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

   $\forall A, B, C \in G \quad (AB)C = A(BC)$

3. **Identity:** There is identity element

   $I (= 1, e, E)$

   $\forall I \in G \quad \forall A \in G \quad IA = AI = A$

4. **Inverse:** There must be an inverse of each element

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

---

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 $SO(3) (= \mathbb{R}_3)$
Symmetry Operations and Character Tables

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

- 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:

- **$E$**: 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.
- **$C_{nk}$**: 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).
- **$\sigma$**: A mirror plane (from the German word for mirror - Spiegel).
  - **$\sigma_h$**: Horizontal reflection plane - passing through the origin and perpendicular to the axis with the 'highest' symmetry.
  - **$\sigma_v$**: Vertical reflection plane - passing through the origin and the axis with the 'highest' symmetry.
  - **$\sigma_d$**: 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 $\sigma_v$.

http://newton.ex.ac.uk/people/goss/symmetry/CharacterTables.html
HOW TO APPLY POINT GROUP THEORY TO PROBLEMS OF QUANTUM MECHANICS?

REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS

\[ H \psi = E \psi \]
\[ E : \{ \psi_1, \psi_2, \ldots, \psi_g \} \]
- \( g \)-fold degeneracy
- \( g \)-linearly independent functions (different)

\[ H(c_1 \psi_1 + c_2 \psi_2 + \ldots + c_g \psi_g) = E(c_1 \psi_1 + c_2 \psi_2 + \ldots + c_g \psi_g) \]

**Group of Symmetry of Hamiltonian**

\[ [P, H] = 0 \]

\[ \hat{P} H \psi_i = H \hat{P} \psi_i = E \hat{P} \psi_i \]

\( \hat{P} \psi_i \) is also eigenfunction for the same energy \( E \)

!?!

**Symmetry Operations**

**The same conclusion is valid for**

\[ R \psi_i, S \psi_i, \ldots \]

**They have to be linearly dependent!**

\[ \hat{P} \psi_i(\text{xyz}) = P_{i1} \psi_1(\text{xyz}) + P_{i2} \psi_2(\text{xyz}) + \ldots + P_{ig} \psi_g(\text{xyz}) \]

**For all symmetry operations and all functions**

\[ D(\hat{P}) = \begin{pmatrix}
P_{11} & P_{12} & \ldots & P_{1g} \\
P_{21} & P_{22} & \ldots & P_{2g} \\
\vdots & \vdots & \ddots & \vdots \\
P_{g1} & P_{g2} & \ldots & P_{gg}
\end{pmatrix} \]

\[ D(\hat{Q}) = \begin{pmatrix}
Q_{11} & Q_{12} & \ldots & Q_{1g} \\
Q_{21} & Q_{22} & \ldots & Q_{2g} \\
\vdots & \vdots & \ddots & \vdots \\
Q_{g1} & Q_{g2} & \ldots & Q_{gg}
\end{pmatrix} \]

\[ D(\hat{R}) = \ldots \]

**Matrix representation of symmetry operations of group \( G \)**

\[ \{ \psi_1, \psi_2, \ldots, \psi_g \} \]

- Basis of representation
- \( g \)-dimension
Symmetry Group
\( \hat{P}, \hat{Q}, \hat{R}, \hat{S}, \ldots \in G \)

Group of Matrices
Matrix Representation \( T' \)
\[ D(P), D(Q), D(R), D(S), \ldots \]

Group Operation = Multiplication of Matrices

Isomorphism 1:1

Matrix Representation \( D' \) is reducible
Each set of \( D_1'(P), D_1'(Q), \ldots \) is also a matrix repr. of group \( G \)

This is irreducible representation

\[ T = T_1' + T_2' + \ldots T_s' \]

Reducible repr.
Irreducible repr.
(Smallest dimensions)

Symbols:
\[ A, B - 1\text{-dim. repr.} \]
\[ E - 2\text{-dim.} \]
\[ T - 3\text{-dim.} \]

(One element)
\( (2 \times 2) \)
\( (3 \times 3) \)

Transformation properties of \( \psi_1, \psi_2, \ldots \psi_q \) under symmetry operations of group \( G \).

