5.04 Principles of Inorganic Chemistry II
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Lecture 3: Irreducible Representations and Character Tables

Similarity transformations yield **irreducible representations**, Γ_i, which lead to the useful tool in group theory – the **character table**. The general strategy for determining Γ_i is as follows: **A**, **B** and **C** are matrix representations of symmetry operations of an arbitrary basis set (i.e., elements on which symmetry operations are performed). There is some similarity transform operator ν such that

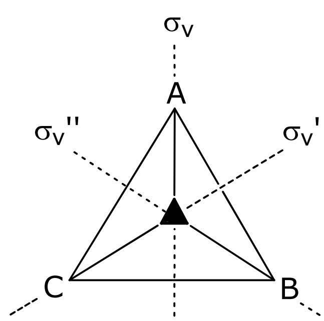
$$\mathbf{A'} = \nu^{-1} \cdot \mathbf{A} \cdot \nu$$
$$\mathbf{B'} = \nu^{-1} \cdot \mathbf{B} \cdot \nu$$
$$\mathbf{C'} = \nu^{-1} \cdot \mathbf{C} \cdot \nu$$

where ν uniquely produces **block-diagonalized** matrices, which are matrices possessing square arrays along the diagonal and zeros outside the blocks

$$\mathbf{A}' = \begin{bmatrix} A_1 & & \\ & A_2 & \\ & & A_3 \end{bmatrix} \qquad \mathbf{B}' = \begin{bmatrix} B_1 & & \\ & B_2 & \\ & & B_3 \end{bmatrix} \qquad \mathbf{C}' = \begin{bmatrix} C_1 & & \\ & C_2 & \\ & & C_3 \end{bmatrix}$$

Matrices **A**, **B**, and **C** are **reducible**. Sub-matrices A_i, B_i and C_i obey the same multiplication properties as **A**, **B** and **C**. If application of the similarity transform does not further block-diagonalize **A′**, **B′** and **C′**, then the blocks are **irreducible representations**. The **character** is the sum of the diagonal elements of Γ_i.

As an example, let's continue with our exemplary group: E, C_3, C_3^2, σ_v, σ_v', σ_v'' by defining an arbitrary basis … a triangle



The basis set is described by the triangles vertices, points A, B and C. The transformation properties of these points under the symmetry operations of the group are:

$$E\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix} \qquad \sigma_V\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}A\\C\\B\end{bmatrix}=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix}$$

$$C_3\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}B\\C\\A\end{bmatrix}=\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix} \qquad \sigma_V{}'\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}B\\A\\C\end{bmatrix}=\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix}$$

$$C_3{}^2\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}C\\A\\B\end{bmatrix}=\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix} \qquad \sigma_V{}''\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}C\\B\\A\end{bmatrix}=\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix}$$

These matrices are not block-diagonalized, however a suitable similarity transformation will accomplish the task,

$$\mathcal{V}=\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{2}{\sqrt{6}}&0\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{2}}\end{bmatrix} \quad ; \quad \mathcal{V}^{-1}=\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}\\\frac{2}{\sqrt{6}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{6}}\\0&\frac{1}{\sqrt{2}}&-\frac{1}{\sqrt{2}}\end{bmatrix}$$

Applying the similarity transformation with C_3 as the example,

$$\mathcal{V}^{-1}\cdot\mathbf{C}_3\cdot\mathcal{V}=\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}\\\frac{2}{\sqrt{6}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{6}}\\0&\frac{1}{\sqrt{2}}&-\frac{1}{\sqrt{2}}\end{bmatrix}\cdot\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}\cdot\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{2}{\sqrt{6}}&0\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{2}}\end{bmatrix}$$

$$\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}\\\frac{2}{\sqrt{6}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{6}}\\0&\frac{1}{\sqrt{2}}&-\frac{1}{\sqrt{2}}\end{bmatrix}\cdot\begin{bmatrix}\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{3}}&\frac{2}{\sqrt{6}}&0\end{bmatrix}=\left[\begin{array}{c|cc}1&0&0\\\hline 0&-\frac{1}{2}&\frac{\sqrt{3}}{2}\\0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{array}\right]=\mathbf{C_3*}$$

if $\nu^{-1} \cdot \mathbf{C_3*} \cdot \nu$ is applied again, the matrix is not block diagonalized any further. The same diagonal sum is obtained *though off-diagonal elements may change). In this case, $\mathbf{C_3*}$ is an irreducible representation, Γ_i.

