Rotating Molecules and Angular Momentum

CHEM 361B: Introduction to Physical Chemistry

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Lecture 11

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Learning Objectives:

- Develop a model for the rigid rotator and then apply it to diatomic molecules to predict their rotational spectra.
- Discuss the solutions to the rigid rotator to understand how it is quantized.

References:

- McQuarrie Chapter 6

Using the Laplacian in the Schrödinger Equation

The Schrödinger equation in three dimensions is

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\psi=E\psi(x,y,z)$$

The laplacian operator (∇^2) is defined as

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

This means that the Schrödinger equation can be expressed as

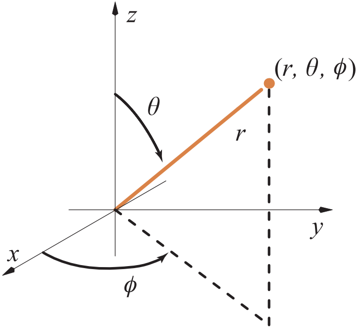
$$-\frac{\hbar^2}{2\mu}\nabla^2\psi+U\psi=E\psi$$

Spherical Coordinates

Using the definition of ∇^2 and the following relationships between cartesian and spherical coordinates:

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

with $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, and $0 \leq r < \infty$



The result is:

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

The Rigid Rotator

Consider a spinning diatomic molecule with two masses, m_1 and m_2, at a fixed distance r_1 and r_2 from their centre of mass. We can treat this system as having one mass fixed at the centre with another mass, the reduced mass μ rotating around the origin at a distance r. The kinetic energy of a rigid rotator is

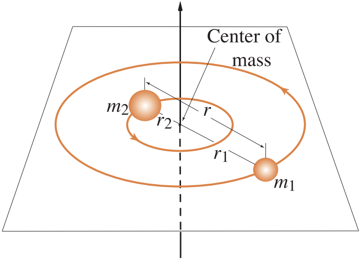
$$E_k = \frac{1}{2} I\omega^2 \quad \text{where } I = \mu r^2$$

ω is the angular velocity. The angular momentum is defined as

$$L = I\omega$$

So the kinetic energy can be expressed as

$$E_k = \frac{L^2}{2I}$$



The Rigid Rotator (cont.)

Since there is no potential present, the Hamiltonian is simply the kinetic energy operator

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2$$

and since the radius of the rotator is fixed then

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

The orientation of the rigid rotator is completely specified by the two angles θ and ϕ so its wave function is denoted as $Y(\theta, \phi)$. The Schrödinger equation then reads

$$\hat{H}Y(\theta, \phi) = EY(\theta, \phi)$$

The Rigid Rotator (cont.)

The Schrödinger equation with the Hamiltonian substituted in is

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

If this is multiplied by $\sin^2\theta$ and substitute

$$\beta=\frac{2IE}{\hbar^2}$$

then rearranging gives

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}+\beta\sin^2\theta Y=0$$

The Rigid Rotator (cont.)

To solve, it will be assumed that

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

When this is substituted into the Schrödinger equation then

$$\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \beta\sin^2\theta + \frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2} = 0$$

Since θ and ϕ are independent variables then

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

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

The Rigid Rotator ($\Phi(\phi)$)

Rearranging the $\Phi(\phi)$ differential equation gives

$$\frac{d^2\Phi}{d\phi^2} + m^2\Phi(\phi) = 0$$

where the solution to this is

$$\Phi(\phi) = Ae^{im\phi} + Be^{-im\phi}$$

Given the initial conditions that $\Phi(\phi + 2\pi) = \Phi(\phi)$ then

$$\Phi_m(\phi) = Ae^{im\phi} \quad m = 0, \pm 1, \pm 2, \ldots$$

Normalizing gives

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

The Rigid Rotator ($\Theta(\theta)$)

Rearranging the $\Theta(\theta)$ differential equation gives

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + (\beta \sin^2\theta - m^2)\Theta(\theta) = 0$$

To solve this difficult differential equation, three substitutions will be made

$$x = \cos\theta, \quad \Theta(\theta) = P(x), \quad \text{and} \quad \beta = \ell(\ell+1)$$

Rearranging gives

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

whose solutions are the associated Legendre functions.

