Unit II – Quantum Mechanics of simple systems

The Schrodinger's wave equation can be applied to any physical system and the solution of the wave equation yields the wave function of the system. The wave function is probability amplitude and contains information about the physical state (observables of the system). The wave function has then to be a well behaved wave function to represent a moving particle.

The template for solving the Schrodinger's wave equation is:

1. Define / set up the physical system (define particle nature, boundaries of potential, total energy of the particle etc)
2. Write the Schrodinger's wave equation and apply the known conditions
3. Obtain the general form of the wave function
4. Check / verify the wave function for it's characteristics
   - finiteness, discreteness and continuity of ψ and its derivatives,
   - normalization of the wave functions
5. Interpret the solution and get the implications on the quantum system.

Free Particle solution

A particle is said to be a free particle when it experiences no external forces.

Thus the force given by $F = -\frac{dV}{dx} = 0$. This implies that either V is zero or V is a constant.

The simplest case then could be when the particle is experiencing no potential i.e., V=0.

The Schrödinger's time independent one dimensional wave equation for the system simplifies to

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x).}{dx^2} + E\psi(x) = 0 \quad \text{or} \quad \frac{d^2\psi(x).}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

$\frac{d^2\psi(x).}{dx^2} + k^2\psi = 0$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$ is the propagation constant.

The solution of this differential equation is $\psi = Ae^{ikx} + Be^{-ikx}$ where A and B are constants.

The energy of the particle is given by $E = \frac{\hbar^2 k^2}{2m}$.

Since the free particle is moving in a zero potential region and there is no restriction on wave number or the energy of the particle, we conclude that the total energy of the particle is kinetic in nature with no implications of quantization.

Potential Steps

The behavior of a moving particle when it encounters a potential field along its path is the first step in solving problems in Quantum Mechanics. In reality the potential field varies inversely as the distance from the source of the potential (i.e., $V \propto \frac{1}{r}$). However the solution of the Schrödinger's wave equation becomes difficult if the actual potential variations are considered. It is therefore necessary and sufficient if the potentials are approximated to simpler (solvable) systems.

This leads to the concept of potential steps where the potential energy vs. distance graphs show a discrete jump from a zero value to a constant value V_0. However the behavior of the wave function (representing the particle) can have different responses depending on the energy of the particle as compared to the energy of the potential step. The energy of the particle can be greater or less than the energy of the potential step.

The problem can be divided as a two region problem, region I in which the potential V=0 and the region II in which the potential V= V_0.

The Schrödinger's wave equation $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$

for the region I with V=0 this becomes $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

The solution of the equation in region I is given by

$$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$$

where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ and the debroglie wavelength $\lambda_1 = \frac{h}{\sqrt{2mE}}$

The component with the positive exponent represents the oncoming wave and the negative exponent represents the reflected wave at the boundary x=0

In region II the nature of the wave function will depend on the energy E of the particle in comparison to the energy of the potential step.

<u>Case I .</u> If the energy E of the particle is greater than the energy of the potential (E>V_o) step then the Schrödinger's wave equation for the region II can be written as

$$\frac{\partial^2\psi_2}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_o)\psi_2 = 0$$

with the solution being $\psi_2 = De^{ik_2x}$ where $k_2 = \sqrt{\frac{2m(E-V_o)}{\hbar^2}}$. The nature of the wavefunction remains the cyclic and the particle propagates in region II with reduced kinetic energy (E-V_o). The momentum is given by $\hbar k_2 = \sqrt{2m(E - V_o)}$ and the corresponding debroglie wavelength $\lambda_2 = \frac{h}{\sqrt{2m(E-V_o)}}$ which is longer than the debroglie wavelength in region I.

In this case the constants B and D can be found in terms of A by applying the boundary condition that the wave function and its derivatives are finite and continuous at x=0.

$$at\ x = 0 \quad \psi_{1(x=0)} = \psi_{II(x=0)}\ gives\ A + B = D$$

$$at\ x = 0 \quad d\psi_{1(x=0)} = d\psi_{II(x=0)}\ gives\ (A - B)k_I = Dk_{II}$$

Solving the simultaneous equations we get

$D = 2A * \left(\frac{k_I}{k_I+k_{II}}\right)$ and $B = A * \left(\frac{k_I - k_{II}}{k_I+k_{II}}\right)$

It is seen that the coefficient B of the reflected component is non zero implying that there is a small probability of reflection at x=0 even if the energy of the particle is greater than the potential step V_o.

The reflection coefficient can be written as $R = \frac{reflected\ \ flux}{incident\ \ flux} = \frac{B^*B\,v_1}{A^*A\,v_1}$ and the transmission coefficient $T = \frac{transmitted\ \ flux}{incident\ \ flux} = \frac{D^*D\,v_2}{A^*A\,v_1}$ where v_1 and v_2 are the velocities of the particles in the two regions.

It is observed that R+T = 1, i.e. the flux incident has to be partially reflected and partially transmitted.

R and T are the relative probabilities of reflection and transmission at the potential step.

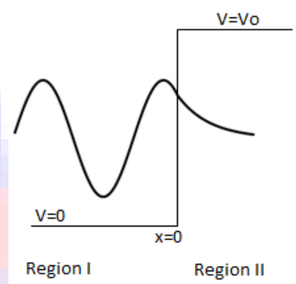
Case II .

