QM(21017) Lecture Notes

Part-IV Spherically Symmetric Potentials

A Course of Lectures to Be Given at IIT Bhubaneswar

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§1 Angular Momentum in Coordinate Representation

The orbital angular momentum of a particle is given by $\vec{L} = \vec{r} \times \vec{p}$ and the components of the angular momentum operator in coordinate representation are

$$\hat{L}_x = -i\hbar\hat{y}\frac{\partial}{\partial z} - \hat{z}\frac{\partial}{\partial y} \quad (1)$$

$$\hat{L}_y = -i\hbar\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z} \quad (2)$$

$$\hat{L}_z = -i\hbar\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x} \quad (3)$$

Here $\hat{A}$ means operator corresponding to the dynamical variable A. In terms of spherical polar coordinates these expressions take the form

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{4}$$

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \tag{5}$$

$$\hat{L}_z = i\hbar\frac{\partial}{\partial\phi} \tag{6}$$

The operator $\vec{L}^2$ given by

$$\vec{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \tag{7}$$

takes the form

$$\vec{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{8}$$

The components of orbital angular momentum satisfy the same commutation relations as angular momentum.

$$[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y;$$

§1.1 Eigenvalues and Eigenvectors

These commutation relations of angular momentum imply that $\vec{L}^2$ commutes with $\vec{n}\cdot\hat{L}$ for all numerical$\hat{n}$. Hence we can find simultaneous eigenfunctions of $\vec{L}^2$ and a component of $\vec{L}$. along any direction $\vec{n}$. Taking $\hat{n}$ to be along $z-$ axis the eigenvalue equations

$$\vec{L}^2 Y(\theta,\phi) = \lambda\hbar^2 Y(\theta,\phi) \tag{9}$$

$$L_z Y(\theta,\phi) = \mu\hbar Y(\theta,\phi) \tag{10}$$

become differential equations

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] Y(\theta,\phi) + \lambda Y(\theta,\phi) = 0 \tag{11}$$

and

$$-i\frac{\partial}{\partial\phi}Y(\theta,\phi) = \mu Y(\theta,\phi) \tag{12}$$

We shall now show that acceptable solutions exist only for

$$\lambda = \ell(\ell+1); \qquad \mu = m \tag{13}$$

where ℓ can take only positive integral values $0, 1, 2, \cdots$ and m must satisfy

$$m = \ell, \ell-1, \cdots, -\ell+1, -\ell, \qquad (-\ell \le m \le \ell) \tag{14}$$

There are $(2\ell+1)$ eigenvalues of L_z for a fixed $\vec{L}^2$ and the spherical harmonics $Y_{\ell m}\theta,\phi$ will be seen to be the corresponding eigenfunctions. These results on eigenvalues and eigenfunctions of $\vec{L}^2$ and L_z will be proved by solving the differential equations by the method of separation of variables.

§1.2 Separation of Variables

To solve the differential equations we substitute

$$Y(\theta,\phi) = Q(\theta)E(\phi) \tag{15}$$

in Eq.(11) and (12) and divide by $Y(\theta,\phi) = Q(\theta)E(\phi)$. This gives

$$-i\frac{dE(\phi)}{d\phi} = \mu E(\phi) \tag{16}$$

Similarly, (11) gives

$$\left[\frac{1}{Q(\theta)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Q(\theta)\right) + \frac{1}{\sin^2\theta}\frac{1}{E(\phi)}\frac{\partial^2 E(\phi)}{\partial\phi^2}\right] + \lambda = 0 \tag{17}$$

On using Eq.(16) in (17) we get

$$\sin^2\theta\left\{\frac{1}{Q(\theta)}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Q(\theta)\right)\right\} + \lambda\sin^2\theta = -\frac{1}{E(\phi)}\frac{d^2E(\phi)}{d\phi^2} \tag{18}$$

While the left hand side of the above equation is a function of θ, the right hand side is a function of ϕ alone. Hence each side must be a constant, from Eq.(16) this constant is μ. Thus we get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Q(\theta)\right) + \left(\lambda - \frac{\mu^2}{\sin^2\theta}\right)Q(\theta) = 0 \tag{19}$$

§1.3 Solution of ϕ equation

General solution of Eq.(16) is

$$E(\phi) = \begin{cases} A\exp(i\sqrt{\mu}\phi) + B\exp(-i\sqrt{\mu}\phi), & \text{if } \mu \neq 0 \\ C + D\phi, & \text{if } \mu = 0 \end{cases} \tag{20}$$

A wave function must be single valued function. For a fixed r,θ,ϕ the values of ϕ and $\phi + 2\pi$ correspond to the same point. Hence the solution should have the same value for ϕ and $\phi + 2\pi$. Thus we demand that $E(\phi)$ must satisfy

$$E(\phi + 2\pi) = E(\phi) \tag{21}$$

for all ϕ. For $\mu = 0$ this implies that $D = 0$.
Next, when $\mu \neq 0$ we must have

$$A\exp(i\sqrt{\mu}\phi + 2\pi) + B\exp(-i\sqrt{\mu}(\phi + 2\pi)) = A\exp(i\sqrt{\mu}\phi) + B\exp(-i\sqrt{\mu}\phi) \tag{22}$$

or

$$A\exp(i\sqrt{\mu}\phi)\exp(2\pi) + B\exp(-i\sqrt{\mu}\phi)\exp(2\pi)) = A\exp(i\sqrt{\mu}\phi) + B\exp(-i\sqrt{\mu}\phi). \tag{23}$$

