Rotational motion

We consider two types of rotational motion: in two dimensions (particle on a ring) and in three dimensions (particle on a sphere).

Particle on a ring

Let us consider a particle of mass \( m \) moving a circular path of radius \( r \). The potential energy is zero everywhere and therefore the total energy is equal to the kinetic energy:

\[ E = \frac{p^2}{2m} \]

According to classical mechanics, the magnitude of angular momentum is \( J = pr \), and so the energy can be expressed as \( E = \frac{J^2}{2mr^2} \). Since the moment of inertia is \( I = mr^2 \), \( E = \frac{J^2}{2I} \).

We shall see that not all the values of the angular momentum are permitted in quantum mechanics and therefore that the energy is quantized.

The qualitative origin of quantized rotation

Since \( J = pr \) and \( p = \frac{h}{\lambda} \), the magnitude of the angular momentum is \( J = \frac{hr}{\lambda} \). The smaller the wavelength of the particle on the ring, the greater its angular momentum. It follows that if we can see why the wavelength is restricted to discrete values, we shall understand why the angular momentum is restricted. Suppose that \( \lambda \) can take an arbitrary value. When the azimuthal angle \( \phi \) increases beyond \( 2\pi \), the wavefunction continues to change, but for an arbitrary wavelength it gives rise to a different amplitude at each point. Since different values are given on successive circuits, the wavefunction is not single-valued, but multiple-valued wavefunction is unacceptable.
An acceptable solution is obtained if the wavefunction reproduces itself on successive circuits. Then, since only some wavefunctions have this property, only some angular momenta are acceptable, and therefore only some energies exist. Hence, the energy of the particle is quantized. In particular, the wavelength must be a whole-number fraction of the circumference if its ends are to match after each circuit. That is,

$$\lambda = \frac{2\pi r}{n} \quad \text{with } n = 0, 1, 2, \ldots$$

($n = 0$, which gives an infinite wavelength, corresponds to a uniform amplitude.) At this stage, therefore, it looks as though the angular momentum is limited to the values

$$J = \frac{n\hbar r}{2\pi r} = n\hbar$$

and that the energy is limited to the values

$$E = \frac{J^2}{2I} = \frac{n^2\hbar^2}{2I} \quad \text{with } n = 0, 1, 2, \ldots$$

However, this solution cannot be complete. The angular momentum can arise from motion in either direction, and so $J$, like $p$, ought to carry a sign, $J = +n\hbar$ indicating one sense of rotation and $J = -n\hbar$ indicating the other. We should therefore expect the quantum number for rotational motion to take both positive and negative values.
The formal solution

The two dimensional Schrödinger equation for a particle in a plane (with $V = 0$):

$$\frac{-\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) = E\psi$$

It is better to transform this equation to polar coordinates:

$$x = r \cos \phi \quad y = r \sin \phi$$

Since $r$ is constant for a particle moving on a ring, we can obtain

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r^2} \frac{d}{d \phi^2}$$

and the Schrödinger equation is transformed into

$$\frac{-\hbar^2}{2mr^2} \frac{d^2 \psi}{d \phi^2} = E\psi$$

The moment of inertia $I = mr^2$ has appeared automatically:

$$\frac{d^2 \psi}{d \phi^2} = \frac{-2IE\psi}{\hbar^2}$$

The normalized general solutions of the equation are

$$\psi_{m_l} = \left( \frac{1}{2\pi} \right)^{1/2} e^{im_l \phi} \quad m_l = \pm \left( \frac{2IE}{\hbar^2} \right)^{1/2}$$
$m_l$ is some dimensionless number at this stage; it will soon be promoted to the status of a quantum number and the origin of the notation $m_l$ will be explained. We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued.

That is, the wavefunction $\psi$ must satisfy the **cyclic boundary condition** and match at points separated by a complete revolution:

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

On substituting the general form into this condition, we obtain

$$\psi_{m_l}(\phi + 2\pi) = \left(\frac{1}{2\pi}\right)^{1/2} e^{im_l(\phi+2\pi)} = \left(\frac{1}{2\pi}\right)^{1/2} e^{im_l\phi} e^{2\pi im_l} = \psi_{m_l}(\phi)e^{2i\pi m_l}$$

As $e^{i\pi} = -1$, this is equivalent to

$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l} \psi_{m_l}(\phi)$$

Hence, $2m_l$ must be a positive or negative **even** integer, and therefore $m_l$ must be an integer: $m_l = 0, \pm 1, \ldots$

**Quantization of rotation**

Since the energy is related to the value of $m_l$, and the cyclic boundary conditions restrict $m_l$ to integer values, we conclude that the energy is quantized, and that the allowed values are given by

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \ldots$$
The occurrence of $m_l$ as its square means that the energy of rotation is independent on the sense of rotation (the sign of $m_l$), as one could expect physically. Furthermore, although the result has been derived for the rotation of a single mass point, it also applies to any body of moment of inertia $I$ constrained to rotate about one axis.

