

# CHEM 30100 (Advanced Inorganic Chemistry I) Notes

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# Week 1

## A Rigorous Definition of Symmetry

### 1.1 Symmetry: Symmetry Elements and Operations

- 9/28:
- Dr. Anna Wuttig (AH-nuh WUH-tig).
    - Teaches exclusively on the blackboard.
    - Will record lectures, however; if there is a technical error, she will upload last year's lecture.
  - Syllabus.
    - PSets graded on completion, not accuracy.
    - Two exams: One on the first half of the course; one on the second half of the course.
      - Cumulativeness: You'll need to understand the first half to do the second half, but there won't be questions specifically targeted to first-half material.
    - No final.
    - Participation. Showing up to class and working in groups.
  - Chris, Dan, Amy, Matt, Jintong, Yibin, Ben, Sara, Ryan, Joe, Owen, Isabella, Pierce are the people.
    - People come from a diversity of chemistry subfields (physical, inorganic, organic, materials, biological).
  - Every day will have a handout that we will write on (in pencil).
  - Study the learning objectives!
  - (Local) symmetry of a molecule helps us predict and describe bonding, spectroscopic properties, and reactivity.
    - We describe symmetry with group theory.
  - **Symmetry operation:** An operation which moves a molecule into a new orientation equivalent to its original one (geometrically indistinguishable).
    - Symmetry operations that can be applied to an object always form a **group**.
  - **Symmetry element:** A point, line, or plane about which a symmetry operation is applied.
  - Symmetry operations.
    1. Identity operation ( $E$ ): Do nothing; null operation.
    2. Reflection through a plane ( $\sigma$ ): Subdivided into...

- $\sigma_d$ : dihedral mirror planes, which contain the principle  $C_n$  axis and bisect the angles formed between adjacent  $C_2$  axes;
  - $\sigma_h$ : horizontal mirror planes, in which the mirror plane is perpendicular to the principal  $C_n$  axis;
  - $\sigma_v$ : vertical mirror planes, which contain the  $C_n$  axis and are not dihedral mirror planes.
3. Rotation about an axis ( $C_n$ ): A clockwise<sup>[1]</sup> rotation about the  $C_n$  axis.
  4. Improper rotation ( $S_n$ ): A two-step symmetry operation consisting of a  $C_n$  followed by a  $\sigma$  that is perpendicular to  $C_n$  (i.e.,  $\sigma_h$ ).
  5. Inversion ( $i$ ): Take any point with coordinates  $(x, y, z)$  to  $(-x, -y, -z)$ .
- To describe the operations, we'll introduce **stereographic projections**.



Table 1.1: Symbols for stereographic projections.

- We have a working area (the plane of the page is the  $xy$ -plane). It is useful to draw quadrants.
- We describe a general point which experiences our symmetry operation.
  - When the point reflects through the working area, we denote the image with an “X” instead of a circle.
- We need a gear symbol in the middle for rotations and improper rotations (see Table 1.1).
  - Must stereographic projections be drawn one at a time because it seems that the squares should not be in a reflection?
  - No — the symbols are to help us and should be included somewhere, but there are no hard-and-fast rules.
- Stereographic projections for each of the five elementary symmetry operations.

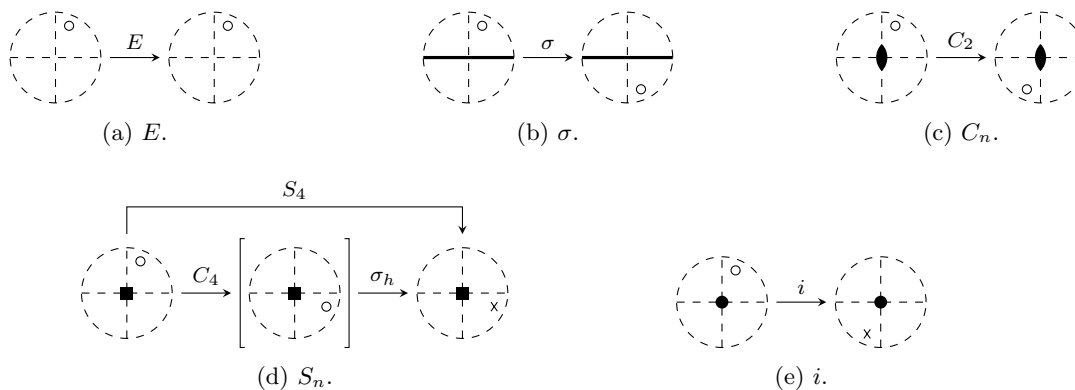


Figure 1.1: Stereographic projections of the elementary symmetry operations.