For $\mu \neq 0$, the linear independence of the $\exp(\pm i\sqrt{\mu}\phi)$ implies that the corresponding coefficients must be equal separately giving where m is an integer and the solutions of Eq.(16) are

$$E(\phi) = \exp(im\phi), \qquad m = 0, \pm 1, \pm 2, \cdots \tag{24}$$

§1.4 Solution of θ equation

If we substitute $w = \cos\theta$ in Eq.(19) takes the form

$$\frac{d}{dw}(1-w^2)\frac{dP(w)}{dw} + \left(\lambda - \frac{m^2}{1-w^2}\right)P(w) = 0 \tag{25}$$

where we have introduced $P(w) \equiv Q(\cos\theta)$ and have used

$$\frac{dP(w)}{d\theta} = \frac{dP(w)}{dw}\cdot\frac{dw}{d\theta} = -\sin\theta\frac{dP(w)}{dw}$$

The equation (25) is known as associated Legendre equation. This equation can be solved by the method of series solution. Since (25) is a second order differential equation, there are two linearly independent solutions of this equation. For general values of λ both the solutions become infinite at $w = \pm 1$ corresponding to $\theta = 0, \pi$ These solutions are therefore unacceptable. For special values $\lambda = \ell(\ell+1)$, where ℓ is a positive integer, and with $|m| \leq \ell$, one solution remains finite , but not the other solution. Thus we fix

$$\lambda = \ell(\ell+1) \qquad |m| \leq \ell \tag{26}$$

For the above choice, the non singular solution for $P(w)$ is known as the associated Legendre function and has the form

$$P_m^\ell(w) = (1-w^2)^{|m|/2}\frac{d^{|m|}}{dw^{|m|}}P_\ell(w) \tag{27}$$

where $P_\ell(w)$ is Legendre polynomial of degree ℓ.Thus the eigenfunctions of $\vec{L}^2$ and L_z are the

$$Y_{\ell m}(\theta,\phi) = NP_m^\ell(\cos\theta)e^{im\phi}, \qquad m = \ell, \ell-1, \cdots, \ell \tag{28}$$

The normalization is fixed by demanding

$$\int_0^{2\pi} d\phi \int_0^\pi Y^*_{\ell m}(\theta,\phi)Y_{\ell m}(\theta,\phi)d\theta = 1 \tag{29}$$

The functions $Y_{\ell m}(\theta,\phi)$ in Eq.(28) are known as spherical harmonics.

§2 Spherically Symmetric Potentials

§2.1 Solution of radial equation for a constant potential

Some Spherical Bessel functions

We shall now tabulate first few spherical Bessel functions.

$$j_0(\rho) = \frac{\sin\rho}{\rho} \tag{30}$$

$$j_1(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho} \tag{31}$$

$$j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin\rho - \frac{3}{\rho^2}\cos\rho \tag{32}$$

$$n_0(\rho) = -\frac{\cos\rho}{\rho} \tag{33}$$

$$n_1\rho = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho} \tag{34}$$

$$n_2\rho = -\left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\cos\rho - \frac{3}{\rho}\sin\rho \tag{35}$$

$$h_0^{(1)}(i\rho) = -\frac{1}{\rho}\exp(-\rho) \tag{36}$$

$$h_1^{(1)}(i\rho) = i\left(\frac{1}{\rho}+\frac{1}{\rho^2}\right) \tag{37}$$

$$h_2^{(2)}(i\rho) = \left(\frac{1}{\rho}+\frac{3}{\rho}+\frac{3}{\rho^3}\right)\exp(-\rho) \tag{38}$$

The functions $h_\ell^{(2)}(\rho)$ have $\exp(\rho)$ as a factor which is bad for large ρ; only $h^{(1)}(i\rho)$ is useful when one needs a solution valid for large ρ. When one needs a solution valid for intermediate values of ρ, one can take linear combination of $j_\ell(\rho)$ and $n_\ell(\rho)$.

Piecewise constant potentials

The solutions of the radial equation for a constant potential are known in terms of Bessel functions. We shall list these solutions and discuss their properties before taking specific examples such as free particle, square well potential. Let us assume $V(r) = V_0$for some range of values of r. Then for this range of values the radial equation takes the form

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2m}{\hbar^2}\left(E-V_0)-\frac{\ell(\ell+1)}{r^2}\right)R(r)=0 \tag{39}$$

We shall consider the cases $E-V_0>0$ and $E-V_0<0$ separately.

CASE I: $E-V_0>0$

We define $\dfrac{2m(E-V_0)}{\hbar^2} = k^2$ and the two linearly independent solutions of the radial equation are given by $j_\ell(kr)$ and $n_\ell(kr)$ known as spherical Bessel functions.Angular Momentum in coordinate representation; Separation of variables in polar coordinates; Solution of radial equation for a constant potential; Free particle solution in polar coordinates ;Square well and hard sphere; General properties of solutions; Isotropic oscillator in three dimension; Hydrogen atom energy levels in Schrödinger mechanics; Accidental degeneracy; Energy levels of positronium and alkali Atoms These are related to the Bessel functions $J_-\nu(kr)$ as follows

$$j_\ell(kr) = \left(\frac{\pi}{2kr}\right)^{1/2}J_{\ell+\frac{1}{2}}(kr) \tag{40}$$

$$n_\ell(kr) = \left(\frac{\pi}{2kr}\right)^{1/2}(-1)^{\ell+1}J_{-\ell-\frac{1}{2}}(kr) \tag{41}$$

and the most general solution of the radial equation is a linear combination of the above solutions.

$$R(r) = Aj_\ell(kr)+Bn_\ell(kr) \tag{42}$$

We need to know the behaviour of the solutions for $r \approx 0$ and for $r \to \infty$.

