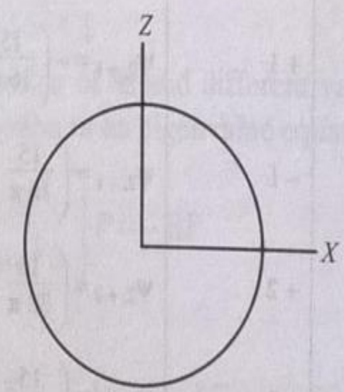
6.2.3 Physical Representation of Spherical Harmonics

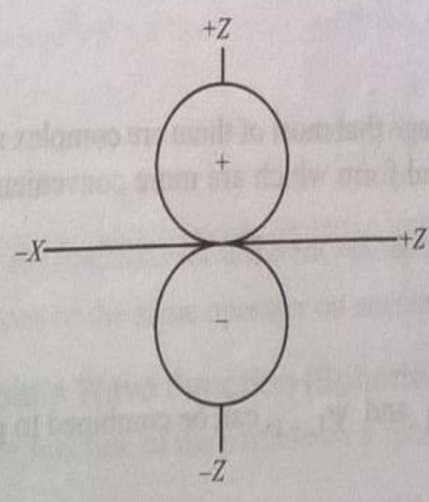
The spherical harmonics in real form can be visualised pictorially.

The function $\psi_{0,0} = \dfrac{1}{2\sqrt{\pi}}$ is a constant for all values of θ and φ; so it can be represented by the surface of the sphere and has no specific orientation [Figure 6.2 (*a*)].

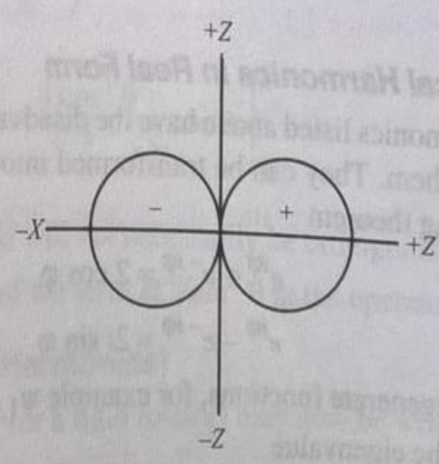
The function $\psi_{1,0} = \left(\dfrac{3}{4\pi}\right)^{1/2} \cos\theta$ has the largest positive value $\left[= + \left(\dfrac{3}{4\pi}\right)^{1/2} \right]$ when $\theta = 0$, *i.e.*, along the $+z$ axis and gradually decreases as θ increases till it vanishes at $\theta = \dfrac{\pi}{2}$ *i.e.*, along the *x*-axis. The



(*a*) $\psi_{0,0}$: No specific orientation, no node



(*b*) $\psi_{1,0}$: Oriented along *z*-axis; *xy* plane is nodal (*y*-axis is not shown)



(*c*) ψ_{1+} : Oriented along *x*-axis; *yz* plane is nodal; (*y*-axis is not shown)

Figure 6.2 : Cross-sections of spherical harmonics

value becomes increasingly negative till it is maximum negative $\left[=-\left(\frac{3}{4\pi}\right)^{1/2}\right]$ at $\theta=\pi$, *i.e.*, along $-z$ axis.

Being independent of φ this function has the same value for all values of φ. As a result, the function $\psi_{1,0}$ looks as sketched in Figure 6.2 (*b*) which consists of two spherical lobes, one + ve and the other – ve, the *xy* plane being the "nodal plane". In other words, this function is specifically oriented along the *z*-axis.

The function $\psi_{1+}=\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\varphi$ has the largest positive value for $\theta=\pi/2$, $\varphi=0$, *i.e.*, along $+x$ axis and the largest negative value for $\theta=3\pi/2$, $\varphi=\pi$, *i.e.*, along $-x$ axis. Thus the function is oriented along *x*-axis with *xz* plane as the "nodal plane" [Figure 6.2 (*c*)].

Similarly, the function $\psi_{1-}=\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\varphi$ can be seen to be oriented along *y*-axis with *xy* plane as the nodal plane.

6.2.4 Introduction to Angular Momentum

Analogous to linear momentum (p) in translational motion, a rotating particle has angular momentum (L) by virtue of its mass and angular velocity. Classically, it is a vector $\vec{L}$ whose direction is along the axis of rotation and the axis is perpendicular to the plane of rotation. Like any other vector it has cartesian components L_x, L_y and L_z in 3-dimensional place.

If the rotation is 2-dimensional, as in the case of a particle in a ring, the axis of rotation may be taken as the *z*-axis if the plane of rotation is the *xy*-plane. Then the components $L_x=L_y=0$, and $L_z=L$. (Figure 6.3).

