Group theory, representations and their applications in solid state

TMS 2018

Why group theory?

Powerful: Lets you extract *all* the physical consequences of the symetries of a system, in a *systematic* and *reliable* way

Simple: At the user level, it is one of the simplest, least demanding theoretical techniques

(Besides the four rules, you just need the most basic acquaintance with matrices)

What symmetries?

Space-time symmetries: Rotations, translations, parity, TRS, Lorentz boosts, Galileo boosts,...

Internal symmetries: SU(2) isospin, SU(2)xU(1) electroweak, SU(3) color,...

In condensed matter we will be concerned with space-time symmetries (parity, TRS, rotations and translations).

What symmetries?

Continuous symmetries: Lie groups (*Casimirs, Cartan subalgebra, Dynkin diagrams, Young tableaux,...*)

Discrete symmetries: Discrete groups (*characters, orthogonality of characters of IRs, projectors,...*)

In condensed matter we will be concerned with *discrete* symmetries, more concreteley with discrete subgroups of O(3), lattice translations and TRS.

What consequences?

Continuous symmetries: Symmetries → Conservation laws → Degeneracies + selection rules,...

Discrete symmetries: Symmetries → Degeneracies + selection rules,...

It is relatively easy to obtain physical consequences from conservation laws, even without (explicitly) using group theory.

In the absence of conservation laws, the use of group theory to obtain the consequences of the system symmetry is virtually unavoidable.

Continuous symmetries

Conservation laws

Degeneracies,
selection rules, ...

Discrete symmetries

Degeneracies,
selection rules, ...

Applications of Group Theory in Quantum Mechanics

M I Petrashen, E D Trifonov

Foreword
1 Introduction
2 Abstract Groups
3 Representations of Point Groups
4 Composition of Representations and the Direct Products of Groups
5 Wigner's Theorem
6 Point Groups
7 Decomposition of a Reducible Representation into an Irreducible Representation
8 Space Groups and their Irreducible Representations
9 Classification of the Vibrational and Electronic States of a Crystal
10 Continuous Groups
11 Irreducible Representations of the Three-Dimensional Rotation Group
12 The Properties of Irreducible Representations of the Rotation Group
13 Some Applications of the Theory of Representation of the Rotation Group in Quantum Mechanics

Outline of the course

1. Introduction: Symmetries, degeneracies and representations.

2. Irreducible representations as building blocks. Application to molecular vibrations.

3. Operations with representations: Physical properties and spectra.

4. Spin and double valued representations. Splitting of atomic orbitals in crystals.

5. Representation theory and electronic bands.

Outline of the course

1. Introduction: Symmetries, degeneracies and representations.

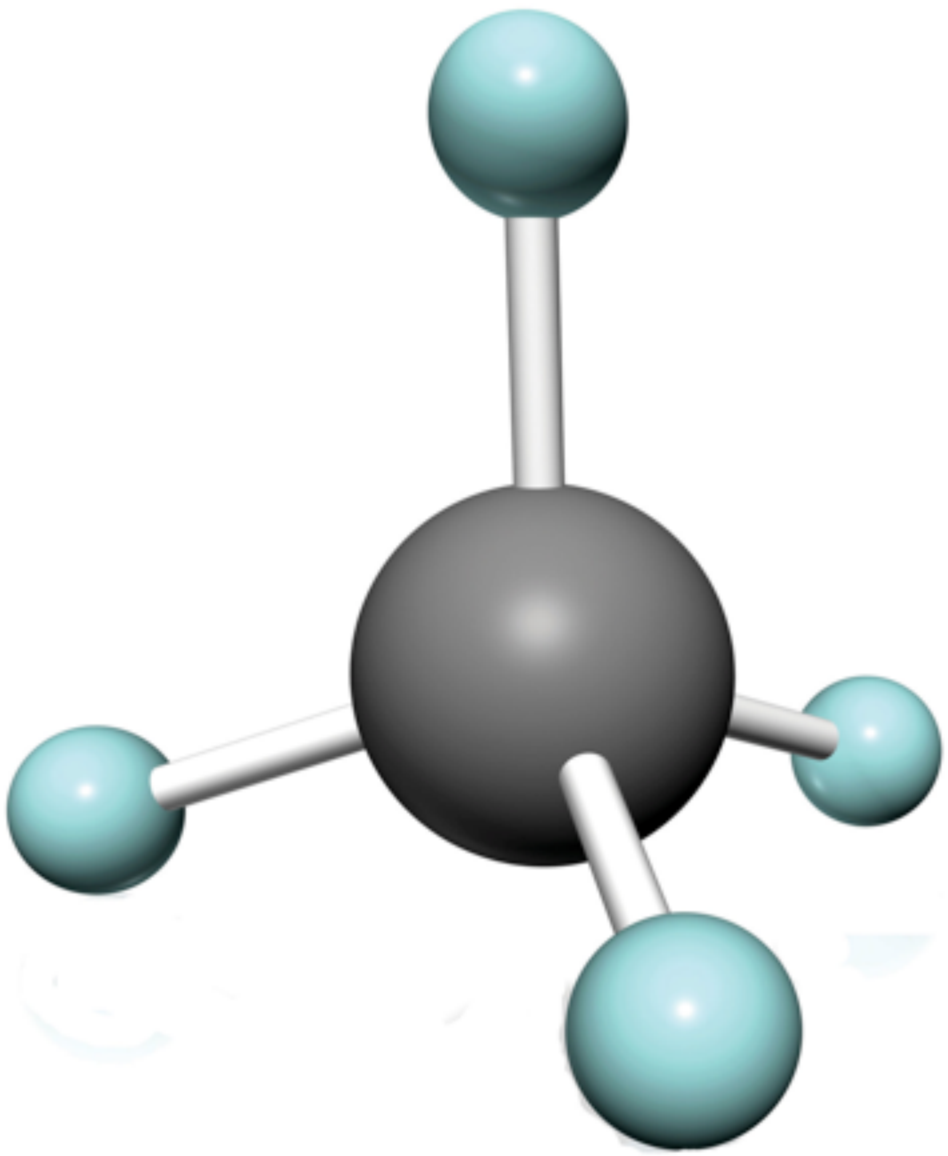
2. Irreducible representations as building blocks. Application to molecular vibrations.