- Principal  $C_n$  axis: The  $C_n$  axis for which  $n$  is the highest.
  - In a stereographic projection, the  $C_n$  axis is the one that is perpendicular to the working area (goes in/out of the page).

<sup>1</sup>Really?

- Example: Give the symmetry elements of  $\text{NH}_3$ .
  - $C_3$  axis, 3  $\sigma_v$  mirror planes (denoted  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ ).
  - The symmetry operations are  $E$ ,  $C_3$ ,  $C_3^2$ ,  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$ . These operations form the  $C_{3v}$  point group.
- Direct products of symmetry operations:  $YX = Z$  means “operation  $X$  is carried out first and then operation  $Y$ ,” giving the same net effect as would the carrying out of the single operation  $Z$ .
  - If  $YX = XY = Z$ , then the two operations  $Y$  and  $X$  commute.
- What is the direct product of  $C_2$  and  $\sigma_h$ ?
  - $\sigma_h C_2 = S_2 = i$ . They do commute.
- Do  $C_4$  and  $\sigma_{x,z}$  commute? Take the plane of this page as  $xy$ .
  - They do not (determine by drawing out both sets of stereographic projections).
- Don't get careless, Steven. This is easy, but it's also easy to make easy mistakes.
- New symmetry operations *of your group* are generated by taking the direct product of two.

## 1.2 Point Groups

9/30:

- The symmetry operations that apply to a given molecule collectively possess the properties of a mathematical **group**.
- **Group**: A set of symmetry operations that satisfy the following conditions.
  - *Closure*: All binary products must be in the group, i.e., the product of any two operators must also be a member of the group.
  - *Identity*: Must contain an identity, i.e.,  $E$  must be part of the group.
  - *Inverse*: All elements must have an inverse in the group, and they must commute with their inverse.
  - *Associativity*: The associative law  $(A \cdot B) \cdot C = A \cdot (B \cdot C)$  must hold.
- **Abelian** (group): A group in which all direct products commute.
  - Not all groups are Abelian.
- Question: Do  $C_3$  and  $\sigma_v$  form a group?
  - No: No identity (for example).
  - Wuttig draws out a stereographic projection for  $C_3 \cdot \sigma_v$  and overlays the first and last picture, showing that  $C_3 \cdot \sigma_v$  is a reflection over a new mirror plane  $\sigma'_v$ .
  - $C_3$  and  $\sigma_v$  do **generate** the set of operations  $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$ , which collectively form the **point group  $C_{3v}$** .
- To prove something on a pset or exam, it's probably a good idea to do it in terms of stereographic projections!
- **Point group**: A group such that at least one point in space is invariant to all operations in the group.
- **Group order**: The number of symmetry operations in the group. *Given by  $h$* .
- Table activity: Finding  $E$ , principal  $C_n$ ,  $\sigma$ ,  $C_2 \perp C_n$ ,  $C_n$  position relative to  $\sigma$  (collinear or perpendicular), and  $i$  for various point groups.

- These properties are the ones that distinguish each point group from every other point group.
- Notes on the pedagogy: Animations and/or tangible models should be used to discuss this stuff. PowerPoint slides are definitely the way to go — far more tangible tools; blackboard should be a supplement. It is key to be careful what you say (*element* and *operation* must be consistently used). Dr. Wuttig is skipping a lot of key points (like naming point groups).
- Developing a flow chart that distinguishes between  $D_{nh}$ ,  $D_{nd}$ ,  $D_n$ ,  $C_{nh}$ ,  $C_{nv}$ ,  $C_n$ , and  $S_n$ .



