CHEM481. Lab Identification and Symmetry and Point Groups and Applying Symmetry to Create Molecular Orbital Diagrams

Overview

In this lab you will learn how to locate elements of symmetry in molecules and how to demonstrate the results of symmetry operations and their application in chemistry sepcifically creating MO diagrams.

1) Make following molecules: H_2O, BF_3, CH_4, PCl_5, C_2H_6 (staggered), C_2H_6 (eclipsed), SF_6, $Fe(\eta\text{-}C_5H_5)_2$ (staggered), $Fe(\eta\text{-}C_5H_5)_2$ (eclipsed), Cr(acac)$_3$

2)Using balls and sticks given. see back of page for drawings

rotation of 120° each step.

C_3 (3) → 3 rotations

~~Draw them below:~~

H_2O, BF_3, CH_4, PCl_5, C_2H_6 (staggered), **C_2H_6**(eclipsed) **SF_6,**

$Fe(\eta\text{-}C_5H_5)_2$ (staggered), **$Fe(\eta\text{-}C_5H_5)$** (eclipsed), **Cr(en)$_3$**

Background

Molecular symmetry is of great value in understanding molecular bonding and spectroscopy. The symmetry of a molecule is expressed as a collection of symmetry operations or elements of symmetry.

A molecule with a particular set of symmetry elements is said to belong to a particular point group. Molecular orbitals and vibrations within molecules also have symmetry properties. Symmetry operations are manipulations of a molecule which result in indistinguishable representations of the molecule; that is, a molecule looks no different before and following a symmetry operation. The operation may exchange two identical atoms, or it may leave one or more atoms unmoved.

The symmetry operations are as follows:

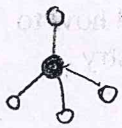
A) Identity (E): The identity is a trivial symmetry operation which involves doing nothing to the molecule. It is mentioned here only for the sake of completeness. All molecules possess an identity and, in some molecules, the identity is the only element of symmetry. same thing when rotate 360°

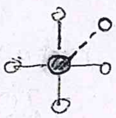
3) Write how identity (E) is obtained for BF_3, CH_4, PCl_5, C_2H_6, SF_6.

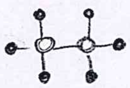
see back of page

H_2O  $C_2^1, C_2^2 = E$

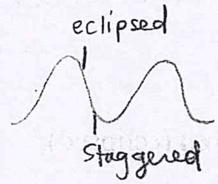
BF_3  $C_3^1, C_3^2, C_3^3 = E$ $C^3 \rightarrow C_3^3 = E$

