Angular Momemtum

Classical Mechanics of One Particle Angular Momentum

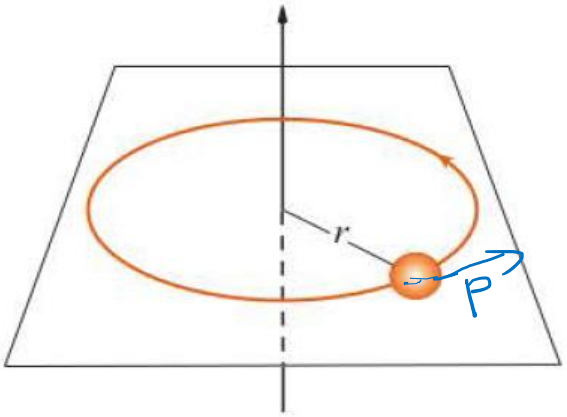
Consider a particle of mass m moving around in a circle at a distance r from the origin.

The particle's angular momentum L with respect to the coordinate origin is defined in classical mechanics as

$\mathbf{L} = \mathbf{r} \times \mathbf{p}$

$\mathbf{L} =$

i	j	k
x	y	z
p_x	p_y	p_z



$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x$

$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar y\frac{\partial}{\partial z} + i\hbar z\frac{\partial}{\partial y}$

$\hat{L}_y = -i\hbar z\frac{\partial}{\partial x} + i\hbar x\frac{\partial}{\partial z}$

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

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

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

Magnitude of the total angular momentum, **L**

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

Commutation Relation

Let a function f depend on x,y,z

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

$$\hat{L}_x\hat{L}_y f = -\hbar^2\left(y\frac{\partial f}{\partial x} + yz\frac{\partial^2 f}{\partial z\,\partial x} - yx\frac{\partial^2 f}{\partial z^2} - z^2\frac{\partial^2 f}{\partial y\,\partial x} + zx\frac{\partial^2 f}{\partial y\,\partial z}\right)$$

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

$$\hat{L}_y\hat{L}_x f = -\hbar^2\left(zy\frac{\partial^2 f}{\partial x\,\partial z} - z^2\frac{\partial^2 f}{\partial x\,\partial y} - xy\frac{\partial^2 f}{\partial z^2} + x\frac{\partial f}{\partial y} + xz\frac{\partial^2 f}{\partial z\,\partial y}\right)$$

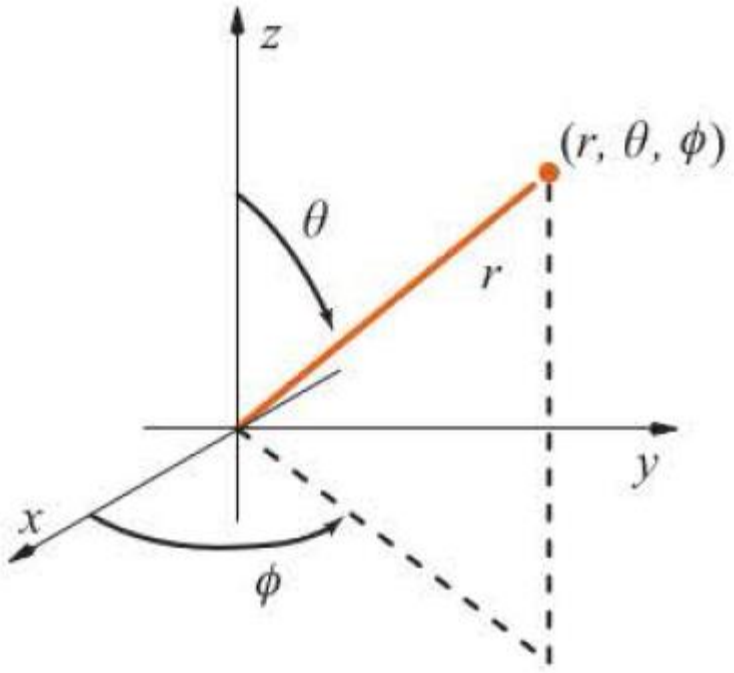
$$\hat{L}_x\hat{L}_y f - \hat{L}_y\hat{L}_x f = -\hbar^2\left(y\frac{\partial f}{\partial x} - x\frac{\partial f}{\partial y}\right)$$