Small r : The solution $j_\ell(kr)$ goes to zero but $n_\ell(kr)$ is singular for $r \approx 0$.In fact as $\rho \to 0$, we have

$$j_\ell(\rho) \rightarrow \frac{\rho^\ell}{(2\ell+1)!!} \tag{43}$$

$$n_\ell(\rho) \rightarrow (2\ell-1)!!\rho^{-\ell-1} \tag{44}$$

Large r : For large ρ both j_ℓ and n_ℓ are oscillatory. As $\rho \to \infty$

$$j_\ell(\rho) \rightarrow \frac{1}{\rho}\cos(\rho - (\ell+1)\pi/2) \tag{45}$$

$$n_\ell(\rho) \rightarrow \frac{1}{\rho}\sin(\rho - (\ell+1)\pi/2) \tag{46}$$

Thus for $E > V_0$ both $j_\ell(\rho)$ and $n_\ell(\rho)$ are acceptable solutions as $\rho \to \infty$

CASE II : $E - V_0 < 0$

In this case we define

$$\frac{2m(E-V_0)}{\hbar^2} = -\alpha^2, \qquad \alpha = \text{real} \tag{47}$$

In this case two linearly indepndent solutions are $j_\ell(i\alpha r)$ and $n_\ell(i\alpha r)$ and the most general solution is

$$R(r) = Aj_\ell(i\alpha r) + Bn_\ell(i\alpha r) \tag{48}$$

Again $n_\ell(i\alpha r)$ has unacceptable singular behaviour at $r = 0$. To discuss large r behaviour, introduce Hankel functions of first and second kinds by

$$h_\ell^{(1)}(\rho) = j_\ell\rho + in_\ell(\rho) \tag{49}$$

$$h_\ell^{(2)}(\rho) = j_\ell\rho - in_\ell(\rho) \tag{50}$$

Then, as $\rho \to \infty$, we have

$$h_\ell^{(1)}(\rho) \to -\frac{1}{\rho}\exp(-\rho) \tag{51}$$

and $h_e^{(2)}ll(\rho)$ blows up and becomes infinite as $\rho \to \infty$. and is unacceptable. It may be remarked that the solutions $j_\ell(\rho)$ and $n_\ell(\rho)$ are linear combinations of $\cos\rho, \sin\rho$ multiplied by powers of ρ. Similarly, $h_\ell^{(1,2)}(\rho)$ are exponentials multiplied by terms containing powers of ρ.

Table: Forms of acceptable solutions of radial equation

	Near $r = 0$	For large r	r in (a, b)
$E - V_0 > 0$	$j_\ell(kr)$	$Aj_\ell(kr) + Bn_\ell(kr)$	$Aj_\ell(kr) + Bn_\ell(kr)$
$E - V_0 < 0$	$j_\ell(ikr)$	$j_\ell(ikr) + in_\ell(ikr)$ $\equiv h_\ell^{(1)}(ikr)$	$Aj_\ell(ikr) + Bn_\ell(ikr)$ $\equiv h_\ell^{(1)}(ikr)$

§2.2 Free particle solution in polar coordinates

Prerequisites Free Particle Solution [**?**]

The radial equation for a free particle, $V(r) = 0$, for all r is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \left(k^2 - \frac{\ell(\ell+1)}{r^2}\right)R = 0, \tag{52}$$

where $k^2 = \dfrac{2mE}{\hbar^2}$. The solution of the radial equation has the most general form

$$R(r) = Aj_\ell(kr) + Bn_\ell(kr) \tag{53}$$

but we must set $B = 0$ because $n_\ell(kr) \to \infty$ as $r \to 0$. Hence we get

$$R_\ell(r) = Aj_\ell(kr) \tag{54}$$

and the full free particle wave function is

$$\Psi(r, \theta, \phi) = Nj_\ell(kr)Y_{\ell m}(\theta, \phi) \tag{55}$$

For a given value of energy E, ℓ can take all values $0, 1, 2, \ldots$ and m has $2(\ell + 1)$ values from $-\ell$ to ℓ. Therefore, for every energy value $E > 0$ there are infinte number of solutions. If we take linear combinations of solutions with fixed energy E we get most general form of the solution for a given energy as

$$\Phi(\vec{r}) = \sum C_{\ell m}j_\ell(kr)Y_{\ell m}(\theta, \phi) \tag{56}$$

In cartesian coordinates the free particle solutions for energy E are plane waves

$$\exp(i\vec{k} \cdot \vec{r})$$

Thus it is possible to write each of these two type of solutions as a linear combination of the other type. In particular we have

$$\exp(\vec{k} \cdot \vec{r}) = \sum C_{\ell m}j_\ell(kr)Y_{\ell m}(\theta, \phi) \tag{57}$$

In a particular case of this equation, when k is along the z axis and $\vec{k}\cdot\vec{r} = kz$, we have the expansion of plane waves

$$\exp(ikz) = \sum_{0}^{\infty}(2\ell+1)i^{\ell}j_{\ell}(kr)P_{\ell}(\cos\theta) \tag{58}$$

Note that only $m = 0$ terms contribute in the above equation.

§2.3 Hard sphere

The potential for a rigid spherical box can be written as

$$V(r) = \begin{cases} 0, & 0 < r < a \\ \infty, & r > a \end{cases}. \tag{59}$$

The problem is separable in spherical polar coordinates and form of the full wave function is

$$\psi(r,\theta,\phi) = R(r)Y_{\ell m}(\theta,\phi). \tag{60}$$

We need to consider solutions of the radial equation only. No solution can be found for $E < 0$, therefore we consider $E > 0$. For $0r > a$ the potential is infinite and hence the radial wave function must be zero, Next we consider $r < a$, where the potential is zero. The radial equation assumes the form

$$-\frac{1}{r^2}\frac{d}{dr}r^2\frac{dR(r)}{dr} + \frac{\ell(\ell+1)\hbar^2}{2mr^2}R(r) - ER(r) = 0. \tag{61}$$

The most general solution of this equation is given in terms of spherical Bessel functions j_ℓ, n_ℓ and we write it as

$$R_{E\ell(r)} = Aj_{\ell}(kr) + Bn_{\ell}(kr), \qquad k^2 = \frac{2mE}{\hbar^2}. \tag{62}$$