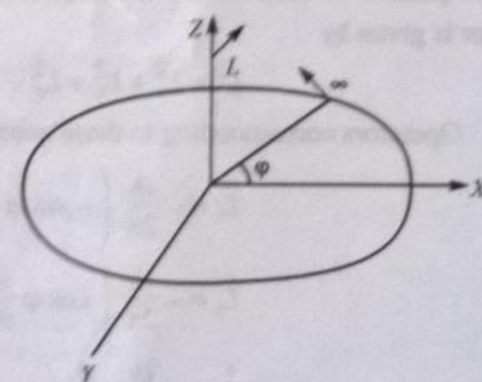


Figure 6.3 : The direction of the angular momentum vector $\vec{L}$ for a particle in a ring

In cartesian coordinate system, L_z is expressed as

$$L_z=xp_y-yp_x \qquad \text{(Vide Equation (3.25) page 43)}$$

where p_x and p_y are the components of the linear momentum p associated with the particle at the point (x, y) on the ring. The corresponding operator for L_z is

$$\hat{L}_z=-\frac{ih}{2\pi}\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$$

Since the motion is rotational it is more convenient to use polar coordinates wherein

$$\hat{L}_z=-\frac{ih}{2\pi}\frac{\partial}{\partial\varphi} \qquad \text{(See Appendix 2)}$$

where φ is the single polar variable (see Figure 6.3).

The important feature of it is that the functions

$$\psi=\frac{1}{\sqrt{2\pi}}e^{iM\varphi} \qquad \text{...(6.12)}$$

which are eigenfunctions of the Hamiltonion operator are also the eigenfunctions of $\hat{L}_z$; in the former case we get energy (E) and in the latter case the angular momentum (L_z) as eigenvalue.

$$\hat{H}\psi = -\frac{h^2}{8\pi^2 I}\frac{d^2}{d\varphi^2}\left(\frac{1}{\sqrt{2\pi}}e^{iM\varphi}\right) = \frac{M^2h^2}{8\pi^2 I}\left(\frac{1}{\sqrt{2\pi}}e^{iM\varphi}\right) = \frac{M^2h^2}{8\pi^2 I}\psi = E\,\psi$$

and
$$\hat{L}_z\,\psi = -\frac{ih}{2\pi}\frac{d}{d\varphi}\left(\frac{1}{\sqrt{2\pi}}e^{iM\varphi}\right) = \frac{Mh}{2\pi}\left[\frac{1}{\sqrt{2\pi}}e^{iM\varphi}\right] = \frac{Mh}{2\pi}\psi = L_z\,\psi$$

It has to be noted, however, that eigenfunctions of $\hat{H}$ in real form are not the eigenfunctions of $\hat{L}_z$,

$$\hat{L}_z\,\psi = -\frac{ih}{2\pi}\frac{d}{d\varphi}\left(\frac{1}{\sqrt{\pi}}\sin M\varphi\right) = -\frac{ihM}{2\pi}\left(\frac{1}{\sqrt{\pi}}\cos M\varphi\right)$$

6.2.4.1 Three Dimensional Rotation

When the particle rotates in three dimensional space, as in the case of particle on a sphere, the axis of rotation is still perpendicular to the plane of rotation but now the axis is free to take any orientation and the vector need not be parallel to the z-axis. The components L_x and L_y are no longer zero now and the magnitude of the vector is given by

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

Operators corresponding to these quantities in spherical coordinates are given below (see Appendix 2)

$$\hat{L}_x = -\frac{ih}{2\pi}\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cos\varphi\cot\theta\frac{\partial}{\partial\varphi}\right) \quad ...(6.36)$$

$$\hat{L}_y = -\frac{ih}{2\pi}\left(\cos\varphi\frac{\partial}{\partial\theta} - \sin\varphi\cot\theta\frac{\partial}{\partial\varphi}\right) \quad ...(6.37)$$

$$\hat{L}_z = -\frac{ih}{2\pi}\frac{d}{d\varphi} \quad ...(6.38)$$

$$\hat{L}^2 = -\frac{h^2}{4\pi^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \quad ...(6.39)$$

The feature of interest here is that there exist eigenfunctions of $\hat{H}$ that are eigenfunctions of $\hat{L}^2$ and of only one of the components. This means that if the system is described by such an eigenfunction then we can obtain definite values of the total energy E, the angular momentum L and one of its components. By convention the component L_z is chosen (perhaps due to the simplicity of its operator in spherical coordinates).

