Molecular Orbitals in Inorganic Chemistry

Prof. P. Hunt
p.hunt@imperial.ac.uk
Rm 110F (MSRH)
http://www.ch.ic.ac.uk/hunt/

Resources

- **Use Socrative**
  - www.socrative.com
  - student login!!
  - join

WHZ9KBWC3

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

Resources

Web

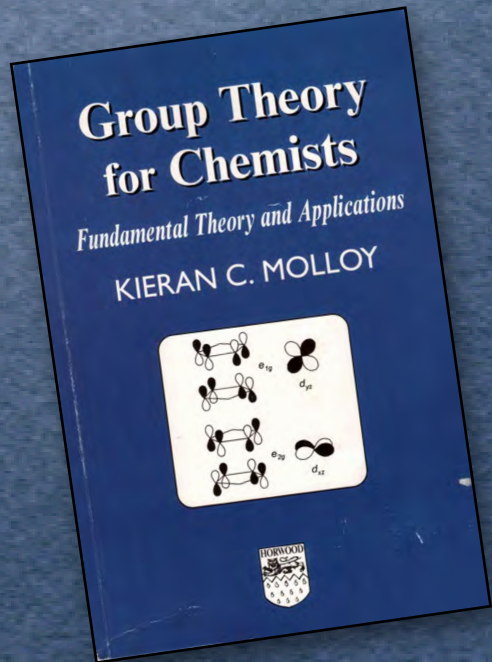
- notes AND slides
- link to panopto when it becomes available
- model answers to “in class activity” questions
- model answers to self-study problems / exam prep
- optional background support for beginners
- questions answered section (from student queries)
- files for visualising MOs
- optional material 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!!



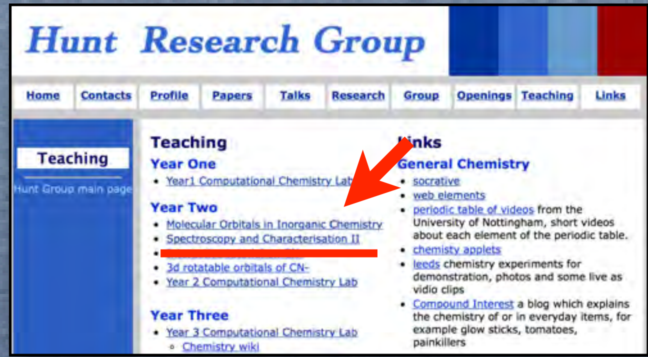
Resources

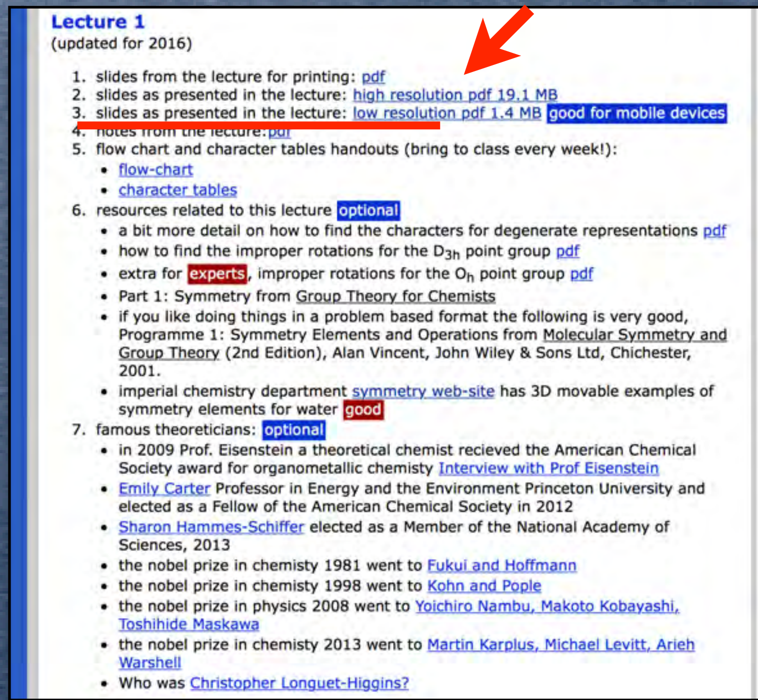
- **Find my web page**
  - type "Hunt theoretical chemistry" into search engine
  - top hit should be my website

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





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)

Supersedes Crystal Field Theory

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

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

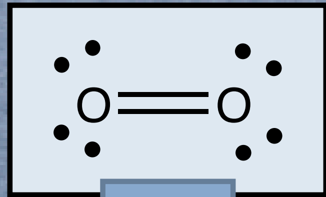


Fig. 1

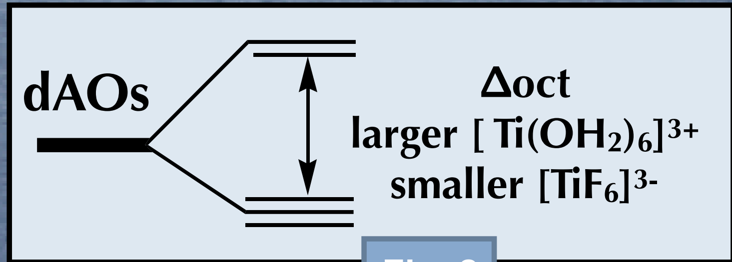


Fig. 2

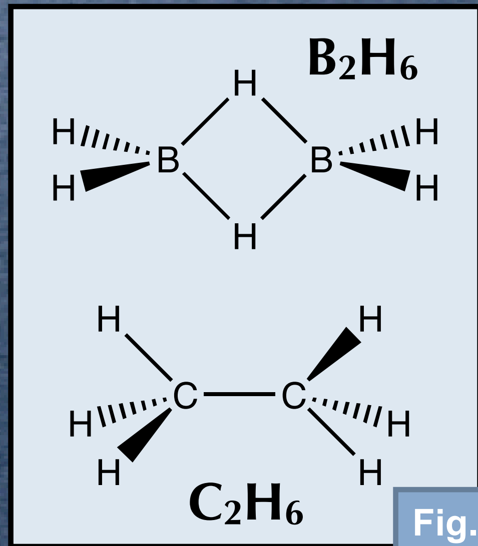


Fig. 3

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

http://nobelprize.org/nobel_prizes/chemistry/laureates

Fig.4

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”

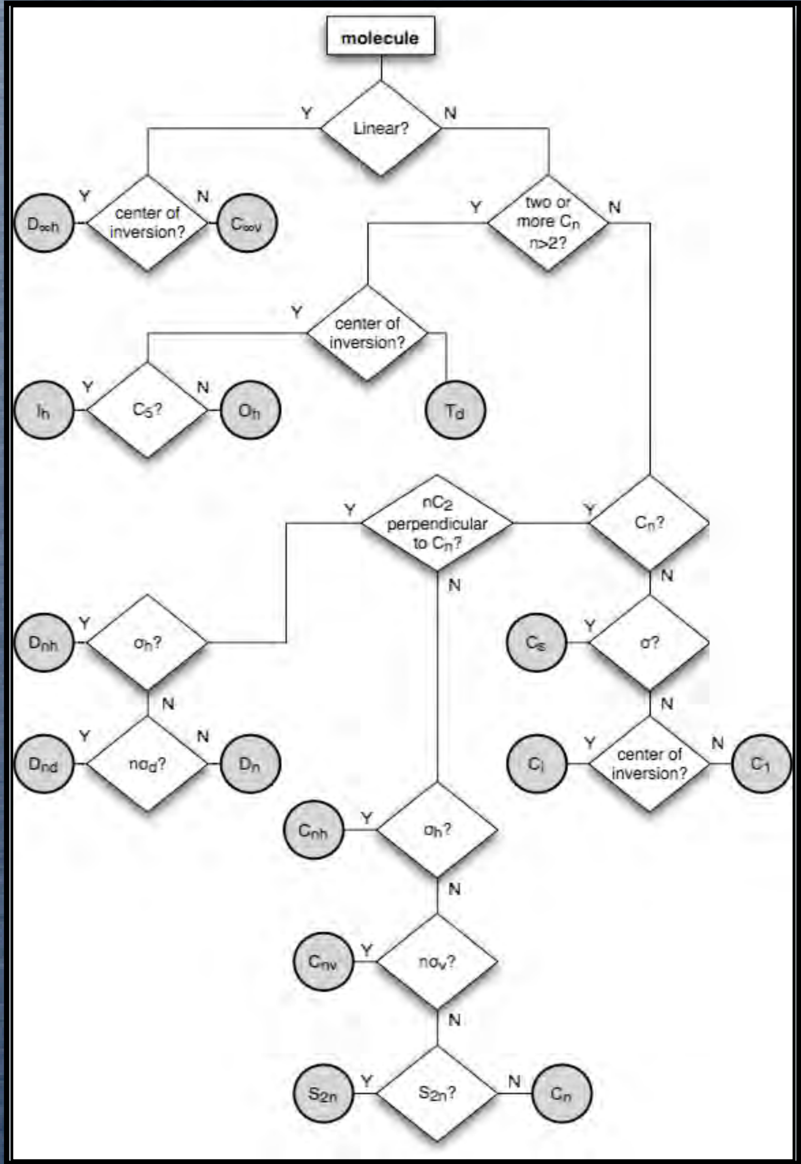
Fig. 6 http://nobelprize.org/nobel_prizes/chemistry/laureates

