SEM IV
PHYSICAL CHEMISTRY HONOURS

PAPER : CEMACOR08T

Angular momentum in spherical coordinates

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Recapitulation

$$\widehat{L_x} = \hat{y}\widehat{p_z} - \hat{z}\widehat{p_y} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\widehat{L_y} = \hat{z}\widehat{p_x} - \hat{x}\widehat{p_z} = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

ns of angular momentum

$$\widehat{L_z} = \hat{x}\widehat{p_y} - \hat{y}\widehat{p_x} = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

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

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

ns of angular momentum

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

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

$$\left[\widehat{L^2}, \widehat{L_x}\right] = 0$$

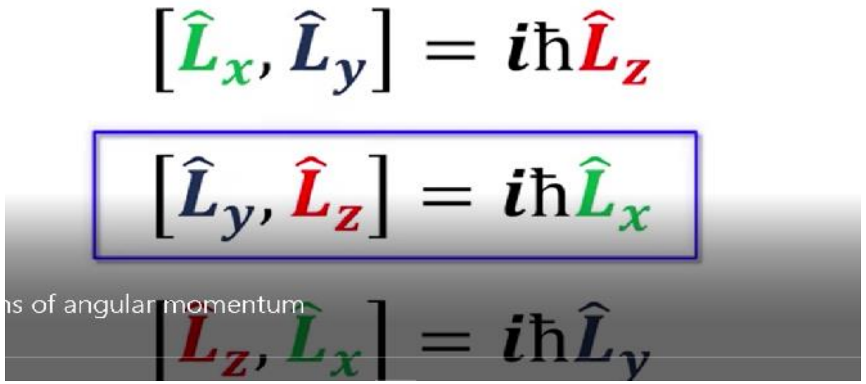
$$\left[\widehat{L^2}, \widehat{L_y}\right] = 0$$

omentum

$$\left[\widehat{L^2}, \widehat{L_z}\right] = 0$$

- The technical term is "**canonically conjugate**" **variables.** For the moving electron, the **canonically conjugate variables** are in two pairs: momentum and position are one pair, and energy and time are another.

- A pair of physical variables describing a quantum-mechanical system such that their commutator is a nonzero constant; either of them, but not both, can be precisely specified at the same time.



A. If the operators **A** and **B** commute, then it is possible to find a simultaneous set of eigenfunctions.

$$[\widehat{L^2}, \widehat{L_x}] = 0$$

$$[\widehat{L^2}, \widehat{L_y}] = 0$$

$$[\widehat{L^2}, \widehat{L_z}] = 0$$

B. If the observables **A** and **B** are compatible, that is, if there exists a simultaneous set of eigenfunctions of the operators **A** and **B**, then these operators must commute; [A , B] = 0.

C. If the operators **A** and **B** do not commute, that is, if [**A** , **B**] $\neq$ 0, then there does not exist a common set of eigenfunctions of the two operators. This means that the corresponding observables **can not** have sharp values simultaneously; they are not compatible.

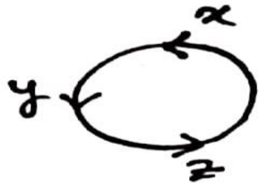
■ $[x_i, p_j] = i\hbar\, \delta_{ij}$

Heisenberg's Uncertainty principle

δ_{ij} = Kronecker delta fn.

ie, if $i=j$ $\delta_{ij}=1$

if $i \neq j$ $\delta_{ij}=0$



$[x\ p_x] = i\hbar$ $[z\ p_z] = ih$

$[y\ p_x] = 0$

■ $[L_x, L_y] = i\hbar L_z$

$[L_x, p_y] = i\hbar p_z$

$[L_x, y] = i\hbar z$

COMMUTATORS = 0

$[y\ p_x]=0$

$[z\ p_x]=0$

$[p_x\ z]=0$

$[x_i, x_j]=0$

$[p_i, p_j]=0$

■ Unlike their classical analogs which are scalars, the ang. momentum operators do not commute

$[L_x, L_x]=0$ $[L^2, L]=0$

$[L_y, L_y]=0$ $[L^2, L_x^2]=0$

$[L_z, L_z]=0$ $[L^2, L_y^2]=0$

$[L^2, L_z^2]=0$

■ $[H\ L]=0$

$[V\ L]=0$

when a particle is under the influence of a central (symmetrical) potential, then L commutes with potential ergy $V(r)$.

Operators in other coordinates

Kinetic energy in spherical coordinates:

$$\hat{K} = -\frac{\hbar^2}{2m}\nabla^2$$

$$\hat{K} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Angular momentum operators in spherical coordinates:

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

Combined:

$$\hat{K} = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{\hbar^2 r^2}\hat{L}^2\right]$$

∇^2 is the *Laplacian operator:*

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{6-34}$$

The Laplacian operator ∇^2 occurs frequently in quantum mechanics. Equation 6-34 expresses ∇^2 in Cartesian coordinates. If the system has a center of symmetry, such as the hydrogen atom with a central proton and an electron around it, then it is more convenient to express ∇^2 in spherical coordinates. Therefore, it is necessary for us to be able to convert ∇^2 from Cartesian coordinates to spherical coordinates. The conversion of ∇^2 from Cartesian coordinates to some other system of coordinates requires that we use the chain rule of partial differentiation. For example, suppose we consider the conversion of ∇^2 from Cartesian coordinates to plane polar coordinates. The relation between these two coordinate systems is shown in [redacted]. Suppose that a function $f(r, \theta)$ depends on the polar coordinates r and θ. Then the chain rule of partial differentiation says that

