One –Particle Orbital –Angular –Momentum Eigenfunctions and Eigenvalues

Now it is time to find the common eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, which is denoted by Y. Since these operators involves only θ and φ, Y is a function of these two ccordinates:Y=Y(θ,φ). Now we have to solve –

$$\hat{L}_z Y(\theta, \phi) = bY(\theta, \phi) \quad \text{………………………………………….. (68)}$$

$$\hat{L}^2 Y(\theta, \phi) = cY(\theta, \phi) \quad \text{…………………………………………..(69)}$$

where b and c are the eigenvalues of $\hat{L}_z$ and $\hat{L}^2$.
Using the $\hat{L}_z$ operator, we have

$$-i\hbar \frac{\partial}{\partial \phi} Y(\theta, \phi) = bY(\theta, \phi) \quad \text{…………………..(70)}$$

Since the operator in (eq. 70) does not involve θ, now separation of variable is introduced –

$$Y(\theta, \phi) = S(\theta)T(\phi) \quad \text{……………….. (71)}$$

Equation (70) becomes

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

$$-i\hbar S(\theta) \frac{dT(\phi)}{d\phi} = bS(\theta)T(\phi)$$

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

$$T(\phi) = Ae^{ib\phi/\hbar} \quad \text{……………………………….. (72)}$$

Where A is an arbitrary constant.

Is T suitable as an eigenfunction ? The answer is no, since it is not, in general, a single –valued function. If we add 2π to φ, we will still be at the same point in space, and hence we want no change in T when this is done. For T to be single- valued, we have the restriction

$$T(\phi + 2\pi) = T(\phi)$$
$$Ae^{ib\phi/\hbar}e^{ib2\pi/\hbar} = Ae^{ib\phi/\hbar}$$
$$e^{ib2\pi/\hbar} = 1 \qquad \ldots\ldots (73)$$

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

$$m = 0, \pm 1, \pm 2, \pm \cdots$$

Therefore (Eqn 73) gives

$$2\pi b/\hbar = 2\pi m \qquad \ldots\ldots (74)$$

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

and eqn 72 becomes

$$T(\phi) = Ae^{im\phi}\,, \qquad m = 0, \pm 1, \pm 2, \ldots \qquad \ldots\ldots (75)$$

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We fix A by normalizing T. First let us consider normalizing some function F of r, θ, and ϕ. The ranges of the independent variables are (see Fig. 6)

$$0 \leqslant r \leqslant \infty, \quad 0 \leqslant \theta \leqslant \pi, \quad 0 \leqslant \phi \leqslant 2\pi \quad \text{........ (76)}$$

The infinitesimal volume element in spherical coordinates is

$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi \quad \text{................. (77)}$$

The quantity (eq.77) is the volume of an infinitesimal region of space for which the spherical coordinates lie in the ranges r to $r + dr$, θ to $\theta + d\theta$, and ϕ to $\phi + d\phi$. The normalization condition for F in spherical coordinates is therefore

$$\int_0^{\infty} \left[\int_0^{\pi} \left[\int_0^{2\pi} |F^2(r, \theta, \phi)| \, d\phi \right] \sin\theta \, d\theta \right] r^2 \, dr = 1 \quad \text{.................. (78)}$$

If F happens to have the form

$$F(r, \theta, \phi) = R(r)S(\theta)T(\phi)$$

then use of the integral identity gives for (Eqn 78)

$$\int_0^{\infty} |R^2(r)| r^2 \, dr \int_0^{\pi} |S^2(\theta)| \sin\theta \, d\theta \int_0^{2\pi} |T^2(\phi)| \, d\phi = 1$$

and it is convenient to normalize each factor of F separately:

$$\int_0^{\infty} |R^2| r^2 \, dr = 1, \quad \int_0^{\pi} |S^2| \sin\theta \, d\theta = 1, \quad \int_0^{2\pi} |T^2| \, d\phi = 1 \quad \text{.......... (79)}$$

(we did the same thing for the wave function of the particle in a three dimensional box). Therefore

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

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

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

…………………………….. (80)

We now solve $\hat{L}^2 Y = cY$ [Eq. 69) for the eigen values c of $\hat{L}^2$. Using (eq. 67) for $\hat{L}^2$. (Eq. 71) for Y and (Eq. 80),we have

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

$$\frac{d^2S}{d\theta^2}+\cot\theta\frac{dS}{d\theta}-\frac{m^2}{\sin^2\theta}S=-\frac{c}{\hbar^2}S \quad \text{.................... (81)}$$

To solve (Eq. 81), we carry out some tedious manipulations.

