Subject: Physics

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Paper No. : Physics at Nanoscale - III

Module : **Confinement of a particle in a box and** in 3D (Quantum Dot)

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Development Team

Principal Investigator	
Paper Coordinator	Prof. Subhasis Ghosh, School of Physical Sciences, Jawaharlal Nehru University, New Delhi
Content Writer	Prof. Subhasis Ghosh, School of Physical Sciences, Jawaharlal Nehru University, New Delhi
Content Reviewer	

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3.1 CONFINEMENT

The properties of materials are strongly influenced by the size of the particle. For example Carbon is a non-metal but when considered at the nanoscale single layer allotrope of carbon i.e. Graphene is one of the best conductors. The phenomenon that can be used to explain the size dependent characteristics of materials is Quantum confinement.

Quantum confinement effects are generally observed when the size of the particle is small and comparable to the de Broglie wavelength of the electron. The effect describes the phenomenon resulting due to squeezing the particles (electrons and holes) into a dimension that approaches a classical limit so that various quantum effects are manifested. In this regime, energy of the particle is no longer continuous, but discrete.

Quantum confinement effects are observed in low dimension, two, one or zero dimension. When a particle is confined in two dimension (2D) or in a plane, then particle's motion is quantized along the direction of confinement, say z-axis and the particle motion is classical i.e. is free to move in the x-y plane. The systems in 2D is also known as "quantum well". In case one dimension (1D), particle's motion is quantized due to confinement in 2D (say in x-y plane) and classical in 1D along z-axis. The system in 1D is also known as "quantum wire". In case of zero dimension (0D), particle's motion is quantized in all three dimension due to confinement along x,y and z directions and known as "quantum dot". In these systems, the spatial dimensions are of the order of the de Broglie wavelength of the carriers and therefore, the carrier energy states become quantised. As a result, the electronic, electrical and optical behaviour of the carriers are governed by quantum mechanics along one dimension, two dimension and all three dimensions in quantum well (2D), quamtum wire (1D) and quantum dot (0D), respectively.

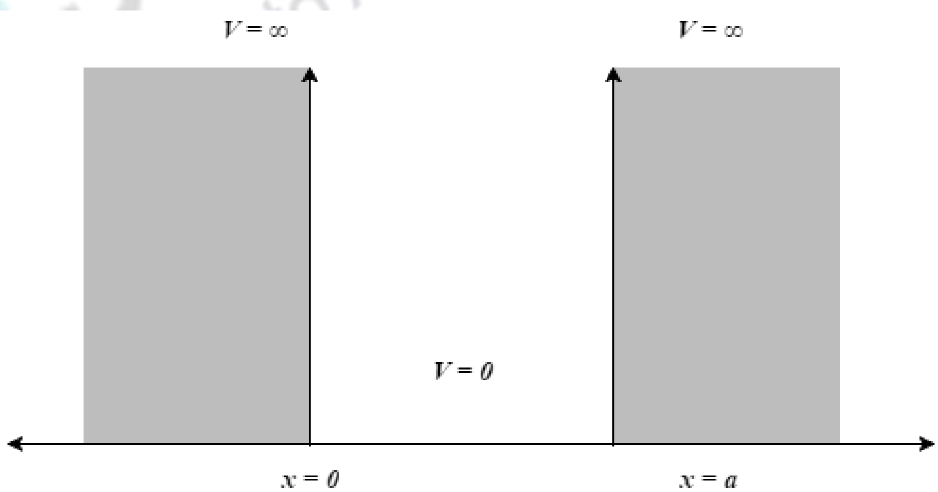
Calculation of eigenstates and eigenvalues for different system

The particle's motion in quantum wells, wires and dots can be described using the analogy to a particle in 1D box, a 2D box, and a 3D box, respectively. The energies of the carrier along the direction of confinement are no longer continuous as in the case where there is no confinement. The emergence of discrete states from continuum states is the most fundamental signature of nanomaterials or nanosystems. One has to solve the Schrodinger equation of the carrier to find out particle's eigenvalues and eigenfunctions. This is achieved by solving differential equations with particular boundary conditions which can be used to predict the actual shape of a quantum well, wire or dot.