Solutions to $P_\ell^{|m|}(x)$

$$
\begin{aligned}
P_0^0 &= 1 \\
P_1^0 &= x = \cos\theta \\
P_1^1 &= (1-x^2)^{1/2} = \sin\theta \\
P_2^0 &= \frac{1}{2}(3x^2-1) = \frac{1}{2}(3\cos^2\theta - 1) \\
P_2^1 &= 3x(1-x^2)^{1/2} = 3\cos\theta\sin\theta \\
P_2^2 &= 3(1-x^2) = 3\sin^2\theta \\
P_3^0 &= \frac{1}{2}(5x^3-3x) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta) \\
P_3^1 &= \frac{3}{2}(5x^2-1)(1-x^2)^{1/2} = \frac{3}{2}(5\cos^2\theta - 1)\sin\theta \\
P_3^2 &= 15x(1-x^2) = 15\cos\theta\sin^2\theta \\
P_3^3 &= 15(1-x^2)^{3/2} = 15\sin^3\theta
\end{aligned}
$$

Nomalizing $P_\ell^{|m|}(x)$

The associated Legendre polynomials satisfy the relation

$$\int_{-1}^{1} P_\ell^{|m|}(x) P_\ell^{|m|}(x) dx = \int_0^\pi \sin\theta P_\ell^{|m|}(\cos\theta) P_\ell^{|m|}(\cos\theta) d\theta$$

$$= \frac{2}{(2\ell+1)} \frac{(\ell+|m|)!}{(\ell-|m|)!}$$

From this, the normalization constant is

$$N_{\ell m} = \left[\frac{(2\ell+1)}{2} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2}$$

The Rigid Rotator Solutions

Returning to the original problem, the solution to the rigid rotator ($Y(\theta,\phi)$) was

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

Substituting in gives

$$\begin{aligned} Y_\ell^m(\theta,\phi) &= \left[\frac{(2\ell+1)}{2}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta)\left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi} \\ &= \left[\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta)e^{im\phi} \end{aligned}$$

The Rigid Rotator Solutions

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{i\phi}$$

$$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{-i\phi}$$

$$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{2i\phi}$$

$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$$

Energy of a Rigid Rotator

Recall that

$$\frac{2IE}{\hbar^2} = \beta = \ell(\ell+1)$$

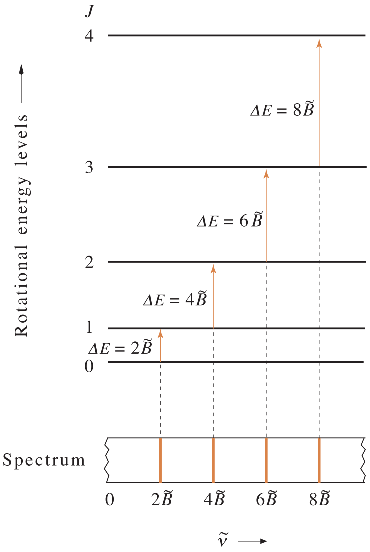
Rearranging for E gives

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) \quad \ell = 0, 1, 2, \ldots$$

This means that

$$\hat{H}Y_\ell^m(\theta,\phi) = \frac{\hbar^2\ell(\ell+1)}{2I}Y_\ell^m(\theta,\phi)$$

Rigid Rotator Example



1. Find the frequency of the photon required to promote a rotator from state ℓ to $\ell + 1$.
2. To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by 6.26×10^{11} Hz. Calculate the bond length of $H^{35}Cl$.

Angular Momentum

Recall that

$$E_k = \frac{L^2}{2I}$$

This means that $\hat{H}$ and $\hat{L}^2$ only differ by a factor of $2I$ for a rigid rotator. As a result,

$$\hat{L}^2 Y_\ell^m(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta, \phi)$$

These same solutions to the Hamiltonian are also eigenfunctions of the square of the angular momentum operator which can only have values given by

$$L^2 = \hbar^2 \ell(\ell+1) \quad \ell = 0, 1, 2, \ldots$$

Angular Momentum (cont.)