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First for convenience, we change the independent variable by making the substitution

w=cosθ ……………………………………….(82)

This transforms S into some new function of w:

S(θ)=G(w) ………………………………….(83)

The chain rule gives

$$\frac{dS}{d\theta}=\frac{dG}{dw}\frac{dw}{d\theta}=-\sin\theta\frac{dG}{dw}=-(1-w^2)^{1/2}\frac{dG}{dw} \quad \text{..............................(84)}$$

To calculate $d^2S/d\theta^2$, we use some operator algebra:

$$\frac{d}{d\theta}=-(1-w^2)^{1/2}\frac{d}{dw}$$

$$\frac{d^2}{d\theta^2}=(1-w^2)^{1/2}\frac{d}{dw}(1-w^2)^{1/2}\frac{d}{dw}$$

$$\frac{d^2}{d\theta^2}=(1-w^2)\frac{d^2}{dw^2}+(1-w^2)^{1/2}(\tfrac{1}{2})(1-w^2)^{-1/2}(-2w)\frac{d}{dw}$$

$$\frac{d^2S}{d\theta^2}=(1-w^2)\frac{d^2G}{dw^2}-w\frac{dG}{dw} \quad \text{...........................(85)}$$

Using (Eq.85), ((Eq.84), and $\cot\theta=\cos\theta/\sin\theta=w/(1-w^2)^{1/2}$, we find that ((Eq.81) becomes

$$(1-w^2)\frac{d^2G}{dw^2}-2w\frac{dG}{dw}+\left[\frac{c}{\hbar^2}-\frac{m^2}{1-w^2}\right]G(w)=0 \quad \text{........................(86)}$$

The range of w is $-1 \le w \le 1$.

To get a two-term recursion relation when we try a power-series solution, we make the following change of dependent variable.

$G(w) = (1-w^2)^{|m|/2} H(w)$ ……………………….(87)

Differentiating (Eq.87), we evaluate G' and G'', and (Eq.86) becomes, after we divided by $(1-w^2)^{|m|/2}$,

$$(1 - w^2)H'' - 2(|m| + 1)wH' + [c\hbar^{-2} - |m|(|m| + 1)]H = 0$$ …………….(88)

We now try a power series for H:

$$H(w) = \sum_{j=0}^{\infty} a_j w^j$$ ……………………………………..(89)

Differentiating , we have

$$H'(w) = \sum_{j=0}^{\infty} j a_j w^{j-1}$$

$$H''(w) = \sum_{j=0}^{\infty} j(j-1)a_j w^{j-2} = \sum_{j=0}^{\infty} (j+2)(j+1)a_{j+2} w^j$$

Substitution of these power series into (Eq.88) yields, after combining sums,

$$\sum_{j=0}^{\infty} \left[(j+2)(j+1)a_{j+2} + \left(-j^2 - j - 2|m|j + \frac{c}{\hbar^2} - |m|^2 - |m| \right) a_j \right] w^j = 0$$

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Setting the coefficient of w^j equal to zero, we have the recursion relation

$$a_{j+2} = \frac{[(j + |m|)(j + |m| + 1) - c/\hbar^2]}{(j+1)(j+2)} a_j$$ ……(90)

Just as in the harmonic-oscillator case, the general solution of (Eq.88) is an arbitrary linear combination of a series of even powers (whose coefficients are determined by a_0) and a series of odd powers (whose coefficients are determined by a_1). It can be shown that the infinite series defined by the recursion relation (Eq.90) does not give well-behaved eigenfunctions. Hence as in the harmonic-oscillator case, we must cause one of the series to break off, its last term being $a_k w^k$. We eliminate the other series by setting a_0 or a_1 equal to zero, depending on whether k is odd or even.

