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 \( r_0 \); 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:

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

\[
x = r \sin \theta \cos \phi
\]

\[
y = r \sin \theta \sin \phi
\]

\[
z = r \cos \theta
\]

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

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

**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:

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

\[ m = 0, \pm 1, \pm 2, \pm 3, \ldots \]

\( m \) is the magnetic quantum number. Thus:

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

Normalization gives:

\[
\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots
\]
Now we’ll consider the function:

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

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:

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

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

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

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

\[
E = \frac{\hbar^2}{2I} l(l + 1) \quad l = 0, 1, 2, 3, \ldots
\]

The wavefunctions are the associated Legendre Polynomials, \( P_l^{|m|}:\)

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

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

\[
P_2^0(\cos \theta) = \frac{1}{2} \left(3\cos^2 \theta - 1\right) \quad P_2^1(\cos \theta) = 3\cos \theta \sin \theta
\]

Putting things together:

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

From normalization:

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

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

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

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