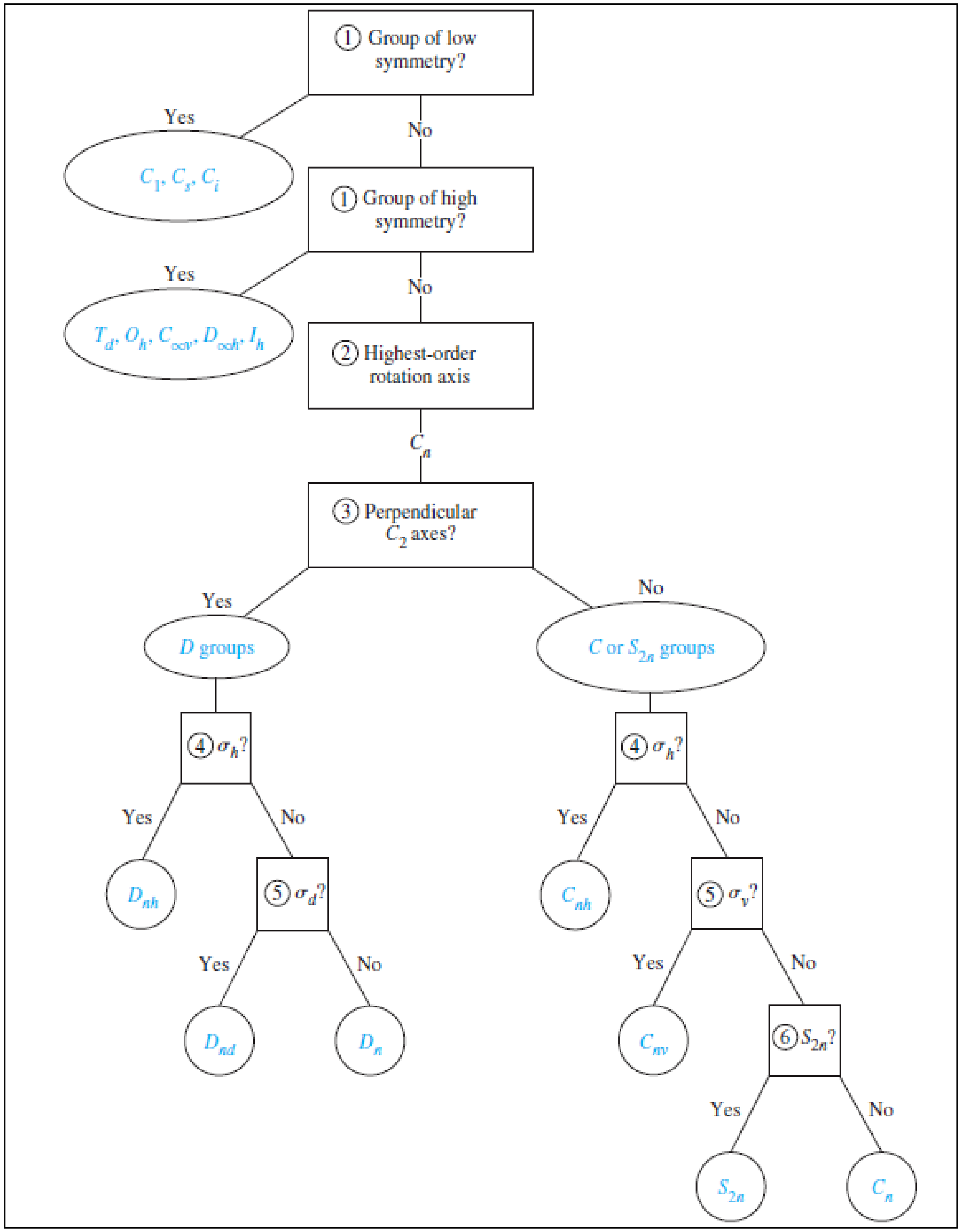
Point Groups Continued

Chapter 4

Wednesday, September 30, 2015

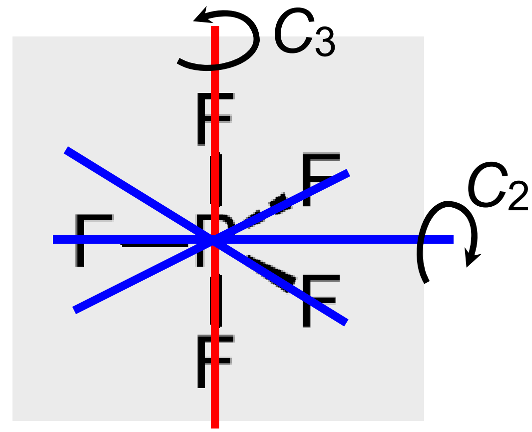
Identifying Point Groups

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



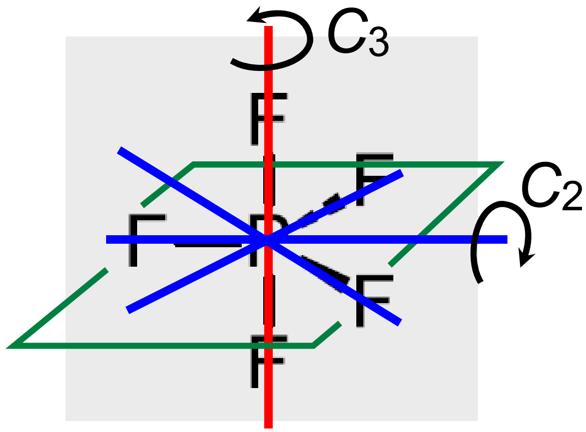
See p. 81, Figure 4.7

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_2s. PF_5 must be D_3, D_{3d}, or D_{3h}.**

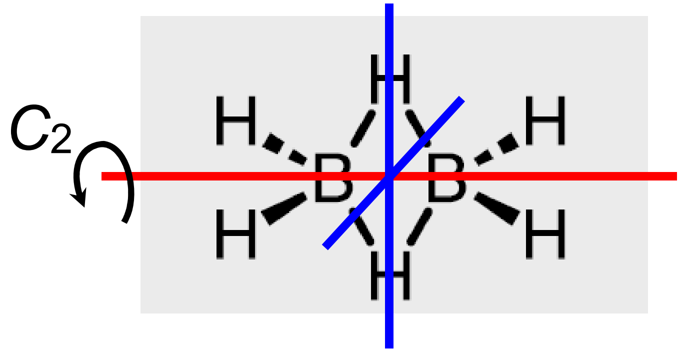
Example: phosphorous pentafluoride