In region I the behavior of the particle is the same at the previous case (since V=0) and the wave function will be

$$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$$

If the energy E of the particle is lesser than the energy of the potential step ($E < V_o$), then the Schrödinger's wave equation for the region II can be written as

$$\frac{\partial^2\psi_2}{\partial x^2} - \frac{2m}{\hbar^2}(V_o - E)\psi_2 = 0$$



with the solution being $\psi_2 = Fe^{-\alpha x} + Ge^{\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o - E)}{\hbar^2}}$

The second part of the wave function $Ge^{\alpha x}$, makes ψ_2 infinite for large values of x and hence cannot be part of the wave function. Setting the coefficient G to be zero the wave function reduces to

$$\psi_2 = Fe^{-\alpha x}$$

The wave function has a finite value and decays exponentially in region II. Thus there exists a finite probability for the particle to be found in region II ($since\ \psi_2{}^*\psi_2\ is\ non\ zero$) which is unlike the classical solution.

(In an exponential decay the wave function decays to $\frac{1}{e}$ it's value at x=0. At x=0 the value of the function $\psi_2 = F$. The changes in this $\psi_2 = Fe^{-\alpha x}$ function becomes insignificant at some Δx.

At Δx the function $\psi_2(\Delta x) = Fe^{-\alpha\Delta x} = F * \frac{1}{e} = F * e^{-1}$.

This gives us $\alpha\Delta x = 1$ or $\Delta x = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_o - E)}}$).

The wave function becomes insignificant at a distance $\Delta x = \frac{\hbar}{\sqrt{2m(V_o - E)}}$ which is the penetration depth in region II. The penetration depth increases as the energy of the particle increases.

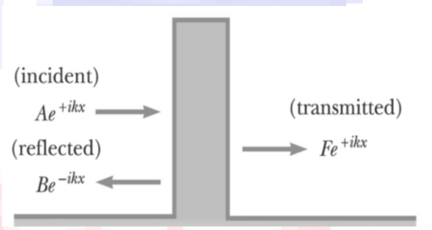
In the second region the kinetic energy of the particle is negative which implies that the particle cannot physically exist in the second region.

We conclude that when a particle (or beam of particles with identical E) is incident on a potential step, there is a quantum mechanical effect which -

- the particle can be reflected back even if the energy of the particle E > V_o.
- the particle can have a small but finite probability of being in the second region even if E<V_o.

Potential Barrier

The potential barrier is a region in space where the potential is a constant V_o for all 0<x<L and V=0 for the all x<0 and x>L



A particle of mass m and energy E < V_o, incident on the potential barrier is represented by a forward moving wave. Since E <V_o classically we expect the particle to be reflected back at the potential barrier and there is no probability of finding the particle in the region beyond the barrier.

In **region I** with V=0 the Schrödinger's wave equation becomes $\boldsymbol{\frac{\partial^2\psi_1}{\partial x^2}+\frac{2m}{\hbar^2}E\psi_1=0}$ (1)

The solution of the equation in region I is given by

$$\boldsymbol{\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}} \qquad (2)$$

where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ and the debroglie wavelength $\lambda_1 = \frac{h}{\sqrt{2mE}}$

The first term in equation 2 represents the incident wave and the second term represents the reflected component.

In **region II** since E<V$_O$, the Schrödinger's wave equation for the region II can be written as

$$\boldsymbol{\frac{\partial^2\psi_2}{\partial x^2}-\frac{2m}{\hbar^2}(V_o-E)\psi_2=0} \qquad (3)$$

with the solution being $\boldsymbol{\psi_2 = De^{-\alpha x}}$ where $\boldsymbol{\alpha = \sqrt{\frac{2m(V_o-E)}{\hbar^2}}}$ (4)

In region II the nature of the wave function changes to an exponentially decaying function. The penetration depth is given by $\Delta x = \frac{\hbar}{\sqrt{2m(V_o-E)}}$ (5)

And in **region III,** the potential being 0, the wave equation is $\frac{\partial^2\psi_3}{\partial x^2}+\frac{2m}{\hbar^2}E\psi_3 = 0$

and the wave function is given by $\psi_3 = Ge^{ik_3x}$ (6)

where $k_3 = \sqrt{\frac{2mE}{\hbar^2}}$ and the debroglie wavelength $\lambda_3 = \frac{h}{\sqrt{2mE}}$

The strength of the reflected and transmitted waves can be evaluated by applying the boundary conditions

$$\psi_1 = \psi_2 \; at \; x = 0 \quad and \quad \psi_2 = \psi_3 \; at \; x = L$$

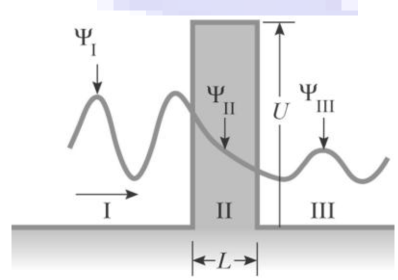
and $\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx} \; at \; x = 0 \quad and \quad \frac{d\psi_2}{dx} = \frac{d\psi_3}{dx} \; at \; x = L$

The transmission coefficient $T = \frac{transmitted \;\; flux}{incident \;\; flux} = \frac{G^*G\, v_3}{A^*A\, v_1}$

where v_1 and v_3 are the velocities of the particle in region I and III. Since the energy of the particle is the same in the two regions the velocities are also same and

the transmission coefficient can be evaluated approximately as

$$T = \frac{G^*G}{A^*A} \approx 16\frac{E}{V_o}\left[1-\left(\frac{E}{V_o}\right)^2\right] e^{-2k_2a} \cong e^{-2k_2a}$$



Thus the probability of transmission is more if either $\boldsymbol{k_2}$ or $\boldsymbol{a}$ is small. Smaller $\boldsymbol{k_2}$ implies smaller $(V_o - E)$. Thus particles with higher energy have higher transmission probability through the barrier.