## Week 2

# Introduction to Representation Theory

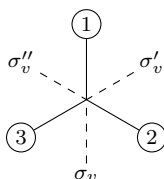
## 2.1 Matrix Representations of Symmetry Operations

- 10/3:
- Tools for identifying symmetry elements.
    - Chem 3D (visualization).
    - Otterbein University symmetry gallery (examples of molecules that satisfy all of the point groups).
  - Gives examples of molecules that satisfy the high-symmetry point groups.
    - $C_{\infty v}$ : CO.
    - $D_{\infty h}$ : CO<sub>2</sub>.
    - $T_d$ : CH<sub>4</sub>.
    - $T_h$ : [Co(NO<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>.
      - $T_h$  is  $T_d$  with  $\sigma_h$  symmetry.
    - $O_h$ : [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
    - $I_h$ : N/a.
      - 120 symmetry elements in total; we will not be asked to identify all of these!
    - $K_h$ : N/a.
      - Symmetry of the sphere.
    - $T, O, I$  are subgroups of  $T_h, O_h, I_h$ , respectively, and only have proper (not improper) rotations. These are very rare point groups. An example of a molecule in the  $T$  point group is [Ca(THF)<sub>6</sub>]<sup>2+</sup>.
  - Learn  $T, O, I$  from Otterbein University example and ask questions!
  - Low symmetry:  $C_1, C_i, C_s$ .
  - The mirror plane in a  $C_s$  molecule is denoted by  $\sigma$  (no subscript).
  - **Vector**: A series of numbers which we write in a row or a column.
  - **Matrix**: Any rectangular array of numbers set between two brackets.
  - Basics of matrix multiplication:  $A \cdot \vec{x} = \vec{y}$  given in terms of matrix multiplication, e.g., if  $A$  is  $n \times m$  and  $\vec{x} \in \mathbb{R}^m$ , then

$$y_i = \sum_{j=1}^m a_{ij} x_j$$

for  $i = 1, \dots, n$ .

- Matrix representations:
  - $E$ : What matrix  $A$  satisfies  $A \cdot \vec{x} = \vec{x}$  for all  $\vec{x}$ ? The  $3 \times 3$  matrix  $I$  does.
  - $i$ : What matrix  $A$  satisfies  $A \cdot \vec{x} = -\vec{x}$  for all  $\vec{x}$ ? The  $3 \times 3$  matrix  $-I$  does.
  - $\sigma_{xy}$ : What matrix  $A$  flips the sign of the  $z$ -coordinate of  $\vec{x}$ ? The  $3 \times 3$  matrix  $\text{diag}(1, 1, -1)$  does.
  - $C_2$ : What matrix  $A$  flips the sign of the  $x, y$ -coordinates of  $\vec{x}$ ? The  $3 \times 3$  matrix  $\text{diag}(-1, -1, 1)$  does.
  - $C_3$ : Consider a  $C_{3v}$  molecule.

Figure 2.1:  $C_3$  matrix representation setup.

Instead of describing a rotation in  $\mathbb{R}^3$  using radians, we can think of a rotation as a permutation of the numbered atoms. So in this example,

$$\underbrace{\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}}_{C_3} \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \\ 1 \end{bmatrix}$$

- We will only be asked for matrix representations of very simple things, e.g., these or  $90^\circ$  or  $180^\circ$  turns.
- The above matrices form a mathematical group, which obeys the same multiplication table as the operations.
  - For example,

$$\underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}_{C_2} \underbrace{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_{\sigma_h} = \underbrace{\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}}_i$$

- The matrix representations given above are not the “simplest” way of describing these symmetry operations.
  - The simplest way is using the **character**.
  - We find the character using a **similarity transformation** to take our matrix representations to block-diagonalized forms and then compute the characters of the blocks from there.
  - Recall that analogous blocks multiply in a block-diagonal matrix.
- **Character** (of a symmetry operation): The trace (sum of the diagonal elements) of the matrix representation of that operation. *Denoted by  $\chi$ .*
- **Similarity transformation** (matrix): The matrix which, when conjugated with a matrix representation of a symmetry operation, yields the block-diagonalized form of that matrix. *Denoted by  $R$ .*
  - We don’t need to know how to compute these.

