

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.**

From vectors to tensors

Molecular polarizability

To lowest order, the *induced* dipole moment of a molecule is proportional to the applied electric field

$$\vec{P} = \alpha \vec{E}$$

α is the polarizability tensor. In components

$$P_i = \alpha_{ij} E_j$$

The transformation properties of the polarizability are those of a tensor

$$\forall g \in G : \alpha_{ij} \rightarrow V_{ik}(g) V_{jl}(g) \alpha_{kl} = V(g) \alpha V^t(g)$$

From vectors to tensors

Molecular polarizability

The polarizability describes a property of the molecule in equilibrium and *must be invariant under all its symmetries*

$$\alpha_g = V(g)\alpha V(g)^t = \alpha \Rightarrow [\alpha, V(g)] = 0, \forall g \in G$$

We will use group theory to find the most general form of the polarizability compatible with the symmetry constraints

This is easier if we consider the electrostatic energy

$$\mathcal{E} \sim \vec{P} \cdot \vec{E} \sim \alpha_{ij} E_i E_j$$

From vectors to tensors

Molecular polarizability

The energy is *quadratic* in the electric field.

The energy must be a *linear combination of quadratic invariants* in the electric field.

The electric field belongs to the vector representation. For the group C_{3v}

$$V(E_x, E_y, E_z) = A_1(E_z) + E(E_x, E_y)$$

All the representations in this equation are unitary: *norms and scalar products are invariant under the symmetry group*

From vectors to tensors

$$V(E_x, E_y, E_z) = A_1(E_z) + E(E_x, E_y)$$

$$A_1(E_z) \times A_1(E_z) \rightarrow E_z^2$$

$$E(E_x, E_y) \times E(E_x, E_y) \rightarrow E_x^2 + E_y^2$$

This implies

$$\alpha_{ij} E_i E_j = a(E_x^2 + E_y^2) + bE_z^2$$

or

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

This is valid for *any* molecule with symmetry group C_{3v}

From vectors to tensors

Molecular polarizability

For any molecule with symmetry T_d

$$V(E_x, E_y, E_z) = T_2(E_x, E_y, E_z)$$

the only quadratic invariant is $E_x^2 + E_y^2 + E_z^2$

This implies an isotropic polarizability

$$\alpha = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

Molecular vibrations

If the molecule has A atoms, its configuration is described by a $3A$ dimensional vector $u = (\vec{u}_1, \vec{u}_2, \dots, \vec{u}_A)$ with

$$\vec{r}_\alpha = \vec{R}_\alpha + \vec{u}_\alpha$$

The kinetic energy is given by

$$T = \sum_{\alpha=1}^A \frac{1}{2} m_\alpha \dot{\vec{u}}_\alpha^2 \equiv \frac{1}{2} \dot{u}^t M \dot{u}$$

where M is the diagonal mass matrix

$$M = [m_1, m_1, m_1, \dots, m_A, m_A, m_A]$$

Molecular vibrations

The potential energy is expanded about the equilibrium configuration keeping only second order contributions

$$U(u_i) \simeq \sum_{i,j=1}^{3A} \frac{1}{2} U_{ij} u_i u_j = \frac{1}{2} u^t U u$$

where U is the symmetric, but non-diagonal potential matrix

$$U_{ij} = \frac{\partial^2 U}{\partial u_i \partial u_j}$$

The lagrangian is thus given by

$$\mathcal{L} = \frac{1}{2} \dot{u}^t M \dot{u} - \frac{1}{2} u^t U u$$

Molecular vibrations

This lagrangian gives rise to a set of coupled linear differential equations

$$M\ddot{u} + Uu = 0$$

The normal modes and frequencies are found by making the ansatz $u(t) = ne^{i\omega t}$ which gives

$$(U - M\omega^2)n = 0$$

This is not a standard eigenvalue problem due to the presence of the matrix M . To solve it, we make the change of coordinates $\tilde{u} = M^{1/2}u$.

Molecular vibrations

The lagrangian in the new variables

$$\mathcal{L} = \frac{1}{2} \dot{\tilde{u}}^t \dot{\tilde{u}} - \frac{1}{2} \tilde{u}^t \tilde{U} \tilde{u}$$

with $\tilde{U} = M^{-1/2} U M^{-1/2}$ gives rise to an ordinary eigenvalue problem.

$$(\tilde{U} - \omega^2) \tilde{n} = 0$$

Solving the eigenvalue problem yields $3A$ frequencies ω_α^2 .
The corresponding normal modes satisfy $\tilde{n}_\alpha^t \tilde{n}_\beta = \delta_{\alpha\beta}$.

