Point Groups Continued

Chapter 4

Wednesday, September 30, 2015
Identifying Point Groups

The point group of an object or molecule can be determined by following this decision tree:

See p. 81, Figure 4.7
Example: phosphorous pentafluoride

Does it belong to one of the special low- or high-symmetry point groups?
- NO.

Find the principal axis.

Does it have perpendicular $C_2$ axes?
- YES. The principal axis is a $C_3$ and there are three perpendicular $C_2$s. PF$_5$ must be $D_3$, $D_{3d}$, or $D_{3h}$. 
Example: phosphorous pentafluoride

- Does it belong to one of the special low- or high-symmetry point groups?
  - NO.

- Find the principal axis.

- Does it have perpendicular $C_2$ axes?
  - YES. The principal axis is a $C_3$ and there are three perpendicular $C_2$s. PF$_5$ must be $D_3$, $D_{3d}$, or $D_{3h}$.

- Is there a horizontal mirror plane?
  - YES. The horizontal mirror plane is defined by the phosphorous atom and the three equatorial fluorine atoms.

$D_{3h} \{ E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v \}$
Example: diborane

- Does it belong to one of the special low- or high-symmetry point groups?
  - NO.
- Find the principal axis.
- Does it have perpendicular $C_2$ axes?
  - YES. In this case the principal axis as well as the perpendicular axes are all $C_2$s. Diborane must be $D_2$, $D_{2d}$, or $D_{2h}$.
Example: diborane

- Does it belong to one of the special low- or high-symmetry point groups?
  - NO.

- Find the principal axis.

- Does it have perpendicular $C_2$ axes?
  - YES. In this case the principal axis as well as the perpendicular axes are all $C_2$s. Diborane must be $D_2$, $D_{2d}$, or $D_{2h}$.

- Is there a horizontal mirror plane?
  - YES. It turns out that there are three mirror planes. Each one is perpendicular to one $C_2$ axis.

$$D_{2h} \{E, C_2(z), C_2(y), C_2(x), i, \sigma(xy), \sigma(xz), \sigma(yz)\}$$
Example: 18-crown-6 ether

- Does it belong to one of the special low- or high-symmetry point groups?  
  - NO.
- Find the principal axis.
- Does it have perpendicular $C_2$ axes?  
  - NO.

1,4,7,10,13,16-hexaoxacyclooctadecane
Example: 18-crown-6 ether

- Does it belong to one of the special low- or high-symmetry point groups?
  - NO.

- Find the principal axis.

- Does it have perpendicular $C_2$ axes?
  - NO.

- Is there a horizontal mirror plane?
  - NO, but there are vertical and dihedral mirror planes. The vertical mirror planes contain two O atoms and are parallel to the $C_6$ axis. The dihedral mirror planes bisect opposite C–C bonds and are parallel to the $C_6$ axis.

$$C_{6v} \{E, 2C_6, 2C_3, C_2, 3\sigma_v, 3\sigma_d\}$$
Self Test

Use the decision tree (if needed) to determine the point groups of the following four molecules.

- $D_{2d}$
- $C_s$
- $C_{2h}$
- $C_{4v}$
Point group of a baseball?

\[ D_{2d} \{ E, 2S_4, C_2, 2C_2', 2\sigma_d \} \]
Point groups of atomic orbitals?

$C_{\infty v}$

$D_{2h}$

$T_d$
Properties of Mathematical Groups

A point group is an example of an algebraic structure called a group, a collection of elements that obey certain algebraic rules.

The four key rules that define a group are:

1. Each group contains an identity operation that commutes with all other members of the group and leaves them unchanged (i.e., \( EA = AE = A \)).*

2. Each operation has an **inverse** operation that yields the identity when multiplied together. For example, in \( C_{3v} \{E, 2C_3, 3\sigma_v\} \):
   \[
   \sigma_v \sigma_v = E \quad \text{and} \quad C_3 C_3^2 = E.
   \]

3. The product of any two operations in the group must also be a member of the group. For example, in \( C_{4v} \{E, 2C_4, C_2, 2\sigma_v, 2\sigma_d\} \):
   \[
   C_4 C_4 = C_2, \quad C_4 \sigma_v = \sigma_d, \quad \sigma_d \sigma_v = C_4, \quad \text{etc.}
   \]

4. The associative law of multiplication holds, i.e., \( A(BC) = (AB)C \).

*Note that we operate (multiply) from right to left, as with matrices