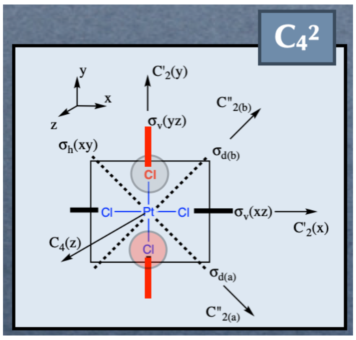
In-Class Problems / Self-study Problems / Test Preparation: Lecture 2

- **In-Class P1** C_4^2 is equivalent to another operation (in addition to $C'_2(x)$), which one is it?



  - The Cl could also be reflected in the $\sigma_v(xz)$ plane

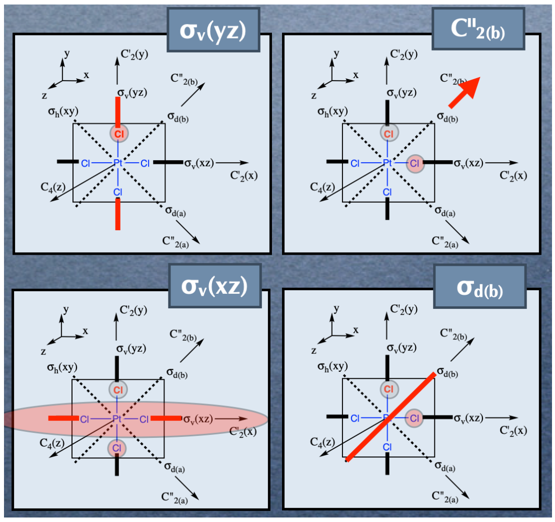


Figure 1 $[PtCl_4]^{2-}$ symmetry elements

- **In-Class P2** What operation is S_3^2 equivalent to? Draw a diagram proving the equality.
  - $S_3^2 = C_3^2$
  - in the figure below make sure you always rotate in the same direction, here the S_n was rotated anticlockwise, so the C_n must also be rotated anticlockwise

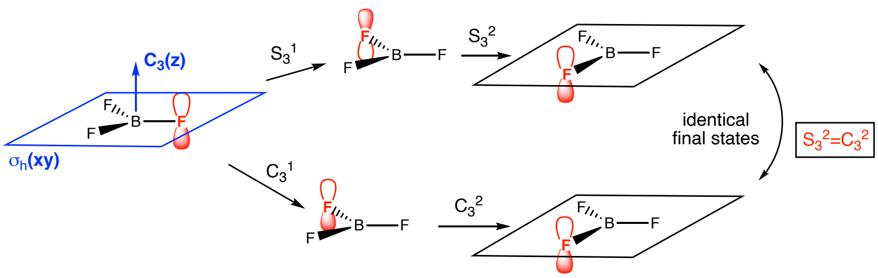


Figure 2 improper rotation

- **In-Class P3** Use a representation table to determine the symmetry label for MO2.

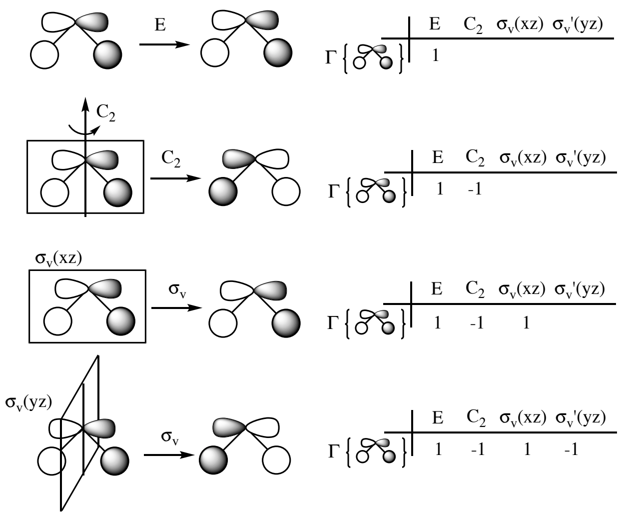
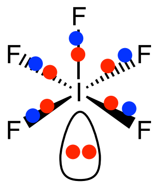


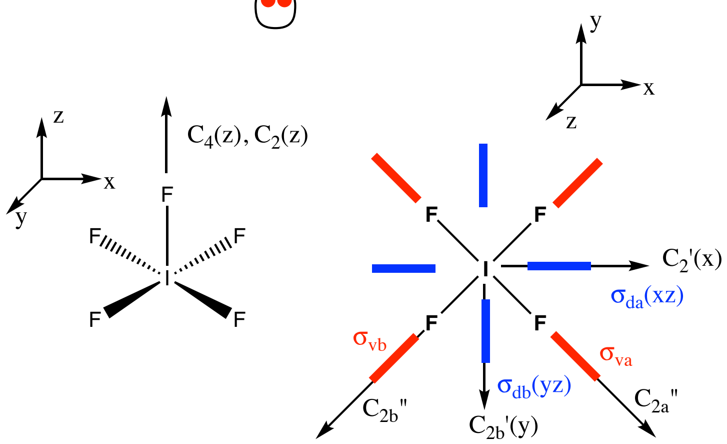
Figure 3 Filling out the representation table for MO2