- Similarity transformation example: The  $C_3$  matrix representation given above is not block diagonal, but there exists a matrix  $R$  (that we don't have to know how to find) such that

$$RC_3R^{-1} = \left[ \begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array} \right]$$

- The characters of the blocks of the above matrix are 1 and  $-1$ , respectively. The character of the overall matrix is still 0.

## 2.2 Characters and Irreducible Representations

10/5:

- The PSet has been posted — remember that its graded for completion.
  - Answer key will be posted the day it's due.
  - Submit via email or give her a printed copy/write it out on blank paper (preferred).
- Review:  $\text{NH}_3$  is in the  $C_{3v}$  point group.
- Denote the bond vectors of  $\text{NH}_3$  by  $d_1, d_2, d_3$ . Let's use them as a basis of the representation  $\Gamma$ . Also label the hydrogen atoms 1-3.

Symmetry element	Matrix	Character
$E$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix}$	3
$C_3$	$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_2 \\ H_3 \\ H_1 \end{bmatrix}$	0
$C_3^2$	$\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_3 \\ H_1 \\ H_2 \end{bmatrix}$	0
$\sigma_v$ (along $d_1$ )	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_1 \\ H_3 \\ H_2 \end{bmatrix}$	1
$\sigma'_v$ (along $d_2$ )	$\begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_3 \\ H_2 \\ H_1 \end{bmatrix}$	1
$\sigma_v$ (along $d_1$ )	$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} = \begin{bmatrix} H_2 \\ H_1 \\ H_3 \end{bmatrix}$	1

Table 2.1:  $\text{NH}_3$  symmetry operations, matrices, and characters.

- Draw out each symmetry operation, its effect on each H atom, and the matrix representation of each. What is the character for each matrix representation? See the above table.
- The characters for each matrix divide the symmetry operations into three classes (the identity, rotation, and reflection classes).

- If we use the Cartesian axes as our basis, we get the following transformation matrices.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_a = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_b = \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_c = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- All of these are block-diagonal, so there must be some similarity transformation that gets us from the matrices in Table 2.1 to these matrices.
- Notice that the character is preserved under similarity transformation.
- The matrix representations in  $\vec{e}$  have blocks, which we can call the 2D block and the 1D block.
- Building a character table with different representations.

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$\Gamma_e$	3	0	1
$\Gamma_{2D}$	2	-1	0
$\Gamma_{1D}$	1	1	1

Table 2.2: Some representations of  $C_{3v}$ .

- $\Gamma_e$  is the representation corresponding to the full  $3 \times 3$  matrices.
- $\Gamma_{2D}$  is the representation corresponding to the 2D blocks.
- $\Gamma_{1D}$  is the representation corresponding to the 1D blocks.
- The latter two are called the irreducible representations; the first one is called a reducible representations. In fact,

$$\Gamma_e = \Gamma_{2D} + \Gamma_{1D}$$

- Every point group has a specific number of irreducible representations (IRRs); are  $\Gamma_{2D}, \Gamma_{1D}$  it?
  - No — we will use the rules to find the others.
- IRRs have 4 rules.
  1. The number of IRRs: The number of non-equivalent IRRs is equal to the number of classes in the group.
  2. Dimensionality of IRRs: The sum of the squares of the dimensions  $\ell$  of IRRs in a class is equal to the order of the group.

$$\sum_i \ell_i^2 = \sum \chi_i^2(\text{class}) = h$$

3. Characters of IRRs: The sum of the squares of the characters under any IRR equals the order of the group.

$$\sum_R g(R) \chi_i^2(R) = h$$

4. Orthogonality rule: The sum of the products of characters under any two irreducible representations is equal to zero.

$$\sum_R g(R) \chi_i(R) \chi_j(R) = 0$$

- Examples of the rules in  $C_{3v}$ .

– Rule 1:  $C_{3v}$  has three classes, so it must have there must be one more IRR than listed in Table 2.2.

