Irreducible Representations and Character Tables

C734b

Irreducible Representations

Suppose {Γ(A), Γ(B), …} for an l-dimensional matrix representation of G.
Then if **S** is any non-singular lxl matrix (det**S** ≠ 0) the {Γ'(A), Γ'(B), …} also form a l-dimensional representation of G where

$$\Gamma'(A) = \underbrace{\tilde{S}^{-1}\Gamma(A)\tilde{S}}_{\text{similarity transform}}$$

similarity transform

Note:
$$\Gamma'(A)\Gamma(B) = \tilde{S}^{-1}\Gamma(A)\tilde{S}\tilde{S}^{-1}\Gamma(B)\tilde{S} = \tilde{S}^{-1}\Gamma(A)\Gamma(B)\tilde{S}$$
$$= \tilde{S}^{-1}\Gamma(AB)\tilde{S} = \Gamma'(AB)$$

$\Longrightarrow$ {Γ'(A), Γ'(B), …} is also a representation of G

Two representations related by a similarity transformation are said to be **equivalent**.

Suppose that Γ¹ and Γ² are matrix representations of G with dimensions l_1 and l_2, respectively, and that for every operation A of G a $(l_1 + l_2)$-dimensional matrix is defined by:

$$\Gamma(A) = \begin{pmatrix} \Gamma^1(A) & 0 \\ 0 & \Gamma^2(A) \end{pmatrix}$$

$$\Rightarrow \Gamma(A)\Gamma(B) = \begin{pmatrix} \Gamma^1(A) & 0 \\ 0 & \Gamma^2(A) \end{pmatrix}\begin{pmatrix} \Gamma^1(B) & 0 \\ 0 & \Gamma^2(B) \end{pmatrix}$$

$$= \begin{pmatrix} \Gamma^1(A)\Gamma^1(B) & 0 \\ 0 & \Gamma^2(A)\Gamma^2(B) \end{pmatrix} = \begin{pmatrix} \Gamma^1(AB) & 0 \\ 0 & \Gamma^2(AB) \end{pmatrix} = \Gamma(AB)$$

⟹ {Γ(A), Γ(B),…} as defined also form a representation of G

This representation of G is called the direct sum of Γ¹ and Γ²

$$\Rightarrow \boxed{\Gamma = \Gamma^1 \oplus \Gamma^2}$$

Alternatively, we can regard Γ as reduced into Γ¹ and Γ²

A representation of G is **reducible** if it can transformed by a similarity transformation into an equivalent representation, each matrix which has the same block diagonal form. Then each of the smaller representations Γ¹, Γ², Γ³ etc are also representations of G

A representation that can not be reduced any further is called an **irreducible representation**, IR

↑

of fundamental importance

Properties of Irreducible Representations

Great Orthogonality Theorem: (no proof)

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{\ell_i \ell_j}} \delta_{ij}\delta_{mm'}\delta_{nn'}$$

Interpretation: in a set of matrices constituting any one IR, and the set of matrix elements, one from each matrix, behaves as the components of a vector in a h-dimensional space. All these vectors are orthogonal and each is normalized so the square of its length = h/ℓ_i.

a) $$\sum_R \Gamma_i(R)_{mn}\Gamma_j(R)_{mn} = 0 \text{ if } i \neq j$$

Vectors chosen from matrices of different representations are orthogonal.

b) $$\sum_R \Gamma_i(R)_{mn}\Gamma_i(R)_{m'n'} = 0 \text{ if } m \neq m' \text{ or } n \neq n'$$

Vectors chosen from the same representation but different matrix elements are orthogonal.

c) $$\sum_R \Gamma_i(R)_{mn}\Gamma_i(R)_{mn} = \frac{h}{\ell_i}$$

Vectors chosen from the same representation and same matrix elements have a magnitude = h/l_i.

Five important rules about IRs, Γ_i and their characters, χ_i

Rule 1.) the sum of the squares of the dimensions of the IRs of a group is equal to the order of the group, h (no proof):

$$\sum_i \ell_i^2 = \ell_1^2 + \ell_2^2 + \cdots = h$$

Rule 1.) can be written as: $$\sum_i [\chi_i(E)]^2 = h$$

since $\chi_i(E)$, the character of the representation of E in the i^{th} IR = order of the representation.