Reverting to the original coordinates shows that normal modes satisfy

$$n_\alpha^t M n_\beta = \delta_{\alpha\beta}$$

Molecular vibrations

PURE VIBRATIONS

The mechanical representation acts on

$$L_M = L_{trans} \oplus L_{rot} \oplus L_{Vib}$$

$$L_{trans} : u = (\vec{t}, \dots, \vec{t})$$

$$L_{rot} : u = (\vec{\omega} \times \vec{R}_1, \dots, \vec{\omega} \times \vec{R}_A)$$

L_{Vib} is defined by the constraints

$$\sum_{\alpha=1}^A m_{\alpha} \vec{u}_{\alpha} = 0 \quad , \quad \sum_{\alpha=1}^A m_{\alpha} (\vec{R}_{\alpha} \times \vec{u}_{\alpha}) = 0$$

that imply $L_{Vib} \perp L_{trans}$ and $L_{Vib} \perp L_{rot}$ with respect to the mass metric $(u_1, u_2) = u_1^t M u_2$

Molecular vibrations

Molecular vibrations

Consider the methane molecule with symmetry T_d .

Assume we have obtained *symmetry-adapted* coordinates for the IRs in the vibrational representation

$$V_{ib} = A_1(q_1) + E(q_2, q_3) + T_2(q_4, q_5, q_6) + T_2(q_7, q_8, q_9)$$

The normal modes and frequencies are obtained by diagonalizing the potential matrix $\tilde{U} = M^{-1/2}UM^{-1/2}$

$$(\tilde{U} - \omega^2)\tilde{n} = 0$$

Molecular vibrations

Molecular vibrations

The potential matrix has to be invariant under all the elements of the group T_d .

$$[\tilde{U}, M(g)] = 0, \quad \forall g \in T_d$$

These constraints can be solved more easily by considering the invariance of the potential energy

$$\mathcal{E}_P = \frac{1}{2} \tilde{u}^t \tilde{U} \tilde{u}$$

This must be a linear combination of quadratic invariants in the symmetric coordinates $\{q_1, q_2, \dots, q_9\}$

Molecular vibrations

Molecular vibrations

$$Vib = A_1(q_1) + E(q_2, q_3) + T_2(q_4, q_5, q_6) + T_2(q_7, q_8, q_9)$$

$$A_1(q_1) \times A_1(q_1) \rightarrow q_1^2$$

$$E(q_2, q_3) \times E(q_2, q_3) \rightarrow q_2^2 + q_3^2$$

$$T_2(q_4, q_5, q_6) \times T_2(q_4, q_5, q_6) \rightarrow q_4^2 + q_5^2 + q_6^2$$

$$T_2(q_7, q_8, q_9) \times T_2(q_7, q_8, q_9) \rightarrow q_7^2 + q_8^2 + q_9^2$$

$$T_2(q_4, q_5, q_6) \times T_2(q_7, q_8, q_9) \rightarrow q_4q_7 + q_5q_8 + q_6q_9$$

This shows that the most general potential energy for the methane molecule depends only on **5** free parameters.

Molecular vibrations

Molecular vibrations

$$\begin{aligned}\tilde{U}_{ij}q_iq_j = & aq_1^2 + b(q_2^2 + q_3^2) + c(q_4^2 + q_5^2 + q_6^2) \\ & + d(q_7^2 + q_8^2 + q_9^2) + 2e(q_4q_7 + q_5q_8 + q_6q_9)\end{aligned}$$

or

$$\tilde{U} = \begin{pmatrix} a & & & & & & & & \\ & b & & & & & & & \\ & & b & & & & & & \\ & & & c & & & & & \\ & & & & c & & & & \\ & & & & & c & & & \\ & & & e & & & d & & \\ & & & & e & & & d & \\ & & & & & e & & & d \end{pmatrix}$$