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

$$\begin{aligned}
[\hat{L}^2, \hat{L}_x] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] \\
&= [\hat{L}_x^2, \hat{L}_x] + [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\
&= [\hat{L}_y, \hat{L}_x]\hat{L}_y + \hat{L}_y[\hat{L}_y, \hat{L}_x] + [\hat{L}_z, \hat{L}_x]\hat{L}_z + \hat{L}_z[\hat{L}_z, \hat{L}_x] \\
&= -i\hbar\hat{L}_z\hat{L}_y - i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_y\hat{L}_z + i\hbar\hat{L}_z\hat{L}_y \\
&= 0
\end{aligned}$$

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



$0 \le r \le \infty, \quad 0 \le \theta \le \pi \quad 0 \le \varphi \le 2\pi$

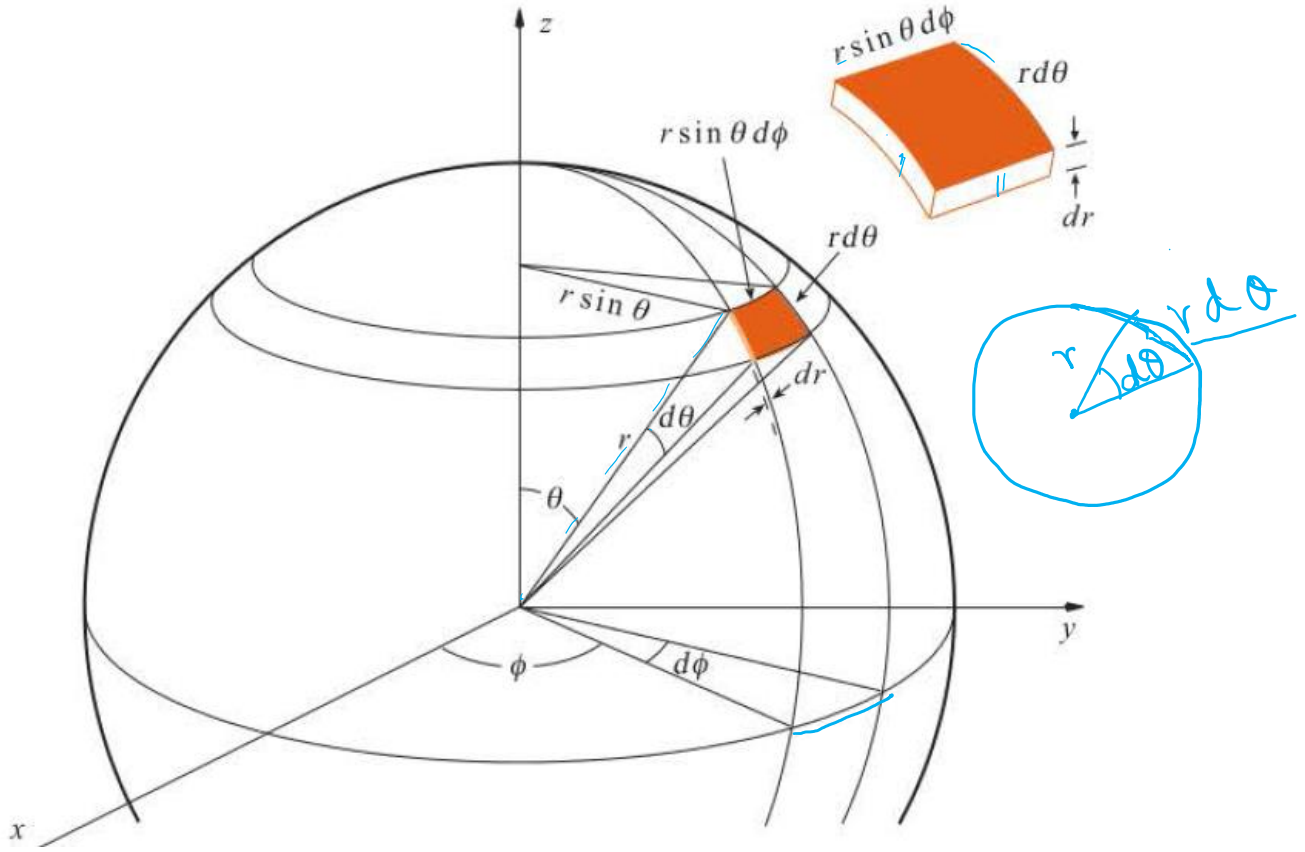
$$x = r \sin\theta \cos\phi\,, \qquad y = r \sin\theta \sin\phi\,, \qquad z = r \cos\theta$$

