Topic II

Symmetry and Group Theory in Chemistry

II.1 Module 3: Symmetry Elements and Operations

1/13:

- He will upload lecture slides in advance in the future.
- An object is symmetric if one part is the same as other parts.
- The symmetry of discrete objects is described using **Point Symmetry**.
- **Point groups** (~ 32 for molecules) provide us with a way to indicate the symmetry unambiguously.
- Point groups have symmetry about a single point at the center of mass of the system.
- Extended objects (e.g., crystals) have **translational symmetry** described by **Space groups**[1] (230 total).
- Reading: Miessler et al. (2014) Chapter 4 and https://en.wikipedia.org/wiki/Molecular_symmetry.
- **Symmetry elements**: Geometric entities about which a **symmetry operation** can be performed. In a point group, all symmetry elements must pass through the center of mass (the point).
- **Symmetry operation**: The action that produces an object identical to the initial object.

Element	Operation
Identity, E	nothing
Rotation axis, C_n	n-fold rotation
Improper rotation axis, S_n	n-fold improper rotation
Plane of symmetry, σ	Reflection
Center of symmetry, i	Inversion

- **Identity**: Does nothing to the object, but is necessary for mathematical completeness.
- ***n*-fold rotation**: A rotation of $360^\circ/n$ about the C_n axis ($n \in [1, \infty)$).
  - In H_2O, there is a C_2 axis, so we can perform a 2-fold (180°) rotation to get the same molecule.
    - Remember, because of quantum mechanical properties, the hydrogens are indistinguishable so when we rotate it 180°, we cannot tell it apart from the unrotated molecule.
  - Rotations are considered positive in the counterclockwise direction.

[1] Not covered in this course.

  - Each possible rotation operation is assigned using a superscript integer m of the form ${C_n}^m$. m is the number of sequential applications.
  - The rotation ${C_n}^n \equiv E$ is equivalent to the identity operation (nothing is moved).
  - Linear molecules have an infinite number of rotational options C_∞ because any rotation on the molecular axis will give the same arrangement.

- **Principal axis**: The highest order rotation axis.
  - By convention, the principal axis is assigned to the z-axis if we are using Cartesian coordinates.
- **Reflection**: Exchanges one half of the object with the reflection of the other half.
- **Vertical mirror plane**: A mirror plane that contains the principal axis. *Also known as* $\boldsymbol{\sigma_v}$.
- **Horizontal mirror plane**: A mirror plane that is perpendicular to the principal axis. *Also known as* $\boldsymbol{\sigma_h}$.
- **Dihedral mirror planes**: A special type of σ_v that is between sides or planes. *Also known as* $\boldsymbol{\sigma_d}$.
  - For example, we might have vertical mirror planes in the xz- or yz-planes. In this case, the dihedral planes would contain the lines $y = \pm x$.
- Two successive reflections are equivalent to the identity operation.
- **Inversion**: Every part of the object is reflected through the inversion center, which must be at the center of mass of the object.
  - $(x, y, z) \xrightarrow{i} (-x, -y, -z)$.
- ***n*-fold improper rotation**: This operation involves a rotation of $360°/n$ followed by a reflection perpendicular to the axis. It is a single operation and is labeled in the same manner as "proper" rotations. *Also known as* $\boldsymbol{{S_n}^m}$, **rotation-reflection operation**.

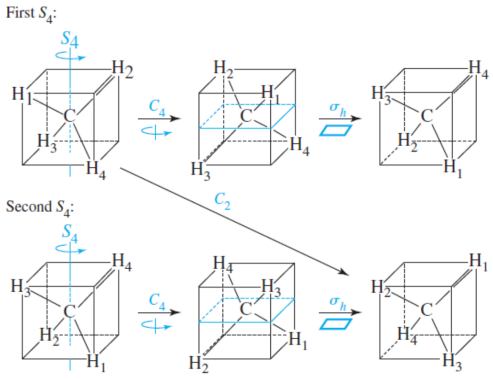
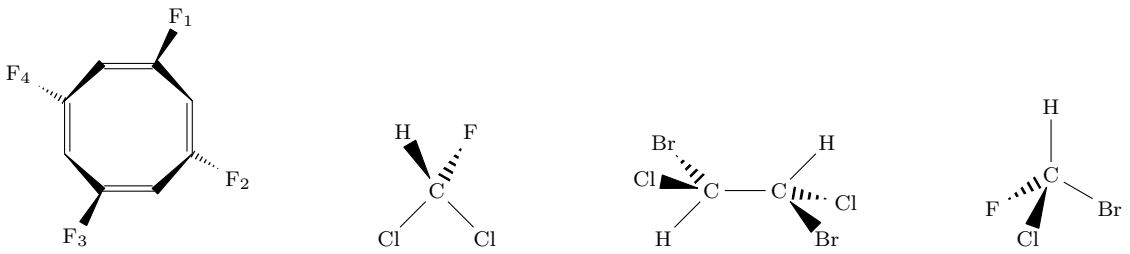