3.1.1a Particle in 1D infinite box

The potential is

$$V(x) = \begin{cases} \infty \; if \; x < 0 \\ 0 \; if \; 0 < x < a \\ \infty \; if \; x \geq a \end{cases} \tag{3.1}$$



For this the boundary conditions are

$$\Psi(0) = 0$$
$$\Psi(a) = 0 \qquad (3.2)$$

The Schrodinger equation to solve is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = E\Psi \qquad (3.3)$$

Rearranging to yield in the box region where V=0

$$\frac{d^2\Psi}{dx^2} + k^2\Psi = 0 \qquad (3.4)$$

Where $k^2 = \frac{2mE}{\hbar^2}$ and general solution is

$$\Psi = Ae^{ikx} + Be^{-ikx}$$

Applying the boundary conditions

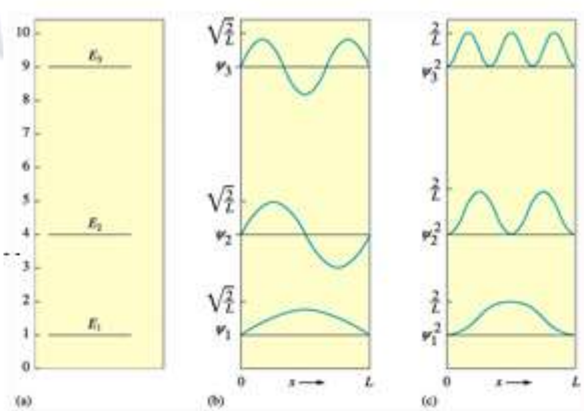
$$\Psi(0) = A + B = 0 \rightarrow B = -A$$
$$\Psi(a) = Ae^{ika} - Ae^{-ika} = 0$$

This leads to

$$2i\sin(ka) = 0$$
$$E = \frac{n^2h^2}{8ma^2} \qquad (3.5)$$

And by normalizing the wave function we get,

$$\Psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \qquad (3.6)$$



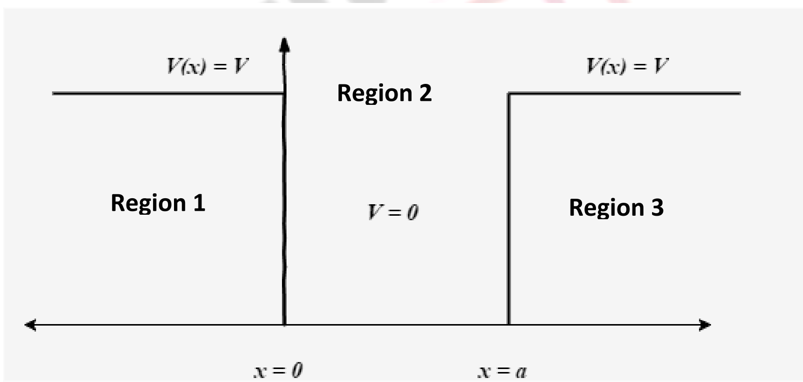
E Ψ Ψ*Ψ

Particle energies, wavefunctions, and probability densities for n = 0, 1 and 2.

3.1.1b Particle in a 1D finite box

From quantum mechanics we know that as the potential is zero inside box, the solutions in the box region will be wavelike and in the barrier region the solution will be exponentially decaying. The potential is

$$V(x) = \begin{cases} V & if\ x \le 0 \\ 0 & if\ 0 < x < a \\ V & if\ x \ge a \end{cases} \tag{3.7}$$



The solutions in the three regions indicated are

$$\begin{aligned} \Psi_1(x) &= Ae^{\beta x} + Be^{-\beta x} \\ \Psi_2(x) &= Ce^{ikx} + De^{-ikx} \\ \Psi_3(x) &= Fe^{\beta x} + De^{-\beta x} \end{aligned} \tag{3.8}$$

Where $\beta = \sqrt{\frac{2m(V-E)}{\hbar^2}}$ and $k = \sqrt{\frac{2mE}{\hbar^2}}$

By applying the boundary conditions, B=0 and F=0 due to finiteness of the wavefunction outside the box, we get

$$\Psi_1(x) = Ae^{\beta x}$$

$$\Psi_2(x) = Ce^{ikx} + De^{-ikx} \tag{3.9}$$

$$\Psi_3(x) = De^{-\beta x}$$

Now by applying the boundary conditions at the interface, one gets

$$\begin{aligned} \Psi_1(0) &= \Psi_2(0) \\ \Psi_1'(0) &= \Psi_2'(0) \\ \Psi_2(a) &= \Psi_3(a) \\ \Psi_2'(a) &= \Psi_3'(a) \end{aligned} \tag{3.10a}$$

We have

$$A = C + D \tag{3.10b}$$

$$A\beta = ikC - ikD$$

$$Ce^{ika} + De^{-ika} = Ge^{-\beta a}$$

$$ikCe^{ika} - ikDe^{-ika} = -\beta Ge^{-\beta a}$$

We have

$$\begin{pmatrix} 1 & -1 & -1 & 0 \\ \beta & -ik & ik & 0 \\ 0 & e^{ika} & e^{-ka} & -e^{\beta a} \\ 0 & ike^{ika} & -ike^{-ka} & \beta e^{\beta a} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = 0 \tag{3.11a}$$