Setting the coefficient of a_k in eq.90 equal to zero, we have

$$c = \hbar^2(k + |m|)(k + |m| + 1), \qquad k = 0, 1, 2, \cdots \qquad \text{.............................(91)}$$

Since │m│ takes on the values 0,1,2,….., the quantity k+│m│takes on the values 0,1,2,……We therefore defined the quantum number l as

$$l \equiv k + |m| \qquad \text{...(92)}$$

and the eigenvalues for the square of the magnitude of angular momentum are

$$c = l(l + 1)\hbar^2, \qquad l = 0,1,2\ldots\ldots\ldots \qquad \text{......................(93)}$$

The magnitude of the orbital angular momentum of a particle is

$$|\mathbf{L}| = [l(l + 1)]^{1/2}\hbar \qquad \text{... (94)}$$

From (Eq. 92), it follows that │m│≤ l. The possible values for m are thus

$$m = -l, -l+1, -l+2, \ldots\ldots -1, 0, 1, \ldots, l-2, l, l-1, l \qquad \text{...................(95)}$$

Let us examine the angular-momentum eigenfunctions. From (Eq. 82) (Eq.83) (Eq.84) ,(Eq.87), (Eq.89) and (Eq.93), the theta factor in the eigenfunction is

$$S_{l,m}(\theta) = \sin^{|m|}\theta \sum_{\substack{j=1,3\ldots \\ \text{or } j=0,2,\ldots}}^{l-|m|} a_j \cos^j\theta \qquad \text{..................................... (96)}$$

Where the sum is over even or odd values of j, depending on whether l-│m│is even or odd. The coefficients a_j satisfy the recursion relation (Eq.90), which using (Eq.93) becomes

$$a_{j+2} = \frac{[(j + |m|)(j + |m| + 1) - l(l + 1)]}{(j + 1)(j + 2)} a_j \qquad \text{..........................(97)}$$

The $\hat{L}^2$ and $\hat{L}_z$ eigenfunctions are given by Eq.71 and Eq.80 as

$$Y_l^m(\theta,\phi) = S_{l,m}(\theta)T(\phi) = \frac{1}{\sqrt{2\pi}} S_{l,m}(\theta)e^{im\phi}$$ ……………….(98)

………………………….Example...

Find $Y_l^m(\theta,\phi)$ and the $\hat{L}^2$ and $\hat{L}_z$ eigenvalues for (a) l=0 ; (b) l=1

(a) For l=0, Eq. 95 gives m=0 and Eq. 96 becomes

$S_{0,0}(\theta) = a_0$ ………………………………………………….(99)

The normalization condition Eq. 79 gives

$$\int_0^{\pi} |a_0^2| \sin\theta \, d\theta = 1 = 2|a_0^2|$$

$$|a_0| = 2^{-1/2}$$

Eq. 98 gives

$$Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$$ ……………………………(100)

[Obviously, Eq. 100 is an eigenfunction of the operators $\hat{L}^2$,$\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$, Eq.64- Eq. 67]

For l=0, there is no angular dependence in the eigenfunction; we say that the eigenfunctions are **Spherical symmetric** for l=0.

For l=0 and m=0, Eq. 68, Eq. 69, Eq.74 and Eq. 93 give the $\hat{L}^2$ eigenvalues as c=0 and the $\hat{L}_z$ eigenvalue as b=0.

(b) For $l = 1$, the possible values for m in Eq. 95) are $-1, 0$, and 1. For $|m| = 1$, (Eq.96) gives

$$S_{1,\pm 1}(\theta) = a_0 \sin\theta \qquad (101)$$

a_0 in (Eq10.1) is not necessarily the same as a_0 in(Eq.99)Normalization gives

$$1 = |a_0^2| \int_0^{\pi} \sin^2\theta \sin\theta \, d\theta = |a_0^2| \int_{-1}^{1} (1 - w^2)\, dw$$

$$|a_0| = \sqrt{3}/2$$

where the substitution $w = \cos\theta$ was made. Thus $S_{1,\pm 1} = (3^{1/2}/2)\sin\theta$ and (Eq.98) gives

$$Y_1^1 = (3/8\pi)^{1/2} \sin\theta \, e^{i\phi}, \qquad Y_1^{-1} = (3/8\pi)^{1/2} \sin\theta \, e^{-i\phi} \qquad (102)$$

For $l = 1$ and $m = 0$,(Eq.96)gives $S_{1,0} = a_1 \cos\theta$. Normalizing, we find $S_{1,0} = (3/2)^{1/2}\cos\theta$. Hence $Y_1^0 = (3/4\pi)^{1/2}\cos\theta$.