Figure II.1: Methane's S_4 symmetry.

  - Methane has S_4 symmetry.
  - Note that $S_1 \equiv \sigma_h$, $S_2 \equiv i$, and sometimes $S_{2n} \equiv C_n$. In methane, for example, ${S_4}^2 \equiv C_2$.
  - Applied to a triangular prism, is a good example.
  - If n is even, we have n unique operations. There should be $C_{n/2}$.
  - If n is odd, we have $2n$ unique operations. There should be C_n and σ_h.
- The absence of an S_n axis is the defining symmetry property of **chiral** molecules.
  - Formerly, we learned that chiral molecules should not have mirror planes and inversion centers.
  - Rigorously, chiral molecules must not have any improper rotation axes.

II.2 Module 4: Symmetry Point Groups

- Identifying the point groups:
  1. Determine if the symmetry is special (e.g., octahedral).
  2. Determine if there is a principal rotation axis.
  3. Determine if there are rotation axes perpendicular to the principal axis.
  4. Determine if there are mirror planes.
  5. Assign point groups.
- High symmetry and low symmetry groups are the most difficult to identify.
- High symmetry:
  - Perfect tetrahedral (T_d), e.g., P_4 and CH_4.
  - Perfect octahedral (O_h), e.g., SF_6.
  - Perfect icosahedral (I_h), e.g., C_{60} and $B_{12}H_{12}{}^{2-}$.
- Low symmetry:



(a) S_4. (b) C_s (c) C_i (d) C_1

Figure II.2: Low symmetry point groups.

  - Only an improper axis: S_n.
  - Only a mirror plane: C_s.
  - Only an inversion center: C_i.
  - No symmetry: C_1.
- C_n groups:
  - Only a C_n axis. Note that conformation is important.
- C_{nh} groups have a C_n axis and a σ_h reflection plane (such as $B(OH)_3$).
  - H_2O_2 has C_{2h} symmetry.
- All symmetry elements are listed in the top row of the corresponding characters table (Appendix C in Miessler et al. (2014)).
- C_{nv} groups have a C_n axis and a σ_v reflection plane.
  - NH_3 has C_{3v} symmetry.
  - CO has $C_{\infty v}$ symmetry since there are an infinite number of both C_n axes and σ_v mirror planes.
- D_{nh} groups: A C_n axis, n perpendicular C_2 axes, and a σ_h reflection plane.
  - BH_3 has D_{3h} symmetry.

  - A square prism has D_{4h} symmetry.
  - CO_2 has $D_{\infty h}$ symmetry.
- D_n groups: A C_n axis, n perpendicular C_2 axes, and no mirror planes.
  - A 3-bladed propeller has D_3 symmetry.
- D_{nd} groups: A C_n axis, n perpendicular C_2 axes, and a σ_d.
  - Ethane in the staggered conformation has D_{3d} symmetry.
- Local symmetry:
  - Sometimes, rigorous math analysis needs to be adjusted to physical reality.
  - If a cyclopentane ring is bonded through the center to $Mn(CO)_3$, this molecule has only C_s symmetry.
  - However, spectroscopically, there is fast rotation about the Mn−Cp bond. This means that the $Mn(CO)_3$ fragment exhibits pseudo-C_{3v} symmetry while the C_5H_5 ligand exhibits pseudo-C_{5v} symmetry.
  - Often, the absolute symmetry of a molecule is very low, but the interactions are far away from the centers of interest, and do not perturb them significantly.
  - If we have platinum as a central atom bonded to two chlorines and two $P(Et)_3$ groups, this molecule technically has C_1 symmetry due to the orientations of atoms within R groups (staggered), but IR spectroscopy is characteristic of highly symmetric species (D_{2h}).

