Why is it a group? Look at the multiplication rule:

\[(A_k \otimes B_e) (A_{k'} \otimes B_{e'}) = (A_k A_{k'}) \otimes (B_e B_{e'})\]

in group \(G_a\) \in group \(G_b\)

And in terms of representation by matrices,

\[\left[ T(A \otimes B) \right]_{ik, j'k'} = T(A)_{ij} T(B)_{k'k}\]

Class structure of the direct product group \(G_a \otimes G_b\)

Since \(G_a\) commutes with \(G_b\) => the # of classes
in \(G_a \otimes G_b\) = product of the # classes in each separate group,

=> each class in \(G_a \otimes G_b\) is labelled by
2 class labels for the separate groups.

i.e. \(C_{\alpha} \otimes C_{\beta} = C_{\alpha \beta}\)

And the character of the class is

\[\chi^{(ab)}_{\alpha \beta} = \chi^{(a)}_{\alpha} \chi^{(b)}_{\beta}\]

Why? \(\sum_{i \in G_a} \sum_{k \in G_b} T(A_{ki}) T(B_{k'k}) = \left( \sum_i T(A_{ki}) \right) \left( \sum_k T(B_{k'}) \right)\)

= \(\chi^{(a)}_{\alpha} \chi^{(b)}_{\beta}\)
This has the permutations we've discussed, but reflection through the plane of the 3 F-atoms is not a good quantum number since above and below are very different, i.e., $[0, H] \neq 0$.

On the other hand, some molecules really ARE the same above and below, e.g., $\mathbf{H}_3^+$.

And for such a molecule, reflection through the plane is ALSO a good quantum number, i.e., $[0, H] = 0$.

So the new group symmetry that INCLUDES both $D_3$ and $\sigma_h$ symmetry is called

$D_{3h} = D_3 \times \sigma_h$
\[
\begin{array}{c|cccc}
D_3 & E & 3C_2 & 2C_3 \\
\hline
A_1 & 1 & 1 & 1 \\
A_2 & 1 & -1 & 1 \\
E & 2 & 0 & -1 \\
\end{array}
\]

\[
\Sigma_h = \begin{pmatrix} E & \sigma_h \\ \sigma_h & \Sigma_h \end{pmatrix}
\]

\[\Sigma_h = \{ E, \sigma_h, g \}
\]

Then let

\[D_{3h} = D_3 \otimes \Sigma_h\]

(6-classes)

\[
\begin{array}{c|cccc|cccc|cccc}
D_{3h} & E & 3C_2 & 2C_3 & \sigma_h & 3C_2 \sigma_h & 2C_3 \sigma_h \\
\hline
A_1^+ & 1 & 1 & \frac{1}{2} & 1 & 1 & 1 \\
A_2^+ & 1 & -1 & \frac{1}{2} & 1 & -1 & 1 \\
E^+ & 2 & 0 & 0 & 2 & 0 & -1 \\
A_1^- & 1 & 1 & \frac{1}{2} & -1 & -1 & -1 \\
A_2^- & 1 & -1 & \frac{1}{2} & -1 & 1 & -1 \\
E^- & 2 & 0 & 0 & -2 & 0 & +1 \\
\end{array}
\]
Symmetry Covering Operations

3 types we consider

1. Rotations about axes through the origin
2. Reflections through planes containing the origin
3. Inversions that take \( \mathbb{R}^3 \) into \( -\mathbb{R}^3 \)
   (Note that inversion = \( \pi \) rotation + reflection through a plane perpendicular to the rotation axis)

What happens when successive operations are carried out?

Answer

1. Product of any 2 rotations is a rotation
2. The product of any 2 reflections is a rotation by an angle \( \phi_{AB} \), where the angle between the planes.
3. Product of a rotation and a reflection in a plane \( \mathcal{A} \) containing the rotation axis \( \mathcal{O} \) is a reflection in another plane \( \mathcal{B} \) passing through the axis. The angle between planes \( \mathcal{A}, \mathcal{B} \) is \( \frac{1}{2} \) the rotation angle

4. The product of two \( \pi \) rotations about intersecting axes \( \mathbf{u}, \mathbf{v} \) is a rotation about an axis \( \perp \) to both \( \mathbf{u}, \mathbf{v} \), (i.e., along \( \mathbf{u} \times \mathbf{v} \)) through an angle of rotation double the angle between \( \mathbf{u}, \mathbf{v} \).
Commuting Operations:

i) Two rotations about the same axis
ii) Two reflections in planes
iii) Two $\pi$-rotations about axes
iv) A rotation and a reflection through a plane to the rotation axis (called an "improper rotation")
v) Inversion and any rotation or reflection.