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**

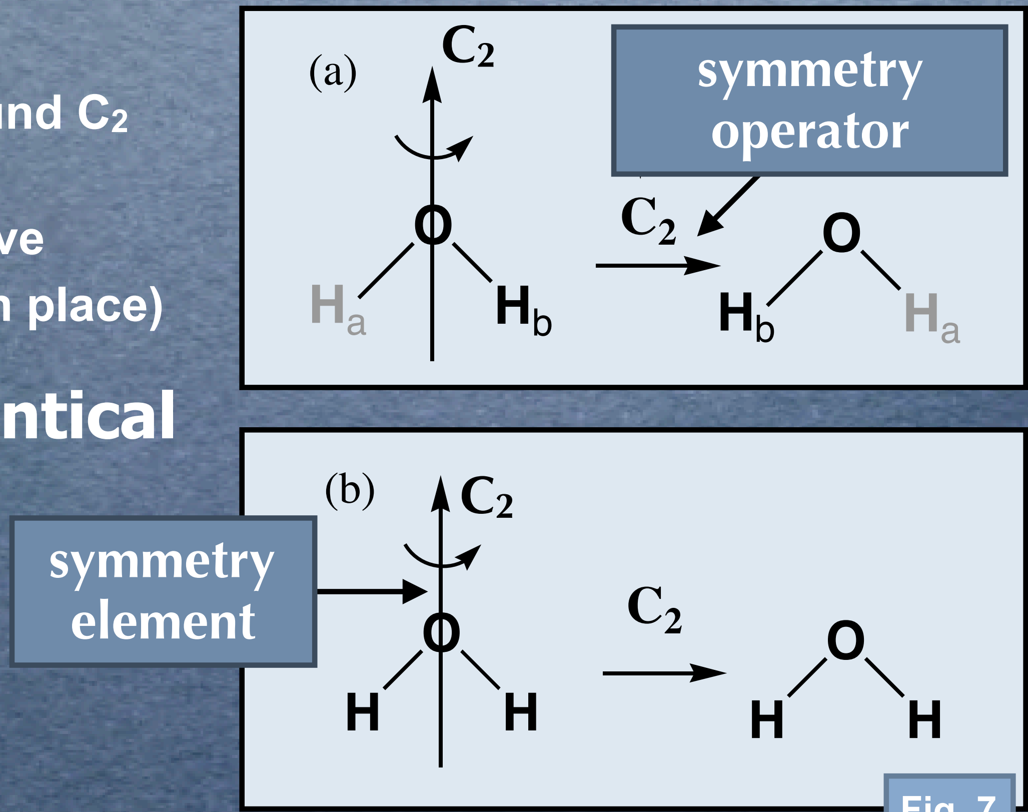


Fig. 7

C_2 operation

you should be able to draw neat diagrams showing symmetry operations

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!

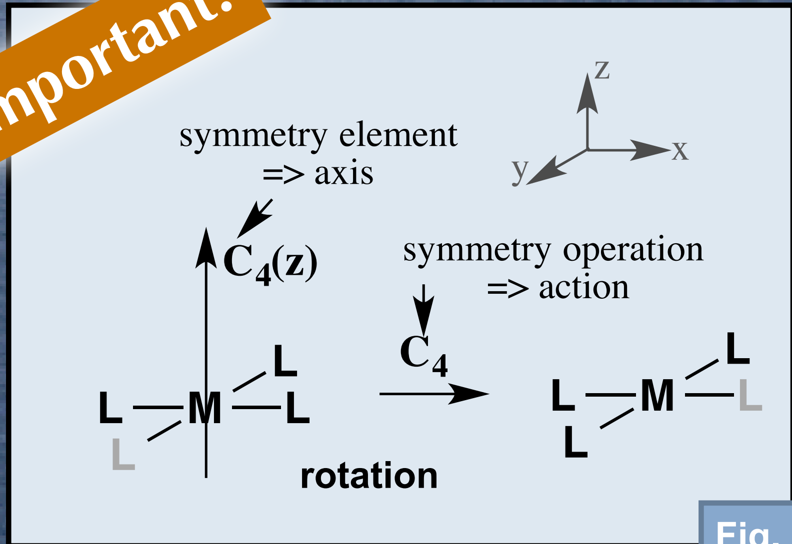


Fig. 8

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

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

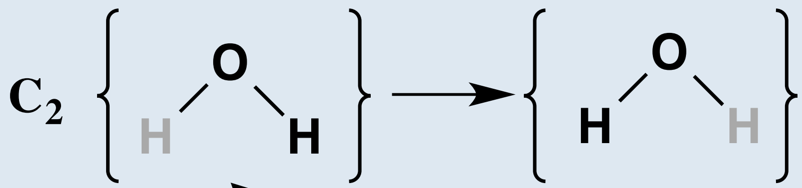


Fig. 9

operator C_2 acts on molecule

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

C_2 operation

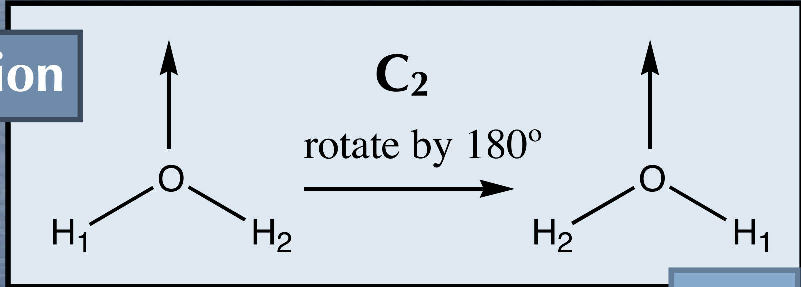


Fig. 7

C_2 element

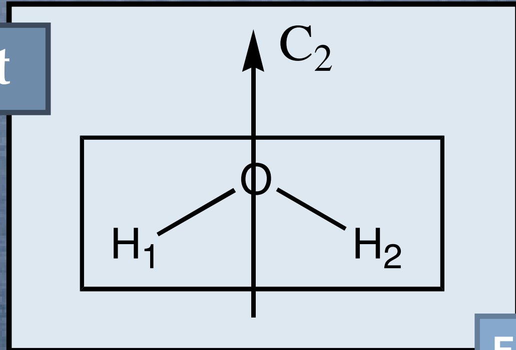


Fig. 8

C_2 operator

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

Fig. 9

Example: H_2O

Symmetry elements for H_2O:

- identity E
- C_2 rotation axis
- reflection plane $\sigma_v(yz)$
- reflection plane $\sigma_v(xz)$

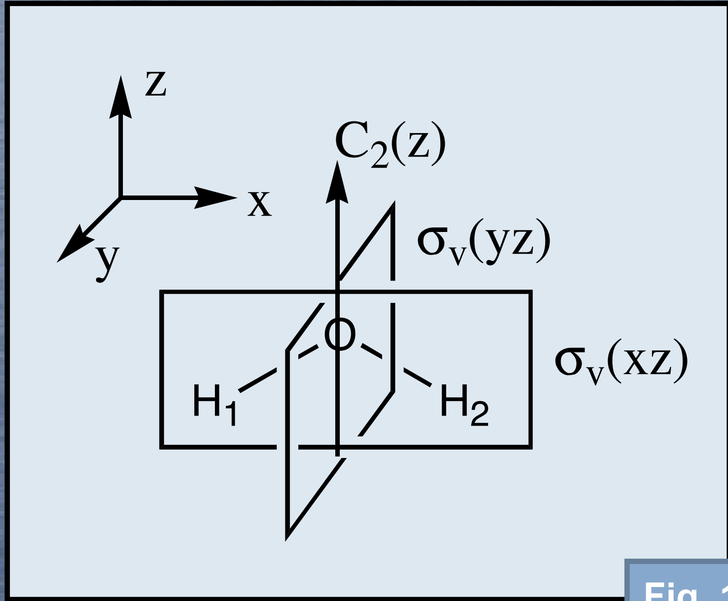


Fig. 10

Flow chart for identifying the point group

- is the molecule linear? NO
- are there two or more C_n N>2? NO
- is there a C_n? YES
- are there nC_2 perpendicular to C_n? NO
- is there a σ_h? NO
- is there a σ_v? YES

point group: C_{2v}

In-Class Activity

socrative quiz!