II.3 Module 5: Group Theory 101

1/15:
- **Group**: A set of elements together with an operation that combines any two of its elements to form a third element satisfying four conditions called the group axioms.
- **Closure**: All binary products must be members of the group.
- **Associativity**: Associative law of multiplication must hold.
- **Identity**: A group must contain the identity operator.
- **Inverse**: Every operator must have an inverse.
- The integers with the addition operation form a group, for example.
- History:
  - Early group theory was driven by the quest for solutions of polynomial equations of degree 5 and above.
  - Early 1800s: Évariste Galois realized that the algebraic solution to a polynomial equation is related to the structure of a group of permutations associated with the roots off the polynomial, the Galois group of the polynomial.
    - Link to Galois video here.
  - 1920s: Group theory was applied to physics and chemistry.
  - 1931: It is often hard or even impossible to obtain a solution of the Schrödinger equation — however, a large part of qualitative results can be obtained by group theory. Almost all the rules of spectroscopy follow from the symmetry of a problem.
- We will use group theory for describing symmetry of molecules. We will use group theory to understand the bonding and spectroscopic features of molecules.

- For us, a group consists of a set of symmetry elements (and associated symmetry operations) that completely describes the symmetry of a molecule.
- **Order** (of a group): The total number of elements (i.e., symmetry operations) in the group. *Also known as* $\boldsymbol{h}$.
- Rule 1: Closure.

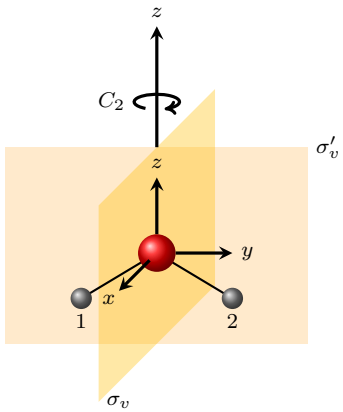


Figure II.3: Symmetry elements for H_2O.

  - H_2O is of the C_{2v} point group (refer to Figure II.3).
    - Symmetry operations: E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$.
    - $\sigma_v \cdot C_2 = \sigma'_v = C_2 \cdot \sigma_v$.
    - The above property (order *does not* matter) shows that C_{2v} is an **Abelian group**.
  - NH_3 is of the C_{2v} point group.
    - Symmetry operations: E, ${C_3}^+$, ${C_3}^-$, σ_v, σ'_v, and σ''_v.
    - $\sigma''_v \cdot C_3 = \sigma_v$, but $C_3 \cdot \sigma''_v = {C_3}^- = {C_3}^2$.
    - The above property (order *does* matter) shows that C_{3v} is a **non-Abelian group**.
- Rule 2: Associativity.
  - H_2O is of the C_{2v} point group (refer to Figure II.3).

$$\begin{aligned}\sigma'_v C_2 \sigma_v(1,2) &= \sigma'_v C_2(2,1) \\ &= \sigma'_v(1,2) \\ &= (1,2)\end{aligned} \qquad \begin{aligned}\sigma'_v(C_2\sigma_v)(1,2) &= \sigma'_v E(1,2) \\ &= \sigma'_v(1,2) \\ &= (1,2)\end{aligned} \qquad \begin{aligned}(\sigma'_v C_2)\sigma_v(1,2) &= \sigma_v\sigma_v(1,2) \\ &= \sigma_v(2,1) \\ &= (1,2)\end{aligned}$$

- Rule 3: Identity.
- Rule 4: Inverse.
  - For a C_{2v} point group:

$$E \cdot E = E \qquad C_2 \cdot C_2 = E \qquad \sigma_v \cdot \sigma_v = E \qquad \sigma'_v \cdot \sigma'_v = E$$

- Group multiplication tables.

C_{2h}	$\boldsymbol{E}$	$\boldsymbol{C_2}$	$\boldsymbol{\sigma_h}$	$\boldsymbol{i}$
$\boldsymbol{E}$	E	C_2	σ_h	i
$\boldsymbol{C_2}$	C_2	E	i	σ_h
$\boldsymbol{\sigma_h}$	σ_h	i	E	C_2
$\boldsymbol{i}$	i	σ_h	C_2	E

Table II.1: Group multiplication table for the C_{2h} point group.

