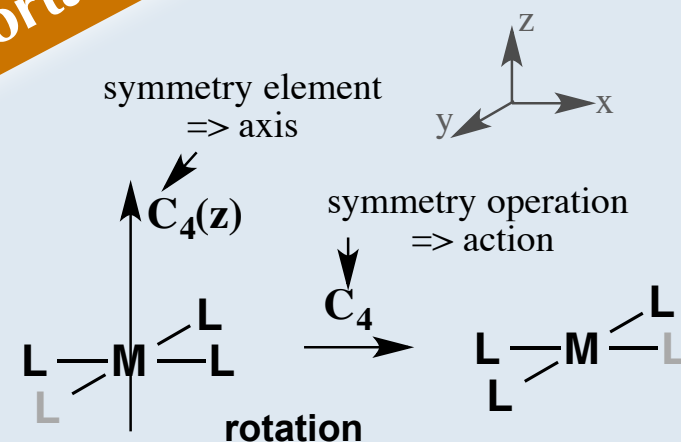


Fig. 8

# Symmetry Operators

## ● Symmetry operator

- ◆ mathematical representation of the action
- ◆ operator “acts on” the wavefunction or molecule (hence brackets)

## ● Advanced (not required)

- ◆ operator is a matrix
- ◆ ie  $C_2$  rotation matrix

Chemical Bonding course

Math courses

Spectroscopy and  
Characterisation course

Quantum mechanics

operator  $C_2$  acts  
on wavefunction

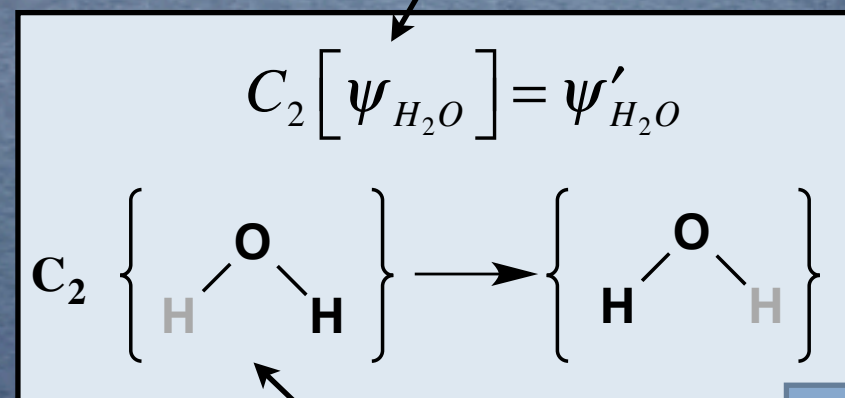


Fig. 9

operator  $C_2$  acts  
on molecule

# Same Notation!

## Symmetry operation

- ◆ the act of performing a motion

## Symmetry elements

- ◆ objects about which symmetry operations occur

## Symmetry operator

- ◆ mathematical representation of the action

$C_2$  operation

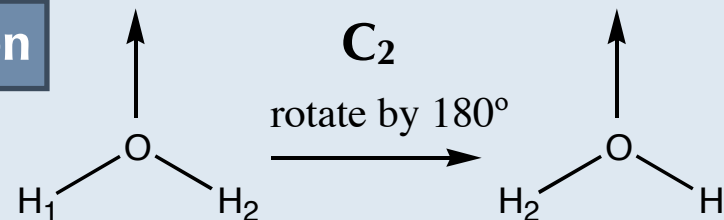


Fig. 7

$C_2$  element

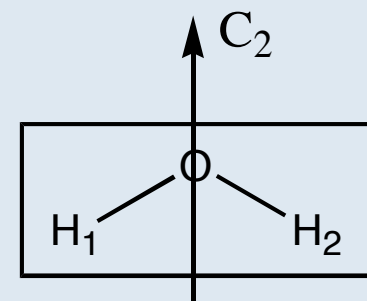


Fig. 8

$C_2$  operator

$$C_2 [\psi_{H_2O}] = \psi'_{H_2O}$$

Fig. 9

# Example: H<sub>2</sub>O

## Symmetry elements for H<sub>2</sub>O:

- ◆ identity E
- ◆ C<sub>2</sub> rotation axis
- ◆ reflection plane  $\sigma_v(yz)$
- ◆ reflection plane  $\sigma_v(xz)$

## Flow chart for identifying the point group

- ◆ is the molecule linear? NO
- ◆ are there two or more C<sub>n</sub> N>2? NO
- ◆ is there a C<sub>n</sub>? YES
- ◆ are there nC<sub>2</sub> perpendicular to C<sub>n</sub>? NO
- ◆ is there a  $\sigma_h$ ? NO
- ◆ is there a  $\sigma_v$ ? YES

point group: C<sub>2v</sub>

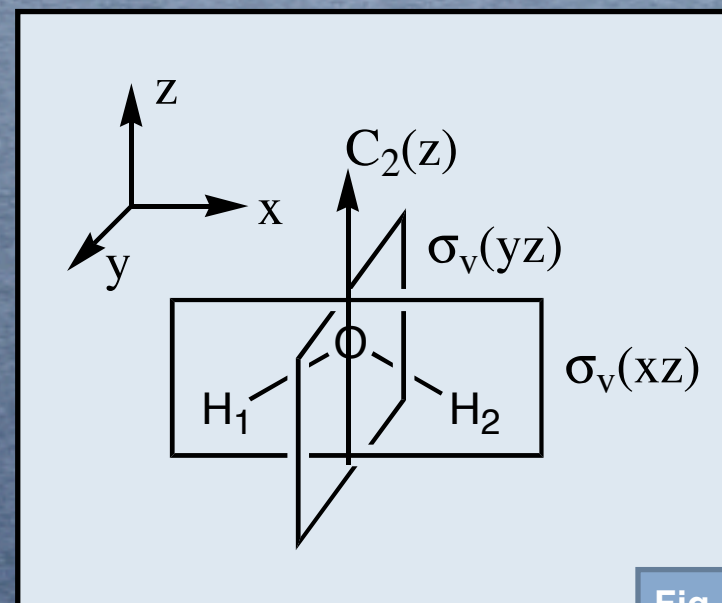


Fig. 10



# In-Class Activity

socratic quiz!

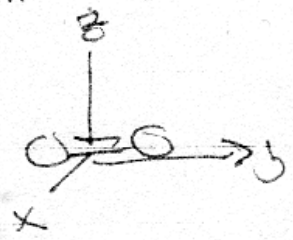
WHZ9KBWC3

- The question was part of an exam and related to a MO diagram for  $O_2$

what is wrong with this answer!

write in this margin

di point group @  $C_{2v}$



write in this margin

Fig. 11

- ◆ What is the point group of this molecule?
- ◆ The z-axis should align ...
- ◆ The principle axis is ...

# In-Class Activity

What is wrong with this answer to part of the 2006 exam?

- ◆ wrong point group
- ◆ wrong principle axis

What is the point group of this molecule?

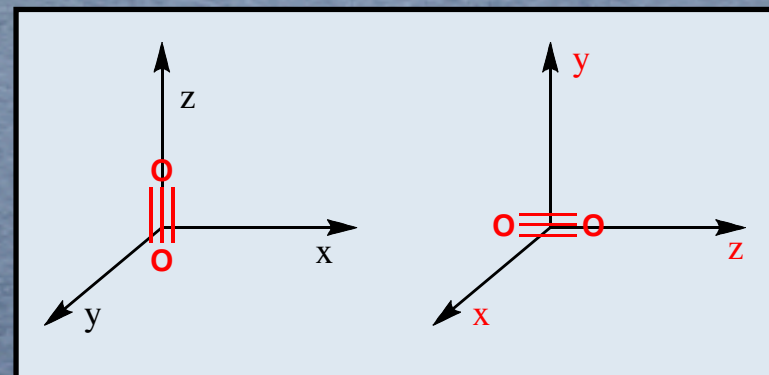
- ◆ point group:  $D_{\infty h}$

The z-axis should align ...

- ◆ along the bond
- ◆ with the principle axis of the molecule

The principle axis is ...

- ◆ principle axis is highest C axis,  $C_{\infty}$  axis



Problems?

