Lecture 16 — Symmetry Elements, Symmetry Operations & Point Groups

Reading: Engel 4th ed., Chapter 16 (Sections 16.1–16.3)

Learning Objectives

- Define symmetry elements and symmetry operations and distinguish between them
- Identify the five types of symmetry operations in molecules
- Apply a systematic procedure to assign a molecule to its point group
- Recognize common point groups and associate them with familiar molecules

1. Symmetry Elements and Symmetry Operations

A **symmetry operation** is a geometric transformation that leaves a molecule indistinguishable from its original configuration (though individual atoms may be permuted).

A **symmetry element** is the geometric entity (point, axis, or plane) about which the symmetry operation is performed.

Symmetry Element	Symbol	Operation	Description
Identity	E	Do nothing	Every molecule has this
Proper rotation axis	C_n	Rotation by $360°/n$	n-fold rotation axis
Mirror plane	σ	Reflection	σ_v (vertical), σ_h (horizontal), σ_d (dihedral)
Inversion center	i	Inversion through center	$(x, y, z) \rightarrow (-x, -y, -z)$
Improper rotation axis	S_n	Rotation by $360°/n$ + reflection through $\perp$ plane	Combined operation

> [!NOTE] **Concept Check 16.1** Explain the difference between a symmetry operation and a symmetry element. For example, in a water molecule, what is the symmetry element and what is the corresponding operation?

2. Detailed Look at Each Operation

Identity (E)

Every molecule possesses the identity element. It serves as the "do nothing" operation, analogous to multiplying by 1 or adding 0.

Proper Rotation (C_n)

Rotation by $360°/n$ about an axis. The axis with the highest n is the **principal axis**.

Examples:

- **H₂O**: C_2 axis (bisects the H–O–H angle)
- **NH₃**: C_3 axis (along the N and the center of the H triangle)
- **BF₃**: C_3 (principal) and three C_2 axes
- **Benzene**: C_6 (principal), six C_2 axes

Note: C_n generates operations $C_n^1, C_n^2, \ldots, C_n^{n-1}, C_n^n = E$.

Mirror Planes (σ)

- σ_v **(vertical)**: Contains the principal axis
- σ_h **(horizontal)**: Perpendicular to the principal axis
- σ_d **(dihedral)**: Contains the principal axis and bisects two C_2 axes

Examples:

- H₂O has two σ_v planes (the molecular plane and the perpendicular plane through O)
- BF₃ has one σ_h (the molecular plane) and three σ_v

Inversion (i)

Every point (x, y, z) is mapped to $(-x, -y, -z)$ through a center of symmetry.

Has i: SF$_6$, benzene, ethane (staggered), CO$_2$ **Lacks** i: H$_2$O, NH$_3$, CH$_4$, CHCl$_3$

Improper Rotation (S_n)
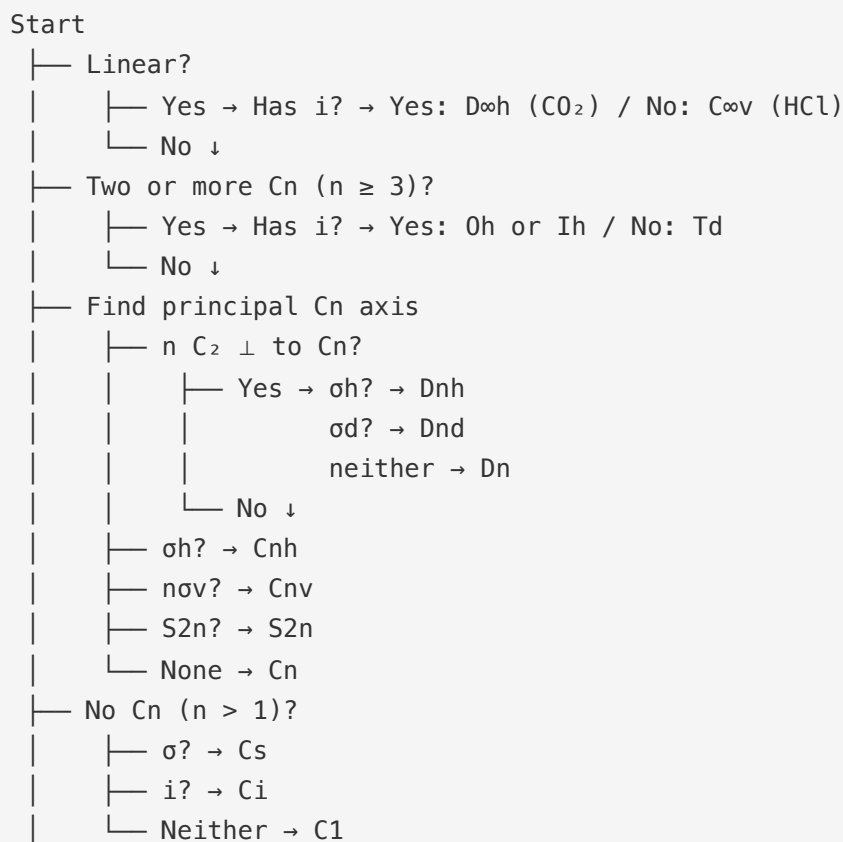
$S_n = \sigma_h \times C_n$ (rotate by $360°/n$, then reflect through the perpendicular plane).

