Particle motion in three dimensions

For a particle moving in three dimensions, the Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\Psi(\vec{r},t) = i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} \quad \text{- - - (1)}$$

where ∇^2 is the Laplacian operator. In a Cartesian coordinate system, the Laplacian operator is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{- - - - - (2)}$$

We now look for solutions of definite energy. Such solutions are of the form

$$\Psi(\vec{r},t) = \psi(\vec{r})\,e^{-iEt/\hbar} \quad \text{- - - - (3)}$$

If we substitute (3) in (1), we find that $\psi(\vec{r})$ must be an eigenfunction of the Hamiltonian with eigenvalue E, i.e.,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}), \quad \text{- - - - (4)}$$

We shall assume that V is spherically symmetric, i.e.,

$$V(\vec{r}) = V(|\vec{r}|) = V(r) .$$

In other words, a spherically symmetric potential is a function of the magnitude of $\vec{r}$ only.

We will use spherical polar coordinates to solve Eq. (4). In spherical polar coordinates, the variables are r, θ and φ as shown in the figure below:

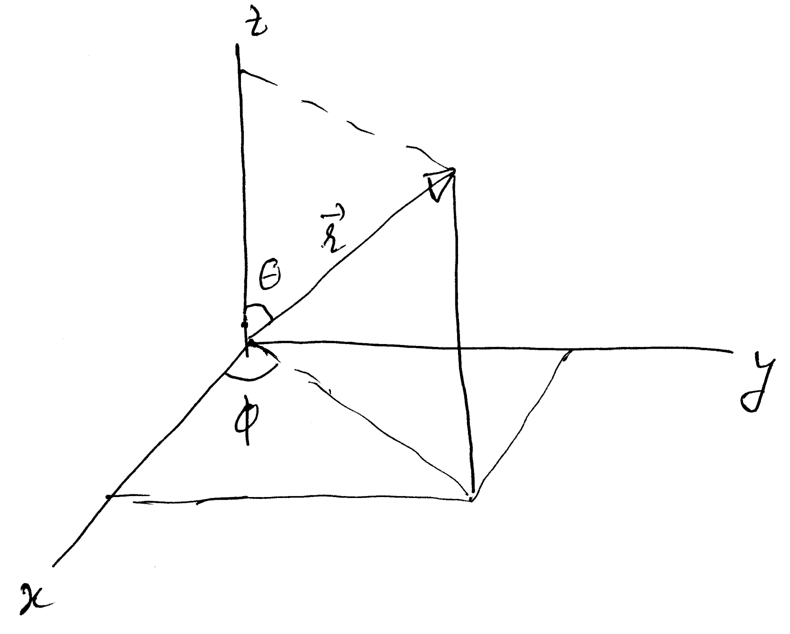


Fig 1: The relation between rectangular and spherical polar coordinates.

We have

$$x = r \sin\theta \cos\varphi$$
$$y = r \sin\theta \sin\varphi \qquad \text{------------} \quad (5)$$
$$z = r \cos\theta$$

In spherical polar coordinates, the Laplacian operator is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}. \quad \text{---} (6)$$

The Schrödinger equation (Eq. (4)) in spherical polar coordinates is then

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(\vec{r})$$
$$+ \frac{2m}{\hbar^2}\left(E - V(r)\right)\psi(\vec{r}) = 0 \quad \text{----} (7)$$

We can solve Eq. (7) by the method of separation of variables. We first separate the radial and the angular parts by substituting

$$\psi(r,\theta,\phi) = R(r)\, Y(\theta,\phi)$$

into Eq. (7) and dividing by ψ. We get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(E - V(r)\right)$$
$$= -\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]. \quad --(8)$$

Since the left side of Eq. (8) depends only on r and the right hand side depends only on θ, ϕ, both sides must be equal to a constant which we call λ. Thus, Eq. (8) gives us a radial equation and an angular equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left\{\frac{2m}{\hbar^2}\left(E-V(r)\right)-\frac{\lambda}{r^2}\right\}R=0 \quad \text{---} (9)$$

and

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}+\lambda Y=0. \quad \text{----} (10)$$

Separation of the angular equation.

The angular equation, i.e., Eq. (10), can be further separated by substituting

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

into it and following the same procedure, i.e, dividing by Y :

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

or $$\frac{1}{\Theta(\theta)}\cdot\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta=-\frac{1}{\Phi(\varphi)}\frac{d^2\Phi}{d\varphi^2}$$

The left hand side depends on θ only and the right hand side depends upon φ only. Therefore, each side must be equal to a constant. Call the constant ν. Therefore, we get

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = \nu$$

or
$$\frac{d^2\Phi}{d\varphi^2} + \nu\Phi = 0 \qquad \cdots\cdots (11)$$

and

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\sin^2\theta = \nu$$

or
$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{\nu}{\sin^2\theta}\right)\Theta = 0 \quad \cdots (12)$$

<u>Solution of Φ (Eq (11))</u>

The Φ equation, Eq. (11), can be solved at once. Its general solution may be written as

$$\Phi(\varphi) = A e^{i\nu^{1/2}\varphi} + B e^{-i\nu^{1/2}\phi} \quad (\nu \neq 0) \quad \cdots (13)$$

$$\Phi(\varphi) = A + B\varphi \quad (\nu = 0). \quad \cdots (14)$$

The requirement that $\Phi(\varphi)$ and $d\Phi/d\varphi$ be continuous throughout the domain 0 to 2π of φ requires that if ν is nonzero (Eq. (13)), then $\nu^{1/2}$ must must be a positive or a negative integer, i.e., $\nu^{1/2} = m$. If $\nu = 0$, we must choose $B = 0$. Therefore, linearly independent solutions are of the ~~ros~~ form

$$\Phi_m(\varphi) = A\, e^{im\varphi} \quad ; \quad m = 0, \pm 1, \pm 2, \ldots$$

We can fix A by requiring that $\Phi_m(\varphi)$ is normalized, i.e.,

$$\int_0^{2\pi} \Phi_m^*(\varphi)\, \Phi_m(\varphi)\, d\varphi = 1$$

or $$|A|^2\, 2\pi = 1$$

or $$A = \frac{1}{\sqrt{2\pi}}.$$

Then

$$\boxed{\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\, e^{im\varphi} \; ; \; m = 0, \pm 1, \pm 2, \ldots} \qquad (15)$$

Associated Legendre polynomial.

Now, we will look at the Θ equation, Eq. (12). With $\nu = m^2$, Eq. (12) is

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \quad ---(16)$$

It is convenient to substitute $\omega = \cos\theta$, so that $\Theta(\theta) = P(\omega)$ and $d\omega = -\sin\theta\, d\theta$. In terms of ω, Eq. (16) becomes

$$\frac{d}{d\omega}\left[(1-\omega^2)\frac{dP}{d\omega}\right] + \left(\lambda - \frac{m^2}{1-\omega^2}\right)P = 0 \quad --(17)$$

In the above equation the domain of ω is -1 to $+1$, since the domain of θ is from 0 to π.

Since Eq. (17) is a second order linear ordinary differential equation, it has two linearly independent solutions. Except for particular values of λ, both of these are infinite at $\omega = \pm 1$ and hence ~~not~~ are not physically acceptable. If, however, $\lambda = \ell(\ell+1)$ with ℓ a positive integer or zero, one of the solutions is finite everywhere, including $\omega = \pm 1$, provided $|m| \le \ell$, and the other is not finite at $\omega = \pm 1$ for any value of m. This finite solution is of the form

$$P(\omega) \sim (1-\omega^2)^{|m|/2} \times \text{polynomial of order } \ell - |m| .$$

Legendre polynomials.

