Group theory, representations and their applications in solid state

TMS 2018

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.

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

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

$$W(C_3^+) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{2} & \frac{1}{4} & -\frac{3}{4} \\ \frac{\sqrt{3}}{2} & -\frac{3}{4} & \frac{1}{4} \end{pmatrix} \qquad W(\sigma_{d2}) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{4} & -\frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{2} & \frac{3}{4} & -\frac{1}{4} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{4} & \frac{3}{4} \end{pmatrix}$$

$$W(C_3^-) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} \\ -\frac{\sqrt{3}}{2} & \frac{1}{4} & -\frac{3}{4} \\ -\frac{\sqrt{3}}{2} & -\frac{3}{4} & \frac{1}{4} \end{pmatrix} \qquad W(\sigma_{d3}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{2} & \frac{3}{4} & -\frac{1}{4} \\ \frac{\sqrt{3}}{2} & -\frac{1}{4} & \frac{3}{4} \end{pmatrix}$$

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')

Characters

Traces are invariant under changes of basis

$$tr(AT(g)A^{-1}) = tr(T(g))$$

As a consequence, equivalent representations have identical traces. The converse is also true

$$\boxed{T_1 \equiv T_2 \Leftrightarrow tr(T_1(g)) = tr(T_2(g)) \ \ \forall g \in G}$$

A representation is thus fully characterized by the set of traces of the elements of the group *G*.

The set of traces of *T(g)* for all the elements of the group *G* is kown as the *character of the representation T.*

Character tables

C_{3v}	E	C_3^+	C_3^-	σ_{d1}	σ_{d2}	σ_{d3}
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
V	3	0	0	1	1	1

Reducible and irreducible representations

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

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

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

Character tables

C_{3v}	E	C_3^+	C_3^-	σ_{d1}	σ_{d2}	σ_{d3}
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
V	3	0	0	1	1	1

$$\boxed{V = A_1 + E \Leftrightarrow \chi_V = \chi_{A_1} + \chi_E}$$

Two elements g_1 and g_2 of *G* belong to the same class if there is an element *h* in *G* such that $g_2 = h \circ g_1 \circ h^{-1}$

There are three classes in C_{3v}

$$\boxed{\{E\}, \{C_3^+, C_3^-\}, \{\sigma_{d1}, \sigma_{d2}, \sigma_{d3}\}}$$

Character tables

C_{3v}	E	$C_3^{\pm}$	σ_{di}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
V	3	0	1

$$\boxed{V = A_1 + E \Leftrightarrow \chi_V = \chi_{A_1} + \chi_E}$$

Two elements g_1 and g_2 of *G* belong to the same class if there is an element *h* in *G* such that $g_2 = h \circ g_1 \circ h^{-1}$

There are three classes in C_{3v}

$$\boxed{\{E\}, \{C_3^+, C_3^-\}, \{\sigma_{d1}, \sigma_{d2}, \sigma_{d3}\}}$$

How many non-equivalent IRs?

THEOREM: The number of non-equivalent irreducible representations for a finite group *G* is equal to the *number of classes* in *G*.

THEOREM: The sum of the squares of the dimensions of the non-equivalent irreducible representations of a finite group *G* is equal to the *order of the group* (i.e., the number of elements of *G*).

$$\boxed{d_1^2 + d_2^2 + \ldots + d_C^2 = N}$$

COROLLARY: The IRs of *abelian* groups are always one-dimensional.

Decomposing a reducible representation

DEFINITION: Given two representations T_1 and T_2 of a group *G*, we define the following scalar product:

$$\boxed{(\chi_1, \chi_2) = \frac{1}{N} \sum_{g \in G} \chi_1^*(g) \chi_2(g)}$$

THEOREM: If τ_i and τ_j are irreducible representations of a group *G*, then

$$\boxed{(\chi_i, \chi_j) = \delta_{ij}}$$

Character tables

C_{3v}	E	C_3^+	C_3^-	σ_{d1}	σ_{d2}	σ_{d3}
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
V	3	0	0	1	1	1

