# Physical Chemistry

Lecture 31

Reducing Reducible Representations

## Reducible representations

- In degenerate groups
  - Products of irreducible representations may give reducible representations
  - Products of wave functions may be represented by reducible representations
- Need to describe reducible representations in terms of irreducible representations

## Direct sums

- A reducible representation is expressible as a direct sum of irreducible representations
- A direct sum is given by the representation with characters that are sum of characters

| $D_{3h}$ | $E$ | $2\,C_3$ | $3\,C_2$ | $\sigma_h$ | $2\,S_3$ | $3\,\sigma_v$ |
|---|---|---|---|---|---|---|
| $A_1'$ | 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 |

| | $E$ | $2\,C_3$ | $3\,C_2$ | $\sigma_h$ | $2\,S_3$ | $3\,\sigma_v$ |
|---|---|---|---|---|---|---|
| $A_1' \oplus A_2'$ | 2 | 2 | 0 | 2 | 2 | 0 |
| $A_1' \oplus E'$ | 3 | 0 | 1 | 3 | 0 | 1 |
| $E' \oplus E'$ | 4 | -2 | 0 | 4 | -2 | 0 |

## Direct product

- Direct products are expressible as direct sums of irreducible representations
- Examples in $C_{3v}$
- Important in determining the representation of a multi-electron wave function
  - Gives a means to decompose a multi-electron wave function into terms

| $C_{3v}$ | $E$ | $2\,C_3$ | $3\,\sigma_v$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 |
| $E$ | 2 | -1 | 0 |

$$E \otimes E \quad = \quad A_1 \oplus A_2 \oplus E$$

| $C_{3v}$ | $E$ | $2\,C_3$ | $3\,\sigma_v$ |
|---|---|---|---|
| $E \otimes E$ | 4 | 1 | 0 |
| $A_1 \oplus A_2 \oplus E$ | 4 | 1 | 0 |

## Definitions in group theory

- Dimension of the group ($\equiv h$)
  - Sum of squares of the characters of the identity operator
  - Number of operations in the group
- Number of elements in a class ($\equiv N_c$)
  - Number of similar operations in a class

| $C_{3v}$ | $E$ | $2\,C_3$ | $3\,\sigma_v$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 |
| $E$ | 2 | -1 | 0 |

$$h = 6$$

$$N_{C_3} = 2$$

$$N_{\sigma_v} = 3$$

## Projection operators

- Projection operator produces the number of irreducible representations in a reducible representation
  - Like dot product of a basis vector with a vector in space
  - Use projection operators to “decompose” reducible representation into irreducible components
- Mulliken symbols convenient
  - Form projection operator for an irreducible representation by multiplying the number of operations in the class times the character
  - “Normalized” by the dimension of the group

| $C_{3v}$ | $E$ | $2\,C_3$ | $3\,\sigma_v$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 |
| $E$ | 2 | -1 | 0 |

$$P_{A_1} = \frac{1}{6}(1\times1, 2\times1, 3\times1) = \frac{1}{6}(1, 2, 3)$$

$$P_{A_2} = \frac{1}{6}(1\times1, 2\times1, 3\times(-1)) = \frac{1}{6}(1, 2, -3)$$

$$P_E = \frac{1}{6}(1\times2, 2\times(-1), 3\times0) = \frac{1}{6}(2, -2, 0)$$

## Reducing a representation with projection operators

- Inner product of the projection operator with the reducible representation gives the number of representations present in the reducible representation
- Example in $C_3v$

$$E \otimes E = A_1 \oplus A_2 \oplus E$$

$$\begin{aligned} P_{A_1} \bullet (E \otimes E) &= \frac{1}{6}(1,2,3) \bullet (4,1,0) \\ &= \frac{1}{6}(1 \bullet 4 + 2 \bullet 1 + 3 \bullet 0) \\ &= \frac{6}{6} = 1 \end{aligned}$$

$$\begin{aligned} P_{A_2} \bullet (E \otimes E) &= \frac{1}{6}(1,2,-3) \bullet (4,1,0) \\ &= \frac{1}{6}(1 \bullet 4 + 2 \bullet 1 - 3 \bullet 0) \\ &= \frac{6}{6} = 1 \end{aligned}$$

$$\begin{aligned} P_{E} \bullet (E \otimes E) &= \frac{1}{6}(2,-2,0) \bullet (4,1,0) \\ &= \frac{1}{6}(2 \bullet 4 - 2 \bullet 1 + 0 \bullet 0) \\ &= \frac{6}{6} = 1 \end{aligned}$$

## Applications to $H_2O$ wave functions

- Configuration results in a direct product of one-electron wave functions
- Want multi-electron wave functions that conform to known symmetry
- Perform a direct product to find the term
- Reduce the direct product to a direct sum
  - Gives all terms arising from that configtation
- Example: ground term of $H_2O$
  - 10 electrons

Filling order

$$1a_1\ 2a_1\ 1b_2\ 3a_1\ 1b_1\ 4a_1\ 2b_2$$

$$(1a_1)^2\ (2a_1)^2\ (1b_2)^2\ (3a_1)^2\ (1b_1)^2$$

$$\begin{aligned} \Gamma &= A_1 \otimes A_1 \otimes A_1 \otimes A_1 \otimes B_2 \otimes B_2 \otimes A_1 \otimes A_1 \otimes B_1 \otimes B_1 \\ &= A_1 \end{aligned}$$

## Excited state of $H_2O$

- Find first excited state by promoting a single electron
- Consider only partially filled shells
  - Filled shells give totally symmetric representation as a product
- Spins of the two electrons may be paired or unpaired
  - Singlet
  - Triplet

$$\cdots (1b_1)^1 (4a_1)^1$$

$$\begin{aligned} \Gamma &= B_1 \otimes A_1 \\ &= B_1 \end{aligned}$$

$$^1B_1 \qquad ^3B_1$$

## Summary

- Multi-electron wave functions found as direct products of one-electron wave functions
  - Can be classified as reducible or irreducible representations
- Reducible representations can be expressed as a direct sum of irreducible representations
  - Use projection operators to determine the direct sum
- The direct sum gives the terms that arise from a configuration
- Use Pauli's principle to determine possible spin of wave functions
- Terms symbols use irreducible representations of the group