WHZ9KBWC3

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

what is wrong with this answer!

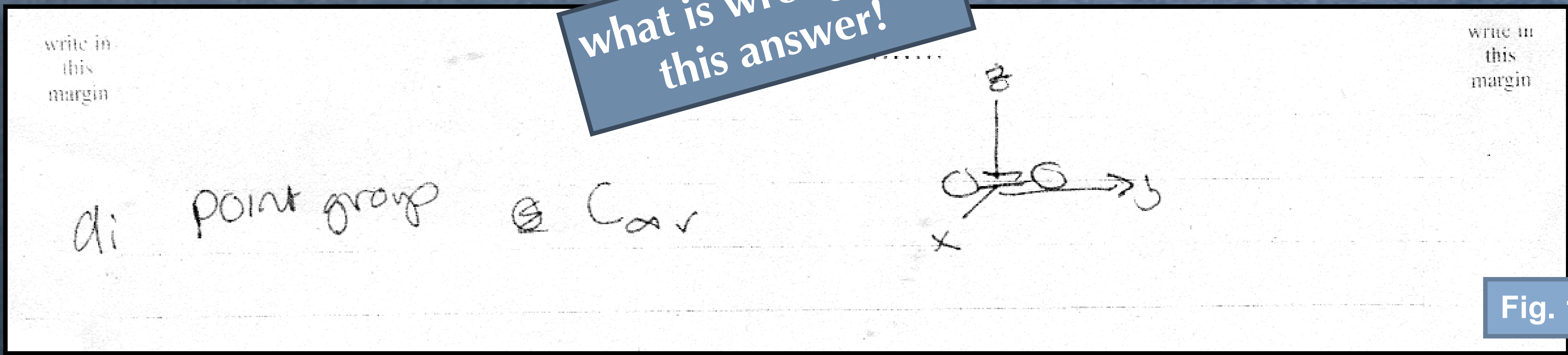
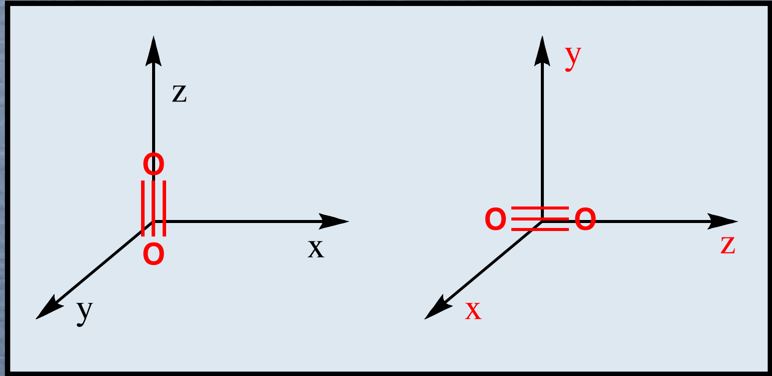


Fig. 11

- 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_{∞} axis

- **Problems?**

see Revision notes

Additional material on my web-site

In-Class Activity

- **The question"Given this molecule of cis-H_4 clearly indicate all of the symmetry elements on a diagram. (4 marks)"**

what is wrong with this answer!

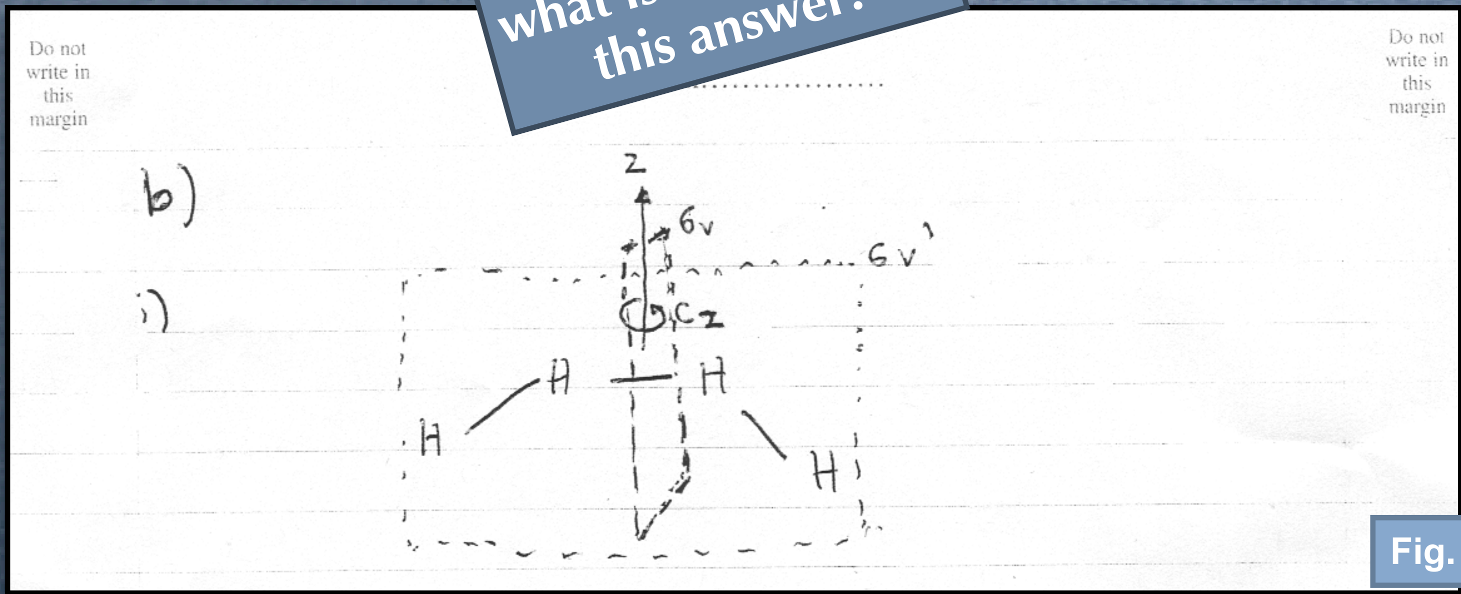
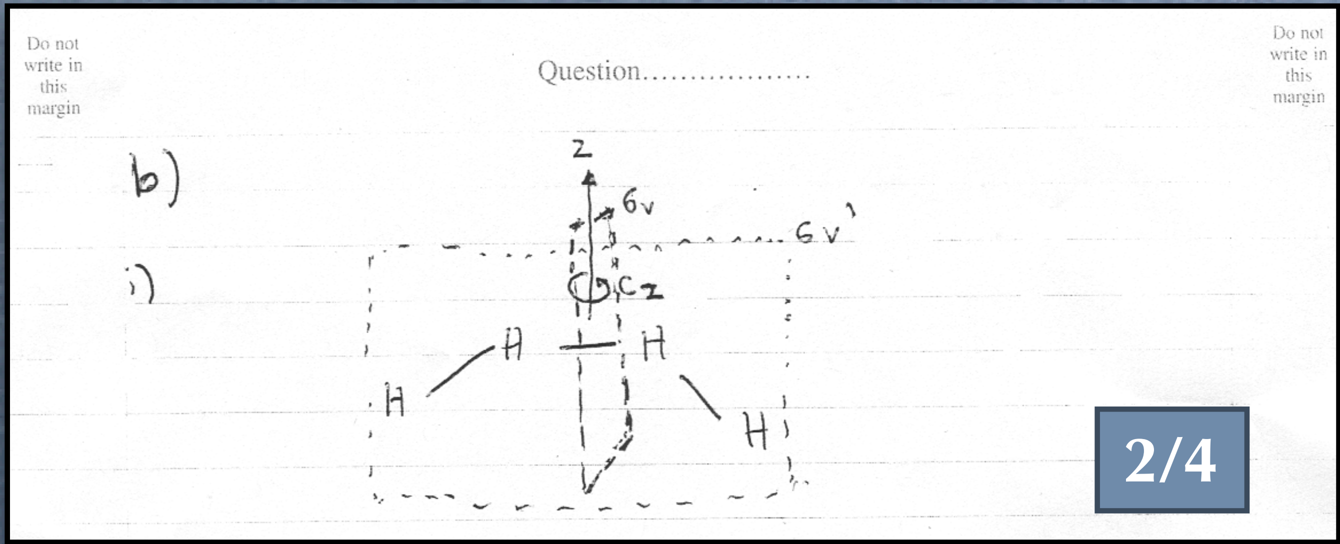


