Module 1 : Atomic Structure

Lecture 3 : Angular Momentum

Objectives

In this Lecture you will learn the following

- Define angular momentum and obtain the operators for angular momentum.
- Solve the problem of the motion of a particle on a ring.
- Obtain the solutions for a particle moving on a sphere.
- Outline the consequences of the above solutions for electronic motion in atoms.

3.1 Angular momentum and rotational kinetic energy.

For a particle of mass m moving in a circular orbit or along any other trajectory at the location $\vec{r}$, the angular momentum is defined as $\vec{r} \times \vec{p}$ where $\vec{r} = x\,\vec{i} + y\,\vec{j} + z\,\vec{k}$, the vector from the center O (the origin of the coordinate system) to the particle and $\vec{p} = m\,\vec{v}$ is the linear momentum of the particle. The velocity of the particle is given by... $\vec{v} = \dot{x}\,\vec{i} + \dot{y}\,\vec{j} + \dot{z}\,\vec{k}$ where $\dot{x}$ is the x component of velocity.

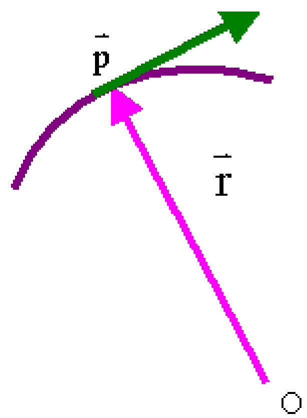


Fig 3.1 : Vectors $\vec{r}$, $\vec{p}$ and $\vec{r} \times \vec{p}$ (see below).

The angular momentum is a vector. In the above case it is directed downward from the plane of paper. The three components of the angular momentum vector can be obtained from

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \qquad (3.1)$$

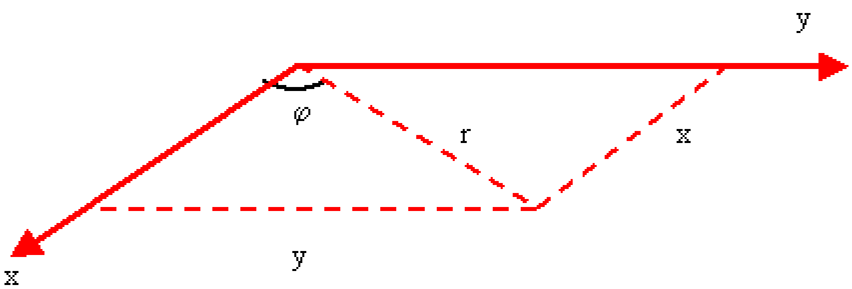
where $\vec{i}$, $\vec{j}$ and $\vec{k}$ are unit vectors and p_x, p_y and p_z are the x, y and z components of linear momentum.

If the potential energy acting on the particle is zero, the total energy $E = T + V = p^2 / 2m$. The magnitude of $\vec{L} = l = pr$ and we get the following formula for energy.

$$E = p^2 / 2m = l^2 / 2mr^2 = l^2 / 2I \qquad (3.2)$$

Where $I = mr^2$ = moment of inertia of the system. One of the issues we want to investigate is whether this angular momentum is quantized (as was assumed by Bohr) and if so, what causes this quantization.

3.2 Operators for K.E and $\vec{L}$



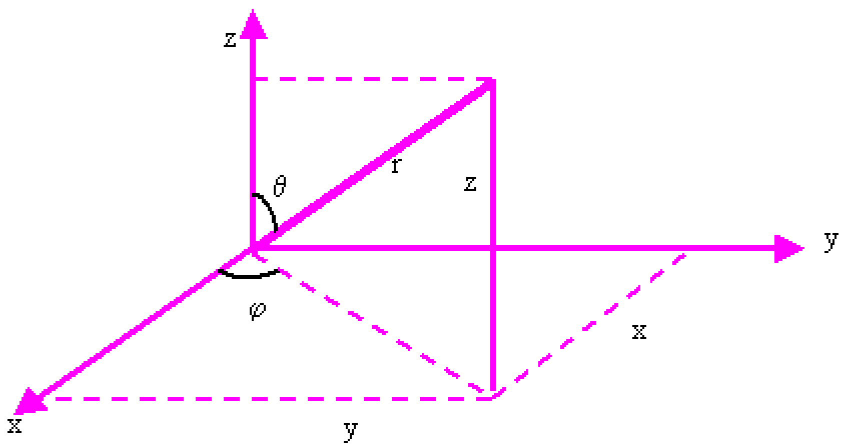


Fig 3.2: a) Plane polar coordinate system, r, φ in the x y plane (two dimensions) and b) Spherical coordinate system r, θ, φ (three dimensions).