– Rule 2: We must have that

$$1^2 + 2^2 + \ell_3^2 = 6$$

– Rule 3: For  $\Gamma_{2D}$ , for example,

$$(1)(2)^2 + 2(-1)^2 + 3(0)^2 = 6$$

– Rule 4: With  $\Gamma_{1D}, \Gamma_{2D}$ , for example,

$$(1)(1)(2) + (2)(1)(-1) + (3)(1)(0) = 0$$

- Finding the last representation of  $C_{3v}$ .

– General procedure: Apply rule 1, then 2, then 4. Check with 3.

– For example, we can find that the last  $\Gamma = (1, 1, -1)$ .

## 2.3 Character Tables and Mulliken Symbols

10/7:

- The algebraic rules discussed last lecture are sufficient to derive a character table. They are summarized in the following procedure.

1. Determine the number of classes in order to find the number of irreducible representations.
2. All groups have a totally symmetric irreducible representation.
3. Determine the dimensionality of the irreducible representations.
4. Apply the orthogonality rule.
5. Verify using the sum of square of characters rule.

- Example: Deriving the  $C_{3v}$  character table using the above strategy.

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$	linear	quadratic
$A_1$	1	1	1	$z$	$z^2$
$A_2$	1	1	-1	$R_z$	
$E$	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

Table 2.3:  $C_{3v}$  character table.

– There are three classes; hence, we will have  $\Gamma_1, \Gamma_2, \Gamma_3$ .

■ See below for an explanation of their labels.

– Let  $\Gamma_1 = (1, 1, 1)$  be the totally symmetric irreducible representation.

– If we want the sum of the squares of the dimensionalities to be natural numbers which add to  $h = 6$ , then we must choose  $\ell_2 = 1$  and  $\ell_3 = 2$ .

– Applying the orthogonality rule, we can find the remaining four values in the table (those in the lower-right block) by inspection.

– We may, indeed, confirm using the sum of the squares rule.

– Also see below for an explanation of the Cartesian coordinates on the right-hand side.

- It will be beneficial to have a standard method for naming our irreducible representations.

- **Mulliken symbol:** The designation of an irreducible representation assigned according to the following procedure. *Given by*
  1. All 1D representations are  $A$  or  $B$ . 2D is  $E$ . 3D is  $T$ .
  2. Distinguishing  $A$  and  $B$ .
    - (a)  $\chi(C_n) = +1 \implies A$ .
    - (b)  $\chi(C_n) = -1 \implies B$ .
  3. Numerical subscripts: For groups that contain a secondary  $C_2$  axis (or in its absence,  $\sigma_v$ ).
    - (a)  $\chi(C_2 \text{ or } \sigma_v) = +1 \implies \text{Subscript 1}$ .
    - (b)  $\chi(C_2 \text{ or } \sigma_v) = -1 \implies \text{Subscript 2}$ .
  4. Alphabetical subscripts: For groups that contain  $i$ .
    - (a)  $\chi(i) = +1 \implies \text{Subscript } g$ .
    - (b)  $\chi(i) = -1 \implies \text{Subscript } u$ .
  5. Prime subscripts: For groups that contain  $\sigma_h$ .
    - (a)  $\chi(\sigma_h) = +1 \implies \text{Superscript '}$ .
    - (b)  $\chi(\sigma_h) = -1 \implies \text{Superscript ''}$ .
- **Symmetric** (IRR wrt. a symmetry operation): An IRR for which the character of the symmetry operation in question is  $+1$ .
- **Unsymmetric** (IRR wrt. a symmetry operation): An IRR for which the character of the symmetry operation in question is  $-1$ . *Also known as antisymmetric.*
- Based on the above rules, we can conclude that for  $C_{3v}$ ,  $\Gamma_1 = A_1$ ,  $\Gamma_2 = A_2$ , and  $\Gamma_3 = E$ .
- The last two elements we need to construct the  $C_{3v}$  character table are the Cartesian coordinates. These are easy to derive for  $z$ -axis elements and groups that contain  $x$ - and  $y$ -axis rotations (e.g.,  $C_2, C_4$ ). If  $n$  is odd, these latter ones will be given to you.
  - There are two types of linear bases to consider:  $x, y, z$  and  $R_x, R_y, R_z$ . The former corresponds to  $p$  orbitals. The latter corresponds to rotations about one of the Cartesian axes.
  - There is one type of quadratic base to consider:  $z^2, x^2 - y^2, xy, xz, yz$ . These correspond to  $d$  orbitals.
  - Wuttig draws out the effect of each symmetry operation in  $C_{3v}$  on  $p_z, d_{z^2}$ , and  $R_z$ . She concludes for the first two that they are totally symmetric with respect to the operations; hence, they are  $A_1$ . She also concludes with respect to the last one that it is symmetric to the identity and to rotation, but unsymmetric to reflection about the  $z$ -axis; hence, it is  $A_2$ .
  - The others are filled in toward us.
- **Summary: Anatomy of a character table.**
  1. Point group.
  2. Irreducible representations, as denoted by Mulliken symbols.
  3. Classes of symmetry operations.
  4. Characters of irreducible representations.
  5. Linear basis: Axes and rotations (basis functions for the irreducible representations).
    - (a)  $p$  orbitals: Denoted as  $z, x, y$ .
    - (b) Rotations around  $z, x, y$ : Denoted as  $R_z, R_x, R_y$ .
  6. Quadratic basis (basis functions for the irreducible representations).
    - (a)  $d$  orbitals: Denoted as  $z^2, x^2 - y^2, xy, xz, yz$ .