We can conclude that the angular momentum is also quantized. This is our first example of an observable other than energy that is confined to discrete values. In the present case, we can find, using the above expression and the classical expression for the energy, that the angular momentum is limited to the values

$$J_z = m_l \hbar$$

$m_l = 0, \pm 1, \pm 2, ...$

(The subscript $z$ is there to remind us that the angular momentum corresponds to motion about the $z$–axis.) The increasing angular momentum is associated with the increasing number of nodes in the wavefunction: the wavelength decreases stepwise as $m_l$ increases, and so the momentum with which the particle travels round the ring increases.

In our discussion of free motion in one dimension, we saw that the opposite signs in the wavefunctions $e^{ikx}$ and $e^{-ikx}$ corresponded to opposite directions of travel, and that the linear momentum was given by the eigenvalue of the linear momentum operator. The same conclusions can be drawn here, but now we need the eigenvalues of the angular momentum operator. In classical mechanics the orbital angular momentum $l_z$ about the $z$–axis is defined as

$$l_z = xp_y - yp_x$$
$p_x$ is the component of linear momentum parallel to the $x$–axis and $p_y$ is the component parallel to the $y$–axis. The operators for the two linear momentum components are differentiation with respect to $x$ and $y$, so in quantum mechanics the operator for angular momentum about the $z$–axis is

$$\hat{l}_z = \frac{\hat{\hbar}}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

In terms of polar coordinates:

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

With the angular momentum operator available, we can test the wavefunction for a particle on a ring. Disregarding the normalization constant, we find

$$\hat{l}_z \psi_{m_l} = \frac{\hat{\hbar}}{i} \frac{d e^{i m_l \phi}}{d \phi} = i m_l \times \frac{\hat{\hbar}}{i} e^{i m_l \phi} = m_l \hat{\hbar} \psi_{m_l}$$

That is, $\psi_{m_l}$ is an eigenfunction of the orbital angular momentum and corresponds to an angular momentum $m_l \hat{\hbar}$. When $m_l$ is positive, the angular momentum is positive (clockwise when seen from below); when $m_l$ is negative, the angular momentum is negative (counter-clockwise when seen from below). This is the origin of the vector presentation of the angular momentum, in which the magnitude is represented by the length of a vector and the direction of motion by its orientation.
We can explore the question of the position of the particle when it is in a state of definite angular momentum. We form the probability density:

$$\psi_{m_l}^* \psi_{m_l} = \frac{1}{2\pi} \times e^{-im_l \phi} \times e^{im_l \phi} = \frac{1}{2\pi}$$

Since $\psi^* \psi$ is independent on $\phi$, the probability of locating the particle at any point on the ring is also independent of $\phi$. Hence, the location of the particle is completely indefinite, and knowing the angular momentum precisely eliminates the possibility of specifying the particle’s position. Angular momentum and angle are a pair of complementary observables, and the inability to specify them simultaneously to arbitrary precision is another example of the uncertainty principle.

In the system we consider there is no zero-point energy, for $m_l$ can be equal to 0. This is not in conflict with the uncertainty principle, for even though we then know that the angular momentum is precisely zero, we are totally uncertain about the position of the particle.

**Rotation in three dimensions (a particle on a sphere)**

We now consider a mass point free to move over the surface of a sphere of radius $r$. The requirement that the wavefunction should match as a path is traced over the poles as well as round the equator introduces a second cyclic boundary condition and therefore a second quantum number.
We shall later use the results of this calculation when we come to describe the states of electrons in atoms and of rotating molecule. The latter application arises from the fact that the rotation of a solid body of mass \( m \) can be represented by a single point of mass \( m \) rotating at a radius \( R_g \), the **radius of gyration** of the body, which is defined so that

\[
I = mR_g^2
\]

**Spherical polar coordinates**

Instead of familiar Cartesian coordinates, we introduce spherical polar coordinates, \( r \), \( \theta \), and \( \phi \), called radius, co-latitude, and azimuth:

\[
\begin{align*}
x &= r \sin \theta \cos \phi \\
y &= r \sin \theta \sin \phi \\
z &= r \cos \theta
\end{align*}
\]