- Table II.1 corresponds to the C_{2h} point group, which has E, C_2, σ_h, and i operations.
- Note that the operation in the top row is the one that's applied first, while the one in the left column will be applied second.

- **Subgroup**: Fractional parts of groups that are groups, too.

C_{3v}	$\boldsymbol{E}$	$\boldsymbol{C_3}$	$\boldsymbol{{C_3}^2}$	$\boldsymbol{\sigma_v}$	$\boldsymbol{\sigma_v'}$	$\boldsymbol{\sigma_v''}$
$\boldsymbol{E}$	E	C_3	${C_3}^2$	σ_v	σ_v'	σ_v''
$\boldsymbol{C_3}$	C_3	${C_3}^2$	E	σ_v''	σ_v	σ_v'
$\boldsymbol{{C_3}^2}$	${C_3}^2$	E	C_3	σ_v'	σ_v''	σ_v
$\boldsymbol{\sigma_v}$	σ_v	σ_v'	σ_v''	E	C_3	${C_3}^2$
$\boldsymbol{\sigma_v'}$	σ_v''	σ_v	σ_v'	C_3	${C_3}^2$	E
$\boldsymbol{\sigma_v''}$	σ_v'	σ_v''	σ_v	${C_3}^2$	E	C_3

Table II.2: Group multiplication table for the C_{3v} point group.

- If $h = 6$ (as in the C_{3v} group), subgroup order can be $h = 3, 2, 1$. Why only these?
- The order 1 and 3 charts are subgroups.
- The order 2 chart is not a subgroup because ${C_3}^2$ is not an operation in the group (therefore, the "subgroup" is not closed).

- We use subgroups because they can make complex problems simpler.
  - For example, calculating the vibrational modes of CO_2.
  - As another example, D_{2h} is a subgroup of $D_{\infty h}$.

II.4 Module 6: Representations

- Items of the same point group have the same vibration modes.
- **Representation** (of a group): Any collection of quantities (or symbols) which obey the multiplication table of a group. *Also known as* Γ.
- For our purposes, these quantities are the matrices that show how certain characteristic of a molecule behave under the symmetry operations of the group.
- Operations (on a point (x, y, z) in Cartesian coordinates):
  - $E(x, y, z) = (x, y, z)$.
  - $\sigma_{xz}(x, y, z) = (x, -y, z)$.
  - $i(x, y, z) = (-x, -y, -z)$.
  - C_n: Convention is a counterclockwise rotation of the point by $\theta = \frac{2\pi}{n}$ radians.
  - S_n: Convention is a clockwise rotation of the point C_n followed by a σ through a plane perpendicular to C.

- Matrix forms of operations:
  - Identity: $E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$.
  - One example of a reflection (there are two more): $\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.
  - Inversion: $i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$.
  - Rotation: Counterclockwise is $C_n(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$ and clockwise is $C_n(\theta) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$.
    - A derivation of this matrix can be found in the slides.
  - Improper rotation: $S_n(\theta) = \sigma_h C_n(\theta)$.
- **Reducible representations** (Γ):
  - A representation of a symmetry operation of a group.
  - Can be expressed in terms of a representation of lower dimension.
  - Can be broken down into a simpler form.
  - Characters can be further diagonalized.
  - Are composed of the direct sum of irreducible representations.
  - Infinite possibilities.
- **Irreducible representations** (Γ_i):
  - A fundamental representation of a symmetry operation of a group.
  - Cannot be expressed in terms of a representation of lower dimension.
  - Cannot be broken down into a simpler form.
  - Characters cannot be further diagonalized.
  - Small finite number dictated by point group.
- Good example of reducible/irreducible representations?
- A representation shows how certain characteristics of an object (a basis) behave under the symmetry operation of the group.
- **Conjugate elements**: Two elements X and Y for which there exists an element Z in the group such that
$$Z^{-1} \cdot X \cdot Z = Y$$
  - Every element is conjugated with itself (let $Z = E$).
  - If X is conjugated with Y, then Y is conjugated with X.
  - If X is conjugated with Y and W, then Y and W are also conjugate.
- **Class**: A complete set of elements of a group that are conjugate to one another.
  - Geometric meaning: operations in the same class can be converted into one another by changing the axis system through application of some symmetry operation of the group.
- Find the conjugates to C_3 in the C_{3v} point group (refer to Table II.2 throughout the following discussion).

