# Group theory, representations and their applications in solid state

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 CH3D
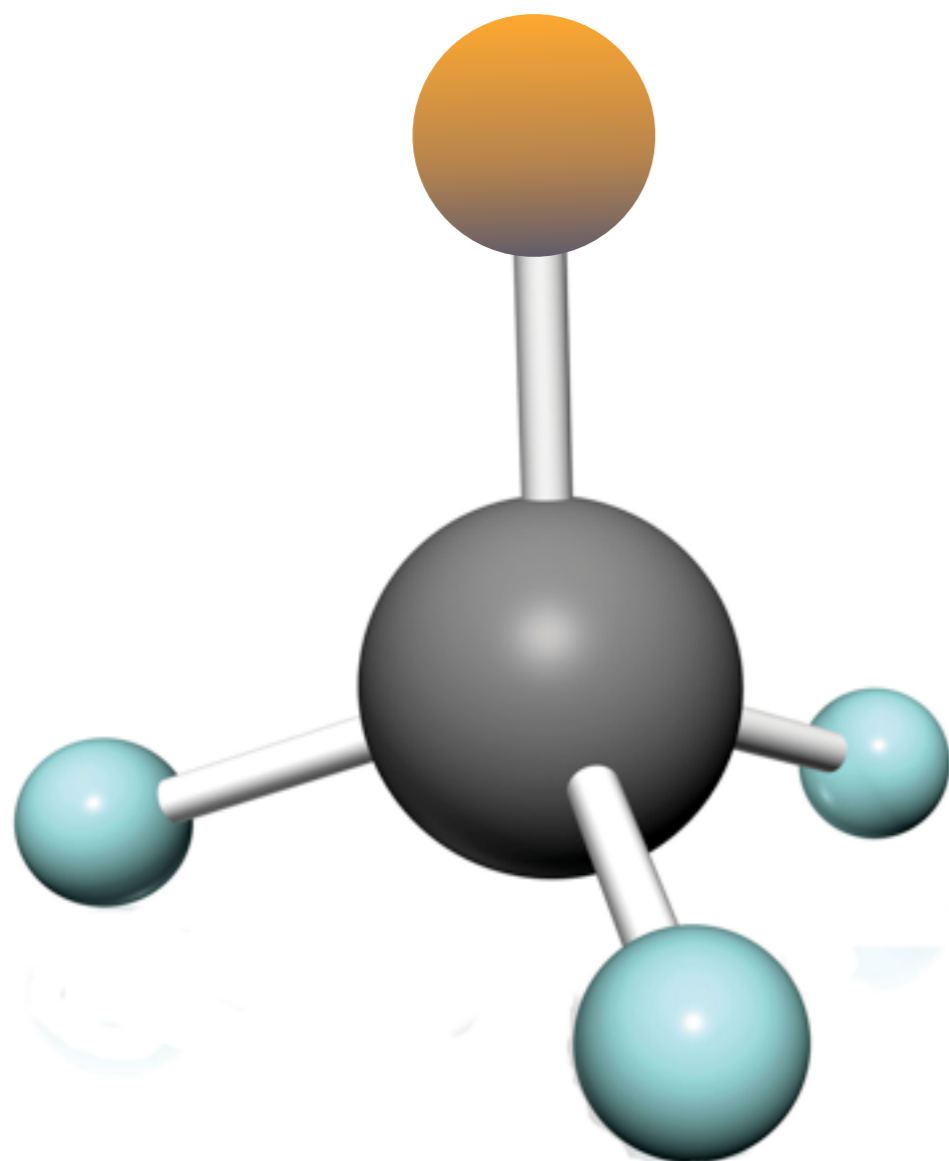
Group theory tells you that each triply degenerate frequency splits: $3 \rightarrow 1+2$:

$$1\text{x}1+1\text{x}2+2\text{x}3=9 \rightarrow 3\text{x}1+3\text{x}2=9$$

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

Subduced representation

If T is a representation of a group G and $G_1 \subset G$ is a subgroup of G, then T subduces the representation T_1 of G_1 according to the obvious rule

$$\forall g \in G_1, \quad T_1(g) = T(g)$$

It often happens that an IR of G subduces a reducible representation T_1 of G_1. Then T_1 can be decomposed as a sum of IRs of G_1.