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y$$

and that

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x \tag{6-35}$$

$$x = f(r, \theta, \phi)$$

$$y = f(r, \theta, \phi)$$

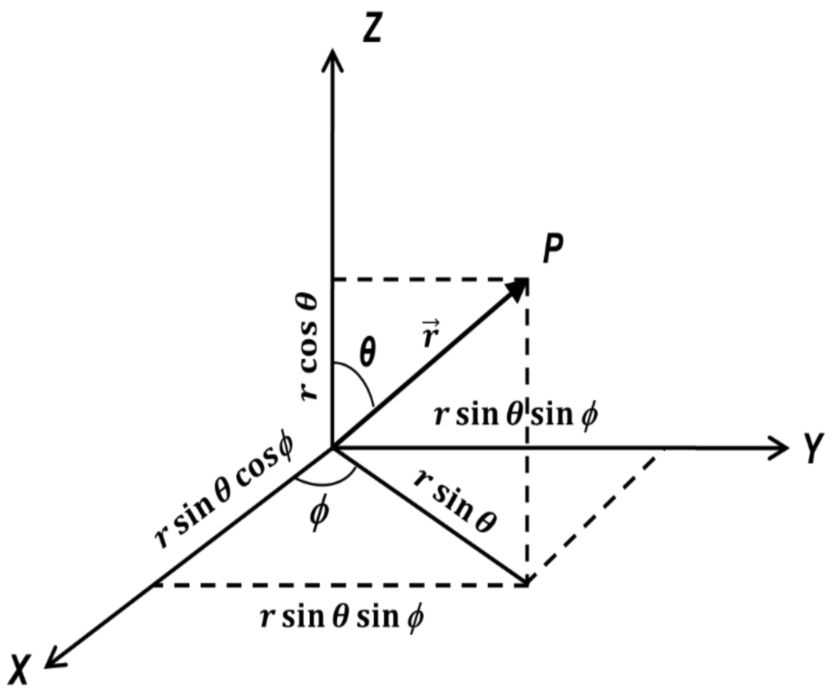
$$z = f(r, \theta, \phi)$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\cdot\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\cdot\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\cdot\frac{\partial}{\partial \phi}$$

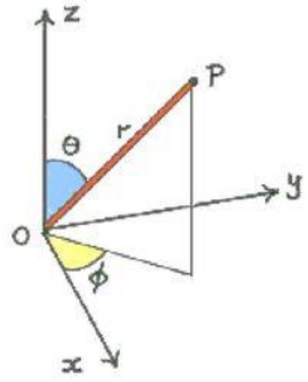
$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\cdot\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\cdot\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\cdot\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\cdot\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\cdot\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\cdot\frac{\partial}{\partial \phi}$$

eigenfunctions of angular momentum



Spherical Polar Coordinates



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

$$r = \sqrt{x^2+y^2+z^2} \qquad 0 \le r$$
$$\theta = \cos^{-1}\frac{z}{r} \qquad 0 \le \theta \le \pi$$
$$\phi = \tan^{-1}\frac{y}{x} \qquad 0 \le \phi \le 2\pi$$

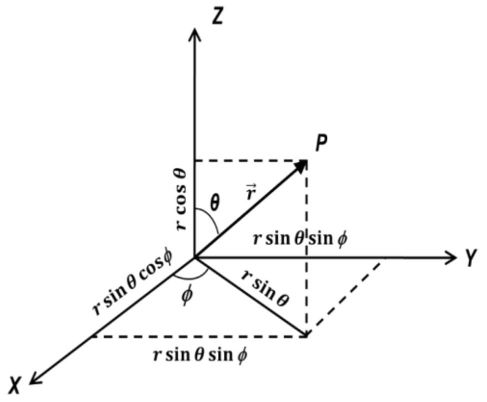
The radius vector $\vec{r}$ is given as

$$\vec{r} = \overrightarrow{OP} = \vec{i}x + \vec{j}y + \vec{k}z$$

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

$$r^2 = x^2 + y^2 + z^2 \quad (8)$$

From Figure 1 we have



$$\left.\begin{array}{r} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{array}\right\} \quad (9)$$

$$\tan\phi = \frac{y}{x}$$
(10)

Hence, $\vec{r} = \overrightarrow{OP} = \vec{i}r\sin\theta\cos\phi + \vec{j}r\sin\theta\sin\phi + \vec{k}r\cos\theta$
(11)

From eqn. 9

$$dx = \sin\theta\cos\phi\,dr + r\cos\theta\cos\phi\,d\theta - r\sin\theta\sin\phi\,d\phi$$
(12)

$$dy = \sin\theta\sin\phi\,dr + r\cos\theta\sin\phi\,d\theta + r\sin\theta\cos\phi\,d\phi$$
(13)

$$dz = \cos\theta\,dr - r\sin\theta\,d\theta$$
(14)

Solving for dr, $d\theta$ and $d\phi$ we have

$$dr = \sin\theta\cos\phi\,dx + \sin\theta\sin\phi\,dy + \cos\theta\,dz$$
(15)

$$d\theta = \frac{1}{r}\cos\theta\cos\phi\,dx + \frac{1}{r}\cos\theta\sin\phi\,dy - \frac{1}{r}\sin\theta\,dz$$
(16)

$$d\phi = \frac{1}{r\sin\theta}(-\sin\phi\,dx + \cos\phi\,dy)$$
(17)

$r^2 = x^2+y^2+z^2$
$2r\,dr = 2x\,dx + 2y\,dy + 2z\,dz$
$r\,dr = x\,dx + y\,dy + z\,dz$
$r\,dr = r\sin\theta\cos\phi\,dx + r\sin\theta\sin\phi\,dy + r\cos\theta\,dz$
or, $dr = \sin\theta\cos\phi\,dx + \sin\theta\sin\phi\,dy + \cos\theta\,dz$.

Using these relationships we have

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial x} = \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial\phi}$$
(18)

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}$$
(19)

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial z}\frac{\partial}{\partial\phi}$$

$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}$$
(20)

From eqn. 8 the following relations can be shown

$$\left.\begin{aligned}\frac{\partial r}{\partial x}&=\frac{x}{r}\\ \frac{\partial r}{\partial y}&=\frac{y}{r}\\ \frac{\partial r}{\partial z}&=\frac{z}{r}\end{aligned}\right\} \qquad (21)$$

From eqn. 9

$$z = r\cos\theta$$

$$\theta = \cos^{-1}\left(\frac{z}{r}\right) = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