- Example: Filling in the  $C_{2v}$  character table.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$	linear	quadratic
$A_1$	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	$y, R_x$	$yz$

Table 2.4:  $C_{2v}$  character table.

- Special case where the two  $\sigma$  have different characters: With respect to determining which of the bottom two representations is  $B_1$  and which is  $B_2$ , we must pick a  $\sigma_v$  to use as a reference and stick with it.

## Week 3

# Applications of Representation Theory

### 3.1 Reducible Representations and Direct Products

10/10:

- PSet is due at the beginning of next class. Email or submit in paper. Show your work!
- Since molecules have more than one point, we need to work with the characters of reducible representations. In particular, when applying group theory to chemical problems, we need to find the IRRs whose sum is the reducible representation.
- **Reduction formula:** The formula which takes a  $\Gamma_{\text{red}}$  and decomposes it into a sum of  $\Gamma_{\text{IRRS}}$ . *Given by*

$$n(\Gamma_A) = \frac{1}{h} \sum_i g(R) \chi_{\text{IRR}}(R) \chi_{\text{RR}}(R)$$

- $n(\Gamma_A)$  is the number of times the IRR  $A$  occurs in  $\Gamma_{\text{red}}$ .
- $h$  is the order of the group.
- $g(R)$  is the order of the class under the symmetry operation  $R$ .
- $\chi_{\text{IRR}}(R)$  is the character of the IRR under the symmetry operation  $R$ .
- $\chi_{\text{RR}}(R)$  is the character of the reducible representation under the symmetry operation  $R$ .
- Recall  $\Gamma_{\text{red}} = (3, 0, 1)$  in  $C_{3v}$  from Lecture 2.2.
  - The number of times each IRR appears is, according to the reduction formula:

$$n(A_1) = \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot 1 \cdot 1) = 1$$

$$n(A_2) = \frac{1}{6}(1 \cdot 1 \cdot 3 + 2 \cdot 1 \cdot 0 + 3 \cdot -1 \cdot 1) = 0$$

$$n(E) = \frac{1}{6}(1 \cdot 2 \cdot 3 + 2 \cdot -1 \cdot 0 + 3 \cdot 0 \cdot 1) = 1$$

- Simple cases (like this and the next one) we can often do by inspection.
- Example:  $\Gamma_{\text{RR}} = (6, 0, 0)$ .
  - Decompose it into  $A_1 + A_2 + 2E$ .
- **Direct product** (of two representations): The (reducible or irreducible) representation obtained by multiplying the characters of the two representations which correspond under each operation. *Denoted by  $M \times N$ , where  $M, N$  are Mulliken symbols.*



