

## Topic II

# Symmetry and Group Theory in Chemistry

### II.1 Module 3: Symmetry Elements and Operations

1/13:

- He will upload lecture slides in advance in the future.
- An object is symmetric if one part is the same as other parts.
- The symmetry of discrete objects is described using **Point Symmetry**.
- **Point groups** ( $\sim 32$  for molecules) provide us with a way to indicate the symmetry unambiguously.
- Point groups have symmetry about a single point at the center of mass of the system.
- Extended objects (e.g., crystals) have **translational symmetry** described by **Space groups**<sup>[1]</sup> (230 total).
- Reading: Miessler et al. (2014) Chapter 4 and [https://en.wikipedia.org/wiki/Molecular\\_symmetry](https://en.wikipedia.org/wiki/Molecular_symmetry).
- **Symmetry elements**: Geometric entities about which a **symmetry operation** can be performed. In a point group, all symmetry elements must pass through the center of mass (the point).
- **Symmetry operation**: The action that produces an object identical to the initial object.

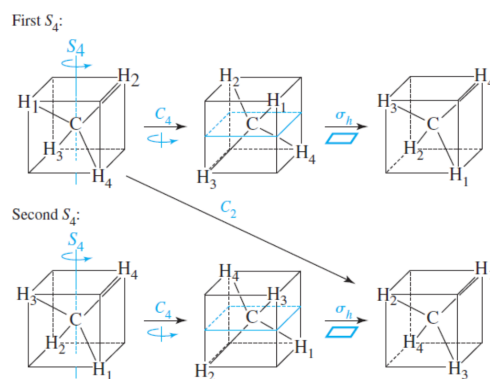
Element	Operation
Identity, $E$	nothing
Rotation axis, $C_n$	$n$ -fold rotation
Improper rotation axis, $S_n$	$n$ -fold improper rotation
Plane of symmetry, $\sigma$	Reflection
Center of symmetry, $i$	Inversion

- **Identity**: Does nothing to the object, but is necessary for mathematical completeness.
- **$n$ -fold rotation**: A rotation of  $360^\circ/n$  about the  $C_n$  axis ( $n \in [1, \infty)$ ).
  - In  $\text{H}_2\text{O}$ , there is a  $C_2$  axis, so we can perform a 2-fold ( $180^\circ$ ) rotation to get the same molecule.
    - Remember, because of quantum mechanical properties, the hydrogens are indistinguishable so when we rotate it  $180^\circ$ , we cannot tell it apart from the unrotated molecule.
  - Rotations are considered positive in the counterclockwise direction.

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<sup>1</sup>Not covered in this course.

- Each possible rotation operation is assigned using a superscript integer  $m$  of the form  $C_n^m$ .  $m$  is the number of sequential applications.
- The rotation  $C_n^n \equiv E$  is equivalent to the identity operation (nothing is moved).
- Linear molecules have an infinite number of rotational options  $C_\infty$  because any rotation on the molecular axis will give the same arrangement.
- **Principal axis:** The highest order rotation axis.
  - By convention, the principal axis is assigned to the  $z$ -axis if we are using Cartesian coordinates.
- **Reflection:** Exchanges one half of the object with the reflection of the other half.
- **Vertical mirror plane:** A mirror plane that contains the principal axis. *Also known as  $\sigma_v$ .*
- **Horizontal mirror plane:** A mirror plane that is perpendicular to the principal axis. *Also known as  $\sigma_h$ .*
- **Dihedral mirror planes:** A special type of  $\sigma_v$  that is between sides or planes. *Also known as  $\sigma_d$ .*
  - For example, we might have vertical mirror planes in the  $xz$ - or  $yz$ -planes. In this case, the dihedral planes would contain the lines  $y = \pm x$ .
- Two successive reflections are equivalent to the identity operation.
- **Inversion:** Every part of the object is reflected through the inversion center, which must be at the center of mass of the object.
  - $(x, y, z) \xrightarrow{i} (-x, -y, -z)$ .
- **$n$ -fold improper rotation:** This operation involves a rotation of  $360^\circ/n$  followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as “proper” rotations. *Also known as  $S_n^m$ , rotation-reflection operation.*

Figure II.1: Methane's  $S_4$  symmetry.

- Methane has  $S_4$  symmetry.
- Note that  $S_1 \equiv \sigma_h$ ,  $S_2 \equiv i$ , and sometimes  $S_{2n} \equiv C_n$ . In methane, for example,  $S_4^2 \equiv C_2$ .
- Applied to a triangular prism, is a good example.
- If  $n$  is even, we have  $n$  unique operations. There should be  $C_{n/2}$ .
- If  $n$  is odd, we have  $2n$  unique operations. There should be  $C_n$  and  $\sigma_h$ .
- The absence of an  $S_n$  axis is the defining symmetry property of **chiral** molecules.
  - Formerly, we learned that chiral molecules should not have mirror planes and inversion centers.
  - Rigorously, chiral molecules must not have any improper rotation axes.

