

Physical Chemistry

Lecture 29
Groups and Representations

Groups and wave functions

- ◆ Groups are sets of operations
 - Objects belonging to a group are eigenfunctions of the operations
- ◆ Electron density is a specific kind of object
 - Must transform exactly into itself under every symmetry operation
- ◆ Wave functions may either transform into itself or the negative of itself

$$O\Psi = \pm 1\Psi$$

Representations

- ◆ In group theory, objects are defined in terms of **representations**
- ◆ **Reducible representations** are objects that are not eigenfunctions of every operation of the group
- ◆ **Irreducible representations** are eigenfunctions of all operations of the group
- ◆ Each irreducible representation must have a different set of eigenvalues

Character

- ◆ The **character** of a representation under an operation is the eigenvalue
- ◆ For irreducible representations in nondegenerate groups, the character must be either +1 or -1
- ◆ Types of groups
 - In **nondegenerate groups**, every irreducible representation consists of one object
 - In **degenerate groups**, some irreducible representations consist of more than one object, considered in pairs, triples, or quartets, ...

Character table

- ◆ For finite groups, ones not containing infinite operations, the number of irreducible representations is finite
- ◆ Irreducible representation defined by the set of characters under the operations of a group
- ◆ The possible values of characters arrayed to display the variation with irreducible representation is called a **character table**

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	Functions
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

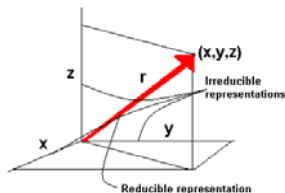
Classes of operations

- ◆ Some operations are so similar they do not have separate entries in character tables
 - Operations are parsed into **classes**
- ◆ Nondegenerate groups have irreducible representations with more than one object
 - Identity character tells the size of the representation
 - Some operations have a character of 0
 - Operation transforms the objects in the representation into each other

C_{3v}	E	$2 C_3(z)$	$3 \sigma_v$	Functions
A_1	1	1	1	z, x^2+y^2, z^2
A_2	1	1	-1	
E	2	-1	0	$(x,y) (x^2-y^2, xy) (xz, yz)$

Analogy to vectors

- ◆ The mathematics of group theory is something like vector algebra
- ◆ Irreducible representations are similar to the basis vectors of a space
 - They are orthogonal to each other
 - They have a "size"
 - Reducible representations may be described as linear combinations of irreducible representations
- ◆ Mulliken symbols
 - Similar to vector notation



$$A_1 = (1, 1, 1, 1)$$

$$A_2 = (1, 1, -1, -1)$$

Inner product

- ◆ Inner product of two representations
 - Like dot product of vectors
 - Sum of weighted products of characters
- ◆ Irreducible representations are orthogonal
 - Inner product of two different representations is zero
 - Inner product of a representation with itself is the group dimension

C_2	E	$2C_2(z)$	$3\sigma_v$	Functions
A_1	1	1	1	z, x^2+y^2, z^2
A_2	1	1	-1	
E	2	-1	0	$(x,y), (x^2-y^2, xy)$

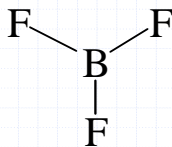
$$A_2 \bullet E = 1 \times 2 + 2(1 \times (-1)) + 3(-1 \times 0) = 2 - 2 = 0$$

$$A_1 \bullet A_2 = 1 \times 1 + 2(1 \times 1) + 3(1 \times (-1)) = 1 + 2 - 3 = 0$$

$$A_1 \bullet A_1 = 1 \times 1 + 2(1 \times 1) + 3(1 \times 1) = 1 + 2 + 3 = 6$$

Relation to quantum mechanics

- ◆ Wave function may be classified as an object in the symmetry group of the molecule
 - Irreducible representation
 - Reducible representation
 - Can be reduced to a sum of irreducible functions
- ◆ Objective is to determine the representation of each wave function
 - Determine character under group operations
 - Compare to irreducible representations
 - Produces a label for the MO wave function consistent with the group symmetry



Example

$$\Psi = C(\Psi_{1s,F_1} + \Psi_{1s,F_2} + \Psi_{1s,F_3})$$

Summary

- ◆ Mathematics of groups is abstract
 - Like the algebra of vectors
 - Character table gives eigenvalues under the operations
- ◆ Groups classified as
 - Nondegenerate
 - Degenerate
- ◆ Point-group symmetry of objects allows classification
 - Irreducible representation
 - Reducible representation
- ◆ Inner product
 - Is zero for two irreducible representations
 - Is the dimension of the group for an irreducible representation with itself