- **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_2s. 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.**

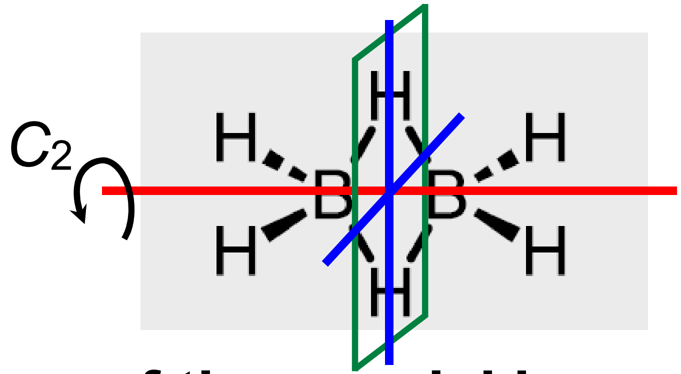
$\boldsymbol{D_{3h}}$ $\{E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v\}$

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_2s. Diborane must be D_2, D_{2d}, or D_{2h}.**

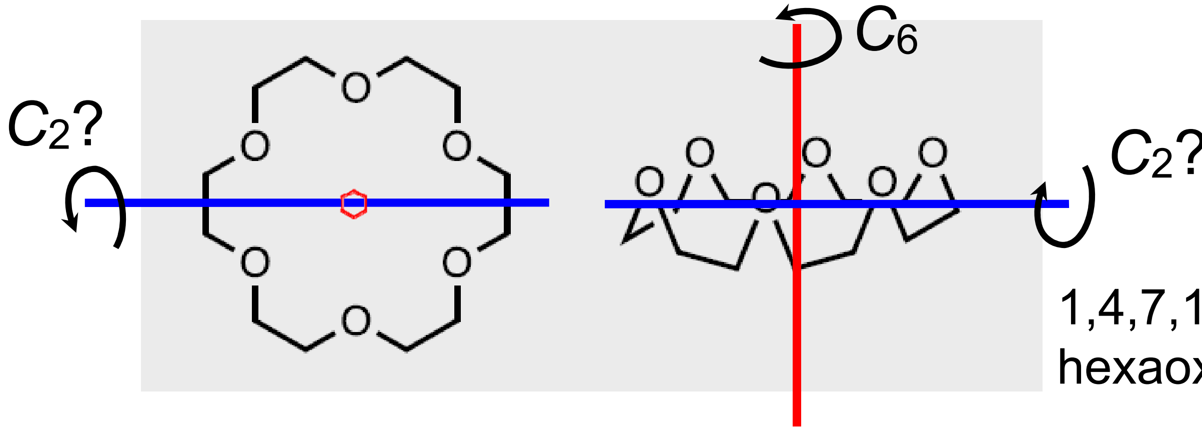
Example: diborane



- **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_2s. 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, $\sigma(xy)$, $\sigma(xz)$, $\sigma(yz)$}

