In-Class Problems / Self-study Problems / Test Preparation: Lecture 2

- **In-Class P1** Use a representation table to determine the symmetry label for MO2.

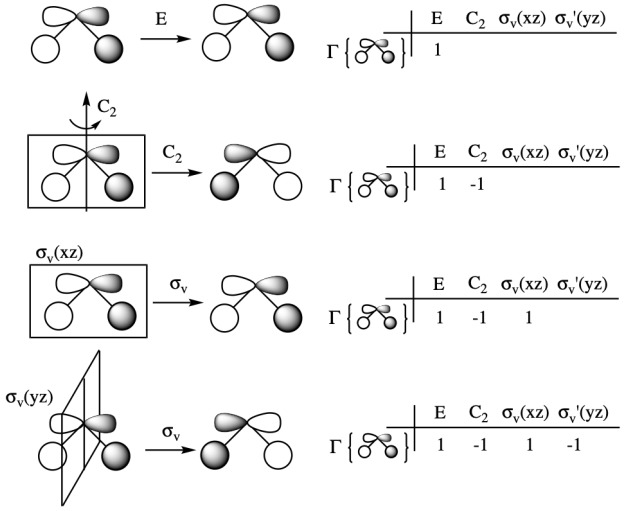


Figure 1 Filling out the representation table for MO2

  - matching the representation table against the C_{2v} point group table we see that MO2 has b_1 symmetry (note the small letter!)
- **In-Class P2** for What is the symmetry of the p_x and p_y AOs of Pt? and What is the symmetry of the dxy AO of Pt?
  - symmetry of the p_x and p_y AOs of Pt is eg
  - symmetry of the dxy AO of Pt is b2g
- **In-Class Activity P3** Determine the symmetry of these MOs identifying appropriate "short-cut" through a relationship to cartesian functions.

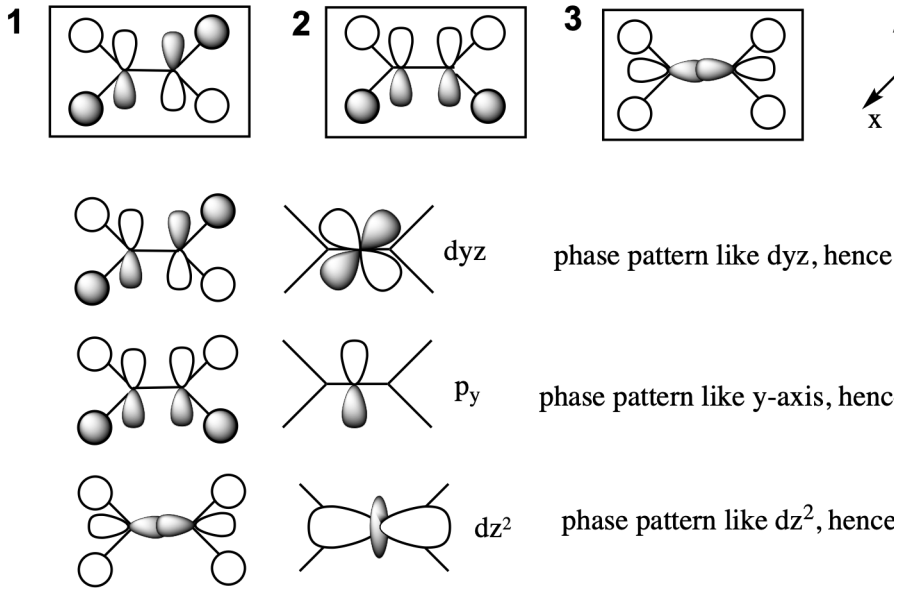
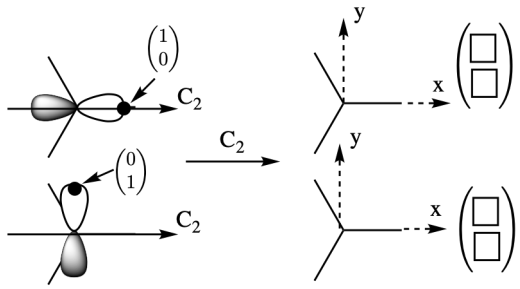
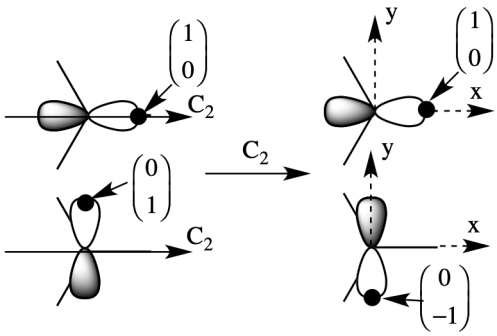