In two dimensions, the kinetic energy is $p_x^2 / 2m + p_y^2 / 2m$. We are assuming that the motion is in the x,y plane.

The operator for p_x is $(\hbar / i)\, \partial / \partial x$ and that for p_x^2 is $-\hbar^2\, \partial^2 / \partial x^2$ (lecture 2). The operator for K.E is.......... . $-\hbar^2 / 2m\, (\partial^2 / \partial x^2 + \partial^2 / \partial y^2)$. In spherical polar coordinates wherein the variables are r, θ, φ in place of xyz (in 3 dimensions). In a plane, the polar coordinates are r and φ (in two dimensions) in place of x and y and it is possible to show that in two dimensions, we obtain the following forms for the operators for energy and angular momentum.

$$(\partial^2 / \partial x^2 + \partial^2 / \partial y^2) = 1/r^2\, \partial^2 / \partial \varphi^2 \qquad (3.3)$$

The relations used are

$$x = r\cos\varphi \quad y = r\sin\varphi \quad \partial / \partial x = (\partial r / \partial x)\, \partial / \partial r + (\partial \varphi / \partial x)\, \partial / \partial \varphi \qquad (3.4)$$

A similar relation can be written for $\partial / \partial y$. The Schrodinger equation for K.E. becomes

$$(-\hbar^2 / 2mr^2)\, \partial^2 \psi / \partial \varphi^2 = E\psi \qquad (3.5)$$

The operator for z component of angular momentum is

$$l_z = y p_z - z p_y \longrightarrow (y \hbar / i)\, \partial / \partial z - (z \hbar / i)\, \partial / \partial y \qquad (3.6)$$

and in polar coordinates , this becomes

$l_z = (\hbar / i)\, \partial / \partial \varphi$ (3.7)

This is one of the simplest forms for an operator.

3.3 Eigenfunctions for the L_z and the K.E. operators :

We need to look for those functions whose derivatives are a constant multiplied by the functions themselves. Examples are $e^{\pm i m \varphi}$ and $e^{\pm i m \varphi}$.The first function $e^{\pm i m \varphi}$ on being operated by $(\hbar / i)\, \partial / \partial \varphi$ gives........ $\pm(\hbar / i)m$ as the constant multiplier for $e^{\pm i m \varphi}$.While this appears all right, there is a problem that it is imaginary. Dynamical variables can not have imaginary values as they can be and are observed in real experiments. Therefore we choose

$e^{\pm i m \varphi}$ as a solution. We have,

$$(\hbar / i)\, \partial / \partial \varphi\, e^{i m \varphi} = \hbar m\, e^{i m \varphi} \quad (3.8)$$

Figure 3.3: Showing the values of $e^{i m \varphi}$ vs φ on a ring. In (a), the function is single valued and in (b), it is not.

The eigenvalue is $\hbar m$. The next question is what are the allowed values of m. When we go around the ring through an angle of 2π, we come to the original point or the original angle. When we return to the original point (original value of φ, see Fig 3.3) the wave function should have the same value (else we have two or more different values of the probability of finding the electron for a given value of φ, which is physically unacceptable).This criterion is expressed through the wavefunction being a single valued function of the variable φ.

$$e^{i m (\varphi + 2\pi)} = e^{i m \varphi}, \text{ because, } e^{im 2\pi} = 1 \quad (3.9)$$

The allowed values of m are therefore integers, 0 , ± 1, ± 2,....... We thus see that quantization (restricted and not continuous values of m) is a consequence of boundary conditions such as $\varphi = 0$ at the boundaries or the single valued requirement on the wave function as shown in Figure 3.3 (a).

Energy of a two dimensional "rotor"

We shall now obtain the energy levels of an object rotating in a plane on a circle of radius r. The operator for the kinetic energy has already been seen in 3.3 to be$(-\hbar^2/2mr^2)\,\partial^2/\partial\varphi^2$. The eigenvalue equation becomes

$$-\hbar^2/2mr^2\,\partial^2/\partial\varphi^2\,\psi = E\,\psi \quad\text{or}\quad \partial^2\psi/\partial\varphi^2 = (-2mr^2E/\hbar^2)\,\psi \qquad (3.10)$$