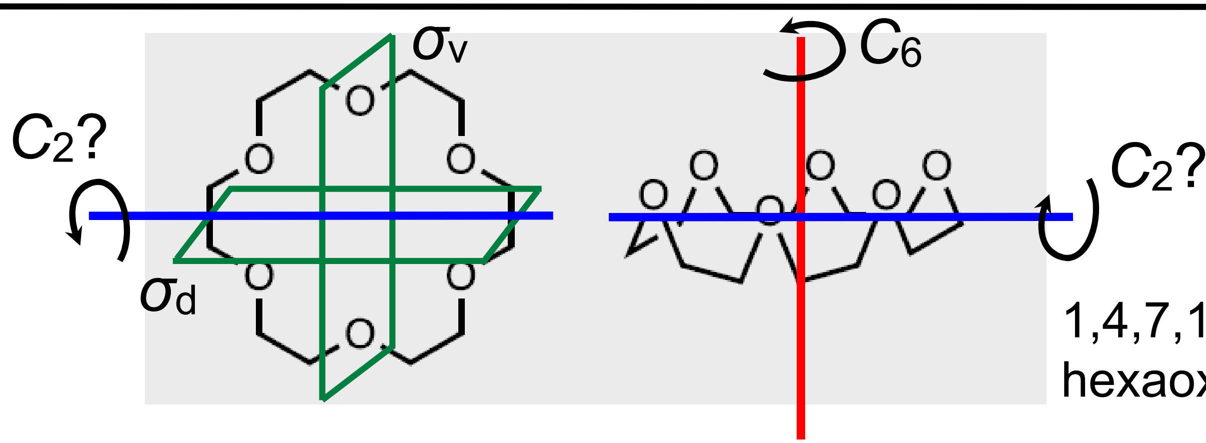
Example: 18-crown-6 ether



1,4,7,10,13,16-
hexaoxacyclooctadecane

- **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.**

Example: 18-crown-6 ether



1,4,7,10,13,16-hexaoxacyclooctadecane

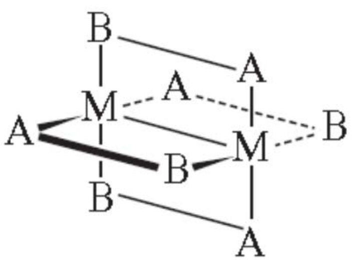
- **Does it belong to one of the special low- or high-symmetry point groups?**
  - **NO.**
- **Find the principal axis.**
- **Does it have perpendicular C_2 axes?**
  - **NO.**
- **Is there a horizontal mirror plane?**
  - **NO, but there are vertical and dihedral mirror planes. The vertical mirror planes 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.**

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

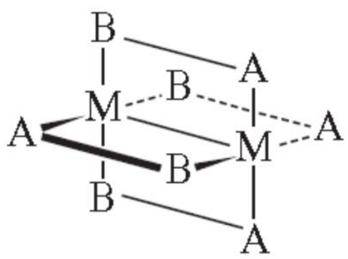
Self Test

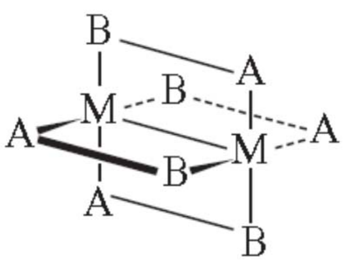
Use the decision tree (if needed) to determine the point groups of the following four molecules.