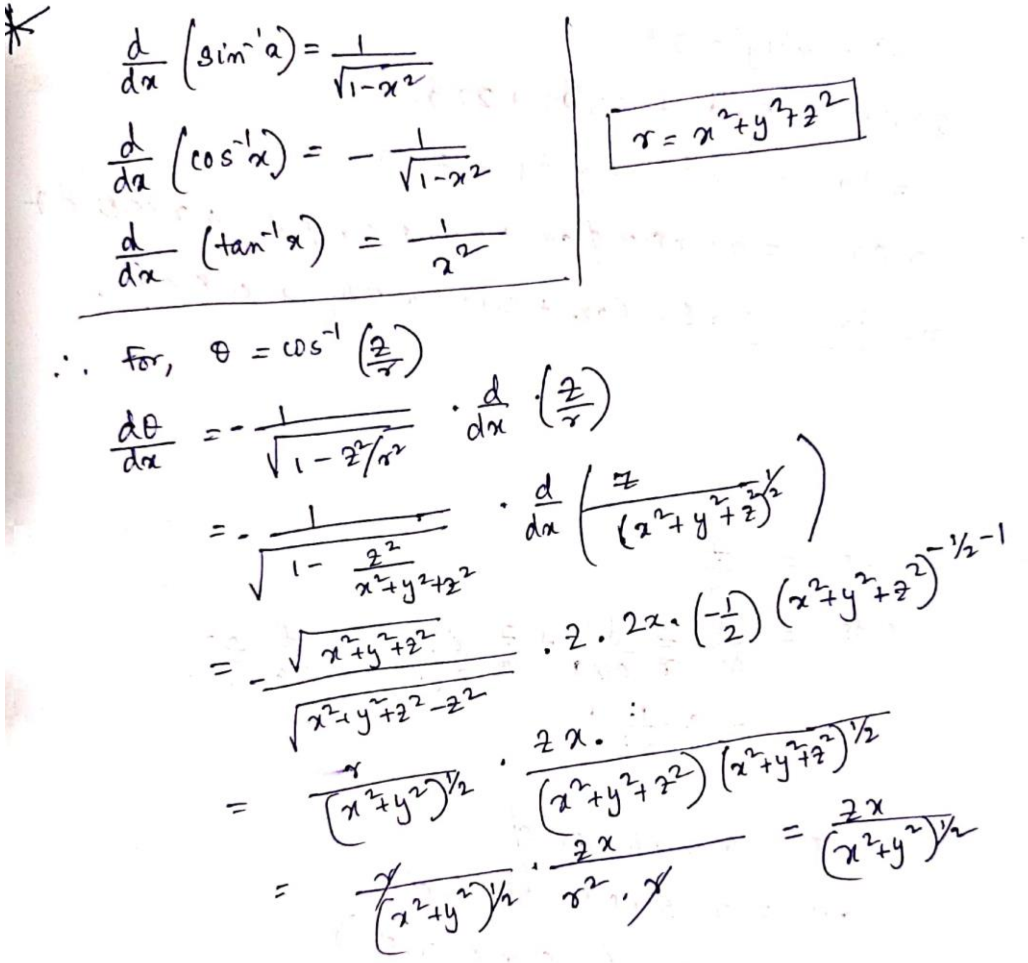
$$\left.\begin{aligned}\frac{\partial \theta}{\partial x}&=\frac{xz}{(x^2+y^2)^{1/2}r^2}\\ \frac{\partial \theta}{\partial y}&=\frac{yz}{(x^2+y^2)^{1/2}r^2}\\ \frac{\partial \theta}{\partial z}&=\frac{-(x^2+y^2)^{1/2}}{r^2}\end{aligned}\right\} \qquad (22)$$

From eqn. 10

$$\tan\phi = \frac{y}{x}$$

$$\phi = \tan^{-1}\left(\frac{y}{x}\right)$$

$$\left.\begin{aligned}\frac{\partial \phi}{\partial x}&=-\frac{y}{x^2+y^2}\\ \frac{\partial \phi}{\partial y}&=\frac{x}{x^2+y^2}\end{aligned}\right\} \qquad (23)$$



Lx in spherical polar coordinates

Hence, $\widehat{L_x}$ is spherical polar coordinate is given as

$$\widehat{L_x} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\widehat{L_x} = i\hbar\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right)$$

$$\widehat{L_x} = i\hbar\left\{z\left[\frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}\right] - y\left[\frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}\right]\right\}$$

$$\widehat{L_x} = i\hbar\left\{\left(z\frac{\partial r}{\partial y} - y\frac{\partial r}{\partial z}\right)\frac{\partial}{\partial r} + \left(z\frac{\partial \theta}{\partial y} - y\frac{\partial \theta}{\partial z}\right)\frac{\partial}{\partial \theta} + \left(z\frac{\partial \phi}{\partial y} - y\frac{\partial \phi}{\partial z}\right)\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_x} = i\hbar\left\{\left[z\left(\frac{y}{r}\right) - y\left(\frac{z}{r}\right)\right]\frac{\partial}{\partial r} + \left[\frac{yz^2}{(x^2+y^2)^{1/2}r^2} + \frac{y(x^2+y^2)^{1/2}}{r^2}\right]\frac{\partial}{\partial \theta} + \frac{xz}{x^2+y^2}\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_x} = i\hbar\left\{\frac{y}{r^2}\left[\frac{z^2}{(x^2+y^2)^{1/2}} + (x^2+y^2)^{1/2}\right]\frac{\partial}{\partial \theta} + \frac{xz}{x^2+y^2}\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_x} = i\hbar\left\{\frac{y}{r^2}\left[\frac{z^2+x^2+y^2}{(x^2+y^2)^{1/2}}\right]\frac{\partial}{\partial \theta} + \frac{xz}{x^2+y^2}\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_x} = i\hbar\left\{\frac{y}{r^2}\left[\frac{r^2}{(x^2+y^2)^{1/2}}\right]\frac{\partial}{\partial \theta} + \frac{xz}{x^2+y^2}\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_x} = i\hbar\left\{\frac{y}{(x^2+y^2)^{1/2}}\frac{\partial}{\partial \theta} + \frac{xz}{x^2+y^2}\frac{\partial}{\partial \phi}\right\}$$

Now,

$$\frac{y}{(x^2+y^2)^{1/2}}$$

$$= \frac{y}{(r^2-z^2)^{1/2}}$$

$$= \frac{y}{(r^2-r^2\cos^2\theta)^{1/2}}$$

$$= \frac{y}{(r^2\sin^2\theta)^{1/2}}$$

$$= \frac{y}{r\sin\theta}$$

$$= \frac{r\sin\theta\sin\phi}{r\sin\theta} = \sin\phi$$

and

$$\frac{xz}{x^2+y^2}$$

$$= \frac{xz}{r^2-z^2}$$

$$= \frac{(r\sin\theta\cos\phi)(r\cos\theta)}{r^2\sin^2\theta}$$

$$= \frac{\cos\theta}{\sin\theta}\cos\phi = \cot\theta\cos\phi$$

With this the above equation simplifies to

$$\widehat{L_x} = i\hbar\left(\sin\phi\frac{\partial}{\partial \theta} + \cot\theta\cos\phi\frac{\partial}{\partial \phi}\right) \quad (24)$$