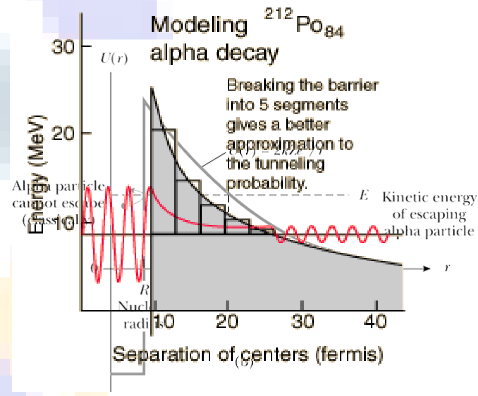
If the width of the barrier ***L* is less than the penetration depth** Δx then there is a finite probability that the particle is transmitted across the barrier.

This process of transmission through a potential barrier even when the energy of the particle is lesser than the barrier potential is known as barrier tunneling or the quantum mechanical tunneling.

It is also noted that for all values of E, there is always a reflected component which is given by **R = 1 – T** which is higher than the transmitted coefficient.

[The particle in the second region has a negative Kinetic energy and this is not a physical reality. However, the particle can exchange energies with the field (potential) without violating the uncertainty principle $\Delta E.\Delta t = \frac{h}{4\pi}$*. Thus the energy exchange has to happen in a time interval of* $\Delta t = \frac{h}{4\pi\Delta E}$*. This gives a time interval which is extremely small of the order of femto seconds. Thus the particle has to cross the barrier almost instantaneously]*

<u>Radioactive alpha decay as a case of barrier tunneling</u>



Emission of α particles (helium nucleii) in the decay of radioactive elements can be example of tunneling.

The positive charge on the nucleus creates a non linear potential barrier around the nucleus. This potential barrier is estimated to be as high as 20MeV at the surface.

In the radioactive α decay of the nucleus, two protons and two neutrons are emitted as a single entity (a doubly charged He nucleus). The process of radioactive decay of α particles with low energies compared to the barrier potential could be explained as a case of barrier tunneling.

The potential which varies inversely as the distance from the surface of the nucleus can be approximated to a triangular potential. This can then be modeled as a series of rectangular potentials of thin slices of thickness Δr. The potential barrier for each of these slices decrease by a small ΔV.

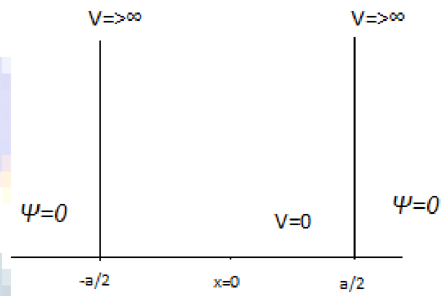
The transmission coefficients for each of the slice of potential barrier can evaluated with T = $e^{-2\alpha a}$ and the total transmission probability is the product of all these individual transmission probabilities. This gives a reasonable estimate of the tunneling probabilities of alpha particles.

Tunneling rate is very sensitive to small changes in energy and size of the nucleus and account for the wide range of decay times to different radioactive nuclei.

Taking the alpha particles to be in a state of constant motion with a very high kinetic energy, the frequency of approach to the nuclear surface can be estimated to be the diameter of the nucleus divided by the velocity of the particles. This frequency when multiplied by the transmission co-efficient gives us the probability that an alpha particle is emitted out of the nucleus. The inverse of this probability is then the mean life time for alpha decay of the radioactive nucleus.

Particle in a Box with infinite potentials at the walls

A particle with mass m and energy E is confined in a one dimensional box with infinite potential at the boundaries. Defining the boundaries to be $x = -\frac{a}{2}$ and $x = +\frac{a}{2}$ where the potential tends to infinity. The particle is confined to the region $-\frac{a}{2} < x < +\frac{a}{2}$ and cannot be found in regions outside the boundaries $x < -\frac{a}{2}$ and $x > \frac{a}{2}$. The potential inside the region $-\frac{a}{2} < x < +\frac{a}{2}$ is V=0.



The Schrödinger's wave equation $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$

in the region within the well V=0 this becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$$

$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$

The solution of the equation in region $-\frac{a}{2} < x < \frac{a}{2}$ is given by

$$\psi(x) = Asin(kx) + Bcos(kx)$$

Applying the boundary condition that $\psi = 0$ at $x = -\frac{a}{2}$ and $x = \frac{a}{2}$

At $x = -\frac{a}{2}$ $\psi\left(x = \frac{a}{2}\right) = Asin\left(-k\frac{a}{2}\right) + Bcos\left(k\frac{a}{2}\right) = 0$ $gives$

$$-Asin\left(k\frac{a}{2}\right) + Bcos\left(k\frac{a}{2}\right) = 0 \qquad [1]$$

At $x = \frac{a}{2}$ $\psi\left(x = \frac{a}{2}\right) = Asin\left(k\frac{a}{2}\right) + Bcos\left(k\frac{a}{2}\right) = 0$ $gives$

$$Asin\left(k\frac{a}{2}\right) + Bcos\left(k\frac{a}{2}\right) = 0 \qquad [2]$$

The above two conditions imply that if $A = 0$ $then$ $B \neq 0$ and if $A = 0$ $then$ $B \neq 0$ since when $sin\left(k\frac{a}{2}\right) = 0,$ $cos\left(k\frac{a}{2}\right) \neq 0$ and $vice$ $versa.$