$$r^2 = x^2 + y^2 + z^2\,, \qquad \cos\theta = \frac{z}{(x^2 + y^2 + z^2)^{1/2}}\,, \qquad \tan\phi = y/x$$

The differential volume element in Cartesian coordinates is dxdydz

The differential volume element in spherical polar cordinates is

$$dV = (r\sin\theta d\phi)(rd\theta)dr = r^2\sin\theta dr d\theta d\phi$$



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

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

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

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right)$$

$f(x,y,z) \equiv g(r,\theta,\phi)$ $\left[r \equiv r(x,y,z),\ \theta \equiv \theta(x,y,z),\ \phi = \phi(x,y,z)\right]$

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = \frac{\partial g(r,\theta,\phi)}{\partial x}$$

$$= \left(\frac{\partial g}{\partial r}\right)_{\theta,\phi}\left(\frac{\partial r}{\partial x}\right)_{y,z} + \left(\frac{\partial g}{\partial\theta}\right)_{r,\phi}\left(\frac{\partial\theta}{\partial x}\right)_{y,z} + \left(\frac{\partial g}{\partial\phi}\right)_{r,\theta}\left(\frac{\partial\phi}{\partial x}\right)_{y,z}$$

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial r}\left(\frac{\partial r}{\partial x}\right)_{y,z} + \frac{\partial}{\partial\theta}\left(\frac{\partial\theta}{\partial x}\right)_{y,z} + \left(\frac{\partial}{\partial\phi}\right)\left(\frac{\partial\phi}{\partial x}\right)_{y,z}$$

One Particle orbital angular momentum eigenfunction and eigenvalue

We now find the common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, which we denote by Y. Since these operators involve only θ and ϕ, Y is a function of these two coordinates:

$$\hat{L}_z Y(\theta, \phi) = bY(\theta, \phi)$$
$$\hat{L}^2 Y(\theta, \phi) = cY(\theta, \phi)$$

$Y(\theta, \phi)$ is known as spherical harmonics

$$-i\hbar \frac{\partial}{\partial \phi} Y(\theta, \phi) = bY(\theta, \phi) \qquad Y(\theta, \phi) = S(\theta)T(\phi)$$

$$-i\hbar \frac{\partial}{\partial \phi} [S(\theta)T(\phi)] = bS(\theta)T(\phi)$$

$$\frac{dT(\phi)}{T(\phi)} = \frac{ib}{\hbar} d\phi$$

$$T(\phi) = Ae^{ib\phi/\hbar}$$

$T(\phi + 2\pi) = A e^{ib(\phi + 2\pi)/\hbar}$

The requirement that T(φ) be a single-valued function of φ is

$$T(\phi + 2\pi) = T(\phi)$$

$$Ae^{ib\phi/\hbar}e^{ib2\pi/\hbar} = Ae^{ib\phi/\hbar}$$

$$e^{ib2\pi/\hbar} = 1$$

To satisfy $e^{i\alpha} = \cos\alpha + i\sin\alpha = 1$, we must have $\alpha = 2\pi m$, where