Ly in spherical polar coordinates

Similarly, $\widehat{L_y}$ in spherical polar coordinates is given as

$$\widehat{L_y} = i\hbar\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right)$$

$$\widehat{L_y} = i\hbar\left\{\left(x\frac{\partial r}{\partial z} - z\frac{\partial r}{\partial x}\right)\frac{\partial}{\partial r} + \left(x\frac{\partial \theta}{\partial z} - z\frac{\partial \theta}{\partial x}\right)\frac{\partial}{\partial \theta} + \left(x\frac{\partial \phi}{\partial z} - z\frac{\partial \phi}{\partial x}\right)\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_y} = i\hbar\left\{\left(\frac{xz}{r} - \frac{zx}{r}\right)\frac{\partial}{\partial r} + \left[\frac{-x(x^2+y^2)^{1/2}}{r^2} - \frac{xz^2}{(x^2+y^2)^{1/2}r^2}\right]\frac{\partial}{\partial \theta} + \left[\frac{yz}{x^2+y^2}\right]\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_y} = i\hbar\left\{-\frac{x}{r^2}\left[\frac{x^2+y^2+z^2}{(x^2+y^2)^{1/2}}\right]\frac{\partial}{\partial \theta} + \left[\frac{yz}{x^2+y^2}\right]\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_y} = i\hbar\left\{\left[-\frac{x}{(x^2+y^2)^{1/2}}\right]\frac{\partial}{\partial \theta} + \left[\frac{yz}{x^2+y^2}\right]\frac{\partial}{\partial \phi}\right\}$$

$$\widehat{L_y} = i\hbar\left[-\frac{r\sin\theta\cos\phi}{r\sin\theta}\frac{\partial}{\partial \theta} + \frac{(r\sin\theta\sin\phi)(r\cos\theta)}{r^2\sin^2\theta}\frac{\partial}{\partial \phi}\right]$$

$$\widehat{L_y} = i\hbar\left(-\cos\phi\frac{\partial}{\partial \theta} + \frac{\cos\theta}{\sin\theta}\sin\phi\frac{\partial}{\partial \phi}\right)$$

$$\widehat{L_y} = i\hbar\left(-\cos\phi\frac{\partial}{\partial \theta} + \cot\theta\sin\phi\frac{\partial}{\partial \phi}\right)$$

(25)

Lz in spherical polar coordinates

Similarly, $\widehat{L_z}$ in spherical polar coordinates is given as

$$\widehat{L_z} = i\hbar\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$$

$$\widehat{L_z} = -i\hbar\frac{\partial}{\partial \phi}$$

(26)

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L2 in spherical polar coordinates

Say, Ψ is an arbitrary function of θ and ϕ, that is $\Psi = \Psi(\theta, \phi)$

$\widehat{L_x}^2\Psi$

$= \widehat{L_x}(\widehat{L_x}\Psi)$

$= -\hbar^2\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\left(\sin\phi\frac{\partial\Psi}{\partial\theta} + \cot\theta\cos\phi\frac{\partial\Psi}{\partial\phi}\right)$ (from eqm. 24)

Similarly,

$\widehat{L_y}^2\Psi$

$= \widehat{L_y}(\widehat{L_y}\Psi)$

$= -\hbar^2\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\left(-\cos\phi\frac{\partial\Psi}{\partial\theta} + \cot\theta\sin\phi\frac{\partial\Psi}{\partial\phi}\right)$ (from eqn. 25)

and$\widehat{L_z}^2\Psi$

$= \widehat{L_z}(\widehat{L_z}\Psi)$

$= -\hbar^2\frac{\partial^2\Psi}{\partial\phi^2}$ (from eqn. 26)

Hence, $L^2\Psi = (L_x^2 + L_y^2 + L_z^2)\Psi$ $(\vec{L} = \vec{L}.\vec{L} = L_x^2 + L_y^2 + L_z^2)$

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

This follows that

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

(27)

Final values :

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

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

eigenfunctions of angular momentum

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

$$\hat{L}^2 = -\hbar^2[\frac{\partial^2}{\partial\theta^2} + cot\theta\frac{\partial}{\partial\theta} + (1 + cot^2\theta).\frac{\partial^2}{\partial\phi^2}$$

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eigenfunctions of angular momentum

$$\left[\frac{\partial^2}{\partial\theta^2} + cot\theta\frac{\partial}{\partial\theta}\right] = \frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)$$

$$[(1 + cot^2\theta)] = \frac{1}{sin^2\theta}$$

eigenfunctions of angular momentum

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

eigenfunctions of angular momentum

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

eigenfunctions of angular momentum

Spherical Polar Coordinates

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

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

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

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

The derivation is lengthy; if you want I can send you; but final results are more important

Do not depend on r

Simultaneous eigen function of L^2 and Lz: Y l,m

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

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

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

$$[\widehat{L^2}, \widehat{L_x}] = 0$$

$$[\widehat{L^2}, \widehat{L_y}] = 0$$

$$[\widehat{L^2}, \widehat{L_z}] = 0$$

none of the two components of angular momentum can be measured simultaneously (they from canonically conjugate pair and hence Heisenberg uncertainty principle is applicable). On the contrary, the operator $\hat{L}^2$ commutes with any component of $\hat{L}$ implying that simultaneous measurement of $\hat{L}^2$ and one of the components of $\hat{L}$ (say $\widehat{L_z}$) may be possible. So to say, simultaneous eigenfunctions of any two components of $\hat{L}$ is not possible but simultaneous eigenfunctions of $\hat{L}^2$ and $\widehat{L_z}$ (or any other component of $\hat{L}$) may be obtained

Simultaneous eigen function of L^2 and Lz: Y l,m

Question

The eigenvalue of $\widehat{L_z}$ is customarily designated as $m\hbar$ where m is a constant which is to be evaluated from solution of the corresponding eigenvalue equation. It is, however, noteworthy in this context that angular momentum has the dimension $[M][L^2][T^{-2}][T]$, that is, the dimension of product of energy and time (e.g., joule-second). Given that the dimension of ħ is exactly the same (unit of ħ is joule-second), it is not irrational to designate the eigenvalues of $\widehat{L_z}$ by $m\hbar$ (m being constant). Similarly, the eigenvalue of $\hat{L}^2$ would be denoted as $\beta\hbar^2$ (α being a constant).

