20. Representations (Γ)

Defn. sets of numbers or matrices that follow the group multiplication table.

$$R \underset{\sim}{B} = (\quad) B$$ representation

basis : function, axis helpful

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	Basis
Γ_5	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	(x, y)
⋮					

Example : 2-D matrices with x, y as basis.

$$R\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} & \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} \qquad E\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$C_2\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ -y \end{pmatrix} \doteq \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$\sigma_{xz}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x \\ -y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

$$\sigma_{yz}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -x \\ y \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

and $C_2 \sigma_{xz} = \sigma_{yz}$ etc.

Example : numbers with z axis as basis $\uparrow$

$$C_2 \uparrow = \uparrow = 1 \uparrow$$ or coordinate
$$\sigma_{xz} \uparrow = \uparrow = 1 \uparrow$$
$$\sigma_{yz} \uparrow = \uparrow = 1 \uparrow$$

One Dimensional Representations :

A_1 $\chi_1 = \Gamma_1$	1	1	1	1	z axis symmetric
A_2 $\chi_2 = \Gamma_2$	1	1	-1	-1	xy
B_1 $\chi_3 = \Gamma_3$	1	-1	1	-1	x xz
B_2 $\chi_4 = \Gamma_4$	1	-1	-1	1	y yz

Although the number of representations is infinite, virtually all are "reducible" in the sense that they

a) are diagonal matrices consisting of 1-D representations (see Γ_5) Γ_5 breaks down into Γ_3 + Γ_4

b) can be transformed into such diagonal matrices or into matrices with $n \times n$ blocks where $n <$ dimensionality of matrix.

<u>Irreducible Representations</u>: cannot be reduced

Some theorems:

(1) The number of irreducible representations can be shown to be equal to the number of classes s in a group.

For C_{2v} $s = h = 4 \Rightarrow 4$ irreducible representations ($\Gamma_1 - \Gamma_4$)

(2) $$\underbrace{h}_{\substack{\text{no. group elements} \\ \text{"order of group"}}} = \underbrace{\sum_{i=1}^{s}}_{\substack{\text{sum over} \\ \text{classes}}} l_i^2$$ l_i: dimensionality of irreducible representation

For C_{2v} $h = 4 = l_1^2 + l_2^2 + l_3^2 + l_4^2$

$l_i = 1 \Rightarrow 4$ 1-D irreducible representations

($h = s \Rightarrow$ 1-D reps only)

Representations are normally tabulated in terms of "<u>characters</u>" χ (<u>traces of matrices</u>)

	E	C_2	σ_{xz}	σ_{yz}	
$\chi(\Gamma_5)$	2	-2	0	0	$= \chi(\Gamma_3) + \chi(\Gamma_4)$
~~$\chi(\Gamma_6)$~~	~~2~~	~~0~~	~~0~~	~~2~~	~~$= \chi(\Gamma_1) + \chi(\Gamma_4)$~~

(3) Matrices representing group elements in the same class have the same trace.

<u>Proof</u>

$RAR^{-1} = B$ $\quad R, A, B$ matrices

$$\chi(B) = \chi(RAR^{-1}) = \sum_i (RAR^{-1})_{ii} = \sum_i \sum_j R_{ij} (AR^{-1})_{ji}$$

$$= \sum_i \sum_j \sum_k R_{ij} A_{jk} R^{-1}_{ki} = \sum_j \sum_k A_{jk} \underbrace{\sum_i R^{-1}_{ki} R_{ij}}_{(R^{-1}R)_{kj}}$$

$$\chi(B) = \sum_j \sum_k A_{jk} \delta_{kj} = \sum_j A_{jj} = \chi(A)$$

Yet another important theorem concerning irreducible representations is the <u>orthogonality theorem</u>:

$$(4) \qquad \sum_{i=1}^{s} N_i \; \chi_j(R_i) \; \chi_k(R_i) = (\quad) \, \delta_{jk}$$

no. elements in class i

[illegible] j

element of class i

[illegible] k

Before we use these theorems, a word concerning notation of representations:

a) One Dimensional — Use A & B with various subscripts and primes

$$\chi(C_p) = \begin{cases} 1 & \text{Use label } A \\ -1 & \text{Use label } B \end{cases}$$

$$\begin{matrix} \chi(\sigma_v) \\ \chi(\perp C_2) \end{matrix} = \begin{cases} 1 & \text{Use subscript } 1 \\ -1 & \text{Use subscript } 2 \end{cases} \quad \text{unclear if } > 1 \text{ such plane}$$

$$\chi(\sigma_h) = \begin{cases} 1 & \text{Use } ' \\ -1 & \text{Use } '' \end{cases}$$

$$\chi(i) = \begin{cases} 1 & \text{Use subscript } g \\ -1 & \text{Use subscript } u \end{cases}$$

b) Two Dimensional E   c) Three dimensional F, T

C_{2v} $\Gamma_1 \rightarrow A_1$ $\Gamma_2 \rightarrow A_2$ $\Gamma_3 \rightarrow B_1$? $\Gamma_4 \rightarrow B_2$?

<u>Use of Theorems To Determine Irreducible Representations</u>

The group C_{3v} has $6 = h$ elements: $E, 2C_3, 3\sigma_v$ (NH_3)

$s = 3$ Theorem (1) No. irred. reps = 3

Theorem (2) $6 = \sum_{i=1}^{3} l_i^2 = l_1^2 + l_2^2 + l_3^2$

$l_1 = l_2 = 1$ $l_3 = 2$ Two 1-D reps of which one must be totally symmetric
1 non-diagonal 2-D rep.

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	} orthogonality theorem
A_2	1	1	−1	$1 \times 1 + 2(1 \times 1) + 3(1 \times -1) = 0$
E	2	−1	0	— orthogonal to both 1-D reps.

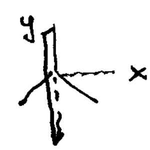
trace of identity matrix

Possible matrices for E: (x y) basis

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix} ✓$$

$$\begin{pmatrix} -\cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$

$\theta = 120°, 240°$



(5) <u>Reduction Theorem</u>

To reduce a reducible representation, use the theorem:

$$N(\text{Rep. } j) = \frac{1}{h} \sum_{i=1}^{s} N_i \, \chi_{red}(R_i) \, \chi_j(R_i)$$

<u>Example</u> C_{3v} group

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
χ_{red}	4	1	0

trace of matrices

Later, we will learn how to generate reducible representations → χ_{red} (4×4 matrices)

$$N(A_1) = \frac{1}{6}\left(1\times4\times1 + 2\times1\times1 + 3\times0\times1\right) = 1$$

$$N(A_2) = \frac{1}{6}\left(1\times4\times1 + 2\times1\times1 + 3\times0\times-1\right) = 1$$

$$N(E) = \frac{1}{6}\left(1\times4\times2 + 2\times1\times-1 + 3\times0\times0\right) = 1$$

$$\chi_{red} = \chi(A_1) + \chi(A_2) + \chi(E)$$

4-D matrices

$$\begin{pmatrix} 1 & & \\ & 1 & \\ & & (\ \ ) \end{pmatrix}$$

2×2 with off diagonal elements except for E

21. Character Tables

- contain, for a given group, group elements, irreducible representations (in the form of characters), and bases

basis: a function, axis, or set of variables that can be used to generate a representation.

$$R\,(B) = (\quad)\,(B)$$

group element   basis   representation   basis

C_{2v} Character Table

elements by classes (e.g. $2C_3$)

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	(bases)	
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

all 1-D bases here

R_z: circular motion around z

"z" stands for a component (e.g. μ_z) of any simple vector
"R_z" can be viewed as a circular vector or as an angular momentum $R_z = xp_y - yp_x$ (which transforms as xy)

Language: "z transforms as A_1"
"z has full symmetry of group"

Ψ_{elec} as Basis (spatial part only)