The solutions are once again $e^{im_l\varphi}$ as in the previous section. $\psi = e^{im_l\varphi}$ is not permitted as its second derivative will not have the negative sign as in (3), ie $\partial^2/\partial\varphi^2\, e^{m_l\varphi} = m_l^2\,\psi$ .Therefore,

$$\partial^2/\partial\varphi\; e^{im_l\varphi} = -m_l^2 e^{im_l\varphi} \qquad (3.11)$$
$$\therefore m_l^2 = 2mr^2E/\hbar^2 = 2\,\mathbf{I}\,E/\hbar^2$$

$$\text{or } m_l = \pm(2IE)^{1/2}/\hbar \text{ or } E = m_l^2\hbar^2/2\,\mathbf{I} \qquad (3.12)$$

Due to the "cyclic" boundary condition, ie, $\psi(\varphi) = \psi(\varphi + 2\varphi)$, m_l has to be an integer, 0, ± 1, ± 2,

We have thus seen that the angular momentum as well as rotational energy are quantized. In Bohr's theory , $mvr = n\hbar$ was a postulate, but in the new quantum theory , this quantization occurs because of the physically reasonable (single valuedness) condition imposed on the wavefunction.

Normalization.

The requirement for normalization is that $\int \psi^* \psi\, d\tau = 1$. In the present case,

$$\int_0^{2\pi} e^{im_l\varphi}\, e^{-im_l\varphi}\, d\varphi = \int d\varphi = 2\pi \qquad (3.13a)$$

Therefore, the normalized wavefunction for rotational motion in 2 dimensions is $(2\pi)^{-1/2} e^{im\varphi}$

Let us now compute the probability of finding the particle in a range of d φ for a given angel φ /.

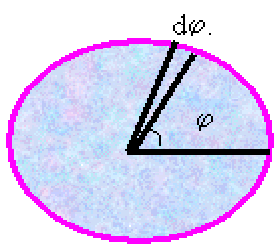


Figure 3.4: Probability of finding a particle in angle d φ .

The probability of finding the particle in this range of dφ is

$$\psi^*\psi\, d\varphi = 1/2\pi\, e^{im\varphi}\, e^{-im\varphi}\, d\varphi = d\varphi/2\pi \qquad (3.13b)$$

which is independent of φ.This means that the probability of finding the particle in a circular range d φ is independent of φ . Since the rotation is "free" (ie in the absence of a potential energy depending on φ), this result is to be expected.

3.4 Rotations on a 3 dimensional sphere.

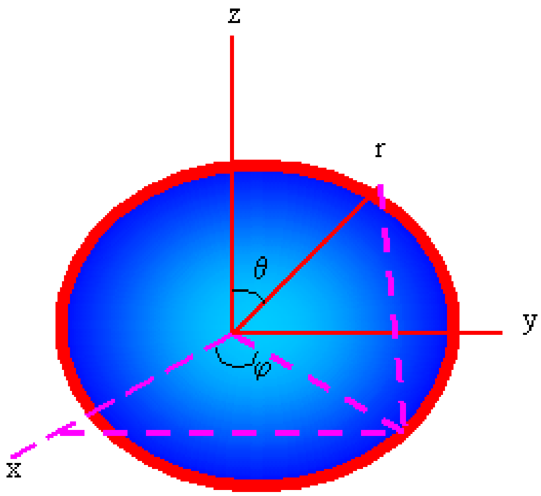


Figure 3.5 Particle moving on a sphere of radius r.

In three dimensional rotation on a sphere of radius r, in addition to the angle φ, in there is a polar angle θ and the wavefunction ψ is a function of both θ and φ ie, $\psi(\theta, \varphi)$. The particle is rotating in a field (potential) which is independent of θ and φ, ie V = 0, just as in the case of particle in box. The kinetic energy operator is $L^2 / 2I$ where L is the angular momentum operator.
By using a procedure outlined in section 3.2, the operator $L^2 / 2I$ can be written in terms of θ and, φ as

$$L^2/2I = -\hbar^2/2I\,[(1/\sin^2\theta)\,\partial^2/\partial\varphi^2 + (1/\sin\theta)\,\partial/\partial\theta\,\sin\theta\,\partial/\partial\theta] = -(\hbar^2/2I)\,\Lambda^2 \qquad (3.14)$$

Although this appears a lot more threatening than the operator for a particle in box , there is no conceptual difference. The same ideas of separation of variables will be employed. The details of mathematical techniques will be introduced to you in the course on differential equations.

As is true for any operator the operations must be performed from left to right. Eg, to evaluate the effect of the second term on a function of θ, $f(\theta)$, first take the derivative $df(\theta)/d\theta$, multiply this by sin θ on the left and take the derivative of the product, $\sin\theta\, df(\theta)/d\theta$. Divide this further by $\sin\theta$ to get the result .Use $f(\theta) = 3\cos^2\theta - 1$ and perform these operations.