Thus, the eigenvalue equation can be written as

$$\hat{L}^2 Y_{l,m} Y(\theta,\phi) = \beta\hbar^2 Y_{l,m}(\theta,\phi)$$

$$\widehat{L_z} Y_{l,m}(\theta,\phi) = m\hbar Y_{l,m}(\theta,\phi)$$

Proof is there; if you want it , it can be sent

$$\hat{L}^2 Y_{l,m} Y(\theta,\phi) = \beta\hbar^2 Y_{l,m}(\theta,\phi)$$

$$\widehat{L_z} Y_{l,m}(\theta,\phi) = m\hbar Y_{l,m}(\theta,\phi)$$

Recalling the expressions for $\widehat{L_z}$ and $\hat{L}^2$ in spherical polar coordinates the above equations are represented as

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] Y_{l,m}(\theta,\phi) = \beta\hbar^2 Y_{l,m}(\theta,\phi)$$

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

igenfunctions of angular momentum

$$-i\hbar\frac{\partial Y_{l,m}(\theta,\phi)}{\partial\phi} = m\hbar Y_{l,m}(\theta,\phi)$$

Applying the technique of separation of variables, that is,

Question : separate the variables

$$Y_{l,m}(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

To Find eigen function of Lz

$$-i\hbar \frac{\partial Y(\theta,\phi)}{\partial \phi} = m\hbar Y(\theta,\phi)$$

Applying the technique of separation of variables,

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

$$-i\hbar \frac{\partial \Theta(\theta)\Phi(\phi)}{\partial \phi} = m\hbar \Theta(\theta)\Phi(\phi)$$

Question : Find the eigen function of Lz

$$-i\hbar \Theta(\theta)\frac{\partial \Phi(\phi)}{\partial \phi} = m\hbar \Theta(\theta)\Phi(\phi)$$

Dividing throughout by $\Theta(\theta)\Phi(\phi)$

$$-i\hbar \frac{1}{\Phi(\phi)}\frac{\partial \Phi(\phi)}{\partial \phi} = m\hbar$$

$$\frac{\partial \ln \Phi(\phi)}{\partial \phi} = im$$

$$\partial \ln \Phi(\phi) = im\partial\phi$$

On integration

$$\ln \Phi(\phi) = im\phi + C \ (integration\ constant)$$

$$\Phi(\phi) = e^{im\phi+C}$$

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

A is the normalization constant.

Remembering the range of the angular variable ϕ, that is, $0 \leq \phi \leq 2\pi$, the solution requires

$\Phi(\phi) = \Phi(\phi + 2\pi)$ in order to satisfy the condition of single-valuedness, hence,

$$\Phi(\phi) = Ae^{im\phi} = \Phi(\phi + 2\pi) = Ae^{im(\phi+2\pi)} = Ae^{im\phi}e^{im2\pi}$$

This follows that

$$e^{im2\pi} = 1$$

which is possible when $m = 0, \pm 1, \pm 2, \pm 3, \dots \dots \dots$

- **Evaluation of the normalization constant A**

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

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

$$A^* A \int_0^{2\pi} e^{-im\phi} e^{im\phi} d\phi = 1$$

$$|A|^2 \int_0^{2\pi} d\phi = 1$$

$$|A|^2 (2\pi) = 1$$

Hence, $|A| = \frac{1}{\sqrt{2\pi}}$

With this the complete solution for the ϕ-part may be given as

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

■ Orthonormality of the function $\Phi(\phi)$

$$\int_0^{2\pi} \Phi_m(\phi)^* \Phi_n(\phi) d\phi$$

$$= \int_0^{2\pi} \left(\frac{1}{\sqrt{2\pi}} e^{im\phi}\right)^* \left(\frac{1}{\sqrt{2\pi}} e^{in\phi}\right) d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{i(n-m)\phi} d\phi$$

$$= \frac{1}{2\pi} \left| \frac{e^{i(n-m)\phi}}{(n-m)} \right|_0^{2\pi}$$ only when $n \neq m$

$$= \frac{1}{2\pi(n-m)} \left[e^{i(n-m)2\pi} - 1\right] = 0$$ when $n \neq m$

Remembering $e^{i\theta} = \cos\theta + i\sin\theta$, and m and n both being integers $(n - m)$ will also be an integer.

Now for $m = n$

$$\int_0^{2\pi} \Phi_m(\phi)^* \Phi_m(\phi) d\phi$$

$$= \int_0^{2\pi} \left(\frac{1}{\sqrt{2\pi}} e^{im\phi}\right)^* \left(\frac{1}{\sqrt{2\pi}} e^{im\phi}\right) d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{i(m-m)\phi} d\phi$$

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

$$= \frac{1}{2\pi} |\phi|_0^{2\pi}$$

$$= \frac{1}{2\pi}(2\pi) = 1$$

Question :Prove orthonormality

In general we can write

$$\int_0^{2\pi} \Phi_m(\phi)^* \Phi_n(\phi) d\phi = \delta_{mn}$$

where, $\delta_{mn} = \left.\begin{matrix} 0\ if\ m \neq n \\ 1\ if\ m = n \end{matrix}\right\}$

that is, the eigenfunctions of $\widehat{L_z}$ form an orthonormal set of functions, $\{\Phi_m(\phi)\}$, where, $m = 0, \pm 1, \pm 2, \pm 3, \dots \dots \dots$

**To solve the θ part of the equation(Sepn of variables)

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

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}+\beta Y(\theta,\phi)=0$$

Question : Separate theta and phi

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

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

Dividing throughout by $\Theta(\theta)\Phi(\phi)$

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

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

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

$$\frac{\sin^2\theta}{\Theta(\theta)}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)+\beta\Theta(\theta)\right]=m^2$$

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

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

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

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

$$x = \cos\theta \qquad \text{and} \qquad P(x) = \Theta(\theta)$$

and hence, $$\frac{dP(\lambda)}{dx} = \frac{d\Theta(\theta)}{dx} = \frac{d\Theta(\theta)}{d(\cos\theta)} = -\frac{1}{\sin\theta}\frac{d\Theta(\theta)}{d\theta}$$

$$\frac{d(\theta)}{d\theta} = -\sin\theta \frac{dP(x)}{dx}$$

and from $x = \cos\theta$

$$\frac{dx}{d\theta} = -\sin\theta$$

$$-\frac{1}{\sin\theta}\frac{d}{d\theta} = \frac{d\theta}{dx}\frac{d}{d\theta} = \frac{d}{dx}$$

With these transformations eqn becomes

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

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

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

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

where, the range of $\lambda = \cos\theta$ would be $-1 \leq \lambda \leq +1$ ($\cos\theta$ varies from – 1 to + 1).