## II.2 Module 4: Symmetry Point Groups

- Identifying the point groups:
  - Determine if the symmetry is special (e.g., octahedral).
  - Determine if there is a principal rotation axis.
  - Determine if there are rotation axes perpendicular to the principal axis.
  - Determine if there are mirror planes.
  - Assign point groups.
- High symmetry and low symmetry groups are the most difficult to identify.
- High symmetry:
  - Perfect tetrahedral ( $T_d$ ), e.g.,  $P_4$  and  $CH_4$ .
  - Perfect octahedral ( $O_h$ ), e.g.,  $SF_6$ .
  - Perfect icosahedral ( $I_h$ ), e.g.,  $C_{60}$  and  $B_{12}H_{12}^{2-}$ .

- Low symmetry:

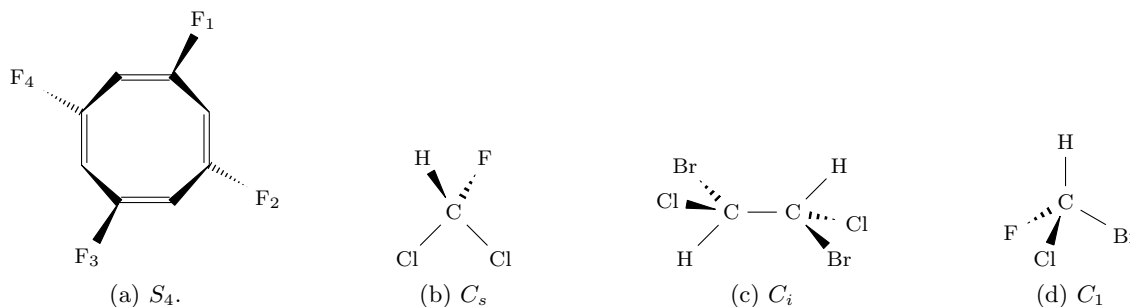


Figure II.2: Low symmetry point groups.

- Only an improper axis:  $S_n$ .
- Only a mirror plane:  $C_s$ .
- Only an inversion center:  $C_i$ .
- No symmetry:  $C_1$ .
- $C_n$  groups:
  - Only a  $C_n$  axis. Note that conformation is important.
- $C_{nh}$  groups have a  $C_n$  axis and a  $\sigma_h$  reflection plane (such as  $B(OH)_3$ ).
  - $H_2O_2$  has  $C_{2h}$  symmetry.
- All symmetry elements are listed in the top row of the corresponding characters table (Appendix C in Miessler et al. (2014)).
- $C_{nv}$  groups have a  $C_n$  axis and a  $\sigma_v$  reflection plane.
  - $NH_3$  has  $C_{3v}$  symmetry.
  - $CO$  has  $C_{\infty v}$  symmetry since there are an infinite number of both  $C_n$  axes and  $\sigma_v$  mirror planes.
- $D_{nh}$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and a  $\sigma_h$  reflection plane.

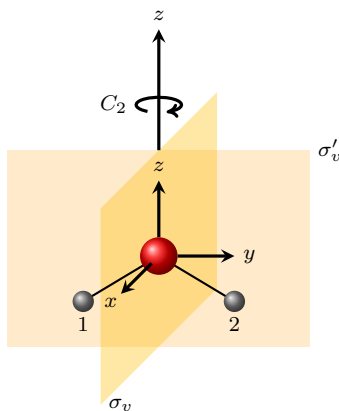
- $\text{BH}_3$  has  $D_{3h}$  symmetry.
- A square prism has  $D_{4h}$  symmetry.
- $\text{CO}_2$  has  $D_{\infty h}$  symmetry.
- $D_n$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and no mirror planes.
  - A 3-bladed propeller has  $D_3$  symmetry.
- $D_{nd}$  groups: A  $C_n$  axis,  $n$  perpendicular  $C_2$  axes, and a  $\sigma_d$ .
  - Ethane in the staggered conformation has  $D_{3d}$  symmetry.
- Local symmetry:
  - Sometimes, rigorous math analysis needs to be adjusted to physical reality.
  - If a cyclopentane ring is bonded through the center to  $\text{Mn}(\text{CO})_3$ , this molecule has only  $C_s$  symmetry.
  - However, spectroscopically, there is fast rotation about the Mn–Cp bond. This means that the  $\text{Mn}(\text{CO})_3$  fragment exhibits pseudo- $C_{3v}$  symmetry while the  $\text{C}_5\text{H}_5$  ligand exhibits pseudo- $C_{5v}$  symmetry.
  - Often, the absolute symmetry of a molecule is very low, but the interactions are far away from the centers of interest, and do not perturb them significantly.
  - If we have platinum as a central atom bonded to two chlorines and two  $\text{P}(\text{Et})_3$  groups, this molecule technically has  $C_1$  symmetry due to the orientations of atoms within R groups (staggered), but IR spectroscopy is characteristic of highly symmetric species ( $D_{2h}$ ).

