In-Class Problems / Self-study Problems / Test Preparation: Lecture 1

- **In-Class P1** What is the principle axis for PCl_5?
  - the principle axis is the highest Cn axis, ie the axis with the largest n, thus the C_3 axis is the principle axis

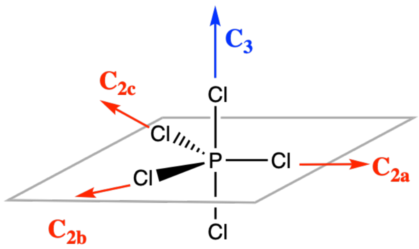
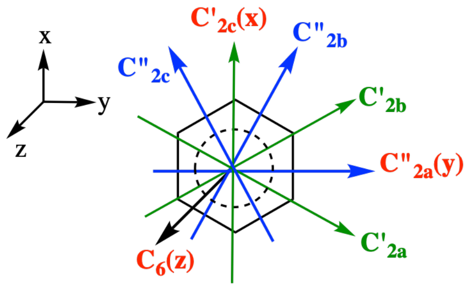
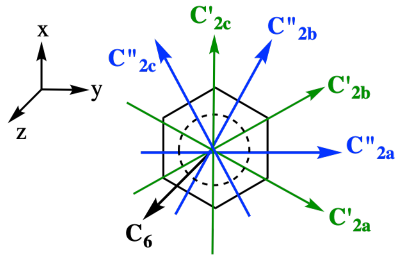


Figure 1 PCl_5 rotation axes

- **In-Class P2** Add the cartesian labels to the relevant axes shown on benzene in **Figure 2**





C_6 comes out of the page
C'_2 go through atoms
C''_2 go through bonds

Figure 2 benzene rotation axes

- **In-Class P3** on a molecule of $[PtCl_4]^{2-}$ draw a diagram for the sequential rotations $C_4^1 \rightarrow C_4^2 \rightarrow C_4^3 \rightarrow C_4^4$
  - C_4 is the principle axis so defines the z-axis position $C_4(z)$, this is easiest drawn as a plan view
  - red Cl is moving after each rotation of 90º, **Figure 4**

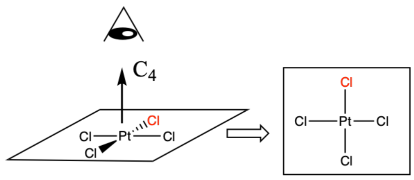
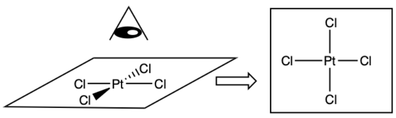


Figure 3 $[PtCl_4]^{2-}$



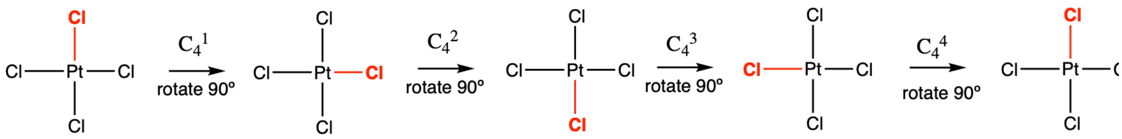


Figure 4 C_4 rotations

- **In-Class P4** Determine the point group of NH_3
  - NH_3 is trigonal pyramidal
  - symmetry elements for NH_3 are E, C_3, and $3\sigma_v$ planes, **Figure 5**
  - use the flow chart
    1. is the molecule linear? NO
    2. is the molecule T_d or O_h? NO
    3. is there a principle C_n axis? YES (C_3 so n=3)
    4. are there nC_2 perpendicular to the principle axis (ie $3C_2$ axes)? NO
    5. is there a σ_h? NO
    6. are there $n\sigma_v$? YES (n=3)
  - therefor the point group of **NH_3 is C_{3v}**