Taking the first condition that $A = 0$ and $B \neq 0$

This gives the result that when

$$\boldsymbol{cos\left(k\frac{a}{2}\right) = 0, \quad k\frac{a}{2} = (2n-1)\frac{\pi}{2} \ or \ k = (2n-1)\frac{\pi}{a}}$$ **(an odd multiple of $\frac{\pi}{a}$)**

The second condition $B = 0$ $then$ $A \neq 0$ which implies that

$$\boldsymbol{sin\left(k\frac{a}{2}\right) = 0 \ or \ k\frac{a}{2} = n\pi \ or \ k = 2n\frac{\pi}{a}}$$ **(an even multiple of $\frac{\pi}{a}$)**

The above two conditions can be combined and generalized to give the allowed values of the wave number

$$\boldsymbol{k = \frac{n\pi}{a}} \ with \ \mathbf{n} = \mathbf{1, 2, 3} \ldots.$$

The wave function then reduces to

$$\boldsymbol{\psi(x) = B\,cos(kx) \quad for \ n \ odd \ and}$$

$$\boldsymbol{\psi(x) = Asin(kx) \quad for \ n \ even}$$

The allowed values of k give the allowed states with energy $\boldsymbol{E_n = \frac{h^2n^2}{8ma^2}}$

The wave functions can be normalized for the individual states to give the constants A and B.

The constant A can be evaluated by normalizing the wave function ie., integrating the function between limits of $-\frac{a}{2}$ and $\frac{a}{2}$ $\int \psi^*\psi\, dx = 1$

$$\int_{-a/2}^{a/2}\left[Asin(\frac{n\pi}{a}x)\right]^2 dx = \frac{A^2}{2}\int_{-a/2}^{a/2}\left[1-\cos(\frac{2n\pi}{a}x)\right]dx$$

This on integration gives $\frac{A^2}{2}\left[x-\frac{L}{2n\pi}\sin(\frac{2n\pi}{a}x)\right]_{-a/2}^{a/2} = \frac{A^2}{2}[a-0] = 1$

This gives a value of $A = \sqrt{\frac{2}{a}}$

The exact form of the wave function becomes

$$\psi_n(x) = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right) \quad for\ n\ odd \qquad \text{(even parity)}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \quad for\ n\ even \qquad \text{(odd parity)}$$

[Parity *of a function is determined by changing the sign of the variable. If the function remains unchanged then it is defined as an even parity function and if the function changes sign then it is an odd parity function.*

$If\ \psi(-x) = \psi(x)\ then\ the\ function\ has\ an\ even\ parity\ and$

$if\ \ \psi(-x) = -\psi(x)\ then\ the\ function\ has\ an\ odd\ parity.$]

Eigen functions and Eigen values

Eigen functions are exact wave functions which represent the state of the system completely. Eigen functions are exact solutions of the Schrodinger's wave equation.

The even parity Eigen function of a particle in a infinite potential well $\psi_n = \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi}{a}x\right)$ and odd parity Eigen function of a particle in a infinite potential well $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$

The first three states correspond to n=1,2 and 3

The Eigen functions are

$$\psi_1 = \sqrt{\frac{2}{a}}\cos\left(\frac{\pi x}{a}\right)$$

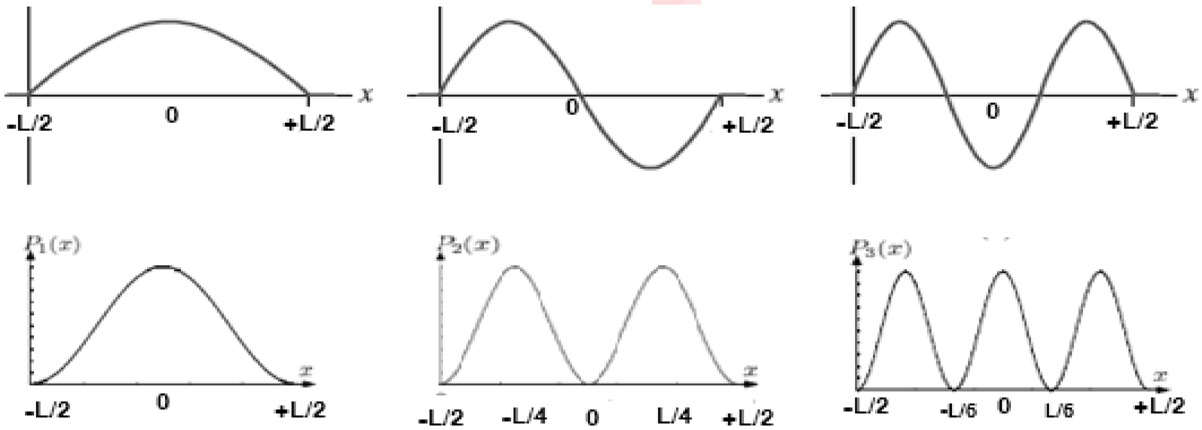
$$\psi_2 = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)$$

$$\psi_3 = \sqrt{\frac{2}{a}}\cos\left(\frac{3\pi x}{a}\right)$$

Eigen values of the system are the exact values of the physical parameters of the system obtained from an Eigen function using operators.