For $m = 0$, eqn reduces to

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

$$\mathbf{\frac{d^2P(\lambda)}{dx^2} - 2x\frac{dP(x)}{dx} - x^2\frac{d^2P(\lambda)}{d\lambda^2} + \beta P(x) = 0}$$

$$\frac{d^2P(\lambda)}{dx^2} - 2x\frac{dP(x)}{dx} - x^2\frac{d^2P(\lambda)}{d\lambda^2} + \beta P(x) = 0 \quad \text{(for m = 0)}$$

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

The above eqn. is a Legendre differential equation whose solutions can be expressed in terms of a power series in x subject to the restriction that

$$\hat{L}^2Y(\theta,\phi) = \beta\hbar^2Y(\theta,\phi)$$

$$\beta = l(l+1)$$

$$\hat{L}_zY(\theta,\phi) = m\hbar Y(\theta,\phi)$$

where, $l = 0,1,2,3,\ldots\ldots\ldots$, l is the "orbital angular momentum quantum number"

Thus, the eigenvalues of $\hat{L}^2$ are given as $\beta\hbar^2 = l(l+1)\hbar^2$.

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Therefore, $$(1- x^2)\frac{d^2P(x)}{dx^2} - 2x\frac{dP(x)}{dx} + [l(l+1) - \frac{m^2}{1-x^2}]P(x) = 0$$

Therefore, $(1-x^2)\frac{d^2P(x)}{dx^2} - 2x\frac{dP(x)}{dx} + [l(l+1) - \frac{m^2}{1-x^2}]P(x) = 0$

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

- The solutions to the above equation when m = 0 are called ***Legendre's plynomials ; -1*** $\leq x \leq$ ***+1*** $(0 \leq \theta \leq \pi)$

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

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

Associated Legendre Polynomials; m≠ 0

$$\int_{-1}^{1} P_l(x)P_n(x)\,dx = \int_0^\pi d\theta \sin\theta P_l(\cos\theta)P_n(\cos\theta) = \frac{2\delta_{ln}}{2l+1}$$

$$d\tau = r^2 \sin\theta\, dr\, d\theta\, d\varphi$$

$\sin\theta\, d\theta$, is the "θ part" of $d\tau$

$$\int_{-1}^{1} dx\, P_l^{|m|}(x)P_n^{|m|}(x) = \int_0^\pi d\theta \sin\theta P_l^{|m|}(\cos\theta)P_n^{|m|}(\cos\theta) = \frac{2}{(2l+1)}\frac{(l+|m|)!}{(l-|m|)!}\delta_{ln}$$

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

The overall solution to the θ-part can be written as

$$\Theta_l(\theta) = \left[\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right]^{1/2} (-1)^m P_l^m(\cos\theta)$$

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

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

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

$X = \cos\theta$

The First Few Associated Legendre Functions $P_l^{|m|}(x)$

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

The overall solution to the θ-part can be written as

$$\Theta_l(\theta) = \left[\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right]^{1/2} (-1)^m P_l^m(\cos\theta)$$

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

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

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

l=0, m=0	$\left[\frac{2.0+1}{2}\frac{(0-0)!}{(0+0)!}\right]^{1/2} = \frac{1}{\sqrt{2}}$	$P_0(x) = \frac{1}{2^0 0!}\frac{d^0}{dx^0}(x^2-1)^0 = 1$	$P_0^{\|0\|}(x) = (1 - x^2)^{\|0\|/2}\frac{d^0}{dx^0}P_0(x) = 1$
l=1, m=0	$\left[\frac{2.1+1}{2}\frac{(1-0)!}{(1+0)!}\right]^{1/2} = \sqrt{\frac{3}{2}}$	$P_1(x) = \frac{1}{2^1 1!}\frac{d^1}{dx^1}(x^2-1)^1 = x$	$P_1^{\|0\|}(x) = (1 - x^2)^{\|0\|/2}\frac{d^0}{dx^0}P_0(x) = x$
l=2, m=0	$\left[\frac{2.2+1}{2}\frac{(2-0)!}{(2+0)!}\right]^{1/2} = \sqrt{\frac{5}{2}}$	$P_2(x) = \frac{1}{2^2 2!}\frac{d^2}{dx^2}(x^2-1)^2 = \frac{3x^2-1}{2}$	$P_2^{\|0\|}(x) = (1 - x^2)^{\|0\|/2}\frac{d^0}{dx^0}P_0(x) = \frac{3x^2-1}{2}$
l=1, 1	$\left[\frac{2.1+1}{2}\frac{(1-1)!}{(1+1)!}\right]^{1/2} = \sqrt{\frac{3}{4}}$	$P_1(x) = \frac{1}{2^1 1!}\frac{d^1}{dx^1}(x^2-1)^1 = x$	$P_1^{\|1\|}(x) = (1 - x^2)^{\|1\|/2}\frac{d^1}{dx^1}P_1(x) = (1 - x^2)^{\|1\|/2}$

Table 6.2 Some Associated Legendre Functions

$\|M\|$	l	$P_l^M(\cos\theta)$	N
0	0	1	$1/\sqrt{2}$
	1	$\cos\theta$	$\sqrt{3/2}$
	2	$1/2\,(3\cos^2\theta - 1)$	$\sqrt{5/2}$
	3	$3/2\,(5/3\cos^3\theta - \cos\theta)$	$\sqrt{7/2}$
1	1	$\sin\theta$	$\sqrt{3/4}$
	2	$3\sin\theta\cos\theta$	$\sqrt{5/12}$
	3	$3/2\sin\theta\,(5\cos^2\theta - 1)$	$\sqrt{7/24}$
2	2	$3\sin^2\theta$	$\sqrt{5/48}$
	3	$15\sin^2\theta\cos\theta$	$\sqrt{7/240}$

$$Y_{l,m}(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

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

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$$

The First Few Spherical Harmonics

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

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

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

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

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

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

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

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

$$\left(\frac{15}{\ldots}\right)^{1/2}$$

The spherical harmonics is an eigen function of Lz with eigen values integral multiples of ħ

Furthermore, because $\hat{L}_z$ acts upon only ϕ, we also have that the spherical harmonics are eigenfunctions of $\hat{L}_z$:

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

Restrictions imposed on values of l, m

What are the values of l and m ?