The laplacian can be expressed as

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r} \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \Lambda^2 \psi
\]

\[
\Lambda^2 \psi = \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right)
\]

\( \Lambda^2 \) is known as the *legendrian*, and is the angular dependent part of the laplacian.
The Schrödinger equation

The Schrödinger equation in three dimensions is

\[-\frac{\hbar^2}{2mr^2} \nabla^2 \psi + V\psi = E\psi\]

Using the spherical polar coordinates and the expressions for laplacian and legendrian, the equation can be written as

\[-\frac{\hbar^2}{2mr^2} \Lambda^2 \psi = E\psi\]

Notice that the moment of inertia \( I = mr^2 \) has appeared automatically.

\[-\frac{\hbar^2}{2I} \Lambda^2 \psi = E\psi \quad \Lambda^2 \psi = \frac{-2IE\psi}{\hbar^2}\]

This equation is still partial differential equation in the two angular variables \( \theta \) and \( \phi \), but it separates into two equations one for \( \theta \) and the other for \( \phi \). To solve this equation we use the separation of variables technique and write the wavefunction as the product \( \psi = \Theta \Phi \) where \( \Theta \) is a function only of \( \theta \), and \( \Phi \) is a function only of \( \phi \). Then

\[\Lambda^2 \psi = \frac{1}{\sin^2 \theta} \Theta \frac{d^2 \Phi}{d\phi^2} + \Phi \frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d\Theta}{d\theta} = \frac{-2IE}{\hbar^2} \Theta \Phi\]
Division through by $\Theta\Phi$ gives
\[ \frac{1}{\sin^2 \theta} \frac{\Phi''}{\Phi} + \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \Theta' \sin \theta \right) = \frac{-2IE}{\hbar^2} \]

where $\Theta' = d\Theta / d\theta$ and $\Phi' = d\Phi / d\phi$. We ensure that each term depends on only one variable by multiplying through by $\sin^2 \theta$:
\[ \frac{\Phi''}{\Phi} \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \Theta' \sin \theta \right) = \frac{-2IE}{\hbar^2} \sin^2 \theta \]

The first term depends only on $\phi$, and the rest depends only on $\theta$. Therefore, the first term must be equal to a constant, which we write as $-m_i^2$ (because it will turn out to have the same significance as the $m_i$ we have already encountered). The separation is therefore successful, and after some rearrangement the two ordinary differential equations we must solve are the following:

\[ \Phi'' = -m_i^2 \Phi \]
\[ \sin \theta \frac{d}{d\theta} \left( \Theta' \sin \theta \right) + \left( \frac{2IE}{\hbar^2} \sin^2 \theta - m_i^2 \right) \Theta = 0 \]
The first of this pair of equations is the same as for a particle on a ring. The cyclic boundary conditions are also the same, and so the acceptable solutions are the same:

$$\Phi_{m_l} = \left(\frac{1}{2\pi}\right)^{1/2} e^{im\phi} \quad m_l = 0, \pm 1, \pm 2, \ldots$$

However, since $m_l$ also occurs in the equation for $\Theta$, it may be the case that the boundary conditions that $\Theta$ must satisfy also limit the values that $m_l$ may take.

The equation for $\theta$ is one that has been studied extensively by mathematicians. We turn it into a standard form by making the substitutions

$$\zeta = \cos \theta \quad l(l+1) = \frac{2IE}{\hbar^2}$$

where $l$ is a dimensionless number (shortly to be promoted to a quantum number).

$$\frac{d}{d\theta} = \left(\frac{d\zeta}{d\theta}\right) \frac{d}{d\zeta} = -\sin \theta \frac{d}{d\zeta}$$

$$\sin \theta = \left(1 - \cos^2 \theta\right)^{1/2} = \left(1 - \zeta^2\right)^{1/2}$$

and the equation transforms into

$$\left(1 - \zeta^2\right)\Theta'' - 2\zeta\Theta' + \left\{l(l+1) - \frac{m_l^2}{1-\zeta^2}\right\}\Theta = 0 \quad \text{where now } \Theta' = d\Theta / d\zeta.$$
This is known as the **associated Legendre equation**. It has acceptable solutions (i.e., solutions that are single valued and do not become infinite anywhere) so long as two conditions are fulfilled:

(a) \( l = 0, 1, 2, \ldots \)  
(b) \( |m_l| \leq l \)

That is, acceptable solutions exist only for *positive* integer \( l \), and the absolute value of the number \( m_l \) must not exceed \( l \) (this is the second constraint on \( m_l \) mentioned above). When these conditions are satisfied, the functions \( \Theta \), which now must be denoted \( \Theta_{l,m_l} \), are the **associated Legendre functions**.