The Eigen energy values is given function $E_n = \frac{h^2n^2}{8mL^2}$ where n = 1,2 3…

And the Eigen values are $E_1 = \frac{h^2}{8ma^2}$ $\quad E_2 = \frac{h^2 2^2}{8ma^2}$ $\quad E_3 = \frac{h^2 3^2}{8ma^2}$



Probability density $\psi^*\psi$ for the first three states is obtained by squaring the corresponding wave functions $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ or $\psi_n = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right)$. The square of the function is close to a gaussian shape.

In the first state n=1, the probability of finding the particle is maximum at $x = 0$ and the area under the curve represents the total probability of finding the particle in the ground state which is 1.00

In the second state n=2, the probability of finding the particle is maximum at $x = -{}^{a}/_{4}$ and $x = +{}^{a}/_{4}$ .The area under one segment of the curve represents the probability of finding the particle in the first excited state and is ${}^{1}/_{2} = 0.5$.

In the third state n=3,the probability of finding the particle is maximum at $x = -{}^{a}/_{3}, x = 0$ and $x = +{}^{a}/_{3}$ .The area under one segment of the curve represents the probability of finding the particle in the first excited state and is ${}^{1}/_{3} = 0.333$.

In general, the probability of finding the particle in the nth state, in a segment of length ${}^{L}/_{n}$ is ${}^{1}/_{n}$.

Particle in a 2D well of infinite potential at the boundaries

A particle in a two dimensional well has two degrees of freedom and can move in XY plane. This can be treated as a case of particle confined in a well with infinite potentials at the boundaries of the x and y directions. The momentum **P** of a particle moving in the x y plane can be resolved into two independent momentum components $\mathbf{P_x}$ and $\mathbf{P_y}$ along the x and y directions.

The problem can be analyzed as two independent problems for the x and y directions and the solutions would be similar to the one dimensional infinite potential well problem.

The Schrodinger's equation can be written as $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2} E\psi = 0$

$\frac{\partial^2\psi}{\partial x^2} + {k_x}^2\psi = 0$ where $k_x = \sqrt{\frac{2mE_x}{\hbar^2}}$ and the solutions to this are

The eigen functions for the x direction

$$\psi_n(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_x\pi}{a} x\right) \; for \; n_x \; odd \qquad \text{(even parity)}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x\pi}{a}x\right) \quad for\ n_x\ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_x = \frac{h^2 {n_x}^2}{8mL^2}$ where n_x can take values 1,2,3,4,5….

The particle's movement in the y direction can be analysed similarly.

The Schrodinger's equation can be written as $\frac{\partial^2\psi}{\partial y^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2\psi}{\partial y^2} + k^2\psi = 0$ where $k_y = \sqrt{\frac{2mE_y}{\hbar^2}}$ and the solutions to this are

The eigen functions for the y direction

$$\psi_n(y) = \sqrt{\frac{2}{a}} \cos\left(\frac{n_y\pi}{a}y\right) \quad for\ n_y\ odd \qquad \text{(even parity)}$$

$$\psi_n(y) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_y\pi}{a}y\right) \quad for\ n_y\ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_y = \frac{h^2 {n_y}^2}{8mL^2}$ where n_y can take values 1,2,3,4,5….

The total energy of the system is then $E_n = E_x + E_y = \frac{h^2 {n_x}^2}{8mL^2} + \frac{h^2 {n_y}^2}{8mL^2} = \frac{h^2}{8mL^2}({n_x}^2 + {n_y}^2)$

The allowed energy states of the particle are then decided by the allowed values of n_x and n_y.

The first allowed state is the ground state of the system and given by $E_{11} = 2\frac{h^2}{8mL^2} = 2E_o$ where $E_o = \frac{h^2}{8mL^2}$.

The second allowed state of the system is given by $E_{21} = 5E_o$ which is also the energy of the state E_{12}. There are two allowed states for the same energy value of $5E_o$. This state is then doubly degenerate.

In general for a 2D system in when $n_x = n_y$ the energy state is a single state and when $n_x \neq n_y$ the energy state has a degeneracy factor of 2.

The separation between energy states does not increase monotonically as in the 1D system.

The wave functions of the corresponding states can be written as

$\psi_{11} = \frac{2}{a}\cos\left(\frac{\pi}{a}x\right) \cos\left(\frac{\pi}{a}y\right)$ for the first allowed state with $n_x = n_y = 1$

$\psi_{21} = \frac{2}{a}\sin\left(\frac{2\pi}{a}x\right) \cos\left(\frac{\pi}{a}y\right)$ for the second allowed state with $n_x = 2\ and\ n_y = 1$

$\psi_{12} = \frac{2}{a}\cos\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}y\right)$ for the allowed state with $n_x = 1\ and\ n_y = 2$

From the wave functions we realize that the two states are different but has the energy eigen value of $5E_o$.

Particle in a 3D Box of infinite potential at the boundaries

A particle in a three dimensional well has three degrees of freedom and can move in 3D space. This can be treated as a case of particle confined in a box of sides L with infinite potentials at the boundaries of the x, y and z directions. The momentum **P** of a particle moving in space can be resolved into three independent momentum components $\mathbf{P_x}$, $\mathbf{P_y}$ and $\mathbf{P_z}$ along the coordinate axes.

This problem can be analysed as three independent problems for the x, y and z directions and the individual solutions will be similar to the one dimensional infinite potential well problem.