## II.3 Module 5: Group Theory 101

1/15:

- **Group:** A set of elements together with an operation that combines any two of its elements to form a third element satisfying four conditions called the group axioms.
- **Closure:** All binary products must be members of the group.
- **Associativity:** Associative law of multiplication must hold.
- **Identity:** A group must contain the identity operator.
- **Inverse:** Every operator must have an inverse.
- The integers with the addition operation form a group, for example.
- History:
  - Early group theory was driven by the quest for solutions of polynomial equations of degree 5 and above.
  - Early 1800s: Évariste Galois realized that the algebraic solution to a polynomial equation is related to the structure of a group of permutations associated with the roots of the polynomial, the Galois group of the polynomial.
    - [Link to Galois video here.](#)
  - 1920s: Group theory was applied to physics and chemistry.
  - 1931: It is often hard or even impossible to obtain a solution of the Schrödinger equation — however, a large part of qualitative results can be obtained by group theory. Almost all the rules of spectroscopy follow from the symmetry of a problem.
- We will use group theory for describing symmetry of molecules. We will use group theory to understand the bonding and spectroscopic features of molecules.

- For us, a group consists of a set of symmetry elements (and associated symmetry operations) that completely describes the symmetry of a molecule.
- **Order** (of a group): The total number of elements (i.e., symmetry operations) in the group. *Also known as  $h$ .*
- Rule 1: Closure.

Figure II.3: Symmetry elements for H<sub>2</sub>O.

- H<sub>2</sub>O is of the  $C_{2v}$  point group (refer to Figure II.3).
  - Symmetry operations:  $E$ ,  $C_2$ ,  $\sigma_{v(xz)}$ , and  $\sigma'_{v(yz)}$ .
  - $\sigma_v \cdot C_2 = \sigma'_v = C_2 \cdot \sigma_v$ .
  - The above property (order *does not* matter) shows that  $C_{2v}$  is an **Abelian group**.
- NH<sub>3</sub> is of the  $C_{3v}$  point group.
  - Symmetry operations:  $E$ ,  $C_3^+$ ,  $C_3^-$ ,  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ .
  - $\sigma''_v \cdot C_3 = \sigma_v$ , but  $C_3 \cdot \sigma''_v = C_3^- = C_3^2$ .
  - The above property (order *does* matter) shows that  $C_{3v}$  is a **non-Abelian group**.
- Rule 2: Associativity.
  - H<sub>2</sub>O is of the  $C_{2v}$  point group (refer to Figure II.3).
 

$\sigma'_v C_2 \sigma_v(1, 2) = \sigma'_v C_2(2, 1)$	$\sigma'_v(C_2 \sigma_v)(1, 2) = \sigma'_v E(1, 2)$	$(\sigma'_v C_2) \sigma_v(1, 2) = \sigma_v \sigma_v(1, 2)$
$= \sigma'_v(1, 2)$	$= \sigma'_v(1, 2)$	$= \sigma_v(2, 1)$
$= (1, 2)$	$= (1, 2)$	$= (1, 2)$
- Rule 3: Identity.
- Rule 4: Inverse.
  - For a  $C_{2v}$  point group:
 

$E \cdot E = E$	$C_2 \cdot C_2 = E$	$\sigma_v \cdot \sigma_v = E$	$\sigma'_v \cdot \sigma'_v = E$
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- Group multiplication tables.

$C_{2h}$	$E$	$C_2$	$\sigma_h$	$i$
$E$	$E$	$C_2$	$\sigma_h$	$i$
$C_2$	$C_2$	$E$	$i$	$\sigma_h$
$\sigma_h$	$\sigma_h$	$i$	$E$	$C_2$
$i$	$i$	$\sigma_h$	$C_2$	$E$

Table II.1: Group multiplication table for the  $C_{2h}$  point group.

- Table II.1 corresponds to the  $C_{2h}$  point group, which has  $E$ ,  $C_2$ ,  $\sigma_h$ , and  $i$  operations.
- Note that the operation in the top row is the one that's applied first, while the one in the left column will be applied second.

- **Subgroup:** Fractional parts of groups that are groups, too.