When this is done for all the IRs of the parent group G, we have a *subduction table.*

Subduced representation

Example: $T_d \to C_{3v}$

T_d	E	$C_{3j}^{\pm}$	C_{2m}	σ_{dp}	$S_{4m}^{\pm}$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_2	3	0	-1	1	-1
T_1	3	0	-1	-1	1

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

Subduction table:

T_d	A_1	A_2	E	T_2	T_1
C_{3v}	A_1	A_2	E	$A_1 + E$	$A_2 + E$

Subduced representation

Example: $T_d \rightarrow C_{3v}$

T_d	A_1	A_2	E	T_2	T_1
C_{3v}	A_1	A_2	E	$A_1 + E$	$A_2 + E$

According to this table, any triply degenerate level of a system with symmetry T_d will split into two levels, one of them doubly degenerate, when the symmetry is broken down to C_{3v}

$$\boxed{\mathbf{3 \rightarrow 1 + 2}}$$

Subduced representation

Application to $CH_4 \to CH_3D$

T_d	A_1	A_2	E	T_2	T_1
C_{3v}	A_1	A_2	E	$A_1 + E$	$A_2 + E$

CH_4   **CH_3D**

$$Vib = A_1 + E + 2T_2 \longrightarrow Vib = 3A_1 + 3E$$

Splitting of atomic levels in crystals

Atomic orbitals

In the central field approximation

$$\mathcal{H}_C \psi_{nlm}(\vec{r}) = E_{nl} \psi_{nlm}(\vec{r})$$

and each single-electron energy has a degeneracy *2(2l+1)* with the factor of two from the spin degeneracy (neglecting spin-orbit couplings).

In a crystal, the symmetry will be reduced from *O(3)* to the *local point group G*

$$O(3) \rightarrow G$$

Splitting of atomic levels in crystals

As a consequence of the reduction of the symmetry from *O(3)* to the local group *G*, some *degeneracies may be broken.*

For instance, when the local group is C_{3v} the atomic orbitals split according to

$$s \rightarrow a_1$$

$$p \rightarrow a_1 + e$$

$$d \rightarrow a_1 + 2e$$

$$f \rightarrow 2a_1 + a_2 + 2e$$

The irreducible representations of **SO(3)**

SO(3) is the group of all possible rotations in $\mathbb{R}_3$.

SO(3) is a Lie group. It can be shown that the multiplets studied in quantum mechanics define the IRs D_l of *SO(3)*:

$$D_l = D_l(\{|l, m\rangle\}), \quad dim(D_l) = 2l + 1$$

Thus *SO(3)* has infinitely many (unitary) IRs.

The characters are easily determined by taking as representative of each class a rotation about the *OZ* axis

The irreducible representations of **SO(3)**

The character of D_l

Every element of SO(3) can be written as an exponential

$$R(\vec{\theta}) = \exp \frac{i\vec{\theta} \cdot \vec{L}}{\hbar}$$

Using $L_z|l, m\rangle = \hbar m|l, m\rangle$ gives

$$\chi_l(C_\theta) = tr\left(\exp\frac{i\theta L_z}{\hbar}\right) = \sum_{m=-l}^{l} e^{im\theta} = \frac{e^{i(l+1)\theta} - e^{-il\theta}}{e^{i\theta} - 1}$$

$$\chi_l(C_\theta) = \frac{\sin(l + \frac{1}{2})\theta}{\sin\frac{\theta}{2}}$$

The irreducible representations of **O(3)**

O(3) contains both proper and improper operations, and can be written as a direct product

$$O(3) = SO(3) \otimes C_i \;, \quad C_i = \{E, I\}$$

As a consequence, the IRs of O(3) are obtained from those of *SO(3)* and C_i .

Concretely, one has to specify the value of l in D_l and the behaviour under the inversion or parity. Thus, *for each IR of SO(3) there are two different IRs of O(3) denoted $D_l^{\pm}$.*

The irreducible representations of **O(3)**

The character of $D_l^P (P = \pm)$

$$\chi_l(E) = 2l + 1$$

$$\chi_l(C_\theta) = \frac{\sin(l + \frac{1}{2})\theta}{\sin \frac{\theta}{2}}$$

$$\chi_l(I) = (2l + 1)P$$

$$\chi_l(\sigma) = \chi_l(C_\pi)P$$

$$\chi_l(S_\theta) = \chi_l(C_{\pi-\theta})P$$

The second column has been obtained by using

$$\sigma = IC_\pi$$

$$S_\theta = \sigma_\perp C_\theta = IC_{\pi-\theta}$$

Splitting of atomic levels in crystals

Atomic orbitals

In the *central field approximation* to multielectron atoms each electron moves in a spherically symmetric effective potential, independently of the other electrons.

