RIGID ROTOR

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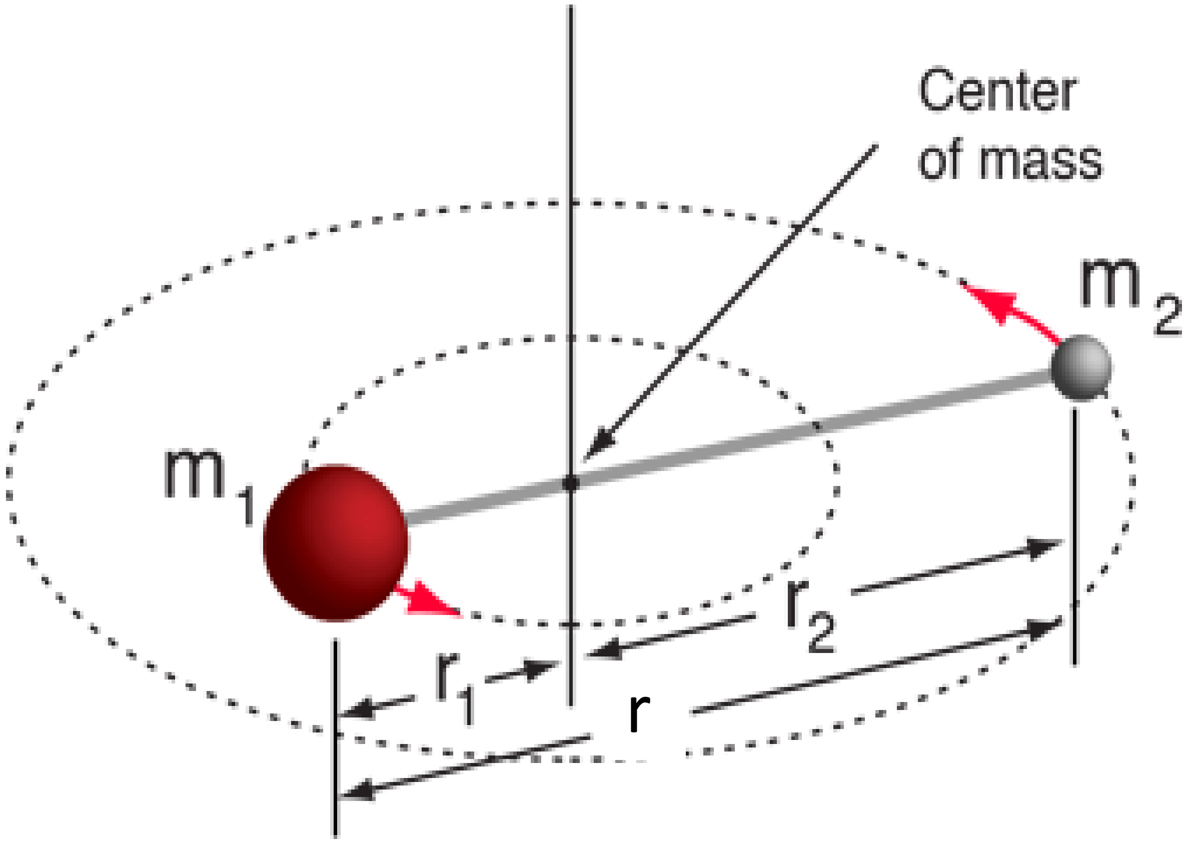