3. Operations with representations: Physical properties and spectra.

4. Spin and double valued representations. Splitting of atomic orbitals in crystals.

5. Representation theory and electronic bands.

Vibrational spectrum of methane (CH4)



Can we say anything about the spectrum just by looking at the molecule?

4+1=5 atoms
5x3 =**15** degrees of freedom

In the harmonic approximation, the frequencies and normal modes can be found by diagonalizing a **15x15** symmetric matrix.

Diagonalizing a generic 15x15 matrix yields **15** frequencies

Vibrational spectrum of methane (CH_4)

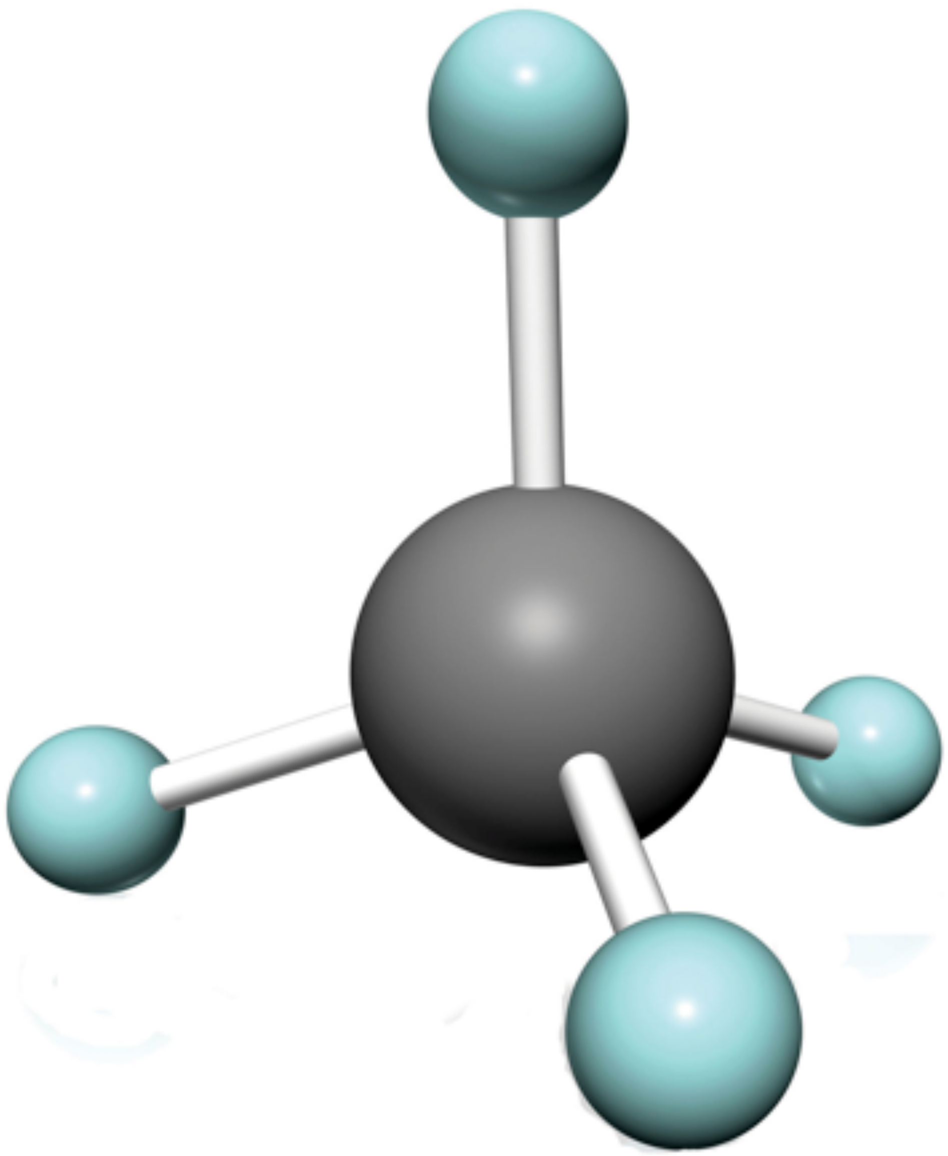
BUT: Our 15x15 matrix is *not* generic. It describes the dynamics of a molecule.