Figure 2 Determining orbital symmetry via short-cuts

- **In-Class Activity P4** What is the character of the degenerate B p_x and p_y AOs under the C_2 axis? Complete the diagram below and determine the transformation matrix and the hence the character.
  - see below the character is the trace =1+(-1)=0



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

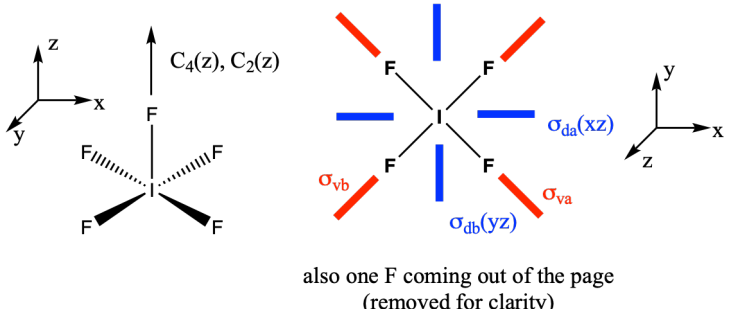


$$C_2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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	

Figure 3 transformation of the p_x and p_y AOs under C_2

- **In-Class P5** Draw a Lewis bonding diagram for IF_5 and identify the molecular shape of IF_5 using VSEPR theory. Determine the point group and draw all of the symmetry elements on a diagram of the molecule. Identify if multiple operations in the character table are due to multiple operations on the same element or multiple elements. For the highest rotation axis identify, for any operations that are not-unique, the equivalent operation.
  - each F contributes 7ve 6 of these will be in lone pairs, and 1e will contribute to a covalent bond with I. The I has 7ve, 5 of these will contribute to covalent bonds with the F atoms, 2 will remain non-bonding as a lone pair.



also one F coming out of the page (removed for clarity)

Figure 4 identifying the symmetry operations of IF_5

- point group
  linear?NO
  T_d or O_h? NO
  principle axis? YES C_4
  $4C_2$ perpendicular to C_4? NO
  σ_h? NO
  $4\sigma_v$? YES
  therefor C_{4v}
- there are 4 possible C_4 operations C_4^1, C_4^2, C_4^3, C_4^4
- C_4^2 is the same as C_2^1 and C_4^4 is the same as E, therefore C_4^1 and C_4^3 are unique,
- The 2C4 operations occur around the same element, the C4 axis
- the $2\sigma_d$ and $2\sigma_v$ operations are due to the presence of different symmetry elements (mirror planes)

- **Q1** determine the symmetry label for the molecular orbitals shown for BH_3 using the "long method" of forming a representation table, for (b) check your answer using a "short-cut" method
  - for each example
    1. draw a "representation table" for the MO
    2. determine how the MO transforms under each symmetry operation
    3. compare the representation to the irreducible representations on the character table
  - (a) has a_1' symmetry
  - (b) has a_2'' symmetry (working shown below) **Figure 5**
  - compare the answer for (b) to the T_z on D_{3h} character table which is a_2'' symmetry, **Figure 6**

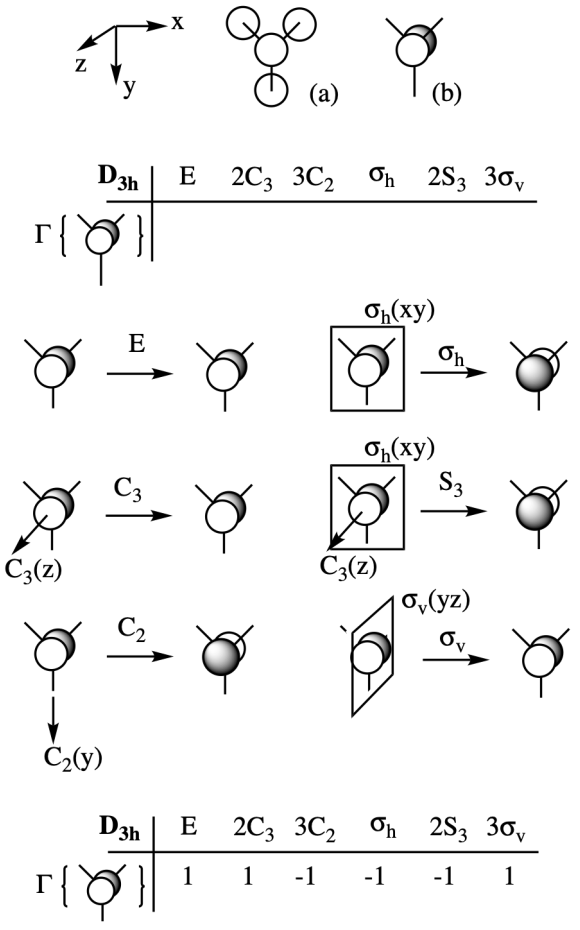


Figure 5 determining the symmetry label for MO (b)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	σ_v		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(T_x, T_y)	x^2-y^2, xy
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	(R_x, R_y)	xz, yz