They can be written in terms of sine and cosine functions and they are components of the spherical harmonics, \( Y = \Theta \Phi \).

That is, the wavefunction can be written as \( \psi = \Theta \Phi \), where \( \Theta \) is a function of \( \theta \) alone, and \( \Phi \) is a function of \( \phi \) alone.

**The properties of the solutions**

The acceptable wavefunctions are specified by *two* quantum numbers \( l \) and \( m_l \). (There are two cyclic boundary conditions to satisfy, one arising from the angle \( \phi \) and the other from the angle \( \theta \).) These quantum numbers are restricted to the values

\[
l = 0, 1, 2, \ldots \quad m_l = 0, \pm 1, \pm 2, \ldots, \pm l
\]

or, equivalently,

\[
m_l = l, l - 1, l - 2, \ldots, -l
\]

Note that \( l \) is positive and that, for a given value of \( l \), there are \( 2l+l \) permitted values of \( m_l \). The normalized wavefunctions are usually denoted \( Y_{l,m_l} \) and are called **spherical harmonics**.
The energy $E$ of the particle is restricted to the values

\[
E = l(l + 1) \frac{\hbar^2}{2I}
\]

$l = 0, 1, 2, ...$
We see that the energies is quantized and independent of $m_l$. Since there are $2l+1$ different wavefunctions (one for each value of $m_l$) that correspond to the same energy, a level with quantum number $l$ is $(2l+1)$ degenerate.

**Angular momentum**

The energy of a rotating particle is related classically to its angular momentum by $E = J^2 / 2I$. Therefore, we can deduce that the magnitude of the angular momentum is quantized, and confined to the values

$$J = \left\{ l(l + 1) \right\}^{1/2} \hbar$$

$l = 0, 1, 2, ...$

We have already seen that the angular momentum about the $z$-axis is quantized, and that it has values

$$J_z = m_l \hbar$$

$m_l = 0, \pm 1, \pm 2, ..., \pm l$

The higher the value of $l$, the larger the number of nodal lines (the positions at which $\psi = 0$) in the wavefunction. This reflects the fact that higher angular momentum implies higher kinetic energy, and therefore a more sharply buckled wavefunction. We can also see that the states corresponding to high angular momentum around the $z$-axis are those in which most nodes cut the equator: this indicates a high kinetic energy arising from motion parallel to the equator because the curvature is greatest in that direction.
We can also write the Schrödinger equation in terms of $l$, so giving the differential equation satisfied by the spherical harmonics:

$$\Lambda^2 Y_{l,m_l} = -l(l + 1)Y_{l,m_l}$$

One can demonstrate that the spherical harmonics are in fact solutions of this equation. Let’s take, for example

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

$$\Lambda^2 Y_{1,0} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta =$$

$$- \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{\sin \theta} \frac{d}{d \theta} \sin^2 \theta = - \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{\sin \theta} 2 \sin \theta \cos \theta = 2Y_{1,0}$$

**Space quantization**

The result that $m_l$ is confined to the discrete values $l$, $l-1$, ..., $-l$ for a given value of $l$ means that the component of angular momentum about the $z$-axis may take only $2l+1$ values. If the angular momentum is represented by a vector of length proportional to its magnitude (i.e. of length $\{l(l+1)\}^{1/2}$ units), then to represent correctly the value of the component of angular momentum, the vector must be oriented so that its projection on the $z$-axis is of length $m_l$. In classical terms, this means that the plane of rotation of the particle can take only a discrete range of orientations. The remarkable implication is that the orientation of a rotating body is quantized.
The vector model

So far, we have referred to the $z$-component of angular momentum, and have made no reference to the $x$- and $y$-components. The reason is that the uncertainty principle forbids the simultaneous, exact specification of more than one component. Therefore, if $l_z$ is known, it is impossible to ascribe values to the other two components. It follows that the illustration on the left gives a false impression of the state of the system, because it suggests definite values for the $x$- and $y$-components. A better picture must reflect the indeterminance of $l_x$ and $l_y$ if $l_z$ is known. The vector model of angular momentum is shown on the figure. The cones are drawn with side $\{l(l+1)\}^{1/2}$ units, and represent the magnitude of the angular momentum. Each cone has a definite projection (of $m_l$ units) on the $z$-axis, representing the system’s precise value of $l_z$. The $l_x$ and $l_y$ projections, however, are indefinite. The vector representing the state of angular momentum can be thought as lying with its tip on any point on the mouth of the cone.