$C_{3v}$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$E$	$E$	$C_3$	$C_3^2$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$
$C_3$	$C_3$	$C_3^2$	$E$	$\sigma''_v$	$\sigma_v$	$\sigma'_v$
$C_3^2$	$C_3^2$	$E$	$C_3$	$\sigma'_v$	$\sigma''_v$	$\sigma_v$
$\sigma_v$	$\sigma_v$	$\sigma'_v$	$\sigma''_v$	$E$	$C_3$	$C_3^2$
$\sigma'_v$	$\sigma''_v$	$\sigma_v$	$\sigma'_v$	$C_3$	$C_3^2$	$E$
$\sigma''_v$	$\sigma'_v$	$\sigma''_v$	$\sigma_v$	$C_3^2$	$E$	$C_3$

Table II.2: Group multiplication table for the  $C_{3v}$  point group.

- If  $h = 6$  (as in the  $C_{3v}$  group), subgroup order can be  $h = 3, 2, 1$ . Why only these?
- The order 1 and 3 charts are subgroups.
- The order 2 chart is not a subgroup because  $C_3^2$  is not an operation in the group (therefore, the “subgroup” is not closed).
- We use subgroups because they can make complex problems simpler.
  - For example, calculating the vibrational modes of  $\text{CO}_2$ .
  - As another example,  $D_{2h}$  is a subgroup of  $D_{\infty h}$ .

## II.4 Module 6: Representations

- Items of the same point group have the same vibration modes.
- **Representation** (of a group): Any collection of quantities (or symbols) which obey the multiplication table of a group. *Also known as*  $\Gamma$ .
- For our purposes, these quantities are the matrices that show how certain characteristic of a molecule behave under the symmetry operations of the group.
- Operations (on a point  $(x, y, z)$  in Cartesian coordinates):
  - $E(x, y, z) = (x, y, z)$ .
  - $\sigma_{xz}(x, y, z) = (x, -y, z)$ .
  - $i(x, y, z) = (-x, -y, -z)$ .
  - $C_n$ : Convention is a counterclockwise rotation of the point by  $\theta = \frac{2\pi}{n}$  radians.
  - $S_n$ : Convention is a clockwise rotation of the point  $C_n$  followed by a  $\sigma$  through a plane perpendicular to  $C$ .

- Matrix forms of operations:

– Identity:  $E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ .

– One example of a reflection (there are two more):  $\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$ .

– Inversion:  $i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$ .

– Rotation: Counterclockwise is  $C_n(\theta) = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$  and clockwise is  $C_n(\theta) = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$ .

■ A derivation of this matrix can be found in the slides.

– Improper rotation:  $S_n(\theta) = \sigma_h C_n(\theta)$ .

- **Reducible representations** ( $\Gamma$ ):

- A representation of a symmetry operation of a group.
- Can be expressed in terms of a representation of lower dimension.
- Can be broken down into a simpler form.
- Characters can be further diagonalized.
- Are composed of the direct sum of irreducible representations.
- Infinite possibilities.

- **Irreducible representations** ( $\Gamma_i$ ):

- A fundamental representation of a symmetry operation of a group.
- Cannot be expressed in terms of a representation of lower dimension.
- Cannot be broken down into a simpler form.
- Characters cannot be further diagonalized.
- Small finite number dictated by point group.

- Good example of reducible/irreducible representations?

- A representation shows how certain characteristics of an object (a basis) behave under the symmetry operation of the group.

- **Conjugate elements:** Two elements  $X$  and  $Y$  for which there exists an element  $Z$  in the group such that

$$Z^{-1} \cdot X \cdot Z = Y$$

- Every element is conjugated with itself (let  $Z = E$ ).
- If  $X$  is conjugated with  $Y$ , then  $Y$  is conjugated with  $X$ .
- If  $X$  is conjugated with  $Y$  and  $W$ , then  $Y$  and  $W$  are also conjugate.

- **Class:** A complete set of elements of a group that are conjugate to one another.

- Geometric meaning: operations in the same class can be converted into one another by changing the axis system through application of some symmetry operation of the group.

- Find the conjugates to  $C_3$  in the  $C_{3v}$  point group (refer to Table II.2 throughout the following discussion).

- Let  $X = C_3$ , let  $Z$  iterate through the six symmetry elements ( $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$ ), and let  $Z^{-1}$  iterate through the corresponding inverses ( $E, C_3^2, C_3, \sigma_v, \sigma'_v, \sigma''_v$ ).
- Thus, we have

$$\begin{aligned} E \cdot C_3 \cdot E &= C_3 \\ C_3^2 \cdot C_3 \cdot C_3 &= C_3 \\ C_3 \cdot C_3 \cdot C_3^2 &= C_3 \\ \sigma_v \cdot C_3 \cdot \sigma_v &= C_3^2 \\ \sigma'_v \cdot C_3 \cdot \sigma'_v &= C_3^2 \\ \sigma''_v \cdot C_3 \cdot \sigma''_v &= C_3^2 \end{aligned}$$

- It follows from the above that  $C_3$  and  $C_3^2$  are conjugates, and  $C_3$  and  $C_3^2$  are conjugates.
- Thus,  $C_3$  and  $C_3^2$  are in the same class.
- We can use a similar method to prove that  $\sigma_v, \sigma'_v$ , and  $\sigma''_v$  are all in the same class within the  $C_{3v}$  point group.
- Likewise  $E$  is in a class by itself.
- Thus, for the  $C_{3v}$  point group,  $E$  forms a class of order 1,  $C_3, C_3^2$  form a class of order 2, and  $\sigma_v, \sigma'_v, \sigma''_v$  form a class of order 3.