Rule 2.) The sum of the squares of the characters in any IR = h

$$\sum_R [\chi_i(R)]^2 = h$$ *(simple test of irreducibility)*

Rule 3.) the vectors whose components are the characters of two different IRs are orthogonal:

$$\sum_R \chi_i(R)\chi_j(R) = 0$$

Rule 4.): In a given reducible or irreducible representation the character of all matrices belong to the same class are identical.

Rule 5.): The number of IRs = number of classes in a group.

From rules 2.) and 3.): $$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}$$

Denote the number of elements in the m^{th} class by g_m, the number in the n^{th} class by g_n, etc. and let there be k classes.

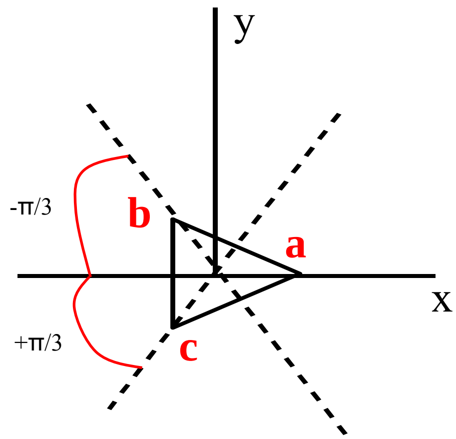
Then: $$\sum_p^k \chi_i(R_p)\chi_j(R_p)g_p = h\delta_{ij}$$

Here R_p is any one of the operations in the p^{th} class.

This means the k $\chi_i(R_p)$ quantities in the Γ_i IR behave like components of a k-dimensional vector which is orthogonal to the k-1 other vectors.

Example: C_{3v} $\{E, C_3^+, C_3^-, \sigma_a, \sigma_b, \sigma_3\}$

defined w.r.t. the xz plane



Matrix representations

$$\Gamma(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma(C_3^+) = \begin{pmatrix} \cos\left(\frac{2\pi}{3}\right) & -\sin\left(\frac{2\pi}{3}\right) & 0 \\ +\sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$C_3^- = C_3^2 = \begin{pmatrix} \cos\left(-\frac{2\pi}{3}\right) & -\sin\left(-\frac{2\pi}{3}\right) & 0 \\ \sin\left(-\frac{2\pi}{3}\right) & \cos\left(-\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) & 0 \\ -\sin\left(\frac{2\pi}{3}\right) & \cos\left(\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$$

$$\sigma_A = \sigma_{xz} = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$$

$$\sigma_B = \begin{pmatrix} \cos(2\theta) & \sin(2\theta) & 0 \\ \sin(2\theta) & -\cos(2\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

θ = -π/3

$$\therefore \sigma_B = \begin{pmatrix} \cos\left(-\frac{2\pi}{3}\right) & \sin\left(-\frac{2\pi}{3}\right) & 0 \\ \sin\left(-\frac{2\pi}{3}\right) & -\cos\left(-\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos\left(\frac{2\pi}{3}\right) & -\sin\left(\frac{2\pi}{3}\right) & 0 \\ -\sin\left(\frac{2\pi}{3}\right) & -\cos\left(\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$$

Lastly:

$$\sigma_C = \begin{pmatrix} \cos\left(\frac{2\pi}{3}\right) & \sin\left(\frac{2\pi}{3}\right) & 0 \\ \sin\left(\frac{2\pi}{3}\right) & -\cos\left(\frac{2\pi}{3}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Each matrix is block diagonal into two representations by inspection:

$$\Gamma^1 \oplus \Gamma^2$$

$\chi(\Gamma^1)$ =	{E,	C_3^+, C_3^-,	σ_A, σ_B, σ_C}	Point 4
	={2,	-1, -1,	0, 0, 0 }	
	= 1st class	2nd class	3rd class	
$\chi(\Gamma^2)$ =	{1	1, 1	1, 1, 1}	

i) Are Γ^1 and Γ^2 irreducible? Yes if $\sum_R |\chi_i(R)|^2 = h$ point 1.)

h = 6

Γ^1: $(2)^2 + (-1)^2 + (-1)^2 + 0^2 + 0^2 + 0^2$
= 4 + 1+ 1 = 6 **irreducible**

Γ^2: $(1)^2 + (1)^2 + (1)^2 + (1)^2 + (1)^2 + (1)^2 = 6$ **irreducible**

ii) Is $\chi(\Gamma^1)$ orthogonal to $\chi(\Gamma^2)$? point 3.)

(2)(1) + (-1)(1) +(-1)(1) +(0)(1) + (0)(1) + (0)(1)
= 2 – 2 = 0 **yes**

iii) Are Γ^1 and Γ^2 the only irreducible representations?