$$\hat{L}_z^2 Y_l^m(\theta, \phi) = m^2\hbar^2 Y_l^m(\theta, \phi)$$

and because

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

and

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

then

$$(\hat{L}^2 - \hat{L}_z^2)Y_l^m(\theta, \phi) = (\hat{L}_x^2 + \hat{L}_y^2)Y_l^m(\theta, \phi) = [l(l+1) - m^2]\hbar^2 Y_l^m(\theta, \phi) \quad (6\text{-}88)$$

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 that

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

or that

$$l(l+1) \geq m^2 \quad (6\text{-}89)$$

Equation 6-89 says that

$$|m| \leq l$$

or that the only possible values of the integer m are

$$m = 0, \pm 1, \pm 2, \ldots, \pm l \quad (6\text{-}90)$$

- ***Therefore there are (2l +1) values of m for each value of l***

- ***Each energy level is (2l + 1) – fold degenerate***

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

$$\widehat{L_z} Y_{l,m}(\theta, \phi) = m\hbar Y_{l,m}(\theta, \phi)$$

- **Hence, the magnitude of orbital angular momentum of a particle, $|\vec{L}|$, is governed by the quantum number *l* and is given as**

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

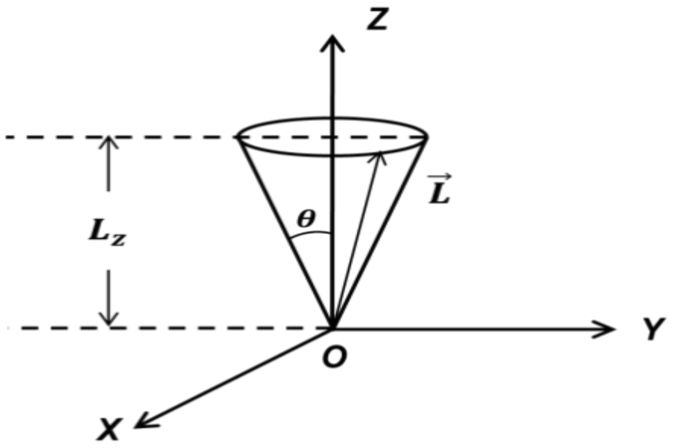


Figure 2: Angular momentum $\vec{L}$ for a given value of L_z. Here $\cos\theta = L_z/L$. Note that $\vec{L}$ may be oriented along any radial direction along the surface of the cone.

Let us now consider an example of a case for $\boldsymbol{l} = 2$ then

$|\boldsymbol{L}| = \sqrt{\boldsymbol{l}(\boldsymbol{l}+\mathbf{1})\hbar^2} = \sqrt{\mathbf{2}(\mathbf{2}+\mathbf{1})\hbar^2} = \sqrt{\mathbf{6}}\hbar^2$

andL_z may have $(2l+1) = (2 \times 2 + 1) = 5$ values for $m = -2, -1, 0, 1, 2$, that is, the eigenvalues of L_z will be given as $-2\hbar, -\hbar, 0, \hbar, 2\hbar$, this is pictorially represented in Figure 3.

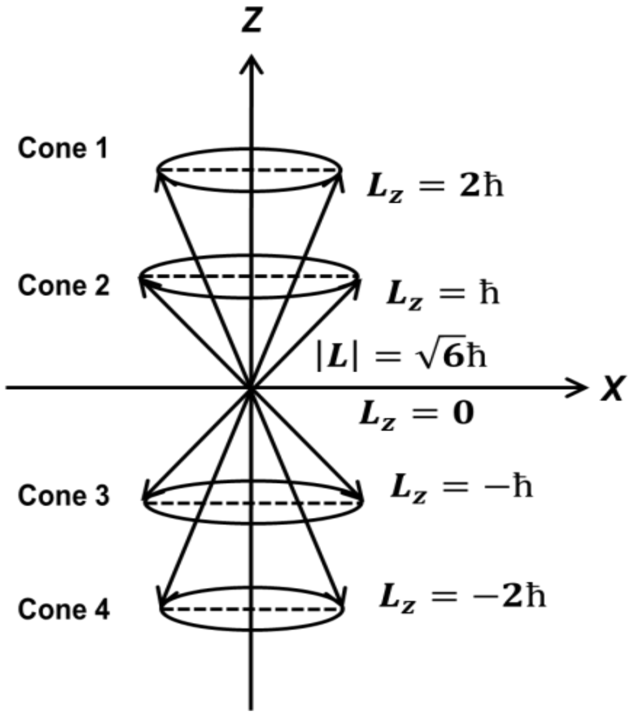


Figure 3: Angular momentum vector $|\boldsymbol{L}| = \sqrt{6}\hbar$for $\boldsymbol{l} = 2$, and the $(2\boldsymbol{l}+1) = 5$ different values of $\boldsymbol{L_z}$.

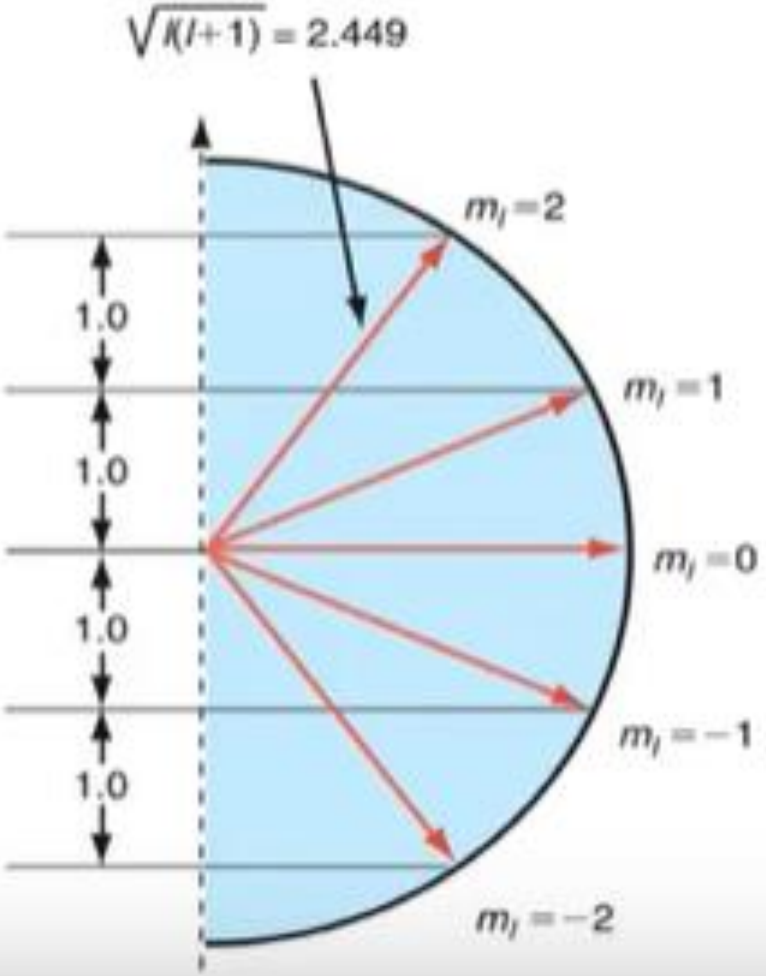
What is the difference between $|\boldsymbol{L}|$ and $\boldsymbol{L_z}$