CH_4  Tetrahedral point group C_3 & C_2 $C_4^4 = E$

PCl_5  C_3 & C_2 $C_3^3 = E$

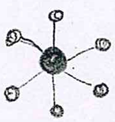
C_2H_6 

eclipse > staggered energys

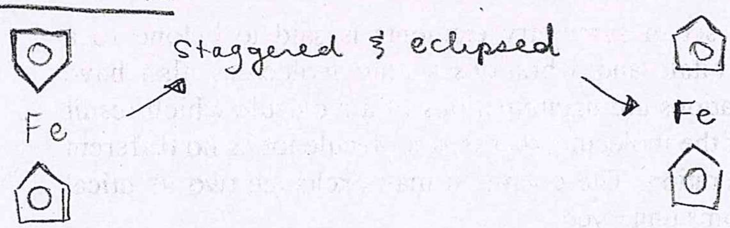


$C_3^3 = E$

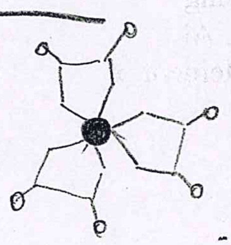
eclipsE

SF_6  octehedral point group - very symmetrical $C_4^4 = E$

$Fe(\eta - C_5H_2)_2$

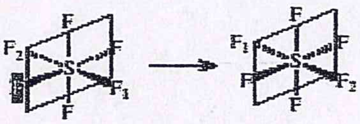


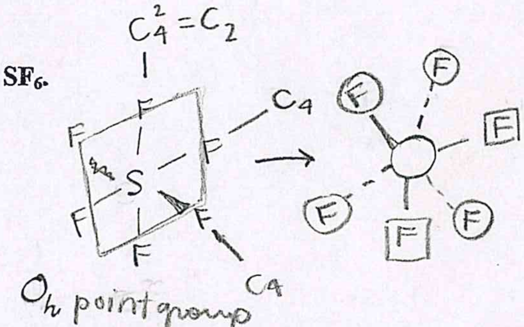
$Cr(en)_3$ $Cr(Ox)_3^{3+}$



B) Axis of Rotation (C_n): An n-fold axis of rotation is a rotation about an axis by 360°/n. Often, but not always, rotation axes correspond to bond axes. For example, SF_6 possesses a C_4 axis which passes through opposing S-F bonds. Rotation by 90° about the axis rotates each fluorine atom perpendicular to the axis into a position previously occupied by another fluorine atom.

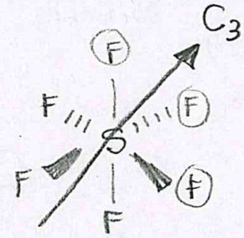
4) Draw a model depicting C_4^2 axis of SF_6.





SF_6 also possesses 3 C_3 axes of rotation which do not pass through bonds. In the following representation, the C_3 axis is perpendicular to the plane of the paper and passes through the sulfur atom.

4) Draw a model depicting C_3 axes of SF_6.



Rotate a molecule

1. Center the molecule in the window by selecting the entire molecule and pressing f on the keyboard. It may resize the molecule in the process of centering it. If the molecule is not centered in the window, it will wobble as the rotation commands are executed.
2. Rotate the molecule until the rotation axis is perpendicular to the screen. You should now be looking directly down the rotation axis, which should be centered in the window.
3. Press r on the keyboard to enter rotation mode.
4. Press z to rotate in the clockwise direction and Z to rotate counter-clockwise. Rotate around the x and y axes by pressing x, X, y or Y. Rotation occurs by 15° each time. Thus three operations result in a 45°rotation, 4 - 60°, 6 - 90°, 8 -120°, etc. You may rotate continuously by pressing the Space bar while in rotate mode. To halt continuous rotation, press the Space bar again.

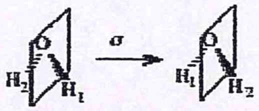
Plane of Symmetry or Reflection (σ): A mirror plane of symmetry is an operation in which reflection of an atom from one side of the plane to the other results in an indistinguishable representation of the molecule. Atoms which lie within the plane are unmoved.

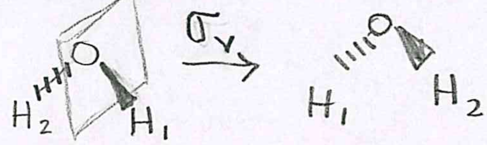
$\sigma_H \rightarrow \sigma_{Horizontal}$

$\sigma_v \rightarrow \sigma_{vertical}$

$\sigma_d \Rightarrow \sigma_{diagonal}$

5) Make a drawing of your model of H_2O depicting mirror planes.

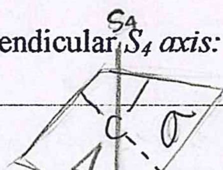




Reflect through a mirror plane

Improper Rotation or rotation-reflection (S_n): An improper rotation is the result of two operations in sequence; rotation by 360°/n, followed by reflection through a mirror plane perpendicular to the axis of rotation. An example of an improper axis of rotation is shown below. $C_1 \perp \sigma = S_1$