Recall that near $r = 0$, $n_\ell(r) \sim r^{-\ell-1}$ and blows up as $r \to 0$. Therefore we must set $B = 0$ if the solution is to remain finite at $r = 0$. Thus we get

$$R_{\ell}(r) = \begin{cases} Aj_{\ell}(kr), & 0 < r < a \\ 0 & r > a \end{cases}. \tag{63}$$

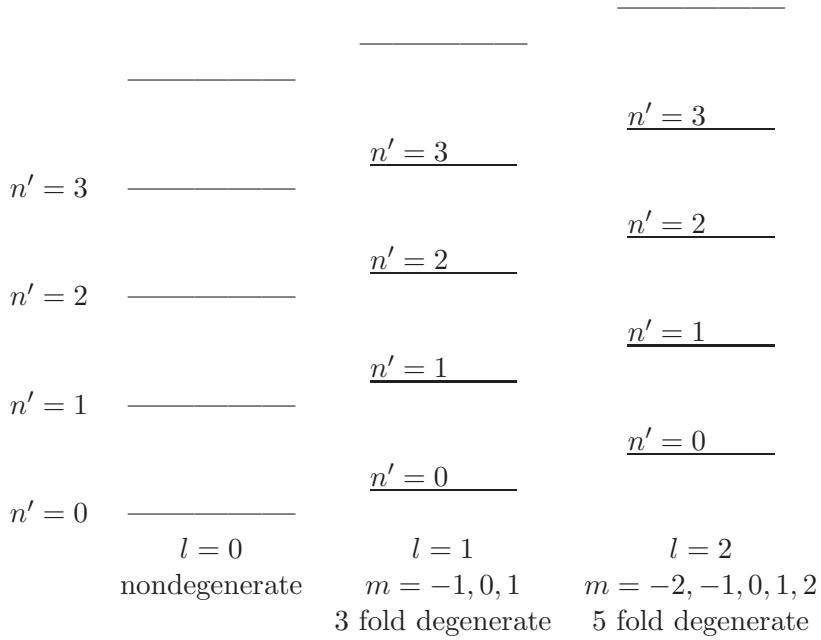
Next we must demand that the radial wave function $R(r)$ must be continuous at $r = 0$ Remember that there is no corresponding requirement on the derivative for this case of infinite jump in the potential at $r = a$ The continuity requirement of $R_{E\ell}(r)$ becomes

$$j_{\ell}(ka) = 0. \tag{64}$$

The solutions of the above equation determine allowed values of k and hence allowed bound state energies.

Energy levels and degeneracy

To get all the solutions, one proceeds as follows. First set $\ell = 0$ and locate the roots of $j_0(ka) = 0$. We call the roots as $\rho_{0n}, n = 0, 1, 2, \ldots$ and the corresponding energies are given by $E = \frac{\hbar^2 \rho_{0n}^2}{2ma^2}$.. Here n denotes the number of nodes of the radial wave function for $\ell = 0$. Next, we set $\ell = 1$ and find the roots of $j_1(kr) = 0$, calling these roots as $\rho_{1n}, n = 0, 1, 2, \ldots$ the $\ell = 1$ energy levels are given by $E = \frac{\hbar^2 \rho_{1n}^2}{2ma^2}$. This process is to be repeated for all values of angular momentum ℓ and the number of bound states for each ℓ turns out to be infinite. The states of definite energy depend on quantum numbers $n\ell m$ and the energy does not depend on magnetic quantum number m. Therefore for a given azimuthal quantum number ℓ we have $(2\ell+1)$ wave functions $N_{n\ell} R_{n\ell}(r/\rho_{n\ell}) Y_{\ell m}(\theta, \phi), (m = -\ell, -\ell+1, \cdots, \ell)$ and the energy levels $E_{n\ell}$ are $(2\ell+1)$ fold degenerate. The energy increases with ℓ and also with increasing n. Thus schematic energy level diagram would appear as follows.


$n' = 3$
$n' = 2$
$n' = 1$
$n' = 0$
$n' = 3$
$n' = 2$
$n' = 1$
$n' = 0$
$n' = 3$
$n' = 2$
$n' = 1$
$n' = 0$
$l = 0$
nondegenerate
$l = 1$
$m = -1, 0, 1$
3 fold degenerate
$l = 2$
$m = -2, -1, 0, 1, 2$
5 fold degenerate

§2.4 Spherically symmetric square Well

The potential for a spherical well can be written as

$$V(r) = \begin{cases} -V_0, & 0 < r < a, \qquad V_0 > 0, \\ 0, & r > a \end{cases}. \tag{65}$$

The problem is separable in spherical polar coordinates and form of the full wave function is

$$\psi(r, \theta, \phi) = R(r) Y_{\ell m}(\theta, \phi). \tag{66}$$

We need to consider solutions of the radial equation only. No solution can be found for $E < -V_0$, therefore we consider $E > -V_0$. We shall consider two cases of

(a) $-V_0 < E < 0$. This case corresponds to bound states,

(b) $E > 0$. In this case the there is no bound state. This case is of interest for scattering from the potential.