The Schrodinger's equation can be written as $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0$ where $k_x = \sqrt{\frac{2mE_x}{\hbar^2}}$ and the solutions to this are

The eigen function for the x directions

$$\psi_n(x) = \sqrt{\frac{2}{a}}\cos\left(\frac{n_x\pi}{a}x\right) \quad for\ n_x\ odd \qquad \text{(even parity)}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi}{a}x\right) \quad for\ n_x\ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_x = \frac{h^2 n_x{}^2}{8mL^2}$ where n_x can take values 1,2,3,4,5….

The particle's movement in the y direction can be analysed.

The Schrodinger's equation can be written as $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2\psi}{\partial y^2} + k^2\psi = 0$ where $k_y = \sqrt{\frac{2mE_y}{\hbar^2}}$ and the solutions to this are

The eigen function for the y directions

$$\psi_n(y) = \sqrt{\frac{2}{a}}\cos\left(\frac{n_y\pi}{a}y\right) \quad for\ n_y\ odd \qquad \text{(even parity)}$$

$$\psi_n(y) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_y\pi}{a}y\right) \quad for\ n_y\ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_y = \frac{h^2 n_y{}^2}{8mL^2}$ where n_y can take values 1,2,3,4,5….

The particle's movement in the z direction can be analysed.

The Schrodinger's equation can be written as $\frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2\psi}{\partial y^2} + k_z{}^2\psi = 0$ where $k_z = \sqrt{\frac{2mE_z}{\hbar^2}}$ and the solutions to this are

The eigen functions for the z direction

$$\psi_n(z) = \sqrt{\frac{2}{a}}\cos\left(\frac{n_z\pi}{a}y\right) \quad for\ n_z\ odd \qquad \text{(even parity)}$$

$$\psi_n(z) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_z\pi}{a}y\right) \quad for\ n_z\ even \qquad \text{(odd parity)}$$

with the eigen values for energy as $E_y = \frac{h^2 n_y{}^2}{8mL^2}$ where n_y can take values 1,2,3,4,5….

The total energy of the system is then

$$E_n = E_x + E_y + E_z = \frac{h^2 n_x{}^2}{8mL^2} + \frac{h^2 n_y{}^2}{8mL^2} + \frac{h^2 n_z{}^2}{8mL^2} = \frac{h^2}{8mL^2}(n_x{}^2 + n_y{}^2 + n_z{}^2)$$

The allowed energy states of the particle are then decided by the allowed values of n_x, n_y and n_z.

The first allowed state is the ground state of the system and has an energy

$E_{111} = 3\frac{h^2}{8mL^2} = 3E_o$ where $E_o = \frac{h^2}{8mL^2}$.

The second allowed state of the system is given by $E_{211} = 6E_o$ which is also the energy of the state E_{121} *and* E_{123}. There are three allowed states for the same energy value of $6E_o$. This state is then triply degenerate.

The analysis of the first few states reveal that the states are non degenerate when $n_x = n_y = n_z$. The states have a degeneracy factor of 3 whenever two of the numbers $n_x,\ n_y$ *and* n_z are equal and not equal to the third.

When all the three numbers n_x, n_y *and* n_z are unequal then the energy state would have a degeneracy of 6.

Further the separation between energy states does not increase monotonically as in the 1D system.

The wave functions of the corresponding states can be written as

for the first allowed state with $n_x = 1,\ n_y = 1$ *and* $n_z = 1$

$$\psi_{111} = \left(\frac{2}{a}\right)^{\frac{3}{2}} \cos\left(\frac{\pi}{a}x\right)\ \cos\left(\frac{\pi}{a}y\right)\ \cos\left(\frac{\pi}{a}z\right)$$

the second allowed state with $n_x = 2,\ n_y = 1$ *and* $n_z = 1$

$$\psi_{211} = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{2\pi}{a}x\right)\ \cos\left(\frac{\pi}{a}y\right)\ \cos\left(\frac{\pi}{a}z\right)$$

the allowed state with $n_x = 1,\ n_y = 2$ *and* $n_z = 1$

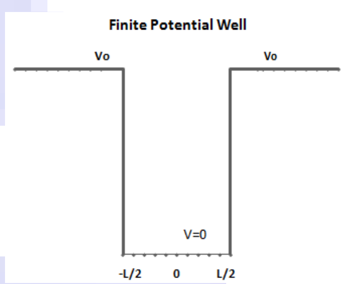
$$\psi_{121} = \frac{2}{a}\cos\left(\frac{\pi}{a}x\right)\ \sin\left(\frac{2\pi}{a}y\right)\ \cos\left(\frac{\pi}{a}z\right)$$

for the allowed state with $n_x = 1,\ n_y = 1$ *and* $n_z = 2$

$$\psi_{112} = \left(\frac{2}{a}\right)^{\frac{3}{2}} \cos\left(\frac{\pi}{a}x\right)\ \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{n_z\pi}{a}z\right)$$

From the wave functions we realize that the three states are different but has the energy eigen value of $6E_o$.

<u>Finite potential well</u>

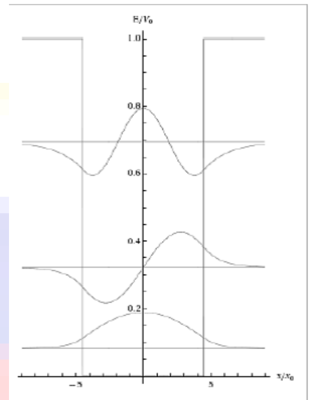


The finite potential well is a closer approximation to real potentials in solids. The particle can be confined to a region with constant potential V_O at the walls $|x| > \frac{L}{2}$.. Inside the potential well region of –L/2 to +L/2 the potential is zero. In this case the SWE for the three regions can can be solved to get the solutions.