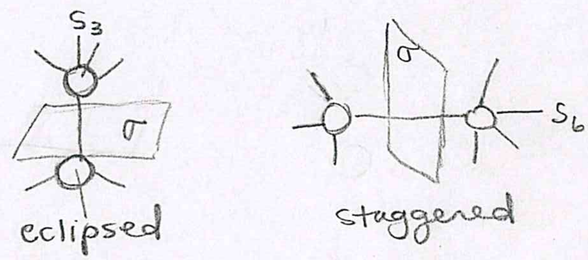
In CH_4 show plane perpendicular *S_4 axis:* plane perpendicular to S_4 is σ



In CH_4 show *S_4 axis:*

In C_2H_6, ethane, show improper rotation axis (S_6) :

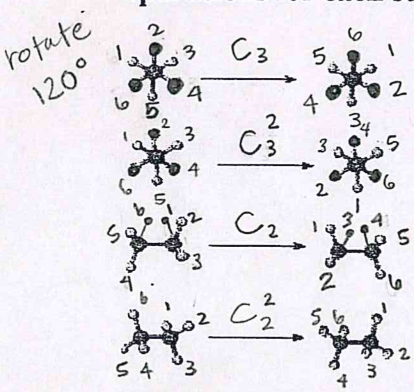
In C_2H_6, show plane perpendicular to S_6 :



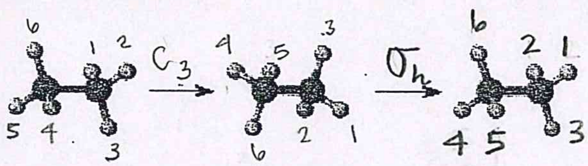
Execute and demonstrate an improper rotation

Follow the procedures for rotation and reflection in sequence.

6) To demonstrate in C_2H_6 label carbon and hydrogen atoms, identify and write the operations for each step

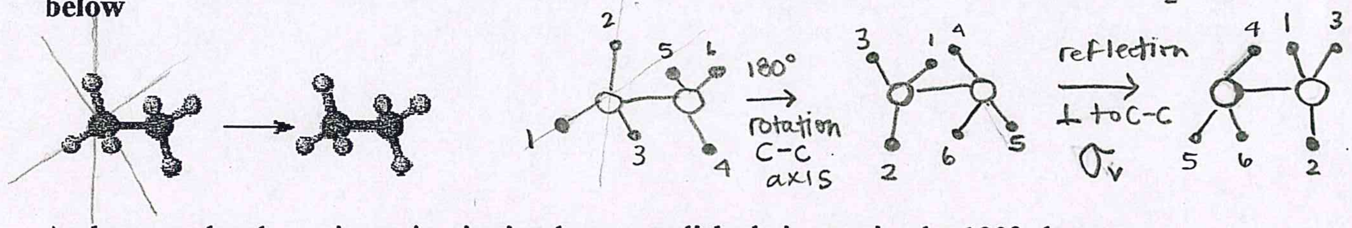


7) Label carbon and hydrogen atoms and write two operations (C_3 and σ) of on the diagram below



Inversion (*i*): An inversion through the center of a molecule can usually be accomplished by a rotation by 180° followed by reflection through a plane (Mirror operation) perpendicular to the rotation. Note that this is identical to an S_2 as in the example below (rotation by 180° about the C-C axis followed by reflection through a plane perpendicular to the C-C axis).

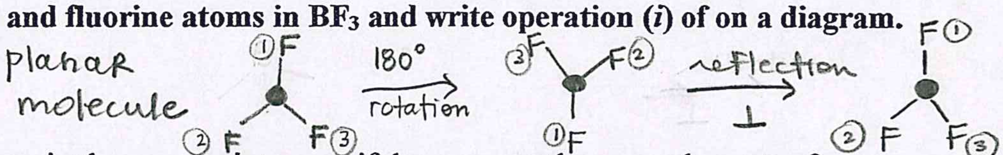
8) Label carbon and hydrogen atoms and write operation (*i*) of on the diagram below $S_2 = i$



A planar molecule, an inversion is simply accomplished via rotation by 180° about an axis perpendicular to the plane since subsequent reflection through the plane leaves the molecule unchanged.