The conventional symbol used for $f(\theta)$ is $\Theta(\theta)$, Θ is Greek symbol for capital theta, and we will stick to this convention as it will help you when you refer to other books. Similarly Φ denotes a function of φ, $\Phi(\varphi)$.

Seperating the variables, $\psi(\theta, \varphi) = \Theta(\theta)\,\Phi(\varphi)$.

$(L^2/2I)\,\psi = E\,\psi$

Substituting

$$\Lambda^2\,\Theta\,\Phi = -2IE/\hbar^2\,\Theta\,\Phi \qquad (3.15)$$

$$= [(1/\sin^2\theta)\,\partial^2/\partial\varphi^2 + (1/\sin\theta)\,\partial/\partial\theta\sin\theta\,\partial/\partial\theta]\,\Theta\,\Phi$$

$$= \Theta\,(1/\sin^2\theta)\,(\partial^2/\partial\varphi^2)\,\Phi + \Phi\,(1/\sin\theta)\,\partial/\partial\theta\,\sin\theta\,\partial/\partial\theta\,\Theta \qquad (3.16)$$

Dividing by Q Φ, multiplying by $\sin^2\theta$ and rearranging,

$$1/\Phi\,\partial^2\Phi/\partial\varphi^2 = -1/\Theta\,\sin\theta\,\partial/\partial\theta\sin\theta\,\partial\Theta/\partial\theta - 2IE/\hbar^2\sin^2\theta \qquad (3.17)$$

we see that the left hand side depends only on φ and the right hand side depends only on θ. Since

θ and φ are independent, each side must be equal to the same constant. Calling this constant $-m'^2$ we get

$$\partial^2 \Phi / \partial \varphi^2 = -m_l^2 \Phi \tag{3.18}$$

setting $x = \cos\theta$, $\sin\theta$ becomes $\sqrt{1-\cos^2\theta} = (1-x^2)^{1/2}$

Setting $2IE / \hbar^2 = l(l+1)$

And by using (3.18), (3.17) becomes

$$(1-x^2)\, d^2\Theta/d\theta^2 - 2x\, d\Theta/d\theta + \{ l(l+1) - m_l^2/(1-x^2) \}\Theta = 0 \tag{3.19}$$

This is called the associated Legendre equation. The solutions for this equation are "well behaved" (ie, single valued, differentiable and finite) for the following conditions

a) $l = 0,1,2,\ldots\ldots$

b) $1 \leq m_l \leq l$ (3.20)

This implies that only when l is a positive integer and the absolute value of m_l is less than or equal to the value of l, acceptable or well behaved solutions exist. The normalized solutions for equation (3.15) for l = 0, 1 and 2 are given in the Table 3.1. Substitute the first three solutions in eq (3.15) and verify that these satisfy the equation

Table 3.1 A few normalized solutions to equation 3.15. The literature symbol for these solutions is $Y_{lm}(\theta, \varphi)$, and for simplicity, we take $m = m_l$.

l	$m = m_l$	$Y_{lm}(\theta, \varphi)$
0	0	$(4\pi)^{-1/2}$
1	0	$(3/4\pi)^{1/2} \cos\theta$
1	± 1	$\pm(3/8\pi)^{1/2} \sin\theta\, e^{\pm i\varphi}$
2	0	$(5/16\pi)^{1/2}(3\cos^2\theta - 1)$
2	± 1	$(15/16\pi)^{1/2} \cos\theta \sin\theta\, e^{\pm i\varphi}$
2	± 2	$(15/32\pi)^{1/2} \sin^2\theta\, e^{\pm 2i\varphi}$

3.5 Energy, angular momentum and probability

As $2IE/\hbar^2$ is restricted to $l(l+1)$, the rotational Kinetic energy takes on only discrete values as

$$E = l(l+1)\hbar^2/2I, \quad l = 0,1,2,\ldots \tag{3.21}$$

The magnitude of angular momentum takes the values

$[\, l(l+1)\,]^{1/2}\, \hbar$ (3.22)

because $L^2 \psi = \hbar^2 \, l\,(l+1)\, \psi$. For a given value of l , m_l can take on values

$m_l = 0,\ \pm 1,\ \pm 2\ \ldots .\ \pm l$ (3.23)

ie ($2l + 1$) values of m_l .Therefore , for a given l , there are $2l + 1$ values of m_l and this level is said to be ($2l + 1$) fold degenerate. The z component of angular momentum takes on values of

$\pm\, m_l\, \hbar$ (3.24)

which we have already seen in section 3.3.