D_{2d}

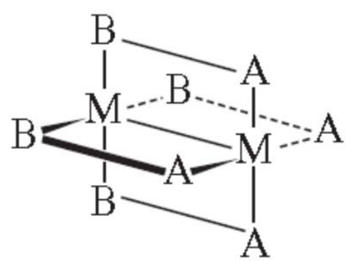


C_s

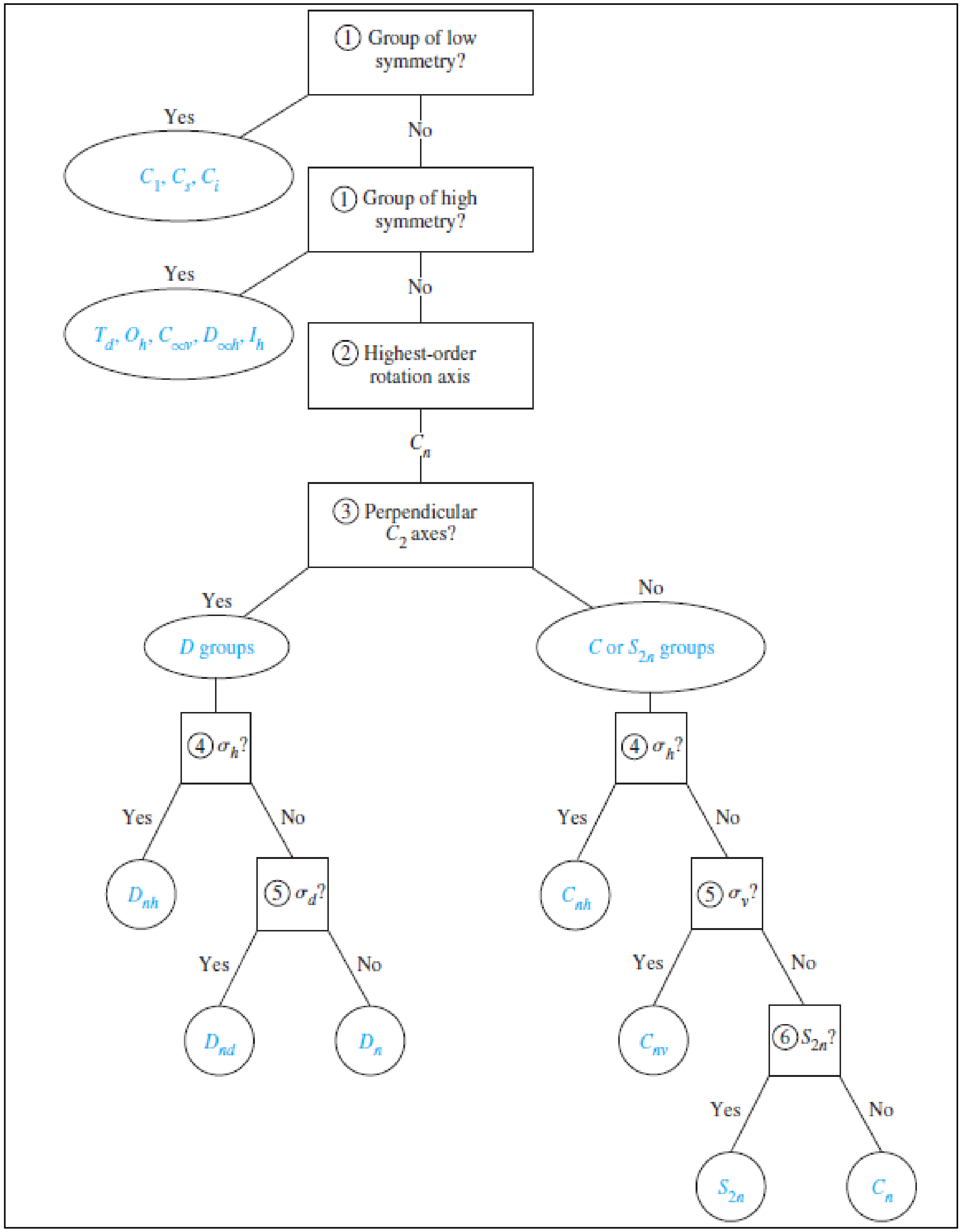




C_{2h}

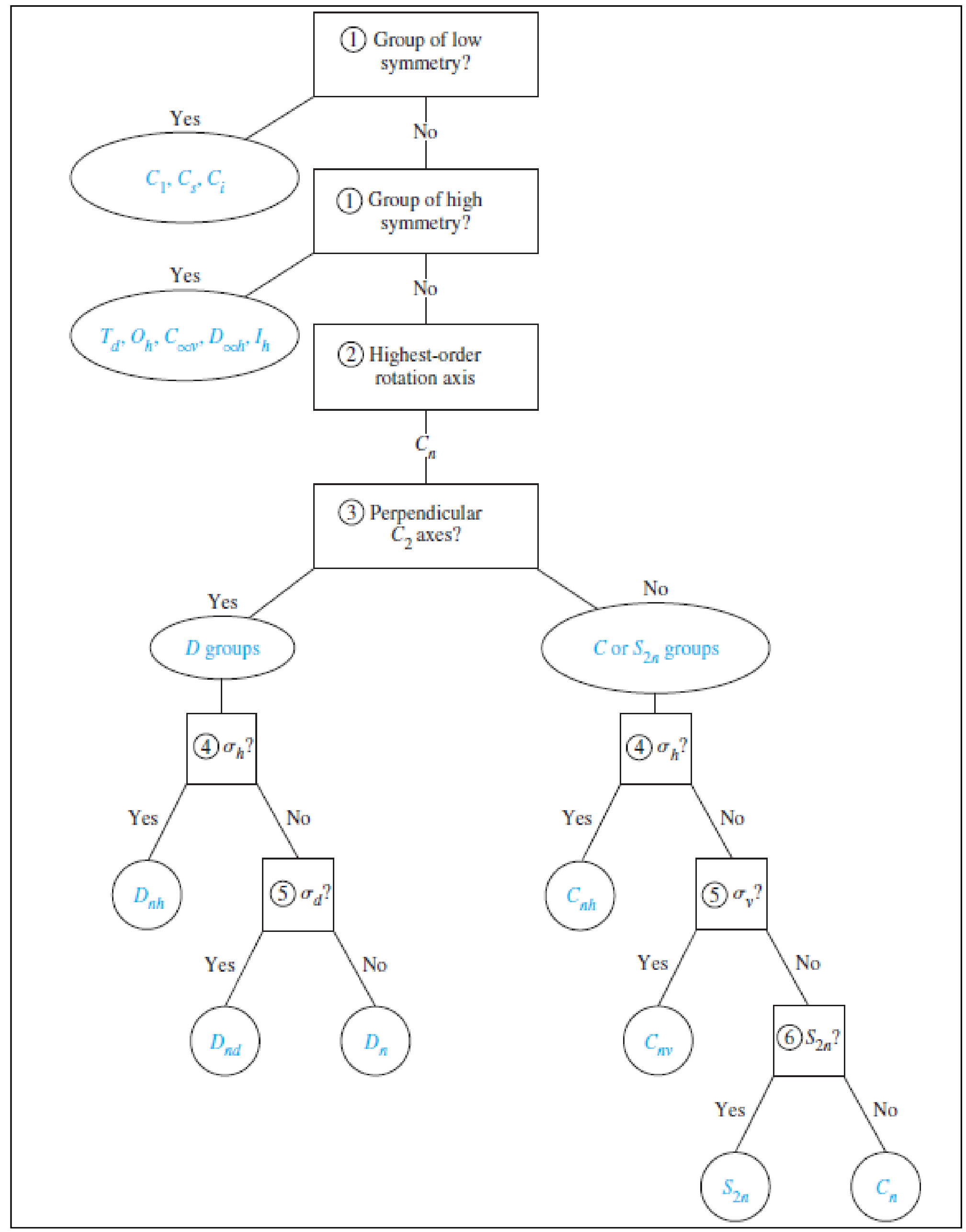


C_{4v}

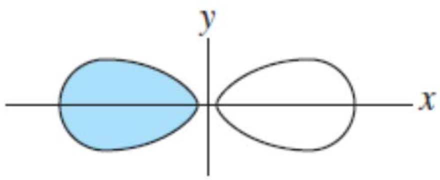


Point group of a baseball?

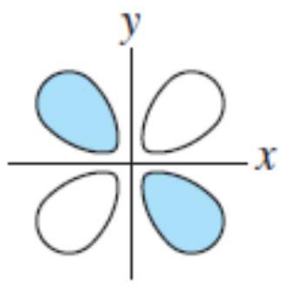
D_{2d} $\{E, 2S_4, C_2, 2C_2', 2\sigma_d\}$



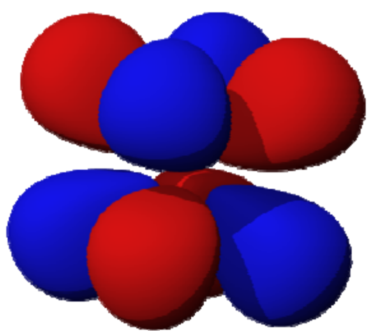
Point groups of atomic orbitals?