The physically acceptable solutions when $m = 0$ are called Legendre polynomials. If $m = 0$, then physically acceptable solutions exist for any value of $\ell = 0, 1, 2, \ldots$. With $m = 0$ and $\lambda = \ell(\ell+1)$, Eq. (17) becomes

$$\frac{d}{d\omega}\left[(1-\omega^2)\frac{dP_\ell}{d\omega}\right] + \ell(\ell+1)P_\ell(\omega) = 0 \quad - - - \quad (8)$$

where $P_\ell(\omega)$ are the Legendre polynomials.

We can show that $P_\ell(\omega)$ is given by the Rodrigues formula

$$P_\ell(\omega) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{d\omega^\ell} (\omega^2 - 1)^\ell \quad \text{.} \quad \text{- - - - - (19)}$$

We also have a generating function for the Legendre polynomials

$$T(\omega, s) = (1 - 2s\omega + s^2)^{-1/2}$$
$$= \sum_{\ell=0}^{\infty} P_\ell(\omega) s^\ell \quad (s < 1) \quad \text{.} \quad \text{- - - - (20)}$$

Using the Rodrigues formula, we can work out the first few Legendre polynomials. We find

$$P_0(\omega) = 1$$
$$P_1(\omega) = \omega$$
$$P_2(\omega) = \frac{1}{2}(3\omega^2 - 1) \qquad \text{- - - - (21)}$$
$$P_3(\omega) = \frac{1}{2}(5\omega^3 - 3\omega)$$

From Eq. (19) we see that

$$P_l(-\omega) = (-1)^l P_l(\omega)$$

i.e., $P_l(\omega)$ is an even function of ω if l is even, and $P_l(\omega)$ is an odd function of ω is l is odd. This can be seen explicitly from Eq. (21).

Legendre polynomials satisfy the orthogonality condition

$$\int_{-1}^{+1} P_l(\omega) P_{l'}(\omega)\, d\omega = \frac{2}{2l+1}\,\delta_{ll'} \quad \cdots \quad (21)$$

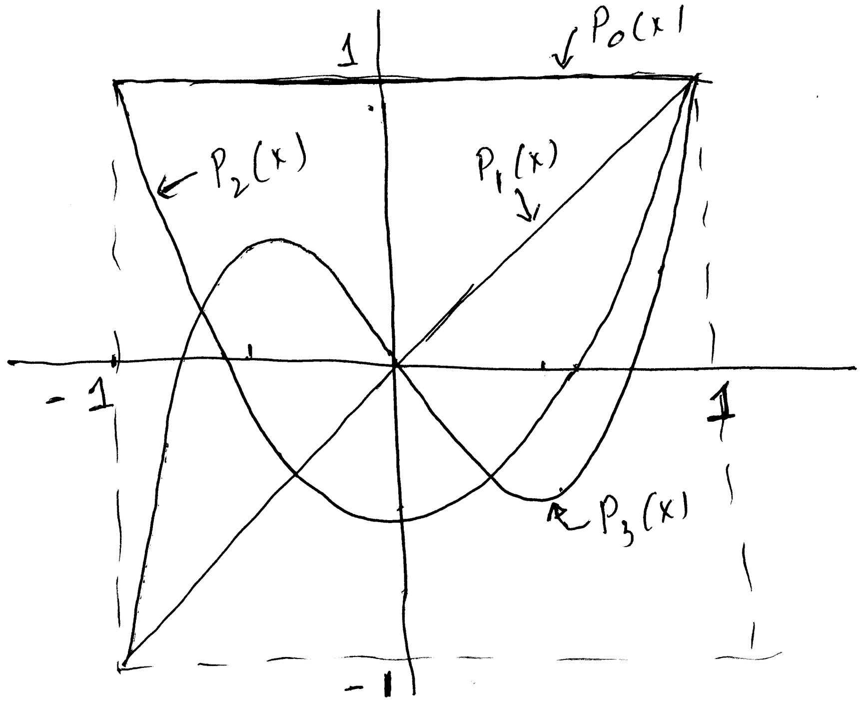
i.e.,

$$\int_0^{2\pi} P_l(\cos\theta)\, P_{l'}(\cos\theta)\, \sin\theta\, d\theta = \frac{2}{2l+1}\,\delta_{ll'}. \quad -(22)$$

The Legendre polynomials also obey the closure or completeness condition

$$\frac{1}{2}\sum_l (2l+1)\, P_l(x)\, P_l(x') = \delta(x-x') \quad \cdots \quad (22)$$

Graph of Legendre polynomials



Associated Legendre polynomials

If $m \neq 0$, Eq. (17) has acceptable solutions if $\lambda = l(l+1)$ and $|m| \leq l$. These solutions are called associated Legendre polynomials and are denoted by $P_l^m(\omega)$. They satisfy the differential equation (Eq (17) with $\lambda = l(l+1)$):

$$\frac{d}{d\omega}\left[(1-\omega^2)\frac{dP_l^m(\omega)}{d\omega}\right] + \left(l(l+1) - \frac{m^2}{1-\omega^2}\right)P_l^m(\omega) = 0.$$

$$(|m| \leq l)$$

If $m = 0$, the associated Legendre polynomial is simply the Legendre polynomial $P_l(\omega)$.

The associated Legendre polynomials can be expressed as

$$P_l^m(\omega) = (1-\omega^2)^{\frac{1}{2}|m|} \frac{d^{|m|}}{d\omega^{|m|}} P_l(\omega). \quad \cdots (23)$$

Note the differential equation for $P_l^m(\omega)$ involves m^2. Therefore, $P_l^m(\omega)$ and $P_l^{-m}(\omega)$ are basically the same functions except for a multiplicative constant. We chosen $P_l^m(\omega)$ and $P_l^{-m}(\omega)$ to be equal in Eq. (23).

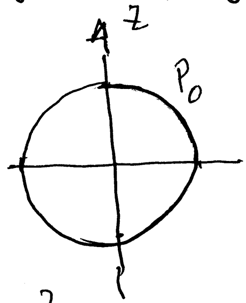
It can be shown that the associated Legendre polynomials satisfy the following orthogonality relation

$$\int_0^\pi P_l^m(\cos\theta)\, P_{l'}^m(\cos\theta) \sin\theta \, d\theta$$

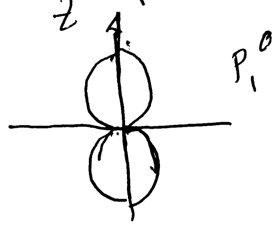
$$= \int_{-1}^{+1} P_l^m(\omega)\, P_{l'}^m(\omega)\, d\omega = \frac{2}{2l+1} \frac{(l+|m|)!}{(l-|m|)!} \delta_{ll'} .$$

In the figure below we show the parametric plots of the first few associated Legendre polynomials.

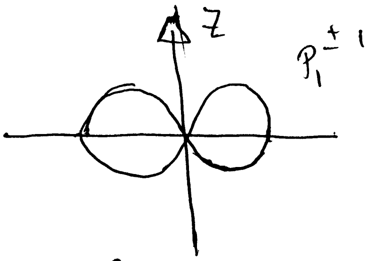
$$P_0^0 = P_0 = 1$$



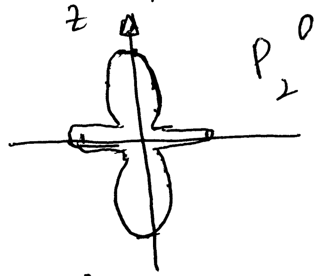
$$P_1^0 = \cos\theta$$



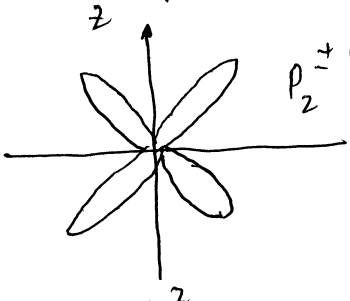
$$P_1^{\pm 1} = \sin\theta$$



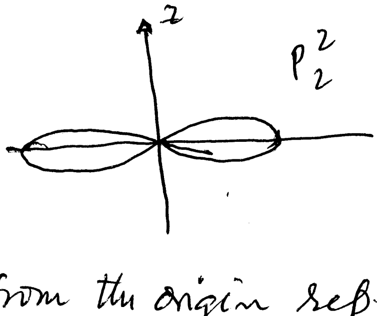
$$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$$



$$P_2^{\pm 1} = 3\sin\theta\cos\theta$$



$$P_2^2 = 3\sin^2\theta$$



Note: In the graphs, distance from the origin represents the magnitude of $P_\ell^m(\cos\theta)$ in the direction θ.