No! There are 3 classes: E, $\{C_3^+, C_3^-\}$, $\{\sigma_A, \sigma_B, \sigma_C\}$

$\therefore$ There must be one more. point 5.)

Let that representation be Γ^3

$$\because \ell_1^2 + \ell_2^2 + \ell_3^2 = 6 \quad \text{point 1.)}$$

and $\ell_1 = 2, \ell_2 = 1 \quad \Rightarrow \ell_3^2 = 6 - 4 - 1 = 1$

$\therefore$ $\chi(E)$ for Γ^3 =1; the IR is 1-dimensional point 1.)

$$\therefore \sum_R \chi(\Gamma^1)\chi(\Gamma^3) = 0 \quad \text{and} \quad \sum_R \chi(\Gamma^2)\chi(\Gamma^3) = 0$$

\# in class

$\therefore$ $(1)(2)(1) + (2)(-1)\chi_3(C_3) + (3)(0)\chi_3(\sigma) = 0$ (i)

and

$(1)(1)(1) + (2)(1)\chi_3(C_3) + (3)(1)\chi_3(\sigma) = 0$ (ii)

$\therefore$ From (i): $-2\chi_3(C_3) = -2 \quad \Longrightarrow \quad \chi(C_3) = 1$

$\therefore$ From (ii): $1+(2)(1)(1) + 3\chi_3(\sigma) = 0 \quad \Longrightarrow \quad 3\chi_3(\sigma) = -3$

$\therefore$ $\chi_3(\sigma) = -1$

$\therefore$ $\chi(\Gamma^3) = \{1, 1, 1, -1, -1, -1\}$

Note: $\sum_R \left|\chi\left(\Gamma^3\right)\right| = 6 \Rightarrow$ IR point 2.)

Will find that we will be constructing many reducible representations and therefore, we will want to know how many IRs are within a reducible one.

A first glance might think we need to find a matrix similarity transformation to block diagonalize the reducible matrix.

Yikes!

However: recall that the character of a matrix is **not** changed by a similarity transformation. Therefore, we will only work with characters.

$$\chi(R) = \sum_j a_j \chi_j(R)$$

Character of matrix representing operation R in a reducible representation

times block of j^{th} IR appears along diagonal

Character of matrix representing operation R in j^{th} IR

$\therefore$ Multiply by $\chi_i(R)$ and sum over R

$$\sum_R \chi(R)\chi_i(R) = \sum_R \sum_j a_j \chi_j(R)\chi_i(R)$$

but $$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}$$

$$\Rightarrow \sum_R \chi(R)\chi_i(R) = ha_i$$

$$\therefore a_i = \frac{1}{h}\sum_R \chi(R)\chi_i(R)$$

Character Tables

Tabulation by class the characters of the IRs of a point group

The Schonflies symbol is in the upper left-hand corner

Each column is headed by the number of elements in class x symbol for that element. For example $2C_3$ for $\{C_3^+, C_3^-\}$ in C_{3v}

Each row ≡ Γ label for the IR given by Mulliken notation:

a) 1-D IRs symmetric to C_n rotation; that is, $\chi(C_n) = +1$: **A** otherwise if $\chi(C_n) = -1$: **B**

b) Subscripts 1 or 2 are used depending on whether the IR is symmetric or anti-symmetric, $\chi = +1$ or -1, to a perpendicular C_2 axis or σ_v

c) Prime or double prime superscripts to indicate IRs which are symmetric or anti-symmetric to σ_h (if it exists).

d) g or u subscripts depending if IR is symmetric or anti-symmetric with respect to I (if it exists). g ≡ *gerade* and u ≡ *ungerade*.

e) 2-D or 3-D IRs are labelled by **E** and **T**, respectively. (Don't confuse this with R = E or T groups).

Right-hand side of character table tells how components of

$\vec{r} = \hat{e}_1 x + \hat{e}_2 y + \hat{e}_3 z$ or how quadratic functions, xy, z^2, etc. transform.

These will be useful down the road for understanding the IRs for p and d orbitals.

R_x, R_y, R_z tell how rotations about x, y, and z, transform, respectively.

The notation for the IRs of the axial groups $C_{\infty v}$ and $D_{\infty h}$ is different.

