

Quantum Mechanics: Vibration and Rotation of Molecules

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I. Recap: Rigid Rotation and Q. M. Orbital Angular Momentum

- For 3-D rigid body rotation in absence of external potential, the kinetic energy (thus total energy) operator in spherical, polar coordinates becomes:

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

- The **energy** eigenvalues are

$$E_l = \frac{1}{2I} \hbar^2 l(l+1)$$

- The **energy** eigenstates are:

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

- Angular momentum is related to the **total energy** in the classical sense as:

$$2 I E_{total} = |l^2|$$

- The quantum mechanical formulation for the relation between operators is then:

$$2 I \hat{H} = \hat{l}^2$$

- Thus, angular momentum is **quantized** and the angular momentum eigenvalues are:

$$l^2 = \hbar^2 l(l+1)$$
$$l = \sqrt{\hbar^2 l(l+1)}$$

- The eigenvalues for the z-component of the total angular momentum are:

$$l_z = \pm \hbar m$$

- Note, only one component of the total angular momentum operator commutes with the operator for the total angular momentum squared operator:

$$[\hat{l}^2, \hat{l}_z] = 0$$

- This relation defines the range of the m quantum number for a given l quantum number.

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

- At this point, we see that the energy is only dependent on l . Since there are several states associated with different m for a given l , the energy states associated with rigid rotation are degenerate. The degeneracy is $2l + 1$.