Spherical harmonics

Our solution of the angular wave function is of the form

$$Y_{lm}(\theta,\phi) = C_{lm}\, P_l^m(\cos\theta)\, \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$$

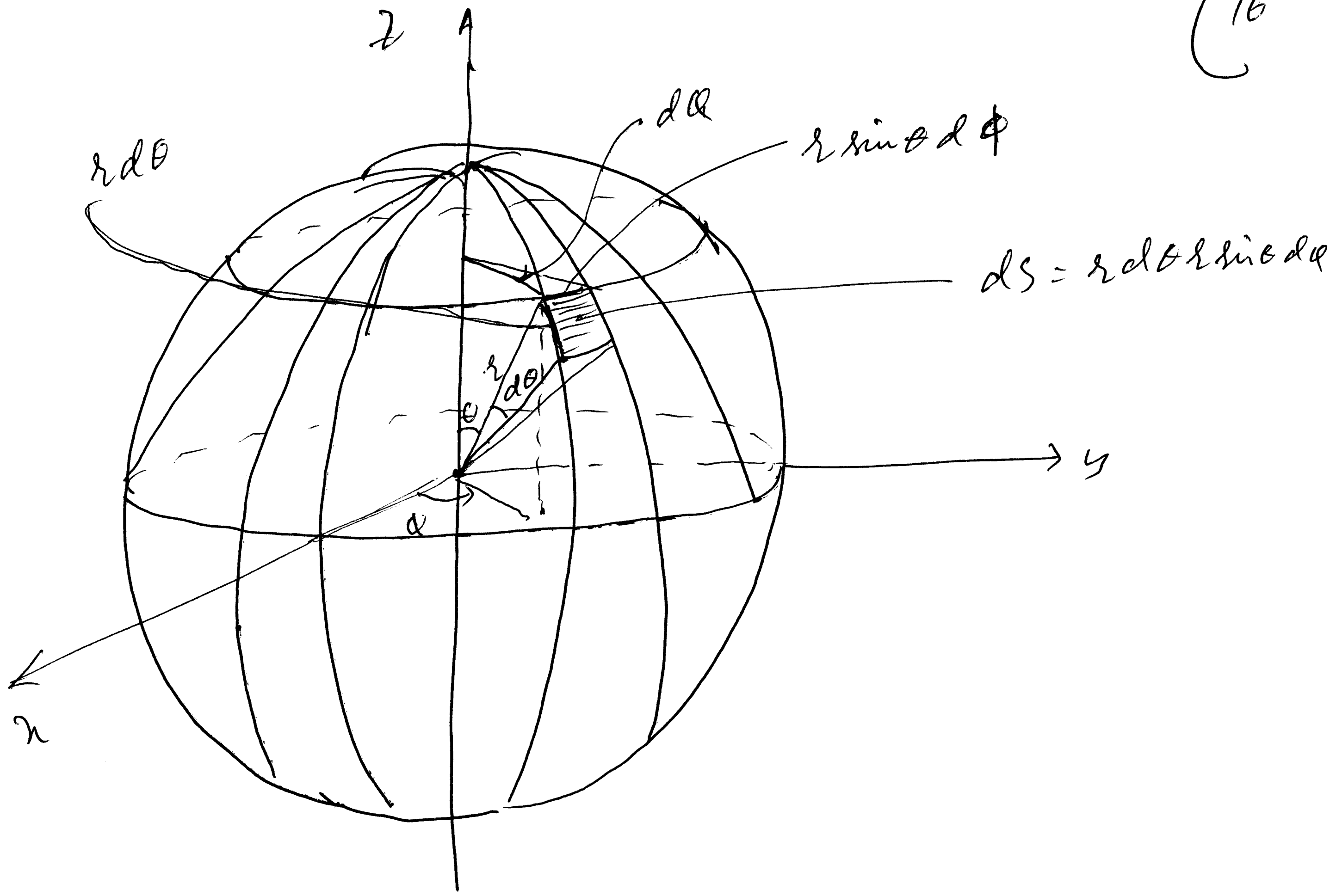
i.e., $$Y_{lm}(\theta,\phi) = N_{lm}\, P_l^m(\cos\theta)\, e^{im\phi} \quad \text{-- -- -- (24)}$$

where N_{lm} is a constant. We note that l is a positive integer or zero, i.e., $l = 0, 1, 2, \cdots$ and $|m| \leq l$. Thus, for a given l, m can assumes $2l+1$ values: $m = -l, -l+1, \cdots l-1, l$.

We now choose N_{lm} by requiring that $Y_{lm}(\theta,\phi)$ is normalized, i.e.,

$$\int Y^{*}_{lm}(\theta,\phi)\, Y_{l'm'}(\theta,\phi)\, d\Omega = \delta_{ll'}\,\delta_{mm'} \quad \text{-- -- (25)}$$

where $d\Omega$ is an element of solid angle in the direction θ, ϕ.



Now $$d\Omega = \frac{ds}{r^2}$$

where ds is an infinitesimal area perpendicular to r in the direction θ, ϕ. In spherical polar coordinates $ds = r\,d\theta . r\sin\theta\,d\varphi = r^2 \sin\theta\,d\theta\,d\varphi$.

$$\therefore\ d\Omega = \frac{r^2 \sin\theta\,d\theta\,d\varphi}{r^2} = \sin\theta\,d\theta\,d\varphi .$$

Now, we can write Eq. (25) as

$$N^*_{\ell m} N_{\ell' m'} \int P_\ell^m(\cos\theta) e^{-im\phi} P_{\ell'}^{m'}(\cos\theta) e^{im'\phi} \sin\theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'}$$

We can do the ϕ integral very easily:

$$\int_0^{2\pi} e^{i(m'-m)\phi} d\phi = 2\pi \, \delta_{mm'}$$

Hence

$$N^*_{\ell m} N_{\ell' m'} \, 2\pi \, \delta_{mm'} \int_0^\pi P_\ell^m(\cos\theta) P_{\ell'}^{m'}(\cos\theta) \sin\theta \, d\theta = \delta_{\ell\ell'} \delta_{mm'}$$

or $$2\pi N^*_{\ell m} N_{\ell' m} \int_0^\pi P_\ell^m(\cos\theta) P_{\ell'}^m(\cos\theta) \sin\theta \, d\theta = \delta_{\ell\ell'}$$

or $$2\pi N^*_{\ell m} N_{\ell' m} \cdot \frac{2}{2\ell+1} \frac{(\ell+|m|)!}{(\ell-|m|)!} \delta_{\ell\ell'} = \delta_{\ell\ell'}$$

or $$|N_{\ell m}|^2 \frac{4\pi}{(2\ell+1)} \frac{(\ell+|m|)!}{(\ell-|m|)!} = 1$$

or,

$$N_{\ell m} = \epsilon \left[\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2},$$

where ϵ is a complex phase factor with unit modulus. Different authors choose ϵ in different ways. We can simply choose $\epsilon = 1$ (Schiff). Another ~~phase~~ choice of the phase ϵ, called the Condon - Shortley phase convention is to choose $\epsilon = (-1)^m$ for $m > 0$ and $\epsilon = 1$ for $m \leq 0$. In the Condon Shortley phase convention, the first few spherical harmonics are:

$$Y_{00} = \frac{1}{(4\pi)^{1/2}}, \quad Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_{1\pm1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{\pm i\phi}$$

$$Y_{20} = \left(\frac{3}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_{2\pm1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta \, e^{\pm i\phi}$$

$$Y_{2\pm2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta \, e^{\pm 2i\phi}$$