- **Similarity transformation:** The transformation

$$v^{-1} \cdot A \cdot v = A'$$

- $A$  is a representation for some type of symmetry operation.
- $v$  is a similarity transform operator.
- $v^{-1}$  is the inverse of the similarity transform operator.
- $A'$  is the product.
- $A$  and  $A'$  are conjugates, and we say that  $A'$  is the similarity transform of  $A$  by  $v$ .
- **Block-diagonal (matrix):** A matrix with nonzero values only in square blocks along the diagonal from the top left to the bottom right.

$$\begin{bmatrix} 2 & 3 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{bmatrix}$$

- The above matrix is an example of a block-diagonal matrix.
- Irreducible representations are the ones where the matrices have the most block-diagonalized form that they can.

## II.5 Module 7: Characters and Character Tables

1/19:

- Nocera Lecture 3 notes (on Canvas) explain how reducible and irreducible transformations are related to each other through the similarity transformations.
- For  $H_2O$ , each atom has 3 Cartesian coordinates, so our transformation matrix<sup>[2]</sup> is 9-square.

<sup>2</sup>Some values in it are negative because of the cosine/sine definition of a rotation matrix for  $\theta = 180^\circ$ .



- However, we can also apply a smaller matrix to the molecule as a whole and invoke symmetry to find the position of the individual atoms.
- **Characters** (of a representation): The traces (i.e., sums of the diagonal matrix elements) of the representation matrices for each operation. *Also known as  $\chi$ .*
  - The character is an invariant for each type of symmetry operation (e.g., regardless of the axis about which a  $C_n$  operation is performed, the trace of the corresponding matrix will be the same).
- Common characters:
  - $C_n$  character:  $\chi = 2 \cos \theta + 1$ .
  - $\sigma_v, \sigma_d$  character:  $\chi = 1$ .
  - $S_2 \equiv i$  character:  $\chi = -3$ .
  - $S_n$  character:  $\chi = 2 \cos \theta - 1$ .
  - $\perp C_2$  axes character:  $\chi = -1$ .
- **Character table:** The collection of characters for a given irreducible representation, under the operations of a group.

Irreducible Representations	Group Symbol	Symmetry Elements				linear	quadratic
	$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
	$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
	$A_2$	1	1	-1	-1	$R_z$	$xy$
	$B_1$	1	-1	1	-1	$x, R_y$	$xz$
	$B_2$	1	-1	-1	1	$y, R_x$	$yz$
		Characters				Basis Functions	

Figure II.4: A character table.

- Character tables for all point groups are listed in Appendix C of Miessler et al. (2014).
- **Mulliken symbols** are used to classify irreducible representations based on degeneracy and symmetry.
  - A or B: singly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $1 \times 1$ ).
  - E: Doubly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $2 \times 2$ ).
  - T: Triply degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is  $3 \times 3$ ).
  - A: symmetric (+) with respect to  $C_n$ .
  - B: anti-symmetric (–) with respect to  $C_n$ .
  - Subscript g: symmetric (+) with respect to  $i$ . *Etymology* short for gerade (German for symmetric).
  - Subscript u: anti-symmetric (–) with respect to  $i$ . *Etymology* short for ungerade (German for unsymmetric).
  - If the molecule has a center of inversion, we label irreducible representations with  $g$  or  $u$ .
  - Subscript 1: symmetric (+) with respect to  $\perp C_2$  or  $\sigma_v$ .
  - Subscript 2: anti-symmetric (–) with respect to  $\perp C_2$  or  $\sigma_v$ .
  - Superscript ': symmetric (+) under  $\sigma_h$  (if no  $i$ ).
  - Superscript ": anti-symmetric (–) under  $\sigma_h$  (if no  $i$ ).