Bound states

The bound states correspond to $-V_0 < E < 0$. The radial equation in regions $r < a$ and $r > a$ assumes the forms

$$\frac{1}{r^2}\frac{d}{dr} r^2 \frac{dR(r)}{dr} + \Big(q^2 - \frac{\ell(\ell+1)}{r^2}\Big) R(r) \;=\; 0, \qquad r > 0, \tag{67}$$

$$\frac{1}{r^2}\frac{d}{dr} r^2 \frac{dR(r)}{dr} + \Big(-\alpha^2 + \frac{\ell(\ell+1)}{r^2}\Big) R(r) = 0, \qquad r > 0. \tag{68}$$

where

$$q^2 = \frac{2m(E + V_0)}{\hbar^2}, \quad \alpha^2 = \frac{2m|E|}{\hbar^2}. \tag{69}$$

The most general solution of this equation is given in terms of spherical Bessel functions j_ℓ, n_ℓ and is given by

$$R(r) = \begin{cases} A j_\ell(qr) + B n_\ell(qr), & r < a \\ C h^{(1)}(\alpha r) + D h^{(2)}(\alpha r) & r > a \end{cases}. \tag{70}$$

Recall that near $r = 0$, $n_\ell(r) \sim r^{-\ell-1}$ and blows up as $r \to 0$. Therefore we must set $B = 0$ if the solution is to remain finite at $r = 0$. Also as $r \to \infty$ the Hankel function $h^{(2)}(\alpha r)$ increases exponentially, hence we must set $D =$. Thus we get

$$R_\ell(r) = \begin{cases} A j_\ell(qr), & 0 < r < a \\ C h_\ell^{(1)}(\alpha r) & r > a \end{cases}. \tag{71}$$

Next we must demand that the radial wave function $R(r)$ and its derivative must be continuous at $r = 0$. These continuity requirements become give the following restrictions of the coefficients A, C.

$$Aj_\ell(qa) = Ch_\ell^{(1)}(\alpha a). \tag{72}$$

$$A\frac{dj_\ell(qr)}{dr}\Big|_{r=a} = C\frac{dh_\ell^{(1)}(\alpha r)}{dr}\Big|_{r=a}. \tag{73}$$

Noting that A, C cannot be zero and eliminating A and C we get condition on the bound state energy to be

$$\frac{1}{j_\ell(qr)}\frac{dj_\ell(qr)}{dr}\Big|_{r=a} = \frac{1}{h_\ell(qr)}\frac{dh_\ell^{(1)}(\alpha r)}{dr}\Big|_{r=a}.. \tag{74}$$

The above equation can be solved numerically to obtain allowed values energies. In this case of square well only a finite number of states exist for a given ℓ below a maximum value. In general there will be no bound state for ℓ greater that a certain values. The states of definite energy depend on quantum number $n\ell$ and the energy does not depend on magnetic quantum number m. Therefore for a given azimuthal quantum number ℓ we have $(2\ell + 1)$ wave functions $N_{n\ell}R_{n\ell}(\rho)Y_{\ell m}(\theta, \phi)$ and the energy levels $E_{n\ell}$ are $(2\ell + 1)$ fold degenerate. The energy increases with ℓ and also with increasing n. Thus energy level diagram would appear as follows.

Continuous energy solutions

The energy levels for $E > 0$ are continuous. We shall write the corresponding solutions which are important for discussion of scattering from a square well. When $E > 0$ we define

$$q^2 = \frac{2m(E + V_0)}{\hbar^2}, \quad k^2 = \frac{2mE}{\hbar^2}. \tag{75}$$

A most general form of the solution of the radial equation is given by

$$R_\ell(r) = \begin{cases} Aj_\ell(qr) + Bn_\ell(qr), & r < a \\ Cj_\ell(kr) + Bn_\ell(kr), & r < a \end{cases}. \tag{76}$$

In order that the radial wave function be finite at $r = 0$, we must set $B = 0$. This gives

$$R_\ell(r) = \begin{cases} Aj_\ell(qr), & r < a \\ Cj_\ell(kr) + Bn_\ell(kr), & r < a \end{cases}. \tag{77}$$

Next we demand continuity of the radial wave function and its derivative at $r = a$ and get

$$Aj_\ell(qa) = Cj_\ell(ka) + Bn_\ell(ka) \tag{78}$$

$$A\frac{d}{dr}j_\ell(qr)\Big|_{r=a} = C\frac{d}{dr}j_\ell(kr)\Big|_{r=a} + B\frac{d}{dr}n_\ell(kr)\Big|_{r=a} \tag{79}$$

These two equations constrain the three constants A, B, C and determine their ratios, the overall normalization constant remains, as expected, undetermined. For a given energy E there is solution for each $\ell = 0, 1, 2, ...$ and $m = -\ell, ..., \ell$ giving rise to infinite degeneracy for $E > 0$. These continuous energy solutions will be required for physical applications to scattering problems.

§3 Hydrogen Atom

§4 Hydrogen Atom

The classical Hamiltonian for an electron and a nucleus of charge Ze is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_2|} \tag{80}$$

where m_1, m_2 are the masses of the electron and the nucleus and $\vec{r}_1, \vec{r}_2$ denote their respective positions.The case $Z = 1$ corresponds to H atom, $Z = 2$ singly ionized He atom and $Z = 3$ doubly ionized Li atom and so on.

The Schrödinger equation for the electron nucleus system takes the form

$$-\frac{\hbar^2}{2m_1}\Big(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\Big)\Psi - \frac{\hbar^2}{2m_1}\Big(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\Big)\Psi - \frac{Ze^2}{|\vec{r}_1 - \vec{r}_2|}\Psi = \mathcal{E}\Psi. \tag{81}$$

Since the potential depends on relative position only, the two body problem can be reduced to an equivalent one body problem with reduced mass by changing the frame of reference to the centre of mass frame. Introducing the centre of mass and relative coordinates defined by

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}, \qquad \vec{r} = \vec{r_1} - \vec{r_2}. \tag{82}$$

The centre of mass will move like a free particle, and the relative motion reduces to that of a particle of reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ Therefore it is not surprising that the separation of variables in the Schrödinger equation can be achieved by changing to these new variables $\vec{r}$ and $\vec{R}$. In terms of these variables the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2M}\Big(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\Big)\Psi(\vec{R},\vec{r}) \tag{83}$$

$$-\frac{\hbar^2}{2\mu}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\Big)\Psi(\vec{R},\vec{r})-\frac{Ze^2}{r}\Psi(\vec{R},\vec{r})=\mathcal{E}\Psi(\vec{R},\vec{r}). \tag{84}$$