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The kinetic energy of the system:

$$KE = \tfrac{1}{2} I\omega^2$$
$$= L^2/ 2I \qquad \text{since: } L= I\omega$$

where L = Angular momentum

I = Moment of Inertia

ω= Angular velocity

$$I = \mu r^2$$

where μ is the reduced mass = $m_1m_2/(m_1+m_2)$

Now the Schrodinger equation is

$$\hat{H}\Psi = E\Psi$$

Where $\hat{H} = T + V$

Since the potential energy is assumed to be zero

$$\hat{H} = T = L^2 / 2I$$

Now the angular momentum operator L^2 can be written as

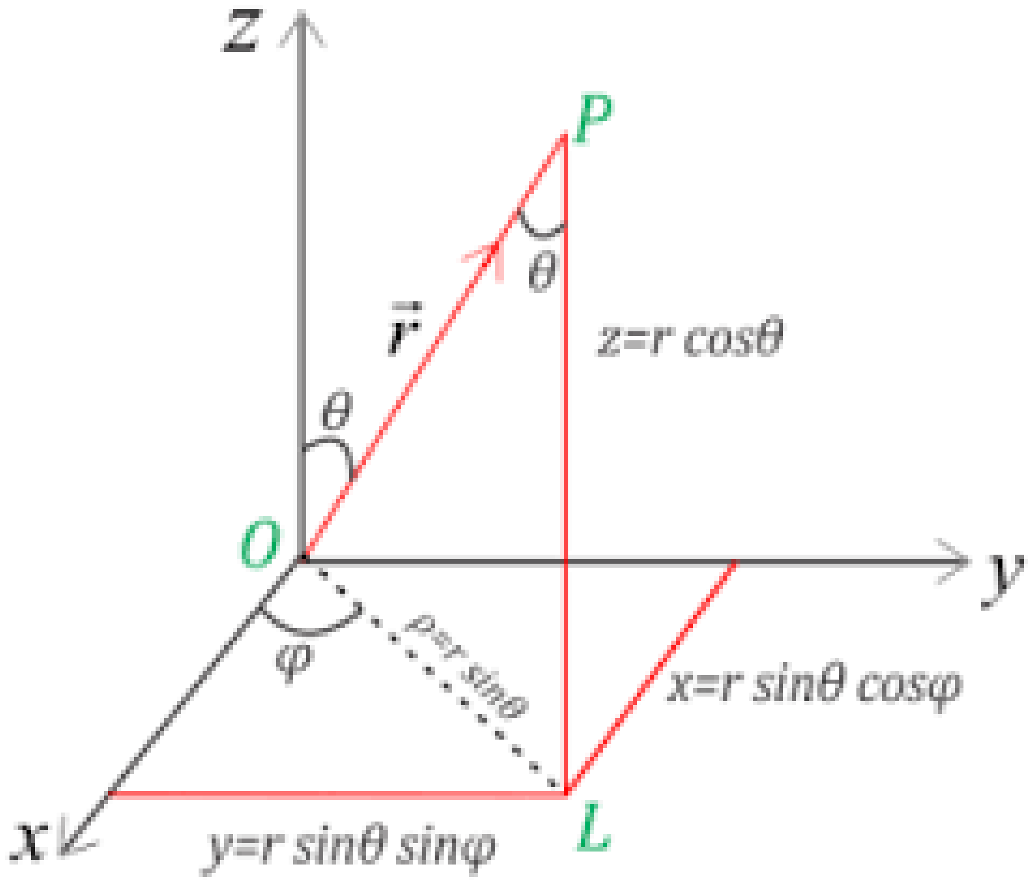
$$\boxed{L^2 = L_x^2 + L_y^2 + L_z^2}$$

$$L_x = y\hat{P}_z - z\hat{P}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)$$

$$L_y = z\hat{P}_x - x\hat{P}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right)$$

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

TRANSFORMATION OF CO-ORDINATES



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

$r^2 = x^2 + y^2 + z^2$

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$$\hat{L}_x = i\hbar\left[\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right]$$

$$\hat{L}_y = i\hbar\left[\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right]$$

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

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

Now putting the value of L^2 in the Schrodinger equation

$$\frac{\hat{L}^2}{2I}\psi = E\psi$$

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

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]+\frac{2I}{\hbar^2}E\psi = 0$$

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]+\frac{8\pi^2 I}{h^2}E\psi = 0$$