- Don't mistake the operation  $E$  for the Mulliken symbol  $E$ !
- To assign Mulliken symbols, use the character table.
  - Assigning the main letter:
    - If  $E$ -character = 1 and  $C_n$ -character = 1:  $A$ .
    - If  $E$ -character = 1 and  $C_n$ -character =  $-1$ :  $B$ .
    - If  $E$ -character = 2:  $E$ .
    - If  $E$ -character = 3:  $T$ .
  - Assigning a subscript  $g$  or  $u$ :
    - If  $i$ -character = 1:  $g$ .
    - If  $i$ -character =  $-1$ :  $u$ .
    - This subscript can be assigned to  $A, B, E, T$  representations.
  - Assigning a superscript  $'$  or  $''$ :
    - If  $\sigma_h$ -character = 1:  $'$ .
    - If  $\sigma_h$ -character =  $-1$ :  $''$ .
    - This subscript can be assigned to  $A, B$  representations.
  - Assigning a subscript 1 or 2:
    - If  $\perp C_2$  or  $\sigma_v$ -character = 1: 1.
    - If  $\perp C_2$  or  $\sigma_v$ -character =  $-1$ : 2.
    - This subscript can be assigned to  $A, B$  representations.
- $\sigma$ ,  $\pi$ , and  $\delta$  bonds come from the Mulliken symbols!
  - Infinity tables use Greek rather than Latin letters.

$D_3$	$E$	$2C_3(z)$	$3C'_2$	linear	quadratic
$A_1$	1	1	1		$x^2 + y^2, z^2$
$A_2$	1	1	$-1$	$z, R_z$	
$E$	2	$-1$	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$ .

Table II.3: Character table for the  $D_3$  point group.

- In character tables, we need to multiply each symmetry operation by the number of types there are (see Table II.3).
- Basis functions show us how different functions transform under different symmetry operations.
- In the  $C_{2v}$  point group:
  - The  $p_x$  orbital has  $B_1$  symmetry.
  - $p_x$  transforms as  $B_1$ .
  - $p_x$  has the same symmetry as  $B_1$ .
  - $p_x$  forms a basis for the  $B_1$  irreducible representation.
  - $p_x$  is  $B_1$  because (see Table 0.2 and Figure II.4) it does not change under  $E$ , it inverts under  $C_2$ , it does not change under  $\sigma_v(xz)$ , and it inverts under  $\sigma'_v(yz)$ .
- We can apply the same procedure to other more complex functions.
  - For example, in the  $C_{2v}$  point group, we know that (with respect to orbitals):
    - $p_y$  is  $B_2$ .

- $p_z$  is  $A_1$ .
  - $d_{z^2}$  is  $A_1$ .
  - $d_{x^2-y^2}$  is  $A_1$ .
  - $d_{yz}$  is  $B_2$ .
  - $d_{xy}$  is  $A_2$ .
  - $d_{xz}$  is  $B_1$ .
  - We can even go into the cubic functions describing the  $f$  orbitals and assign them Mulliken symbols.
- Essentially, the right hand side of a character table tells you how atomic orbitals will transform under certain symmetry operations.
  - Properties of a character table:
    1. The characters of all matrices belonging to the operations in the same class are identical in a given irreducible representation.
      - As such, we form **classes** of operations.
      - We most commonly form a **rotational class** and a **reflection class**.
    2. The number of irreducible representations in a group is equal to the number of classes of that group.
    3. There is always a totally symmetric representation for any group.
      - I.e., a representation where every character is 1.
    4. The sum of the squares of the dimensionality of all the irreducible representations is equal to the order of the group. Mathematically,

$$h = \sum_i [\chi_i(E)]^2$$

- For example, the dimensionalities (characters under  $E$ ) of the  $D_3$  point group (see Table II.3) are 1, 1, and 2, and the order is, indeed,  $6 = 1^2 + 1^2 + 2^2$ .
- 5. The sum of the squares of the characters multiplied by the number of operations in the class equals the order of the group. Mathematically,

$$h = \sum_{R_c} g_c [\chi_i(R_c)]^2$$

- For example, with respect to the  $D_3$  point group (see Table II.3),
 
$$\begin{aligned} 6 &= (1)(1)^2 + (2)(1)^2 + (3)(1)^2 \\ &= (1)(1)^2 + (2)(1)^2 + (3)(-1)^2 \\ &= (1)(2)^2 + (2)(-1)^2 + (3)(0)^2 \end{aligned}$$
- 6. The sum of the products of the corresponding characters of any two different irreducible representations of the same group is zero. Mathematically,

$$\sum_{R_c} g_c \chi_i(R_c) \chi_f(R_c) = 0$$

- Basically, this means that if we treat irreducible representations as vectors in  $h$ -space, they are orthogonal.
- For example, with respect to the  $D_3$  point group (see Table II.3),

$$\begin{aligned} 0 &= 1(1)(1) + 2(1)(1) + 3(1)(-1) \\ &= 1(1)(2) + 2(1)(-1) + 3(1)(0) \\ &= 1(1)(2) + 2(1)(-1) + 3(-1)(0) \end{aligned}$$

## II.6 Module 8: Using Character Tables

- A reducible representation of a group is any representation  $\Gamma$  of the form

$$\Gamma = \sum_i a_i \Gamma_i$$

where each  $\Gamma_i$  is an irreducible representation of the group and  $a_i$  is a real scalar.