Finally, the differential equation satisfied by $Y_{\ell m}$ is (put $\lambda = \ell(\ell+1)$ in Eq. (10))

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] Y_{\ell m}(\theta,\phi) = -\ell(\ell+1) Y_{\ell m}(\theta,\phi). \quad \text{-- (27)}$$

Spherical harmonics form a complete set. Any function of θ and ϕ, $f(\theta,\phi)$, can always be expanded in terms of the spherical harmonics:

$$f(\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m} Y_{\ell m}(\theta,\phi).$$

The expansion coefficients can be found as follows:

$$\int Y^*_{\ell' m'}(\theta,\phi) f(\theta,\phi)\, d\Omega = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m}\int Y^*_{\ell' m'}(\theta,\phi) Y_{\ell m}(\theta,\phi)\, d\Omega$$

$$= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m}\,\delta_{\ell\ell'}\,\delta_{mm'} = c_{\ell' m'}$$

Since ℓ' and m' are arbitrary

$$c_{\ell m} = \int Y^*_{\ell m}(\theta,\phi) f(\theta,\phi)\, d\Omega.$$

Full wave function.

The full wavefunction with definite energy E can now be written as

$$\psi_{E\ell m}(\vec{r}) = R_{E\ell}(r)\, Y_{\ell m}(\theta,\phi) \quad \cdots \quad (28)$$

where $R_{E\ell}(r)$ satisfies Eq. (9) with $\lambda = \ell(\ell+1)$,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR_{E\ell}}{dr}\right) + \left[\frac{2m}{\hbar^2}(E - V(r)) - \frac{\ell(\ell+1)}{r^2}\right] R_{E\ell}(r) = 0. \quad \cdots (29)$$

This radial equation can be rewritten in a form that resembles one-dimensional Schrödinger by putting

$$R_{E\ell}(r) = \frac{u_{E\ell}(r)}{r}.$$

Then Eq. (29) becomes

$$\frac{d^2 u_{E\ell}(r)}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right] u_{E\ell}(r) = 0$$

or

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{E\ell}}{dr^2} + \left[V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right] u_{E\ell} = E\, u_{E\ell} \quad \cdots (30)$$

Thus the radial motion is similar to the one-dimensional motion of a particle with the effective potential

$$V_{eff}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \quad \text{- - - - - . (31)}$$

Classical particle

Consider a classical particle moving in a central force field with potential $V(r)$ where r is the distance of the particle from the force center. For a central ~~force~~ potential, we have

$$\vec{F} = -\vec{\nabla}V = -\hat{r}\,\frac{dV(r)}{dr}$$

i.e $\vec{F}$ is radial, pointing either towards the center of the force if $\frac{\partial V}{\partial r}$ is +ve, or pointing radially outward from the center of the force if $\frac{dV}{dr}$ is -ve. The center of the force is taken as the origin of the coordinate system.

Now, the orbital angular momentum of the particle about the origin is defined as

$$\vec{L} = \vec{r} \times \vec{p}.$$

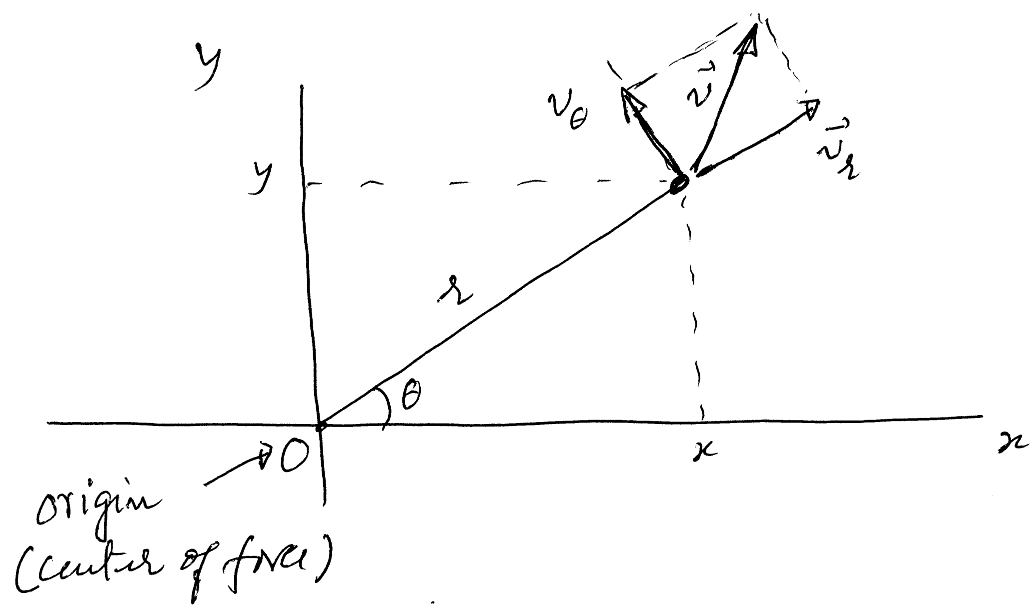
If the force is radial, we can show that $\vec{L}$ is a constant vector.

To show this we calculate the time derivative of $\vec{L}$ and show that it is zero for a central force.

$$
\begin{aligned}
\frac{d\vec{L}}{dt} &= \frac{d}{dt}(\vec{r}\times\vec{p}) = \frac{d\vec{r}}{dt}\times\vec{p} + \vec{r}\times\frac{d\vec{p}}{dt} \\
&= \vec{v}\times m\vec{v} + \vec{r}\times\vec{F} \\
&= 0 + 0 \,(\text{if } \vec{F} \text{ is radial}) \\
&= 0 .
\end{aligned}
$$

Thus $\vec{L}$ is a constant vector, i.e., both the magnitude and the direction of the angular momentum vector about the center of force are constants. Now, according to the definition of cross product of two vectors, $\vec{r}$ and $\vec{p}$ ~~is~~ are perpendicular to $\vec{L}$ and ~~B~~ since $\vec{L}$ has a fixed direction in space, $\vec{r}$ and $\vec{p}$ always lie in a plane perpendicular to $\vec{L}$. Thus the motion occurs in a plane and the angular momentum points perpendicular to the plane. Call the plane of motion the $x-y$ plane.

To describe the motion of a particle moving in the $x-y$ plane under a central force, it is convenient to use plane polar coordinates, rather than Cartesian coordinates.



The relations between cartesian coordinates (x, y) and plane polar coordinates ~~are~~ $(r\,\theta)$ are

$$x = r\cos\theta$$
$$y = r\sin\theta,$$

The velocity vector $\vec{v}$ in Cartesian coordinates is

$$\vec{v} = v_x\,\hat{i} + v_y\,\hat{j} = \dot{x}\,\hat{i} + \dot{y}\,\hat{j}$$

while in plane polar coordinates,

$$\vec{v} = v_r\,\hat{r} + v_\theta\,\hat{\theta} = \dot{r}\,\hat{r} + \hat{\theta}\,r\dot{\theta}$$

$v_r = \dot{r}$ is called the radial component of $\vec{v}$ and $v_\theta = r\dot{\theta}$ is called the tangential component of $\vec{v}$.

