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 by 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 as the group operation
- The set of symmetry operations on a physical system, which could be reflections, translations, rotations, improper rotations (rotation and reflection)
- There are many other "important" groups which are not so relevant for us

A simple example

Symmetry operations on e.g. NH_3, CH_3Cl

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

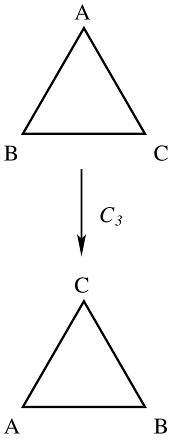

Figure: Definition of system and action of C_3

Group tables

- All combinations of $x * y$ form the group table for $\mathscr{C}_{3v}$

$x *^y$	E	C_3	C_3^2	σ_A	σ_B	σ_C
E	E	C_3	C_3^2	σ_A	σ_B	σ_C
C_3	C_3	C_3^2	E	σ_C	σ_A	σ_B
C_3^2	C_3^2	E	C_3	σ_B	σ_C	σ_A
σ_A	σ_A	σ_B	σ_C	E	C_3	C_3^2
σ_B	σ_B	σ_C	σ_A	C_3^2	E	C_3
σ_C	σ_C	σ_A	σ_B	C_3	C_3^2	E

- Observe that e.g. the rotations here form a subgroup: successive rotations only ever form other rotations

Representations of groups

Mapping

- A representation of a group G associates a matrix with every element of G, such that the matrix product implements the group operation (and so on wrt. inversion, identity)
- More specifically, if $R_1, R_2, R_3 \in G$ have respective matrices $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$, then

$$R_1 * R_2 = R_3 \implies \mathbf{R}_1\mathbf{R}_2 = \mathbf{R}_3$$

- The representation of a group is also a group. If the matrices are $n \times n$, the representation is called n-dimensional
- A group can have multiple representations, possibly of different dimension

Alternative representations

Two examples of matrices for C_3 in $\mathscr{C}_{3v}$ representations

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

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

- 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 former example would yield even more dimensions!

Reducibility

Block diagonalization in $\mathscr{C}_{3v}$

- When using $\hat{\mathbf{z}}$ as a basis vector, it turns out (not surprisingly) that every symmetry operation R in $\mathscr{C}_{3v}$ has a matrix of the block-diagonal form

$$\mathbf{R} = \begin{bmatrix} r_{11} & r_{12} & 0 \\ r_{21} & r_{22} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- It is always possible to obtain "maximally" block diagonalized matrices by choosing a suitable basis. We say that the matrix is written in reduced form

Reducibility, continued

Generally

- In reduced form, all symmetry operations R have matrices with the same block structure, which we can write as

$$\mathbf{R} = \begin{bmatrix} [\mathbf{R}_1] & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & [\mathbf{R}_2] & & \vdots \\ \vdots & & \ddots & \mathbf{0} \\ \mathbf{0} & \cdots & \mathbf{0} & [\mathbf{R}_n] \end{bmatrix}$$

- We say that the representation above is reducible into several irreducible representations, each of which corresponds to one block

Irreducible representations

This is why irreducible representations are interesting

- The irreducible representations of a group have dimensions $n_1, \ldots, n_k$ such that

$$n_1^2 + n_2^2 + \cdots + n_k^2 = \{\text{no. of symmetry ops.}\}$$

- In particular, there can never be more irreducible representations of a group than the group's element count
- Spoiler: each irreducible representation will correspond to an energy level of the physical system, giving rise to degeneracies when dimension is larger than 1