Notation for types of symmetry operations

- $E =$ identity
- $C_n =$ rotation through $\frac{2\pi}{n}$ (for periodic crystals, only $n = 1, 2, 3, 4, 6$ are possible)
- $\sigma =$ reflection through a plane
- $\sigma_h =$ reflection through a "horizontal" plane, which means the plane through the origin to the axis of highest rotation symmetry
- $\sigma_v =$ reflection through a "vertical" plane, passing through the axis of highest symmetry
- $\sigma_d =$ reflection through a "diagonal" plane, containing the symmetry axis and bisecting the angle between the 2-fold axes to symm. axis
- $S_n =$ improper rotation through $2\pi/n$
- $i = S_2 =$ inversion.
Other rules

- Intersection of 2 reflection planes must be a symmetry axis. If the angle between planes is $\phi = \frac{\pi}{n}$, it is an n-fold symmetry axis.

- If a reflection plane contains an n-fold axis, there must be n-1 other reflection planes at angles of $\frac{\pi}{n}$.

- Two 2-fold axes separated by $\frac{\pi}{n}$ require a perpendicular n-fold symmetry axis.

- If there is a 2-fold axis and an n-fold axis perpendicular to it, there must be n-1 additional 2-fold axes separated by angles of $\frac{\pi}{n}$.

- An even n-fold axis, a reflection plane perpendicular to it, and an inversion center are interdependent, i.e. Any 2 such elements implies the existence of the third.
Notational Issues for Groups

The Schönflies notation for symmetry groups

$C_s (= C_{1v} = C_{1h} = S_1)$ - means a planar reflection symmetry only, e.g. HDO

$C_n$ - groups where only symmetry is a single $n$-fold axis (these are cyclic abelian groups)

$C_6$ group has $C_6$, $C_6^2 = C_3$, $C_6^3 = C_2$,

$C_6^4 = C_3^{-1}$, $C_6^5 = C_6^{-1}$, $C_6^6 = E$

$C_{nv}$ - groups contain a $\sigma_v$ reflection plane in addition to the $C_n$ axis,

$\Rightarrow 3$ $n$ reflection planes, separated by $\frac{\pi}{n}$ around the $C_n$ axis.

$C_{nh}$ - groups contain a $\sigma_h$ reflection in addition to the $C_n$ axis.

$S_n$ - groups contain an $n$-fold axis for improper rotations. For $n = \text{odd}$, $S_n = C_{nh}$

For $n = \text{even}$, $C_n^2$ will be a subgroup.
$D_n$ - groups have $n$ 2-fold axes $\perp$ to the principal $C_n$ axis.

$D_{nd}$ - groups have elements of $D_n$ plus the diagonal reflection planes $\sigma_1$ bisecting the angle(s) between the 2-fold axes $\perp$ to the $D_n$ principal symmetry axes.

$D_{nh}$ - groups with $D_n$ elements, plus the horizontal reflection plane $\sigma_h$ (i.e. twice as many elements as $D_n$).

+ Groups of "higher symmetry"

$T$ - 12 proper rotational operations that take a regular tetrahedron into itself.

$T_d$ - $T$ plus the reflection operations of a regular tetrahedron. (24 elements)

$T_h$ - $T \times i$

$O$ - octahedral group = group of proper rotations that take a cube (or an octahedron) into itself = 24 elements.

$E$, 8 $C_3$, about body cube diagonals; 3 $C_2$ about $x$, $y$, $z$;

6 $C_4$ about $x$, $y$, $z$; 6 $C_2$ about axes through origin, parallel to face diagonals.

$O_h = O \times i$. $C_{d_{sh}}$ = group of a general 1h. molecule $C_{d_{sh}}$ = homonuclear diatomic, ABA linear.
$A, B = \pm \frac{\pi}{2}$ for the principal rotation elements, $B \neq -1$.

$E = 2$-dim irreps

$T = 3$-dim irreps

And if inversion symmetry is present, use $g$ or $u$ (gerade or ungerade) for even or odd, respectively.