Quantum Mechanics: Vibration and Rotation of Molecules

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

Consider a rotating *diatomic* molecule, 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:

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

$$x = rsin\theta cos\phi$$

$$y = rsin\theta sin\phi$$

$$z = rcos\theta$$

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

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

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

For the **rigid** rotor, $V = 0 \quad (r = r_o) \quad and \quad \mathrm{V} = \infty \quad (r \neq r_o)$. That is, the length between masses is constant.

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

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: $\mu r_0^2 = I$, the moment of Inertia of the rotor.
If we assume that $\psi(r_o,\theta,\phi)$ is more generally $\psi(r_o,\theta,\phi) = BY(\theta,\phi)$, 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 θ and the right is a function only of ϕ. Thus, we can use *separation of variables* to generate a solution:

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

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 ϕ 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 ϕ 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:

$$m=0,\pm1,\pm2,\pm3,.....$$

m is the magnetic quantum number. Thus :

$$\Phi(\phi)=A_m e^{im\phi}\qquad m=0,\pm1,\pm2,\pm3,...$$

Normalization gives:

$$\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi}\qquad m=0,\pm1,\pm2,\pm3,...$$

Now we'll consider the Θ 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:

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

The boundary conditions arise due to the requirement that Θ is continuous; this quantizes β:

$$\beta = l(l+1); \quad l = 0, 1, 2, 3, ... \quad (with\ m\ =\ 0, \pm 1, \pm 2, \pm 3, ...)$$

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

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

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

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

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

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

Putting things togther:

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

From normalization:

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

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

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