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

**Recommended Text**
- only specific sections!!

**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!
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 O₂ diamagnetic (paired electrons) the experimental evidence is that O₂ is paramagnetic (unpaired electrons)

- **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 H₂O

- **Required for “odd” bonding situations**
  - structure of ethane is well known, diborane B₂H₆ 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
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
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

“development of multiscale models for complex chemical systems”
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 C₂ axis
  - if nuclei are labeled specific atoms move
  - Hₐ and Hₜ exchange places (O rotates in place)

- **Initial and final states are identical with respect to nuclei**

  ![C₂ operation diagram](image)

  ![Symmetry operator diagram](image)

  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

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!

Symmetry element => axis
Symmetry operation => action
Rotation

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

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

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

---

Chemical Bonding course
Math courses
Spectroscopy and Characterisation course
Quantum mechanics
Symmetry operation
- the act of performing a motion

Symmetry elements
- objects about with symmetry operations occur

Symmetry operator
- mathematical representation of the action

\[ C_2 \left[ \psi_{H_2O} \right] = \psi'_{H_2O} \]
Example: \( \text{H}_2\text{O} \)

**Symmetry elements for \( \text{H}_2\text{O} \):**

- identity \( E \)
- \( \text{C}_2 \) 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 \( \text{C}_n \) \( N>2 \)? NO
- is there a \( \text{C}_n \)? YES
- are there \( n\text{C}_2 \) perpendicular to \( \text{C}_n \)? NO
- is there a \( \sigma_h \)? NO
- is there a \( \sigma_v \)? YES

point group: \( \text{C}_{2v} \)
The question was part of an exam and related to a MO diagram for $O_2$.

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

- 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
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 character table handout

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

Advanced Spectroscopy

C<sub>2v</sub> character table

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2v&lt;/sub&gt;</th>
<th>E</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;</th>
<th>σ&lt;sub&gt;v&lt;/sub&gt;(xz)</th>
<th>σ&lt;sub&gt;v&lt;/sub&gt;'(yz)</th>
<th>h=4</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>x</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>y</td>
</tr>
</tbody>
</table>

Fig. 13
### Character Table Components

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>C₂</th>
<th>σᵥ(xz)</th>
<th>σᵥ'(yz)</th>
<th>h=4</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Symmetry Operations**
- E (Identity)
- C₂
- σᵥ(xz)
- σᵥ'(yz)

**Symmetry Labels**
- A₁
- A₂
- B₁
- B₂

**Irreducible Representation**
- A₁
- A₂
- B₁
- B₂

**Symmetry of Cartesian Axes**
- x
- y
- z

**Number of Symmetry Operations**
- h=4

**1’s and -1’s**
- These are characters for the irreducible representations.
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

\( \text{H}_2\text{O} \) has \( \text{C}_{2\text{v}} \) symmetry so use \( \text{C}_{2\text{v}} \) character table

start by constructing a representation table:
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

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

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

\[ \chi = \begin{array}{c} \sigma_v(xz) \\ \sigma_v(yz) \end{array} \]

No change under \( \sigma_v \)

\[ \chi = 1 \]

\[ \begin{array}{c|cccc} & C_{2v} & E & C_2 & \sigma_v(xz) & \sigma_v'(yz) \\ \hline \Gamma \{G\} & 1 & 1 & 1 & 1 \end{array} \]

Fig. 16
Using Character Tables

Determine how the orbital transforms under each symmetry operation of the group:
- Orbital is unchanged $\Rightarrow$ character $= 1$
- A sign change $\Rightarrow$ character $= -1$

![Diagram of C2 symmetry](image)

No change under $\sigma_v$

$$\chi = 1$$

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v'(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma { \text{orbital} }$</td>
<td>$1$</td>
<td>$1$</td>
<td>$1$</td>
<td>$1$</td>
</tr>
</tbody>
</table>

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

**Fig. 17**

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>E</th>
<th>( C_2 )</th>
<th>( \sigma_v(xz) )</th>
<th>( \sigma_v'(yz) )</th>
<th>( h=4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( z )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>( x )</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( y )</td>
</tr>
</tbody>
</table>
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

your turn:

$$\Gamma \left\{ \begin{array}{c} C_{2v} \\ E \\ C_2 \\ \sigma_v(xz) \\ \sigma_v'(yz) \end{array} \right\}$$
In-Class Activity

\[ \Gamma \begin{bmatrix} C_{2v} \\ E \\ C_2 \sigma_v(xz) \sigma_v'(yz) \end{bmatrix} \begin{bmatrix} 1 \\ -1 \\ 1 \\ -1 \end{bmatrix} \]

This orbital has \( b_1 \) symmetry.
Find the D$_{3h}$ character table in your set of Character Tables

$$\begin{array}{|c|cccccccc|}
\hline
D_{3h} & E & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
A_1' & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
A_2' & 1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 \\
E' & 2 & -1 & 0 & 2 & -1 & 0 & 2 & 0 \\
A_1'' & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\
A_2'' & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 \\
E'' & 2 & -1 & 0 & -2 & 1 & 0 & 2 & 0 \\
\hline
\end{array}$$

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
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
  - $= 1 + 2 + 3 + 1 + 2 + 3 = 12$

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
2C₃ Rotations

\[ C^{1}_3 \quad C^{2}_3 \quad C^{3}_3 \]

\[ C^{3}_3 = E \]
Rotations in General

Each rotation of order n has n rotations

For example

<table>
<thead>
<tr>
<th>C₁</th>
<th>C₂</th>
<th>C₂</th>
<th>C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂</td>
<td>C₁</td>
<td>C₃</td>
<td>C₃</td>
</tr>
<tr>
<td>C₃</td>
<td>C₂</td>
<td>C₃</td>
<td>C₄</td>
</tr>
<tr>
<td>C₄</td>
<td>C₃</td>
<td>C₄</td>
<td>C₄</td>
</tr>
</tbody>
</table>

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
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: $C_2$ $C'_2$ $C''_2$

Fig. 22
Multiple Operations

2C₃ and 3C₂ appear in the character table of D₃h

- it doesn’t matter if these are the SAME or DIFFERENT symmetry elements
- the table only “cares” about operations

![Diagram](image)

Fig. 22
**Symmetry Labels**

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

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1'}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2'}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A_{1''}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2''}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 19 (Tx, Ty)

$T_z$
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

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S'_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E'$</td>
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<td>2</td>
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<td>0</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 19
**Symmetry Labels**

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- 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

You have already seen e and t symmetry labels!

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
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<tbody>
<tr>
<td>$A_1'$</td>
<td>1</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

(Tx, Ty) Tz

Fig. 19
Degenerate Representations

- **degenerate representations**
  - example: \((p_x, p_y)\) have e’ symmetry in \(D_{3h}\)

![Diagram](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

\[
\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]
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

\[
\begin{pmatrix}
p_x \\
p_y
\end{pmatrix}
\begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\begin{pmatrix}
p_x \\
p_y
\end{pmatrix}
\]
**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

\[
E \begin{pmatrix} 1 & 0 \\
0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\
0 & 1 \end{pmatrix}
\]
Degenerate Representations

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

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

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

Model answer on the web-site
Improper Rotations

- 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)

- 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 $S_3^3 \neq E = \sigma_h$

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

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!!

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