The 15 degrees of freedom include 3 rigid *translations* and 3 rigid *rotations*, where the molecule moves as a whole without changing the geometry of the bonds. This leaves **9** genuine *vibrations*.

$$\boxed{15 = 6 \text{ zero modes} + \mathbf{9} \text{ vibrational modes}}$$

That is as far as we can go without taking into consideration the symmetries of the molecule.

Vibrational spectrum of methane (CH4)



If you know group theory, you can easily obtain:

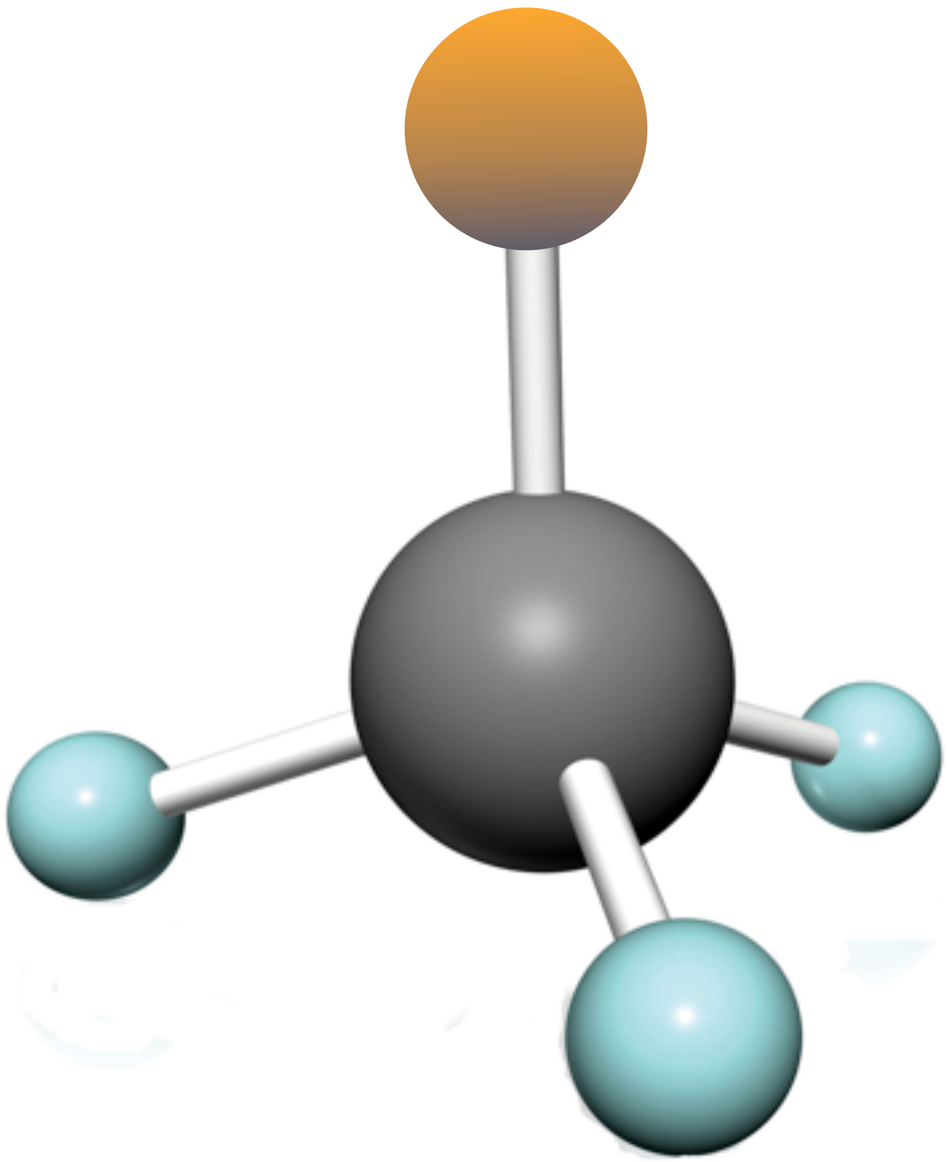
$$\boxed{1 \times \mathbf{1} + 1 \times \mathbf{2} + 2 \times \mathbf{3} = \mathbf{9}}$$

(1 non-degenerate +1 doubly +2 triply degenerate = 4 different frequencies)

You will also know that all 4 frequencies are ***Raman active***, but only the triply degenerate frequencies are ***IR active***.

Moreover, methane is ***MW inactive***.

Vibrational spectrum of CH_3D



Group theory tells you that each triply degenerate frequency splits: **3** ➞**1**+**2**:

$\boxed{1\times\mathbf{1}+1\times\mathbf{2}+2\times\mathbf{3}=\mathbf{9}\rightarrow 3\times\mathbf{1}+3\times\mathbf{2}=\mathbf{9}}$

(3 nondegenerate +3 doubly degenerate = 6 different frequencies)

Now all 6 frequencies are both ***Raman active***, and ***IR active***.