Fig. 12

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

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

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_2O has C_{2v} symmetry so use C_{2v} character table
- start by constructing a representation table:

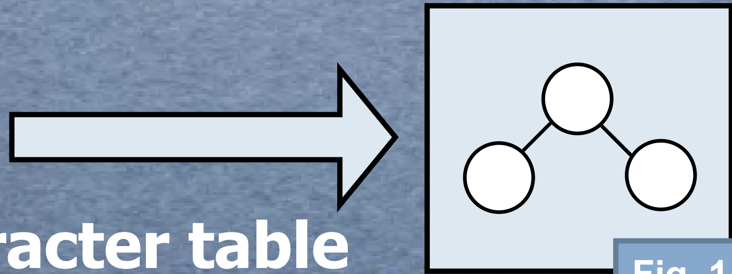


Fig. 14

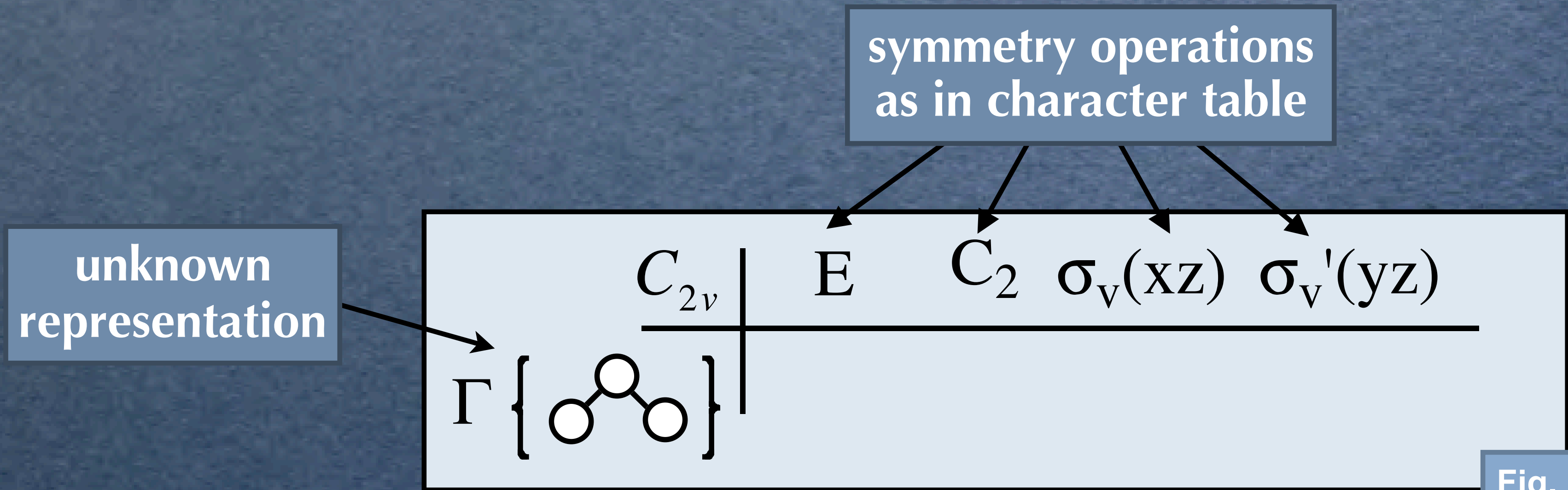
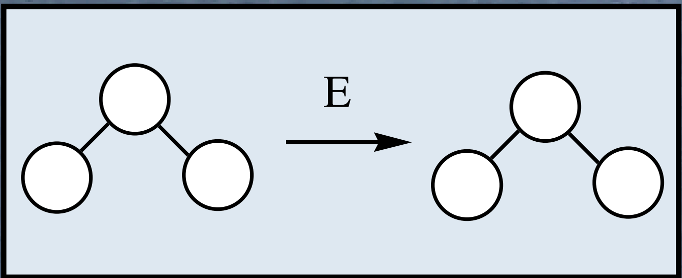


Fig. 15

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 ⇒ $\chi = 1$

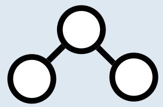
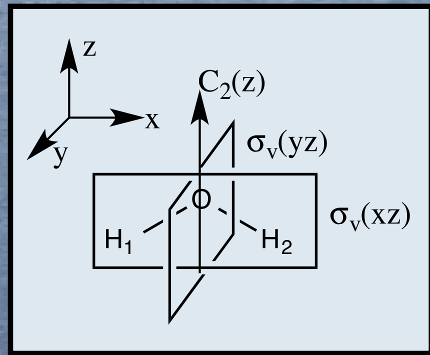
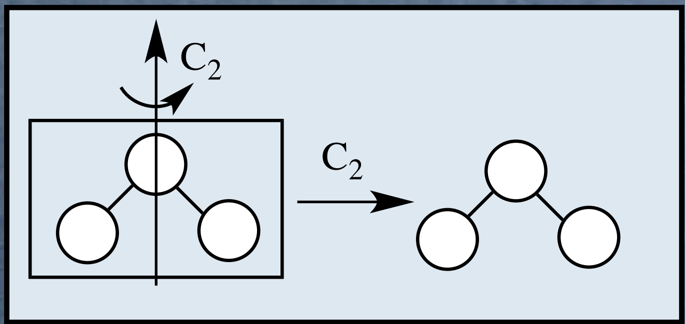
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }	**1**			

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 ⇒ $\chi = 1$

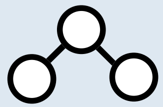
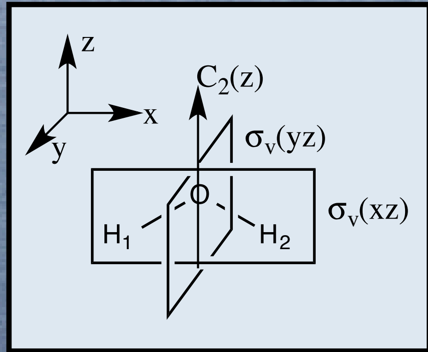
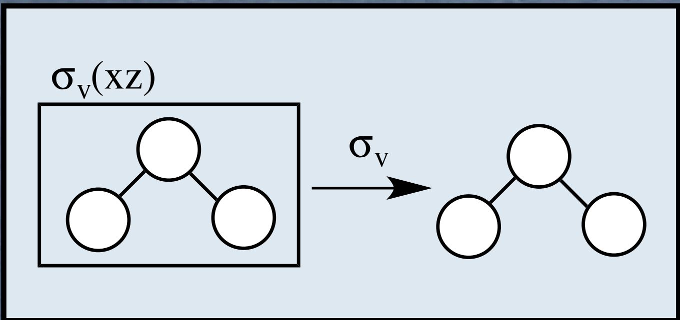
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }	1	1		

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 σ_v ⇒ $\chi = 1$

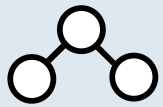
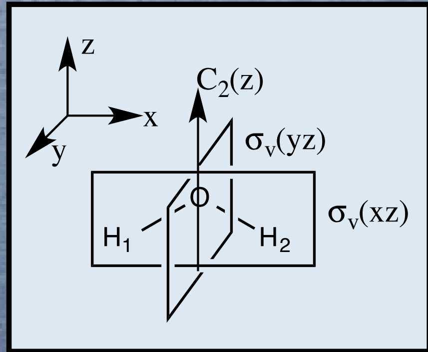
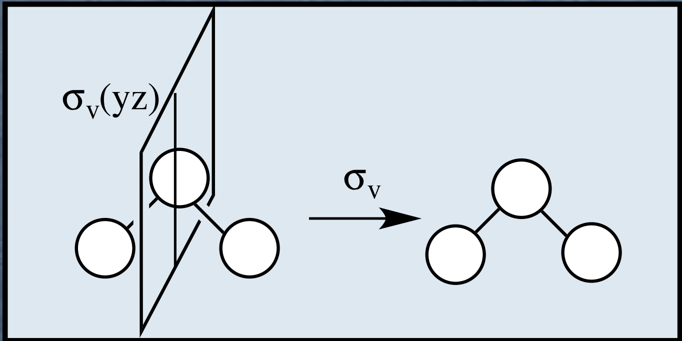
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }	1	1	1	

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 σ_v ⇒ $\chi = 1$

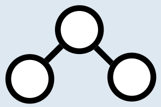
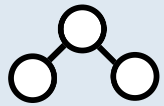
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }	1	1	1	1