Here either we get the trivial solution where A=B=C=D or that the determent of the large matrix is zero

$$\begin{vmatrix} 1 & -1 & -1 & 0 \\ \beta & -ik & ik & 0 \\ 0 & e^{ika} & e^{-ka} & -e^{\beta a} \\ 0 & ike^{ika} & -ike^{-ka} & \beta e^{-\beta a} \end{vmatrix} = 0 \tag{3.11b}$$

To simplify the determent we have apply the following path as

$$-ik(row\ 3) + (row\ 4) \to (row\ 4)$$

$$\begin{vmatrix} 1 & -1 & -1 & 0 \\ \beta & -ik & ik & 0 \\ 0 & e^{ika} & e^{-ka} & -e^{\beta a} \\ 0 & 0 & -2ike^{-ka} & (\beta + ik)e^{-\beta a} \end{vmatrix} = 0$$

Followed by

$$-\frac{1}{\beta - ik}(row\ 2) \rightarrow (row\ 2)$$

$$e^{-ika}(row\ 3) \rightarrow (row\ 3)$$

This gives us

$$\begin{vmatrix} 1 & -1 & \frac{-1}{(\beta+ik)} & 0 \\ 0 & -1 & -\frac{(\beta+ik)}{(\beta-ik)} & 0 \\ 0 & 1 & e^{-2ika} & -e^{-a(\beta+ik)} \\ 0 & 0 & -2ike^{-ika} & (\beta+ik)e^{-\beta a} \end{vmatrix} = 0$$

And final steps are

$$(row\ 2) + (row\ 3) \rightarrow (row\ 3)$$

$$-(row\ 2) \rightarrow (row\ 2)$$

Giving

$$\begin{vmatrix} 1 & -1 & \frac{-1}{(\beta+ik)} & 0 \\ 0 & -1 & \frac{(\beta+ik)}{(\beta-ik)} & 0 \\ 0 & 0 & e^{-2ika} + -\frac{(\beta+ik)}{(\beta-ik)} & -e^{-a(\beta+ik)} \\ 0 & 0 & -2ike^{-ika} & (\beta+ik)e^{-\beta a} \end{vmatrix} = 0$$

And finally we get

$$(\beta+ik)e^{-2ika-\beta a} - \frac{(\beta+ik)^2}{(\beta-ik)}e^{-\beta a} - 2ike^{-2ika-\beta a} = 0$$

$$(\beta-ik)^2 e^{-2ika} = (\beta+ik)^2$$

$$-(\beta - ik)^2 e^{-ika} + (\beta + ik)^2 e^{ika}$$

This gives

$$\tan(ka) = \frac{2\beta k}{(k^2-\beta^2)} \tag{3.12}$$

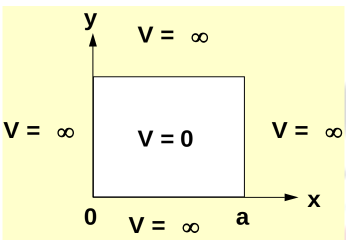
And finally we get

$$tan\left(\sqrt{\frac{2mE}{\hbar^2}}a\right) = \frac{2\sqrt{E(V-E)}}{2E-V} \tag{3.13}$$

3.1.2 Particle in 2D box

3.1.2a Particle in a rectangular box

The potential is



$$V(x,y) = \begin{cases} \infty\ if\ x < 0;\ y < 0 \\ 0\ if\ 0 < x < a;\ 0 < y < b \\ \infty\ if\ x \geq a; y \geq b \end{cases} \tag{3.14}$$

The Schrodinger equation to solve is

$$-\frac{\hbar^2}{2m}\left[\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right) + V(x,y)\right]\Psi(x,y) = E\Psi(x,y) \tag{3.15}$$

Let us consider solution of above equation is $\Psi(x,y) = \Psi_x \Psi_y$; where Ψ_x, Ψ_y are the functions of x and y only.