Moreover, deuterated methane is ***MW active***.

Vibrational spectrum of methane (CH4)

GROUP THEORY COMPUTATIONS:

$$M = A_1 + E + 3\,T_2 + T_1$$
$$V = T_2$$
$$R = T_1$$
$$Vib = M - V - R = A_1 + E + 2\,T_2$$

These are all statements about *representations*.

A **representation** tells you how something transforms under the symmetries of the system.

Vibrational spectrum of methane (CH4)

GROUP THEORY COMPUTATIONS:

$$\boxed{\begin{aligned} M &= A_1 + E + 3\,T_2 + T_1 \\ V &= T_2 \\ R &= T_1 \\ Vib &= M - V - R = A_1 + E + 2\,T_2 \end{aligned}}$$

M: ***Mechanical*** representation. dim (M) = 15
V: ***Vector*** representation. dim (V) = 3
R: ***Rotational*** representation. dim (R) = 3
Vib: ***Vibrational*** representation. dim (Vib) = 9

15=6 zero modes + **9** vibrational modes

Vibrational spectrum of methane (CH4)

GROUP THEORY COMPUTATIONS:

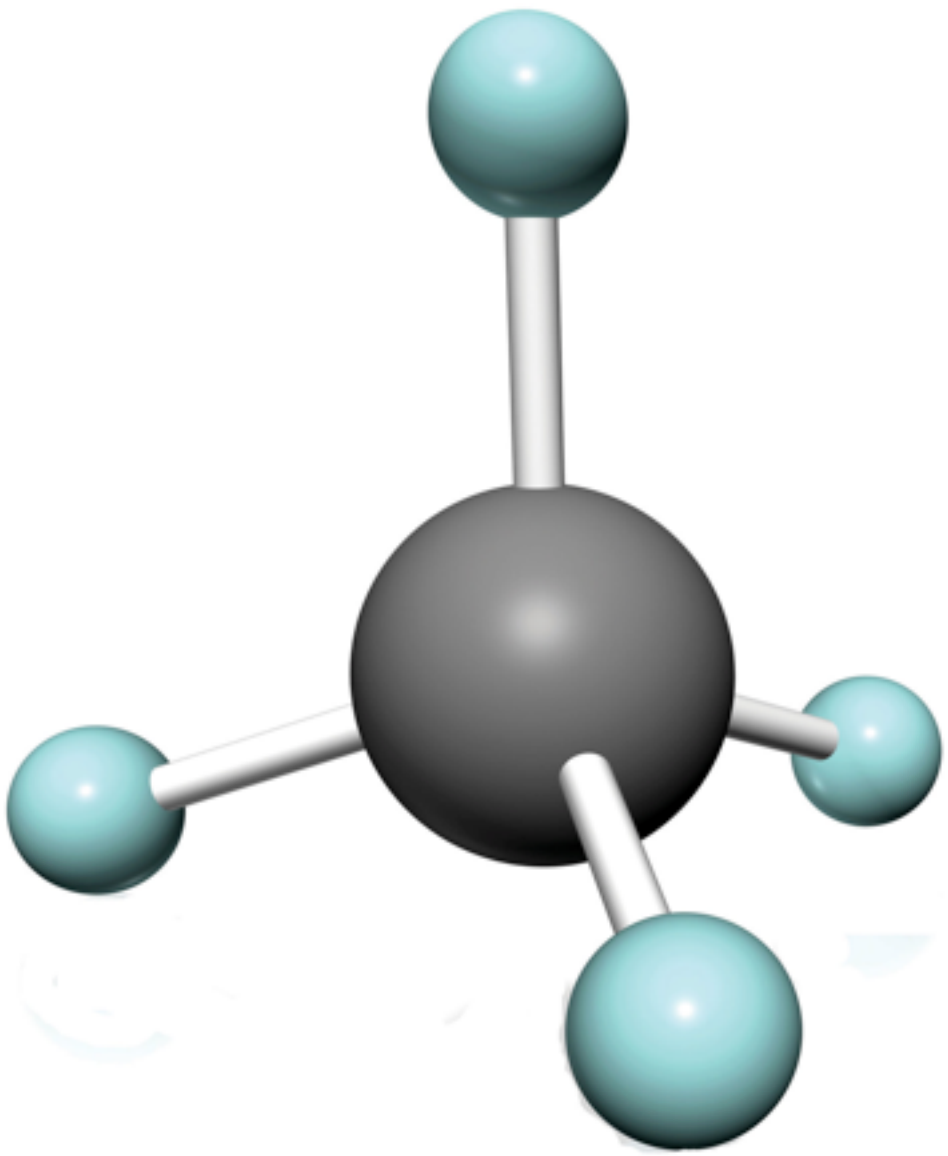
$$\boxed{\begin{aligned} M &= A_1 + E + 3\,T_2 + T_1 \\ V &= T_2 \\ R &= T_1 \\ Vib &= M - V - R = A_1 + E + 2\,T_2 \end{aligned}}$$

$\{A_1, E, T_1, T_2\}$ are *irreducible representations* of the point group $T_d(\bar{4}3m)$

