Lecture 21 — The Rigid Rotor Model

Reading: Engel 4th ed., Chapter 7 (Sections 7.6–7.8)

Learning Objectives

- Solve the Schrödinger equation for the rigid rotor (particle on a sphere)
- Identify the quantum numbers J and m_J and their physical meaning
- Describe the spherical harmonics and their connection to angular momentum
- Calculate rotational energy levels and degeneracies
- Relate moment of inertia, bond length, and rotational constant

1. The Classical Rigid Rotor

Two atoms of masses m_1 and m_2 separated by a fixed distance r_e (bond length), rotating about their center of mass.

Moment of inertia:

$$I = \mu r_e^2$$

Classical rotational energy:

$$E_{\text{rot}} = \frac{L^2}{2I}$$

where L is the angular momentum.

> [!NOTE] **Concept Check 21.1** If the bond length of a rotating diatomic molecule increases by 10% (while the masses stay the same), by what percentage does the moment of inertia I change? How does this affect the rotational energy levels?

2. The Quantum Rigid Rotor — Schrödinger Equation

In spherical coordinates, the rigid rotor Hamiltonian involves only angular variables (θ, ϕ):

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

This is equivalent to:

$$\hat{H} = \frac{\hat{L}^2}{2I}$$

where $\hat{L}^2$ is the angular momentum squared operator.

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3. Spherical Harmonics — Solutions

The eigenfunctions are the **spherical harmonics** $Y_J^{m_J}(\theta, \phi)$:

$$\hat{H}\,Y_J^{m_J}(\theta, \phi) = E_J\,Y_J^{m_J}(\theta, \phi)$$

Energy Levels

$$E_J = \frac{\hbar^2}{2I}J(J+1) = BhcJ(J+1), \quad J = 0, 1, 2, \ldots$$

where the **rotational constant** is:

$$B = \frac{\hbar}{4\pi cI} = \frac{h}{8\pi^2 cI} \quad (\text{in cm}^{-1})$$

Quantum Numbers

Quantum Number	Symbol	Range	Physical Meaning
Rotational	J	$0, 1, 2, \ldots$	Total angular momentum: $\|L\| = \hbar\sqrt{J(J+1)}$
Magnetic	m_J	$-J, \ldots, 0, \ldots, +J$	z-component: $L_z = m_J\hbar$

Degeneracy

Each level J has $(2J+1)$ degenerate states (different m_J values):

$$g_J = 2J + 1$$

This degeneracy reflects the **spherical symmetry** — the energy doesn't depend on the orientation of the angular momentum.

4. Angular Momentum

Operators and Eigenvalues

$$\hat{L}^2\, Y_J^{m_J} = \hbar^2 J(J+1)\, Y_J^{m_J}$$

$$\hat{L}_z\, Y_J^{m_J} = m_J \hbar\, Y_J^{m_J}$$

$\hat{L}^2$ and $\hat{L}_z$ **commute**: $[\hat{L}^2, \hat{L}_z] = 0 \to$ They share eigenfunctions and can be simultaneously specified.

But: $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ (and cyclic permutations) $\to$ Only one component of $\vec{L}$ can be known along with L^2.

Space Quantization

The angular momentum vector $\vec{L}$ has:

- Fixed magnitude: $|\vec{L}| = \hbar\sqrt{J(J+1)}$
- Fixed z-component: $L_z = m_J\hbar$

But L_x and L_y are **uncertain** — the angular momentum vector precesses around the z-axis on a cone.

> [!NOTE] **Concept Check 21.2** For a rigid rotor in the state $J = 1$, what are the possible values of the z-component of angular momentum (L_z)? What is the total magnitude of the angular momentum vector $|\vec{L}|$ in this state?

5. The First Few Spherical Harmonics

J	m_J	$Y_J^{m_J}(\theta, \phi)$
0	0	$\frac{1}{\sqrt{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	±1	$\mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$

J	m_J	$Y_J^{m_J}(\theta, \phi)$
2	0	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$

These same functions appear as the angular parts of atomic orbitals:

- $J = 0 \rightarrow s$ orbitals (spherically symmetric)
- $J = 1 \rightarrow p$ orbitals
- $J = 2 \rightarrow d$ orbitals

Symmetry of Spherical Harmonics

In the full rotation group R_3, spherical harmonics with quantum number J transform as the irreducible representation of dimension $2J + 1$. Under specific point groups:

- $Y_1^0 \sim z$ (transforms like p_z)
- $Y_1^{\pm 1} \sim (x \pm iy)$ (transforms like p_x, p_y)

6. Rotational Constants and Bond Lengths

$$B = \frac{h}{8\pi^2 c\mu r_e^2}$$

Measuring B from the rotational spectrum gives the **bond length** r_e directly:

$$r_e = \sqrt{\frac{h}{8\pi^2 c\mu B}}$$

Molecule	B (cm⁻¹)	r_e (pm)
HCl	10.59	127.5
HBr	8.46	141.4
CO	1.931	112.8
N_2	2.010	109.8

7. Energy Level Spacing

$$E_J - E_{J-1} = 2BhcJ$$

The spacing increases linearly with J:

- $J = 0 \to 1$: gap = $2Bhc$
- $J = 1 \to 2$: gap = $4Bhc$
- $J = 2 \to 3$: gap = $6Bhc$

This contrasts with the harmonic oscillator (constant spacing) and the particle in a box (quadratic spacing).

Key Equations Summary

Equation	Expression
Moment of inertia	$I = \mu r_e^2$
Rotational energies	$E_J = BhcJ(J+1)$
Rotational constant	$B = h/(8\pi^2 cI)$
Angular momentum	$\|L\| = \hbar\sqrt{J(J+1)}$
z-component	$L_z = m_J\hbar$
Degeneracy	$g_J = 2J+1$
Level spacing	$\Delta E = 2BhcJ$

Recent Literature Spotlight

"Rotational-State-Selected Carbon Astrochemistry" *J. Toscano*, Chimia, **2024**, 78, 40–44. DOI

This review describes how state-selected molecular beams, prepared in individual rotational quantum states $|J, M_J\rangle$, are used to study carbon-bearing reactions relevant to astrochemistry. By controlling the rotational angular momentum of reactant molecules, chemists can probe how quantized angular momentum influences reaction dynamics — a direct application of the rigid rotor energy levels taught in this lecture.

Practice Problems

1. **Bond length.** The rotational constant of ¹²C¹⁶O is $B = 1.931$ cm⁻¹. Calculate the bond length.

2. **Energy levels.** Calculate the energies (in cm⁻¹) of the first five rotational levels ($J = 0$ to 4) of HCl. What are the frequencies (in GHz) of the $J = 0 \rightarrow 1$ and $J = 3 \rightarrow 4$ transitions?

3. **Degeneracy and populations.** At 300 K, calculate the ratio of the population in $J = 1$ to $J = 0$ for HCl, including the degeneracy factor. Use the Boltzmann distribution: $N_J/N_0 = (2J + 1)\exp[-E_J/(k_B T)]$.

Next week: Vibrational and Rotational Spectroscopy of Diatomic Molecules