Substituting the solution in eq. 3.15 and rearranging the terms to yield in the box region where V=0, the eq. 3.15 becomes

$$-\frac{\hbar^2}{2m}\left[\left(\frac{1}{\Psi_x}\frac{d^2\Psi_x}{dx^2} + \frac{1}{\Psi_y}\frac{d^2\Psi_y}{dy^2}\right)\right] = E \tag{3.16}$$

Let us consider $E = E_x + E_y$ and using variable separable method for a rectangular box eq. 3.16 transforms into two equations each consisting of one variable only.

$$\frac{d^2\Psi_x}{dx^2} + {k_x}^2\Psi_x = 0$$

$$\frac{d^2\Psi_y}{dy^2} + k_y{}^2\Psi_y = 0 \quad (3.17)$$

Where $k_x{}^2 = \frac{2mE_x}{\hbar^2}$ and $k_y{}^2 = \frac{2mE_y}{\hbar^2}$. The general solution for the above equations is

$$\Psi_x = Ae^{ik_x x} + Be^{-ik_x x};\ \Psi_y = Ce^{ik_y y} + De^{-ik_y y}$$

For this the boundary conditions are

$$\Psi_x(0) = 0$$
$$\Psi_x(a) = 0 \quad (3.18)$$
$$\Psi_y(0) = 0$$
$$\Psi_y(b) = 0$$

Applying the boundary conditions

$$\Psi_x(0) = A + B = 0 \rightarrow B = -A$$
$$\Psi_x(a) = Ae^{ik_x a} + Be^{-ik_x a} = 0$$

This leads to

$$2isin(k_x a) = 0$$
$$sin(k_x a) = \sin(n_x\pi)$$
$$\Rightarrow k_x a = n_x\pi$$
$$\Rightarrow E_x = \frac{n_x{}^2h^2}{8ma^2} \quad (3.19)$$

Similarly solving the equation for y, we get

$$E_y = \frac{n_y{}^2h^2}{8mb^2}$$

Thus total energy,

$$E = \frac{n_x{}^2h^2}{8ma^2} + \frac{n_y{}^2h^2}{8mb^2}$$

And by normalizing the wavefunction we get,

$$\Psi(x,y) = \sqrt{\frac{2}{a}} sin\left(\frac{n_x \pi}{a} x\right) \sqrt{\frac{2}{b}} sin\left(\frac{n_y \pi}{b} y\right) \quad (3.20)$$

3.1.2b Particle in circular box

Now, consider a circular box of radius R. The potential inside the box is 0 and outside of the box is ∞ such that the boundary conditions for the wave function would be

$$\Psi(R,\theta) = 0 \;\forall\; \theta$$

Transforming the Schrodinger question from Cartesian co-ordinates to polar coordinates, the transformation equations are

$$x = rcos\theta$$
$$y = rsin\theta \quad (3.21)$$

Such that $r = \sqrt{x^2 + y^2}$ and $\theta = \tan^{-1}\left(\frac{y}{x}\right)$

Transforming the partial differentiation in terms of r and θ ,

$$\left(\frac{\partial}{\partial x}\right)_y = \left(\frac{\partial r}{\partial x}\right)_y \left(\frac{\partial}{\partial r}\right)_\theta + \left(\frac{\partial \theta}{\partial x}\right)_y \left(\frac{\partial}{\partial \theta}\right)_r$$
$$\left(\frac{\partial}{\partial y}\right)_x = \left(\frac{\partial r}{\partial y}\right)_x \left(\frac{\partial}{\partial r}\right)_\theta + \left(\frac{\partial \theta}{\partial y}\right)_x \left(\frac{\partial}{\partial \theta}\right)_r \quad (3.22)$$

Using transforming equation,

$$\left(\frac{\partial r}{\partial x}\right)_y = \left(\frac{\partial \sqrt{x^2 + y^2}}{\partial x}\right)_y = \frac{1}{2}\frac{2x}{r} = cos\theta$$

And

$$\left(\frac{\partial \theta}{\partial x}\right)_y = \left(\frac{\partial \tan^{-1}\left(\frac{y}{x}\right)}{\partial x}\right)_y = -\frac{sin\theta}{r}$$

Similarly considering x constant,

$$\left(\frac{\partial r}{\partial y}\right)_x = sin\theta$$
$$\left(\frac{\partial \theta}{\partial y}\right)_x = \frac{cos\theta}{r}$$

Substituting the above results eq. 3.22 becomes

$$\left(\frac{\partial}{\partial x}\right)_y = cos\theta\left(\frac{\partial}{\partial r}\right)_\theta - \frac{sin\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r$$

$$\left(\frac{\partial}{\partial y}\right)_x = sin\theta\left(\frac{\partial}{\partial r}\right)_\theta + \frac{cos\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r$$