  - Let $X = C_3$, let Z iterate through the six symmetry elements $(E, C_3, {C_3}^2, \sigma_v, \sigma_v', \sigma_v'')$, and let Z^{-1} iterate through the corresponding inverses $(E, {C_3}^2, C_3, \sigma_v, \sigma_v', \sigma_v'')$.
  - Thus, we have

$$E \cdot C_3 \cdot E = C_3$$
$${C_3}^2 \cdot C_3 \cdot C_3 = C_3$$
$$C_3 \cdot C_3 \cdot {C_3}^2 = C_3$$
$$\sigma_v \cdot C_3 \cdot \sigma_v = {C_3}^2$$
$$\sigma_v' \cdot C_3 \cdot \sigma_v' = {C_3}^2$$
$$\sigma_v'' \cdot C_3 \cdot \sigma_v'' = {C_3}^2$$

  - It follows from the above that C_3 and C_3 are conjugates, and C_3 and ${C_3}^2$ are conjugates.
  - Thus, C_3 and ${C_3}^2$ are in the same class.
  - We can use a similar method to prove that σ_v, σ_v', and σ_v'' are all in the same class within the C_{3v} point group.
  - Likewise E is in a class by itself.
  - Thus, for the C_{3v} point group, E forms a class of order 1, $C_3, {C_3}^2$ form a class of order 2, and $\sigma_v, \sigma_v', \sigma_v''$ form a class of order 3.

- **Similarity transformation**: The transformation

$$v^{-1} \cdot A \cdot v = A'$$

  - A is a representation for some type of symmetry operation.
  - v is a similarity transform operator.
  - v^{-1} is the inverse of the similarity transform operator.
  - A' is the product.
  - A and A' are conjugates, and we say that A' is the similarity transform of A by v.

- **Block-diagonal** (matrix): A matrix with nonzero values only in square blocks along the diagonal from the top left to the bottom right.

$$\begin{bmatrix} 2 & 3 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{bmatrix}$$

  - The above matrix is an example of a block-diagonal matrix.

- Irreducible representations are the ones where the matrices have the most block-diagonalized form that they can.

II.5 Module 7: Characters and Character Tables

1/19:

- Nocera Lecture 3 notes (on Canvas) explain how reducible and irreducible transformations are related to each other through the similarity transformations.
- For H_2O, each atom has 3 Cartesian coordinates, so our transformation matrix[2] is 9-square.

[2] Some values in it are negative because of the cosine/sine definition of a rotation matrix for $\theta = 180°$.

  - However, we can also apply a smaller matrix to the molecule as a whole and invoke symmetry to find the position of the individual atoms.

- **Characters** (of a representation): The traces (i.e., sums of the diagonal matrix elements) of the representation matrices for each operation. *Also known as* $\boldsymbol{\chi}$.
  - The character is an invariant for each type of symmetry operation (e.g., regardless of the axis about which a C_n operation is performed, the trace of the corresponding matrix will be the same).

- Common characters:
  - C_n character: $\chi = 2\cos\theta + 1$.
  - σ_v, σ_d character: $\chi = 1$.
  - $S_2 \equiv i$ character: $\chi = -3$.
  - S_n character: $\chi = 2\cos\theta - 1$.
  - $\perp C_2$ axes character: $\chi = -1$.

- **Character table**: The collection of characters for a given irreducible representation, under the operations of a group.

Group Symbol	Symmetry Elements					
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
Irreducible Representations	Characters				Basis Functions	

Figure II.4: A character table.

  - Character tables for all point groups are listed in Appendix C of Miessler et al. (2014).

- **Mulliken symbols** are used to classify irreducible representations based on degeneracy and symmetry.
  - A or B: singly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is 1×1).
  - E: Doubly degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is 2×2).
  - T: Triply degenerate (the maximum block size in the block-diagonalized irreducible transformation matrix is 3×3).
  - A: symmetric (+) with respect to C_n.
  - B: anti-symmetric (−) with respect to C_n.
  - Subscript g: symmetric (+) with respect to i. *Etymology* short for gerade (German for symmetric).
  - Subscript u: anti-symmetric (−) with respect to i. *Etymology* short for ungerade (German for unsymmetric).
    - If the molecule has a center of inversion, we label irreducible representations with g or u.
  - Subscript 1: symmetric (+) with respect to $\perp C_2$ or σ_v.
  - Subscript 2: anti-symmetric (−) with respect to $\perp C_2$ or σ_v.
  - Superscript $'$: symmetric (+) under σ_h (if no i).
  - Superscript $''$: anti-symmetric (−) under σ_h (if no i).

