

# Quantum Mechanics: Vibration and Rotation of Molecules

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## I. The Rigid Rotor and Q. M. Orbital Angular Momentum

Consider a **rigid** rotating *diatomic* molecule — the rigid rotor — with two masses separated by a distance  $r_o$ ; the distance is fixed, and the rotation occurs in the absence of external potentials. The quantum mechanical description begins with the Hamiltonian:

$$\hat{H} = \hat{K} + V(x, y, z) = \frac{-\hbar^2}{2\mu} \nabla^2 + 0$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

This is simply the kinetic energy operator as we have seen in the past for the particle-in-box and the harmonic oscillator. Now, we can change coordinate systems from Cartesian to polar spherical coordinates. This goes as:

$$\text{Cartesian}(x, y, z) \quad \rightarrow \quad \text{sphericalpolar}(r, \theta, \phi)$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Thus, in spherical polar coordinates,  $\hat{H}(r, \theta, \phi)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$  becomes:

$$\left[ \frac{-\hbar^2}{2\mu} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

For the **rigid** rotor, the length between masses is constant. Thus

$$\psi(r, \theta, \phi) \rightarrow \psi(r_o, \theta, \phi) \rightarrow \frac{\partial}{\partial r} \psi = 0$$

The Schrodinger equation is now:

$$\left[ \frac{-\hbar^2}{2\mu r_o^2} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

Recall:  $\mu r_o^2 = I$ , the moment of Inertia of the rotor.

$$\left[ \frac{-\hbar^2}{2I} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

If we assume that  $\psi(r_o, \theta, \phi)$  is more generally  $\psi(r_o, \theta, \phi) = B(r)Y(\theta, \phi)$  (the function B(r) is some generic function that takes into account the true r-dependence which we are simplifying in the present case by treating the system as a rigid rotor), the problem reduces to:

$$\boxed{\left[ \frac{-\hbar^2}{2I} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) \right] Y(\theta, \phi) = EY(\theta, \phi)}$$

### Solving the Rigid Rotor Problem

Rearranging the previous equation:

$$\left[ \sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{2IE}{\hbar^2} \sin^2\theta \right] Y(\theta, \phi) = -\frac{\partial^2}{\partial \phi^2} Y(\theta, \phi)$$

The left-hand side of the previous equation is a function only of  $\theta$  and the right is a function only of  $\phi$ . Thus, we can use *separation of variables* to generate a solution:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \rightarrow \text{Define: } \beta \equiv \frac{2IE}{\hbar^2}$$

Thus,

$$\left[ \sin\theta \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{2IE}{\hbar^2} \sin^2\theta \right] \Theta(\theta)\Phi(\phi) = -\frac{\partial^2}{\partial\phi^2} \Theta(\theta)\Phi(\phi)$$

Dividing by  $\Theta(\theta)\Phi(\phi)$  and simplifying:

$$\left[ \frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) \Theta(\theta) + \beta \sin^2\theta \right] = -\frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial\phi^2} \Phi(\phi)$$

Since both sides are functions of different variables, each is equal to a constant, which we'll let be  $m^2$ .

$$\frac{1}{\Phi(\phi)} \frac{\partial^2}{\partial\phi^2} \Phi(\phi) = -m^2$$

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) \Theta(\theta) + \beta \sin^2\theta = m^2$$

First consider the  $\phi$  expression:

$$\frac{\partial^2}{\partial\phi^2} \Phi(\phi) = -m^2 \Phi(\phi)$$

Solutions are of the general form:  $\Phi_{\pm}(\phi) = A_{\pm} e^{\pm im\phi}$ . As before, the boundary conditions lead to quantization. Since this expression is related to the z-component of the angular momentum, we can imagine the particle moving along a circular ring. At the values of  $\phi$  separated by an entire revolution, the wavefunction has to be the same; i.e.  $\Phi(\phi) = \Phi(\phi + 2\pi)$ .

The latter constraint leads to:  $e^{\pm i2\pi m} = 1$ . This is valid for values of  $m$ :

$$m = 0, \pm 1, \pm 2, \pm 3, \dots$$

$m$  is the magnetic quantum number. Thus :

$$\Phi(\phi) = A_m e^{im\phi} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots$$

Normalization gives:

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots$$

Now we'll consider the  $\Theta$  function:

$$\frac{\sin\theta}{\Theta(\theta)} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) \Theta(\theta) + \beta \sin^2\theta = m^2$$

First change variables:  $x = \cos\theta$ ,  $\Theta(\theta) = P(x)$ , and  $\frac{dx}{-\sin\theta} = d\theta$ .

Since  $0 \leq \theta \leq \pi$ ,  $-1 \leq x \leq 1$ , conveniently. Also,  $\sin^2\theta = 1 - \cos^2\theta = 1 - x^2$ . After some rearrangement and simplification, one obtains the associated Legendre equation:

$$(1 - x^2) \frac{d^2}{dx^2} P(x) - 2x \frac{d}{dx} P(x) + \left[ \beta - \frac{m^2}{1 - x^2} \right] P(x) = 0$$

The boundary conditions arise due to the requirement that  $\Theta$  is continuous; this quantizes  $\beta$ :

$$\beta = l(l + 1); \quad l = 0, 1, 2, 3, \dots \quad (\text{with } m = 0, \pm 1, \pm 2, \pm 3, \dots)$$

The energy (eigenvalue) is thus quantized from the definition of  $\beta$ .

$$E = \frac{\hbar^2}{2I} l(l + 1) \quad l = 0, 1, 2, 3, \dots$$

The wavefunctions are the associated Legendre Polynomials,  $P_l^{|m|}$ :

$$P_l^{|m|}(x) = P_l^{|m|}(\cos\theta)$$

$$P_0^0(\cos\theta) = 1 \quad P_1^0(\cos\theta) = \cos\theta$$

$$P_2^0(\cos\theta) = \frac{1}{2} (3\cos^2\theta - 1) \quad P_2^1(\cos\theta) = 3\cos\theta\sin\theta$$

Putting things together:

$$\Theta(\theta) = A_{lm} P_l^{|m|}(\cos\theta)$$

From normalization:

$$A_{lm} = \left[ \left( \frac{2l + 1}{2} \right) \frac{(l - |m|)!}{(l + |m|)!} \right]^{1/2} \quad \leftarrow \quad 1 = A_{lm}^2 \int_0^\pi [P_l^{|m|}(\cos\theta)]^2 \sin\theta d\theta$$

The Spherical Harmonics are the eigenfunctions for the 3-D rigid rotor:

$$Y_l^m = \left[ \left( \frac{2l + 1}{4\pi} \right) \frac{(l - |m|)!}{(l + |m|)!} \right]^{1/2} P_l^{|m|}(\cos\theta) e^{im\phi} \quad (\hat{H}Y = EY) \quad \left( E_l = \frac{\hbar^2}{2I} l(l + 1) \right)$$

**But what is the relation between the  $l$  and  $m$  quantum numbers that have arisen? For this, we need to consider Angular Momentum**