IR	A_1	E	T_2	T_1
dim	1	2	3	3

$$\boxed{\begin{aligned} Vib &= A_1 + E + 2\,T_2 \\ 9 &= 1 \times \mathbf{1} + 1 \times \mathbf{2} + 2 \times \mathbf{3} \end{aligned}}$$

Vibrational spectrum of methane (CH4)



If you know group theory, you can easily obtain:

$$\boxed{1\times\mathbf{1}+1\times\mathbf{2}+2\times\mathbf{3}=\mathbf{9}}$$

(1 non-degenerate +1 doubly +2 triply degenerate = 4 different frequencies)

Vibrational spectrum of CH3D

GROUP THEORY COMPUTATIONS:

$$\boxed{\begin{aligned} M &= 4\,A_1 + A_2 + 5\,E \\ V &= A_1 + E \\ R &= A_2 + E \\ Vib &= M - V - R = 3\,A_1 + 3\,E \end{aligned}}$$

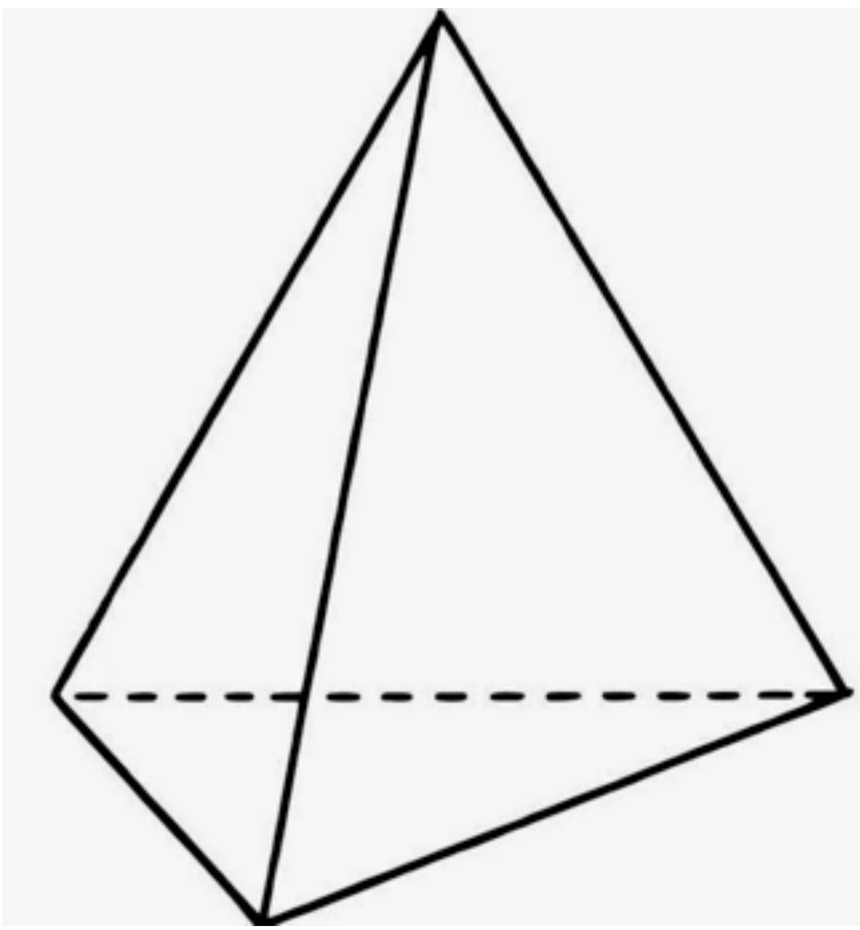
$\{A_1, A_2, E\}$ are irreducible representations of the point group $C_{3v}(3m)$