Fig. 16

Using Character Tables

same set of characters as the irreducible representation a_1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }	**1**	**1**	**1**	**1**

Use lower case when for the symmetry label of MOs
A_1 -> a_1

upper case letters are reserved for vibrations and states

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. 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

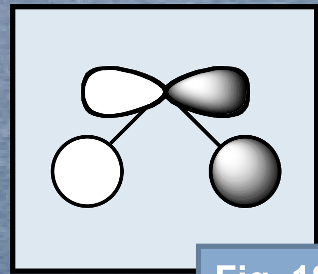
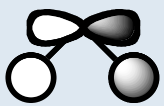
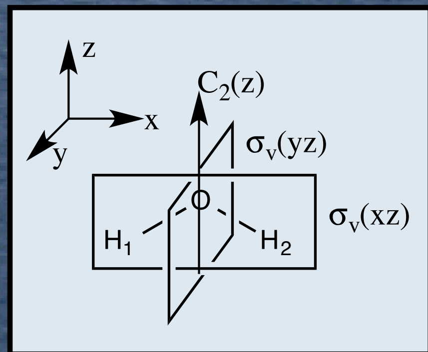


Fig. 18

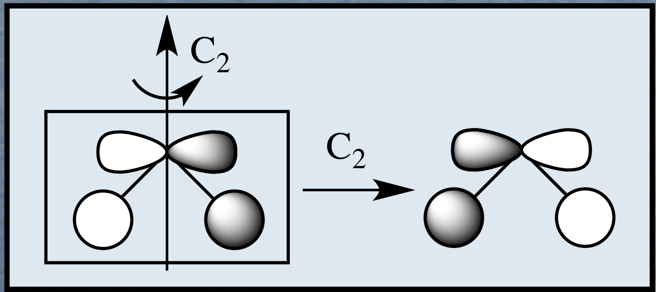
your turn:

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



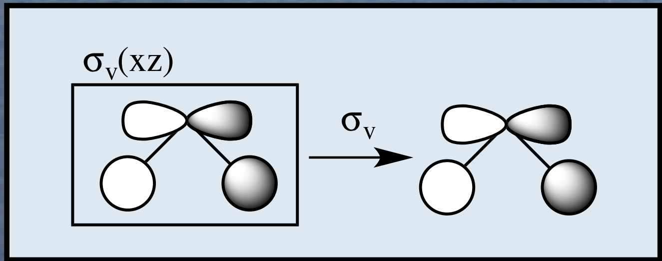
In-Class Activity

C_2



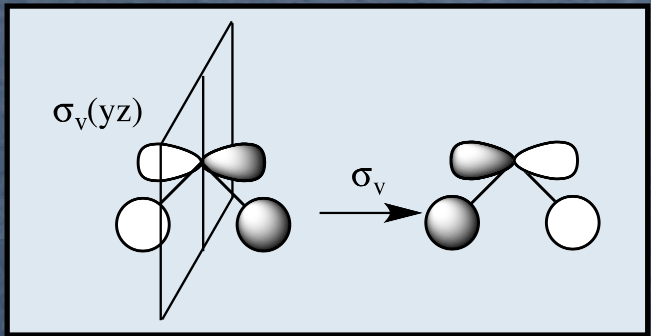
$\chi = -1$

$\sigma_v(xz)$

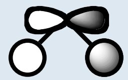


$\chi = 1$

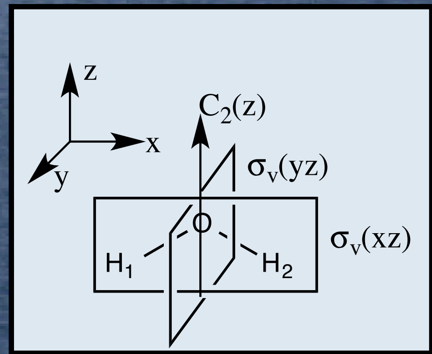
$\sigma_v(yz)$



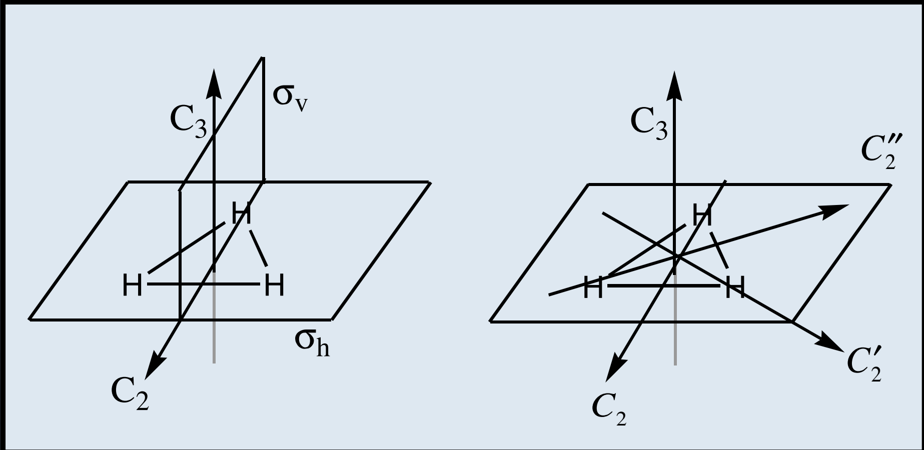
$\chi = -1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ {  }	1	-1	1	-1

this orbital has b_1 symmetry



D_{3h} Character Table



Find the D_{3h} character table in your set of Character Tables

D_{3h}	E	$2C_3$	$3C_2$	σ_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

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

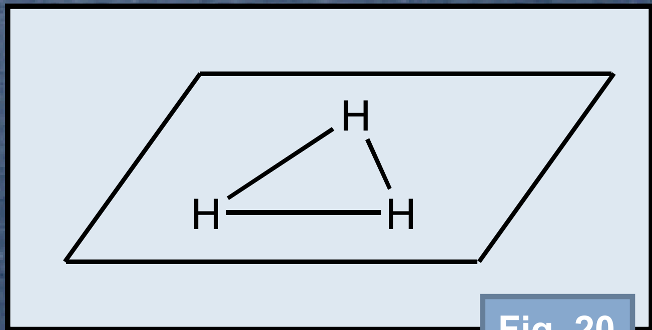


Fig. 20

Multiple Operations

- **Symmetry operations of D_{3h}**
  - 1 E identity
  - 2 C_3 rotations
  - 3 C_2 rotations
  - 1 σ_h reflection
  - 2 S_3 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	$2S_3$	$3\sigma_v$	
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

$2C_3$ Rotations

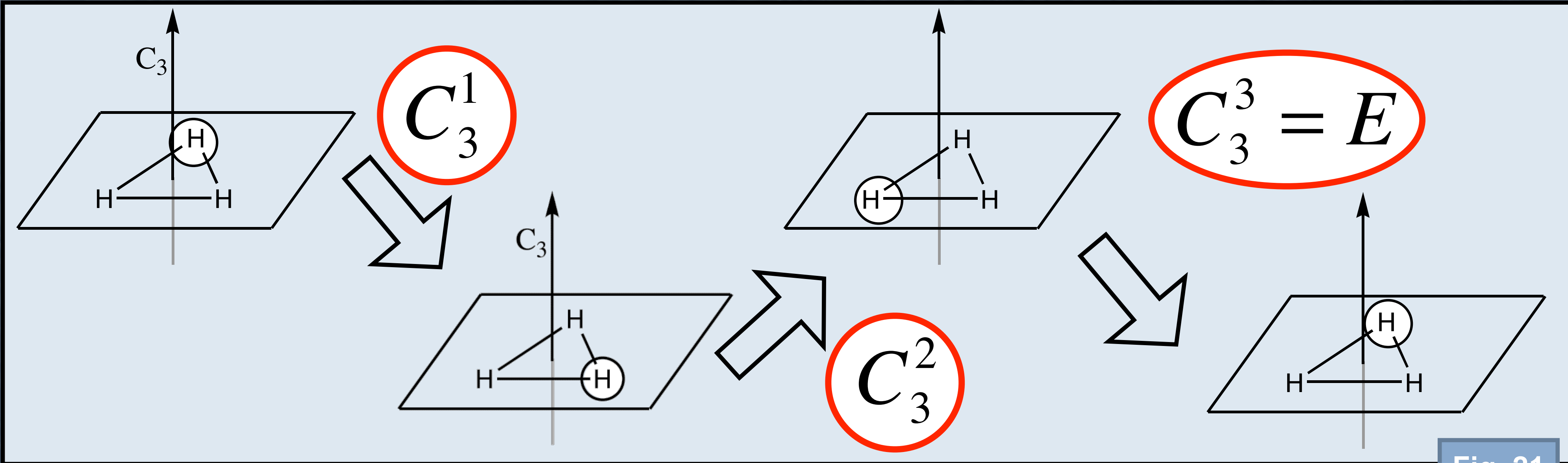


Fig. 21

$$C_3^1 \quad C_3^2 \quad C_3^3$$

Rotations in General

- **Each rotation of order n has n rotations**
- **for example**

$$C_2^1 \quad C_2^2$$
$$C_3^1 \quad C_3^2 \quad C_3^3$$
$$C_4^1 \quad C_4^2 \quad C_4^3 \quad C_4^4$$

each set of rotations forms a group

- **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

$3C_2$ Rotations

- three separate C_2 axes
- each contributes one C_2 rotation
- find one C_2 axis and use C_3 to find the rest
- each element is distinct: $C_2 \quad C_2' \quad C_2''$