The kinetic energy of the particle can be expressed as

$$T = \frac{1}{2}mv^2$$
$$= \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 \quad \text{(Cartesian coordinates)}$$
$$= \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\theta}^2 \quad \text{(plane polar coordinates)}.$$

Now, the angular momentum of the particle about the origin (origin is the center of force) is

$$\vec{L} = \vec{r} \times m\vec{v}$$

$$= \vec{r} \times m(\hat{r}\dot{r} + \hat{\theta}r\dot{\theta})$$

$$= \vec{r} \times m(\hat{\theta}r\dot{\theta})$$

The magnitude of $\vec{L}$ is

$$L = mr^2|\dot{\theta}| = mr^2\omega = \text{constant}$$

where ω is the angular speed of the particle defined as $\omega = |\dot{\theta}|$.

Next, the total energy of the particle is given by

$$E = T + V(r) = \frac{1}{2}mv^2 + V(r)$$

$$= \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\theta}^2 + V(r)$$

But $|\dot{\theta}| = \frac{L}{mr^2}$. Hence

$$E = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\frac{L^2}{m^2r^4} + V(r)$$

i.e.,

$$E = \frac{1}{2}m\dot{r}^2 + \frac{L^2}{2mr^2} + V(r).$$

To get the equation of motion we note that E is a constant, i.e.,

$$\frac{dE}{dt} = 0.$$

Therefore,

$$m\dot{r}\ddot{r} - \frac{L^2}{mr^3}\dot{r} + \frac{\partial V}{\partial r}\dot{r} = 0$$

or $$m\ddot{r} = -\frac{\partial V}{\partial r} + \frac{L^2}{mr^3}.$$

Here $-\frac{\partial V}{\partial r}$ is the force on the particle which is central. In addition, there is an additional term L^2/mr^3 which arises because of the angular motion of the particle. Now, L^2/mr^3 is +ve, i.e., repulsive and hence this term is called ~~a~~ the 'centrifugal' force. Note that the 'centrifugal' force is not a real physical force on the particle. The presence of this term means that the effect of angular motion of the particle on the radial motion is as if a repulsive (i.e., radially outward or centrifugal) force L^2/mr^3 acts on the particle.

Thus, the radial motion of the particle is like that of a particle moving in one dimension with an effective force given by

$$F_r = -\frac{\partial V}{\partial r} + \frac{L^2}{m r^3}$$

$$= -\frac{\partial V}{\partial r} - \frac{\partial}{\partial r}\left(\frac{L^2}{2 m r^2}\right)$$

$$= -\frac{\partial}{\partial r}\left(V + \frac{L^2}{2 m r^2}\right)$$

$$= -\frac{\partial V_{eff}}{\partial r}$$

where V_{eff} is the effective potential of the particle given by

$$\boxed{V_{eff}(r) = V(r) + \frac{L^2}{2 m r^2}} \quad \ldots\ldots (32)$$

The equation of motion for r is then

$$\boxed{m\ddot{r} = -\frac{\partial V_{eff}}{\partial r}}$$

Comparing the effective potential in quantum mechanics (Eq. 31) with the effective potential in classical mechanics (Eq. 32) we see that the angular momentum of a particle in quantum mechanics is

$$L = \sqrt{l(l+1)}\,\hbar \; ; \quad l = 0, 1, 2, \cdots .$$

Thus, in quantum mechanics, angular momentum of a particle can only take on certain discrete values, i.e., angular momentum is quantized.

Angular momentum.

In classical mechanics, angular momentum of a particle about an origin is defined as

$$\vec{L} = \vec{r} \times \vec{p}$$

where $\vec{r}$ is the radius vector of the particle from the origin and $\vec{p} = m\vec{v}$ is the linear momentum of the particle. The three Cartesian components of $\vec{L}$ are

$$\begin{aligned} L_x &= y p_z - z p_y \\ L_y &= z p_x - x p_z \\ L_z &= x p_y - y p_x \end{aligned} \tag{33}$$

In quantum mechanics, all physical observables are represented by operators. In the coordinate representation we have

$$\hat{x} = x, \quad \hat{y} = y, \quad \hat{z} = z \tag{34}$$

and $\hat{p}_x = -i\hbar \dfrac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar \dfrac{\partial}{\partial y}$, $\hat{p}_z = -i\hbar \dfrac{\partial}{\partial z}$

i.e.,

$$\hat{\vec{p}} = -i\hbar \vec{\nabla} \tag{35}$$

Therefore, using Cartesian coordinates (x, y, z), the operators for the components of angular momentum are ;

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad (36).$$
$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

We define the operator corresponding to the square of the angular momentum as

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

In spherical polar coordinates, the angular momentum operators are

$$\hat{L}_x = +i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\varphi}\right)$$
$$\hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \qquad (37)$$
$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$
$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right].$$

Now, we have seen previously that the spherical harmonics $Y_{lm}(\theta,\phi)$ satisfy the differential equation (Eq. 27)

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

Comparing the operator within brackets on the left hand side of this equation with $\hat{L}^2$ (Eq. 37), we get

$$-\frac{1}{\hbar^2}\hat{L}^2 Y_{lm}(\theta,\phi) = -l(l+1)\,Y_{lm}(\theta,\phi)$$

or $$\boxed{\hat{L}^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2\, Y_{lm}(\theta,\phi)} \quad \text{---}(38)$$

i.e., $Y_{lm}(\theta,\phi)$ is an eigenfunction of $\hat{L}^2$ with eigenvalue $l(l+1)\hbar^2$.

Next, $Y_{lm}(\theta,\phi)$ can be written as (Eq. (24))

$$Y_{lm}(\theta,\phi) = N_{lm}\, P_l^m(\cos\theta)\, e^{im\phi}.$$

Operating on $Y_{lm}(\theta,\phi)$ by $\hat{L}_z$ (Eq. 37), we have

$$\hat{L}_z Y_{lm}(\theta,\phi) = -i\hbar\frac{\partial}{\partial\phi}Y_{lm}(\theta,\phi)$$

$$= -i\hbar\,(im)\,Y_{lm}(\theta,\phi)$$

or $$\boxed{\hat{L}_z Y_{lm}(\theta,\phi) = m\hbar\, Y_{lm}(\theta,\phi)} \quad \cdots\cdots (39)$$

i.e., $Y_{lm}(\theta,\phi)$ is an eigenfunction of $\hat{L}_z$ with eigenvalue $m\hbar$. Thus, Y_{lm} is the simultaneous eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues $l(l+1)\hbar^2$ and $m\hbar$ respectively.

The fact that $\hat{L}^2$ and $\hat{L}_z$ have ~~simult~~ simultaneous eigenfunctions is to be expected, since, as we can verify, $\hat{L}^2$ and $\hat{L}_z$ commute, i.e.,

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

However, $Y_{lm}(\theta,\phi)$ is not an eigenfunction of $\hat{L}_x$ and $\hat{L}_y$, since $\hat{L}_x$ and $\hat{L}_y$ do not commute with $\hat{L}_z$.

We now express the Laplacian operator in terms of $\hat{L}^2$. We have

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

or $$\boxed{\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hat{L}^2}{\hbar^2 r^2}} \quad \cdots\cdots (40).$$

Parity of a state

Suppose that the state of a particle is given by the wave function $\psi(\vec{r})$. We ask what might happen to the wave function if we make the replacement $\vec{r} \to -\vec{r}$. Such a transformation of the coordinates is called the parity transformation.

Parity transformation: $\vec{r} \longrightarrow -\vec{r}$.

In a Cartesian coordinate system, the parity transformation is equivalent to

$$x \to -x, \quad y \to -y, \quad z \to -z.$$

In spherical polar coordinates, the parity transformation is

$$\begin{aligned} r &\longrightarrow r \\ \theta &\longrightarrow \pi - \theta \\ \phi &\longrightarrow \pi + \phi \end{aligned}$$

Under a parity transformation, the wave function $\psi(\vec{r})$ changes as

$$\psi(\vec{r}) \xrightarrow{P} \psi^{P}(\vec{r}) = \psi(-\vec{r})$$

If $\psi(-\vec{r}) = \psi(\vec{r})$, i.e, if the wave function is even, then we say that the state has even parity. On the other hand, if $\psi(-\vec{r}) = -\psi(\vec{r})$ the state has odd parity.

