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_2.
  - T_d: CH_4.
  - T_h: $[Co(NO_2)_6]^{3+}$.
    - T_h is T_d with σ_h symmetry.
  - O_h: $[Co(NH_3)_6]^{3+}$
  - 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 $[Ca(THF)_6]^{2+}$.
- 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 σ (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 3×3 matrix I does.
  - i: What matrix A satisfies $A \cdot \vec{x} = -\vec{x}$ for all $\vec{x}$? The 3×3 matrix $-I$ does.
  - σ_{xy}: What matrix A flips the sign of the z-coordinate of $\vec{x}$? The 3×3 matrix $\text{diag}(1, 1, -1)$ does.
  - C_2: What matrix A flips the sign of the x, y-coordinates of $\vec{x}$? The 3×3 matrix $\text{diag}(-1, -1, 1)$ does.
  - C_3: Consider a C_{3v} molecule.

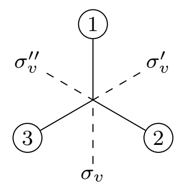

Figure 2.1: C_3 matrix representation setup.

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° or 180° 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* $\boldsymbol{\chi}$.
- **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* $\boldsymbol{R}$.
  - 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: NH_3 is in the C_{3v} point group.
- Denote the bond vectors of NH_3 by d_1, d_2, d_3. Let's use them as a basis of the representation Γ. 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
σ_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
σ_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
σ_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: 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.

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

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

  - 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	$2C_3$	$3\sigma_v$
Γ_e	3	0	1
Γ_{2D}	2	-1	0
Γ_{1D}	1	1	1

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

  - Γ_e is the representation corresponding to the full 3×3 matrices.
  - Γ_{2D} is the representation corresponding to the 2D blocks.
  - Γ_{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 Γ_{2D}, Γ_{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 ℓ 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 Γ_{2D}, for example,
    $$(1)(2)^2 + 2(-1)^2 + 3(0)^2 = 6$$
  - Rule 4: With Γ_{1D}, Γ_{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 $\Gamma = (1, 1, -1)$.