POINT GROUP THEORY

A GROUP **G** IS A FINITE OR INFINITE SET OF ELEMENTS TOGETHER WITH THE GROUP OPERATION

(A SET IS SAID TO BE A GROUP "UNDER" THIS OPERATION)

IF:

1. CLOSURE: IF $A \in G$ AND $B \in G \Rightarrow$

$$AB \in G$$

2. ASSOCIATIVITY: THE GROUP OPERATION (MULTIPLICATION) IS ASSOCIATIVE

$$\bigwedge_{A,B,C \in G} \quad (AB)C = A(BC)$$

3. IDENTITY: THERE IS IDENTITY ELEMENT

$$I\,(=1, e, E)$$

$$\bigvee_{I \in G} \quad \bigwedge_{A \in G} \quad IA = AI = A$$

4. INVERSE: THERE MUST BE AN INVERSE OF EACH ELEMENT

$$\bigvee_{B \in G} \quad \bigwedge_{A \in G} \quad AB = BA = I \Rightarrow B = A^{-1}$$

- A GROUP MUST CONTAIN AT LEAST ONE ELEMENT
  TRIVIAL GROUP
- IF THERE IS A FINITE NUMBER OF ELEMENTS (GROUP ORDER)
  FINITE GROUP (SYMMETRIC GROUP S_n OF PERMUTATIONS)
- A SUBSET OF A GROUP THAT IS ALSO A GROUP
  SUBGROUP
- CONTINUOUS GROUP (LIE GROUP) ROTATIONS IN $SO(3)$ $(=R_3)$

V1.2

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Symmetry Operations and Character Tables

SYMMETRY

All the character tables are laid out in the same way, and some pre-knowledge of group theory is assumed. In brief:

NOTATION OF THE SYMMETRY OPERATIONS:

- The top row and first column consist of the symmetry operations and irreducible representations respectively.
- The table elements are the characters.
- The final two columns show the first and second order combinations of Cartesian coordinates.
- Infinitesimal rotations are listed as I_x, I_y, and I_z

The notation for the symmetry operations is as follows:

IN ALL CASES ONE POINT (ORIGIN) IS NOT CHANGED!

- E The identity transformation (E coming from the German *Einheit*, meaning unity).
- C_n Rotation (clockwise) through an angle of $2\pi/n$ radians, where n is an integer. The axis for which n is greatest is termed the *principle* axis.
- C_n^k Rotation (clockwise) through an angle of $2k\pi/n$ radians. Both n and k are integers.
- S_n An *improper* rotation (clockwise) through an angle of $2\pi/n$ radians. Improper rotations are regular rotations followed by a reflection in the plane perpendicular to the axis of rotation. Also known as *alternating axis of symmetry* and *rotation-reflection axis*.
- i The inversion operator (the same as S_2). In Cartesian coordinates, $(x, y, z) \rightarrow (-x, -y, -z)$. Irreducible representations that are even under this symmetry operation are usually denoted with the subscript *g* for *gerade* (german=even), and those that are odd are denoted with the subscript *u* for *ungerade* (german=odd).
- σ A mirror plane (from the German word for mirror - *Spiegel*).
- σ_h *Horizontal* reflection plane - passing through the origin and perpendicular to the axis with the `highest' symmetry.
- σ_v *Vertical* reflection plane - passing through the origin and the axis with the `highest' symmetry.
- σ_d *Diagonal* or *dihedral* reflection in a plane through the origin and the axis with the `highest' symmetry, but also bisecting the angle between the twofold axes perpendicular to the symmetry axis. This is actually a special case of σ_v.

HOW TO APPLY POINT GROUP THEORY TO PROBLEMS OF QUANTUM MECHANICS ?

REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS

$$H\Psi = E\Psi \qquad E: \begin{cases} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_g \end{cases}$$

g- FOLD DEGENERACY

g- LINEARLY INDEPENDENT FUNCTIONS (DIFFERENT)

$$H(c_1\Psi_1 + c_2\Psi_2 + \dots c_g\Psi_g) = E(c_1\Psi_1 + c_2\Psi_2 + \dots c_g\Psi_g)$$

G GROUP OF SYMMETRY OF HAMILTONIAN

$P, Q, R, \dots$ $\qquad [P, H] = 0$

SYMMETRY OPERATIONS

$$\hat{P} \backslash H\Psi_i = E\Psi_i$$

$$\hat{P}H\Psi_i = H(\hat{P}\Psi_i) = E(\hat{P}\Psi_i)$$

$P\Psi_i$ IS ALSO EIGEN-FUNCTION FOR THE SAME ENERGY E ?!

THE SAME CONCLUSION IS VALID FOR

$R\Psi_i$, $S\Psi_i$, ...