- Don't mistake the operation E for the Mulliken symbol E!
- To assign Mulliken symbols, use the character table.
  - Assigning the main letter:
    - If E-character $= 1$ and C_n-character $= 1$: A.
    - If E-character $= 1$ and C_n-character $= -1$: B.
    - If E-character $= 2$: E.
    - If E-character $= 3$: T.
  - Assigning a subscript g or u:
    - If i-character $= 1$: g.
    - If i-character $= -1$: u.
    - This subscript can be assigned to A, B, E, T representations.
  - Assigning a superscript $'$ or $''$:
    - If σ_h-character $= 1$: $'$.
    - If σ_h-character $= -1$: $''$.
    - This subscript can be assigned to A, B representations.
  - Assigning a subscript 1 or 2:
    - If $\perp C_2$ or σ_v-character $= 1$: 1.
    - If $\perp C_2$ or σ_v-character $= -1$: 2.
    - This subscript can be assigned to A, B representations.
- σ, π, and δ bonds come from the Mulliken symbols!
  - Infinity tables use Greek rather than Latin letters.

D_3	E	$2C_3(z)$	$3C_2'$	linear	quadratic
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x,y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$.

Table II.3: Character table for the D_3 point group.

- In character tables, we need to multiply each symmetry operation by the number of types there are (see Table II.3).
- Basis functions show us how different functions transform under different symmetry operations.
- In the C_{2v} point group:
  - The p_x orbital has B_1 symmetry.
  - p_x transforms as B_1.
  - p_x has the same symmetry as B_1.
  - p_x forms a basis for the B_1 irreducible representation.
  - p_x is B_1 because (see Table 2 and Figure II.4) it does not change under E, it inverts under C_2, it does not change under $\sigma_v(xz)$, and it inverts under $\sigma_v'(yz)$.
- We can apply the same procedure to other more complex functions.
  - For example, in the C_{2v} point group, we know that (with respect to orbitals):
    - p_y is B_2.

- p_z is A_1.
- d_{z^2} is A_1.
- $d_{x^2-y^2}$ is A_1.
- d_{yz} is B_2.
- d_{xy} is A_2.
- d_{xz} is B_1.
- We can even go into the cubic functions describing the f orbitals and assign them Mulliken symbols.

- Essentially, the right hand side of a character table tells you how atomic orbitals will transform under certain symmetry operations.

- Properties of a character table:

1. The characters of all matrices belonging to the operations in the same class are identical in a given irreducible representation.
   - As such, we form **classes** of operations.
   - We most commonly form a **rotational class** and a **reflection class**.
2. The number of irreducible representations in a group is equal to the number of classes of that group.
3. There is always a totally symmetric representation for any group.
   - I.e., a representation where every character is 1.
4. The sum of the squares of the dimensionality of all the irreducible representations is equal to the order of the group. Mathematically,

$$h = \sum_i [\chi_i(E)]^2$$

   - For example, the dimensionalities (characters under E) of the D_3 point group (see Table II.3) are 1, 1, and 2, and the order is, indeed, $6 = 1^2 + 1^2 + 2^2$.
5. The sum of the squares of the characters multiplied by the number of operations in the class equals the order of the group. Mathematically,

$$h = \sum_{R_c} g_c [\chi_i(R_c)]^2$$

   - For example, with respect to the D_3 point group (see Table II.3),

$$\begin{aligned} 6 &= (1)(1)^2 + (2)(1)^2 + (3)(1)^2 \\ &= (1)(1)^2 + (2)(1)^2 + (3)(-1)^2 \\ &= (1)(2)^2 + (2)(-1)^2 + (3)(0)^2 \end{aligned}$$

6. The sum of the products of the corresponding characters of any two different irreducible representations of the same group is zero. Mathematically,

$$\sum_{R_c} g_c \chi_i(R_c) \chi_f(R_c) = 0$$

   - Basically, this means that if we treat irreducible representations as vectors in h-space, they are orthogonal.
   - For example, with respect to the D_3 point group (see Table II.3),

$$\begin{aligned} 0 &= 1(1)(1) + 2(1)(1) + 3(1)(-1) \\ &= 1(1)(2) + 2(1)(-1) + 3(1)(0) \\ &= 1(1)(2) + 2(1)(-1) + 3(-1)(0) \end{aligned}$$

II.6 Module 8: Using Character Tables

- A reducible representation of a group is any representation Γ of the form

$$\Gamma = \sum_i a_i \Gamma_i$$

  where each Γ_i is an irreducible representation of the group and a_i is a real scalar.