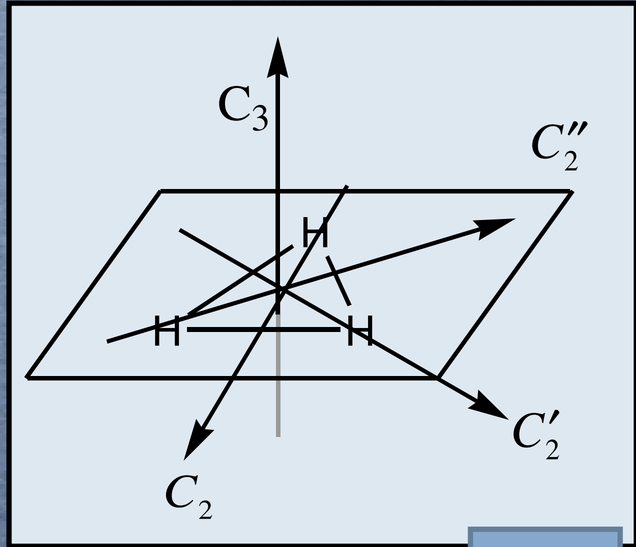
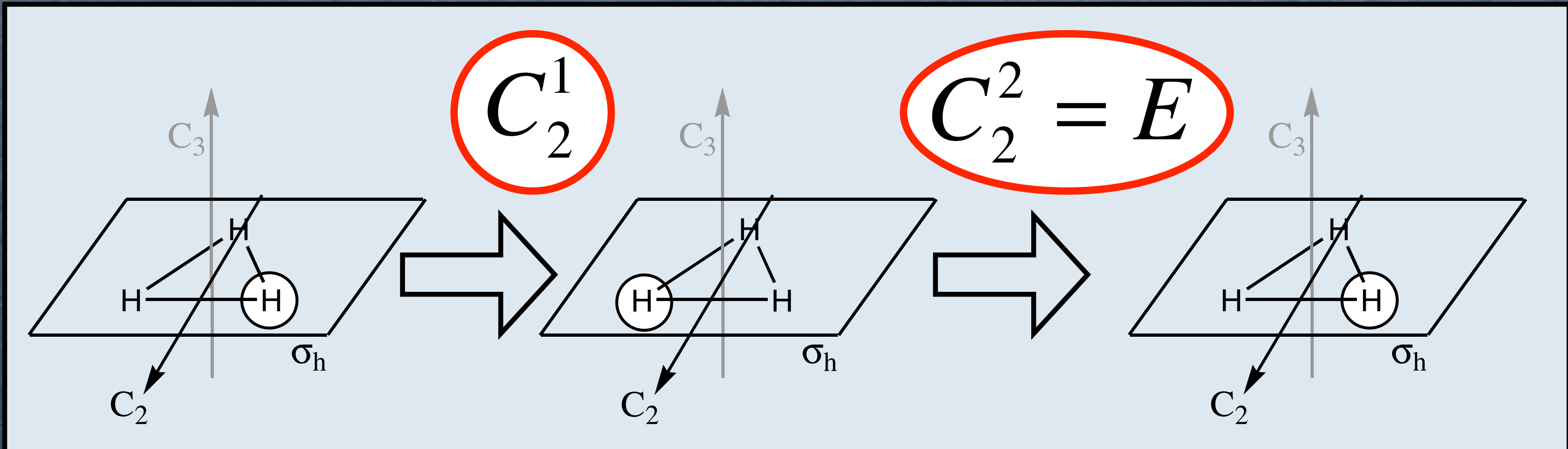


Fig. 22



Multiple Operations

- $2C_3$ and $3C_2$ appear in the character table of D_{3h}
  - it doesn't matter if these are the SAME or DIFFERENT symmetry elements
  - the table only "cares" about operations

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

one element
3 operations

$$C_3^1 \quad C_3^2 \quad C_3^3$$

$$C_2 \quad C_2' \quad C_2''$$

three elements
3 operations

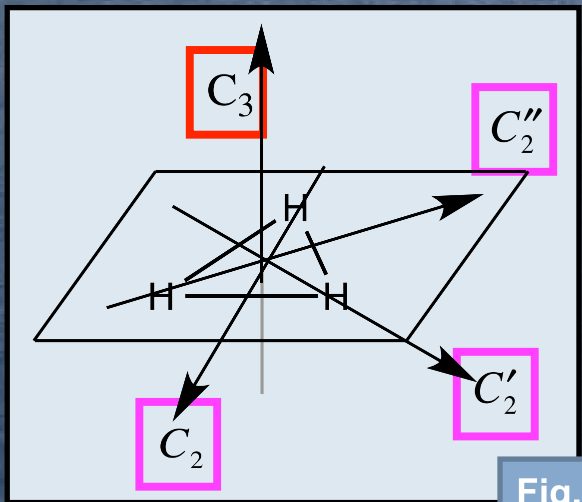


Fig. 22

Symmetry Labels

- **A and B singe representations**
  - atoms/orbitals map onto each other

D_{3h}	E	$2C_3$	$3C_2$	σ_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

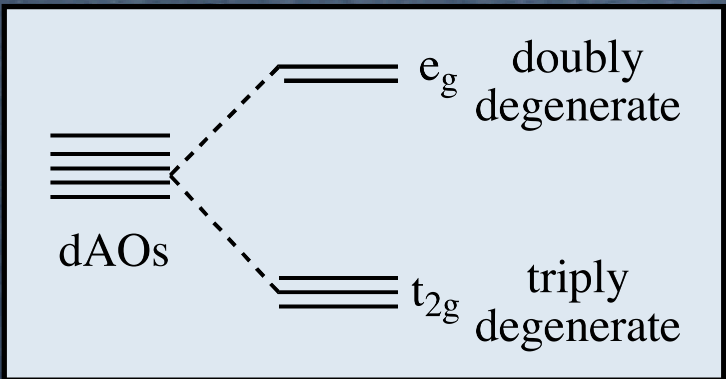
- **A and B singe representations**
  - atoms/orbitals map onto each other
- **E doubly degenerate**
  - don't confuse with E operation!
  - orbitals as a group map onto each other
  - character =2 under E operation
- **T triply degenerate**
  - tetrahedral point groups (Td)
  - character =3 under E operation

D_{3h}	E	$2C_3$	$3C_2$	σ_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 singe 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	$2C_3$	$3C_2$	σ_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

