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.

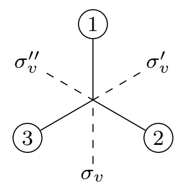

Figure 2.1: C_3 matrix representation setup.

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 $\Gamma = (1, 1, -1)$.

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, σ_v).
     (a) $\chi(C_2 \text{ or } \sigma_v) = +1 \implies$ Subscript 1.
     (b) $\chi(C_2 \text{ or } \sigma_v) = -1 \implies$ Subscript 2.
  4. Alphabetical subscripts: For groups that contain i.
     (a) $\chi(i) = +1 \implies$ Subscript g.
     (b) $\chi(i) = -1 \implies$ Subscript u.
  5. Prime subscripts: For groups that contain σ_h.
     (a) $\chi(\sigma_h) = +1 \implies$ Superscript $'$.
     (b) $\chi(\sigma_h) = -1 \implies$ 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 for 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 σ 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 σ_v to use as a reference and stick with it.