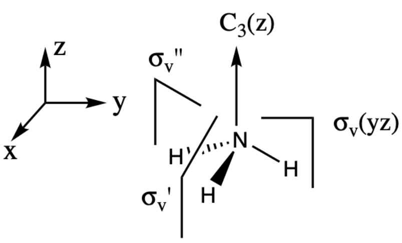


Figure 5 symmetry elements NH_3

- **Q1** find, draw and label all the rotation axes for the square planar $[PtCl_4]^{2-}$ molecular ion
  - see **Figure 6**
  - C_4 is the prinicple axis so defines the z-axis position
  - C_2 and C_4 are coincident, ie in the same place
  - there are two **types** of C_2 axis, ones that go through bonds and ones that go between bonds, different types of axis are labelled with single/double primes
  - only the C_2' axes lie along cartesian axes

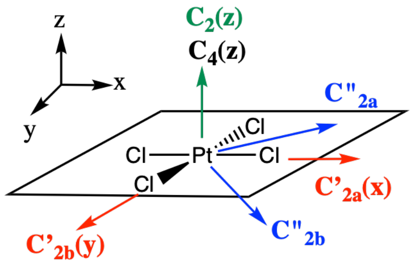


Figure 6 rotation axes for $[PtCl_4]^{2-}$

- **Q2** find, draw and label all the rotation axes and reflection planes for the trigonal planar BH_3 molecule
  - see **Figure 7**
  - diagrams must be clear, you don't need to fit all of the operations on a single diagram
  - you can put some operations on a "side on" diagram and some on an "in-plane" diagram
  - mirror planes can also be represented by a "partial" plane as shown

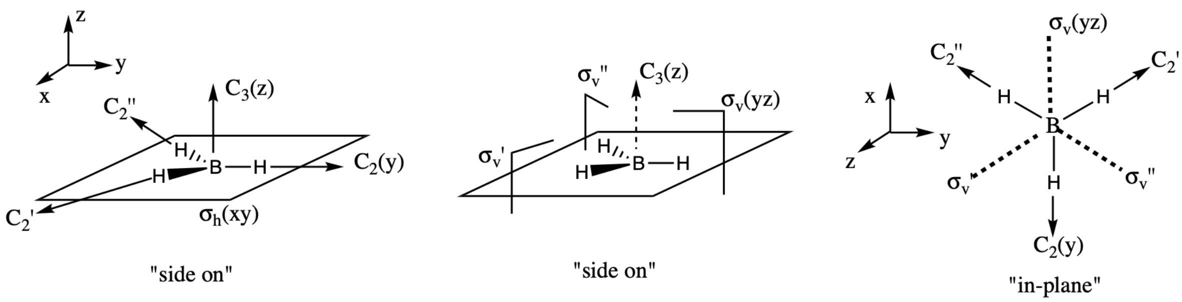
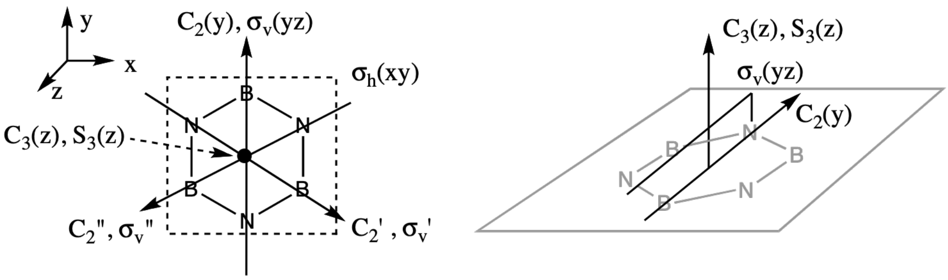


Figure 7 mirror planes and rotation axes for BH_3

- **Q3** On a sketch of borazine illustrate and label the symmetry elements of the D_{3h} point group
  - put in the axial definition, note the z axis is coming out of the page in the first diagram because it has to align with the C_3 axis, **Figure 8**
  - don't crowd your diagrams, use two or three if that will make things clear!
  -



σ_v planes lie perpendicular to the page
and pass through the C_2 axes
S_3 axis is coincident with the C_3 axis

Figure 8 symmetry elements sketched on a molecule of borazine

- **Q4** Draw a diagram showing all the rotation operations for the C_5 group on the cyclopentadienyl anion