The second partial derivatives will be

$$\left(\frac{\partial^2}{\partial x^2}\right)_y = \frac{\partial\left(cos\theta\left(\frac{\partial}{\partial r}\right)_\theta - \frac{sin\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r\right)}{\partial x} \quad (3.23)$$

$$\left(\frac{\partial^2}{\partial y^2}\right)_x = \frac{\partial\left(sin\theta\left(\frac{\partial}{\partial r}\right)_\theta + \frac{cos\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r\right)}{\partial y} \quad (3.24)$$

$$\left(\frac{\partial^2}{\partial x^2}\right)_y = cos\theta\left(\frac{\partial\left(cos\theta\left(\frac{\partial}{\partial r}\right)_\theta - \frac{sin\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r\right)}{\partial r}\right) - \frac{sin\theta}{r}\left(\frac{\partial\left(cos\theta\left(\frac{\partial}{\partial r}\right)_\theta - \frac{sin\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r\right)}{\partial\theta}\right)$$

i.e.

$$\left(\frac{\partial^2}{\partial x^2}\right)_y = cos^2\theta\frac{\partial^2}{\partial r^2} + \frac{sin\theta cos\theta}{r^2}\frac{\partial}{\partial\theta} - \frac{sin\theta cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta} + \frac{sin^2\theta}{r}\frac{\partial}{\partial r} - \frac{sin\theta cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta} + \frac{sin\theta cos\theta}{r^2}\frac{\partial}{\partial\theta} + \frac{sin^2\theta}{r^2}\frac{\partial^2}{\partial\theta^2} \quad (3.25)$$

For y:

$$\left(\frac{\partial^2}{\partial y^2}\right)_x = sin\theta\left(\frac{\partial\left(sin\theta\left(\frac{\partial}{\partial r}\right)_\theta + \frac{cos\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r\right)}{\partial r}\right) + \frac{sin\theta}{r}\left(\frac{\partial\left(sin\theta\left(\frac{\partial}{\partial r}\right)_\theta + \frac{cos\theta}{r}\left(\frac{\partial}{\partial\theta}\right)_r\right)}{\partial\theta}\right)$$

$$\left(\frac{\partial^2}{\partial y^2}\right)_x = sin^2\theta\frac{\partial^2}{\partial r^2} - \frac{sin\theta cos\theta}{r^2}\frac{\partial}{\partial\theta} + \frac{sin\theta cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta} + \frac{cos^2\theta}{r}\frac{\partial}{\partial r} + \frac{sin\theta cos\theta}{r}\frac{\partial^2}{\partial r\partial\theta} - \frac{sin\theta cos\theta}{r^2}\frac{\partial}{\partial\theta} + \frac{cos^2\theta}{r^2}\frac{\partial^2}{\partial\theta^2} \quad (3.26)$$

Adding above two equations,

$$\left(\frac{\partial^2}{\partial x^2}\right)_y + \left(\frac{\partial^2}{\partial y^2}\right)_x = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} \quad (3.27)$$

Schrodinger equation for circular box becomes

$$-\frac{\hbar^2}{2m}\left[\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right)+0\right]\Psi(r,\theta)=E\Psi(r,\theta)$$

Considering the solution for the above equation,

$$\Psi=R_{ml}(r)e^{\pm im_l\theta}$$

Substituting into Schrodinger equation,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 R_{ml}(r)}{\partial r^2}+\frac{1}{r}\frac{\partial R_{ml}(r)}{\partial r}-\frac{m_l^2}{r^2}R_{ml}(r)\right)=ER_{ml}(r)$$

Rearranging above equation,

$$r^2\frac{\partial^2 R_{ml}(r)}{\partial r^2}+r\,\frac{\partial R_{ml}(r)}{\partial r}+\left(\epsilon r^2-\frac{2m}{\hbar^2}m_l^2\right)R_{ml}(r)=0$$

Where $=\frac{2mE}{\hbar^2}$.

This is form of Bessel differential equation. To change into standard form, considering the variable

$$r=k\rho$$

$$\frac{\partial\rho}{\partial r}\frac{\partial}{\partial\rho}=\frac{\partial}{\partial r}=\frac{1}{k}\frac{\partial}{\partial\rho}$$

With $k^2\epsilon=1\Rightarrow k=\sqrt{\frac{1}{\epsilon}}$

The Schrodinger equation finally reduces to,

$$\rho^2\frac{\partial^2 R(\rho)}{\partial\rho^2}+\rho\,\frac{\partial R(\rho)}{\partial\rho}+(\rho^2-m_l^2)R(\rho)=0$$