The quantum mechanical operators for angular momentum can be found with:

$$\hat{L} = -i\hbar(\mathbf{r} \times \nabla)$$

Cartesian

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Spherical

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Angular Momentum - $\hat{L}_z$

Of the three components, $\hat{L}_z$ is the simplest. Applying it to $\Phi(\phi)$ gives

$$\hat{L}_z\Phi(\phi) = -i\hbar\frac{\partial}{\partial\phi}e^{im\phi} = m\hbar e^{im\phi}$$

Thus $e^{im\phi}$ is an eigenfunction of $\hat{L}_z$. Since $\hat{L}_z$ only acts on the ϕ coordinate then

$$\begin{aligned}\hat{L}_z Y_\ell^m(\theta,\phi) =& \hat{L}_z N_{\ell m} P_\ell^{|m|}(\cos\theta)e^{im\phi} \\ =& N_{\ell m} P_\ell^{|m|}(\cos\theta)\hat{L}_z e^{im\phi} \\ =& \hbar m Y_\ell^m(\theta,\phi)\end{aligned}$$

$Y(\theta,\phi)$ is also an eigenfunction of $\hat{L}_z$.

$\hat{L}^2$ and $\hat{L}_z$ commute

$Y(\theta, \phi)$ is an eigenfunction of both $\hat{L}^2$ and $\hat{L}_z$. It can also be shown that they commute since

$$\hat{L}^2 \hat{L}_z f = \hat{L}_z \hat{L}^2 f$$

for some arbitrary test function f. As a result

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

which means that it is possible to know both simultaneously.

Setting limits on m

It is known that

$$\hat{L}_z^2 Y_\ell^m(\theta,\phi) = \hbar^2 m^2 Y_\ell^m(\theta,\phi)$$
$$\hat{L}^2 Y_\ell^m(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\phi)$$

Using the fact that

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Then it can be shown that

$$[\ell(\ell+1) - m^2]\hbar \geq 0$$

or that the only possible values of the integer m are

$$m = 0, \pm 1, \pm 2, \ldots, \pm \ell$$

which is the familiar result for the magnetic quantum number m.

Examining the Rigid Rotator energy degeneracy

For each value of ℓ there are $2\ell + 1$ values of m. Since the energy of the rigid rotator is

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) \quad \ell = 0, 1, 2, \ldots$$

then each energy level is $(2\ell + 1)$-fold degenerate. Taking $\ell = 1$ for example, m can only take values of 0 and ± 1 so

$$\hat{L}^2 Y_1^m(\theta, \phi) = 2\hbar^2 Y_1^m(\theta, \phi) \quad |L| = \sqrt{L^2} = \sqrt{2}\hbar$$

and

$$\hat{L}_z Y_1^m(\theta, \phi) = \hbar m Y_1^m(\theta, \phi) \quad L_z = -\hbar, 0, \hbar$$

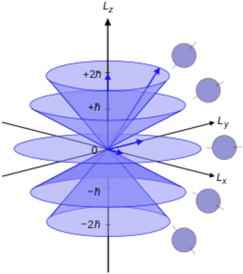
Imagining what this means

It can be shown that

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$

but that each component does not commute with any other component

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= i\hbar\hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar\hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar\hat{L}_y\end{aligned}$$



Thus it can be imagined that the particle precesses around the z-axis mapping out the surface of a cone.

Summary

- The solutions to the rigid rotator take the form

$$Y_\ell^m(\theta,\phi) = \left[\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}(\cos\theta)e^{im\phi}$$

with energy levels defined by

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1)$$

- The quantization of the energy levels is dictated by the solution to the Schrödinger equation and the commutation relationship between the total angular momentum and the components of the angular momentum:

$$\ell = 0, 1, 2, \ldots \quad \text{and} \quad m = 0, \pm 1, \pm 2, \ldots \quad \text{where} \quad |m| \leq \ell$$

- This solution will be used for the hydrogen atom. As a result, this quantization of the states defines how the periodic table is arranged.