Here $M=m_1+m_2$ is the total mass, μ is the reduced mass. If we now write the full wave function $\Psi(\vec{R},\vec{r})$ as

$$\Psi(\vec{r},\vec{r})=U(\vec{R})u(\vec{r}) \tag{85}$$

and substitute it in Eq.(84), the variables $\vec{R}$ and $\vec{r}$ get separated and we would get the following differential equations for $U(\vec{R})$ and $u(\vec{r})$

$$-\frac{\hbar^2}{2M}\Big(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\Big)U(\vec{R})=E_{\rm cm}U(\vec{R}) \tag{86}$$

$$-\frac{\hbar^2}{2\mu}\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\Big)u(\vec{r})-\frac{Ze^2}{r}u(\vec{r})=Eu(\vec{r}). \tag{87}$$

$E_{\rm cm}, E$ are constants appearing from the process of separation of variables so that $E+E_{\rm cm}=\mathcal{E}$. The equation (86) is a free particle equation for the centre of mass and Eq.(87) describes the relative motion of the electron and the nucleus.

The Schrödinger equation (87) can now be solved by separation of variables in spherical polar coordinates r,θ,ϕ. The angular part of the wave function is given by the spherical harmonics $Y_{\ell 2m}(\theta,\phi)$ and therefore we write

$$u(\vec{r})=R(r)Y_{\ell m}(\theta,\phi). \tag{88}$$

The radial equation for $R(r)$ takes the form

$$\frac{1}{r^2}\frac{d}{dr}\Big(r^2\frac{dR}{dr}\Big)+\frac{2\mu E}{\hbar^2}\Big(E+\frac{Ze^2}{r}-\frac{\ell(\ell+1)}{\hbar^2}\Big)R(r) = 0, \tag{89}$$

$$\frac{d^2R(r)}{dr^2}+\frac{2}{r}\frac{dR(r)}{dr}+\frac{2\mu E}{\hbar^2}\Big(E+\frac{Ze^2}{r}-\frac{\ell(\ell+1)}{\hbar^2}\Big)R(r) = 0. \tag{90}$$

The radial equation involves effective potential

$$V_{\rm eff}(r)=-\frac{Ze^2}{r}+\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}. \tag{91}$$

Remembering that $\ell(\ell+1)\hbar^2$ is the eigenvalue of the square of orbital angular momentum, L^2,the second term is seen to be the centrifugal barrier term that appears in classical mechanics. The effective potentail goes to zero fr large r. Hence for $E>0$ the energy

eigenvalues will be continuous and the bound states exist only for negative E, so we write $E = -|E|$. It is convenient to work with dimensionless variables ρ and λ defined by

$$\rho = \alpha r, \qquad \alpha^2 = \frac{8\mu|E|}{\hbar^2} \tag{92}$$

$$\lambda = \frac{2\mu Z e^2}{\alpha\hbar^2} \quad = \quad \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}. \tag{93}$$

The equation for radial wave function written in terms of ρ takes the form

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \Big(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\Big)R = 0. \tag{94}$$

The above equation (94) can be transformed into a form similar to one dimensional Schrödinger equation by introducing $\chi(\rho) = \rho R(\rho)$ which gives the following equation for $\chi(\rho)$

$$\frac{d^2\chi}{d\rho^2} + \Big(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\Big)\chi(\rho) = 0. \tag{95}$$

§4.1 Large ρ behaviour

The behaviour of the radial wave function for large ρ can be easily found by taking large ρ limit of Eq.(95). Neglecting the terms $\frac{\lambda}{\rho}$ and $\frac{\ell(\ell+1)}{\rho^2}$ compared to $1/4$ we get

$$\frac{d^2\chi(\rho)}{d\rho^2} - \frac{1}{4}\chi\rho = 0. \tag{96}$$

showing that the wave function behaves like $\exp(\pm\rho/2)$ for large ρ. The wave function must be bounded everywhere including at infinity, so we must have $\chi(\rho) \approx e^{-\rho/2}$. This suggests that we write $R = e^{-\rho/2}F(\rho)$, and solve for $F(\rho)$. The equation for $F(\rho)$ turns out to be

$$\frac{d^2F(\rho)}{d\rho^2} + \left(\frac{2}{\rho} - 1\right) + \left[\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1}{\rho^2}\right] \tag{97}$$

§4.2 Solution by Frobenius method

We now find solution of the differential equation for $F(\rho)$ by the method of series solution. Assuming the form

$$F(\rho) = \sum_{m=0} a_m \rho^{c+m},, \tag{98}$$

substituting in Eq.(97), and equating coefficients of lowest power of ρ to zero we get

$$c(c+1) - \ell(\ell+1) = 0 \Longrightarrow c = -\ell - 1, \ell \tag{99}$$

Since $\ell > 0$, the value $c = -\ell(\ell+1)$ give solution diverging at $\rho = 0$.

Therefore we choose $c = \ell =$ and the recurrence relation for the coefficients a_m turns out to be

$$a_{m+1} = \frac{(m+\ell+1-\lambda}{(m+1)(m+2\ell+2)} a_m. \tag{100}$$

The ratio of coefficients for large m

$$\frac{a_{m+1}}{a_m} \sim \frac{1}{m} \tag{101}$$

coincides with the corresponding value for the series $\rho^k \exp(\rho)$. Hence if the series does not terminate, the solution $F(\rho)$ gives the radial wave function diverging like $\rho^k \exp(\rho/2)$ for large ρ. This is unacceptable and hence the series must terminate. This happens if all terms vanish after some n' *i.e.* $a_m = 0$ for all $m > n'$. For this to happen we must have $a_{n'+1} = 0$. Hence from Eq.(100) we get

$$\lambda = n' + \ell + 1. \tag{102}$$

The energy is then given by

$$\boxed{E_n = -|E_n| = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2} = \frac{Z\alpha^2}{2n^2}(\mu c^2)}. \tag{103}$$

where c is velocity of light and $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ is the fine structure constant.