Now, Ψ is a function of θ and ϕ and both are independent of each other. Hence,

$$\Psi(\theta,\phi)=\Theta(\theta).\ \Phi(\phi)$$

Now multiplying Sin²θ in the previous equation,

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial\varphi^2}\right]+\frac{8\pi^2 I}{h^2}E\sin^2\theta\psi=0$$

$$Assume,\quad \beta=\frac{8\pi^2 I}{h^2}E$$

Now the equation becomes

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\beta\sin^2\theta\psi=-\frac{\partial^2\psi}{\partial\varphi^2}$$

Substituting the value of ψ

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

Now dividing throughout by ψ

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

As the terms are separated now, they can be equated to one constant, as they are independent of each other.

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

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

Now we have two different equation to solve.
Solving individual equations and then combining will provide the solution for rigid rotor.

θ varies from 0 to π.

ϕ varies from 0 to 2π.

Solution to ϕ equation

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

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

The general solution to such equation is

$$\Phi(\phi)=Ne^{im\phi}$$

N is the normalization constant.

Normalization of ϕ equation

Applying Normalization Condition

$$\int_0^{2\pi} \Phi(\phi)^* \Phi(\phi) \mathrm{d}\phi = 1$$

$$\int_0^{2\pi} N e^{-im\phi} N e^{im\phi} \mathrm{d}\phi = 1$$

$$N^2 \int_0^{2\pi} \mathrm{d}\phi = 1$$

$$\Rightarrow \ N = \frac{1}{\sqrt{2\pi}}$$

Hence the solution becomes

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

Solution to Θ equation

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

It will become easier to solve, if this equation can be transformed to Legendre equation

$$Assume \quad \mathrm{x}=\cos\theta$$

$$Then \quad 1-x^2=\sin^2\theta$$

$$\sqrt{1-x^2}=\sin\theta \quad \Rightarrow dx=-\sin\theta\, d\theta$$

$$Let\ \Theta(\theta)=\mathrm{P(x)}$$

$$\frac{d}{d\theta}=\frac{dx}{d\theta}.\frac{d}{dx}=-\sin\theta\frac{d}{dx}=-\sqrt{1-x^2}\frac{d}{dx}$$

Now the Θ equation becomes

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

This is similar to Legendre equation, where β = l(l+1)
l is the azimuthal quantum number.

Now the solution to the Legendre equation becomes

$$P_l^{|m|}(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)$$

$$P_l(x) = \frac{1}{2^l\, l!}\frac{d^l}{dx^l}(x^2-1)^l$$

$Find\ P_l(x)$ for $l = 0,1,2\ldots$

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Now $|m| \le l$

It can't be greater than l, as the Legendre equation becomes zero.

Using the value of x, we can find solution to Θ equation as

$$\Theta(\theta) = N_{l,m} P_l^{|m|}(x)$$

$N_{l,m}$ is the normalization constant.

$$N_{l,m} = \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}}$$

$$\Theta(\theta) = \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} . P_l^{|m|}(x)$$

Now the complete wavefunction for rigid rotator is

$$\Psi(\theta,\phi)=\Theta(\theta).\Phi(\phi)$$

$$=\sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}}.P_l^{|m|}(x).\frac{1}{\sqrt{2\pi}}e^{im\phi}$$

$$=\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}.P_l^{|m|}(x).e^{im\phi}$$

$$where \quad l=0,1,2,3 \quad \& \quad -l\leq m\leq l$$

$$\beta = l(l+1) = \frac{8\pi^2 IE}{h^2}$$

$$E = \frac{l(l+1)h^2}{8\pi^2 I} \qquad \text{where } l = 0,1,2,3....$$

In Spectroscopy

$$E = \frac{J(J+1)h^2}{8\pi^2 I} \qquad \text{where J} = 0,1,2,3....$$

J is known as rotational quantum number.