THEY HAVE TO BE LINEARLY DEPENDENT !

$$\hat{P}\Psi_i(xyz) = P_{1i}\Psi_1(xyz) + P_{2i}\Psi_2(xyz) + \dots P_{gi}\Psi_g(xyz)$$

FOR ALL SYMMETRY OPERATIONS AND ALL FUNCTIONS

$$D(\hat{P}) = \begin{pmatrix} P_{11} & P_{12} & \dots & P_{1g} \\ P_{21} & P_{22} & \dots & P_{2g} \\ \vdots \\ P_{g1} & P_{g2} & \dots & P_{gg} \end{pmatrix} \qquad D(\hat{Q}) = \begin{pmatrix} Q_{11} & Q_{12} & \dots & Q_{1g} \\ Q_{21} & Q_{22} & \dots & Q_{2g} \\ \vdots \\ Q_{g1} & Q_{g2} & \dots & Q_{gg} \end{pmatrix} \qquad D(\hat{R}) = \dots$$

MATRIX REPRESENTATION OF SYMMETRY OPERATIONS OF GROUP G

$\Psi_1, \Psi_2, \dots \Psi_g$ – BASIS OF REPRESENTATION

g – DIMENSION

SYMMETRY GROUP

$\hat{P}, \hat{Q}, \hat{R}, \hat{S}, \ldots \in G$

$\psi_1 \, \psi_2 \ldots \psi_g$ BASIS FUNCTIONS

GROUP OF MATRICES

MATRIX REPRESENTATION Γ'

$D(P) \quad D(Q) \quad D(R) \quad D(S) \ldots$

ISOMORPHISM 1 : 1

GROUP OPERATION = MULTIPLICATION OF MATRICES

$$\Gamma' : \; D'(P) = \begin{pmatrix} D_1'(P) & 0 & 0 \\ 0 & D_2'(P) & 0 \\ 0 & 0 & D_s'(P) \end{pmatrix} \qquad D'(Q) = \begin{pmatrix} D_1'(Q) & 0 & 0 \\ 0 & D_2'(Q) & 0 \\ 0 & 0 & D_s'(Q) \end{pmatrix} \qquad D'(R) = \ldots$$

(D_1': Γ_1, D_2': Γ_2, D_s': Γ_s)

ALL $D'(P), D'(Q) \ldots$ HAVE THE SAME STRUCTURE (BLOCKS)

ALL $D_i'(P), D_i'(Q) \ldots$ HAVE THE SAME STRUCTURE (DIMENSIONS)

MATRIX REPRESENTATION D' IS REDUCIBLE

EACH SET OF $D_i'(P), D_i'(Q), \ldots$ IS ALSO A MATRIX REPR. OF GROUP G

THIS IS IRREDUCIBLE REPRESENTATION

$$\underset{\text{REDUCIBLE REPR.}}{\Gamma'} = \underbrace{\Gamma_1 + \Gamma_2 + \ldots \Gamma_s}_{\substack{\text{IRREDUCIBLE REPR.} \\ \text{(SMALLEST DIMENSIONS)}}}$$

SYMBOLS:

A, B –	1 – DIM. REPR.	(ONE ELEMENT)
E –	2 – DIM.	(2×2)
T –	3 – DIM.	(3×3)

TRANSFORMATION PROPERTIES OF $\psi_1, \psi_2, \ldots \psi_g$ UNDER SYMMETRY OPERATIONS OF GROUP G.

INSTEAD OF QUANTUM NUMBERS!

SYMBOLS:

$$C_n |\psi|^2 = |\psi|^2$$

ROTATION AROUND THE PRINCIPLE AXIS

$C_n \psi = +\psi$ A $C_n \psi = -\psi$ B

$\mathcal{J}$ (INVERSION) $\mathcal{J}\psi = +\psi$ $\mathcal{J}\psi = -\psi$

EVEN PARITY ψ_g (Γ_g) ODD PARITY ψ_u (Γ_u)

IN THE CASE OF PRODUCT $G \times C_h(E, \sigma_h)$

$\sigma_h \psi = +\psi$ $\sigma_h \psi = -\psi$

$\Downarrow$

REPR. $A', B', \ldots$ $A'', B'' \ldots$

(Γ') (Γ'')

EXAMPLE. ARE THE ORBITALS p_x, p_y, p_z THE BASIS FUNCTIONS OF THE REPRESENTATION OF D_{3h}?