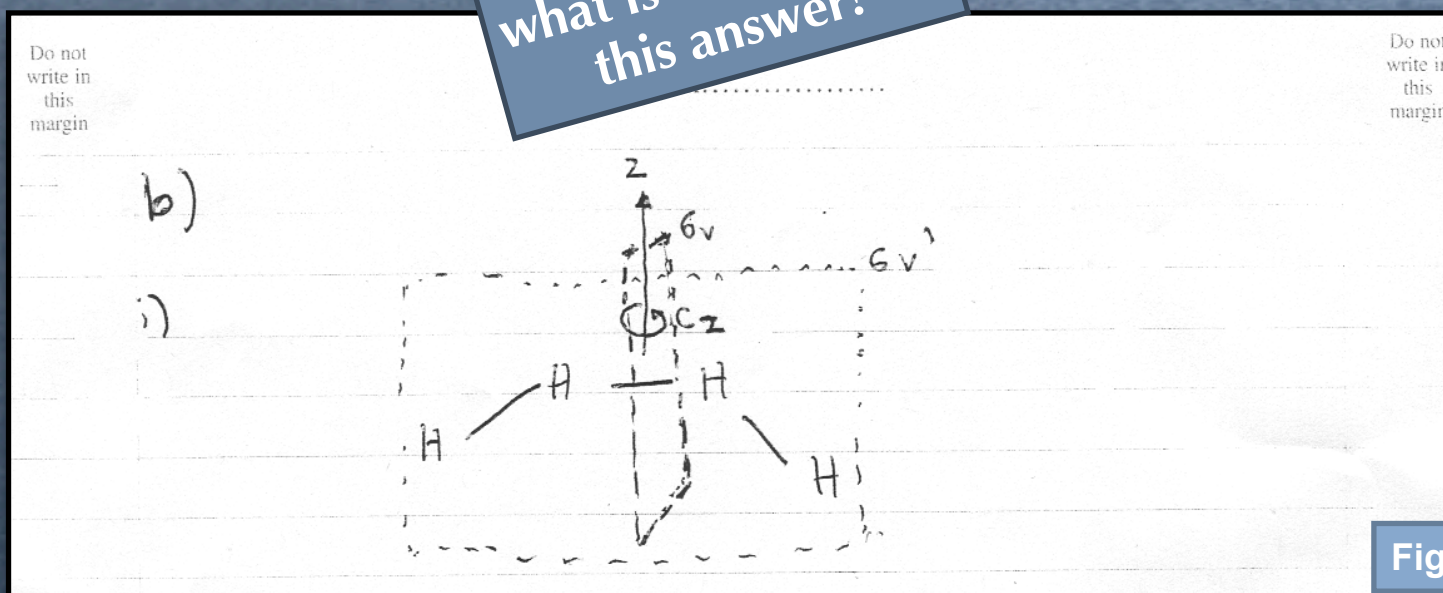
see Revision notes

Additional material  
on my web-site

# In-Class Activity

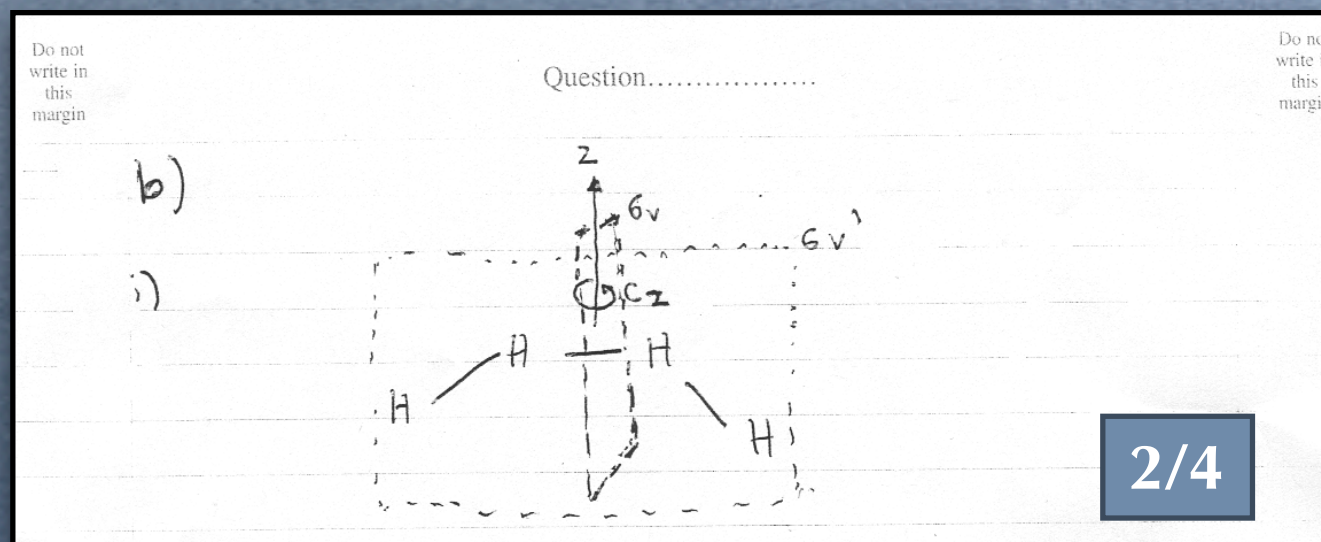
- The question "Given this molecule of cis-H<sub>2</sub> clearly indicate all of the symmetry elements on a diagram. (4 marks)"

what is wrong with this answer!



# In-Class Activity

## What is wrong with this answer?"



what is wrong?

- does not include an axis definition
- does not include axial information in element names

what is correct?

- all of the symmetry elements identified and drawn on the molecule
- molecule is correctly orientated
- diagram is tidy and clear

# Character Tables

## key part of this course is learning how to use character tables

- ◆ determine symmetry of MOs
- ◆ other uses not covered in this course ... but covered next year in

Advanced  
Spectroscopy

## character table handout

- ◆ includes character tables of all main symmetry groups
- ◆ a copy of these character tables will be available to you in the exam

Bring a copy to  
EVERY lecture!

$C_{2v}$  character table

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h=4$
$A_1$	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

Fig. 13

# Character Table Components

symmetry operations

number of symmetry operations

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h=4$
$A_1$	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

symmetry labels

symmetry of cartesian axes

irreducible representation

1's and -1's are characters

# Using Character Tables

- best way to understand character table is to use it
- example: lowest energy MO of water
  - s atomic orbital on each of the H and O atoms
- H<sub>2</sub>O has C<sub>2v</sub> symmetry so use C<sub>2v</sub> character table
- start by constructing a representation table:

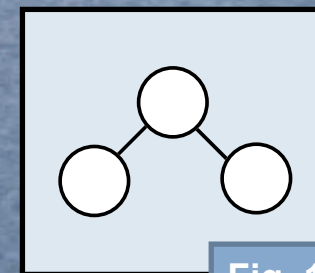
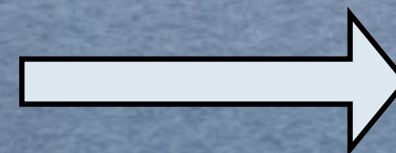


Fig. 14

unknown representation

symmetry operations  
as in character table

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

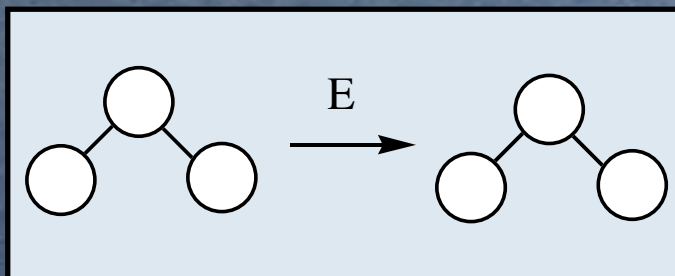
Fig. 15

# Using Character Tables

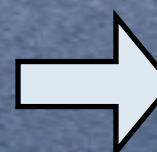
- Determine how the orbital transforms under each symmetry operation of the group

- ◆ orbital is unchanged => character=1
- ◆ a sign change => character= -1

symbol representing a character



No change under E



$$\chi = 1$$

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} \right\}$	<b>1</b>			

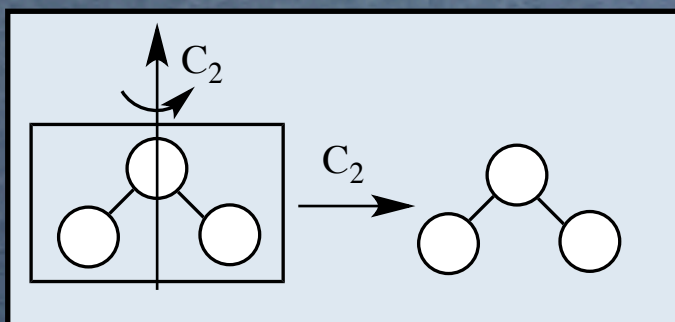
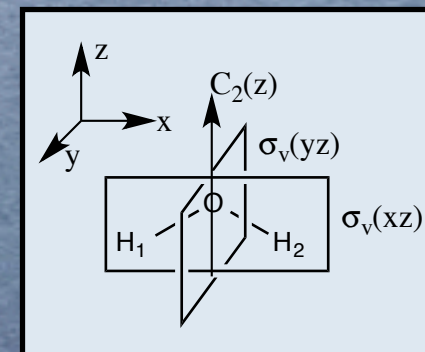
Fig. 16