8) Label boron and fluorine atoms in BF_3 and write operation (*i*) of on a diagram.

Point Groups



Two molecules are in the same point group if they possess the same elements of symmetry. The first step in a group theory analysis of a molecule is to determine the point group of the molecule. There is a systematic way of naming most point groups

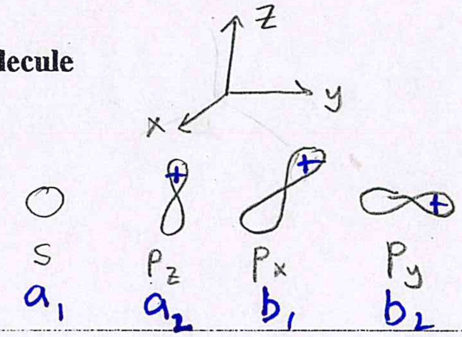
9) Using the chart in the book assign the point group to each of the following molecules

a. **H_2O** C_{2v}
b. **BF_3** D_{3h}
c. **CH_4** T_d
d. **PCl_5** D_{3h}
e. **C_2H_6** (staggered) D_{3d}
f. **C_2H_6** (eclipsed) D_{3h}
g. **Fe(η-C_5H_5)** (staggered) D_{5d}
h. **Fe(η-C_5H_5)** (eclipsed) D_{5h}
i. **Cr(acac)$_3$** D_3
j. **SF_6** O_h

Character Tables

The top row and first column consist of the symmetry operations and irreducible representations respectively. The table elements are the characters. The final two columns show the first and second order combinations of Cartesian coordinates. Infinitesimal rotations are listed as I_x, I_y, and I_z.

Character table for point group C_{2v}, H_2O, water molecule



C_{2v}	E	C_2	s_v	s_v'		
[illegible]	1	1	1	1	z	x^2, y^2, z^2
[illegible]	1	1	-1	-1	R_z	xy
[illegible]	1	-1	1	-1	x, R_y	xz
[illegible]	1	-1	-1	1	y, R_x	yz

Character table for point group O_h, SF_6,

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2'$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2 (=r^2)$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(3z^2-r^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(I_x, I_y, I_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, yz, zx)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

10) Using appropriate character table do the following:

a) Using character table for point group C_{2v}, H_2O, water molecule identify symmetry representation of s, p_x, p_y and p_z atomic orbitals on oxygen atom of water molecule.

$C_{2v} \Rightarrow H_2O$

	s	p_x	p_y	p_z
symmetry representation	a_1	b_1	b_2	a_1

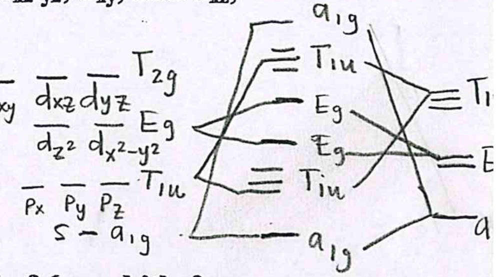
b) From the appendices in the book obtain the pictures of SALC of 2 s orbitls from 2 terminal hydrogen atoms in the H_2O molecule

S

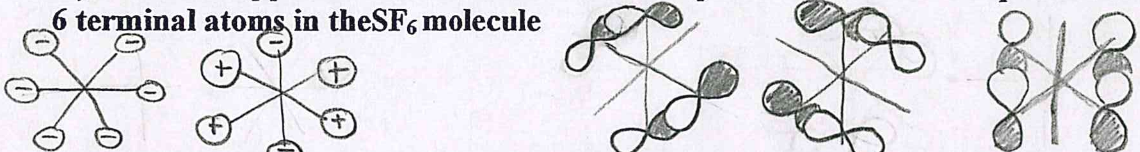
c) Using character table for point group O_h, SF_6, s, p_x, p_y p_z, d_{z2}, d_{x2-y2}, d_{xy}, and d_{xz}, d_{yz} atomic orbitals on sulfur atom of SF_6 molecule.