For $l = 1$, (Eq.93) gives the $\hat{L}^2$ eigenvalue as $2\hbar^2$; for $m = -1, 0$, and 1,(Eq.74)gives the $\hat{L}_z$ eigenvalues as $-\hbar$, 0, and $\hbar$, respectively.

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The functions $S_{l,m}(\theta)$ are well known in mathematics, and are *associated Legendre functions* multiplied by a normalization constant. The associated Legendre functions $P_l^{|m|}(w)$ are defined by

$$P_l^{|m|}(w) \equiv \frac{1}{2^l l!}(1 - w^2)^{|m|/2} \frac{d^{l+|m|}}{dw^{l+|m|}}(w^2 - 1)^l, \qquad l = 0, 1, 2, \ldots \qquad (103)$$

Some associated Legendre functions are

$$P_0^0(w) = 1 \qquad P_2^0(w) = \tfrac{1}{2}(3w^2 - 1)$$
$$P_1^0(w) = w \qquad P_2^1(w) = 3w(1 - w^2)^{1/2} \qquad (104)$$
$$P_1^1(w) = (1 - w^2)^{1/2} \qquad P_2^2(w) = 3 - 3w^2$$

It can be shown that (*Pauling and Wilson*, page 129)

$$S_{l,m}(\theta) = \left[\frac{2l + 1}{2} \frac{(l - |m|)!}{(l + |m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta) \qquad (105)$$

Equations (105) and (103) give the explicit formula for the normalized theta factor in the angular-momentum eigenfunctions. Using (Eq.105) we construct Table 1, which gives the theta factor in the angular-momentum eigenfunctions.

The eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ are called ***spherical harmonics*** (or *surface harmonics*) and are given by Eqs. (105) and (98) as

$$Y_l^m(\theta, \phi) = \left[\frac{2l + 1}{4\pi} \frac{(l - |m|)!}{(l + |m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta) e^{im\phi} \qquad (106)$$

TABLE 1 $S_{l,m}(\theta)$

$l=0$:	$S_{0,0}$	$=\frac{1}{2}\sqrt{2}$
$l=1$:	$S_{1,0}$	$=\frac{1}{2}\sqrt{6}\cos\theta$
	$S_{1,\pm1}$	$=\frac{1}{2}\sqrt{3}\sin\theta$
$l=2$:	$S_{2,0}$	$=\frac{1}{4}\sqrt{10}(3\cos^2\theta-1)$
	$S_{2,\pm1}$	$=\frac{1}{2}\sqrt{15}\sin\theta\cos\theta$
	$S_{2,\pm2}$	$=\frac{1}{4}\sqrt{15}\sin^2\theta$
$l=3$:	$S_{3,0}$	$=\frac{3}{4}\sqrt{14}\left(\frac{5}{3}\cos^3\theta-\cos\theta\right)$
	$S_{3,\pm1}$	$=\frac{1}{8}\sqrt{42}\sin\theta(5\cos^2\theta-1)$
	$S_{3,\pm2}$	$=\frac{1}{4}\sqrt{105}\sin^2\theta\cos\theta$
	$S_{3,\pm3}$	$=\frac{1}{8}\sqrt{70}\sin^3\theta$

In summary, the one particle orbital angular- momentum eigenfunctions and eigenvalues are [(Eq.68), (Eq.69), (Eq.74) and (Eq.93)]

$$\hat{L}^2 Y_l^m(\theta,\phi) = l(l+1)\hbar^2 Y_l^m(\theta,\phi), \quad l = 0, 1, 2, \dots \qquad \text{……………………..(107)}$$

$$\hat{L}_z Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi), \quad m = -l, -l+1, \dots, l-1, l \qquad \text{……………………..(108)}$$

Where the eigenfunctions are given by (Eq. 106).Often the symbol m_l is used instead of m for the L_z quantum number.