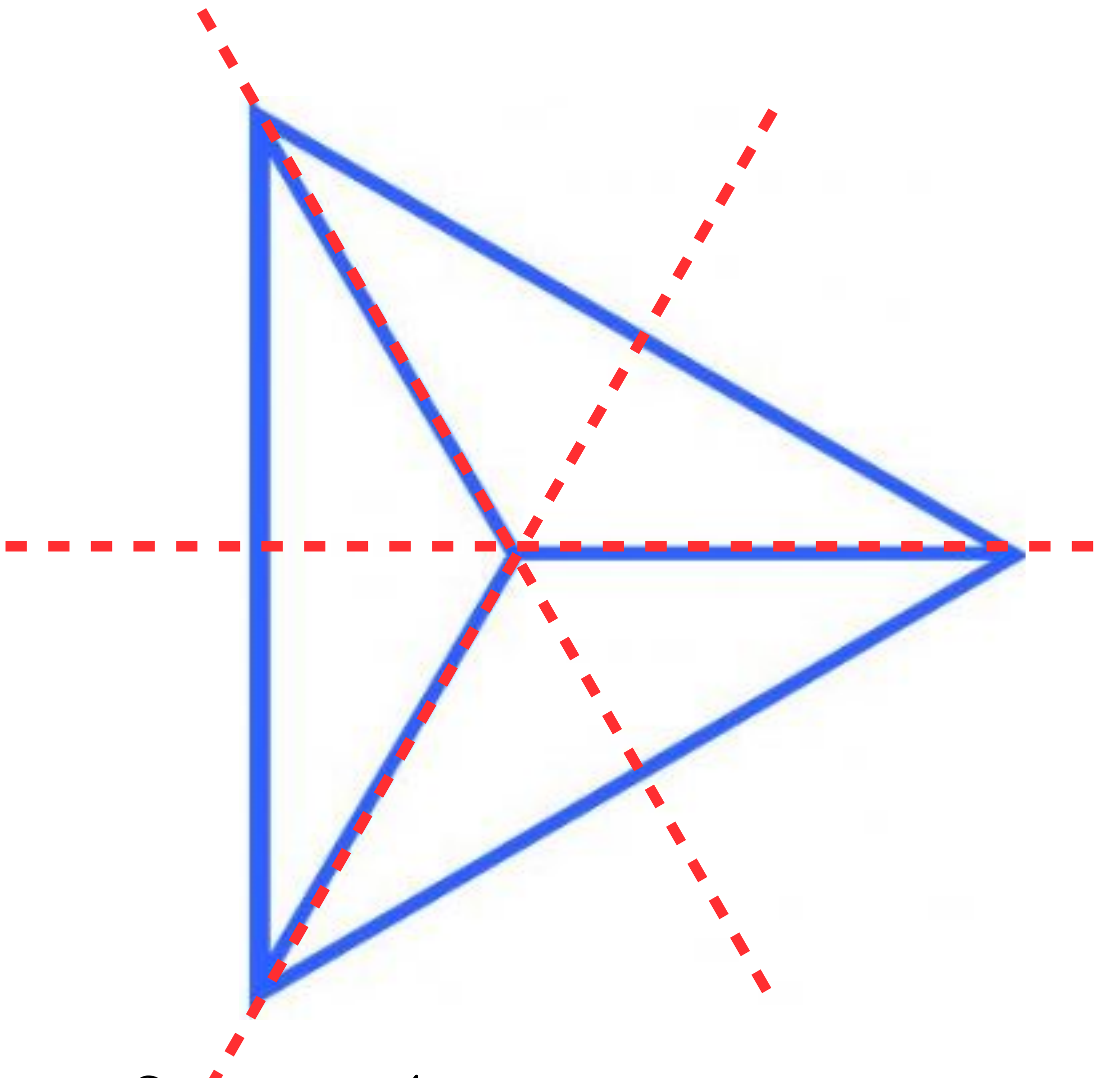
IR	A_1	A_2	E
dim	1	1	2

$$\boxed{\begin{aligned} Vib &= 3\,A_1 + 3\,E \\ \mathbf{9} &= 3 \times \mathbf{1} + 3 \times \mathbf{2} \end{aligned}}$$

The symmetry group

The symmetry group of CH3D is $C_{3v}(3m)$.
C_{3v} is the group of symmetries of a triangular pyramid.



