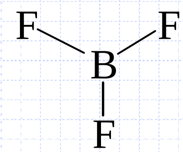
Physical Chemistry

Lecture 30

Wave Functions and Group Theory

Wave functions and group theory

- Wave function 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



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

Example

Finding the irreducible representation of a MO

- Objects belonging to a group are eigenfunctions of the operations
- Find the characters under the operations of the group
- By comparison, identify the representation of the orbital
- Example in BF_3
  - $\psi = 1s_{F1} + 1s_{F2} + 1s_{F3}$
  - Representation is $a_1{}'$ in D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$A_1{}'$	1	1	1	1	1	1
$A_2{}'$	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
$A_1{}''$	1	1	1	-1	-1	-1
$A_2{}''$	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
ψ	1	1	1	1	1	1

Direct product

- Objects may be products of other objects
  - Example: product of two wave functions
- Composite object's representation determined from representations of objects comprising it
- Representation of a product found as direct product of representations of the objects of which it is composed
- Important in determining the representation of a multi-electron wave function

$$h = f\,g$$

$$\Gamma_h = \Gamma_f \otimes \Gamma_g$$

$$O(fg) = (Of)(Og)$$

$$= c_f c_g (fg)$$

Direct product of two representations

- Determining the direct product
  - Multiply characters under each operation
  - Analyze character set to find representation
- Either an irreducible representation or a reducible representation
- For reducible representation
  - Reduce to a direct sum of irreducible representations
- May be continued to find representations of multiple products

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	
A_u	1	1	-1	-1	
B_g	1	-1	1	-1	
B_u	1	-1	-1	1	
$A_g \otimes A_g$	1	1	1	1	A_g
$B_g \otimes B_u$	1	1	-1	-1	A_u
$A_u \otimes B_u$	1	-1	1	-1	B_g

Direct product and the totally symmetric representation

- Totally symmetric representation is special
  - Direct product of the totally symmetric representation with any representation is the representation

$$\Gamma_{sym} \otimes \Gamma_a = \Gamma_a$$

  - An operation like multiplying by 1 in algebra of numbers
- The direct product of wave functions representing a filled shell is always the group's totally symmetric representation
  - Direct product of representation of a filled shell with subsequent wave functions only gives the representation of those shells
  - Can neglect filled shells in finding the representation of a multi-electron state

Finding electronic configurations of molecules

- Must find one-electron MOs for the system
  - Use SALCs
    - A subset of linear combinations which take into account symmetry
- Must know filling order (energy order)
  - Can sometimes guess it by classical theories of bonding
- Create configuration by adding electrons by the aufbau principle

Example:

Linear H—X—H

$$
\begin{aligned}
1\sigma_g &= 1s_X \\
2\sigma_g &= c_1 2s_X + c_2(1s_{HA} + 1s_{HB}) \\
1\sigma_u &= c_5 2p_{zX} - c_6(1s_{HA} - 1s_{HB}) \\
1\pi_u &= (2p_{xX}, 2p_{yX}) \\
3\sigma_g^* &= c_3 2s_X - c_4(1s_{HA} + 1s_{HB}) \\
2\sigma_u^* &= c_7 2p_{zX} + c_8(1s_{HA} - 1s_{HB})
\end{aligned}
$$

Example: BeH_2

- A total of six electrons
- Create configuration by shuttling these into the lowest energy one-electron orbitals
- Perform a direct product to find the term
- Consider spin
  - All spins paired
  - A singlet state
- Could have guessed this because all in the totally symmetric representation

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2$$

$$
\begin{aligned}
\Gamma &= \Sigma_g \otimes \Sigma_g \otimes \Sigma_g \otimes \Sigma_g \otimes \Sigma_u \otimes \Sigma_u \\
&= \Sigma_g
\end{aligned}
$$

Ground term symbol: $^1\Sigma_g$

Example: excited state of BeH_2

- Repeat the aufbau, adding the last electron to the next excited one-electron state
- Do the direct product
  - Inner product of a representation with itself is the group dimension
- Spins of the two electrons may be paired or unpaired
- Apply Hund's rules to determine the term of lower energy

$$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^1(1\pi_u)^1$$

$$
\begin{aligned}
\Gamma &= \\
&\Sigma_g \otimes \Sigma_g \otimes \Sigma_g \otimes \Sigma_g \otimes \Sigma_u \otimes \Pi_u \\
&= \Pi_g
\end{aligned}
$$

Term symbols: $^1\Pi_g$ and $^3\Pi_g$

Summary

- Wave functions are objects in the group of the molecule
  - Can be classified as reducible or irreducible representations
  - Can determine the representation by carrying out operations on the wave function
- SALCs
  - Symmetry-adapted linear combinations of orbitals already conform to the required symmetry of the molecule
  - Combine atomic orbitals of similar energy relative to the dissociation energy
- Aufbau principle
  - Find multi-electron configurations
- Direct product
  - Gives multi-electron terms