

Week 2

Introduction to Representation Theory

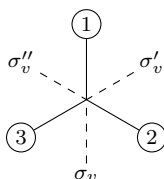
2.1 Matrix Representations of Symmetry Operations

- 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.
 - $D_{\infty h}$: CO₂.
 - T_d : CH₄.
 - T_h : [Co(NO₂)₆]³⁺.
 - T_h is T_d with σ_h symmetry.
 - O_h : [Co(NH₃)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 χ .*
- **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: 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.

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

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

- 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	$2C_3$	$3\sigma_v$
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) $\chi(C_2 \text{ or } \sigma_v) = +1 \implies \text{Subscript 1}$.
 - (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 σ_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 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.