It is easy to see that the spherical harmonics, real or complex, are eigenfunctions of both $\hat{H}$ and $\hat{L}^2$. For the operator $\hat{L}_z$, however, eigenfunctions exist in complex form only. Take for example the spherical harmonics for $l = 1$, $M = 0$, *i.e.*, $\psi_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$. Then, leaving the normalisation factor,

$$\hat{H}\,\psi_{1,0} = -\frac{h^2}{8\pi^2 I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial}{\partial\theta}(\cos\theta)\right\} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}(\cos\theta)\right]$$

$$= \frac{h^2}{8\pi^2 I} \cdot \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin^2\theta)$$

$$= \frac{2h^2}{8\pi^2 I} \cos\theta = \frac{2h^2}{8\pi^2 I} \cdot \psi_{1,0}.$$

Eigen value (E) $= \dfrac{2h^2}{8\pi^2 I}$

Also $\hat{L}^2 \psi_{1,0} = -\dfrac{h^2}{4\pi^2} \left[\dfrac{1}{\sin\theta} \dfrac{\partial}{\partial\theta} \left\{ \sin\theta \dfrac{\partial}{\partial\theta} (\cos\theta) \right\} + \dfrac{1}{\sin^2\theta} \dfrac{\partial^2}{\partial\varphi^2} (\cos\theta) \right]$

$$= \frac{2h^2}{4\pi^2} \cos\theta = \frac{2h^2}{4\pi^2} \psi_{1,0}$$

Eigenvalue (L^2) $= \dfrac{2h^2}{4\pi^2}$

But $\hat{L}_z \psi_{1,0} = -\dfrac{ih}{2\pi} \dfrac{\partial}{\partial\varphi} (\cos\theta) = 0$

which is not eigenvalue equation. However, we could write

$$\hat{L}_z \psi_{1,0} = -\frac{ih}{2\pi} \frac{\partial}{\partial\varphi} (\cos\theta\, e^{i \cdot 0 \cdot \varphi}) = -0 \left(\frac{i^2 h}{2\pi} \right) \cos\theta\, e^{i \cdot 0 \cdot \varphi}$$

$$= 0 \cdot \cos\theta\, e^{i \cdot 0 \cdot \varphi} = 0 \cdot \psi_{1,0}$$

Eigenvalue $= 0$

The eigenvalue equations for $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ may be given, in general, as follows,

$$\hat{H} \psi_{l,M} = \frac{\beta h^2}{8\pi^2 I} \psi_{l,M} = l(l+1) \frac{h^2}{8\pi^2 I} \cdot \psi_{l,M} \quad \text{...(6.40)}$$

$$\hat{L}^2 \psi_{l,M} = \frac{\beta h^2}{4\pi^2} \psi_{l,M} = l(l+1) \frac{h^2}{4\pi^2} \cdot \psi_{l,M} \quad \text{...(6.41)}$$

$$\hat{L}_z \psi_{l,M} = \frac{Mh}{2\pi} \psi_{l,M}. \quad \text{...(6.42)}$$

6.2.5 Quantisation of Energy and Angular Momentum

Spherical harmonics when operated upon by the Hamiltonion ($\hat{H}$) yield energy as eigenvalue expressed as

$$E_l = l(l+1) \frac{h^2}{8\pi^2 I} \quad \text{...(6.43)}$$

where $I = mr^2$ is the moment of inertia of the rotating particle on the surface of radius r. The energy is quantised in units of $\frac{h^2}{8\pi^2 I}$, l being the "quantum number of energy", and is restricted to the values 0, 2, 6, 12, ... units according as $l = 0, 1, 2, 3, ...$ respectively. The system has no zero point energy ($\because E = 0$ when $l = 0$). The energy is determined solely by l and is independent of M. Since for each value of l, there are $2l + 1$ values of M, each energy level is $(2l + 1)$-fold degenerate each state having a definite value of M.

When operated upon by $\hat{L}^2$, the spherical harmonics yield an eigenvalue which represents the square of the length of the angular momentum of the same rotating particle expressed as

$$L^2 = l\,(l+1)\,\frac{h^2}{4\pi^2}, \text{ or } L = \sqrt{l\,(l+1)} \cdot \frac{h}{2\pi} \qquad ...(6.44)$$

Therefore, l is also the "quantum number of angular momentum".

The operator $\hat{L}_z$ leads to the magnitude of the z-component of the angular momentum vector ($\vec{L}$), given as

$$L_z = \frac{Mh}{2\pi} \qquad ...(6.45)$$

Accordingly, M is the "quantum number of the z-component of angular momentum".

References:

1. Quantum Chemistry by R.K.Prasad, 3rd Edition, New Age International Publishers.
2. Engineering Physics by Senthil Kumar.