Figure 6 D_{3h} Character Table

- **Q2** construct a representation table for the "z-axis" and determine which irreducible representation it transforms as.
  - The z-axis has the same **phase** properties as the p_z AO of boron and MO(b) above (which is just the p_z AO of boron, AOs can also be MOs!). Thus we need never actually work out the symmetry labels of the p_x, p_y or p_z atomic orbitals because they will always have the same symmetry labels as the x, y and z axes. The representation table is therefor the same as that for the p_z orbital and the symmetry label is a_2".

- **Q3** *In your own words*, using bullet points, write out the general procedure to determine the symmetry label of a molecular orbital This is my process however you should go through the notes and an example and write out the process **for yourself in your own words**!
  1. determine the point group of the molecule
  2. define the axis system
  3. draw a representation table for the MO
  4. determine how the MO transforms under each symmetry operation
  5. enter +1 for no phase change, -1 for a phase change
  6. compare this representation to the irreducible representations from the character table
  7. use a small letter for the symmetry label of a MO

- **Q4** *In your own words*, using bullet points, write out the general procedure to determine the character of a degenerate set of orbitals? This is my process however you should go through the notes and an example and write out the process for yourself in your own words!
  1. take point on tip of each orbital
  2. form the starting matrix
  3. perform the symmetry operation on the orbitals
  4. write coordinates of each point
  5. form the final matrix by combing the coordinates
  6. the character is the TRACE of the final matrix

- **Q5** The Tetrahedral Point Group (*advanced!*)
  - discuss and illustrate the symmetry operations of the T_d point group.
  - **hint:** there are three useful ways of thinking about a tetrahedral molecule, **Figure 7**, each one emphasises a different aspect of symmetry:
    (a) the C_2 axes
    (b) the C_3 axes
    (c) the cubic structure

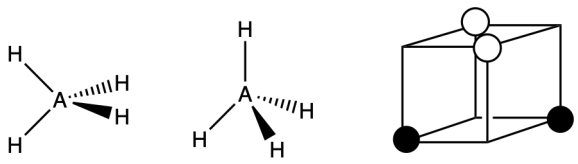


Figure 7 different ways to represent a T_d molecule

- the "cube" may be less familiar to you, think of the H atoms occupying opposite corners of a cube and the central atom A is at the center of the cube
- The character table for the T_d point group is shown to the left, **Figure 8** and it tells us the key symmetry operations in this group are E, $8C_3$ $3C_2$, $6S_4$ and $6\sigma_d$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	h=24
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	
T_1	3	0	-1	1	-1	
T_2	3	0	-1	-1	1	$(T_xT_y\ T_z)$

Figure 8 T_d character table

- there are *8C3 operations*
  - a C_3 axis lies along each bond, one C_3 axis is shown in **Figure 9**, the others are easily predicted because the four H atoms are symmetry equivalent, if one H atom has a C_3 axis passing through it then they all will, hence there are four C_3 axis symmetry elements
  - around each axis there are 3 possible C_3 operations: $C_3^1\ C_3^2\ C_3^3$, the last operation $C_3^3 = E$ is equivalent to the identity and so is already counted, there are then <u>two</u> symmetry operations associated with each C_3 axis
  - thus there are eight distinct C_3 operations in T_d: $8C_3$
- there are $3C_2$ operations
  - a C_2 axis lies between each pair of A-H bonds, **Figure 9**, bisecting each pair of atoms and through the center of each pair of faces in the cube, as there are 3 pairs of faces to each cube, there will be $3C_2$ axes
  - as we associate only one operation with each C_2 axis there are 3 C_2 operations in T_d

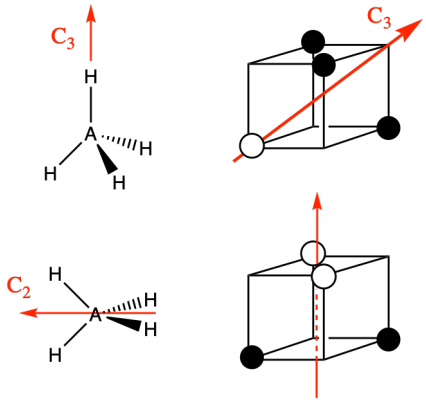


Figure 9 T_d rotation operations

- there are $6\sigma_d$ operations
  - a σ mirror plane passes through each pair of atoms and contains a C_2 axis, ie two mirror planes cross each pair of faces, **Figure 10**, these are dihedral mirror planes σ_d.
  - as there are 3 pairs of faces each with two mirror planes there are $6\sigma_d$ operations in T_d