The one-electron states are atomic orbitals

$$\psi_{nlm}(\vec{r}) = R_{nl}(r) Y_l^m(\theta, \varphi)$$

The radial functions are invariant under *O(3)* and only the *spherical harmonics* transform. The parity of a spherical harmonic is $P = (-)^l$.

$$Y_l^m \in D_l^P \ , \quad P = (-)^l$$

Splitting of atomic levels in crystals

Splitting of atomic orbitals *(weak spin-orbit)*

This is basically a subduction problem. If the *local* point group for the atom is, for instance, C_{3v}, we can use the character formulas to obtain the characters of the subduced representations

C_{3v}	E	$C_3^{\pm}$	σ_{di}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
D_0^+	1	1	1
D_1^-	3	0	1
D_2^+	5	-1	1
D_3^-	7	1	1

s
p
d
f

$$D_0^+ = A_1$$
$$D_1^- = A_1 + E$$
$$D_2^+ = A_1 + 2E$$
$$D_3^- = 2A_1 + A_2 + 2E$$

$$s \to a_1$$
$$p \to a_1 + e$$
$$d \to a_1 + 2e$$
$$f \to 2a_1 + a_2 + 2e$$

Splitting of atomic levels in crystals

Splitting of atomic multiplets *(strong spin-orbit)*

When *spin-orbit interaction* is important, each orbital splits into two multiplets defined by the total angular momentum *j* of the electron according to

$$l \rightarrow j = l \pm 1/2$$

For instance, *p* orbitals split into a multiplet with *j=1/2* and another multiplet with *j=3/2*. In terms of representations of *O(3)*

$$D_1^- \times D_{1/2}^+ = D_{1/2}^- + D_{3/2}^-$$

Note that the parity of the multiplet is always equal to that of the parent orbital.

Splitting of atomic levels in crystals

The character of D_l^P $(P = \pm)$

$$\chi_l(E) = 2l + 1$$

$$\chi_l(C_\theta) = \frac{\sin(l + \frac{1}{2})\theta}{\sin \frac{\theta}{2}}$$

$$\chi_l(I) = (2l + 1)P$$

$$\chi_l(\sigma) = \chi_l(C_\pi)P$$

$$\chi_l(S_\theta) = \chi_l(C_{\pi-\theta})P$$

Splitting of atomic levels in crystals

Splitting of atomic multiplets *(strong spin-orbit)*

C_{3v}	E	$C_3^{\pm}$	σ_{di}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$D_{1/2}^{-}$	2	1	0
$D_{3/2}^{-}$	4	-1	0

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

$$D_{1/2}^{-}: \ m_{A_1} = m_{A_2} = 2/3, \ \ m_E = 1/3$$

$$D_{3/2}^{-}: \ m_{A_1} = m_{A_2} = 1/3, \ \ m_E = 5/3$$

$(!)$

The doubled-valued representations

The trouble with half-integral values of *j* is that the representation is no longer single-valued. In particular

$$\chi_j(\theta) = \frac{\sin(j + \frac{1}{2})\theta}{\sin \frac{\theta}{2}}$$

$$\Rightarrow \boxed{\chi_j(\theta + 2\pi) = -\chi_j(\theta) \,, \forall j = \frac{1}{2}, \frac{3}{2} \cdots}$$

Then we say that we are dealing with *double-valued representations* of *SO(3)*.

The double groups

Alternatively, we may acknowledge that C_θ and $C_{\theta+2\pi}$ are in fact different symmetry operations.

From this viewpoint, the IRs for half-integral *J* are <u>*not*</u> representations of *SO(3)* but of its universal covering *SU(2)*, which is ``twice as large'' as *SO(3)*.

Then, rather than double-valued IRs of the point groups, we will have *representations of the double point groups*.