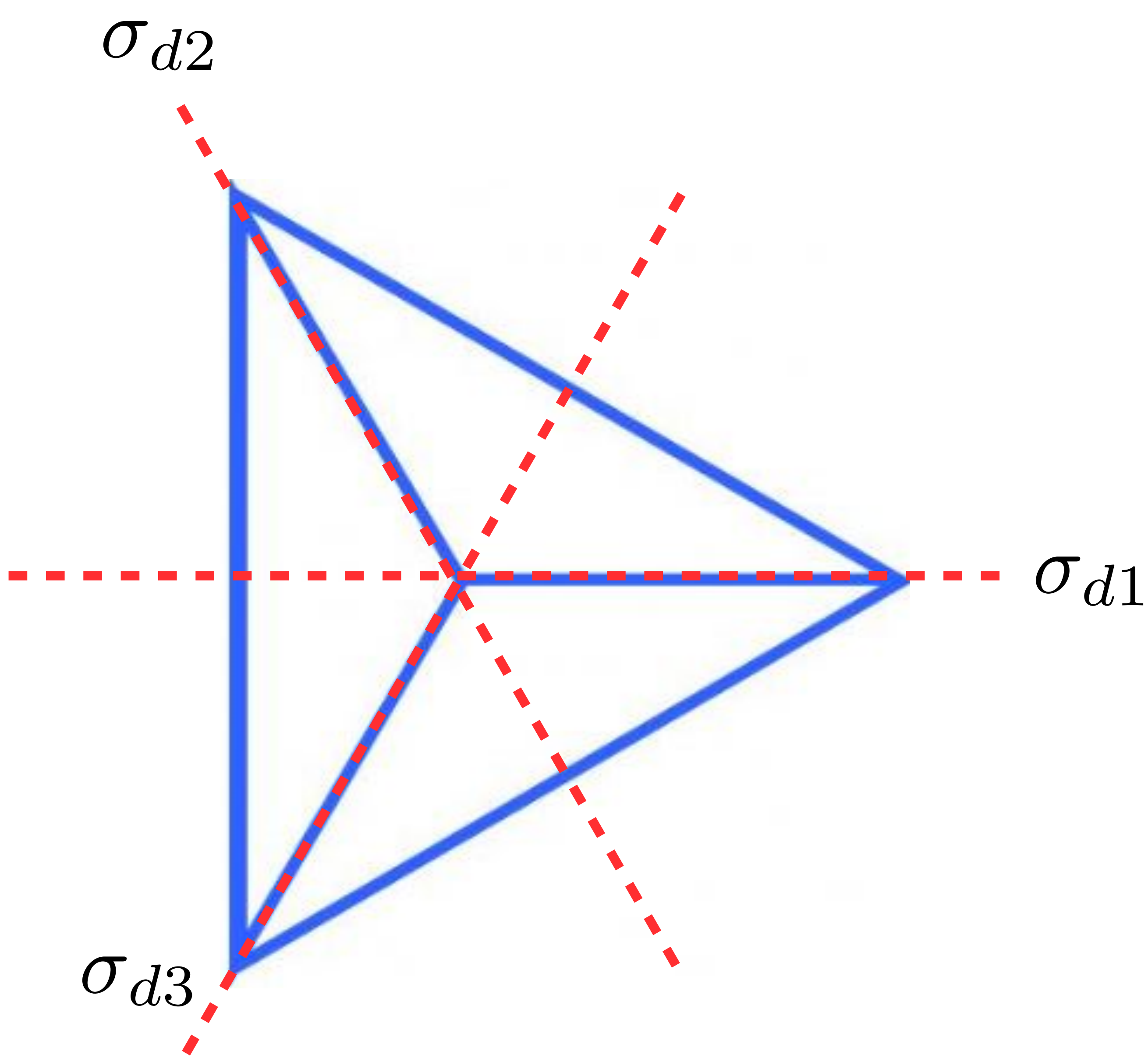


The pyramid is invariant under $\frac{2\pi}{3}$ or $\frac{4\pi}{3}$ rotations and under 3 vertical reflection planes.

The vector representation

Tells you how ordinary vectors transform under the elements of the symmetry group:

$$\boxed{C_{3v} = \{E, C_3^+, C_3^-, \sigma_{d1}, \sigma_{d2}, \sigma_{d3}\}}$$



The vector representation

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

$$V(\sigma_{d1}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

$$V(\sigma_{d2}) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$V(C_3^-) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$V(\sigma_{d3}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The vector representation

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

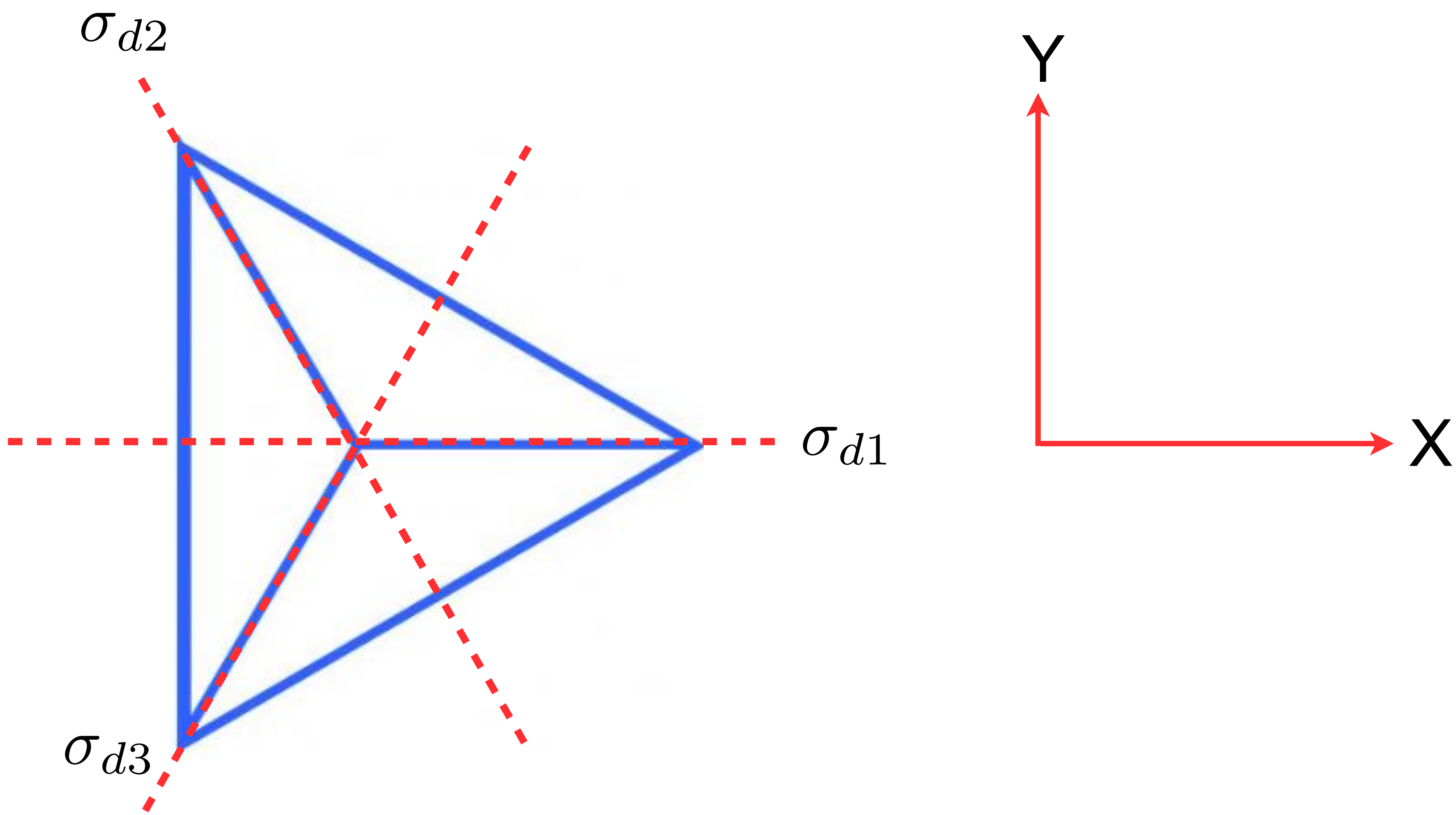
$$V(\sigma_{d1}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