A function $\psi(\vec{r})$ may not have a definite parity, i.e., $\psi(\vec{r})$ may be neither even nor odd. However, we can always write $\psi(\vec{r})$ as a sum of two functions one of which is even and the other odd:

$$\psi(\vec{r}) = \frac{1}{2}\left(\psi(\vec{r}) + \psi(-\vec{r})\right) + \frac{1}{2}\left(\psi(\vec{r}) - \psi(-\vec{r})\right)$$

$$= \underset{\substack{\uparrow \\ \text{even}}}{\psi_{+}(\vec{r})} + \underset{\substack{\uparrow \\ \text{odd}}}{\psi_{-}(\vec{r})}.$$

Now consider the time independent Schrödinger equation for a single particle under a central potential

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\vec{r}) = E\,\psi(\vec{r}).$$

We make the parity transformation $\vec{r} \to -\vec{r}$. The Hamiltonian operator remains unchanged, since V is a function of $r = |\vec{r}|$ only and the Laplacian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is also unchanged. Therefore we get

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(-\vec{r}) = E\,\psi(-\vec{r}).$$

Hence if $\psi(\vec{r})$ is the eigenfunction of $\hat{H}$ with eigenvalue E, then $\psi(-\vec{r})$ is also an eigenfunction of $\hat{H}$ with the same eigenvalue, provided V is a central potential.

If the eigenvalue E is nondegenerate, i.e., if there is only one linearly independent eigenfunction corresponding to E, then $\psi(\vec{r})$ and $\psi(-\vec{r})$ must be linearly linearly dependent, so that we have

$$\psi(-\vec{r}) = \pi\, \psi(\vec{r}) \,. \quad (\pi = \text{constant})$$

Changing the sign of $\vec{r}$

$$\psi(\vec{r}) = \pi\, \psi(-\vec{r}) \,.$$

From these two equations, it follows at once that

$$\pi^2 = 1$$

or $\pi = +1$ or -1. Thus all nondegenerate eigenfunctions of a spherically symmetric Hamiltonian are either even or odd with respect to a change of sign of $\vec{r}$.

If an eigenvalue has more than one linearly independent eigenfunctions, i.e., if the eigenvalue is degenerate, the foregoing arguments break down and these eigenfunctions need not have a definite parity.

Parity of $\psi_{E\ell m}(\vec{r})$

The wave function of a particle moving in a central potential was found to be of the form (Eq. 28)

$$\psi_{E\ell m}(\vec{r}) = R_{E\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

where $Y_{\ell m}(\theta,\phi)$ is given in Eq.(24) and $R_{E\ell}(r)$ satisfies the differential equation shown in Eq. (29).

We have

$$Y_{\ell m}(\theta,\phi) = N_{\ell m}\, P_\ell^m(\cos\theta)\, e^{im\phi}$$

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

with ϵ a phase factor of modulus unity.

Making the parity transformation one has

$$\psi_{E\ell m}(-\vec{r}) = R_{E\ell}(r)\, Y_{\ell m}(\pi-\theta,\, \pi+\phi)$$

From the definition of $Y_{lm}(\theta, \phi)$ we have

$$Y_{lm}(\pi-\theta, \pi+\varphi) = N_{lm}\, P_l^m\big(\cos(\pi-\theta)\big)\, e^{im(\pi+\varphi)}$$

$$= N_{lm}\, P_l^m(-\cos\theta)\, e^{im(\pi+\phi)}.$$

To find $P_l^m(-\cos\theta)$, we have to go back to the definition of $P_l^m(\cos\theta)$ or $P_l^m(\omega)$ where $\omega = \cos\theta$. This definition is given in Eq (23) which we quote here

$$P_l^m(\omega) = (1-\omega^2)^{\frac{1}{2}|m|} \frac{d^{|m|}}{d\omega^{|m|}} P_l(\omega), \quad (\omega = \cos\theta)$$

Therefore

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

But $\quad P_l(-\omega) = (-1)^l P_l(\omega).$

So,

$$P_l^m(-\omega) = (-1)^{l+|m|}(1-\omega^2)^{\frac{1}{2}|m|} \frac{d^{|m|}}{d\omega^{|m|}} P_l(\omega)$$

$$= (-1)^{l+|m|} P_l^m(\omega).$$

Also,

$$e^{im(\pi+\phi)} = e^{im\pi} e^{im\varphi}$$

$$= \left(e^{i\pi}\right)^m e^{im\phi}$$

$$= (-1)^m e^{im\varphi} = (-1)^{|m|} e^{im\varphi}$$

Hence

$$Y_{lm}(\pi-\theta, \pi+\varphi) = (-1)^{l+|m|+|m|} Y_{lm}(\theta,\varphi) = (-1)^l Y_{lm}(\theta,\varphi).$$

Thus, the parity of $Y_{lm}(\pi-\theta, \pi+\varphi)$ is $(-1)^l$ and therefore, parity of $\psi_{Elm}(\vec{r})$ is also $(-1)^l$.

Radial wave function.

We now return to the radial Schrödinger equation (Eq. (29)).

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2m}{\hbar^2}\left(E-V(r)\right)-\frac{l(l+1)}{r^2}\right]R=0.$$

Here we have omitted the subscripts (E,l) in R.

If V is zero ~~case~~ or constant, the solutions of R can be written down in terms of standard functions of mathematical physics.

For constant V, we define a parameter α as

$$\alpha=\sqrt{\frac{2m}{\hbar^2}(E-V_0)}.$$

If $E>V_0$ then α is a real parameter. For a free particle $(V_0=0)$ $\alpha=\sqrt{\frac{2mE}{\hbar^2}}=k$ which is also real and positive since E is positive for a free particle.

If $E<V_0$ then

$$\alpha=i\beta \quad \text{where } \beta=\sqrt{\frac{2m}{\hbar^2}(V_0-E)}$$

i.e., α becomes purely imaginary.

The radial Schrödinger equation is now written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\alpha^2-\frac{l(l+1)}{r^2}\right]R=0 \quad \text{----} (41)$$

If we put $\rho=\alpha r$, the radial wave equation becomes

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{d\rho}+\left[1-\frac{l(l+1)}{\rho^2}\right]R=0 \quad \text{---} (42).$$

The solutions of this equation are standard. The two linearly independent solutions of (42) are the spherical Bessel function $j_l(\rho)$ and the spherical Neumann function $n_l(\rho)$. They are defined as

$$j_l(\rho)=\left(\frac{\pi}{2\rho}\right)^{1/2}J_{l+\frac{1}{2}}(\rho) \quad \text{---------} (43)$$

and

$$n_l(\rho)=\left(\frac{\pi}{2\rho}\right)^{1/2}J_{-l-\frac{1}{2}}(\rho) \quad \text{---} (44)$$

where J is an ordinary Bessel of half-odd-integer order. In particular, the explicit expressions for the first two j's and n's are

$$j_0(\rho) = \frac{\sin\rho}{\rho}\,, \qquad n_0(\rho) = -\frac{\cos\rho}{\rho}$$

$$j_1(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho}$$

$$n_1(\rho) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho}$$

The leading terms for small ρ are

$$j_l(\rho) \xrightarrow[\rho\to 0]{} \frac{\rho^l}{(2l+1)!!}$$

$$n_l(\rho) \xrightarrow[\rho\to 0]{} -\frac{2l+1}{\rho^{l+1}}$$

where $(2l+1)!! = 1\cdot 3\cdot 5 \cdots (2l+1)$.

We see that $j_l(\rho)$ is regular at the origin and n_l tends to infinity, i.e., irregular at the origin.