Decomposing a reducible representation

To find the decomposition of a reducible representation

$$T = m_1\tau_1 + m_2\tau_2 + \ldots m_c\tau_c$$

just take the scalar product of

$$\chi_T = m_1\chi_1 + m_2\chi_2 + \ldots m_c\chi_c$$

with χ_j to get $(\chi_T, \chi_j) = \sum_i m_i(\chi_i, \chi_j) = m_j$

This is the famous **"magic formula"** that gives the multiplicities of the different IRs

$$\boxed{m_j = \frac{1}{N}\sum_{g\in G}\chi^*(g)\chi_j(g)}$$

Decomposing the vector representation

C_{3v}	E	$C_3^{\pm}$	σ_{di}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
V	3	0	1

$$\boxed{m_j = \frac{1}{N}\sum_{g\in G}\chi^*(g)\chi_j(g)}$$

$$m_{A_1} = \frac{1}{6}(3\times 1 + 0\times 1\times 2 + 1\times 1\times 3) = 1$$

$$m_{A_2} = \frac{1}{6}(3\times 1 + 0\times 1\times 2 + 1\times(-1)\times 3) = 0$$

$$m_E = \frac{1}{6}(3\times 2 + 0\times(-1)\times 2 + 1\times 0\times 3) = 1$$

$$\boxed{V = A_1 + E}$$

Computing characters

If the matrices of the representation are known, we just take the traces.

But, in practice, we don’t need all the actual matrices in order to compute the character of a representation. Instead, we use the following tricks:

a) Characters are *class functions*. Therefore, choose the “easiest” element from each class.

b) Traces are *independent of the coordinates*. Therefore, choose the most convenient coordinates *<u>for each element</u>*.

Computing the character of ***V***

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

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

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

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

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

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

Computing the character of ***V***

General formulas

Besides the identity, a point group may contain only four types of elements

C_n	*Rotations*
σ	*Reflection planes*
I	*Inversion*
S_n	*Roto-reflections*

By choosing the appropriate coordinates, one easily finds

$$\boxed{\begin{aligned} \chi_V(C_n) &= 1 + 2\cos\theta_n \\ \chi_V(\sigma) &= 1 \\ \chi_V(I) &= -3 \\ \chi_V(S_n) &= -1 + 2\cos\theta_n \end{aligned}}$$

Computing the character of ***V***

C_{3v}	E	$C_3^{\pm}$	σ_{di}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
V	3	0	1

$$\boxed{\begin{aligned} \chi_V(C_n) &= 1 + 2\cos\theta_n \\ \chi_V(\sigma) &= 1 \\ \chi_V(I) &= -3 \\ \chi_V(S_n) &= -1 + 2\cos\theta_n \end{aligned}}$$

Computing the character of ***R***

General formulas

The rotational representation tells how *pseudovectors* (a.k.a. *axial vectors*) transform.

Axial vectors transform like vectors under rotations, but with a relative minus sign under "improper"operations.

Thus the formulas for the vector representation imply

$$\boxed{\begin{aligned} \chi_R(C_n) &= 1 + 2\cos\theta_n \\ \chi_R(\sigma) &= -1 \\ \chi_R(I) &= 3 \\ \chi_R(S_n) &= 1 - 2\cos\theta_n \end{aligned}}$$