- Basically, a reducible representation is any nontrivial linear combination of irreducible representations.
- For example, with respect to the  $C_{2v}$  point group (see Figure II.4),  $\Gamma = (7, 1, 5, 3) = 4A_1 + 2B_1 + B_2$  is a reducible representation.
- We may “factor” reducible representations by inspection, or by the...
- Decomposition/reduction formula for a reducible representation:

$$a_i = \frac{1}{h} \sum_Q N \cdot \chi(R)_Q \cdot \chi_i(R)_Q$$

- $a_i$  is the number of times the irreducible representation appears in  $\Gamma_1$ .
- $h$  is the order of the group.
- $N$  is the number of operations in class  $Q$ .
- $\chi(R)_Q$  is the character of the reducible representation.
- $\chi_i(R)_Q$  is the character of the irreducible representation.
- This formula cannot be applied to  $D_{\infty h}$  and  $C_{\infty v}$ .
- Let's look at decomposing  $\Gamma = (7, 1, 5, 3)$  into its component irreducible point groups using the above formula.

$$\begin{aligned} a_{A_1} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot 1) = 4 \\ a_{A_2} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot -1) = 0 \\ a_{B_1} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot -1) = 2 \\ a_{B_2} &= \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot 1) = 1 \end{aligned}$$

- You can also find websites that will apply the formula for you.
- Basis  $\rightarrow$  reducible representation  $\rightarrow$  irreducible representations workflow:
  1. Assign a point group.
  2. Choose a basis function (bond, vibration, orbital, angle, etc.).
  3. Apply operations.
    - The following shortcuts allow us to skip matrix math in certain situations.
      - If the basis stays the same: +1.
      - If the basis is reversed: -1.
      - If it is a more complicated change: 0.
  4. Generate a reducible representation.
  5. Reduce to irreducible representation.

- We now look at an example of applying the above method to  $\text{H}_2\text{O}$ .
  - $\text{H}_2\text{O}$  is of the  $C_{2v}$  point group.
  - The  $9 \times 9$  identity matrix represents the identity operation on the 3 atoms in  $\text{H}_2\text{O}$ , each described by 3 Cartesian coordinates. Thus,  $\chi(E) = 9$ .
  - The following matrix represents the  $C_2$  symmetry operation. Thus,  $\chi(C_2) = -1$ .

$$\begin{array}{l} \text{O} \left\{ \begin{array}{l} x' \\ y' \\ z' \end{array} \right\} \\ \text{H}_a \left\{ \begin{array}{l} x' \\ y' \\ z' \end{array} \right\} \\ \text{H}_b \left\{ \begin{array}{l} x' \\ y' \\ z' \end{array} \right\} \end{array} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{array}{l} \left\{ \begin{array}{l} x \\ y \\ z \end{array} \right\} \text{O} \\ \left\{ \begin{array}{l} x \\ y \\ z \end{array} \right\} \text{H}_a \\ \left\{ \begin{array}{l} x \\ y \\ z \end{array} \right\} \text{H}_b \end{array}$$

- Note that atoms moved during the transformation do not contribute to the character of the transformation matrix.
- Since under  $\sigma_v(xz)$  only O is unshifted, we need only consider its part of the transformation matrix (as follows) when looking for the character. Thus,  $\chi(\sigma_v(xz)) = 1$ .

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- Since under  $\sigma_v(yz)$  no atom is shifted, we need to consider each (identical) part of the transformation matrix (as follows) when looking for the character. Thus,  $\chi(\sigma_v(yz)) = 3$ .

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

- Thus, the characters of our final reducible representation is  $\Gamma_{3N} = (9, -1, 1, 3)$ .

■ This representation represents fully unrestricted motion of all 3 ambiguities of freedom.

- Another example:  $\text{XeOF}_4$ .

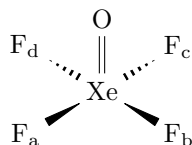


Figure II.5:  $\text{XeOF}_4$ .

- Point group:  $C_{4v}$ .
- Basis function: F atoms.
- Let's see what happens to the fluorine atoms under the  $C_{4v}$  operations (remember that if a basis element (a fluorine atom) stays the same, it contributes +1 to the character of an operation, and if it moves, it contributes 0 to the character).

$E$	all unchanged	4
$C_4$	all move	0
$C_2$	all move	0
$2\sigma_v$	2 move, 2 unchanged	2
$2\sigma_d$	all move	0

Table II.4: Changes in the fluorine atoms of  $\text{XeOF}_4$  under the  $C_{4v}$  symmetry operations.