The leading terms in the asymptotic expansions are:

$$j_l(\rho) \xrightarrow[\rho\to\infty]{} \frac{1}{\rho}\cos\left[\rho - \tfrac{1}{2}(l+1)\pi\right]$$

$$n_l(\rho) \xrightarrow[\rho\to\infty]{} \frac{1}{\rho}\sin\left[\rho - \tfrac{1}{2}(l+1)\pi\right].$$

In some situations it becomes convenient to express the wave function in terms of the spherical Hankel functions which are linear combinations of $j_\ell(\rho)$ and $n_\ell(\rho)$. We define the spherical Hankel functions of the first kind $h_\ell^{(1)}(\rho)$ and of the second kind $h_\ell^{(2)}(\rho)$ as

$$h_\ell^{(1)}(\rho) = j_\ell(\rho) + i\, n_\ell(\rho)$$

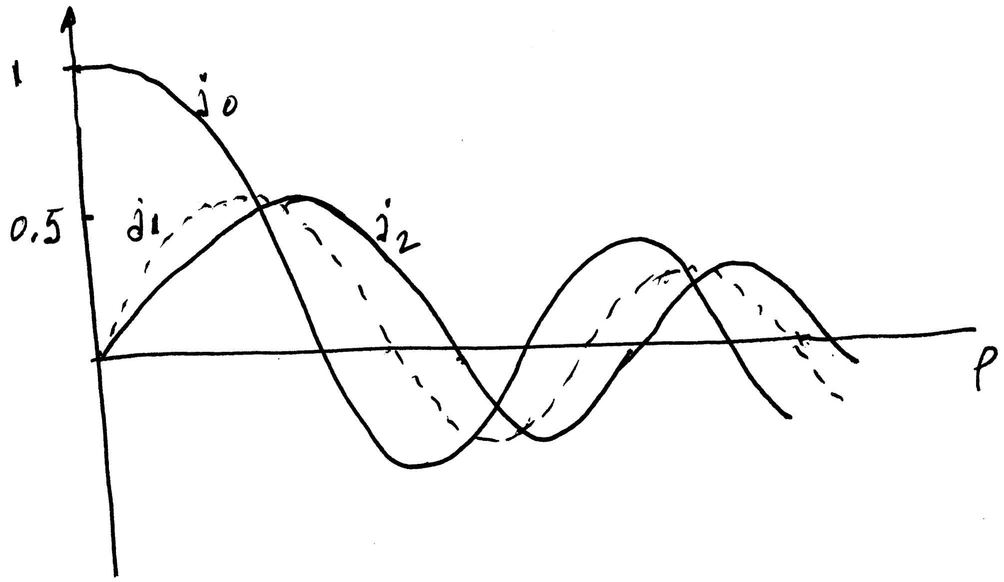
$$h_\ell^{(2)}(\rho) = j_\ell(\rho) - i\, n_\ell(\rho).$$

They have the asymptotic form

$$h_\ell^{(1)}(\rho) \xrightarrow[\rho\to\infty]{} \frac{1}{\rho}\, e^{i[\rho - \frac{1}{2}(\ell+1)\pi]}$$

$$h_\ell^{(2)}(\rho) \xrightarrow[\rho\to\infty]{} \frac{1}{\rho}\, e^{-i[\rho - \frac{1}{2}(\ell+1)\pi]}.$$

In the figure below we show the plots of some low-order spherical Bessel and spherical Neumann functions versus ρ. We assume that α is real, i.e., $\rho = \alpha r$ is also real.



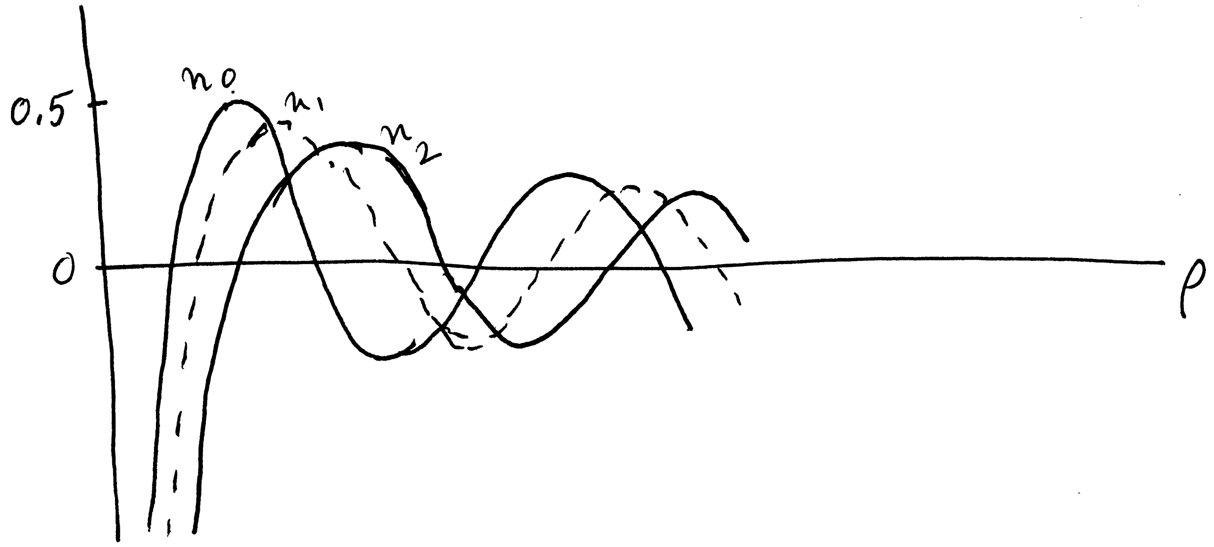


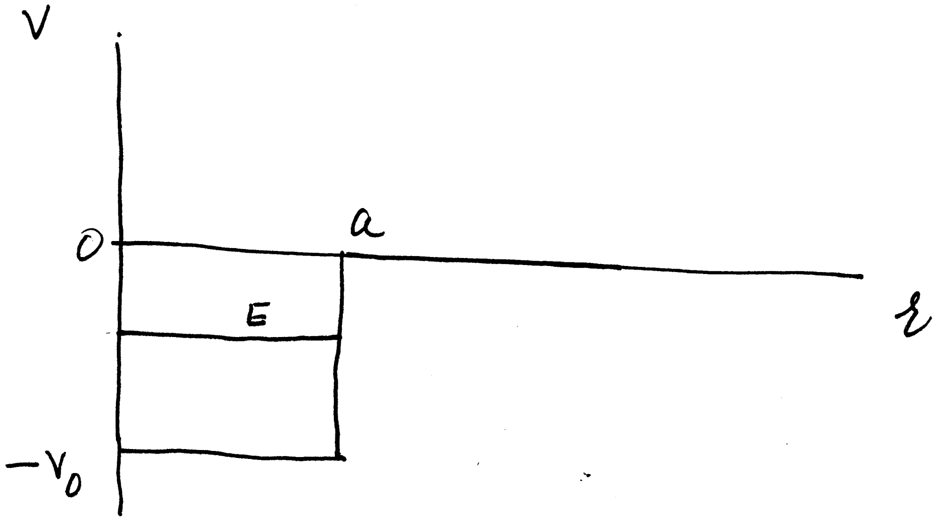
Fig: Spherical Bessel functions $j_\ell(\rho)$ and spherical Neumann functions $n_\ell(\rho)$. Only the Bessel functions are finite at the origin.

In summary, for constant potential the two linearly independent solutions are spherical Bessel functions $j_\ell(\alpha r)$ and the spherical Neuman functions $n_\ell(\alpha r)$. Both functions are finite and oscillatory as $r \to \infty$ provided α is real. $j_\ell(\alpha r)$ is regular at the origin and $n_\ell(\alpha r)$ is irregular.