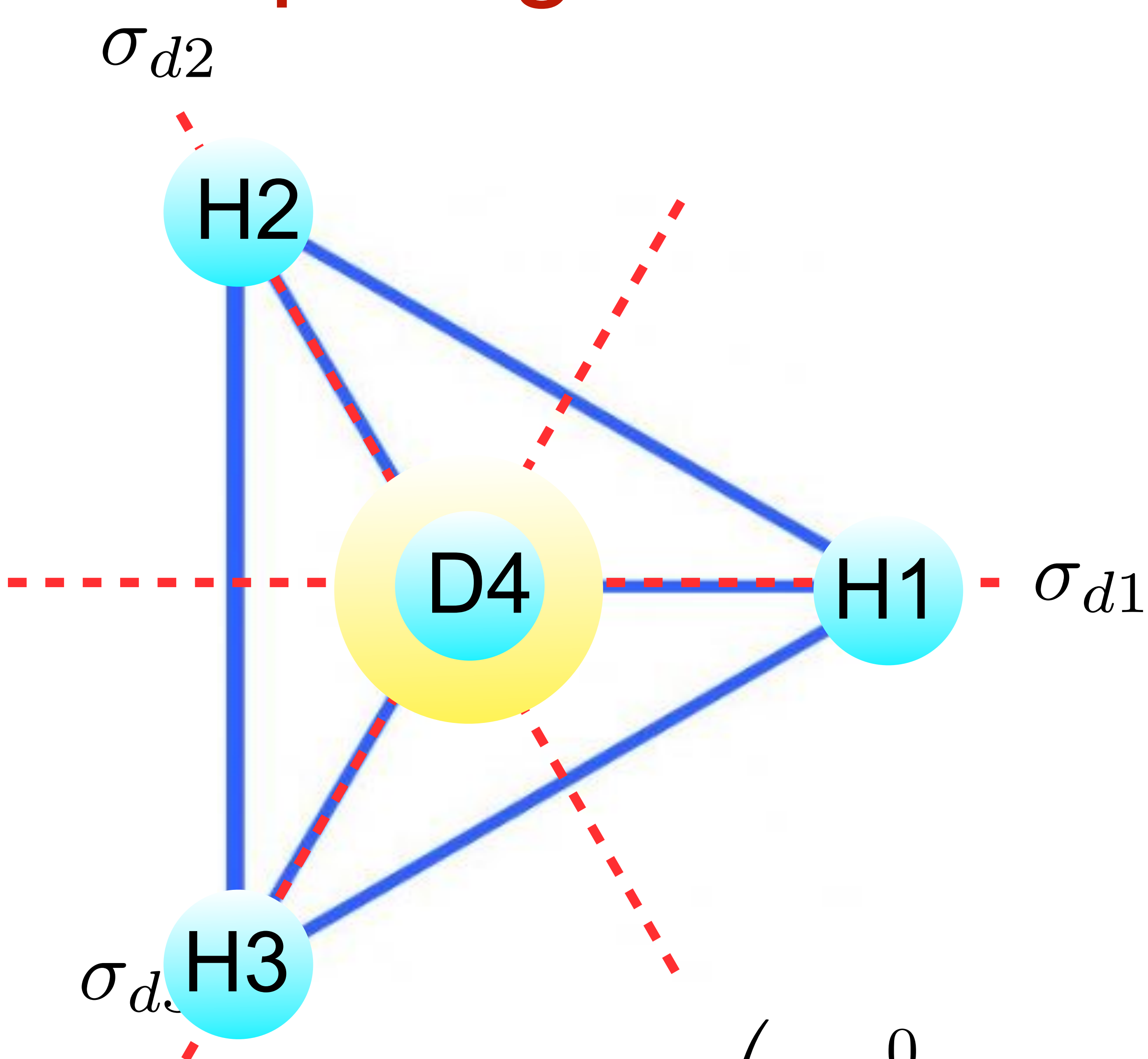
Computing the character of *M*

General formula

The mechanical representation tells how general mechanical deformations of a molecule transform.

The matrices for the mechanical represention have a block structure where the blocks are just the matrices of the vector representation.