$$m = 0, \pm 1, \pm 2, \pm \cdots \quad [\alpha = \frac{2\pi b}{\hbar}]$$

$$b = m\hbar, \qquad m = \cdots -2, -1, 0, 1, 2, \ldots$$

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

$$\int_0^{2\pi} T^*(\phi)\, T(\phi)\, d\phi = 1$$

$$\int_0^{2\pi} (Ae^{im\phi})^* Ae^{im\phi}\, d\phi = 1 = |A|^2 \int_0^{2\pi} d\phi$$

$$|A| = (2\pi)^{-1/2}$$

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

$Y(\theta,\phi) = \frac{1}{\sqrt{2\pi}} S(\theta) e^{im\phi}$

We now solve $\hat{L}^2 Y = cY$ for the eigenvalues c of $\hat{L}^2$

$$-\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \left(S(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi} \right) = cS(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\frac{d^2S}{d\theta^2} + \cot\theta \frac{dS}{d\theta} - \frac{m^2}{\sin^2\theta} S = -\frac{c}{\hbar^2} S$$

$$c = l(l+1)\hbar^2, \qquad l = 0, 1, 2, \ldots$$

$$|\mathbf{L}| = [l(l+1)]^{1/2}\hbar \qquad = \sqrt{l(l+1)}\,\hbar$$

$$Y_l^m(\theta, \phi) = S_{l,m}(\theta)T(\phi) = \frac{1}{\sqrt{2\pi}} S_{l,m}(\theta)e^{im\phi}$$

$S_{l,m}(\theta)$ are well known in mathematics, and are *associated Legendre functions*

case of $l = 1$ for which $l(l+1) = 2$

$$\hat{L}^2 Y_1^m(\theta, \phi) = 1(1+1)\hbar^2 Y_1^m(\theta, \phi) = 2\hbar^2 Y_1^m(\theta, \phi) \qquad m = 0, \pm 1$$

$$\hat{L}_z Y_1^m(\theta, \phi) = m\hbar Y_1^m(\theta, \phi) \qquad m = 0, \pm 1$$

$$|\mathbf{L}| = (L^2)^{1/2} = \sqrt{2}\hbar$$

$$L_z = -\hbar, 0, +\hbar$$

$$(\hat{L}^2 - \hat{L}_z^2)Y_l^m(\theta, \phi) = (\hat{L}_x^2 + \hat{L}_y^2)Y_l^m(\theta, \phi) = \hbar^2[l(l+1) - m^2]\, Y_l^m(\theta, \phi)$$

Thus, the observed values of $L_x^2 + L_y^2$ are $[l(l+1) - m^2]\hbar^2$. But because $L_x^2 + L_y^2$ is the sum of two squared terms, it cannot be negative, and so we have

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

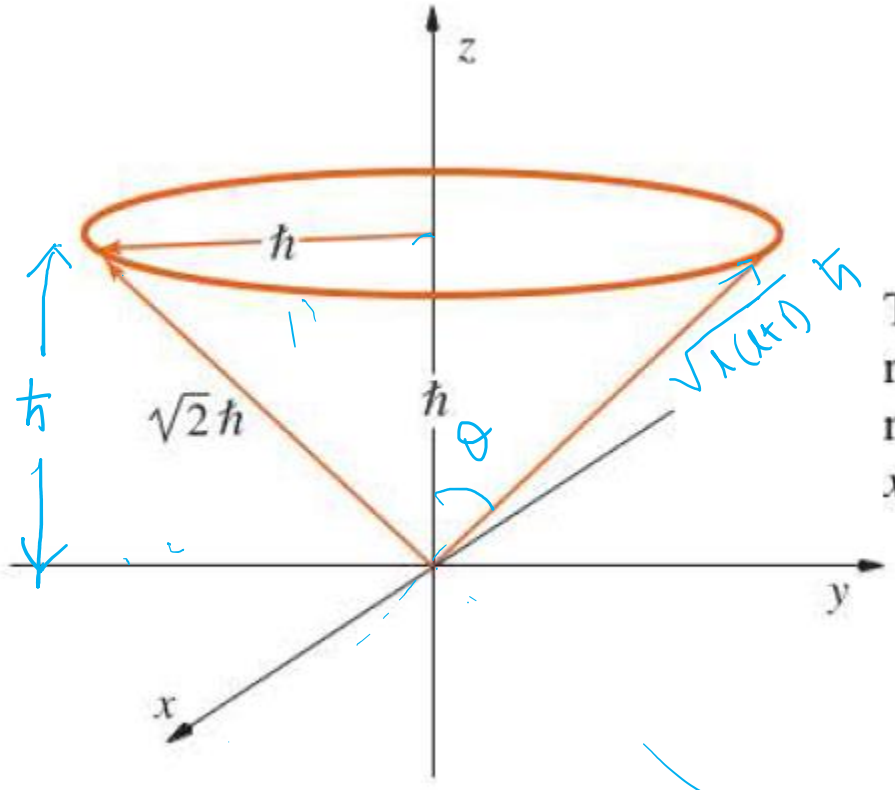
$$l(l+1) \geq m^2$$ Thus, $l \geq \pm m$, or, $m \leq l$ and $m \geq -l$