# Using Character Tables

● Determine how the orbital transforms under each symmetry operation of the group

- ◆ orbital is unchanged => character=1
- ◆ a sign change => character= -1



No change under  $C_2$

$\chi = 1$

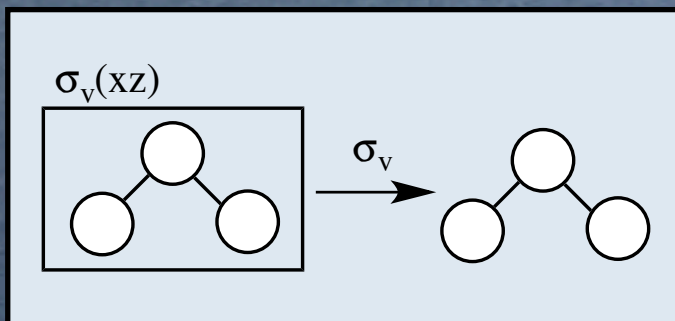
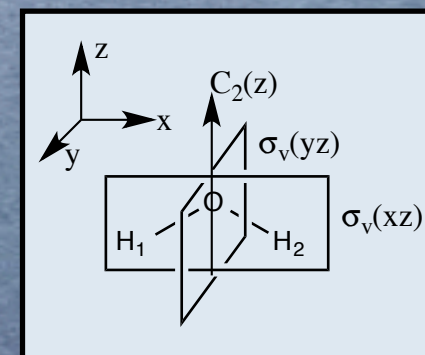
$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array} \right\}$	<b>1</b>	<b>1</b>		

Fig. 16

# Using Character Tables

● Determine how the orbital transforms under each symmetry operation of the group

- ◆ orbital is unchanged => character=1
- ◆ a sign change => character= -1



No change under  $\sigma_v$

$$\chi = 1$$

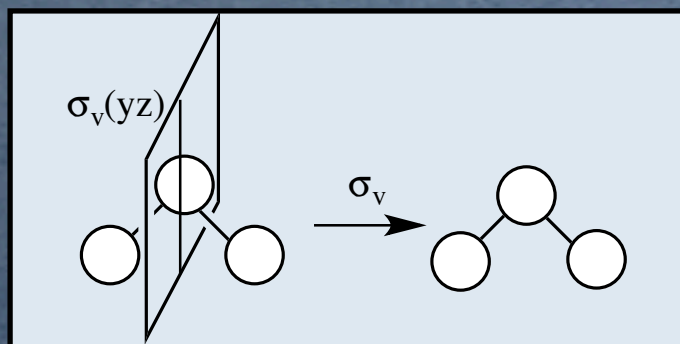
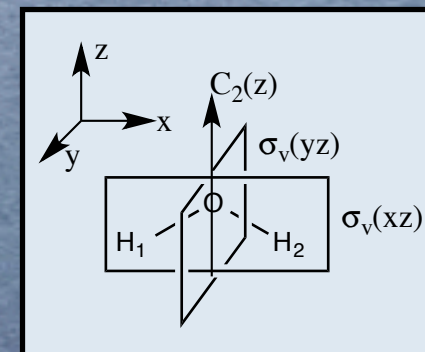
$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \right\}$	<b>1</b>	<b>1</b>	<b>1</b>	

Fig. 16

# Using Character Tables

● Determine how the orbital transforms under each symmetry operation of the group

- ◆ orbital is unchanged => character=1
- ◆ a sign change => character= -1



No change under  $\sigma_v$

$$\chi = 1$$

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} \right\}$	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>

Fig. 16

# Using Character Tables

same set of characters  
as the irreducible  
representation  $a_1$

Use lower case when  
for the symmetry  
label of MOs

$A_1 \rightarrow a_1$

upper case letters are  
reserved for vibrations  
and states

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \circ \\ \diagdown \quad \diagup \\ \circ \quad \circ \end{array} \right\}$	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$	
<b><math>A_1</math></b>	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

Fig. 17

# In-Class Activity

## the second highest energy MO for water

- out of phase s atomic orbitals on the hydrogen atoms and a  $p_x$  atomic orbital on the oxygen atom

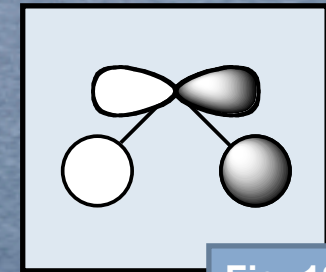
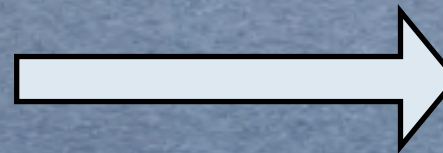
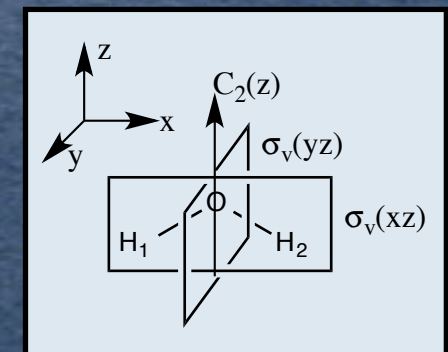
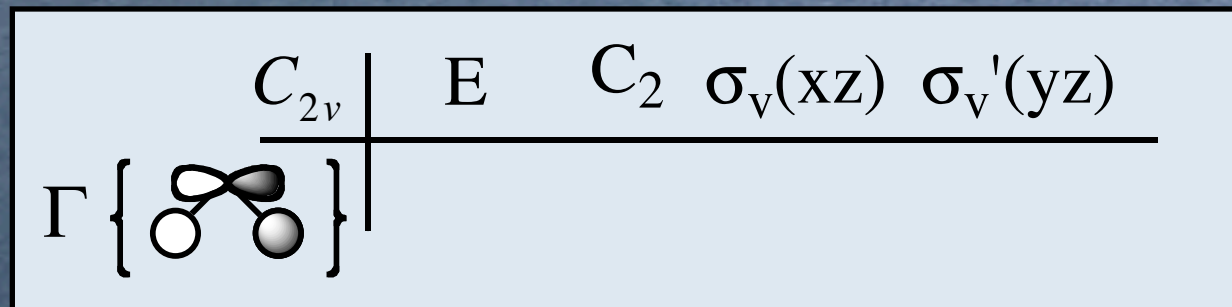
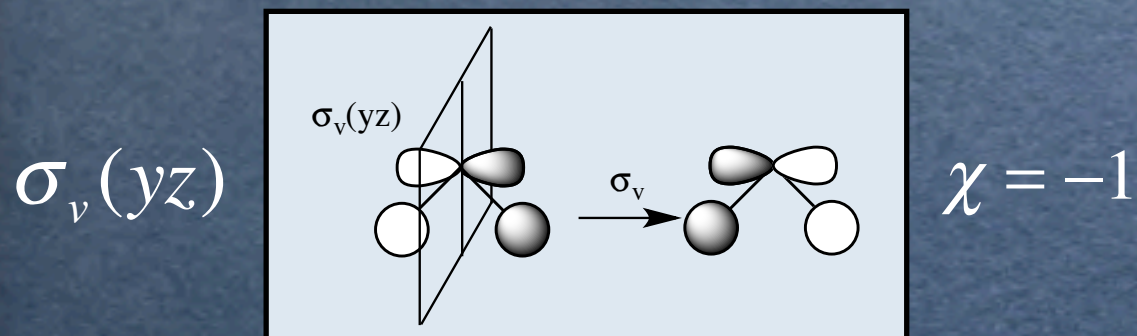
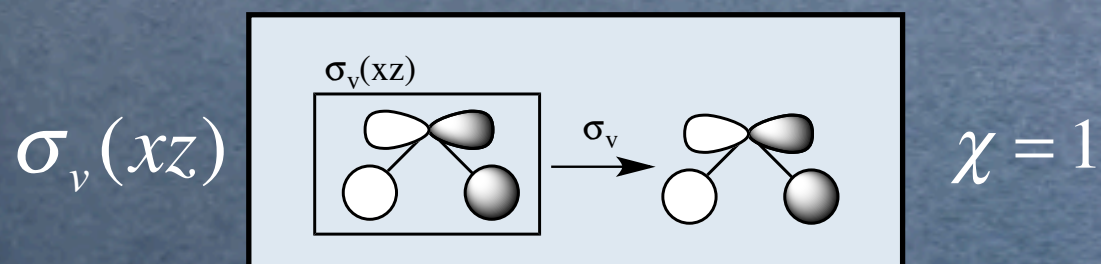
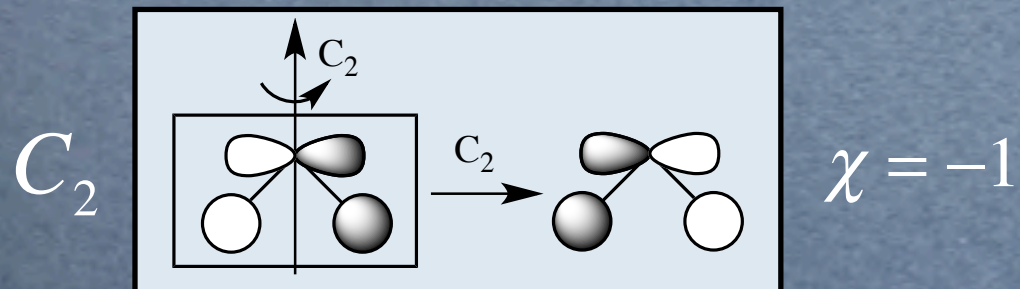