Computing the character of ***M***

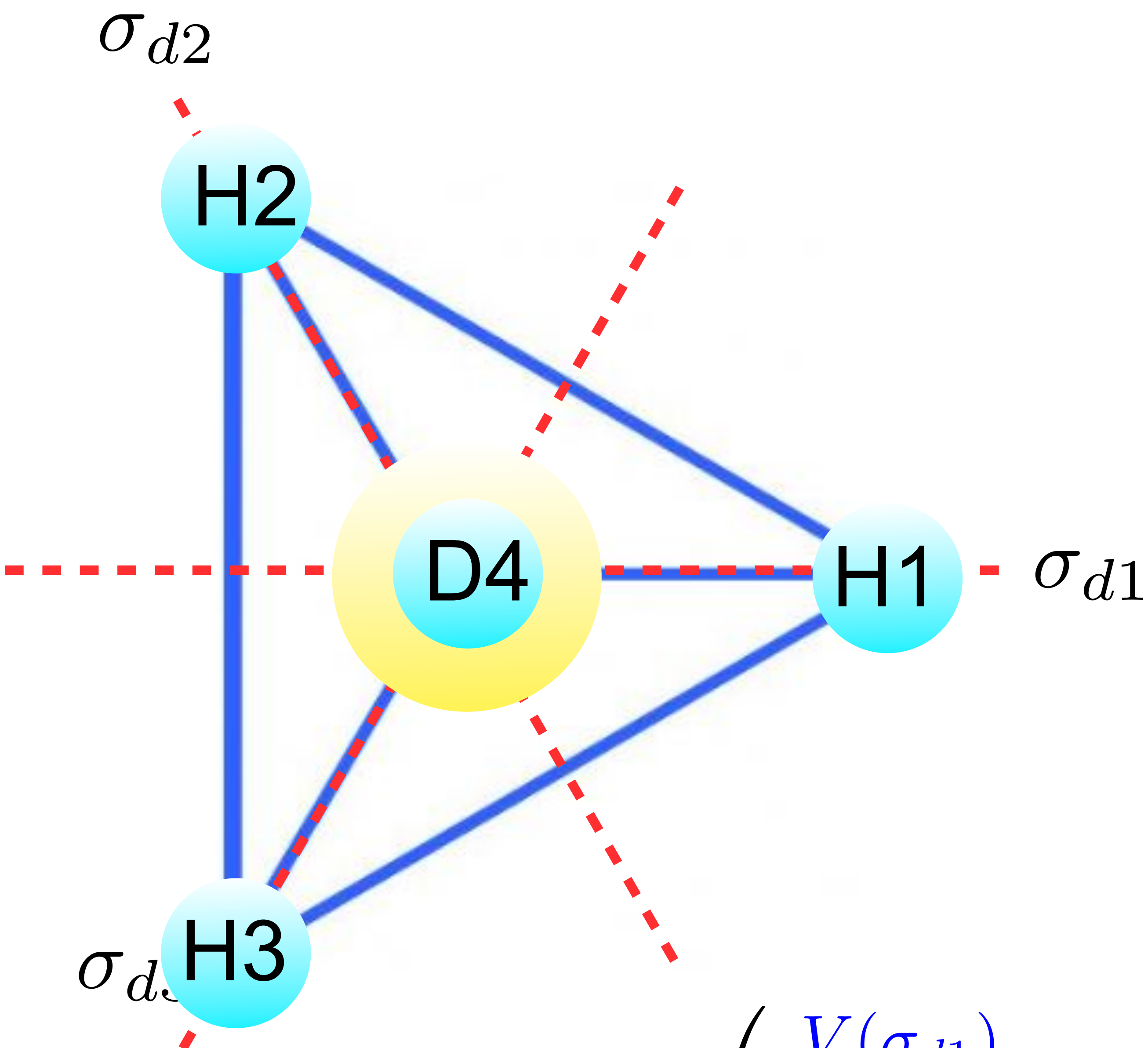


$$u = \begin{pmatrix} \vec{u}_1 \\ \vec{u}_2 \\ \vec{u}_3 \\ \vec{u}_4 \\ \vec{u}_C \end{pmatrix}$$

$$\boxed{u_g = M(g)u}$$

$$M(C_3^+) = \begin{pmatrix} 0 & 0 & V(C_3^+) & 0 & 0 \\ V(C_3^+) & 0 & 0 & 0 & 0 \\ 0 & V(C_3^+) & 0 & 0 & 0 \\ 0 & 0 & & V(C_3^+) & 0 \\ 0 & 0 & 0 & 0 & V(C_3^+) \end{pmatrix}$$

Computing the character of ***M***



$$u = \begin{pmatrix} \vec{u}_1 \\ \vec{u}_2 \\ \vec{u}_3 \\ \vec{u}_4 \\ \vec{u}_C \end{pmatrix}$$

$$\boxed{u_g = M(g)u}$$

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

Computing the character of ***M***

General formula

The mechanical representation tells how general mechanical deformations of a molecule transform.