Molecular vibrations

Molecular vibrations

$$Vib = A_1(q_1) + E(q_2, q_3) + T_2(q_4, q_5, q_6) + T_2(q_7, q_8, q_9)$$

Reorder the coordinates $\{q_1, q_2, q_3, q_4, q_7, q_5, q_8, q_6, q_9\}$

$$\tilde{U} = \left(\begin{array}{ccccccc} \boxed{a} & & & & & & \\ & \boxed{b} & & & & & \\ & & \boxed{b} & & & & \\ & & & \boxed{\begin{matrix} c & e \\ e & d \end{matrix}} & & & \\ & & & & \boxed{\begin{matrix} c & e \\ e & d \end{matrix}} & & \\ & & & & & \boxed{\begin{matrix} c & e \\ e & d \end{matrix}} & \\ & & & & & & \end{array} \right)$$

Molecular vibrations

Molecular vibrations

$$Vib = A_1(q_1) + E(q_2, q_3) + T_2(q_4, q_5, q_6) + T_2(q_7, q_8, q_9)$$

$$\begin{aligned} \tilde{U}_{ij}q_iq_j = & aq_1^2 + b(q_2^2 + q_3^2) + c(q_4^2 + q_5^2 + q_6^2) \\ & + d(q_7^2 + q_8^2 + q_9^2) + 2e(q_4q_7 + q_5q_8 + q_6q_9) \end{aligned}$$

Molecular vibrations

Molecular vibrations

$$Vib = A_1(q_1) + E(q_2, q_3) + T_2(q_4, q_5, q_6) + T_2(q_7, q_8, q_9)$$

Reorder the coordinates $\{q_1, q_2, q_3, q_4, q_7, q_5, q_8, q_6, q_9\}$

$$\tilde{U} = \begin{pmatrix} a & & & & & & & & \\ & b & & & & & & & \\ & & b & & & & & & \\ & & & \begin{pmatrix} c & e \\ e & d \end{pmatrix} & & & & & \\ & & & & \begin{pmatrix} c & e \\ e & d \end{pmatrix} & & & & \\ & & & & & \begin{pmatrix} c & e \\ e & d \end{pmatrix} & & & \\ & & & & & & \begin{pmatrix} c & e \\ e & d \end{pmatrix} & & \\ & & & & & & & \begin{pmatrix} c & e \\ e & d \end{pmatrix} & \\ & & & & & & & & \begin{pmatrix} c & e \\ e & d \end{pmatrix} \end{pmatrix}$$

$\omega^2(A_1) = a$
 $\omega^2(E) = b$
 $\begin{pmatrix} c & e \\ e & d \end{pmatrix}$
 \downarrow
 $\{\omega_1^2(T_2), \omega_2^2(T_2)\}$

Molecular vibrations

Molecular vibrations

$$Vib = \dots + m_i \tau_i + \dots$$

In general, for each IR with dimension d and multiplicity m in the decomposition of Vib , there are d identical $m \times m$ matrices in the diagonal of the potential matrix.

Upon diagonalization, they give rise to m different d -degenerated frequencies.

Appendix: The product representation

Rank-2 tensors t_{ij} live in the 9-dimensional space $\mathbb{R}_3 \otimes \mathbb{R}_3$ and transform like the products $\{x_1x_2, y_1y_2, z_1z_2, x_1y_2, y_1x_2, y_1z_2, z_1y_2, z_1x_2, x_1z_2\}$

Rank-2 tensors belong to the product representation $V \times V \equiv V^2$

General representations

Given two representations T_1 and T_2 acting on representation spaces of dimensions d_1 and d_2 , the tensors in $L_1 \otimes L_2$ belong to the product representation

$$T_3 = T_1 \times T_2$$

with

$$\chi_3(g) = \chi_1(g)\chi_2(g)$$

Number of bilinear invariants

Given two real IRs τ_1 and τ_2 acting on $L_1(x_1, \dots, x_{d_1})$ and $L_2(y_1, \dots, y_{d_2})$, bilinears in their coordinates belong to the product representation $\tau_3 = \tau_1 \times \tau_2$.

The number of bilinear invariants is equal to the number of times the identity representation is contained in $\tau_3 = \tau_1 \times \tau_2$

$$m_1 = \frac{1}{N} \sum_{g \in G} \chi_3^*(g) \cdot 1 = \frac{1}{N} \sum_{g \in G} \chi_1(g) \chi_2(g) = (\chi_1, \chi_2) = \delta_{1,2}$$

There are no invariants if $\tau_1 \neq \tau_2$. And for equivalent IRs, the only bilinear invariant is given by

$$x_1 y_1 + \dots + x_d y_d$$

This form of the invariant is valid only *if the matrices of the two equivalent IRs are identical.*