Fig. 18

your turn:

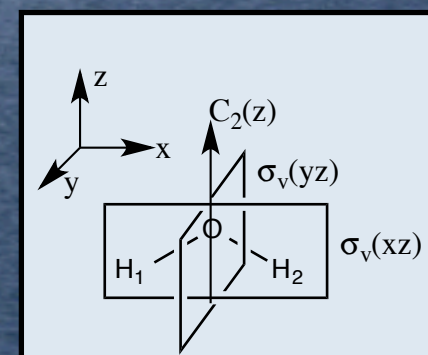


# In-Class Activity

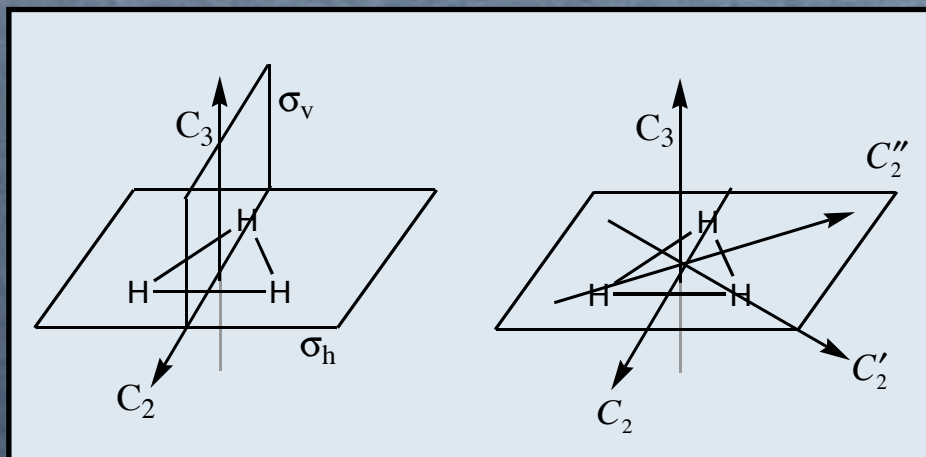


$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \text{orbital} \\ \text{diagram} \end{array} \right\}$	<b>1</b>	<b>-1</b>	<b>1</b>	<b>-1</b>

this orbital has  $b_1$  symmetry



# D<sub>3h</sub> Character Table



Find the D<sub>3h</sub> character table in your set of Character Tables

D <sub>3h</sub>	E	2C <sub>3</sub>	3C <sub>2</sub>	σ <sub>h</sub>	2S <sub>3</sub>	3σ <sub>v</sub>	
A <sub>1</sub> '	1	1	1	1	1	1	
A <sub>2</sub> '	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T <sub>x</sub> , T <sub>y</sub> )
A <sub>1</sub> "	1	1	1	-1	-1	-1	
A <sub>2</sub> "	1	1	-1	-1	-1	1	T <sub>z</sub>
E"	2	-1	0	-2	1	0	

Fig. 19

# $D_{3h}$ Character Table

- Show by example
- Use simple molecule
- $H_3$  or  $H_3^+$
- Planar equilateral triangle
- H common orbital fragment
  - ◆  $BH_3$ ,  $NH_3$ ,  $ER_3$ ,  $ML_3$  etc
- Model for heavier elements
  - ◆ such as  $Au_3$
  - ◆ highest active orbital is 6s orbital

## $H_3^+$ is interesting!

- ◆ Most abundant ion in universe
- ◆ Important for interstellar chemistry
- ◆ Use spectroscopy to detect new interstellar species, also provide information on interstellar chemical and physical conditions

## Links on the web-site

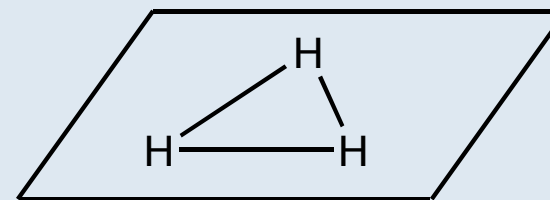


Fig. 20



# Multiple Operations

## ● Symmetry operations of $D_{3h}$

- ◆ 1 E identity
- ◆ 2  $C_3$  rotations
- ◆ 3  $C_2$  rotations
- ◆ 1  $\sigma_h$  reflection
- ◆ 2  $S_3$  improper rotations
- ◆ 3  $\sigma_v$  reflections

## ● number of operations

## ● $h$ =total number of operations

- ◆  $=1+2+3+1+2+3=12$

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	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	

Fig. 19

# 2C<sub>3</sub> Rotations

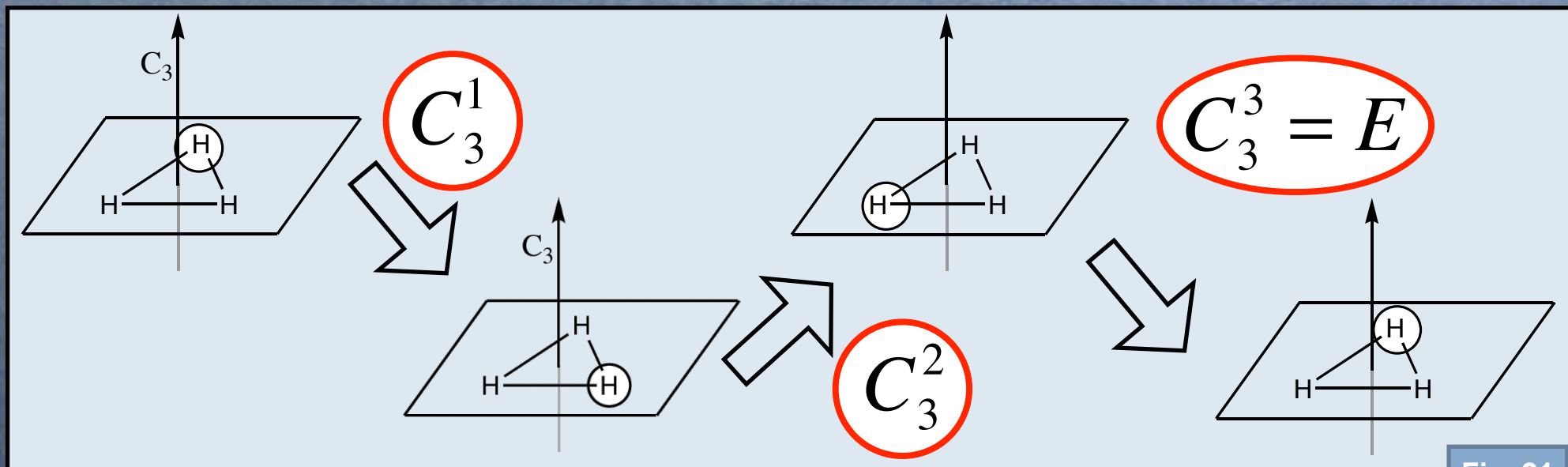


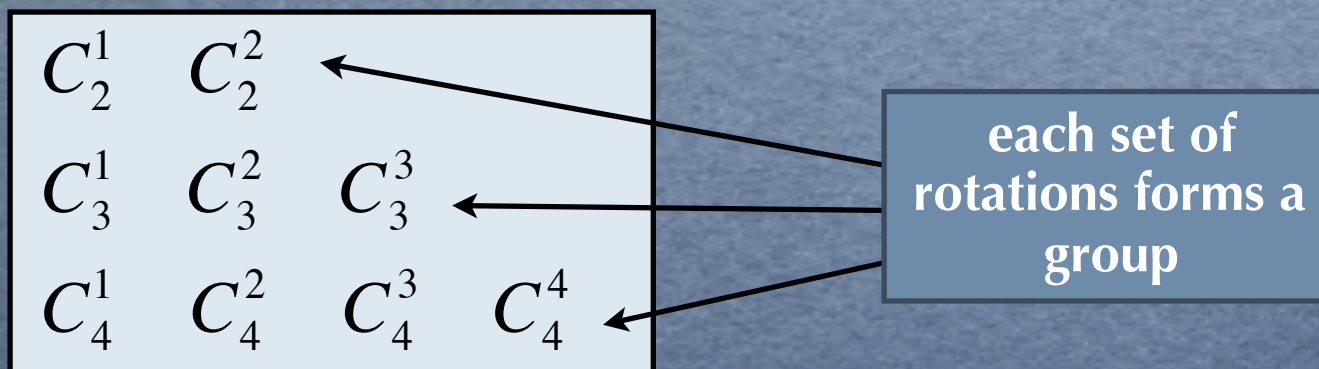
Fig. 21



# Rotations in General

● Each rotation of order  $n$  has  $n$  rotations

● for example



● final rotation returns to starting geometry = E

● 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

● rotation groups

- ◆ mathematical entities
- ◆ whole area of mathematics devoted to groups

# 3C<sub>2</sub> Rotations

- three separate C<sub>2</sub> axes
- each contributes one C<sub>2</sub> rotation
- find one C<sub>2</sub> axis and use C<sub>3</sub> to find the rest
- each element is distinct: C<sub>2</sub> C'<sub>2</sub> C''<sub>2</sub>