Instead of quantum numbers!
SYMBOLS:
\[ C_n \psi^2 = \psi^2 \]

**Rotation around the principle axis**

- \( A \): \( C_n \psi = +\psi \)
- \( B \): \( C_n \psi = -\psi \)

**J (Inversion)**

- \( \gamma \psi = +\psi \)
- \( \gamma \psi = -\psi \)

**Even Parity**

- \( \psi \downarrow \)

**Odd Parity**

- \( \psi \uparrow \)

**In the case of product** \( G \times C_n (E, \sigma_h) \)

- \( \sigma_h \psi = +\psi \)
- \( \sigma_h \psi = -\psi \)

**Reprs.** \( A', B', \ldots \)

**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?

\[
\begin{align*}
\psi_{m10} &= R_{m1}(r) \frac{3}{14\pi} \cos \psi \\
\psi_{m11} &= R_{m1}(r) \frac{3}{18\pi} \sin \psi \cos \psi \\
\psi_{m1-1} &= R_{m1}(r) \frac{3}{18\pi} \sin \psi \sin \psi \\
\end{align*}
\]

**=>**

\[
\begin{align*}
P_z(r) &= \frac{1}{12} \psi_{m10} = x f(r) \\
P_x(r) &= \frac{1}{2} (\psi_{m11} + \psi_{m1-1}) = x f(r) \\
P_y(r) &= \frac{1}{2i} (\psi_{m11} - \psi_{m1-1}) = y f(r)
\end{align*}
\]

**Functions with defined spatial properties**

\[ D_3 \; \{ E, C_3^+, C_3^-, C_2a, C_2b, C_2c \} \]

**Group Order = 6**

**SO3: Sulfur Trioxide**

- **C3**
- **C3'**
- **C3''**
D₃

E: \( x = x', \; y = y', \; z = z' \)

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

\( C_2': x = -\frac{1}{2} x' + \frac{1}{2} \sqrt{3} y', \; y = -\frac{1}{2} \sqrt{3} x' - \frac{1}{2} y', \; z = z' \)

\( C_{2a}: x = -x', \; y = y', \; z = -z' \)

\( C_{2b}: x = \frac{1}{2} x' + \frac{1}{2} \sqrt{3} y', \; y = \frac{1}{2} \sqrt{3} x' - \frac{1}{2} y', \; z = -z' \)

\( C_{2c}: x = \frac{1}{2} x' - \frac{1}{2} \sqrt{3} y', \; y = -\frac{1}{2} \sqrt{3} x' - \frac{1}{2} y', \; z = -z' \)

\[ \begin{align*}
  p_x &= x f(r) \\
  p_y &= y f(r) \\
  p_z &= z f(r)
\end{align*} \]

Are they transformed into themselves?

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

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

\( C_3^{-1} (p_z) = C_3^{-1} z f(r) = \{ z' f(r) \} = p_z \)

\[ C_3^{-1} (p_x p_y p_z) = (p_x p_y p_z) \begin{pmatrix}
  -\frac{1}{2} & -\frac{1}{2} \sqrt{3} & 0 \\
  \frac{1}{2} \sqrt{3} & -\frac{1}{2} & 0 \\
  0 & 0 & 1
\end{pmatrix} = (p_x p_y p_z) D(C_3^{-1}) \]

Matrix representation in the \( p_x p_y p_z \) basis

\( D(C_3') = \begin{pmatrix}
  -\frac{1}{2} & \frac{1}{2} \sqrt{3} & 0 \\
  -\frac{1}{2} \sqrt{3} & -\frac{1}{2} & 0 \\
  0 & 0 & 1
\end{pmatrix} \quad D(E) = \begin{pmatrix}
  1 & 0 & 0 \\
  0 & 1 & 0 \\
  0 & 0 & 1
\end{pmatrix} \)

\( D(C_{2a}) = \begin{pmatrix}
  -1 & 0 & 0 \\
  0 & 1 & 0 \\
  0 & 0 & -1
\end{pmatrix} \quad D(C_{2b}) = \begin{pmatrix}
  \frac{1}{2} & \frac{1}{2} \sqrt{3} & 0 \\
  \frac{1}{2} \sqrt{3} & -\frac{1}{2} & 0 \\
  0 & 0 & 1
\end{pmatrix} \quad D(C_{2c}) = \begin{pmatrix}
  \frac{1}{2} & -\frac{1}{2} \sqrt{3} & 0 \\
  -\frac{1}{2} \sqrt{3} & -\frac{1}{2} & 0 \\
  0 & 0 & 1
\end{pmatrix} \)

Is it reducible or irreducible representation?