Since $l >> |m|$, the magnitude $[l(l+1)]^{1/2}\hbar$ of the orbital angular momentum **L** is greater than the magnitude $|m|\hbar$ of its z component L_z, except for $l=0$. If it were possible to have the angular – momentum magnitude equal to its z component, this would mean that the x and y components were zero, and we would have specified all three components of **L.** However, since the components of angular momentum do not commute with each other, we cannot do this. The one exception is when l is zero. In this case, $|\mathbf{L}|^2 = \mathbf{L}^2\mathbf{x} + \mathbf{L}^2\mathbf{y} + \mathbf{L}^2\mathbf{z}$ has zero for its eigenvalue, and it must be true that allthre components Lx, Ly and Lz have zero eigenvalues. From Eq.12, the uncertainties in angular – momentum components satisfy

$$\Delta L_x \, \Delta L_y \geqslant \frac{1}{2}\left|\int \Psi^*[\hat{L}_x, \hat{L}_y]\Psi \, d\tau\right| = \frac{\hbar}{2}\left|\int \Psi^* \hat{L}_z \Psi \, d\tau\right| \qquad \text{…………………………. (109)}$$

and two similar equations obtained by cycloc permutation. When the eigenvalues of $\hat{L}_z, \hat{L}_x$, and $\hat{L}_y$ are zero, $\hat{L}_x\Psi = 0, \hat{L}_y\Psi = 0, \hat{L}_z\Psi = 0,$ the right-hand sides of Eq. 109 and the two similar equations are zero, and having $\Delta L_x = \Delta L_y = \Delta L_z = 0$ is permitted. But what about the statement in section 1.1 that to have simultaneous eigenfunctions of two operators the operators must commute? The answer is that this theorem refers to the possibility of having a complete set of eigenfunctions of one operator be eigenfunctions of the other operator. Thus, even though $\hat{L}_x$ and $\hat{L}_z$, do not commute, it is possible to have some of the eigenfunctions $\hat{L}_z$ (those with l=0=m) be eigen functions of $\hat{L}_x$.However, it is impossible to have all the $\hat{L}_z$ eigenfunctions also be eigenfunctions of $\hat{L}_x$.

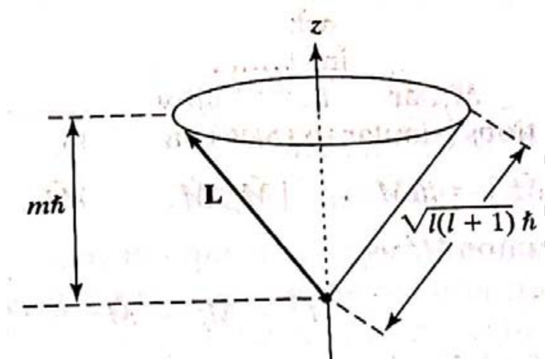

Figure 7. Orientation of L

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 $\sqrt{l(l+1)}\,\hbar$ (Fig7). The possible orientations of **L** with respect to the z axis for the case l=1 are shown in fig 7. For each eigenvalue of $\hat{L}^2$, these are $2l$+1 different eigenfunctions Y_l^m, corresponding to the $2l$+1 values of m. We say that the $\hat{L}^2$ eigenvalues are ($2l$+1)- fold degenerate. The term **degeneracy** is applicable to the eigenvalues of any operator, not just the Hamiltonian.

Of course, there is nothing special about the z axis; all directions of space are equivalent. If we had chosen to specify L^2 and L_x (rather than L_z),we would have gotten the same eigenvalues for L_x as we found for L_z. However, it is easier to solve the $\hat{L}_z$ eigenvalue equation because $\hat{L}_z$ has a simple form in spherical coordinates , which involve the angle of rotation φ about the z-axis.

……………………………………………..End…………………………………………………