The vector model of angular momentum, although only a pictorial representation of aspects of the quantum mechanical properties, turns out to be very useful when we turn to the structure and spectra of atoms.

The quantum mechanical result that a rotating body may not take up an arbitrary orientation with respect to some specified axis (e.g. an axis defined by the direction of an externally applied electric or magnetic field) is called space quantization. It was confirmed by experiment first performed by Stern and Gerlach in 1921.
They shot a beam of silver atoms through an inhomogeneous magnetic field. The idea behind the experiment was that a rotating, charged body behaves like a magnet and interacts with the applied field. According to classical mechanics, since the orientation of the angular momentum can take any value, the associated magnet can take any orientation.

Since the direction in which the magnet is driven by the inhomogeneous field depends on the orientation, it follows that a broad band of atoms is expected to emerge from the region where the magnetic field acts. According to quantum mechanics, since the angular momentum is quantized, the associated magnet lies in a number of discrete orientations, and so several sharp bands of atoms are expected.

In their first experiment, Stern and Gerlach appeared to confirm the classical prediction. However, the experiment is difficult because the atoms in the beam collide with each other and this blurs the bands. When the experiment was repeated with a beam of very low intensity (so that collisions were less frequent) they observed discrete bands, and so confirmed the quantum prediction.
Spin

When Stern and Gerlach used Ag atoms in their experiment, they observed two bands. This seems to conflict with one of the predictions of quantum mechanics, because an angular momentum $l$ gives rise to $2l+1$ orientations, which is equal to 2 only if $l = 1/2$, contrary to the conclusion that $l$ must be an integer. This conflict was resolved by the suggestion that the angular momentum they were observing was not due to the atom’s orbital angular momentum (which arises from the motion of an electron around the atomic nucleus) but arose from the motion of the electron about its own axis. The internal angular momentum of the electron is called its spin.

The wavefunction of an electron spinning at a single point in space does not have to satisfy the same boundary conditions as those for a particle moving over the surface of a sphere, and so the quantum numbers are not subject to the same restrictions. In order to distinguish the spin angular momentum from orbital angular momentum we use the quantum number $s$ (in place of $l$) and $m_s$ for the projection on the $z$-axis. The magnitude of the spin angular momentum is $\left\{s(s+1)\right\}^{1/2}\hbar$ and the component $m_s\hbar$ is restricted to the $2s+1$ values: $m_s = s, s-1, s-2, ..., -s$

The detailed analysis of the spin of a particle is quite sophisticated, and shows that the property should not be taken to be an actual spinning motion. However, this picture can be very useful when used with care. For an electron, it turns out that only one value of $s$ is allowed, and $s = 1/2$, corresponding to an angular momentum of magnitude

$$1/2\sqrt{3}\hbar = 0.866\hbar.$$
This spin angular momentum is an intrinsic property of the electron, like its rest mass and charge, and every electron has exactly the same value. The spin may lie in either of $2s + 1 = 2$ different orientations. One orientation corresponds to $m_s = +1/2$ (this is often called an $\alpha$-electron and denoted $\uparrow$); the other corresponds to $m_s = -1/2$ (and is called a $\beta$-electron and denoted $\downarrow$).

The outcome of the Stern-Gerlach experiment can now be explained if we suppose that each silver atom possesses an angular momentum due to the spin of a single electron, because the two bands of atoms then correspond to the two spin orientations.

Like the electron, other elementary particles have characteristic spins. Few example, protons and neutrons are spin-\(^{1/2}\) particles (i.e. $s = 1/2$) and so invariably spin with angular momentum $1/2\sqrt{3}\hbar = 0.866\hbar$. Since the masses of a proton and a neutron are so much greater than the mass of an electron, yet they all have the same the same angular momentum, the classical picture would be of particles spinning much more slowly than an electron. Some elementary particles have $s = 1$, and so have an intrinsic angular momentum of magnitude $\sqrt{2}\hbar = 1.414\hbar$. Some mesons and some atomic nuclei are spin-1 particles, but perhaps the most important spin-1 particle is the photon.
Summary: Properties of Angular Momentum

The quantum numbers:

Orbital quantum number: \( l = 0, 1, 2, ... \)

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

(\( m_l \) is also known as the magnetic quantum number)

Spin angular momentum quantum number \( s = 1/2 \)

\( m_s = \pm (1/2) \)

In general, an angular momentum is denoted by the quantum numbers \( j \) and \( m_j \). The magnitude of the angular momentum is equal to \( \sqrt{j(j + 1)} \hbar \) and the z-component of angular momentum is equal to \( m_j \hbar \).