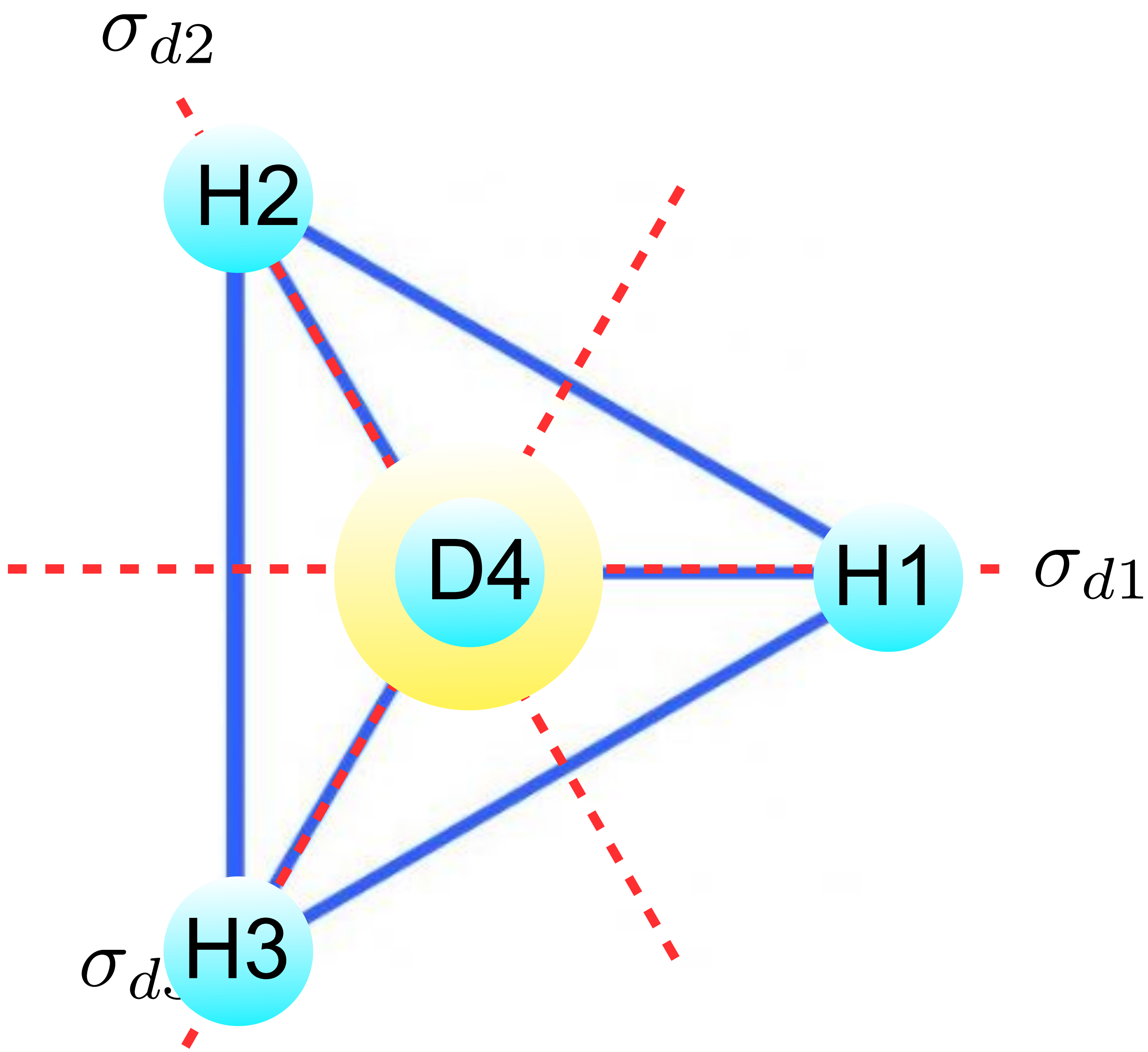
The matrices for the mechanical represention have a block structure where the blocks are just the matrices of the vector representation.

The blocks are on the diagonal when the corresponding atoms are invariant under the symmetry operation. Thus

$$\boxed{\chi_M(g) = n_{inv}(g)\chi_V(g)}$$

where $n_{inv}(g)$ is the number of atoms invariant under *g*.

Computing the character of ***M***



C_{3v}	E	$C_3^{\pm}$	σ_{di}
n_{inv}	5	2	3

Computing the character of *M*

C_{3v}	E	$C_3^{\pm}$	σ_{di}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
V	3	0	1
n_{inv}	5	2	3
M	15	0	3

$$\boxed{m_j = \frac{1}{N} \sum_{g \in G} \chi^*(g) \chi_j(g)}$$

$$\boxed{M = 4A_1 + A_2 + 5E}$$

$$m_{A_1} = \frac{1}{6}(15 \times 1 + 0 \times 1 \times 2 + 3 \times 1 \times 3) = 4$$

$$m_{A_2} = \frac{1}{6}(15 \times 1 + 0 \times 1 \times 2 + 3 \times (-1) \times 3) = 1$$

$$m_E = \frac{1}{6}(15 \times 2 + 0 \times (-1) \times 2 + 3 \times 0 \times 3) = 5$$

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

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

Summary

COMPUTING CHARACTERS

$$\boxed{\begin{aligned}\chi_V(C_n) &= 1 + 2\cos\theta_n \\ \chi_V(\sigma) &= 1 \\ \chi_V(I) &= -3 \\ \chi_V(S_n) &= -1 + 2\cos\theta_n\end{aligned}}$$

$$\boxed{\begin{aligned}\chi_R(C_n) &= 1 + 2\cos\theta_n \\ \chi_R(\sigma) &= -1 \\ \chi_R(I) &= 3 \\ \chi_R(S_n) &= 1 - 2\cos\theta_n\end{aligned}}$$

$$\boxed{\chi_M(g) = n_{inv}(g)\chi_V(g)}$$

DECOMPOSING REPRESENTATIONS

$$\boxed{m_j = \frac{1}{N}\sum_{g\in G}\chi^*(g)\chi_j(g)}$$

$$\boxed{Vib = M - V - R}$$