The similarity transformation applied to other reducible representations yields:

$$\nu^{-1} \cdot \mathbf{E} \cdot \nu = \mathbf{E*} = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right] \qquad \nu^{-1} \cdot \mathbf{C_3^2} \cdot \nu = \mathbf{C_3^2*} = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array}\right]$$

$$\nu^{-1} \cdot \boldsymbol{\sigma_v} \cdot \nu = \boldsymbol{\sigma_v*} = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & -1 \end{array}\right] \qquad \nu^{-1} \cdot \boldsymbol{\sigma_v''} \cdot \nu = \boldsymbol{\sigma_v''*} = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{array}\right]$$

$$\nu^{-1} \cdot \sigma_v' \cdot \nu = \sigma_v'* = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{array}\right]$$

As above, the block-diagonalized matrices do not further reduce under re-application of the similarity transform. All are Γ_{irr}s.

Thus a 3 × 3 reducible representation, Γ_{red}, has been decomposed under a similarity transformation into a 1 (1 × 1) and 1 (2 × 2) block-diagonalized irreducible representations, Γ_i. The traces (i.e. sum of diagonal matrix elements) of the Γ_i's under each operation yield the **characters** (indicated by χ) of the representation. Taking the traces of each of the blocks:

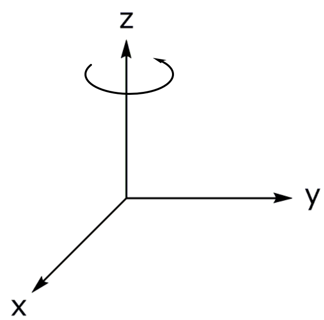
	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
Γ_1	1	1	1	1	1	1
Γ_2	2	−1	−1	0	0	0

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	2	−1	0

Note: characters of operators in the same class are identical

This collection of characters for a given irreducible representation, under the operations of a group is called a **character table**. As this example shows, from a completely arbitrary basis and a similarity transform, a character table is born.

The triangular basis set does not uncover all Γ_{irr} of the group defined by {E, C_3, C_3^2, σ_v, σ_v', σ_v''}. A triangle represents Cartesian coordinate space (x,y,z) for which the Γ_is were determined. May choose other basis functions in an attempt to uncover other Γ_is. For instance, consider a rotation about the z-axis,



The transformation properties of this basis function, R_z, under the operations of the group (will choose only 1 operation from each class, since characters of operators in a class are identical):

E: $R_z \rightarrow R_z$ $\qquad$ C_3: $R_z \rightarrow R_z$ $\qquad$ $\sigma_v(xy)$: $R_z \rightarrow \overline{R}_z$

Note, these transformation properties give rise to a Γ_i that is not contained in a triangular basis. A new (1 x 1) basis is obtained, Γ_3, which describes the transform properties for R_z. A summary of the Γ_i for the group defined by E, C_3, C_3^2, σ_v, σ_v', σ_v'' is:

	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	from triangular basis, i.e. (x, y, z)
Γ_2	2	−1	0	
Γ_3	1	1	−1	from R_z

Is this character table complete? Irreducible representations and their characters obey certain algebraic relationships. From these 5 rules, we can ascertain whether this is a complete character table for these 6 symmetry operations.

Five important rules govern irreducible representations and their characters:

Rule 1

The sum of the squares of the dimensions, ℓ, of irreducible representation Γ_i is equal to the order, h, of the group,

$$\sum_i \ell_i^2 = \ell_1^2 + \ell_2^2 + \ell_3^2 + \ldots = h$$

order of matrix representation of Γ_i (e.g. ℓ = 2 for a 2×2)

Since the character under the identity operation is equal to the dimension of Γ_i (since E is always the unit matrix), the rule can be reformulated as,

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

character under E

Rule 2

The sum of squares of the characters of irreducible representation Γ_i equals h

$$\sum_R \left[\chi_i(R) \right]^2 = h$$

character of Γ_i under operation R

Rule 3

Vectors whose components are characters of two different irreducible representations are orthogonal

$$\sum_R \left[\chi_i(R) \right] \left[\chi_j(R) \right] = 0 \quad \text{for} \quad i \neq j$$

Rule 4

For a given representation, characters of all matrices belonging to operations in the same class are identical

Rule 5

The number of Γ_is of a group is equal to the number of classes in a group.