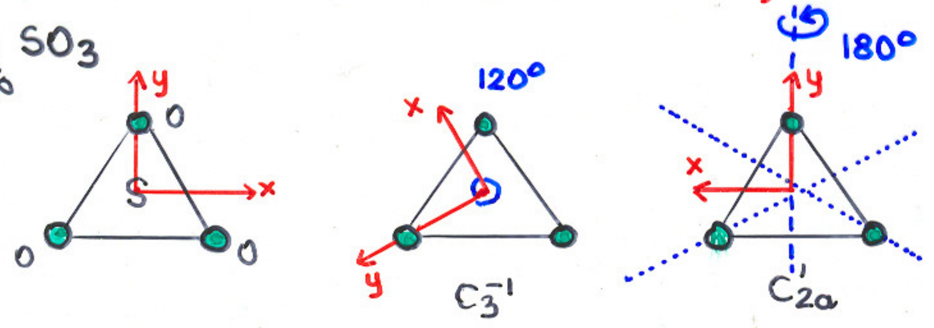
IF SO – IS IT REDUCIBLE OR IRREDUCIBLE REPRESENTATION?

$$\begin{cases} \varphi_{n10} = R_{n1}(r) \frac{3}{\sqrt{4\pi}} \cos\vartheta \\ \varphi_{n11} = R_{n1}(r) \frac{3}{\sqrt{8\pi}} \sin\vartheta\, e^{i\varphi} \\ \qquad \pm \\ \varphi_{n1-1} = R_{n1}(r) \frac{3}{\sqrt{8\pi}} \sin\vartheta\, e^{-i\varphi} \end{cases} \Rightarrow \begin{cases} p_z(\bar{r}) = \frac{1}{\sqrt{2}} \varphi_{n10} = z f(r) \\ p_x(\bar{r}) = \frac{1}{2}(\varphi_{n11} + \varphi_{n1-1}) = x f(r) \\ p_y(\bar{r}) = \frac{1}{2i}(\varphi_{n11} - \varphi_{n1-1}) = y f(r) \end{cases}$$

FUNCTIONS WITH DEFINED SPATIAL PROPERTIES

D_3: $\{E, C_3^{+1}, C_3^{-1}, C'_{2a}, C'_{2b}, C'_{2c}\}$ GROUP ORDER = 6

SULFUR TRIOXIDE SO_3



D_3

$\hat{E}$: $x=x'$, $y=y'$, $z=z'$

$\hat{C}_3^{+1}$: $x=-\frac{1}{2}x'-\frac{1}{2}\sqrt{3}y'$, $y=\frac{1}{2}\sqrt{3}x'-\frac{1}{2}y'$, $z=z'$

$\hat{C}_3^{-1}$: $x=-\frac{1}{2}x'+\frac{1}{2}\sqrt{3}y'$, $y=-\frac{1}{2}\sqrt{3}x'-\frac{1}{2}y'$, $z=z'$

C'_{2a}: $x=-x'$, $y=y'$, $z=-z'$

C'_{2b}: $x=\frac{1}{2}x'+\frac{1}{2}\sqrt{3}y'$, $y=\frac{1}{2}\sqrt{3}x'-\frac{1}{2}y'$, $z=-z'$

C'_{2c}: $x=\frac{1}{2}x'-\frac{1}{2}\sqrt{3}y'$, $y=-\frac{1}{2}\sqrt{3}x'-\frac{1}{2}y'$, $z=-z'$

$$\begin{cases} p_x = x f(r) \\ p_y = y f(r) \\ p_z = z f(r) \end{cases}$$

ARE THEY TRANSFORMED INTO THEMSELVES ?

$$C_3^{-1} p_x = C_3^{-1} x f(r) = \left\{-\frac{1}{2}x' f(r') + \frac{1}{2}\sqrt{3}\,y' f(r')\right\}_{\vec{r}'=\vec{r}} = -\frac{1}{2}p_x + \frac{1}{2}\sqrt{3}\,p_y \qquad (1)$$

$$C_3^{-1} p_y = C_3^{-1} y f(r) = \left\{-\frac{1}{2}\sqrt{3}\,x' f(r') - \frac{1}{2}y' f(r')\right\}_{\vec{r}'=\vec{r}} = -\frac{1}{2}\sqrt{3}\,p_x - \frac{1}{2}p_y \qquad (2)$$

$$C_3^{-1} p_z = C_3^{-1} z f(r) = \left\{z' f(r')\right\}_{\vec{r}'=\vec{r}} = p_z \qquad (3)$$

$$C_3^{-1}(p_x\, p_y\, p_z) = (p_x\, p_y\, p_z)\begin{array}{c}\begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ \begin{array}{ccc} (1) & (2) & (3) \end{array}\end{array} \equiv (p_x\, p_y\, p_z)\,\mathbb{D}(C_3^{-1})$$

MATRIX REPRESENTATION IN THE $p_x\ p_y\ p_z$ BASIS

IS IT REDUCIBLE OR IRREDUCIBLE REPRESENTATION ?

$$\mathbb{D}(C_3^{+1}) = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbb{D}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbb{D}(C'_{2a}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \mathbb{D}(C'_{2b}) = \begin{pmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathbb{D}(C'_{2c}) = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$