- Examples:
  - $A_1 \times E = E$ .
  - $A_2 \times E = E$ .
  - $E \times E = A_1 + A_2 + E$ .
  - $A_2 \times A_2 = A_1$ .
- We now dive into how to use the symmetry properties of a collection of orbitals to determine the states that arise by populating them with electrons. To do this for a given basis set of valence atomic orbitals, we need to ask what set of IRRs they fall into.
- Procedure.
  1. Generate the characters of this representation by examining the trace of the relevant transform matrices.
    - +1 on the diagonal if a particular basis function is left unchanged during the symmetry operation.
    - 0 on the diagonal if the basis function is transformed to another function.
    - -1 on the diagonal if the function is converted into minus itself.
    - Indeed, only basis set elements that do not move contribute to the trace (i.e., character) of the representation.
  2. Check that the dimension is greater than the largest dimension permissible in the point group. If so, we need to reduce to IRRs. This is an important step to construct SALCs.
- Example: Consider the set of  $H_{1s}$  orbitals of  $NH_3$  as the representation.
  - $\Gamma_{3H_{1s}} = (3, 0, 1)$  since all 3 orbitals stay under  $E$ , all orbitals move under  $2C_3$ , and 1 orbital stays under  $3\sigma_v$ .
  - Decompose into  $A_1 + E$ .
  - Therefore, the  $1s$  orbital of H within  $C_{3v}$  of  $NH_3$  transforms in  $a_1 + e$  symmetry.
  - Note that we use lowercase Mulliken symbols for atomic/molecular orbitals and vibrational modes and uppercase Mulliken symbols for electronic states.
  - This  $a_1 + e$  symmetry for the  $H_{1s}$  group orbitals implies that there are 3 SALC orbitals: 1 of  $a_1$  symmetry and 2 of  $e$  symmetry.
- Example:  $H_2O$ .
  - $\Gamma = (2, 0, 0, 2) = A_1 + B_2$ .

## 3.2 Projection Operations and SALCs

10/12:

- PSet 2 is posted and due 10/21.
  - Go over questions on the HW in the review classes prior to exams.
- **Symmetry-Adapted Linear Combination:** An orthonormal linear combination of one or more sets of orthonormal functions (which are either atomic orbitals or internal coordinates of a molecule) taken in such a way that the combinations form bases for irreducible representations of the symmetry group of the molecule. *Also known as SALC.*
- Last time, we investigated the SALCs of  $NH_3$ . We found them by decomposing a reducible representation of the  $H_{1s}$  basis set to its irreducible representations and naming them via the character table.

- Goal: What do the SALCs of  $\text{NH}_3$  look like?
  - We know that we need 3 SALCs, 1 of  $a_1$  symmetry and 2 of  $e$  symmetry.
  - To achieve the goal, we apply the **projection operator** to each irreducible representation.
- **Projection operator** (on an IRR): The operator defined as follows, which acts on IRRs. *Denoted by  $\hat{P}$ . Given by*

$$\hat{P}(\Gamma_i) = \frac{\ell_i}{h} \sum_R \chi_i(R) \hat{R}$$

- $\ell_i$  is the dimension(ality) of the IRR.
- $\Gamma_i$  is the IRR.
- $\hat{R}$  is the symmetry operation to be applied to the basis.
- $\chi_i(R)$  is the character of the given symmetry operation for  $\Gamma_i$ .
- In other words, we need to evaluate what happens to the  $\text{H}_{1s}$  orbitals under each symmetry operation.
- It follows that we need the character table to evaluate what happens to the  $\text{H}_{1s}$  orbitals for each symmetry operation.
  - Note that for the projection operator, we do *not* do this by class (i.e., we do need to apply *every single* symmetry operation)<sup>[1]</sup>.
  - Focus on one orbital in particular, and see to which orbital each symmetry operation takes it.
- $\text{NH}_3$  example.