  - 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 P4** 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.



square based pyramid



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 and C_4^3 are unique, C_4^2 is the same as C_2^1 and C_4^4 is the same as E. 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** Draw a diagram showing all the rotation operations for the C_5 group on the cyclopentadienyl anion

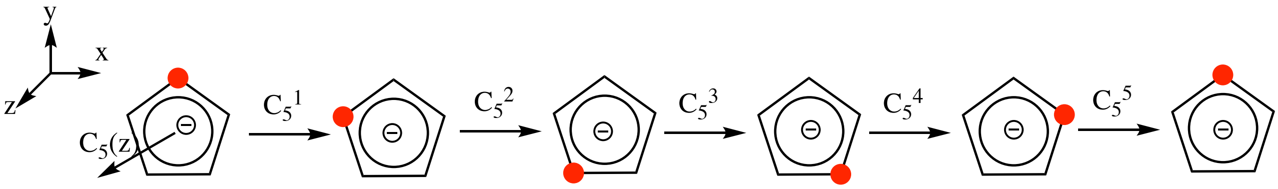


Figure 5 C_5 rotation operations

- **Q2** Work out all of the S_3^n operations up to S_3^6 for D_{3h} $[H_3]^+$ and determine the two unique S_3 operations.
  - although we are using H which has no pAOs, we use a pAO (as a tool) to ensure we take into account the correct symmetry.
  - the unique operations are S_3^1 and S_3^5

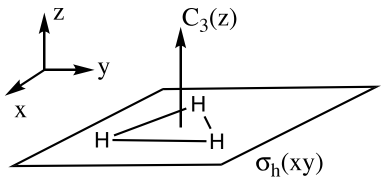


Figure 6 D_{3h} H_3^+

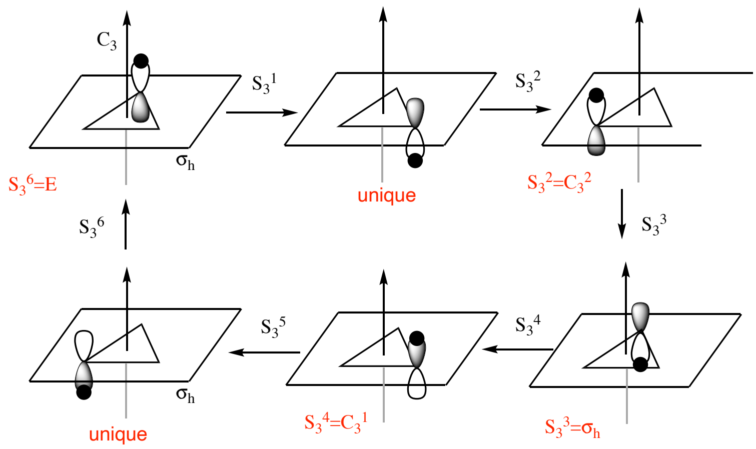


Figure 7 identifying the unique S_3 operations

- **Q3** Which operation is S_3^4 equivalent to? Draw a diagram clearly proving this equality.

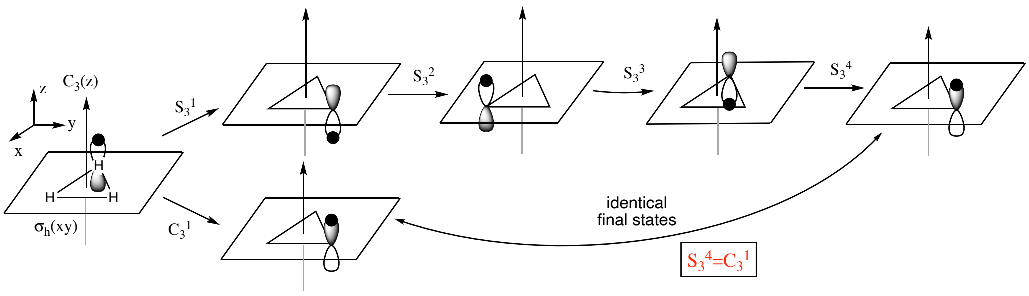


Figure 8 proof that the S_3^4 operation is equivalent to the C_3^1 operation

- **Q4** determine the symmetry label for the molecular orbitals shown for BH_3
  - 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 9**