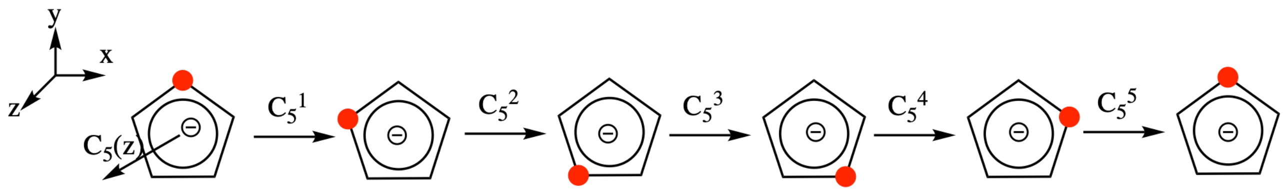


Figure 9 C_5 rotation operations

- **Q5** C_4^2 is equivalent to another operation in addition to $C_2(z)$ and $C'_2(x)$, which one is it?
  1. $\sigma_v(yz)$
  2. $C''_{2(b)}$
  3. $\sigma_v(xz)$
  4. $\sigma_{d(b)}$

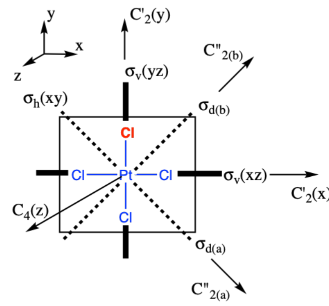


Figure 10 $[PtCl_4]^{2-}$ symmetry elements

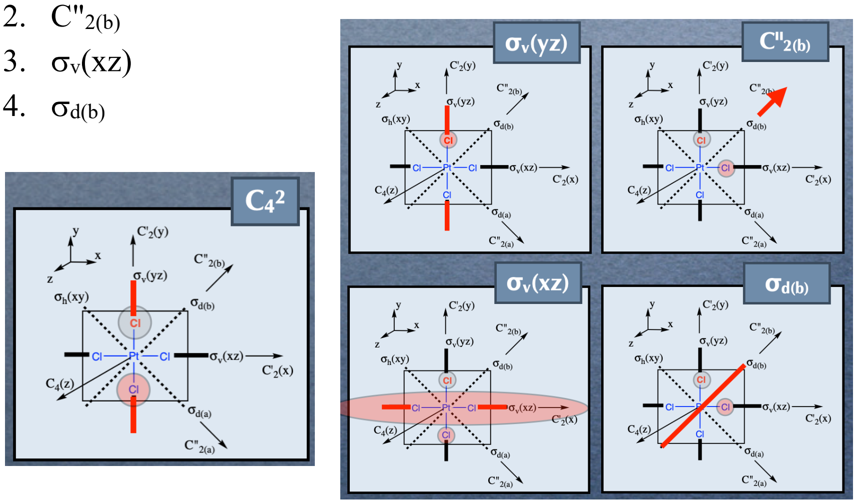


Figure 11 $[PtCl_4]^{2-}$ symmetry elements

- **Q6** What operation is S_3^2 equivalent to? Complete the diagram below and 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

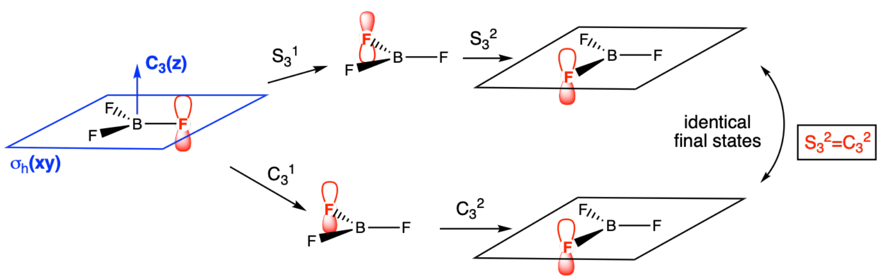


Figure 12 improper rotation

  - If you want something a bit **more challenging** there is a document "Improper rotations of the O_h point group" on my web-site.

- **Q7** Which operation is S_3^4 equivalent to? Draw a diagram clearly proving this equality.

