

Lecture 18 — Applications: Reducible Representations & the Reduction Formula

Reading: Engel 4th ed., Chapter 16 (Sections 16.7–16.9)

Learning Objectives

- Construct reducible representations for sets of basis functions (bonds, orbitals, coordinates)
 - Apply the reduction formula to decompose reducible representations into irreps
 - Use group theory to classify molecular vibrations by symmetry
 - Predict IR and Raman activity using symmetry selection rules
 - Determine which atomic orbitals can combine to form molecular orbitals
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1. The Reduction Formula

Any reducible representation Γ can be written as a sum of irreducible representations:

$$\Gamma = \sum_i n_i \Gamma_i$$

where n_i is the number of times irrep Γ_i appears. The coefficients are found using:

$$n_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

where:

- h = order of the group
- $\chi(R)$ = character of the reducible representation for operation R
- $\chi_i(R)$ = character of irrep Γ_i for operation R
- Sum is over all operations R (or over classes, multiplied by the number of operations in each class)

[!NOTE] **Concept Check 18.1** Why is the reduction formula essential for analyzing complex molecules in quantum chemistry? How does it help us relate a large set of basis functions (like $3N$ displacements) back to the fundamental symmetry properties of the point group?

Using Classes

$$n_i = \frac{1}{h} \sum_{\text{classes}} N_c \chi(C) \chi_i(C)$$

where N_c is the number of operations in class C .

2. Worked Example: Classifying Vibrations of H₂O

Step 1: Identify the Point Group

H₂O belongs to C_{2v} ($h = 4$).

Step 2: Construct the Reducible Representation

Use the $3N$ Cartesian displacement vectors as the basis set. For H₂O ($N = 3$ atoms), we have $3 \times 3 = 9$ basis vectors.

The character $\chi(R)$ for each operation equals the number of atoms **unmoved** by R , multiplied by the contribution per unmoved atom:

Operation	Contribution per unmoved atom
E	+3
C_n	$1 + 2 \cos(360^\circ/n)$
σ	+1
i	−3
S_n	$-1 + 2 \cos(360^\circ/n)$

For H₂O:

	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Unmoved atoms	3	1	1	3
Contribution/atom	3	-1	1	1
χ_{total}	9	-1	1	3

Step 3: Apply the Reduction Formula

$$n_{A_1} = \frac{1}{4}[9(1) + (-1)(1) + 1(1) + 3(1)] = \frac{12}{4} = 3$$

$$n_{A_2} = \frac{1}{4}[9(1) + (-1)(1) + 1(-1) + 3(-1)] = \frac{4}{4} = 1$$

$$n_{B_1} = \frac{1}{4}[9(1) + (-1)(-1) + 1(1) + 3(-1)] = \frac{8}{4} = 2$$

$$n_{B_2} = \frac{1}{4}[9(1) + (-1)(-1) + 1(-1) + 3(1)] = \frac{12}{4} = 3$$

$$\Gamma_{\text{total}} = 3A_1 + A_2 + 2B_1 + 3B_2$$

Step 4: Subtract Translations and Rotations

From the character table:

- Translations: $A_1(z) + B_1(x) + B_2(y)$
- Rotations: $A_2(R_z) + B_1(R_y) + B_2(R_x)$

$$\Gamma_{\text{vib}} = \Gamma_{\text{total}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$$

$$\Gamma_{\text{vib}} = (3A_1 + A_2 + 2B_1 + 3B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2)$$

$$\boxed{\Gamma_{\text{vib}} = 2A_1 + B_2}$$

H₂O has **3 normal modes**: two of A_1 symmetry (symmetric stretch and bend) and one of B_2 symmetry (asymmetric stretch).

3. Selection Rules from Symmetry

Infrared (IR) Activity

A vibration is **IR active** if it belongs to the same symmetry species as one of the translational functions (x , y , or z) in the character table.

For H_2O (C_{2v}):

- A_1 : z is listed \rightarrow **IR active** ✓
- B_2 : y is listed \rightarrow **IR active** ✓

All three modes of H_2O are IR active.