Solutions to the Schrödinger equation must be continuous, and as well as the derivatives must be continuous, which are the boundary conditions. However these do not have a exact solution and can be solved using approximations. The nature of the wave functions can be written as

$\psi_1 = De^{\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o - E)}{\hbar^2}}$ for the region x< $^{-L}/_2$

$\psi_2 = A\cos(k_2x)$ $for\ odd\ values\ of\ n$ or $\psi_2 = A\sin(k_2x)$ for even values of n where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$ for the region $-L/_2 < x < L/_2$



The cosine solutions show even parity (symmetric when sign of the function becomes negative) and the sine solutions exhibit odd parity (anti symmetric when sign of the function becomes negative)

$\psi_3 = Ge^{-\alpha x}$ where $\alpha = \sqrt{\frac{2m(V_o - E)}{\hbar^2}}$ for the region x > $L/_2$

The continuity of the wave functions and it's derivatives at the boundaries $-\frac{L}{2}\ and + \frac{L}{2}$ gives the condition that

$\alpha = k\tan(k\frac{L}{2})$ or $\sqrt{(V_o - E)} = \sqrt{\mathrm{E}}\tan(\sqrt{\frac{2mE}{\hbar^2}} * \frac{L}{2})$.

It can be seen that the right hand side and left hand side of the equations contain the same variable E and the nature of the functions are quite different and hence an exact solution do not exist. (Equations of this type are called transcendental equations.)

The energy values of the particle inside the well region have to be found from graphical or approximate methods. However, since the particle is in the finite potential well at least one solution to the problem exists. Or one energy state exist for the particle in the finite potential well. The number of solutions would obviously depend on the height of the finite potential Vo.

The penetration depths in the regions of the potential V_o is given by $\Delta x = \frac{\hbar}{\sqrt{2m(V_o - E_x)}}$ which is a function of E_x.

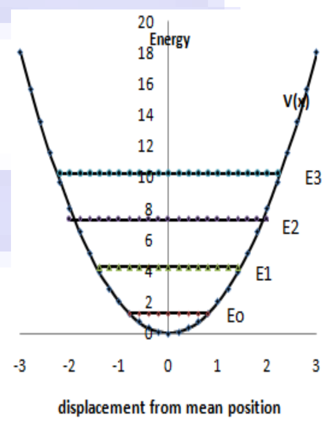
The effective width of the box (defined approx as the points at the wave function becomes insignificant of zero) is then larger and can be approximated as L+2Δx.

Hence the energy values are less than the energy values for the corresponding states of an infinite potential well of the width L.

Harmonic Oscillator

Harmonic oscillator is one of the most fundamental systems in quantum mechanics which gives insight to a variety of problems such as the vibrational molecular spectroscopy.

The classical harmonic oscillator is a bound particle subjected to oscillations about a mean position. However a restoring force that is proportional to the displacement of the particle from a mean position keeps the amplitude of the oscillations within limits . The force equation of such a system in classical physics is $\mathrm{F = ma = m\frac{d^2x}{dt^2} = -kx}$ where k is the force constant given by $\mu\omega^2$ where $\omega = \sqrt{\frac{k}{\mu}}$ is the frequency of vibration and μ is the effective mass of the system.



The potential energy of the system is evaluated as

$\mathrm{V = -\int Fdx = \int kxdx = \frac{1}{2}kx^2 = \frac{1}{2}\mu\omega^2x^2}$.

Using this form of the potential in the Hamiltonian $\mathrm{H}\psi$ we get

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + V\psi(x) = -\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}\mu\omega^2x^2 = E\psi(x)$$

The Schrodinger wave equation can be written as

$$\frac{d^2\psi(x)}{dx^2} + \frac{2\mu}{\hbar^2}\left(E - \frac{1}{2}\mu\omega^2x^2\right)\psi(x) = 0$$

The solution of this equation is of the form

$$\psi(x) = N_n H_n(\xi)e^{-\frac{1}{2}\xi^2} \quad \text{with } n = 0,1,2,3,4..$$

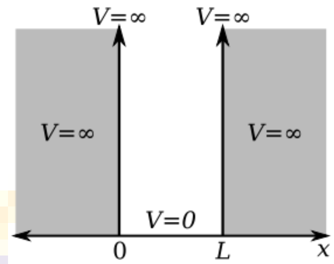
where $\xi = \gamma x$ and $\gamma = \sqrt{\frac{\mu\omega}{\hbar}}$; $N_n = \sqrt{\left[\frac{\gamma}{2^n n!\sqrt{\pi}}\right]}$ and $H_n(\xi)$ are the Hermite polynomials described by $\mathbf{H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi)}$ **for** $\mathbf{n \geq 1}$ and $\mathbf{H_0(\xi)=1}$ and $\mathbf{H_1(\xi) = 2\xi}$

The solutions yield the Eigen energy values of the system as $E_n = (n + \frac{1}{2})\hbar\omega$

This gives the allowed energy states as $\frac{1}{2}\hbar\omega,\ \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega, \dots\dots$

Thus the minimum energy state of the system is a non-zero $\frac{1}{2}\hbar\omega$ where ω is the fundamental frequency of vibration. The higher energy states are then equally spaced at $\hbar\omega$ which is unlike the energy of states in the particle in a box solutions.