This is more accurate, as the double point groups have a *different structure* and *different number of classes*.
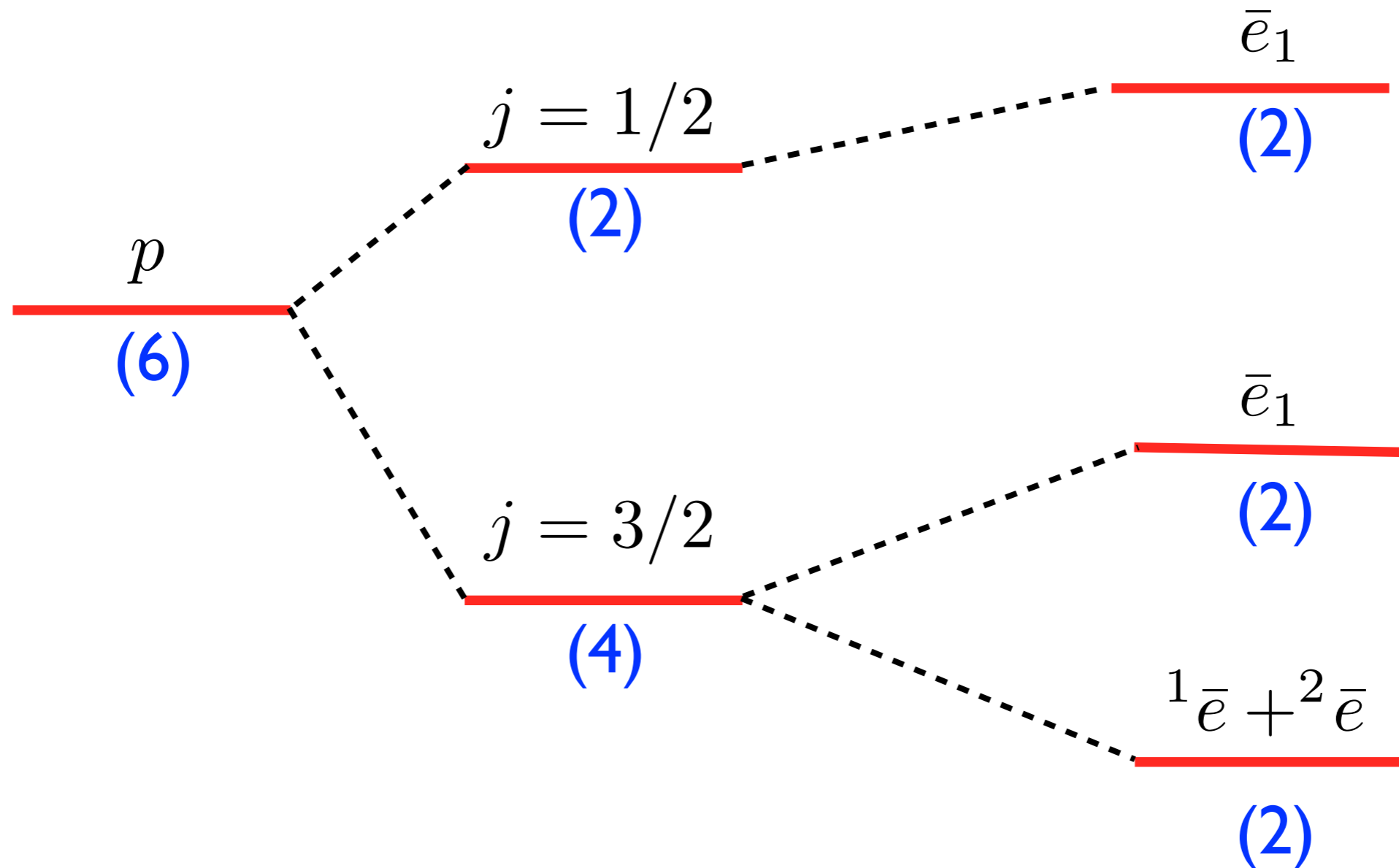
The double groups

$$D_{1/2}^- = \bar{E}_1$$

$$D_{3/2}^- = \bar{E}_1 + {}^1\bar{E} + {}^2\bar{E}$$

Example:

C_{3v}	E	$\bar{E}$	$C_3^\pm$	$\bar{C}_3^\pm$	σ_{di}	$\bar{\sigma}_{di}$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	-1	-1
${}^1\bar{E}$	1	-1	-1	1	i	-i
${}^2\bar{E}$	1	-1	-1	1	-i	i
E	2	2	-1	-1	0	0
$\bar{E}_1$	2	-2	1	-1	0	0
$D_{1/2}^-$	2	-2	1	-1	0	0
$D_{3/2}^-$	4	-4	-1	1	0	0

Note: $\bar{E} \equiv C_{2\pi}$

Splitting of p-orbitals in a crystal field *(strong spin-orbit)*

$$D_1^- \times D_{1/2}^+ = D_{1/2}^- + D_{3/2}^-$$

$$D_{1/2}^- = \bar{E}_1$$
$$D_{3/2}^- = \bar{E}_1 + {}^1\bar{E} + {}^2\bar{E}$$