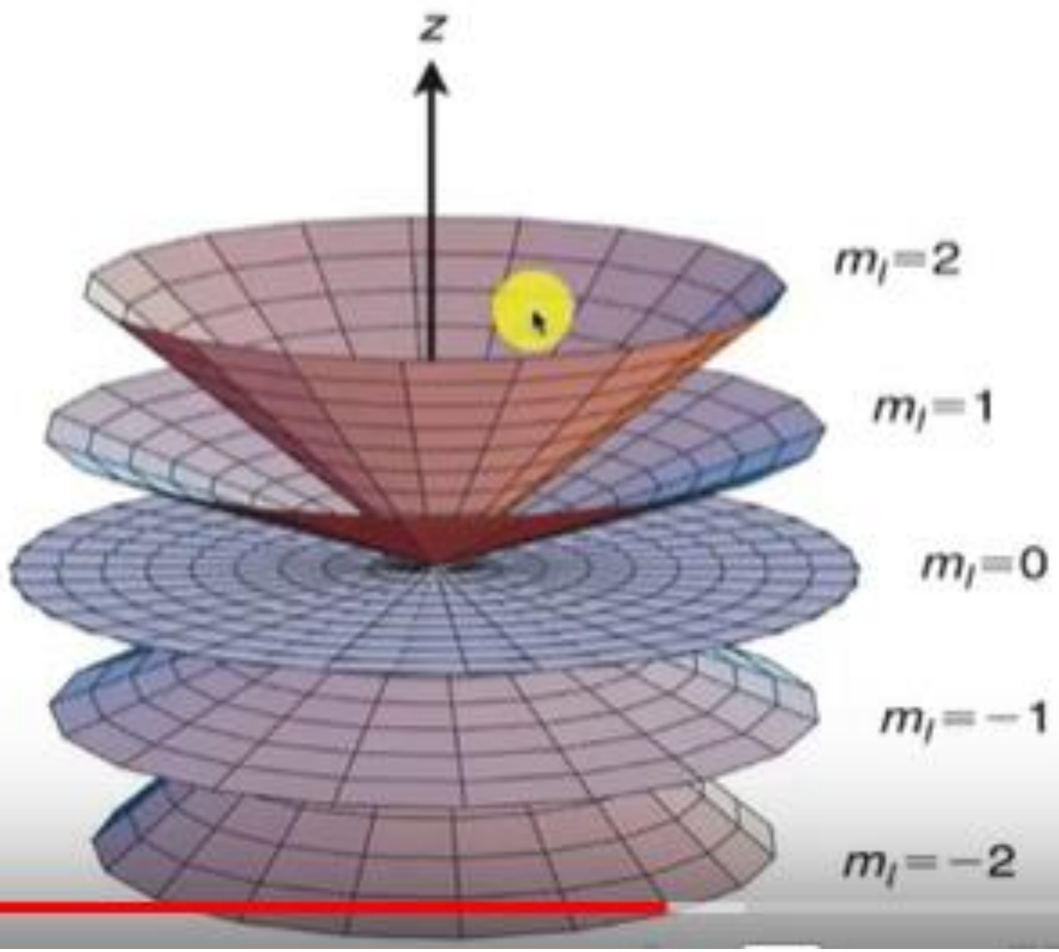
Visualization for l=2

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi)$$

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

$$l = 0,1,2,3\cdots \quad m = 0,\pm1,\pm2\cdots\pm l$$





Rigid Rotator Model

Suppose two masses are held rigidly apart at some fixed distance r_0. For this freely rotating system P.E. = 0, then

$$\hat{T} = \frac{\hat{L}^2}{2I} = \hat{H} \qquad (I = \mu {r_0}^2)$$

Therefore, the Schrödinger equation

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

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

$$\frac{\hat{L}^2}{2I}Y(\theta,\phi) = EY(\theta,\phi)$$

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

What are the energy eigen values of a Rigid rotor ?

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

Solution of this equation $E = E_J = J(J+1)\frac{\hbar^2}{2I}$

where, rotational quantum number $J = 0,1,2,\cdots\cdots\cdots$

Also note that the energy of a rigid rotor according to classical mechanics is $E = \frac{L^2}{2I}$

L is the total angular momentum.

By comparing the dimensionality we can easily see that E_J must be some integral multiple of $\frac{\hbar^2}{2I}$ with J being a dimensionless parameter.

Spherical Harmonics

$\ell = 0,\quad Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$

$$\ell = 1,\quad \begin{cases} Y_1^1(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \\ Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta \end{cases}$$

$$\ell = 2,\quad \begin{cases} Y_2^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{2i\phi} \\ Y_2^1(\theta,\phi) = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi} \\ Y_2^0(\theta,\phi) = \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1) \end{cases}$$

$$\hat{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1) Y_l^m(\theta,\varphi)$$

$$\hat{L}_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi)$$

$l = 0,1,2,3\cdots$

$m = 0,\pm1,\pm2\cdots\pm l$

Why spherical harmonics are useful

1) The spherical harmonics are orthonormal:

$$\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\varphi \, Y^*_{l'm'}(\theta,\varphi) Y_{lm}(\theta,\varphi) = \begin{cases} 0 & \text{if } l \neq l' \text{ or } m \neq m' \\ 1 & \text{if } l = l' \text{ and } m = m' \end{cases}$$

$$\left(\text{or } \int d\Omega \, Y^*_{l'm'} Y_{lm} = \delta_{l'l} \right)$$

2) The spherical harmonics are a complete set of functions:

$$f(\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm} Y_{lm}(\theta,\varphi)$$