Because l and m are integers, $|m| \leq l$

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

So, there are 2l+1 values of m for each value of *l*

This result might be familiar as the condition of the magnetic quantum number associated with the hydrogen atom.



The $m = +1$ component of the angular-momentum state, $l = 1$. The angular momentum describes a cone because the x and y components cannot be specified.

L precesses about the z axis, mapping out the surface of the cone shown there.

Since we cannot specify L_x and L_y, the vector **L** can lie anywhere on the surface

of a cone whose axis is the z axis, whose altitude is $m\hbar$, and whose slant height is $\sqrt{l(l+1)}\,\hbar$

$$\theta = \cos^{-1}\frac{m}{\sqrt{l(l+1)}}$$

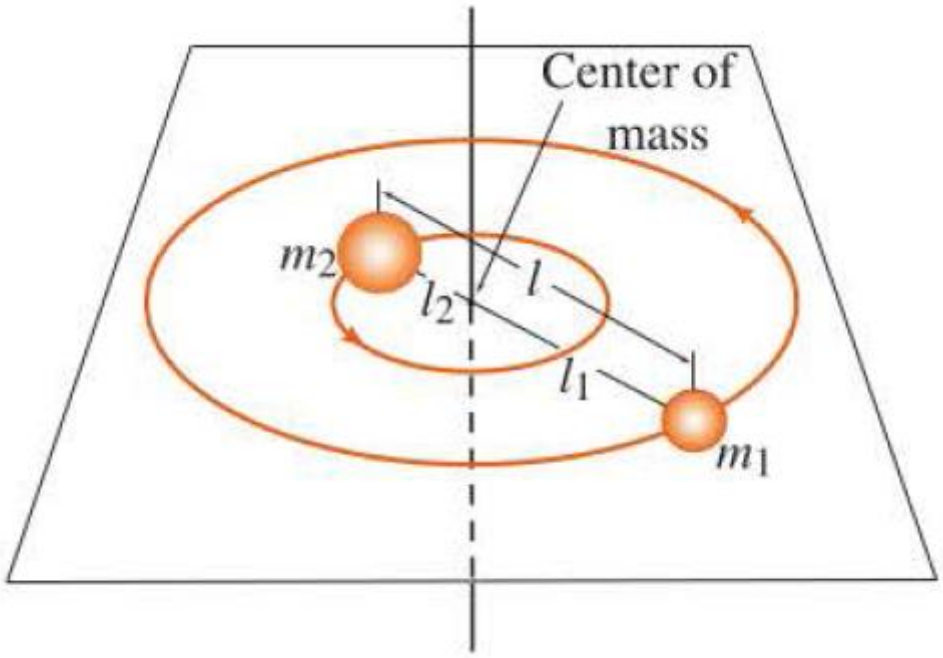
θ is always greater than 0 since m is always less than L except when *l*=0

The average values of $\langle L_x \rangle$ and $\langle L_y \rangle$ are zero. This picture is in nice accord with the uncertainty principle: by specifying L_z exactly, we have a complete uncertainty in the angle ϕ associated with L_z.