With these rules one can algebraically construct a character table. Returning to our example, let's construct the character table in the absence of an arbitrary basis:

Rule 5: $E\ (C_3,\ C_3^2)\ (\sigma_v,\ \sigma_v',\ \sigma_v'')$ … 3 classes $\therefore$ 3 Γ_is

Rule 1: $\ell_1^2 + \ell_2^2 + \ell_3^2 = 6 \quad \therefore \quad \ell_1 = \ell_2 = 1,\ \ell_2 = 2$

Rule 2: All character tables have a totally symmetric representation. Thus one of the irreducible representations, Γ_i, possesses the character set $\chi_1(E) = 1$, $\chi_1(C_3, C_3^2) = 1$, $\chi_1(\sigma_v, \sigma_v', \sigma_v'') = 1$. Applying Rule 2, we find for the other irreducible representation of dimension 1,

$$1 \cdot \chi_1(E) \cdot \chi_2(E) \ + \ 2 \cdot \chi_1(C_3) \cdot \chi_2(C_3) \ + \ 3 \cdot \chi_1(\sigma_v) \cdot \chi_2(\sigma_v) \ = \ 0$$

consequence of Rule 4

$$1 \cdot 1 \cdot \chi_2(E) \ + \ 2 \cdot 1 \cdot \chi_2(C_3) \ + \ 3 \cdot 1 \cdot \chi_2(\sigma_v) \ = \ 0$$

Since $\chi_2(E) = 1$,

$$1 \ + \ 2 \cdot \chi_2(C_3) \ + \ 3 \cdot \chi_2(\sigma_v) \ = \ 0 \quad \therefore \quad \chi_2(C_3) = 1,\ \chi_2(\sigma_v) = -1$$

For the case of Γ_3 ($\ell_3 = 2$) there is not a unique solution to Rule 2

$$2 \ + \ 2 \cdot \chi_3(C_3) \ + \ 3 \cdot \chi_3(\sigma_v) \ = \ 0$$

However, application of Rule 2 to Γ_3 gives us one equation for two unknowns. Have several options to obtain a second independent equation:

Rule 1: $1 \cdot 2^2 \ + \ 2[\chi_3(C_3)]^2 \ + \ 3[\chi_3(\sigma_v)]^2 \ = \ 6$

Rule 3: $1 \cdot 1 \cdot 2 \ + \ 2 \cdot 1 \cdot \chi_3(C_3) \ + \ 3 \cdot 1 \cdot \chi_3(\sigma_v) \ = \ 0$

or

$1 \cdot 1 \cdot 2 \ + \ 2 \cdot 1 \cdot \chi_3(C_3) \ + \ 3 \cdot (-1) \cdot \chi_3(\sigma_v) \ = \ 0$

Solving simultaneously yields $\chi_3(C_3) = -1$, $\chi_3(\sigma_v) = 0$

Thus the same result shown on pg 4 is obtained:

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	2	−1	0
Γ_3	1	1	−1

Note, the derivation of the character table in this section is based solely on the properties of characters; the table was derived algebraically. The derivation on pg 4 was accomplished from first principles.

The complete character table is:

operations

Schoenflies symbol for point group

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x,y)(R_x,R_y)$	$(x^2 - y^2, xy)\ (xz,yz)$

Mulliken symbols for the Γ_i

characters

basis functions

- Γ_is of:

  $\ell = 1 \Rightarrow$ A or B   A is symmetric (+1) with respect to C_n
  B is antisymmetric (−1) with respect to C_n

  $\ell = 2 \Rightarrow$ E

  $\ell = 3 \Rightarrow$ T

- subscripts 1 and 2 designate Γ_is that are symmetric and antisymmetric, respectively to $\perp C_2$s; if $\perp C_2$s do not exist, then with respect to σ_v
- primes (′) and double primes (″) attached to Γ_is that are symmetric and antisymmetric, respectively, to σ_h
- for groups containing i, g subscript attached to Γ_is that are symmetric to i whereas u subscript designates Γ_is that are antisymmetic to i