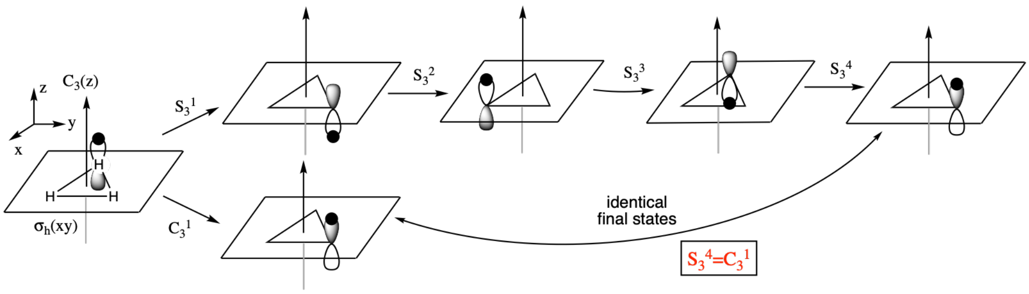


Figure 13 proof that the S_3^4 operation is equivalent to the C_3^1 operation

- **Q8** 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

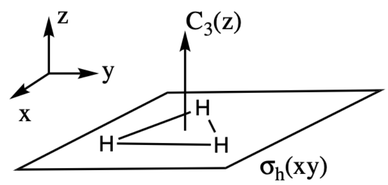


Figure 14 D_{3h} H_3^+

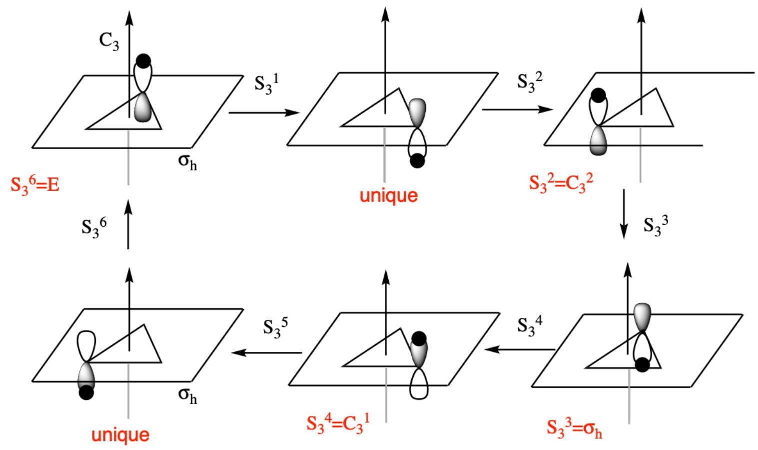


Figure 15 identifying the unique S_3 operations

- **Q9** identify the shape of the following molecules and if they have a center of inversion, if the inversion point lies on an atom, identify that atom. (a)CO_2 (b)$SiCl_4$ (c) SF_6 (d) NH_3 (e) benzene
  - (a) CO_2 is linear, yes, inversion point lies on the C atom
  - (b) $SiCl_4$ is tetrahedral, no inversion point
  - (c) SF_6 is octahedral, yes, inversion point lies on the S atom
  - (d) NH_3 is trigonal pyramidal, no inversion point
  - (e) benzene is hexagonal planar, yes, inversion point lies in the center of the ring

- **Q10** determine the point group of BH_3
  - BH_3 is trigonal planar
  - all of the symmetry elements are shown above in **Figure 7**
  - use the flow chart
    1. is the molecule linear? NO
    2. are there 2 or more C_n $n>2$? NO
    3. is there a princile C_n axis? YES (C_3 so n=3)
    4. are there nC_2 perpendicular to the principle axis (ie $3C_2$ axes)? YES
    5. is there a σ_h? YES
  - therefor the point group of the molecule is D_{3h}

- **Q11** determine the point group of the following molecules (* = more challenging)

a) SH_2	C_{2v}	
b) CO_2	$D_{\infty h}$	
c) $POCl_3$	C_{3v}	
d) trans-N_2F_2	C_{2h}	
e) CCl_4	T_d	
f) $[PtCl_4]^{2-}$	D_{4h}	
g) CHFClBr	C_1	
h) hydrazine N_2H_4	C_2	
i) *cyclohexane (chair)	D_{3d}	https://www.chemtube3d.com/sym-d3dcyclohexane/
j) *cyclohexane (boat)	C_{2v}	https://www.chemtube3d.com/sym-cyclohexaneboat/
k) *benzene	D_{6h}	https://www.chemtube3d.com/symbenzened6h/