  - Basically, a reducible representation is any nontrivial linear combination of irreducible representations.
  - For example, with respect to the C_{2v} point group (see Figure II.4), $\Gamma = (7, 1, 5, 3) = 4A_1 + 2B_1 + B_2$ is a reducible representation.

- We may "factor" reducible representations by inspection, or by the...

- Decomposition/reduction formula for a reducible representation:

$$a_i = \frac{1}{h} \sum_Q N \cdot \chi(R)_Q \cdot \chi_i(R)_Q$$

  - a_i is the number of times the irreducible representation appears in Γ_1.
  - h is the order of the group.
  - N is the number of operations in class Q.
  - $\chi(R)_Q$ is the character of the reducible representation.
  - $\chi_i(R)_Q$ is the character of the irreducible representation.
  - This formula cannot be applied to $D_{\infty h}$ and $C_{\infty v}$.

- Let's look at decomposing $\Gamma = (7, 1, 5, 3)$ into its component irreducible point groups using the above formula.

$$a_{A_1} = \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot 1) = 4$$
$$a_{A_2} = \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot 1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot -1) = 0$$
$$a_{B_1} = \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot 1 + 1 \cdot 3 \cdot -1) = 2$$
$$a_{B_2} = \frac{1}{4}(1 \cdot 7 \cdot 1 + 1 \cdot 1 \cdot -1 + 1 \cdot 5 \cdot -1 + 1 \cdot 3 \cdot 1) = 1$$

- You can also find websites that will apply the formula for you.

- Basis → reducible representation → irreducible representations workflow:

  1. Assign a point group.
  2. Choose a basis function (bond, vibration, orbital, angle, etc.).
  3. Apply operations.
     - The following shortcuts allow us to skip matrix math in certain situations.
       - If the basis stays the same: $+1$.
       - If the basis is reversed: -1.
       - If it is a more complicated change: 0.
  4. Generate a reducible representation.
  5. Reduce to irreducible representation.

- We now look at an example of applying the above method to H_2O.
  - H_2O is of the C_{2v} point group.
  - The 9×9 identity matrix represents the identity operation on the 3 atoms in H_2O, each described by 3 Cartesian coordinates. Thus, $\chi(E) = 9$.
  - The following matrix represents the C_2 symmetry operation. Thus, $\chi(C_2) = -1$.

$$\begin{matrix} \mathrm{O}\left\{\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}\right. \\ \mathrm{H}_a\left\{\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}\right. \\ \mathrm{H}_b\left\{\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}\right. \end{matrix} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} \left.\begin{bmatrix} x \\ y \\ z \end{bmatrix}\right\}\mathrm{O} \\ \left.\begin{bmatrix} x \\ y \\ z \end{bmatrix}\right\}\mathrm{H}_a \\ \left.\begin{bmatrix} x \\ y \\ z \end{bmatrix}\right\}\mathrm{H}_b \end{matrix}$$

    - Note that atoms moved during the transformation do not contribute to the character of the transformation matrix.
  - Since under $\sigma_v(xz)$ only O is unshifted, we need only consider its part of the transformation matrix (as follows) when looking for the character. Thus, $\chi(\sigma_v(xz)) = 1$.

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

  - Since under $\sigma_v(yz)$ no atom is shifted, we need to consider each (identical) part of the transformation matrix (as follows) when looking for the character. Thus, $\chi(\sigma_v(yz)) = 3$.

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

  - Thus, the characters of our final reducible representation is $\Gamma_{3N} = (9, -1, 1, 3)$.
    - This representation represents fully unrestricted motion of all 3 ambiguities of freedom.

- Another example: $XeOF_4$.

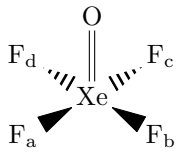


Figure II.5: $XeOF_4$.