$\Delta L_z \Delta \phi \geq \frac{\hbar}{2}$

Rigid Rotator

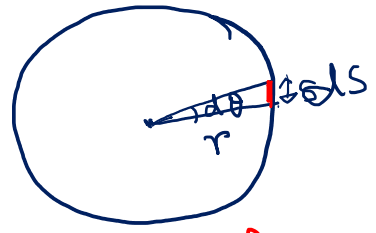
we will discuss a simple model for a rotating diatomic molecule. This model consists of two point masses m_1 and m_2 at fixed distances l_1 and l_2 from their center of mass Because the distance between the two masses is fixed, this model is referred to as the *rigid-rotator model*.



The kinetic energy of the rigid rotator is

$$T = \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 = \frac{1}{2}(m_1 l_1^2 + m_2 l_2^2)\omega^2$$

$$= \frac{1}{2} I \omega^2$$



$ds = r \sin d\theta$

$= r\, d\theta$

$\frac{ds}{dt} = r \frac{d\theta}{dt} \Rightarrow V = \omega r$

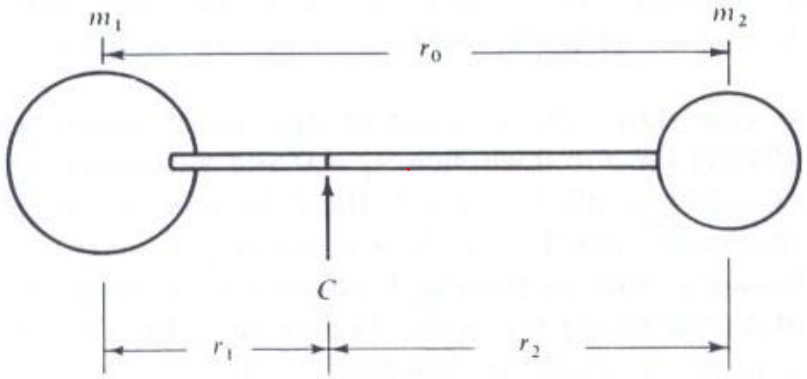
where I, the *moment of inertia*, is given by $I = m_1 l_1^2 + m_2 l_2^2$

Using the fact that the location of the center of mass is given by $m_1 l_1 = m_2 l_2$

$$I = \mu l^2$$

Prove it

where $l = l_1 + l_2$ (the fixed separation of the two masses) and μ is the *reduced mass*



$$r_0 = r_1 + r_2 \quad \Rightarrow \quad r_0 = l, \; r_1 = l_1, \; r_2 = l_2$$

$$m_1 r_1 = m_2 r_2 \quad \Rightarrow \quad m_1 l_1 = m_2 l_2$$

The moment of inertia about C is defined by:

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \\ &= r_1 r_2 (m_1 + m_2) \end{aligned}$$

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

therefore,

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r_0}{m_1 + m_2}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

$\Rightarrow I = \mu l^2$

$$L = I\omega \qquad T = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$$

$H = T + V$, $V \to 0$

There is no potential energy term because in the absence of any external forces (e.g., electric or magnetic forces) the energy of the molecule does not depend on its orientation in space. The Hamiltonian operator of a rigid rotator is therefore just the kinetic energy operator.

$$\hat{H} = \hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 \qquad (r \text{ constant})$$

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

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

Schrödinger Equation for Rigid Rotator

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

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

$$E_J = \frac{\hbar^2}{2I} J(J+1) = BJ(J+1) \qquad J = 0, 1, 2, \ldots$$

where $B = \hbar^2/2I$ is called the *rotational constant* of the molecule.

