Group Theory with Applications to Electronic Structure

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Plan

Topics

- AHL Basics of group theory and representations
- MV Symmetry in quantum mechanics
- GT Systematic characterization with point groups
- FCV Lattices and space groups
- etc Miscellaneous applications

The big spoiler page

Why this is interesting

- Hamiltonian is invariant under symmetry transformations. Symmetries lead to degeneracies, selection rules
- The symmetry operations of a system form a group, for which reason we shall now indulge ourselves in group theory
- Systems can be characterized in terms of point groups and space groups

Groups

Definition

A group is a set G with the following properties:

- There exists a binary operation $*: G \times G \to G$
- The operation $*$ is associative, i.e. for all A, B, C in G,

$$A * (B * C) = (A * B) * C$$

- G contains an identity element $E \in G$ such that for all $A \in G$,

$$A * E = E * A = A$$

- Each element $A \in G$ has an inverse $A^{-1} \in G$ such that

$$A * A^{-1} = A^{-1} * A = E$$

Important groups

- The set of regular $n \times n$ matrices with matrix product, identity matrix as identity element and matrix inversion
- The set of symmetry operations on a physical system, which could be reflections, translations, rotations, improper rotations (rotation and reflection)

A simple example

Symmetry operations on e.g. NH_3, CH_3Cl

- Consider three identical atoms A, B, C (see upper configuration on figure)
- Three rotations C_3, $C_3^2 = C_3^{-1}$, $C_3^3 = E$
- Three reflections σ_A, σ_B, σ_C
- Improper rotations (denoted S_n) are all equivalent to reflections in this case, e.g. $C_3\sigma_A = \sigma_B$
- This six-element group is denoted $\mathscr{C}_{3v}$ (that's a C)

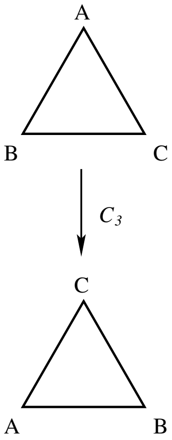

Figure: Definition of system and action of C_3

Matrix representations

Representation

- A symmetry operation is a linear transformation
- Each operation in a symmetry group can be represented by a matrix
- The group operation $*$ now corresponds to matrix multiplication
- If the matrices are $n \times n$, the mapping between group operations and matrices is called a representation of the group
- Actually one can always ascribe matrix representations to finite groups

Alternative representations

Two example representations of C_3 in the $\mathscr{C}_{3v}$ case

- Use atomic sites $\{\mathbf{A}, \mathbf{B}, \mathbf{C}\}$ as basis. Then

$$\mathbf{C}_3' = \begin{bmatrix} \uparrow & \uparrow & \uparrow \\ C_3(\mathbf{A}) & C_3(\mathbf{B}) & C_3(\mathbf{C}) \\ \downarrow & \downarrow & \downarrow \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

- Use axes $\{\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}\}$ as basis. C_3 is then represented by

$$\mathbf{C}_3 = \begin{bmatrix} \uparrow & \uparrow & \uparrow \\ C_3(\hat{\mathbf{x}}) & C_3(\hat{\mathbf{y}}) & C_3(\hat{\mathbf{z}}) \\ \downarrow & \downarrow & \downarrow \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- But our system is essentially 2D, so why would we need 3 dimensions? Moreover, if there were four atoms the second example would yield even more dimensions!

Reducibility

hello