Taking the solution of the above equation to be

$$R(\rho)=\sum_{i=0}a_i\rho^i$$

We have,

$$\frac{\partial R(\rho)}{\partial\rho}=\sum_{i=1}ia_i\rho^{i-1}$$

$$\frac{\partial^2 R(\rho)}{\partial \rho^2} = \sum_{i=2} i(i-1)a_i\rho^{i-2}$$

This implies,

$$\rho^2 \frac{\partial^2 R(\rho)}{\partial \rho^2} \to \sum_{i=2} i(i-1)a_i\rho^{i} \to 2a_2\rho^2 + (3)(2)a_3\rho^3 + (4)(3)a_3\rho^4 + \cdots \quad \text{(a)}$$

$$\rho \frac{\partial R(\rho)}{\partial \rho} \to \sum_{i=1} ia_i\rho^{i} \to a_1\rho + 2a_2\rho^2 + (3)a_3\rho^3 + \cdots \quad \text{(b)}$$

$$(\rho^2)R(\rho) \to \sum_{i=0} a_i\rho^{i+2} \to a_0\rho^2 + a_1\rho^3 + a_2\rho^4 + \cdots \quad \text{(c)}$$

Now, we need $Eq.(a) + Eq.(b) + Eq.(c) = 0$ for the Bessel equation to be satisfied.

Gathering the coefficients of individual powers,

$$a_2 = -a_0/2$$

$$((3)(2) + 3)a_3 = a_1$$

$$((4)(3) + 4)a_4 = -a_2 = \frac{-a_0/2}{((4)(3) + 4)}$$

This Bessel Function's expansion remains an infinite series which never truncates. The quantization occurs only with the boundary conditions i.e. at the perimeter of circular ring. At the boundary (r=R) Bessel function should be zero, let us say it,ρ_0. So,

$$\rho_0 = \frac{R}{k} = \frac{R}{\sqrt{\frac{1}{\epsilon}}}$$

and energy,

$$\left(\frac{\rho_0}{R}\right)^2 = \epsilon = \frac{2mE}{\hbar^2}$$

Ground energy state will be,

$$E_0 = \frac{\hbar^2}{2m}\left(\frac{\rho_0}{R}\right)^2$$

Or,

$$E_0 = \frac{\hbar^2}{2m}\left(\frac{2.4048}{R}\right)^2$$

Where $\rho_0 = 2.4048$ is the first root of Bessel function.

3.2 Particle in 3D box

3.2.1a Particle in an infinite cubical box

Let us consider a general case i.e. a box with dimensions a, b and c:

The potential is

$$V(x, y, z) = \begin{cases} \infty \; if \; x < 0; \; y < 0; z < 0 \\ 0 \; if \; 0 < x < a; \; 0 < y < b; 0 < z < b \\ \infty \; if \; x \geq a; y \geq b; z \geq c \end{cases} \qquad (3.28)$$

The Schrodinger equation to solve is

$$-\frac{\hbar^2}{2m}\left[\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)+V(x,y,z)\right]\Psi(x,y,z)=E\Psi(x,y,z) \qquad (3.29)$$

Let us consider solution of above equation is $\Psi(x,y,z)=\Psi_x\,\Psi_y\,\Psi_z$; where $\Psi_x\,,\Psi_y$ *and* Ψ_z are the functions of only x, y and z respectively.

Substituting the solution in eq. 3.29 and rearranging the terms to yield in the box region where V=0, the eq. 3.29 becomes

$$-\frac{\hbar^2}{2m}\left[\left(\frac{1}{\Psi_x}\frac{d^2\Psi_x}{dx^2}+\frac{1}{\Psi_y}\frac{d^2\Psi_y}{dy^2}+\frac{1}{\Psi_z}\frac{d^2\Psi_z}{dz^2}\right)\right]=E \qquad (3.30)$$

Let us consider $E=E_x+E_y+E_z$ and using variable separable method for a rectangular box eq. 3.30 transforms into two equations each consisting of one variable only.

$$\frac{d^2\Psi_x}{dx^2}+{k_x}^2\Psi_x=0$$

$$\frac{d^2\Psi_y}{dy^2}+{k_y}^2\Psi_y=0 \qquad (3.31)$$

$$\frac{d^2\Psi_z}{dz^2}+{k_z}^2\Psi_z=0$$

Where ${k_x}^2=\frac{2mE_x}{\hbar^2}$, ${k_y}^2=\frac{2mE_y}{\hbar^2}$and ${k_z}^2=\frac{2mE_z}{\hbar^2}$The general solution for the above equations is

$$\Psi_x=Ae^{ik_xx}+Be^{-ik_xx};\ \Psi_y=Ce^{ik_yy}+De^{-ik_yy};\ \Psi_z=Me^{ik_zz}+Ne^{-ik_zz}$$