- $S_1 = \sigma$ (just a reflection)
- $S_2 = i$ (inversion)
- **CH$_4$** has three S_4 axes (but no C_4 or σ_h individually!)

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3. Point Group Classification

A **point group** is the complete set of symmetry operations for a molecule. It is called a "point" group because at least one point (the center of mass) is unmoved by every operation.

Systematic Flowchart for Assigning Point Groups

```
Start
 ├── Linear?
 │     ├── Yes → Has i? → Yes: D∞h (CO₂) / No: C∞v (HCl)
 │     └── No ↓
 ├── Two or more Cn (n ≥ 3)?
 │     ├── Yes → Has i? → Yes: Oh or Ih / No: Td
 │     └── No ↓
 ├── Find principal Cn axis
 │     ├── n C₂ ⊥ to Cn?
 │     │     ├── Yes → σh? → Dnh
 │     │     |          σd? → Dnd
 │     │     |          neither → Dn
 │     │     └── No ↓
 │     ├── σh? → Cnh
 │     ├── nσv? → Cnv
 │     ├── S2n? → S2n
 │     └── None → Cn
 ├── No Cn (n > 1)?
 │     ├── σ? → Cs
 │     ├── i? → Ci
 │     └── Neither → C1
```

Common Point Groups with Examples

Point Group	Key Features	Example Molecules
C_1	No symmetry except E	CHFClBr
C_s	Only a mirror plane	HOCl
C_i	Only inversion	meso-tartaric acid
C_{2v}	$C_2 + 2\sigma_v$	H_2O, CH_2Cl_2, pyridine
C_{3v}	$C_3 + 3\sigma_v$	NH_3, $CHCl_3$, $POCl_3$
$C_{\infty v}$	Linear, no i	HCl, HCN, CO, NO
D_{2h}	Three $C_2 + \sigma_h + 2\sigma_v$	C_2H_4 (ethylene), naphthalene
D_{3h}	$C_3 + 3C_2 + \sigma_h$	BF_3, PCl_5 (eq), CO_3^{2-}
D_{6h}	$C_6 + 6C_2 + \sigma_h$	Benzene
$D_{\infty h}$	Linear, has i	CO_2, N_2, C_2H_2
T_d	Tetrahedral	CH_4, CCl_4, SiH_4
O_h	Octahedral	SF_6, $[Fe(CN)_6]^{4-}$

> [!NOTE] **Concept Check 16.2** Following the point group flowchart, why does water (H_2O) belong to the C_{2v} point group while ammonia (NH_3) belongs to C_{3v}? What specific symmetry element differs between them?

4. Why Symmetry Matters in Chemistry

We will use point groups in the coming weeks to:

1. **Classify molecular vibrations** (Week 7): Determine normal modes and their symmetry species using character tables
2. **Predict IR and Raman activity** (Week 8): A vibration is IR active only if it belongs to the same symmetry species as x, y, or z (translational functions in the character table)
3. **Construct molecular orbitals** (Weeks 11–13): Only atomic orbitals of the same symmetry species can combine

4. **Determine selection rules** for electronic transitions (Week 13): Only transitions with nonzero transition dipole moment are allowed

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Key Equations Summary

Concept	Expression
C_n^k	Rotation by $k \times 360°/n$
S_n	$\sigma_h \circ C_n$
$S_1 = \sigma$, $S_2 = i$	Special cases
Order of group	Total number of symmetry operations

Recent Literature Spotlight

"MolSym: A Python Package for Handling Symmetry in Molecular Quantum Chemistry" *S. M. Goodlett, N. L. Kitzmiller, J. M. Turney, H. F. Schaefer III*, Journal of Chemical Physics, **2024**, 161, 012501. DOI

This paper introduces MolSym, a Python package that automates molecular symmetry analysis for quantum chemistry calculations. The software identifies point groups, generates symmetry-adapted linear combinations of basis functions, and constructs character tables — tasks that are central to the group theory taught in this lecture and that underpin modern computational chemistry.

Practice Problems

1. **Identify operations.** List all symmetry elements and operations for (a) H_2O, (b) NH_3, (c) BF_3, (d) CH_4, (e) benzene.

2. **Point group assignment.** Assign the following molecules to their point groups: (a) $CHCl_3$, (b) trans-1,2-dichloroethylene, (c) allene ($H_2C=C=CH_2$), (d) SF_6, (e) ferrocene (staggered).

3. **Inversion.** For each molecule in Problem 2, determine whether it has an inversion center. Which of these molecules are optically active (chiral)?