each rotational energy level has a degeneracy g_J given by

$$g_J = 2J + 1$$

The Rigid Rotator is a Model for a Rotating Diatomic Molecule

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I}[(J+1)(J+2) - J(J+1)]$$

$$= \frac{\hbar^2}{I}(J+1) = \frac{h^2}{4\pi^2 I}(J+1) \qquad J = 0, 1, 2, \ldots$$

$$\Delta E = h\nu_{\text{obs}},$$

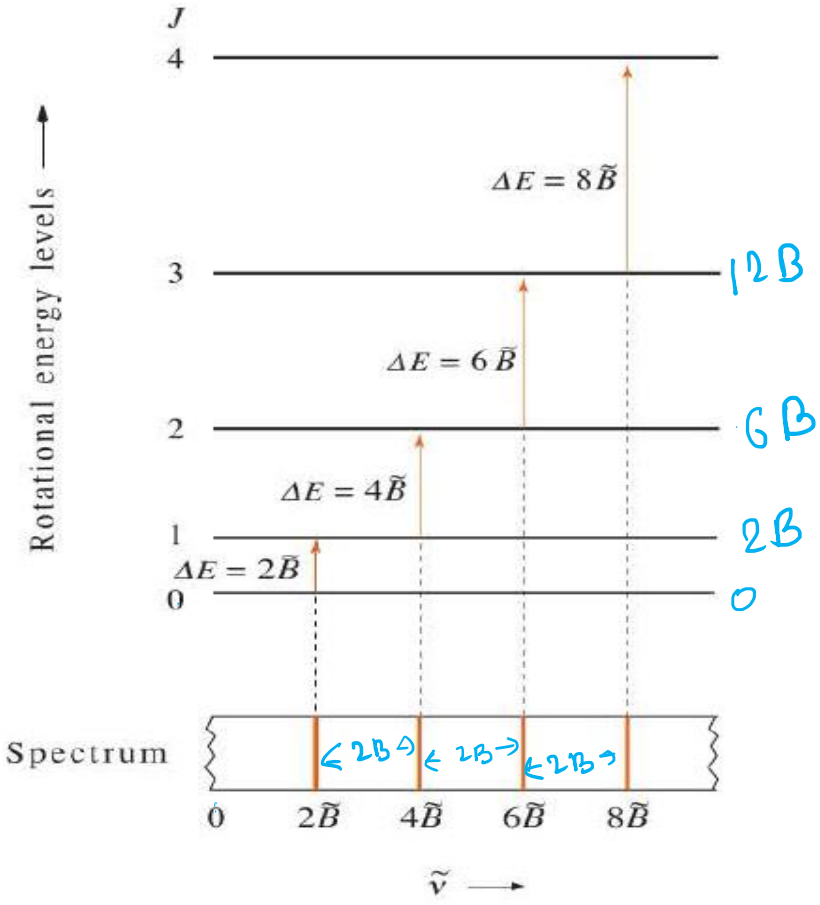
$$\nu_{\text{obs}} = \frac{h}{4\pi^2 I}(J+1) \qquad J = 0, 1, 2, \ldots$$

The frequencies of the pure-rotational spectral lines of a diatomic molecule are

$$\nu = \frac{E_{J+1} - E_J}{h} = \frac{[(J+1)(J+2) - J(J+1)]h}{8\pi^2 I} = 2(J+1)B$$