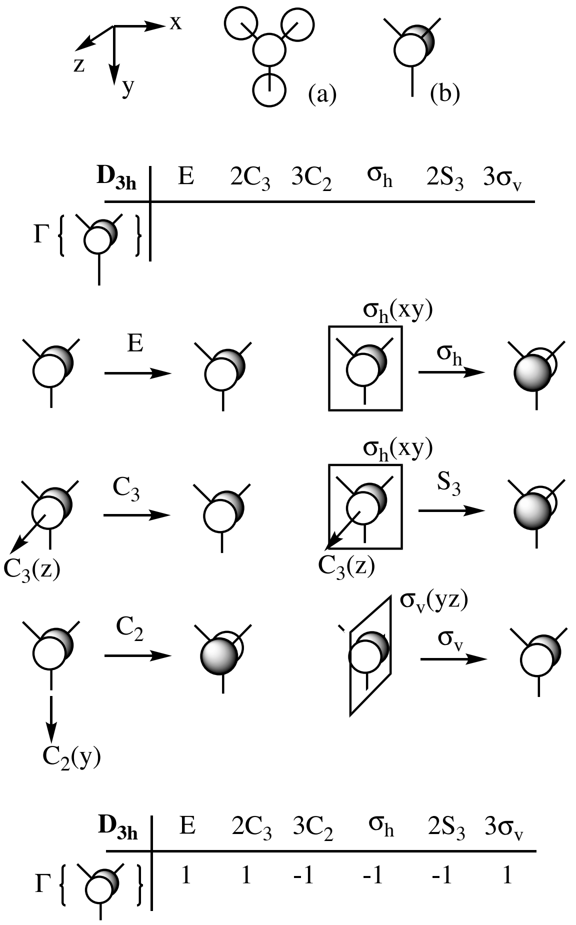


Figure 9 determining the symmetry label for MO (b)

- **Q5** 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''.
- **Q6** *In your own words*, using bullet points, write out the general procedure to determine the symmetry label of a molecular orbital (abstraction from the Kolb cycle!)
  - 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

- **Q7** *In your own words*, using bullet points, write out the general procedure to determine the character of a degenerate set of orbitals? (abstraction from the Kolb cycle!)
  - 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
- **Q8** The Tetrahedral Point Group (challenging but important!)
  - 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 10**, each one emphasises a different aspect of symmetry:
    - (a) the C_2 axes
    - (b) the C_3 axes
    - (c) the cubic structure

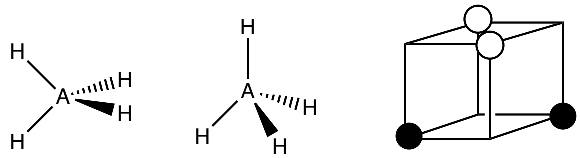


Figure 10 different ways to represent a T_d molecule

  - 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 11** 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	$(T_x T_y T_z)$

Figure 11 T_d character table

- there are *$8C_3$ operations*
  - a C_3 axis lies along each bond, one C_3 axis is shown in **Figure 12**, 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 two 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 12**, 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

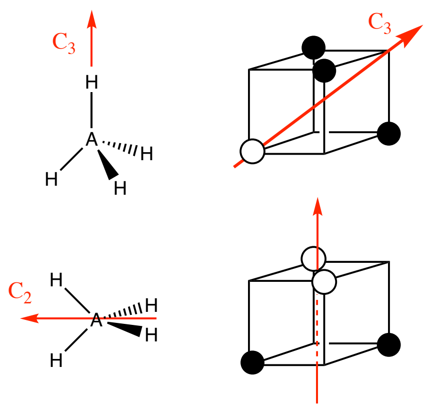


Figure 12 T_d rotation operations

- 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 13**, 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

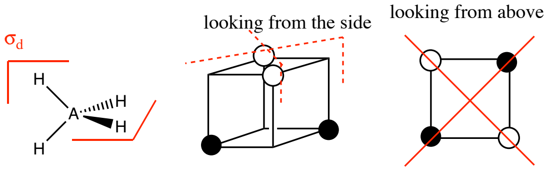


Figure 13 T_d σ_d mirror plane

- there are $6S_4$ operations
  - each C_2 axis has a coincident S_4 axis, consider a rotation of 90° 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 14**Error! Reference source not found..
  - notice that 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}.
  - notice that 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**!!

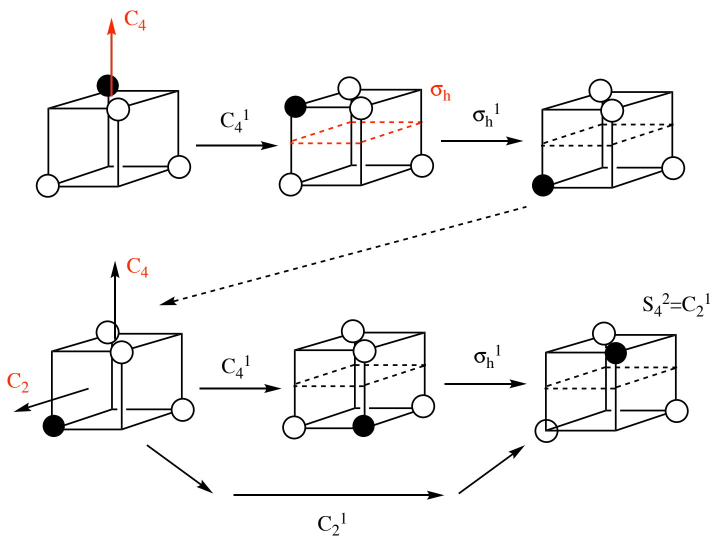


Figure 14 top is the S_4^1 operation, followed by the S_4^2 operation on the bottom

  - S_4^2(**Figure**) 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.