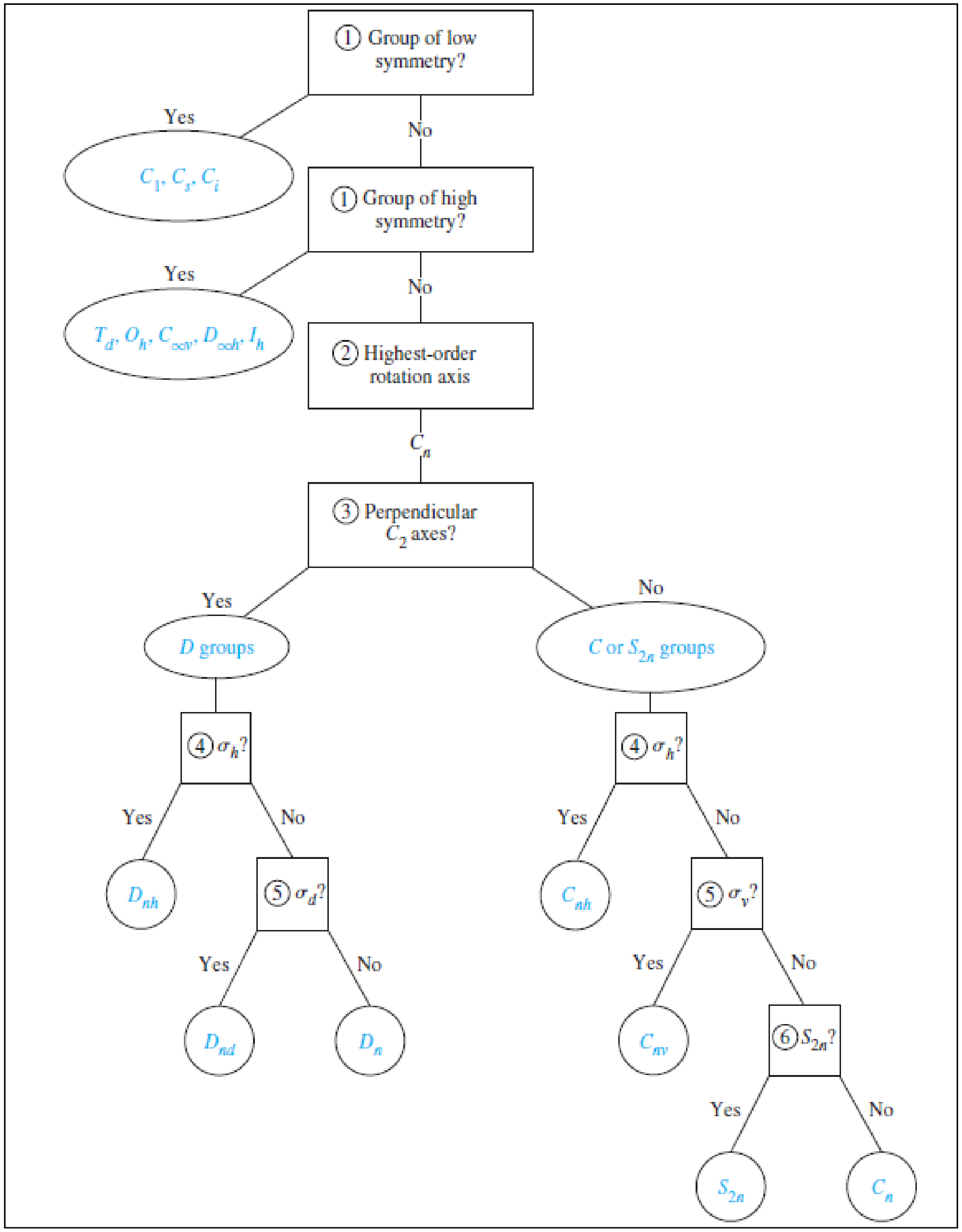
$C_{\infty v}$



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} $\{E, 2C_3, 3\sigma_v\}$:

$$\sigma_v\sigma_v = E \text{ and } C_3C_3^2 = E.$$

3. The product of any two operations in the group must also be a member of the group. For example, in C_{4v} $\{E, 2C_4, C_2, 2\sigma_v, 2\sigma_d\}$:

$$C_4C_4 = C_2 \text{ , } C_4\sigma_v = \sigma_d \text{ , } \sigma_d\sigma_v = C_4 \text{ , etc.}$$

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*