For this the boundary conditions are

$$\Psi_x(0)=0$$

$$\Psi_x(a)=0$$

$$\Psi_y(0)=0 \qquad (3.32)$$

$$\Psi_y(b)=0$$

$$\Psi_z(0)=0$$

$$\Psi_z(c)=0$$

Applying the boundary conditions

$$\Psi_x(0)=A+B=0\rightarrow B=-A$$

$$\Psi_x(a)=Ae^{ik_xa}+Be^{-ik_xa}=0$$

This leads to

$$2isin(k_x a) = 0$$

$$sin(k_x a) = \sin(n_x \pi)$$

$$\Rightarrow k_x a = n_x \pi$$

$$\Rightarrow E_x = \frac{{n_x}^2 h^2}{8ma^2}$$

Similarly solving the equation for y and z, we get

$$E_y = \frac{{n_y}^2 h^2}{8mb^2}$$

$$E_z = \frac{{n_z}^2 h^2}{8mc^2}$$

Thus total energy,

$$E = \frac{{n_x}^2 h^2}{8ma^2} + \frac{{n_y}^2 h^2}{8mb^2} + \frac{{n_z}^2 h^2}{8mc^2} \tag{3.33}$$

and by normalizing the wavefunction we get,

$$\Psi(x, y, z) = \sqrt{\frac{2}{a}} sin\left(\frac{n_x \pi}{a} x\right) \sqrt{\frac{2}{b}} sin\left(\frac{n_y \pi}{b} y\right) \sqrt{\frac{2}{c}} sin\left(\frac{n_z \pi}{c} z\right) \tag{3.34}$$

For a cube: $a = b = c$

Energy: $$E = \frac{({n_x}^2 + {n_y}^2 + {n_z}^2) h^2}{8ma^2}$$

$$\Psi(x, y, z) = \sqrt{\frac{8}{a^3}} sin\left(\frac{n_x \pi}{a} x\right) sin\left(\frac{n_y \pi}{a} y\right) sin\left(\frac{n_z \pi}{a} z\right)$$

3.2.1b Particle in a spherical box

Let us consider a spherical box of radius R. The potential inside the box is 0 and outside of the box is ∞

i.e. $$V(r) = \begin{cases} 0 & if\ 0 < r < R \\ \infty & if\ r \geq R \end{cases}$$

such that the boundary conditions for the wave function would be

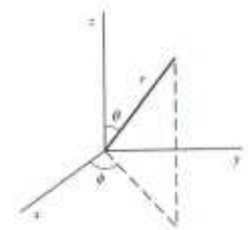
$$\Psi(R, \theta, \phi) = 0 \forall \theta, \phi$$

Transforming the Schrodinger question from Cartesian co-ordinates to polar coordinates, the transformation equation are

$$x = r sin\theta cos\phi$$
$$y = r sin\theta sin\phi \qquad (3.35)$$
$$z = r cos\theta$$

Such that $\quad r = \sqrt{x^2 + y^2 + z^2} \quad$ and $\quad \phi = \tan^{-1}\left(\frac{y}{x}\right)$

$$\theta = \tan^{-1}\left(\frac{\sqrt{x^2+y^2}}{z}\right) \quad \text{or } \theta = \cos^{-1}\left(\frac{z}{r}\right)$$



Transforming the partial differentiation in terms of r and θ ,

$$\left(\frac{\partial}{\partial x}\right)_{y,z} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta}$$

$$\left(\frac{\partial}{\partial y}\right)_{z,x} = \left(\frac{\partial r}{\partial y}\right)_{z,x}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial y}\right)_{z,x}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial y}\right)_{z,x}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta} \qquad (3.36)$$

$$\left(\frac{\partial}{\partial z}\right)_{x,y} = \left(\frac{\partial r}{\partial z}\right)_{x,y}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left(\frac{\partial \theta}{\partial z}\right)_{x,y}\left(\frac{\partial}{\partial \theta}\right)_{r,\phi} + \left(\frac{\partial \phi}{\partial z}\right)_{x,y}\left(\frac{\partial}{\partial \phi}\right)_{r,\theta}$$

Using the transformation

$$\left(\frac{\partial^2}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2}{\partial y^2}\right)_{z,x} + \left(\frac{\partial^2}{\partial z^2}\right)_{x,y} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

Schrodinger equation for spherical box becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial \phi^2} + 0\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

Considering the solution for the above equation,

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

Substituting into Schrodinger equation and separating the variables ,

$$-\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) - 2mr^2E - \frac{\hbar^2}{Y(\theta,\phi)}\left(\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial Y(\theta,\phi)}{\partial \theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial \phi^2}\right) = 0 \qquad (3.37)$$

Let us consider

$$\frac{\hbar^2}{Y(\theta,\phi)}\left(\frac{1}{sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial Y(\theta,\phi)}{\partial \theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial \phi^2}\right) = -L^2 \qquad (3.38)$$

Substituting in eq. 3.37 and rearranging,

$$-\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)-2mr^2E+L^2=0$$

$$-\frac{\hbar^2}{2mr^2R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)+\frac{L^2}{2mr^2}-E=0 \quad (3.39)$$

Equations 3.38 and 3.39 are angular and radial equations respectively.