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

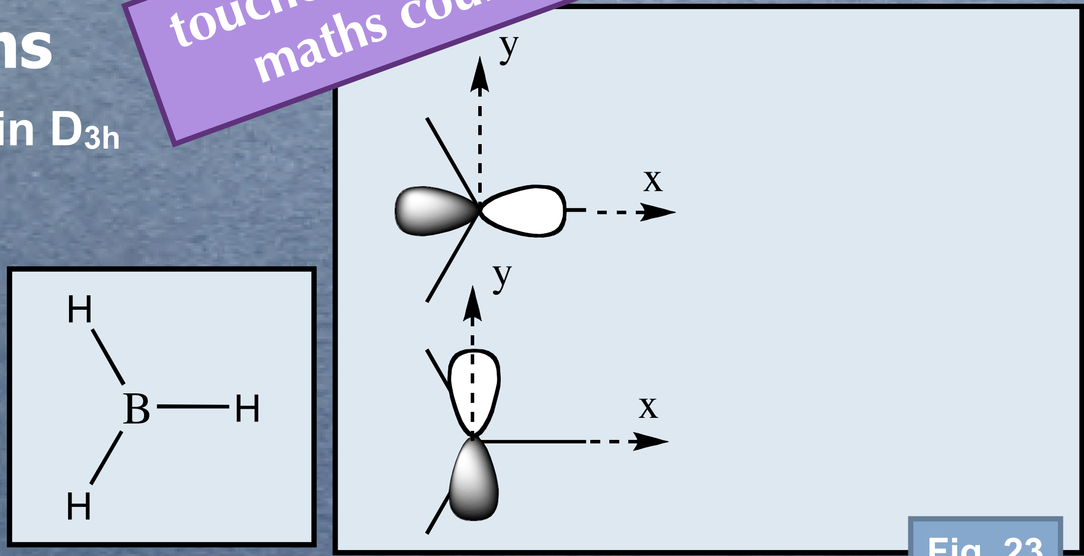


Fig. 23

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

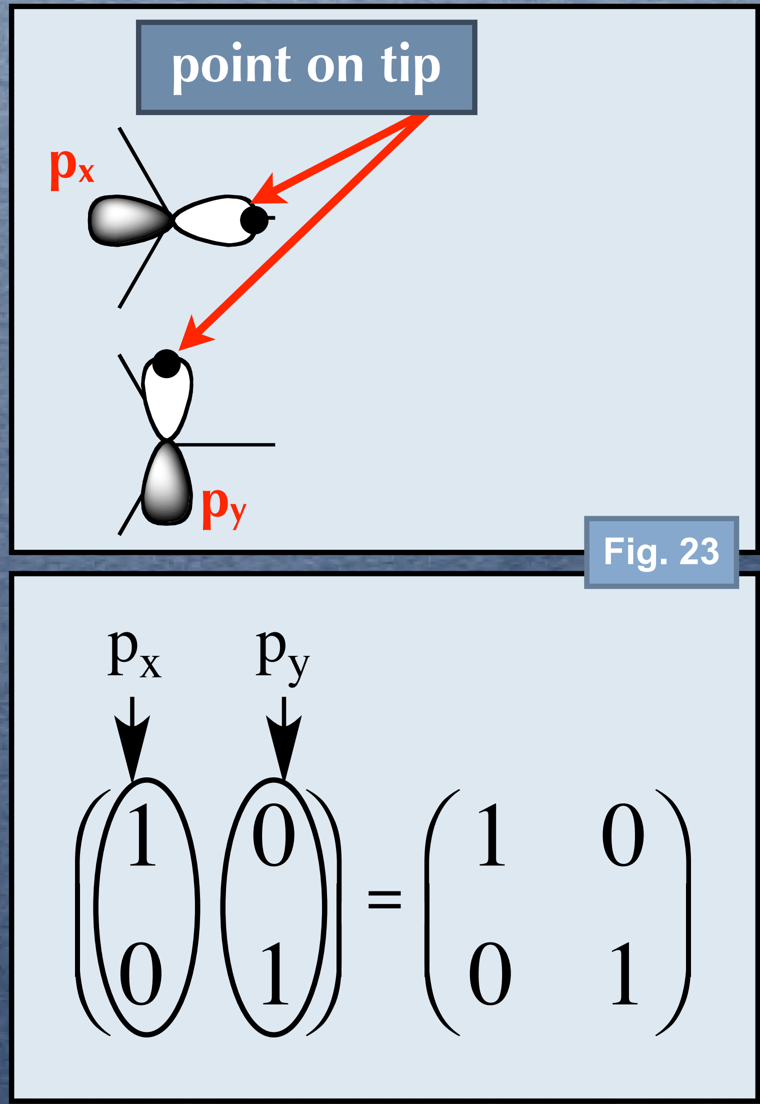


Fig. 23

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

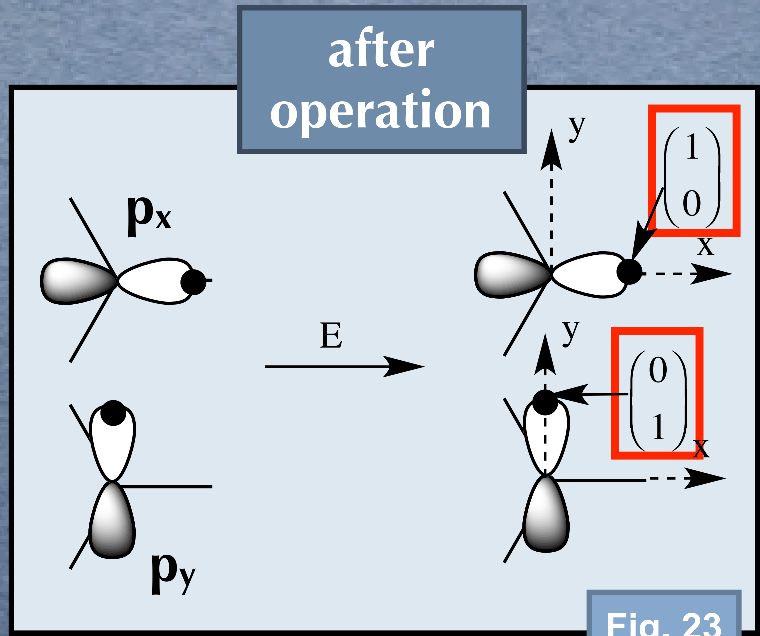


Fig. 23

p_x ↓ p_y ↓

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

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

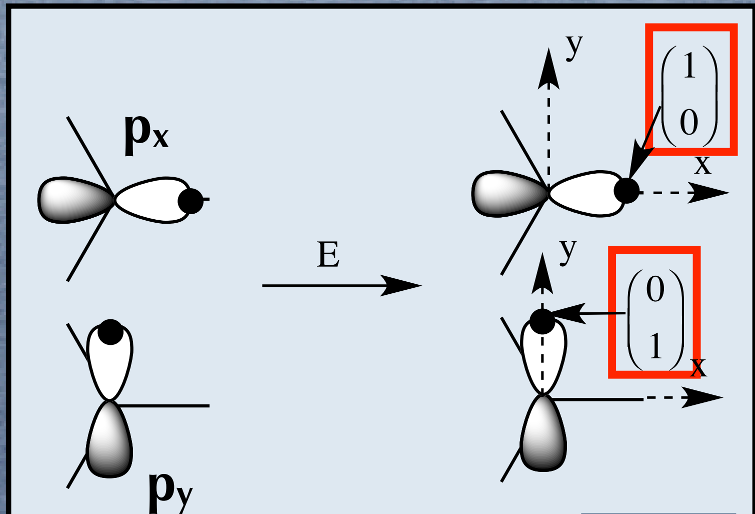


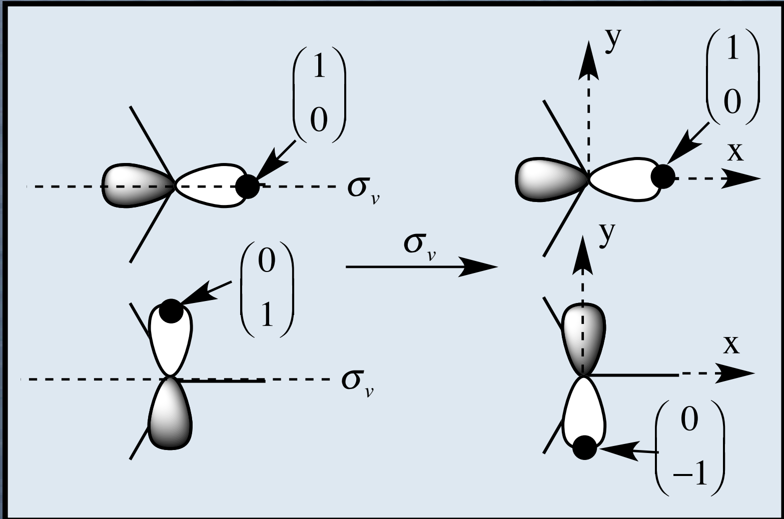
Fig. 23

p_x p_y

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

Degenerate Representations

- the character for the σ_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	$2C_3$	$3C_2$	σ_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	