- We have

$$E : x_1 \mapsto x_1 \quad C_3 : x_1 \mapsto x_2 \quad C_3^2 : x_1 \mapsto x_3 \quad \sigma_v : x_1 \mapsto x_1 \quad \sigma'_v : x_1 \mapsto x_3 \quad \sigma''_v : x_1 \mapsto x_2$$

- We can do the same for where  $x_2, x_3$  go.
- It follows that

$$\hat{P}(A_1)_{x_1} = 1x_1 + 1x_2 + 1x_3 + 1x_1 + 1x_3 + 1x_2 = 2(x_1 + x_2 + x_3) \approx x_1 + x_2 + x_3$$

- This implies that under the totally symmetric representation, all orbitals are the same, as we might expect. Note that the constant factor of 2 does not affect the functional form and therefore does not affect the symmetry properties.
- We don't carry through  $\ell_i/h$  because it's a constant??
- Note that

$$\hat{P}(A_1)_{x_2} = \hat{P}(A_1)_{x_3} = \hat{P}(A_1)_{x_1}$$

- As another example,

$$\hat{P}(E)_{x_1} = 2x_1 - x_2 - x_3 + 0x_1 + 0x_3 + 0x_2 = 2x_1 - x_2 - x_3$$

- Similarly,

$$\hat{P}(E)_{x_2} = 2x_2 - x_3 - x_1$$

$$\hat{P}(E)_{x_3} = 2x_3 - x_1 - x_2$$

- Note that all of these functions must be orthonormal.
  - We have three functions, but we only need 2 in  $e$ ! Thus, we employ the orthonormal rule to figure it out.

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<sup>1</sup>Notice that the order of the class is not present in the projection operator!

- We have that the first and second, and first and third are not orthogonal:

$$(\Psi_{E,x_1}, \Psi_{E,x_2}) = (2)(-1) + (2)(-1) + (-1)(-1) = 3 \neq 0$$

$$(\Psi_{E,x_1}, \Psi_{E,x_3}) = (2)(-1) + (-1)(-1) + (-1)(2) = 3 \neq 0$$

- What we can do is take a linear combination of 2 and 3 so that it's orthogonal to 1.
- Let's try

$$\Psi_{E,\text{new}} = \Psi_{E,x_2} - \Psi_{E,x_3} = 3x_2 - 3x_3 \approx x_2 - x_3$$

- Indeed,

$$(\Psi_{E,x_1}, \Psi_{E,\text{new}}) = (2)(0) + (-1)(1) + (-1)(-1) = 0$$

as desired.

- Note that adding does not get us something orthogonal.

– Normalize the SALCs.

- At this point, we have that

$$\Psi_{A_1 \text{ SALC}} = x_1 + x_2 + x_3 \quad \Psi_{E \text{ SALC}} = 2x_1 - x_2 - x_3 \quad \Psi_{E \text{ SALC}} = x_2 - x_3$$

- Normalization means adjusting the normalization constant  $N$  such that

$$\int [N(x_1 + x_2 + x_3)]^2 = 1$$

- More simply, we multiply each of the above by 1 over the square root of the sum of the squares of the extant coefficients. So

$$\begin{aligned} \Psi_{A_1 \text{ SALC}} &= \frac{1}{\sqrt{1^2 + 1^2 + 1^2}}(x_1 + x_2 + x_3) & \Psi_{E \text{ SALC}} &= \frac{1}{\sqrt{2^2 + (-1)^2 + (-1)^2}}(2x_1 - x_2 - x_3) \\ &= \frac{1}{\sqrt{3}}(x_1 + x_2 + x_3) & &= \frac{1}{\sqrt{6}}(2x_1 - x_2 - x_3) \end{aligned}$$

$$\begin{aligned} \Psi_{E \text{ SALC}} &= \frac{1}{\sqrt{0^2 + 1^2 + (-1)^2}}(x_2 - x_3) \\ &= \frac{1}{\sqrt{2}}(x_2 - x_3) \end{aligned}$$

– Lastly, we can draw the orbitals.

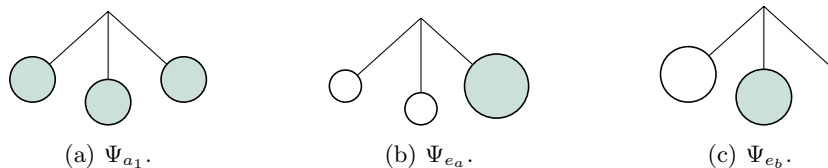


Figure 3.1:  $\text{NH}_3$  SALCs.