  - Point group: C_{4v}.
  - Basis function: F atoms.
  - Let's see what happens to the fluorine atoms under the C_{4v} operations (remember that if a basis element (a fluroine atom) stays the same, it contributes +1 to the character of an operation, and if it moves, it contributes 0 to the character).

E	all unchanged	4
C_4	all move	0
C_2	all move	0
$2\sigma_v$	2 move, 2 unchanged	2
$2\sigma_d$	all move	0

Table II.4: Changes in the fluorine atoms of $XeOF_4$ under the C_{4v} symmetry operations.

- Thus, $\Gamma = (4, 0, 0, 2, 0)$.
- With the C_{4v} character table and the decomposition formula, we can discover that $\Gamma = A_1 + B_1 + E$.

II.7 Chapter 4: Symmetry and Group Theory

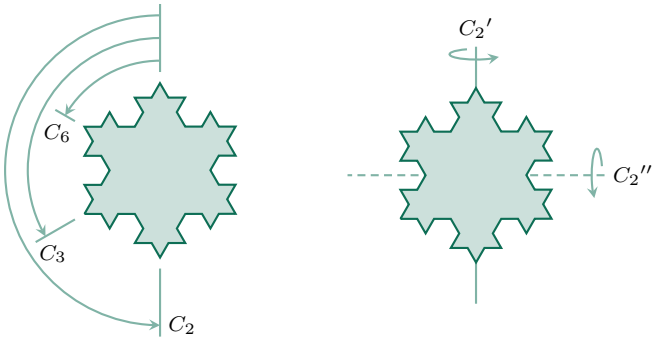
From Miessler et al. (2014).

II.7.1 Notes

1/18:

- **Coincident** (axes): Two identical axes.
  - For example, the C_3 rotation axis of $CHCl_3$ is **coincident** with the C−H bond axis.
- Snowflakes, which are often planar and have hexagonal symmetry, have a twofold (C_2), threefold (C_3), and sixfold (C_6) axis through their center and perpendicular to their plane.
  - Rotations ${C_3}^2$ and ${C_6}^5$ are also symmetry operations.

1/19:



(a) About the principal axis. (b) About perpendicular axes.

Figure II.6: Rotations of a snowflake design.

1/18:

- "When necessary, the C_2 axes perpendicular to the principal axis are designated with primes; a single prime (C_2') indicates that the axis passes through several atoms of the molecule, whereas a double prime (C_2'') indicates that it passes between the outer atoms" (Miessler et al., 2014, p. 77).

1/19:

- Even though $S_2 \equiv i$ and $S_1 \equiv \sigma$, the i and σ notations are preferred because of the group theory requirement of maximizing the number of unique classes of symmetry operations associated with a molecule.
- **Point group**: A set of symmetry operations that describes a molecule's overall symmetry.
- Alternative steps for assigning point groups:
  1. Determine whether the molecule exhibits very low symmetry (C_1, C_s, C_i) or high symmetry (T_d, O_h, $C_{\infty v}$, $D_{\infty h}$, I_h).

2. If not, find the highest order C_n axis for the molecule.
3. Does the molecule have any C_2 axes perpendicular to the principal C_n axis? If it does, there will be n of such C_2 axes, and the molecule is in the D set of groups. If not, it is in the C or S set.
4. Does the molecule have a mirror plane (σ_h) perpendicular to the principal C_n axis? If so, it is classified as C_{nh} or D_{nh}. If not, continue with Step 5.
5. Does the molecule have any mirror planes that contain the principal C_n axis (σ_v or σ_d)? If so, it is classified as C_{nv} or D_{nd}. If not, but it is in the D set, it is classified as D_n. If the molecule is in the C or S set, continue with Step 6.
6. Is there an S_{2n} axis collinear with the principal C_n axis? If so, it is classified as S_{2n}. If not, the molecule is classified as C_n.

- Groups of high symmetry:
  - $C_{\infty v}$ (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.
  - $D_{\infty h}$ (linear): These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.
  - T_d (tetrahedral): Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.
    - Look for C_3 and C_2 axes.
  - O_h (octahedral): These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.
    - Look for C_4, C_3, and C_2 axes.
  - I_h (icosahedral): Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations — 120 in all.
    - Look for C_5, C_3, and C_2 axes.
  - T_h: Adds i to T_d. Example: $W[N(CH_3)_2]_6$.