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 $i = 1, \ldots, n$.

- 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.

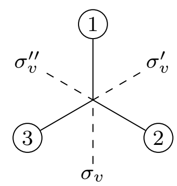

Figure 2.1: C_3 matrix representation setup.

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.