Considering $Y(\theta,\phi)=P(\theta)F(\phi)$

Substituting in eq. 3.38

$$\frac{L^2}{\hbar^2}sin^2\theta-\left(\frac{sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)+\frac{1}{F(\phi)}\frac{\partial^2F(\phi)}{\partial\phi^2}\right)=0$$

Separating the variables,

$$\frac{L^2}{\hbar^2}sin^2\theta-\frac{sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)=0 \quad (3.40)$$

$$\frac{1}{F(\phi)}\frac{\partial^2F(\phi)}{\partial\phi^2}=0 \quad (3.41)$$

Equations (3.39), (3.40) and (3.41) and the functions of only r, θ and ϕ respectively.

Taking, Solution of eq 3.41 be $F(\phi)\propto e^{im_l\phi}$

Eq 3.41 becomes,

$$\frac{\hbar^2}{F(\phi)}\frac{\partial^2F(\phi)}{\partial\phi^2}=-m_l^2\hbar^2 \quad (3.42)$$

And eq. 3.40 becomes

$$\frac{1}{P(\theta)}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial P(\theta)}{\partial\theta}\right)-\frac{m_l^2}{sin^2\theta}=-\frac{L^2}{\hbar^2} \quad (3.43)$$

Taking the substitution x=cosθ, Eq. 3.43 becomes

$$(1-x^2)\frac{d^2P}{dx^2}-2x\frac{dP}{dx}+\left[\frac{L^2}{\hbar^2}-\frac{m_l^2}{(1-x^2)}\right]P=0$$

Which is form of Legendre's equation.

This equation will have a solution only if

$$\frac{L^2}{\hbar^2}=l(l+1)$$

$$\frac{L^2}{\hbar^2}-m_l^2\geq 0; l>|m_l|$$

The solution Legendre's function will be

$$P_{m_l}^l(x) = \frac{(-1)^l}{2^l\, l!}(1-x^2)^{l/2}\frac{d^l}{dx^l}(x^2-1)^l$$

There angular part of the solution will be

$Y_{l,m_l}(\theta,\phi) = P(\theta)F(\phi) = P_{m_l}^l(cos\theta).e^{im_l\phi}$ for $l > |m_l| \& \, l > 0$

Solution of radial part

$$-\frac{\hbar^2}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) - 2mr^2E + L^2 = 0$$

Assuming $u(r) \equiv rR(r)$

The radial equation reduces to

$$\frac{d^2u}{dr^2} = \left(\frac{l(l+1)}{r^2} - \frac{2mE}{\hbar^2}\right)u$$

Where $L^2 = l(l+1)$

Let us define, $k^2 = \frac{2mE}{\hbar^2}$

This equation is of the form of Bessel's equation. R(r) are the spherical Bessel functions then,

$$u_l(r) = arj_l(kr) + brn_l(kr)$$

Where

$$j_p(x) = (-x)^p\left(\frac{1}{x}\frac{d}{dx}\right)^p\frac{sinx}{x} \& n_p(x) = -(-x)^p\left(\frac{1}{x}\frac{d}{dx}\right)^p\frac{cosx}{x}$$

When $r \to 0$

$$j_p(x{\sim}0) = \frac{2^p p!}{(2p+1)!}x^p \& n_p(x{\sim}0) = -\frac{2^p p!}{(2p+1)!}x^{-(p+1)}$$

The spherical Bessel functions are oscillatory in nature and have zero many times. The functions $n_p(x)$ are not square-integrable at r=0, whereas the functions $j_p(x)$ are well defined in the entire region. Hence $n_p(x)$ are unphysical, and that the radial wavefunction $R_{n,l}(r)$ is thus only proportional to $j_p(x)$. The general solution of the Schrodinger equation is

$$\Psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\, Y_{l,m_l}(\theta,\phi)$$

In order to satisfy the boundary condition at r=R, the value of k must be chosen such a way so that z=kR corresponds to one of the zeros of $j_p(x)$ and given by

$$kR = z_{n,l}$$

for n=1,2,3.

Therefore the allowed energy states will be

$$E_{n,l} = {z_{n,l}}^2 \frac{\hbar^2}{2mR^2}$$