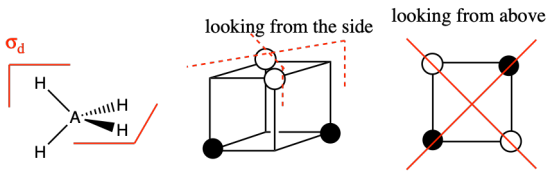


Figure 10 T_d σ_d mirror plane

- there are $6S_4$ operations
  - each C_2 axis has a coincident S_4 axis, consider a rotation of 90º around this axis and then reflection in a plane perpendicular to the axis through the center of the molecule.
  - An example of these elements for the S_4^1 operation is given in **Figure 11**

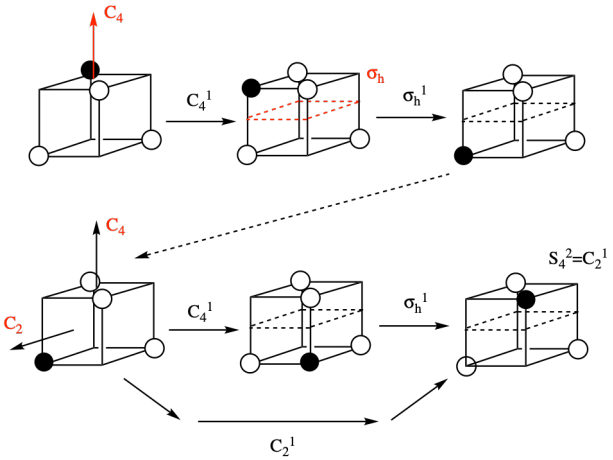
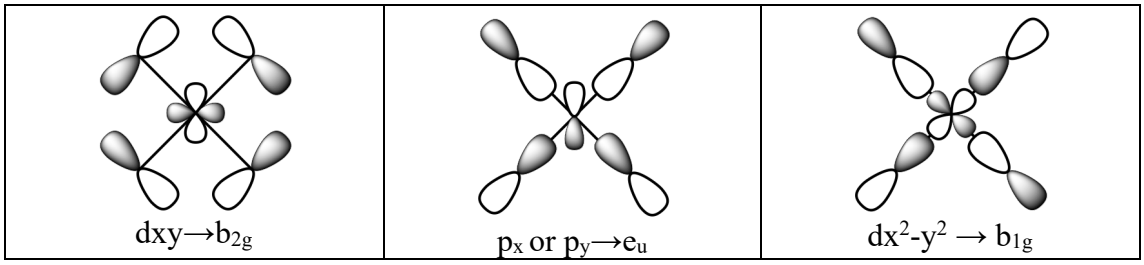


Figure 11 top is the S_4^1 operation, followed by the S_4^2 operation on the bottom

- I am rotating counter clockwise, I can rotate in any direction I like as long as I am consistent for all operations. If I call counter-clockwise the positive direction, then rotating in the opposite direction becomes the "reverse" operation of C_4^{-1}.
- after the C_4^1 operation the "atom" is now "off" the molecule! However, once the whole S_4^1 operation is completed it is back "on" the molecule. This is a consequence of **neither the C_4 nor the σ_h existing within the T_d point group as separate elements**!!
- S_4^2(in **Figure 11**) is the same as C_2^1 operation and C_2 lies to the left of S_4 in the character table and so this operation is not counted with the S_4 operations. In addition the S_4^4 operation is the same as E and so is not counted either
- thus there are $2S_4$ operations per C_2 axis, and as there are $3C_2$ axes there must be $6S_4$ operations in T_d

- Thus we have shown that there are E, $8C_3$ $3C_2$, $6S_4$ and $6\sigma_d$ operations for the T_d point group.
- **Q6** Identify the symmetry of the following MOs of a D_{4h} molecule, use the short-cuts where possible



D_{4h}	E	$2C_4$	C_2	C_2'	C_2''	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	**x^2+y^2, z^2**
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	**x^2-y^2**
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	**xy**
Eg	2	0	-2	0	0	2	0	-2	0	0	**(xz, yz)**
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	**T_z**
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
Eu	2	0	-2	0	0	-2	0	2	0	0	**(T_x, T_y)**

Figure 12 D_{4h} character table