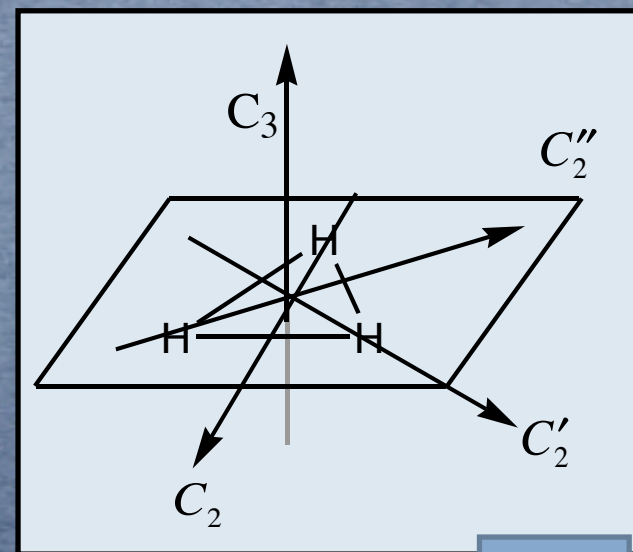
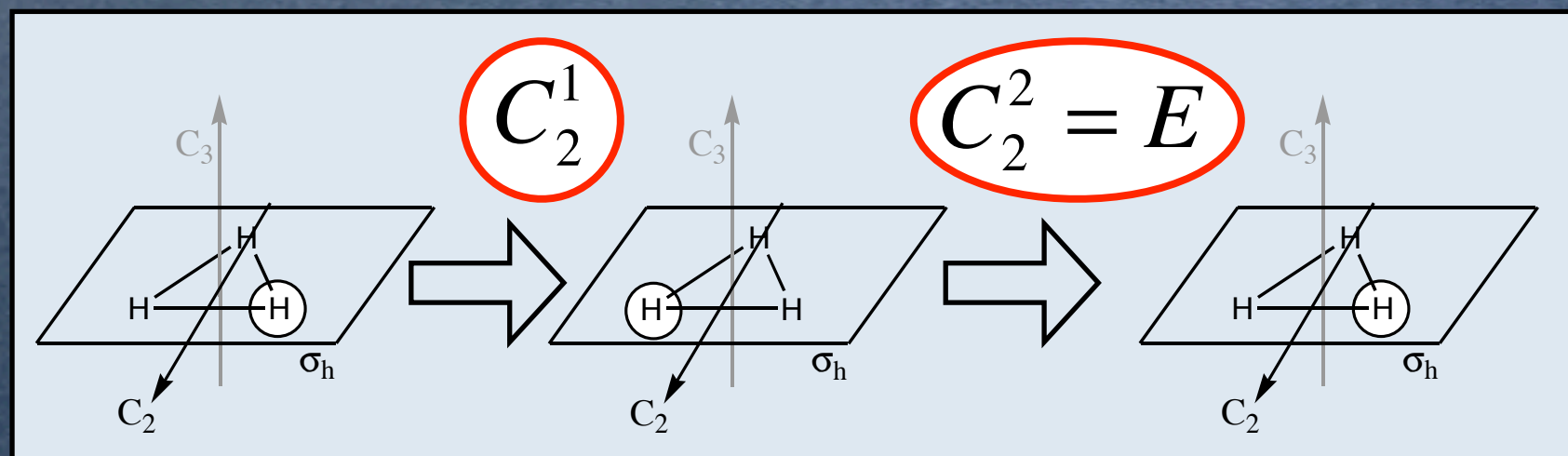


Fig. 22



# Multiple Operations

## 2C<sub>3</sub> and 3C<sub>2</sub> appear in the character table of D<sub>3h</sub>

- ◆ it doesn't matter if these are the SAME or DIFFERENT symmetry elements
- ◆ the table only "cares" about operations

$E$     $2C_3$     $3C_2$     $\sigma_h$     $2S_3$     $3\sigma_v$

one element  
3 operations

$C_3^1$     $C_3^2$     $C_3^3$



$C_2$     $C_2'$     $C_2''$

three elements  
3 operations

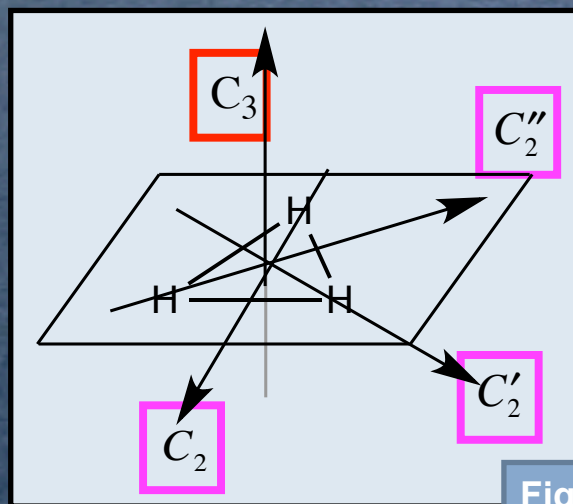


Fig. 22

# Symmetry Labels

## A and B single representations

◆ atoms/orbitals map onto each other

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	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	

Fig. 19

# Symmetry Labels

## A and B single representations

- ◆ atoms/orbitals map onto each other

## E doubly degenerate

- ◆ don't confuse with E operation!
- ◆ orbitals as a group map onto each other
- ◆ character = 2 under E operation

## T triply degenerate

- ◆ tetrahedral point groups (Td)
- ◆ character = 3 under E operation

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	
$A_2'$	1	1	-1	1	1	-1	
<b>E'</b>	<b>2</b>	-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	$T_z$
<b>E''</b>	<b>2</b>	-1	0	-2	1	0	

Fig. 19

# Symmetry Labels

## A and B single representations

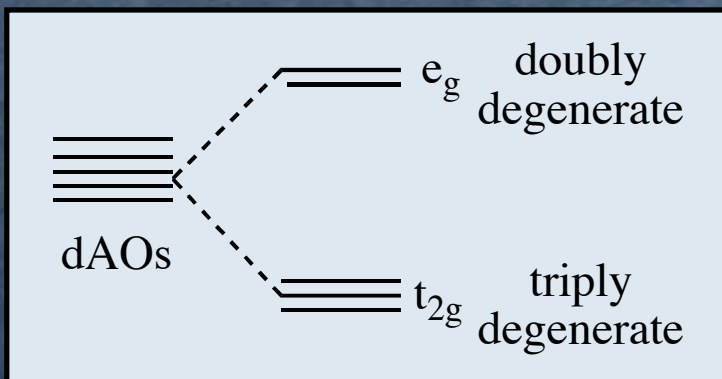
- ◆ atoms/orbitals map onto each other

## E doubly degenerate

- ◆ don't confuse with E operation!
- ◆ orbitals as a group map onto each other
- ◆ character = 2 under E operation

## T triply degenerate

- ◆ tetrahedral point groups (Td)
- ◆ character = 3 under E operation



$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	
$A_2'$	1	1	-1	1	1	-1	
<b>E'</b>	<b>2</b>	-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	$T_z$
<b>E''</b>	<b>2</b>	-1	0	-2	1	0	

Fig. 19

You have already  
seen e and t  
symmetry labels!