IRs are classified according to the magnitude of the z-component of angular momentum L_z along the symmetry axis, z ≡ Λ

$$\Lambda = |L_z| = 0 \quad 1 \quad 2 \quad 3 \ldots$$
$$\Sigma \quad \Pi \quad \Delta \quad \Phi \ldots$$

All IRs are 2-D except Σ. Subscripts g and u are the same but + or – superscripts are used on Σ if $\chi(\sigma_v) = +1$ or -1, respectively.

For L_z . 0, $\chi(C_2^{'})$ and $\chi(\sigma_v) = 0$.

Character table for the point group C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$		
Γ_1 A_1	1	1	1	z	$x^2 + y^2$, z^2
Γ_2 A_2	1	1	-1	R_z	
Γ_3 E	2	-1	0	(x,y) (R_x R_y)	($x^2 - y^2$, xy) (yz , zx)

Mulliken notation for the irreducible representations of the point groups.

l	notation used for IR	$\chi(C_n)$	$\chi(C_2')$ or $\chi(\sigma_v)$ [a]	$\chi(\sigma_h)$	$\chi(I)$
1	A	+1			
	B	-1			
	subscript 1		+1		
	subscript 2		-1		
2	E [b]				
3	T [c]				
1 , 2 or 3	superscript '			+1	
	superscript ''			-1	
	subscript g				+1
	subscript u				-1

[a] If no C_2' present then subscripts 1 or 2 according to whether $\chi(\sigma_v)$ is +1 or -1 .

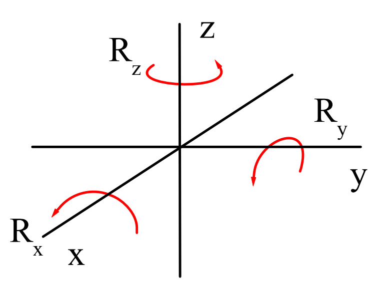
[b] The symbol E for a *two-dimensional irreducible representation* is not to be confused with that used for the *identity operator*.

[c] Sometimes F in the older literature.

Note: by tradition the first IR listed in the character table is the totally symmetric one where all the characters are +1 for every class of symmetry operator

More on the RHS of the character table

As stated the table indicates the IRs for the functions x, y, z, x^2, y^2, xy, and cross products: R_x =j x k; R_y =k x i and R_z = i x j (rotations about the axes).



Should we care?
Yes because many important chemistry items share the same symmetry properties

What else behaves symmetry-wise as x, y, z?

The p-orbitals: p_x, p_y, p_z

The components of the dipole moment: $\hat{\mu} = -e\vec{r} : \mu_x = -ex \quad \mu_y = -ey \quad \mu_z = -ez$

The dipole moment governs the strongest single-photon absorption and emission transitions. Their IRs will help understand electronic spectroscopy

Bond lengths also behave as x, y, z. Their IRs come up in infrared spectroscopy

Translations of molecules behave as x, y, z

What else behaves symmetry-wise as binary properties of x, y, z?

The d-orbitals: $d_{z^2} \quad d_{x^2-y^2} \quad d_{xy} \quad d_{xz} \quad d_{yz}$

Components of the electric quadrupole, Q

$$Q_{ij} \equiv \int \rho(3r_i r_j - r^2\delta_{ij})d^3r$$

Important for weak electric quadrupole transitions; important in solid state NMR

Components of the polarizability tensor α. Their IRs come up in Raman spectroscopy

Binary products also show up as the operator for two-photon transitions in molecules

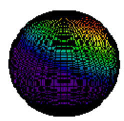
What else behaves symmetry-wise as R_x R_y R_z?

The components of orbital angular momentum: L_x, L_y, L_z

The components of the magnetic dipole: $\vec{\mu}_m = -\mu_B \vec{L}$

Here μ_B is the Bohr magnetron constant.
Important for weak magnetic dipole transitions. Also important in NMR.

What about s-orbitals?



s-orbitals look the same regardless of symmetry operation. Hence their IR is the totally symmetric IR of the point group under discussion.
This is always true and therefore, s is not labeled in the character table.

What about f-orbitals?

There are seven: f_{z^3} f_{xz^2} f_{yz^2} f_{xyz} $f_{z(x^2-y^2)}$ $f_{x(x^2-3y^2)}$ $f_{y(3x^2-y^2)}$

Their IRs are not listed in character tables but if you know how x, y, z, and the binary operators behave you can deduce the triple products by taking direct products of the appropriate IRs.

What about electron spin?

Like every thing to do with electron spin, the behavior is weird. We'll consider this later.

Point: You can learn a lot from a character table without doing a single calculation!