$$V(\sigma_{d2}) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$V(C_3^-) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$V(\sigma_{d3}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$


σ_{d2}
σ_{d1}
σ_{d3}
Y
X

Definition of representation

A representation *T* of a group *G* assigns to each element $g \in G$ a linear operator *T(g)* in such a way that

$$\boxed{g_1 \circ g_2 = g_3 \Rightarrow T(g_1)T(g_2) = T(g_3)}$$

Example:

$$C_3^+ \circ C_3^+ = C_3^- \Rightarrow V(C_3^+)V(C_3^+) = V(C_3^-)$$

$$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = V(C_3^-)$$

Reducible and irreducible representations

$$V(E) = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right) \qquad V(\sigma_{d1}) = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & -1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$$

$$V(C_3^+) = \left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right) \qquad V(\sigma_{d2}) = \left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$$

$$V(C_3^-) = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right) \qquad V(\sigma_{d3}) = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right)$$

The vector representation V decomposes into the two *irreducible representations* (IRs) A_1 and E

$$\boxed{V(x, y, z) = A_1(z) + E(x, y)}$$

Reducible and irreducible representations

A representation *T* of a group *G* assigns to each element $g \in G$ a linear operator *T(g)* in such a way that

$$\boxed{g_1 \circ g_2 = g_3 \Rightarrow T(g_1)T(g_2) = T(g_3)}$$

Example:

$$C_3^+ \circ C_3^+ = C_3^- \Rightarrow V(C_3^+)V(C_3^+) = V(C_3^-)$$

$$\left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right)\left(\begin{array}{cc|c} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right) = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right) = V(C_3^-)$$

$$C_3^+ \circ C_3^+ = C_3^- \Rightarrow E(C_3^+)E(C_3^+) = E(C_3^-)$$

Reducible and irreducible representations

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

$$W(\sigma_{d1}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$W(C_3^+) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{2} & \frac{1}{4} & -\frac{3}{4} \\ \frac{\sqrt{3}}{2} & -\frac{3}{4} & \frac{1}{4} \end{pmatrix}$$

$$W(\sigma_{d2}) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{2} & \frac{3}{4} & -\frac{1}{4} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{4} & \frac{3}{4} \end{pmatrix}$$

$$W(C_3^-) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{2} & \frac{1}{4} & -\frac{3}{4} \\ -\frac{\sqrt{3}}{2} & -\frac{3}{4} & \frac{1}{4} \end{pmatrix}$$

$$W(\sigma_{d3}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{2} & \frac{3}{4} & -\frac{1}{4} \\ \frac{\sqrt{3}}{2} & -\frac{1}{4} & \frac{3}{4} \end{pmatrix}$$

The representation W decomposes into the two irreducible representations A_1 and E

$$\boxed{W(x, y, z) = A_1(y - z) + E(2x, y + z)}$$

Equivalent representations

Two representations T_1 and T_2 of a group *G* are said to be equivalent if there is a non-singular matrix *A* such that

$$\boxed{T_2(g) = AT_2(g)A^{-1} \quad \forall g \in G}$$

In our case, $W(g) = AV(g)A^{-1} \quad \forall g \in C_{3v}$ with

$$A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & -1 \end{pmatrix}$$

This can be interpreted as a change of coordinates, with $u' = Au$, i.e. $x' = x, \quad y' = y + z, \quad z' = y - z$

Thus *W(g)* is just *V(g)* in the coordinate system (x', y', z')

Symmetry-adapted coordinates

The block structure of the matrices of a reducible representation becomes apparent only when *symmetry-adapted coordinates* are used.

(x, y, z) are symmetry-adapted coordinates for the vector representation of C_{3v} .

APPENDIX: Groups

In mathematics, a *group G* is a set of elements $\{g_i\}$ with the following properties

1) There is a composition law that asigns an element g_3 to each ordered pair of elements

$$g_1 \circ g_2 = g_3$$

2) There is a unique unit element *e* such that

$$e \circ g = g \circ e = g, \ \forall g \in G$$

3) For each element *g* there is a unique inverse g^{-1}

$$g \circ g^{-1} = g^{-1} \circ g = e, \ \forall g \in G$$

4) The composition law is associative

$$(g_1 \circ g_2) \circ g_3 = g_1 \circ (g_2 \circ g_3)$$