# Degenerate Representations

## degenerate representations

- ◆ example:  $(p_x, p_y)$  have  $e'$  symmetry in  $D_{3h}$

touched on in your  
maths course

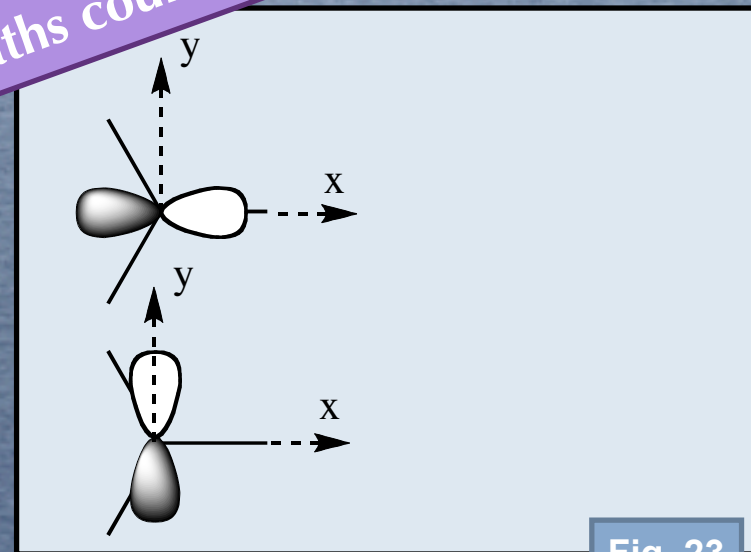
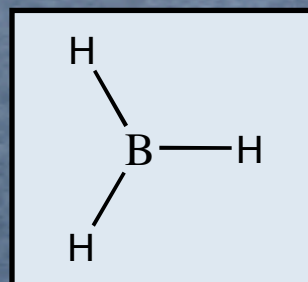


Fig. 23

# Degenerate Representations

## degenerate representations

◆ example: ( $p_x, p_y$ ) have  $e'$  symmetry in  $D_{3h}$

## character refers to BOTH components

◆ how to work out the character?

◆ take point on tip of each orbital

◆ write the position in coordinates as

$$\begin{pmatrix} x \\ y \end{pmatrix}$$

◆ form matrix by combing the coordinates

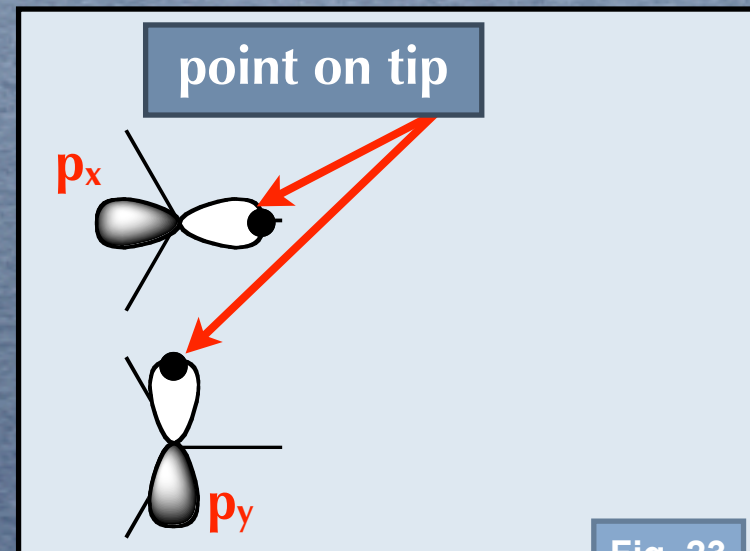


Fig. 23

$$\begin{matrix} p_x & p_y \\ \downarrow & \downarrow \\ \begin{pmatrix} 1 \\ 0 \end{pmatrix} & \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{matrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

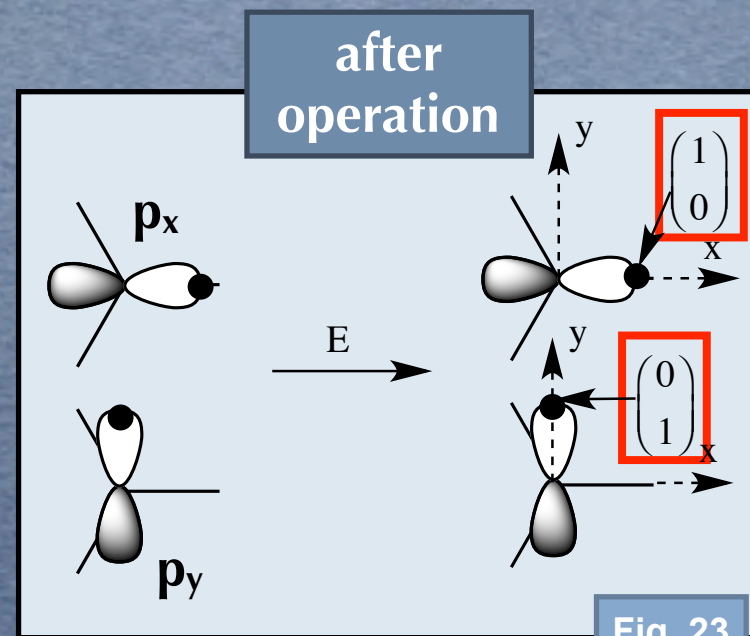
# Degenerate Representations

## degenerate representations

◆ example:  $(p_x, p_y)$  have  $e'$  symmetry in  $D_{3h}$

## character refers to BOTH components

- ◆ how to work out the character?
- ◆ take point on tip of each orbital
- ◆ write the position in coordinates as  $\begin{pmatrix} x \\ y \end{pmatrix}$
- ◆ form matrix by combing the coordinates
- ◆ perform the operation



$$E \begin{pmatrix} p_x & p_y \\ \downarrow & \downarrow \\ 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

# Degenerate Representations

## degenerate representations

◆ example: ( $p_x, p_y$ ) have  $e'$  symmetry in  $D_{3h}$

## character refers to BOTH components

- ◆ how to work out the character?
- ◆ take point on tip of each orbital
- ◆ write the position in coordinates as  $\begin{pmatrix} x \\ y \end{pmatrix}$

- ◆ form matrix by combing the coordinates
- ◆ perform the operation
- ◆ the character is the TRACE of this matrix
- ◆ trace=sum of diagonal terms
- ◆ for this example (E) trace=1+1=2
- ◆ character is 2

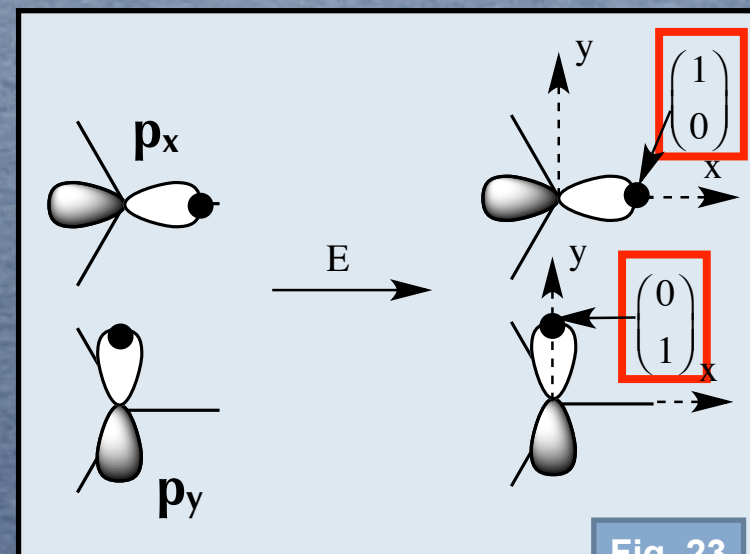
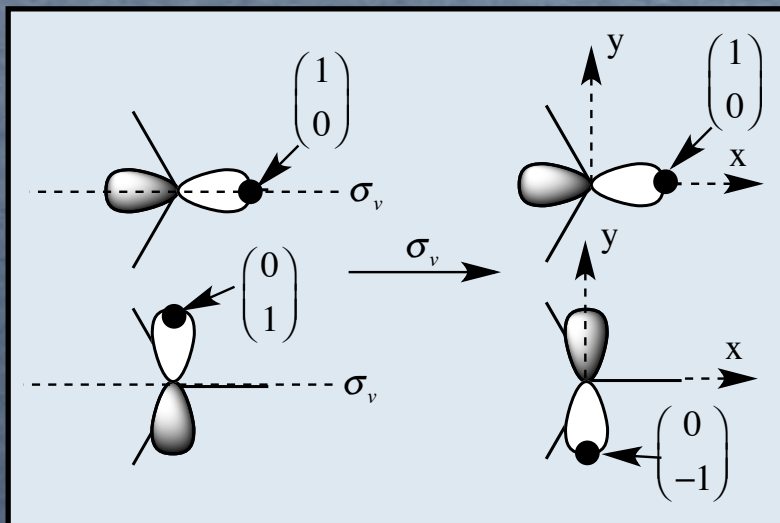


Fig. 23

$$E \begin{pmatrix} p_x & p_y \\ \downarrow & \downarrow \\ 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

# Degenerate Representations

the character for the  $\sigma_v$  operation under  $D_{3h}$



$$\sigma_v \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Fig. 24

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	
$A_2'$	1	1	-1	1	1	-1	
<b>E'</b>	2	-1	0	2	-1	<b>0</b>	<b>(<math>T_x, T_y</math>)</b>
$A_1''$	1	1	1	-1	-1	-1	
$A_2''$	1	1	-1	-1	-1	1	$T_z$
E''	2	-1	0	-2	1	0	