$\underbrace{\hat{H}_{elec}}\Psi_{elec} = E_{elec}\Psi_{elec}$ at given fixed structure

structure built in through V: has full symmetry of group

R: group element $\quad R\hat{H}_{elec} = \hat{H}_{elec}$

Now consider $R(\hat{H}_{elec}\Psi_{elec}) = R(E_{elec}\Psi_{elec})$

compound basis

$$\hat{H}_{elec}(\underbrace{R\Psi_{elec}}) = E_{elec}(R\Psi_{elec})$$

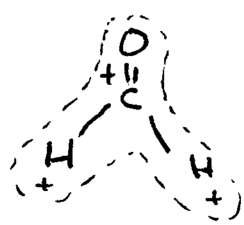
$[\hat{H}_{elec}, R] = 0$ $\quad$ eigenfunctions with energy E_{elec}

Non-degenerate Case

$R\Psi_{elec} = \pm 1\ \underbrace{\Psi_{elec}}_{\text{basis}}$ $\quad$ can be thought of as Ψ_{elec} eigenfunction of R

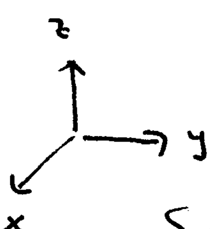
1-D representation →

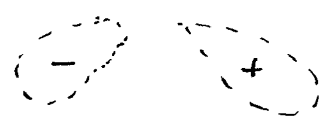
C_{2v} example:



A_1 (symmetric) basis

(multi-electronic function)





B_2 basis

State designation $^{2S+1}$Representation

e.g. $^1A_1$ (common for ground electronic states)

$^3B_2$, $^1B_2$

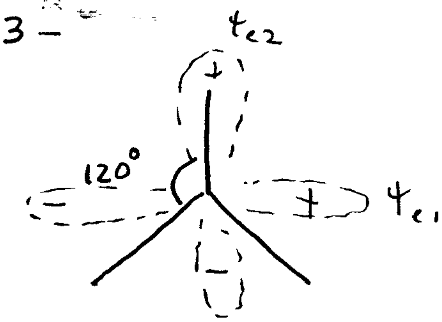
Degenerate Case

e.g. 2-fold $\quad R\Psi_{e1} = a_{11}\Psi_{e1} + a_{12}\Psi_{e2}$ $\quad R\begin{pmatrix}\Psi_{e1}\\ \Psi_{e2}\end{pmatrix} = (\quad)\begin{pmatrix}\Psi_{e1}\\ \Psi_{e2}\end{pmatrix}$

Ψ_{e1}, Ψ_{e2} $\quad \begin{pmatrix}\Psi_{e1}\\ \Psi_{e2}\end{pmatrix}$ 2-D basis for 2-D irreducible representation

– Example (C_{3v} group)

Top View



^1E , ^3E etc.

Direct Products : Selection Rules

If μ_x "transforms" as B_1 and μ_y "transforms" as B_2, $\mu_x \mu_y$ transforms as the "direct product" of the representations.

$$\chi(B_1 \otimes B_2) = \chi_{B_1} \chi_{B_2} \quad \text{or} \quad \chi_{B_1} \otimes \chi_{B_2}$$

$$\chi(B_1) \otimes \chi(B_2)$$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	
A_2	1	1	–1	–1	R_z ,	xy
B_1	1	–1	1	–1	x	
B_2	1	–1	–1	1	y	
$B_1 \otimes B_2$	1	1	–1	–1	(A_2)	

Here, as for all 1-D representations, the direct product is also irreducible.

Rules: $A \otimes A = A$ $B \otimes B = A$ $B_1 \otimes B_2 = A_2$

$A \otimes B = B$ $A_1 \otimes B_2 = B_2$ etc.

For 2-D + 3-D representations (matrices), direct products (can be) are reducible and can be reduced via the reduction theorem.

(example chosen for C_{3v}) $\chi(E \otimes E) = \chi_E \, \chi_E$

$\otimes$ optional

(For identity element $2 \times 2 = 4$)

– **Electronic Transitions** : Consider a molecule with a specific point group. Then:

$$\int_{\text{all space}} \left[\psi_{e,2}\, \hat{O}\, \psi_{e,1}\right] d\tau = 0 \quad \text{unless the}$$