§4.3 Properties of H atom wave functions

The final expressions for wave functions for hydrogen like problems is given by

$$\begin{aligned} u_{n\ell m}(r,\theta,\phi) &= R_{n\ell}(r) Y_{\ell m}(\theta,\phi) && (104)\\ R_{n\ell}(r) &= N_{n\ell}\, \rho^\ell\, L^{2\ell+1}_{n+\ell}(\rho) e^{-\rho/2} && (105)\\ N_{n\ell} &= \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\big((n+\ell)!\big)}} && (106) \end{aligned}$$

with

$$\rho = \Big(\frac{2Z}{na_0}\Big) r, \qquad a_0 = \frac{\hbar^2}{\mu e^2}. \tag{107}$$

and n is the principle quantum number.

Here $L^p_q(\rho)$ are associated Laguerre polynomials and a_0 is the radius of first Bohr orbit of the the electron in hydrogen atom. The energy levels are given by

$$E_n = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2}. \tag{108}$$

The first few radial wave functions are

$$\begin{aligned} R_{10} &= (Z/2a_0)^{\frac{3}{2}} 2\exp(-Zr/2a_0)) && (109)\\ R_{20}(r) &= (Z/2a_0)^{\frac{3}{2}}(2 - Zr/a_0)\exp(-Zr/2a_0)) && (110)\\ R_{20}(r) &= (Z/2a_0)^{\frac{3}{2}}(Zr/\sqrt{3}\,a_0)\exp(-Zr/2a_0)) && (111) \end{aligned}$$

A comment on hydrogen atom energy levels Finally we wish to remind you that the non-relativistic result $-R/n^2$ for the energy levels of H-atom is not the end of story for H-atom levels. Precision experiments show that each level is not a single level. To understand the experimental facts we must take into account of relativistic effects using Dirac theory of electron

$$\text{Dirac Theory} \nearrow \text{Spin orbit coupling} \searrow \text{Fine Structure}$$
$$\text{Dirac Theory} \searrow \text{Relativistic variation of mass} \nearrow \text{Fine Structure}$$

Also a hyperfine structure, seen in the energy levels, requires a treatment of the spin-spin interaction of electron with the nucleus and an explanation of a tiny 'Lamb shift' requires use of quantum field theory.

Hyperfine structure	$\rightarrow$ Effect of Nuclear Spin
Lamb shift	$\rightarrow$ Quantum field Theory, Vacuum Polarization Effect

§5 Accidental degeneracy

General Properties of Bound State Spectra

A potential is spherically symmetric if in polar variables it depends only on r and not on θ and ϕ coordinates . We shall now discuss general properties of solution of 3-dimensional Schrödinger equation $H\psi = E\psi$ where

$$H = \frac{\vec{p}^{\,2}}{2m} + V(r)$$

and the potential $V(r)$ is spherically symmetric.

Conserved quantities

We note that all the three components of $\vec{L}$ commute with Hamiltonian

$$[\vec{L}, H] = 0$$

hence

$$[\vec{L}^2, H] = 0 \ .$$

The parity operator P

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

also commutes with $L^2 L_z$ and H, operators. Therefore, the eigen functions of H will also be eigen functions of L^2, L_z and parity and each level can be assigned a definite value of l, m and parity. For a state with definite value of l, the value of parity is $\equiv (-1)^l$. In this case L^2, L_z and H form a complete commuting set.

$(2\ell + 1)$ **degeneracy**

We use the notation $|El, m\rangle$ to denote the simultaneous eigenvector of H, L^2 and L_z

$$\begin{aligned} H|E, lm\rangle &= E|E, lm\rangle & (112)\\ L^2|E, lm\rangle &= l(l+1)\hbar^2|E, lm\rangle & (113)\\ \text{and} \quad L_z|E, lm\rangle &= m\hbar|E, lm\rangle & (114)\\ P|E, lm\rangle &= (-1)^l|E, lm\rangle & (115) \end{aligned}$$

Applying L_- on $|El, m\rangle$ several times leads successively to

$$|El, m-1>\rangle \ , \ |E, l, m-2\rangle \quad \cdots \quad |El, -l> \tag{116}$$

$$\tag{117}$$

and the action of L_+ on $|E, lm\rangle$ leads to the states

$$|El, m+1\rangle \ , \ |E, l, m+2\rangle \quad \cdots \quad |El, l> \tag{118}$$

All these states will have the same value of energy. This statement can be proved by making use of the fact that H commutes with $L_\pm$ and that action of L_+ (or L_-) on $|Elm>$ leads to states $|El, m+1>$ (or $|El, m-1>$). Thus we see that the bound state energy eigenvalues of a spherically symmetric potential problem with have $(2l+1)$ fold degeneracy. (What about the continuous energy eigenvalues?)