OPTIONAL: More details about degenerate representations on my web-site

# In-Class Activity

- find character for the  $C_2$  operation under  $D_{3h}$

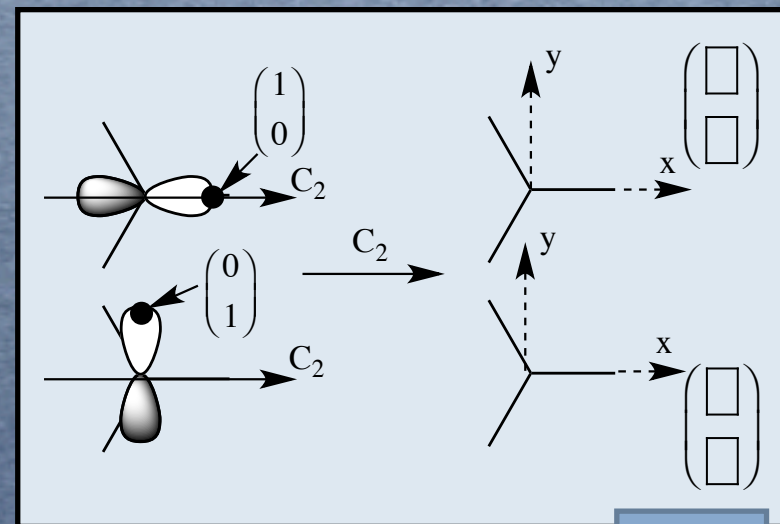
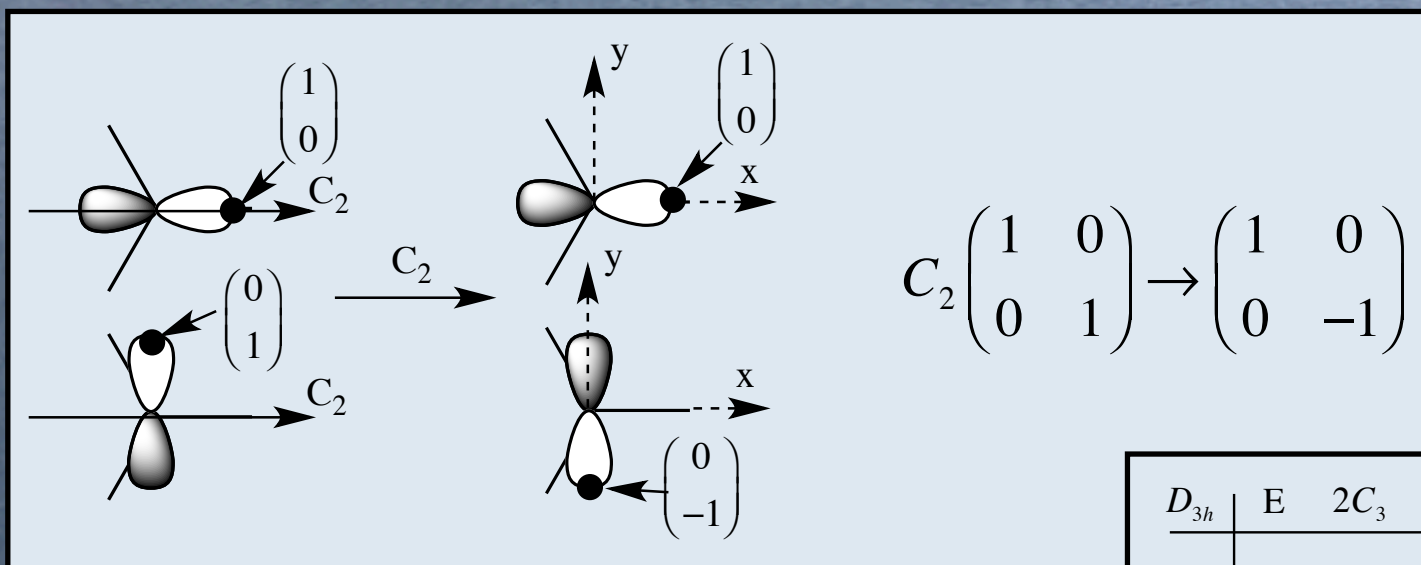


Fig. 25

# In-Class Activity

find character for the  $C_2$  operation under  $D_{3h}$



- ◆ trace=sum of diagonal terms
- ◆ trace=1+-1=0
- ◆ character is 0

$D_{3h}$	E	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A_1'$	1	1	1	1	1	1	
$A_2'$	1	1	-1	1	1	-1	
<b>E'</b>	2	-1	<b>0</b>	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	

Model answer on the web-site

# Improper Rotations

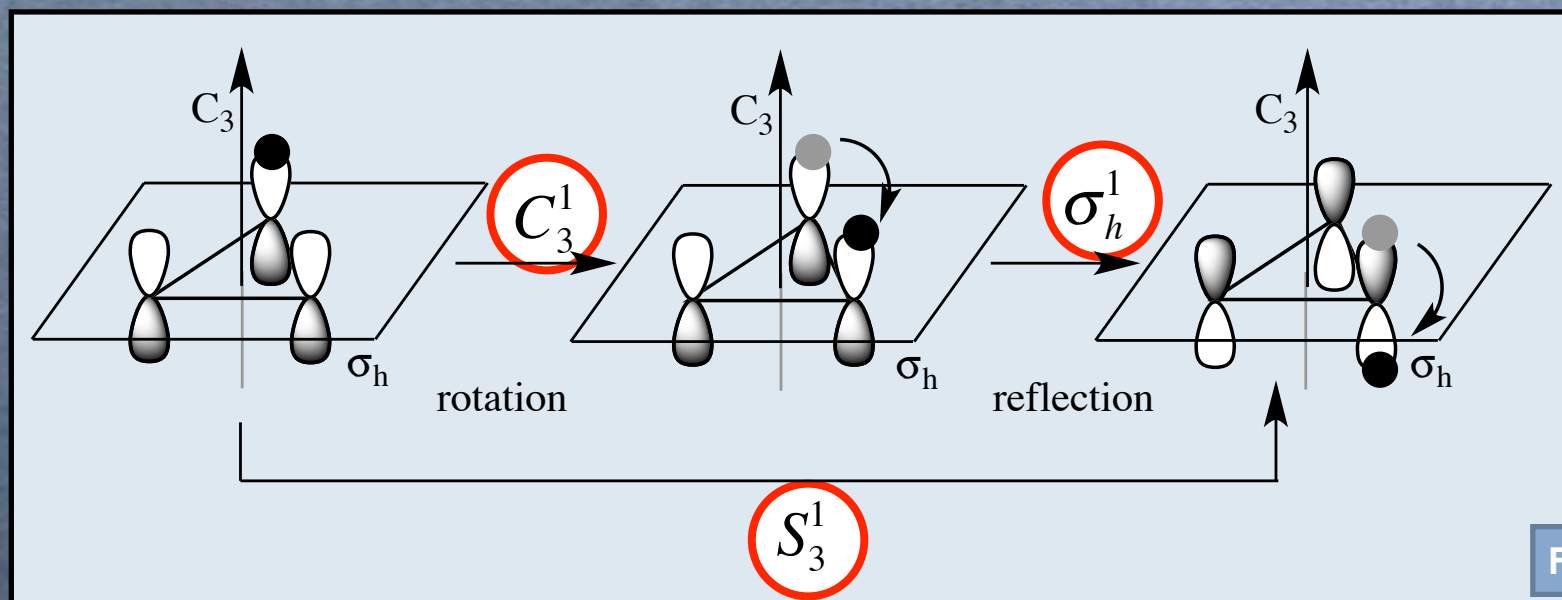


Fig. 26

● rotation followed by reflection in mirror plane perpendicular to the axis of rotation

● phase changes are important

**Important!**

◆ use pAOs to visualise

◆ OR take a point off the mirror plane and axis (black circle above)

● sometimes it requires two full rotations to return to starting state

$$S_3^3 \neq E \quad S_3^6 = E$$



# Equivalent Operations

## ● only keep unique operations

- ◆ “count” symmetry element to the left on the character table
- ◆ does not apply to rotations

