

Atomic and molecular physics
practice course
Group theory appendix

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1 Symmetry group

Symmetry of the system: invariance of \hat{H} against a coordinate transformation. This can be particle exchange, time inversion or spatial symmetry.

Def 1 *Symmetry operator \hat{R} : $[\hat{H}, \hat{R}] = 0$.*

Theorem 1 *The symmetry operators with a multiplication create a group.*

Def 2 *Group: G set with a multiplication, that fulfills the following group axioms.*

- *closeness: $\forall a, b \in G : ab = c \in G$*
- *associative: $(ab)c = a(bc)$*
- *unit: $\exists e \in G, \forall a \in G : ea = a$*
- *inverse: $\exists a^{-1} \in G, \forall a \in G : a^{-1}a = e$*

Def 3 *Point group: group of isometries that keep one point fixed.*

Schönflies notation: n-fold rotation C_n , vertical mirroring σ_v , horizontal mirroring σ_h , inversion i , improper rotation S_n .

Example 1 *The point group of NH_3 molecule*

$$C_{3v} = \{E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v\}$$

Def 4 *$b \in G$ is a conjugate of $a \in G$ if $\exists p \in G : b = pap^{-1}$.*

Theorem 2 *Conjugacy is an equivalence relation and the group is partitioned into equivalence classes called conjugacy classes.*

Example 2 *The partition of C_{3v} point group into conjugacy classes*

$$C_{3v} = \{E\} \cup \{C_3, C_3^2\} \cup \{\sigma_v, \sigma'_v, \sigma''_v\}$$

2 Representation theory

Def 5 Representation $\Gamma : G \rightarrow \text{GL}(n, \mathbb{C})$ homomorphism

where $\text{GL}(n, \mathbb{C})$ is the general linear group of $n \times n$ matrices.

Def 6 Γ and Γ' are equivalent representations if $\exists S \forall a \in G : \Gamma'(a) = S\Gamma(a)S^{-1}$

Def 7 Reducible representation can be partitioned into direct sum of representations, i.e., a block-diagonal form. Irreducible representation cannot be partitioned this way.

Theorem 3 The number of irreducible representations of a group is equal to the number of its conjugacy classes.

Def 8 Character of representation: $\chi(a) = \text{Tr}(\Gamma(a))$

Theorem 4 The characters of equivalent representations and conjugate elements are equal.

Example 3 Representation of an element in each conjugacy class of C_{3v}

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} \cos \frac{2\pi}{3} & \sin \frac{2\pi}{3} & 0 \\ -\sin \frac{2\pi}{3} & \cos \frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_v[xz] = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Theorem 5 Orthogonality relation for characters of irreducible representations

$$\sum_{k=1}^N \frac{n_k}{h} \chi^i(a_k)^* \chi^j(a_k) = \delta_{ij}$$

where i, j are the labels of irreducible representations, k is the label of conjugacy classes, $h = |G|$ is the order of the group, N is the number of conjugacy classes, n_k is the number of elements in the conjugacy class.

Consequence: if $\Gamma = \bigoplus_i m_i \Gamma^i$ then

$$m_i = \sum_{k=1}^N \frac{n_k}{h} \chi^i(a_k)^* \chi(a_k)$$

where $\chi(a_k)$ are the characters of the reducible representation.

3 Vibrational normal modes of water molecule

The vibration of a molecule can be described by the displacement vector of each atom. Arbitrary displacements can describe translational and rotational motion as well, we will subtract these carefully. Let us choose the displacement basis $\{x_i, y_i, z_i\}$ as the linear space of the group representation.

Water molecule has C_{2v} point symmetry

$$C_{2v} = \{E, C_2, \sigma_v[xz], \sigma_v[yz]\}$$

where each group element is a conjugacy class. So C_{2v} has four irreducible representations listed in its character table. We can construct the representations of the symmetry operators by studying their effect on the basis vectors. The twofold rotation permutes the hydrogen atom indices, and changes the sign of x and y basis vectors. The other matrices can be constructed in a similar way.

$$E = \text{diag}(1, 1, 1, 1, 1, 1, 1, 1, 1) \quad \chi(E) = 9$$

$$C_2 = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \chi(C_2) = -1$$

$$\sigma_v[xz] = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \chi(\sigma_v[xz]) = 1$$

$$\sigma_v[yz] = \text{diag}(-1, 1, 1, -1, 1, 1, -1, 1, 1) \quad \chi(\sigma_v[yz]) = 3$$

This reducible representation can be partitioned into a direct sum of irreducible representations

$$\Gamma = \bigoplus_i m_i \Gamma^{(i)}$$

where irrep i has contribution m_i times. m_i can be calculated using the orthogonality theorem.

$$m_{A_1} = \frac{1}{4} (1 \cdot 9 + 1 \cdot (-1) + 1 \cdot 1 + 1 \cdot 3) = 3$$

$$m_{A_2} = \frac{1}{4} (1 \cdot 9 + 1 \cdot (-1) + (-1) \cdot 1 + (-1) \cdot 3) = 1$$

$$m_{B_1} = \frac{1}{4} (1 \cdot 9 + (-1) \cdot (-1) + 1 \cdot 1 + (-1) \cdot 3) = 2$$

$$m_{B_2} = \frac{1}{4} (1 \cdot 9 + (-1) \cdot (-1) + (-1) \cdot 1 + 1 \cdot 3) = 3$$

$$\Gamma = 3A_1 + A_2 + 2B_1 + 3B_2$$

The displacement normal modes of translation transform as the coordinate vectors x, y, z and rotational modes transform as the pseudo-vectors R_x, R_y, R_z , that we can read from the character table:

$$\Gamma_{\text{tr}} = A_1 + B_1 + B_2$$

$$\Gamma_{\text{rot}} = A_2 + B_1 + B_2$$

The remaining modes are the vibrational normal modes of water molecule:

$$\Gamma_{\text{vib}} = \Gamma - \Gamma_{\text{tr}} - \Gamma_{\text{rot}} = 2A_1 + B_2$$