S : s p_x p_y p_z d_{z^2} $d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}

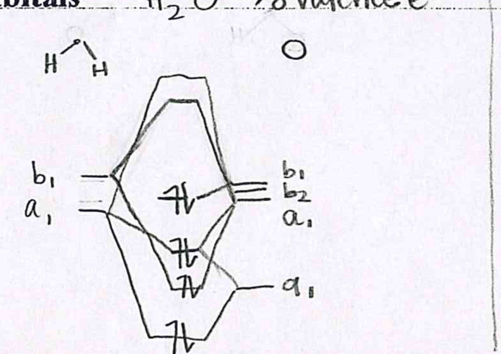
A_{1g} T_{1u} T_{1u} T_{1u} E_g E_g T_{2g} T_{2g} T_{2g}

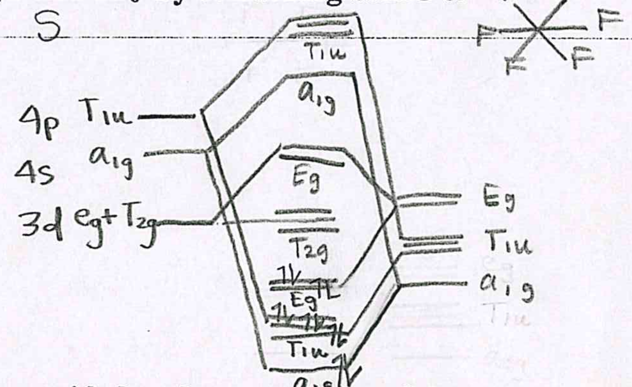


d) From the appendices in the book obtain the pictures of SALC of 6 p orbitls from 6 terminal atoms in theSF$_6$ molecule

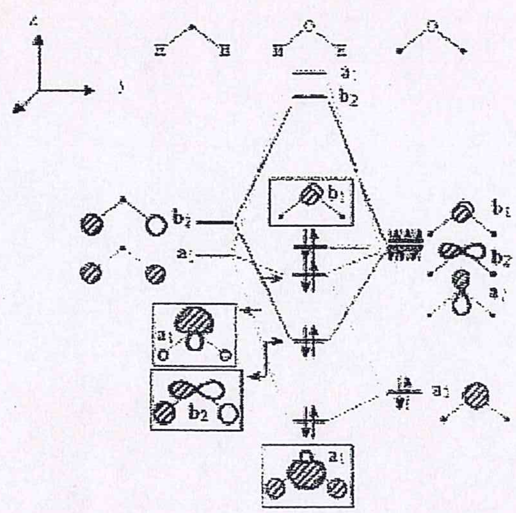


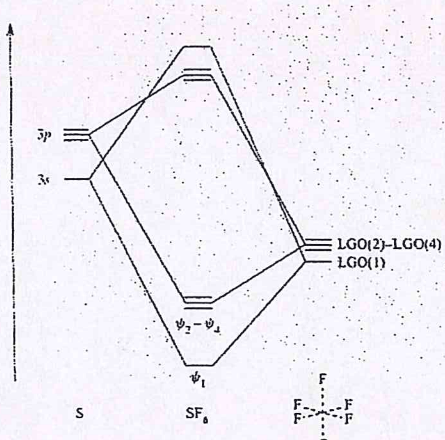
12) Obtain molecular orbital diagram for H_2O and SF_6 by combining SALC of orabitals H_2O → 8 valence e⁻





13) Compare symmetry labels and diagrams provided to the symmetries of the molecular orbital diagrams of H_2O and SF_6





SF_6 : uses A_{1g}, T_{1u}, E_g

H_2O : uses A_1, B_1, B_2