Three-dimensional square well potential

Consider a square-well potential

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r > a \end{cases}$$



We are looking for bound state solutions of a particle trapped in this potential well when the particle has orbital angular momentum with quantum number l. For a bound state E must be less than zero, but greater than $-V_0$. So E is negative in the range $-V_0 < E < 0$.

The radial Schrödinger equation for $r<a$ is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_\ell}{dr}\right)+\left[\alpha^2-\frac{\ell(\ell+1)}{r^2}\right]R_\ell(r)=0 \quad \cdots (45)$$

where α is given by

$$\alpha=\sqrt{\frac{2m}{\hbar^2}(E-V(r))}=\sqrt{\frac{2m}{\hbar^2}(V_0-|E|)} \quad \cdots (46).$$

where E is negative $E=-|E|$. The parameter α is a positive number.

For $r>a$, the radial Schrödinger equation is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_\ell}{dr}\right)+\left[-\beta^2-\frac{\ell(\ell+1)}{r^2}\right]R_\ell(r)=0 \quad \cdots (47)$$

where

$$\beta=\sqrt{\frac{2m}{\hbar^2}|E|} \quad \cdots (48),$$

Solutions

1. Zero angular momentum.

When $l=0$, it is easier to solve the wave equation in terms of the auxiliary function $u_l(r)$ defined as

$$R_l(r) = \frac{u_l(r)}{r} .$$

The differential equation for $u_l(r)$ is (see Eq. (30))

$$\frac{d^2 u_l}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{l(l+1)\hbar^2}{2mr^2}\right) u_l(r) = 0$$

For the s-wave ($l=0$), we have

$$\frac{d^2 u}{dr^2} + \alpha^2 u = 0 \qquad (r<a) \qquad \text{------} (49)$$

$$\frac{d^2 u}{dr^2} - \beta^2 u = 0 \qquad (r>a). \qquad \text{---} (50)$$

Here we have omitted the subscript l in u_l.

Solutions of Eq (49) and Eq (50) are:

$$u(r) = A \sin \alpha r + B \cos \alpha r \quad (r<a) \quad \cdots (51)$$

$$u(r) = C e^{-\beta r} + D e^{\beta r} \quad (r>a). \quad \cdots (52)$$

Now $R_l(r)$ is finite at $r=0$, so $u(r)$ must be zero at the origin. Hence we must choose $B=0$ in Eq. (51). Further, we have to choose $D=0$ in Eq (52) for, otherwise $u(r)$ would become infinity as $r \to \infty$. Thus the wave function is

$$u(r) = \begin{cases} A \sin \alpha r & (r<a) \\ C e^{-\beta r} & (r>a) \end{cases} \qquad (53)$$

Next imposing the continuity of u and its derivative at $r=a$, we have

$$A \sin \alpha a = C e^{-\beta a}$$
$$\alpha A \cos \alpha a = -\beta C e^{-\beta a}$$

From these two equations we obtain

$$\alpha \cot \alpha a = -\beta$$

or $\alpha a \cot \alpha a = -\beta a$ . . . . (54)

This is the same equation obtained for the odd-parity solution of the one-dimensional problem. Then it follows from the discussions on the bound states in a one-dimensional finite square well potential, that there is no energy level unless $V_0 a^2 > \frac{\pi^2 \hbar^2}{8m}$, there is one bound state if $\frac{\pi^2 \hbar^2}{8m} < V_0 a^2 < 9\frac{\pi^2 \hbar^2}{8m}$, etc.

Solutions for arbitrary l.

$r < a$ Eq. (45) has two linearly independent solutions, namely, $j_l(\alpha r)$ and $n_l(\alpha r)$. However, $n_l(\alpha r)$ is irregular at the origin. Therefore

$$R_l(r) = A\, j_l(\alpha r) \quad \ldots \ldots \ldots (55)$$

$r > a$ Outside the potential well ($r > a$), the independent solutions of Eq. (47) are $j_l(i\beta r)$ and $n_l(i\beta r)$ or the Hankel functions $h_l^{(1)}(i\beta r)$ and $h_l^{(2)}(i\beta r)$.

We write the general solution as

$$R_l(r) = B\, h_l^{(1)}(i\beta r) + C\, h_l^{(2)}(i\beta r) \quad \ldots \ldots (56)$$

Now

$$h_l^{(1)}(\rho) \underset{\rho\to\infty}{\sim} \frac{1}{\rho} e^{i\rho}$$

$$h_l^{(2)}(\rho) \underset{\rho\to\infty}{\sim} \frac{1}{\rho} e^{-i\rho}$$

Hence

$$h_l^{(1)}(i\beta r) \underset{r\to\infty}{\sim} \frac{1}{i\beta r} e^{-\beta r}$$

$$h_l^{(2)}(i\beta r) \underset{r\to\infty}{\sim} \frac{1}{i\beta r} e^{+\beta r}$$

Since $R_l(r)$ must be finite as $r \to \infty$, we must choose $C = 0$ in Eq. (56). Therefore, we have

$$R_l(r) = B\, h_l^{(1)}(i\beta r) = B\left(j_l(i\beta r) + i\, n_l(i\beta r)\right). \qquad (r > a) \qquad (57)$$

Energy eigenvalues

The wave function and its derivative must be continuous at $r = a$. Therefore,

$$A\, j_l(\alpha a) = B\left(j_l(i\beta a) + i\, n_l(i\beta a)\right) \quad \cdots (58)$$

$$\alpha A\, j_l'(\alpha a) = B\, i\beta\left(j_l'(i\beta a) + i\, n_l'(i\beta a)\right) \quad \text{--} (59)$$

where the prime means derivative with respect to the argument. Dividing (59) by (58)

$$\alpha \frac{j_l'(\alpha a)}{j_l(\alpha a)} = i\beta \frac{j_l'(i\beta a) + i n_l'(i\beta a)}{j_l(i\beta a) + i n_l(i\beta a)} . \qquad (60)$$

Also, previously we defined α and β as (Eqs. (46) and (47))

$$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - |E|)}$$

$$\beta = \sqrt{\frac{2m}{\hbar^2}|E|} .$$

Therefore,

$$\alpha^2 + \beta^2 = \frac{2mV_0}{\hbar^2} \qquad \text{------ (61)}$$

or

$$(\alpha a)^2 + (\beta a)^2 = \frac{2mV_0 a^2}{\hbar^2} . \qquad \text{------ (62)}.$$

We can solve Eqs (~~6~~ 60) and (62) ~~either~~ numerically to find α and β. Then using either Eq. (46) or Eq. (47) we can find $|E|$ or $E = -|E|$.

We find that if $V_0 a^2$ is small, then no bound state exists. For sufficiently large $V_0 a^2$, several bound states for a given l may exist.

The minimum value of $V_0 a^2$ for a s-wave ($l=0$) bound state to exist is $V_0 a^2 = \pi^2\hbar^2/8m$ and the minimum value for a p-wave ($l=1$) bound state is $V_0 a^2 = \pi^2\hbar^2/2m$.

The smallest value of $V_0 a^2$ for which there exists a bound state with $l=1$ is greater than the corresponding value of $V_0 a^2$ for $l=0$. The minimum value of $V_0 a^2$ for a bound state to exist with a particular l increases with increasing l.

This is reasonable from a physical point of view, considering the effective potential

$$V_{eff} = V + \frac{l(l+1)\hbar^2}{2mr^2}.$$

we see that the larger the value of l, the greater the repulsive 'centrifugal' force. This suggests that a particle having a large angular momentum requires a stronger attractive potential to bind it than a particle having no angular momentum or small angular momentum. Indeed, it turns out that the minimum square-well potential "strength" $V_0 a^2$ required to bind a particle of orbital angular momentum quantum number l increases monotonically with increasing l.