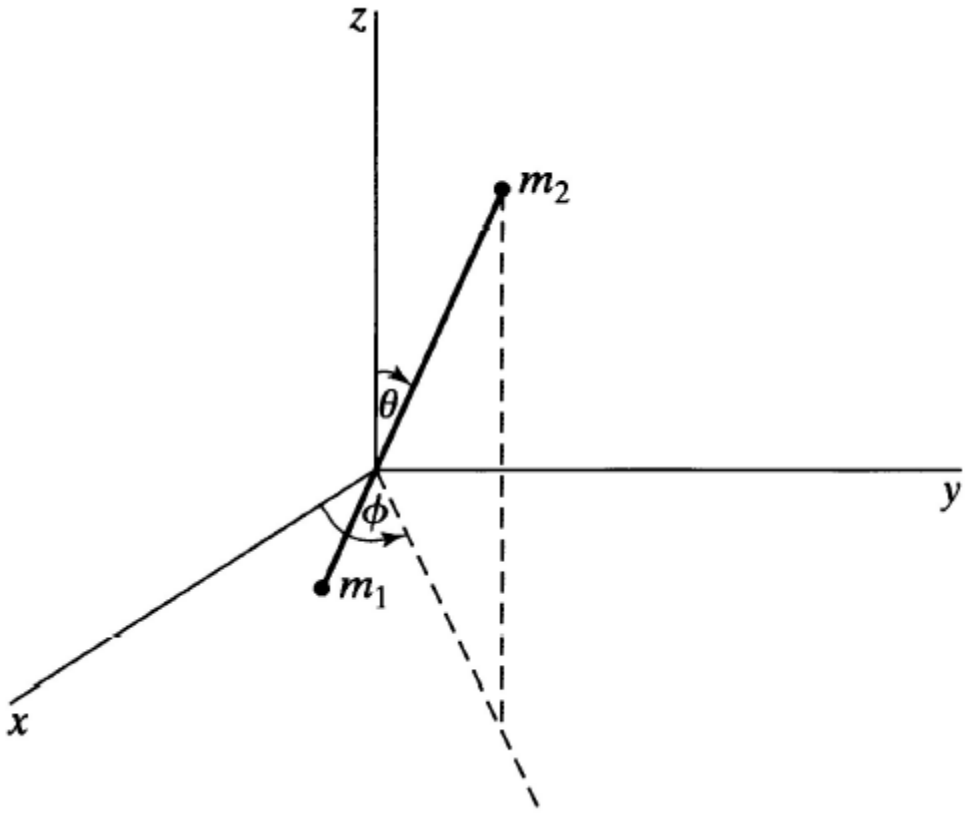
$$B \equiv h/8\pi^2 I\,, \qquad J = 0, 1, 2, \ldots$$

$\Delta E = h\nu$



$E = BJ(J+1)$

The energy levels and absorption transitions of a rigid rotator. The absorption transitions occur between adjacent levels, so the absorption spectrum shown below the energy levels consists of a series of equally spaced lines. The quantity $\tilde{B}$ is $h/8\pi^2 cI$



Coordinate system for the two-particle rigid rotor.

$$\left(-\frac{\hbar^2}{2m_1}\nabla_1^2-\frac{\hbar^2}{2m_2}\nabla_2^2+V(x,y,z)\right)\psi=E\psi$$

where $\psi \equiv \psi(x_1,x_2,y_1,y_2,z_1,z_2)$

$$,x=(x_2-x_1),y=(y_2-y_1),z=(z_2-z_1)$$

V is function only of the relative coordinates, in this particular case V=0

$$H= \left(-\frac{\hbar^2}{2M}\nabla_M^2\right) + \left(-\frac{\hbar^2}{2\mu}\nabla_\mu^2 - V\right)$$

The Hamiltonian can be viewed as the sum of the Hamiltonians of two hypothetical non-interacting particles with masses M and μ. The first term represent Hamiltonian for translational kinetic energy of the hypothetical particle of mass M located at the centre of mass. The second term represents Hamiltonian for kinetic energy of internal motion of the hypothetical particle of mass μ subject to potential energy function V.

$$-\frac{h^2}{8\pi^2 M}\frac{d^2\psi_M}{dX^2} = E_M\psi_M$$

E_M is the translational Energy of a hypothetical particle of mass M located at the centre of mass

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V\right)\psi = E_\mu\psi$$

E_μ is the energy of the hypothetical particle of mass μ that subject to the same potential energy as the original system.

Where $E= E_\mu + E_M$ and $\Psi = \Psi_M . \Psi_\mu$

Internal motion is of two types: the distance between two particles can change (vibration) and direction of the bond or r vector can change (rotation)

Here, V=0

$$\hat{H} = \hat{T} = -\frac{\hbar^2}{2\mu}\nabla^2 \qquad (r \text{ constant})$$

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

This problem becomes equivalent to a particle of mass μ constrained to move on a surface of a sphere of radius r=*l* , the bond length