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

In-Class Activity

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

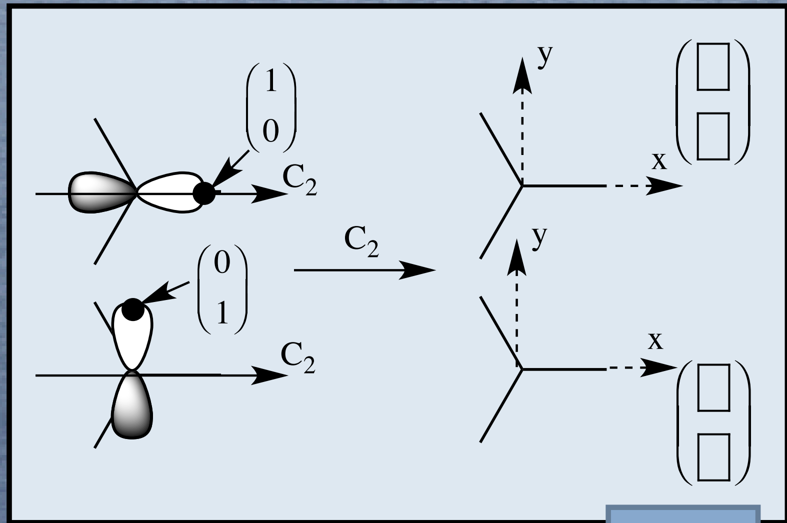
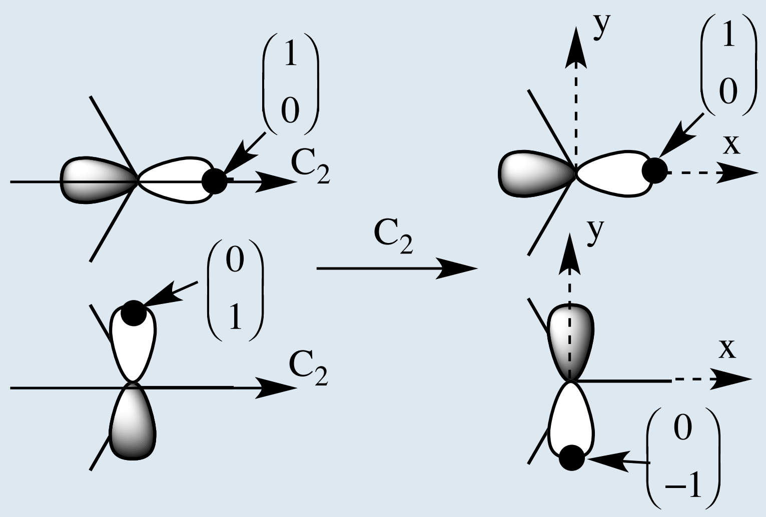


Fig. 25

In-Class Activity

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



$$C_2\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}\rightarrow\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$$

D_{3h}	E	$2C_3$	$3C_2$	σ_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	

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

Model answer on the web-site

Improper Rotations

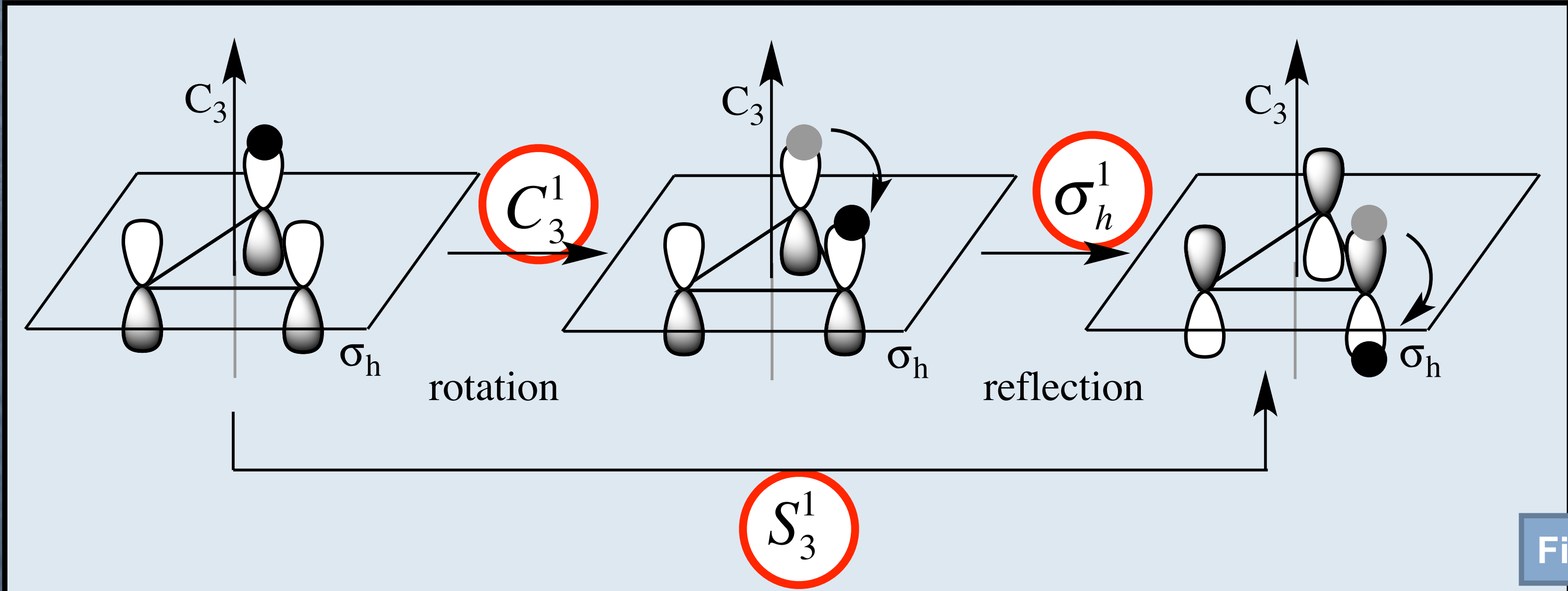


Fig. 26

- **rotation followed by reflection in mirror plane perpendicular to the axis of rotation**
- **phase changes are important**
  - use pAOs to visualise
  - OR take a point off the mirror plane and axis (black circle above)

Important!

- **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=odd $S_n^n \neq E$

Improper Rotations

- **diagram showing** $S_3^3 \neq E = \sigma_h$

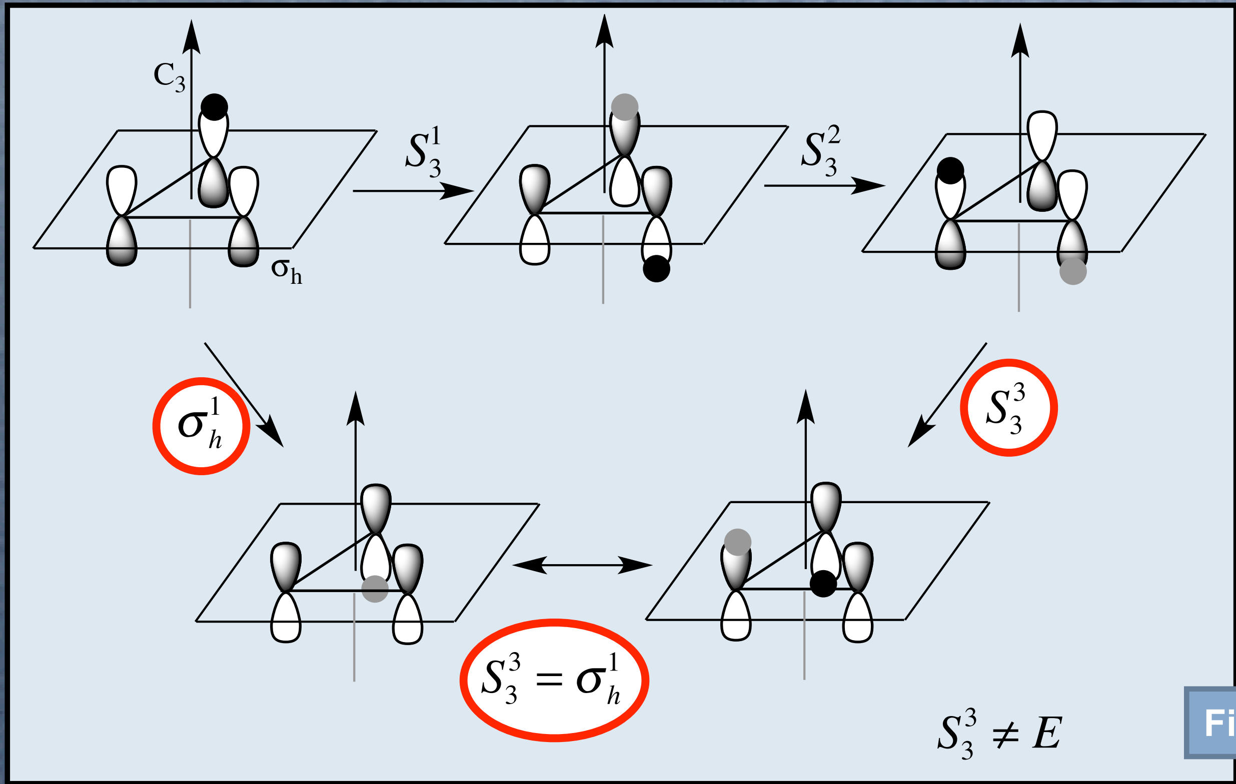


Fig. 27

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 Sn 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!!