Radial wave function

The Schrödinger equation for a spherically symmetric potential can be solved by separation of variables in polar coordinates. The angular part of the wave functions turns out to be a spherical harmonic $Y_{lm}(\theta, \phi)$ and the wave function has the form

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$$

where $R(r)$ is radial wave function satisfying the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}R(r) + \left(V(r) + \frac{l(l+1)\hbar^2}{2mr^2}\right)R(r) = ER(r) \ .$$

If we define $\chi(r) = rR(r)$, the function χ satisfies the equation

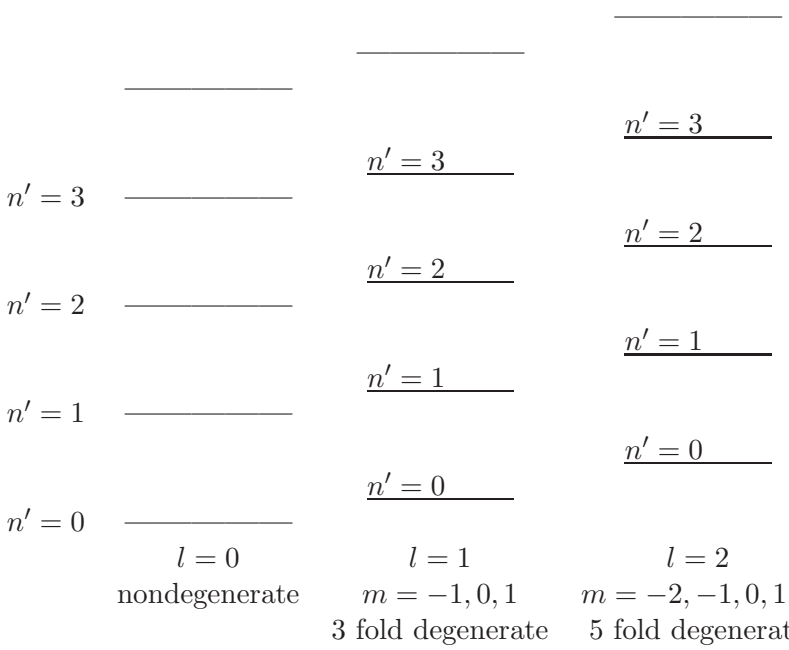
$$-\frac{\hbar^2}{2m}\frac{d^2\chi}{dr^2} + \left(V(r) + \frac{l(l+1)\hbar^2}{2mr^2} - E\right)\chi = 0 \ .$$

with boundary condition $\chi(r)|_{r=o} = 0$, otherwise $R(r)$, the radial wave function will tend to ∞ as $r \to \infty$.

Bound state spectrum

The equation for χ has the form of one dimensional Schrödinger equation. Let n' denote the number of zeros of the radial wave function, excluding $r = 0$ and at $r = \infty$. Then for a fixed value of l, the energy will increase with n', $n' = 0, 1, 2, \cdots$ will correspond to, for a fixed l, the 'ground' state, first excited state, the second excited state etc. Because of the l dependence of the term $\frac{l(l+1)\hbar^2}{2mr^2}$ in the potential appearing in equation for $\chi(r)$, we expect that as l is changed, keeping the number of nodes to be the same, E would also change. Increasing l would lead to increase in E, when n' is kept fixed.

Thus the spectrum would appear as follows



Coulomb problem spectrum

For hydrogen atom the energy levels are given by

$$E = -\frac{Z^2 e^4 m}{2\hbar^2(n' + l + 1)^2}$$

The energy does not depend on n' and l separately but only on the combination $n = (n' + l + 1)$. For a fixed n, l can have values $0, 1, \cdots, n-1$ (because $n' \geq 0$) and all these

solutions correspond to the same energy eigenvalue. The energy level diagram of H-atom, therefore, appears as shown below.

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
$n=7$					
$n=6$					
$n=5$					
$n=4$	$n=4$	$n=4$	$n=4$	$n=4$ 7 fold degenerate	$n=4$ 9 fold degenerate
$n=3$	$n=3$	$n=3$	$n=3$ 5 fold degenerate		
$n=2$	$n=2$	$n=2$ 3 fold degenerate			
$n=1$	$n=1$ non-degenerate				

Putting all the levels which have the same energy together we get the following schematic representation of energy levels of H atom. This table also shows that the allowed values of l for each n, and number of m values for each level. The number of total m values, with the same energy, is n^2 and the degeneracy, after taking spin into account, becomes $2n^2$.

		l values	number of m values	degeneracy
		$0, 1, ..n-1$	n^2	$2n^2$
$n=4$	32	$l=0,1,2,3$	$\sum(2l+1)=16$	$2\times 16=32$
$n=3$	18	$l=0,1,2$	$\sum 2(l+1)=9$	$2\times 9=18$
$n=2$	8	$l=0,1$	$\sum(2l+1)=4$	$2\times 4=8$
$n=1$	degen=2	$l=0$	$\sum(2l+1)=1$	$2\times 1=2$

Accidental degeneracy

Comparing the hydrogen atom levels with those of a general spherically symmetric potential, we find that energies for states with several different values of l $(=0,1,2\ldots n-1)$ are the same. For a general spherically symmetric potential different combinations of n, l values correspond to different bound state energies, and are $(2l+1)$ fold degenerate. Thus there is an extra degeneracy is present for H atom beyond the expected $(2l+1)$ fold degeneracy this phenomenon present in the case of hydrogen atom is known as *accidental degeneracy.* Another well known case of accidental degeneracy is that of isotropic harmonic oscillator ($V(r)=\frac{1}{2}kr^2$) in three dimensions.

Remarks

[1] It must be emphasized that the accidental degeneracy is due to the special symmetry of the Coulomb problem.

[2] Any slight deviation of the potential from $\frac{1}{r}$ will result in splitting of energy levels with different values of l.

[3] It is known that the accidental degeneracy is present whenever the Schrödinger equation $H\psi = E\psi$ can be separated into ordinary differential equations in more than one set of coordinate system.

H atom — Separation of variables for the Coulomb problem is possible in

(a) spherical polar coordinates r, θ, ϕ

(b) parabolic coordinates ξ, η, ϕ defined by

$$\xi = r - z = r(1 - \cos\theta) \quad \eta = r + z = r(1 + \cos\theta) \quad \phi = \phi \tag{119}$$

[4] The isotropic oscillator also exhibits accidental degeneracy. For isotropic harmonic oscillator,$V(r) = \frac{1}{2}kr^2$, the Schrodinger equation can be separated in two set of variables, Cartesian and spherical polar coordinates.