## ● count lowest n for $C_n$ operations first

- ◆ for example count  $C_2^1$  over  $C_4^2$

## ● final rotation in a group = E

## ● many improper rotations will have already been counted

- ◆ watch out for odd  $S_n$   $n=\text{odd}$   $S_n^n \neq E$

# Improper Rotations

● diagram showing  $S_3^3 \neq E = \sigma_h$

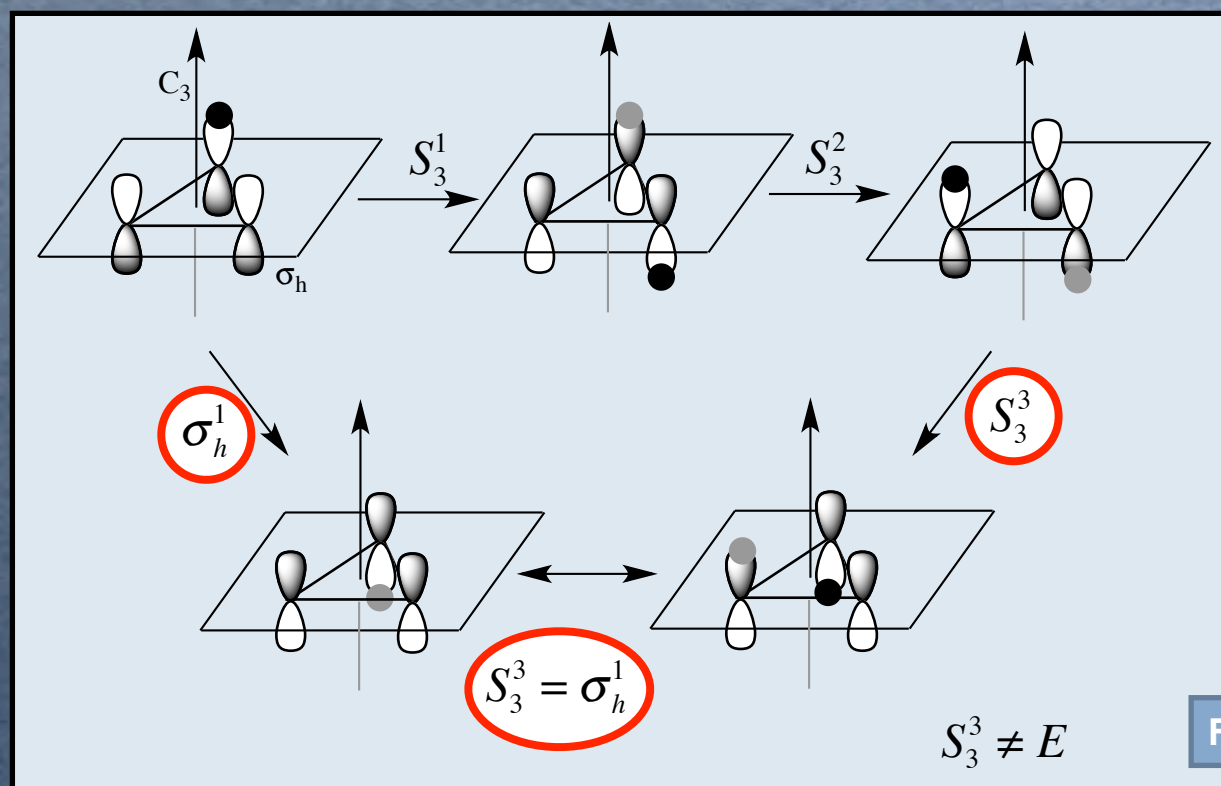


Fig. 27

OPTIONAL: Supporting information about improper rotations on my web-site

# Key Points

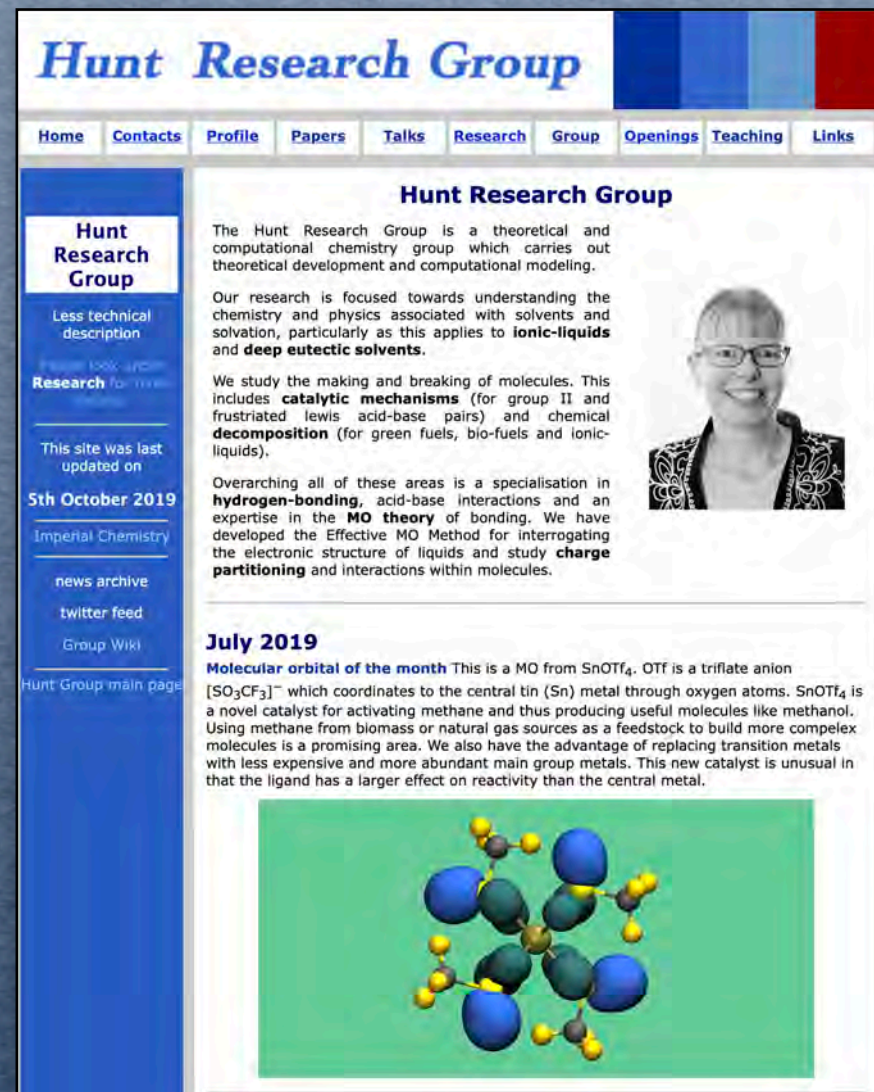
- Be able to define symmetry element, operation and operator
- Be able to draw clear diagrams showing the symmetry elements of a molecule and the action of a symmetry operation
- Be able to define all the components of a character table
- Be able to use character tables to find the symmetry label of MOs
- Be able to identify when operations in the header row are due to multiple symmetry elements or multiple symmetry operations
- Be able to identify degenerate irreducible representations
- Be able to determine the characters of degenerate IRs
- Be able to perform and illustrate  $S_n$  operations
- Be able to identify and show when operations are not unique

# Finally

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

## See my web-site

- ◆ notes AND slides
- ◆ link to panopto when it becomes available
- ◆ optional background support for beginners
- ◆ optional material to take you a little further
- ◆ links to interesting people and web-sites
- ◆ links to relevant research papers on MOs
- ◆ model answers!!



The screenshot shows the homepage of the Hunt Research Group website. The header features the group's name in a blue serif font. A navigation menu includes links for Home, Contacts, Profile, Papers, Talks, Research, Group, Openings, Teaching, and Links. The main content area is divided into a left sidebar and a main text area. The sidebar contains a 'Hunt Research Group' section with a 'Less technical description' link, a 'Research' section, and a date '5th October 2019'. The main text area has a 'Hunt Research Group' heading followed by a paragraph describing the group's focus on theoretical and computational chemistry. A portrait of a woman with glasses is shown to the right. Below this is a 'July 2019' section titled 'Molecular orbital of the month' with a detailed description of a catalyst and a corresponding 3D molecular model.


### Hunt Research Group

The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modeling.

Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to **ionic-liquids** and **deep eutectic solvents**.

We study the making and breaking of molecules. This includes **catalytic mechanisms** (for group II and frustrated Lewis acid-base pairs) and chemical **decomposition** (for green fuels, bio-fuels and ionic-liquids).

Overarching all of these areas is a specialisation in **hydrogen-bonding**, acid-base interactions and an expertise in the **MO theory** of bonding. We have developed the Effective MO Method for interrogating the electronic structure of liquids and study **charge partitioning** and interactions within molecules.



### July 2019

**Molecular orbital of the month** This is a MO from  $\text{SnOTf}_4$ . OTf is a triflate anion  $[\text{SO}_3\text{CF}_3]^-$  which coordinates to the central tin (Sn) metal through oxygen atoms.  $\text{SnOTf}_4$  is a novel catalyst for activating methane and thus producing useful molecules like methanol. Using methane from biomass or natural gas sources as a feedstock to build more complex molecules is a promising area. We also have the advantage of replacing transition metals with less expensive and more abundant main group metals. This new catalyst is unusual in that the ligand has a larger effect on reactivity than the central metal.

