

7.7: Overview of the Rigid Rotor

We found that the rotational wavefunctions are functions called the Spherical Harmonics, and that these functions are products of [Associated Legendre Functions](#) and the $e^{im}\varphi$ function. Two quantum numbers, J and m_J , are associated with the rotational motion of a diatomic molecule. The quantum numbers identify or specify the particular functions that describe particular rotational states. The functions are written as

$$\psi_{J,m_J}(\theta, \varphi) = Y_{J,m_J}(\theta, \varphi) = \Theta_J^{|m_J|}(\theta)\Phi_{m_J}(\varphi) \quad (7.7.1)$$

The absolute square of the wavefunction evaluated at a particular (θ, φ) gives the probability density for finding the internuclear axis aligned at these angles.

Constraints on the wavefunctions arose from boundary conditions, the requirement that the functions be single valued, and the interpretation of the functions as probability amplitudes. The Spherical Harmonic functions for the rigid rotor have these necessary properties only when $|m_J| \leq J$ and m_J is an integer. J is the upper limit to the value of m_J , but there is no upper limit to the value for J . The subscript J is added to m_J as a reminder that J controls the allowed range of m_J .

The angular momentum of a rotating diatomic molecule is quantized by the same constraints that quantize the energy of a rotating system. As summarized in the table below, the rotational angular momentum quantum number, J , specifies both the energy and the square of the angular momentum. The z -component of the angular momentum is specified by m_J .

Rotational spectra consist of multiple lines spaced nearly equally apart because many rotational levels are populated at room temperature and the rotational energy level spacing increases by approximately $2B$ with each increase in J . The rotational constant, B , can be used to calculate the bond length of a diatomic molecule. The spectroscopic selection rules for rotation, shown in the Overview table, allow transitions between neighboring J states with the constraint that m_J change by 0 or 1 unit. Additionally, the molecule must have a non-zero dipole moment in order to move from one state to another by interacting with electromagnetic radiation. The factors that interact to control the line intensities in rotational spectra (γ_{max}) include the magnitude of the transition moment, μ_T , and the population difference between the initial and final states involved in the transition, Δn .

So far you have seen three different quantum mechanical models (the particle-in-a-box, the harmonic oscillator, and the rigid rotor) that can be used to describe chemically interesting phenomena (absorption of light by cyanine dye molecules, the vibration of molecules to determine bond force constants, and the rotation of molecules to determine bond lengths). For these cases, you should remember the chemical problem, the form of the Hamiltonian, and the characteristics of the wavefunctions (i.e. the names of the functions, and their mathematical and graphical forms). Also remember the associated energy level structure, values for the quantum numbers, and selection rules for electric-dipole transitions.

As we shall see in the following chapter, the selection rules for the rigid rotor also apply to the hydrogen atom and other atoms because the atomic wavefunctions include the same spherical harmonic angular functions, eigenfunctions of the angular momentum operators \hat{M}^2 and \hat{M}_z . The selection rules result from transition moment integrals that involve the same angular wavefunctions and therefore are the same for rotational transitions in diatomic molecules and electronic transitions in atoms.

Exercise 7.7.1

Complete the table below. For an example of a completed table, see [Chapter 4](#).

Overview of key concepts and equations for the Rigid Rotor

- Potential energy
- Hamiltonian
- Wavefunctions
- Quantum Numbers
- Energies
- Spectroscopic Selection Rules
- Angular Momentum Properties

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