Raman Activity

A vibration is **Raman active** if it belongs to the same symmetry species as one of the quadratic functions ($x^2, y^2, z^2, xy, xz, yz$) in the character table.

For H_2O :

- A_1 : $x^2, y^2, z^2 \rightarrow$ **Raman active** ✓
- B_2 : $yz \rightarrow$ **Raman active** ✓

The Mutual Exclusion Rule

In a molecule with an **inversion center** (i), no vibration can be both IR active and Raman active.

This is because in centrosymmetric molecules:

- IR-active modes are u (ungerade)
- Raman-active modes are g (gerade)
- No mode can be both g and u

Example: CO_2 ($D_{\infty h}$) — the symmetric stretch is Raman active only; the asymmetric stretch and bends are IR active only.

[!NOTE] **Concept Check 18.2** The mutual exclusion rule states that for molecules with an inversion center, a vibration cannot be both IR active and Raman active. Explain the physical reason for this in terms of the "ungerade" (u) and "gerade" (g) symmetries.

4. Group Theory and Molecular Orbitals (Preview)

Symmetry-Adapted Linear Combinations (SALCs)

Group theory determines which combinations of atomic orbitals transform as each irrep. Only orbitals of the **same symmetry species** can mix to form molecular orbitals.

Projection Operator

The projection operator generates SALCs from a basis function ϕ :

$$\hat{P}_i \phi = \frac{1}{h} \sum_R \chi_i(R) R \phi$$

Example: For H₂O, the two H 1s orbitals generate:

- A_1 : $\phi_{1s,A} + \phi_{1s,B}$ (in-phase, symmetric)
- B_2 : $\phi_{1s,A} - \phi_{1s,B}$ (out-of-phase, antisymmetric)

These SALCs combine with O orbitals of matching symmetry to form MOs.

5. Optical Activity and Symmetry

A molecule is **optically active (chiral)** if and only if it lacks:

- Any S_n axis (including $S_1 = \sigma$ and $S_2 = i$)

Equivalently, a molecule is chiral if its point group contains **only proper rotations** (C_n) and the identity (E).

Chiral point groups: C_1, C_n, D_n, T, O, I

Key Equations Summary

Equation	Expression
Reduction formula	$n_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$
Vibrational modes	$\Gamma_{\text{vib}} = \Gamma_{\text{total}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$
Number of vibrational modes	$3N - 6$ (nonlinear), $3N - 5$ (linear)
IR activity	Mode symmetry = translation symmetry

Equation	Expression
Raman activity	Mode symmetry = quadratic function symmetry
Projection operator	$\hat{P}_i \phi = \frac{l_i}{h} \sum_R \chi_i(R) R \phi$

Recent Literature Spotlight

"Nature of the Charge Density Wave in Kagome Metal CsV₃Sb₅" H. Zhao, H. Li, B. R. Ortiz, S. M. L. Teicher, T. Park, *et al.*, Physical Review X, **2023**, 13, 011032. [DOI](#)

This study reveals how molecular orbital symmetry governs the electronic ordering in the kagome metal CsV₃Sb₅. Using scanning tunneling microscopy, the authors show that charge density waves form through symmetry-driven trimerization of vanadium d-orbitals — a macroscopic quantum phenomenon that directly reflects the MO symmetry principles taught in this lecture.

Practice Problems

- NH₃ vibrations.** Using the C_{3v} character table, determine the symmetry species of the vibrational modes of NH₃. How many modes are IR active? Raman active?
 - CO₂ modes.** CO₂ is linear ($D_{\infty h}$). It has $3(3) - 5 = 4$ vibrational modes. Using symmetry arguments, predict which modes are IR active and which are Raman active. Verify the mutual exclusion rule.
 - SALCs.** For BF₃ (D_{3h}), use the projection operator to construct the symmetry-adapted linear combinations of the three F $2p_z$ orbitals (perpendicular to the molecular plane). What symmetry species do they belong to?
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Next week: Vibration and Rotation of Molecules (using group theory!)