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 representations 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

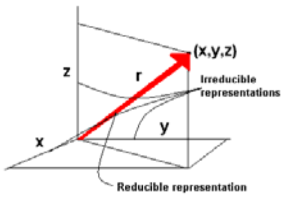
Classes of operations

- Some operations are so similar they do not have separate entries in character tables
  - Operations are parsed into classes
- Degenerate 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_{3v}	E	$2C_3$ (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	$(x,y)\ (x^2-y^2,xy)\ (xz,yz)$

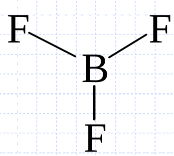
$$A_2 \bullet E = 1\times 2 + 2(1\times(-1)) + 3(-1\times 0) = 2 - 2 = 0$$

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

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

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

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

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