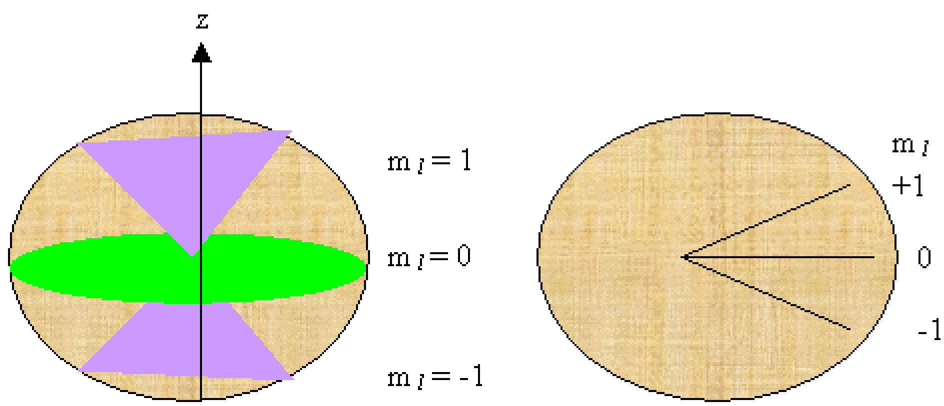


Figure 3.6: Visualisation of quantized z-component of angular momentum.

A nice way of visualization of these for l = 1 is given in fig 3.6. This is commonly referred to as space quantization. For l = 0 , the angular momentum = 0 . For l = 1 and m_l = 0, the angular momentum is oriented along a radius vector on the sphere such that its projection on the z axis is zero. For l =1 and m_l = 1, the angular momentum vector is in the upper cone such that the projection on z axis = $\hbar$. For l = 1 and m_l = -1, the angular momentum is in the lower cone with a projection on z axis = - $\hbar$ .This implies that all regions of space are not accessible to the $\vec{L}$ vector . Only some regions are accessible and this is turned “space quantization”

The probability of finding the rotating object such as an electron or a rotating molecule at given angles θ, and φ in infinitesimal ranges dθ and dφ is given by

$\left| Y_{lml}(\theta, \theta) \right|^2 \sin\theta \, d\theta \, d\varphi$ (3.25)

Most of the excercizes in this chapter involves substituting the numerical values in the formulae and are given in the last section.

3.6 Problems

3.1) An electron is moving in a circular orbit of radius 2 Å with a speed of 10^6 m/s. What is its angular momentum and momentum of inertia? ($m_e = 9.1 \times 10^{-31}$ kg)

3.2) What is the operator for the x component of angular momentum L_x ?

3.3) If l = 3, what are the admissible values of m_l? For each m_l what is the eigenfunction $\Phi(\varphi)$?

3.4) Verify that the functions in Table 3.1 for l = 1 and m_l = 0 and l = 1 and m_l = 1 satisfy the equation (3.15.)

3.5) For the electron in problem 1, what are the quantized values of angular momentum and energy for l = 0, 1 and 2?

3.6) The region of space where the wavefunction is zero is called a node. For the function in Table 3.1 for l = 0 and m_l = 0, what is the shape of the node?

3.7) Real functions can be obtained by combining the functions for positive and negative values of m_l using........ $e^{i\varphi} = \cos\varphi + \sin\varphi$; $\cos\varphi = ½ (e^{i\varphi} + e^{-i\varphi})$; and $\sin\varphi = (e^{i\varphi} - e^{-i\varphi}) /(2i)$. Obtain two real solutions for l = 1 by suitable linear combinations of the two functions for m_l = 1 and m_l = -1. Repeat the process for l = 2 and $m_l = \pm 2$.

3.8) Using the function $(3/4\pi)^{1/2}\cos\theta$, estimate the probability of finding the electron in an angle interval of $d\theta = 0.2^o$ when $\theta = 0^o$, $\theta = 45^o$ and $\theta = 90^o$. Repeat the calculation for the function for l = 2, m_l = 0 for $d\theta = 0.2^o$ and θ = 0, 22.5^o ,45^o ,67.5^o and 90^o .Use the formula of Eq (3.25) without the $d\varphi$ part.

Recap

In this Lecture you have learnt the following

Summary

In this chapter we have studied rotational motion in two and three dimensions. The operators for energy, angular momentum and the z component of angular momentum are constructed in Cartesian (x,y,z), polar (r, φ) and spherical polar (r, θ, φ) coordinates and the solutions, which are functions of θ and φ are obtained .

The quantization of $\vec{L}$ and $\vec{L}_z$ occurs due to the requirement that the wavefunction has to be single valued. These solutions will be used for obtaining the solution of the hydrogen atom to be studied in the next chapter.