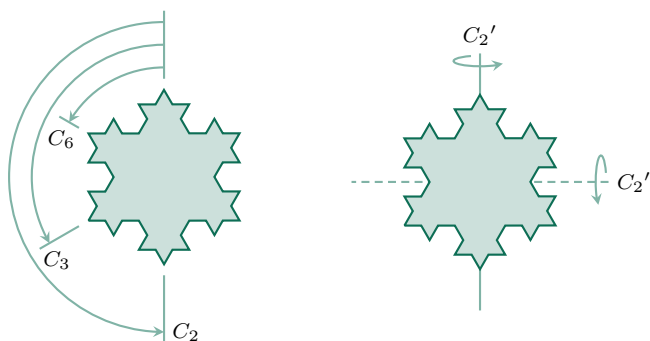
- Thus,  $\Gamma = (4, 0, 0, 2, 0)$ .
- With the  $C_{4v}$  character table and the decomposition formula, we can discover that  $\Gamma = A_1 + B_1 + E$ .

## II.7 Chapter 4: Symmetry and Group Theory

From Miessler et al. (2014).

- 1/18: • **Coincident** (axes): Two identical axes.
- For example, the  $C_3$  rotation axis of  $\text{CHCl}_3$  is **coincident** with the C–H bond axis.
  - Snowflakes, which are often planar and have hexagonal symmetry, have a twofold ( $C_2$ ), threefold ( $C_3$ ), and sixfold ( $C_6$ ) axis through their center and perpendicular to their plane.
  - Rotations  $C_3^2$  and  $C_6^5$  are also symmetry operations.

1/19:



(a) About the principal axis. (b) About perpendicular axes.

Figure II.6: Rotations of a snowflake design.

- 1/18: • “When necessary, the  $C_2$  axes perpendicular to the principal axis are designated with primes; a single prime ( $C_2'$ ) indicates that the axis passes through several atoms of the molecule, whereas a double prime ( $C_2''$ ) indicates that it passes between the outer atoms” (Miessler et al., 2014, p. 77).
- 1/19: • Even though  $S_2 \equiv i$  and  $S_1 \equiv \sigma$ , the  $i$  and  $\sigma$  notations are preferred because of the group theory requirement of maximizing the number of unique classes of symmetry operations associated with a molecule.
- **Point group:** A set of symmetry operations that describes a molecule’s overall symmetry.
  - Alternative steps for assigning point groups:
    1. Determine whether the molecule exhibits very low symmetry ( $C_1$ ,  $C_s$ ,  $C_i$ ) or high symmetry ( $T_d$ ,  $O_h$ ,  $C_{\infty v}$ ,  $D_{\infty h}$ ,  $I_h$ ).
    2. If not, find the highest order  $C_n$  axis for the molecule.

3. Does the molecule have any  $C_2$  axes perpendicular to the principal  $C_n$  axis? If it does, there will be  $n$  of such  $C_2$  axes, and the molecule is in the  $D$  set of groups. If not, it is in the  $C$  or  $S$  set.
  4. Does the molecule have a mirror plane ( $\sigma_h$ ) perpendicular to the principal  $C_n$  axis? If so, it is classified as  $C_{nh}$  or  $D_{nh}$ . If not, continue with Step 5.
  5. Does the molecule have any mirror planes that contain the principal  $C_n$  axis ( $\sigma_v$  or  $\sigma_d$ )? If so, it is classified as  $C_{nv}$  or  $D_{nd}$ . If not, but it is in the  $D$  set, it is classified as  $D_n$ . If the molecule is in the  $C$  or  $S$  set, continue with Step 6.
  6. Is there an  $S_{2n}$  axis collinear with the principal  $C_n$  axis? If so, it is classified as  $S_{2n}$ . If not, the molecule is classified as  $C_n$ .
- Groups of high symmetry:
    - $C_{\infty v}$  (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.
    - $D_{\infty h}$  (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular  $C_2$  axes, a perpendicular reflection plane, and an inversion center.
    - $T_d$  (tetrahedral): Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four  $C_3$  axes, three  $C_2$  axes, three  $S_4$  axes, and six  $\sigma_d$  planes. They have no  $C_4$  axes.
      - Look for  $C_3$  and  $C_2$  axes.
    - $O_h$  (octahedral): These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four  $C_3$  rotations, three  $C_4$  rotations, and an inversion.
      - Look for  $C_4$ ,  $C_3$ , and  $C_2$  axes.
    - $I_h$  (icosahedral): Icosahedral structures are best recognized by their six  $C_5$  axes, as well as many other symmetry operations — 120 in all.
      - Look for  $C_5$ ,  $C_3$ , and  $C_2$  axes.
    - $T_h$ : Adds  $i$  to  $T_d$ . Example:  $\text{W}[\text{N}(\text{CH}_3)_2]_6$ .