[**Particle in a Box with infinite potentials at the walls (boundaries at x=0 to x=L**



A particle in an one dimensional box is confined to be within the boundaries (x=0 and x=L) where the potential tends to infinity. The particle cannot be found outside the boundary x<0 and X>L. The potential inside the well V=0.

The Schrödinger's wave equation $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$

in the region within the well V=0 this becomes $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$

$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0$ where $k = \sqrt{\frac{2mE}{\hbar^2}}$

The solution of the equation in region 0<x<L is given by

$$\psi(x) = Asin(kx) + Bcos(kx)$$

Applying the boundary condition that $\psi = 0\ at\ x = 0\ and\ x = L$

At x=0 $\psi(x=0) = Asin(k0) + Bcos(k0) = 0\ gives\ B = 0$

The wave function then reduces to$\psi(x) = Asin(kx)$

At x=L $\psi(L) = Asin(kL) = 0$.
If A=0 the wave function does not exist and hence $kL = n\pi$

Or $k = n.\frac{\pi}{L}$, thus propagation constant can be only multiples of $\frac{\pi}{L}$

This also gives us the energy $E_n = \frac{h^2n^2}{8mL^2}$

The wave function then reduces to $\psi(x) = Asin(\frac{n\pi}{L}x)$

The constant A can be evaluated by normalizing the wave function ie., $\int_0^L \psi^*\psi\,dx = 1$

$$\int_0^L \left[Asin(\frac{n\pi}{L}x)\right]^2 dx = \frac{A^2}{2}\int_0^L \left[1 - \cos(\frac{2n\pi}{L}x)\right] dx$$

Which on integration gives $\frac{A^2}{2}\left[1 - \frac{L}{2n\pi}\sin(\frac{2n\pi}{L}x)\right]_0^L = \frac{A^2}{2}[L-0] = 1.$

This gives a value of $A = \sqrt{\frac{2}{L}}$

The exact form of the wave function becomes $\psi_n(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi}{L}x)$

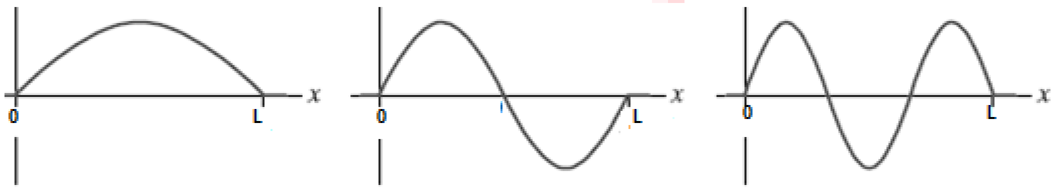
Eigen functions and Eigen values

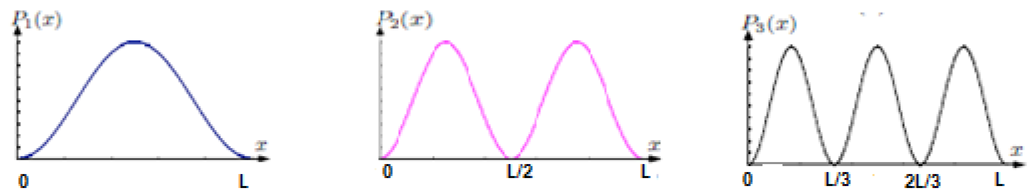
The Eigen function of a particle in a infinite potential well $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ and the Eigen energy values is given function $E_n = \frac{h^2n^2}{8mL^2}$ where n = 1,2 3…

The first three states correspond to n=1,2 and 3

The Eigen fuctions are $\psi_1 = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$ $\psi_2 = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$ $\psi_3 = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi x}{L}\right)$

And the Eigen values are $E_1 = \frac{h^2}{8mL^2}$ $E_2 = \frac{h^2 2^2}{8mL^2}$ $E_3 = \frac{h^2 3^2}{8mL^2}$





Probability density $\psi^*\psi$ for the first three states is obtained by squaring the wave function

$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$. The square of the function is close to a Gaussian shape.

In the first state n=1 the probability of finding the particle is maximum at $L/_2$ and the area under the curve represents the total probability of finding the particle in the ground state which is 1.00

In the second state n=2 the probability of finding the particle is maximum at $L/_4$ and $3L/_4$ .The area under one segment curve represents the probability of finding the particle in the first excited state and is $1/_n = 0.5$.

In the third state n=3 the probability of finding the particle is maximum at $-L/_3$ and $+L/_3$ .The area under one segment curve represents the probability of finding the particle in the first excited state and is $1/_n = 0.333$.

In general, the probability of finding the particle in the nth state, in a segment of length $L/_n$ is $1/_n$.**]**

Numericals

1. Electrons with energies of 0.400 eV are incident on a barrier 3.0 eV high and 0.100 nm wide. Find the probability for these electrons to penetrate the barrier. **(Ans T =19.20%)**

2. A beam of identical electrons is incident on a barrier 6.0 eV high and 2 nm wide. Find the energy of the electrons if 1% of the electrons are to get through the barrier.**(Ans =5.963eV)**

3. An electron and a proton with the same energy E approach a potential barrier whose height U is greater than E. Comment on their tunneling probability.

4. A current beam 10 pico amperes (of identical electrons) is incident on a barrier 5.0 eV high and 1 nm wide. Find the transmitted current strength if the energy of the electrons is 4.9ev.**(Ans = T=3.93%** Transmitted current = 10pA *.0393 = 0.393pA**)**

5. Find the normalisation constant B for the wave function Ψ - B[sin(πx/L)+sin(2πx/L)] **(Ans** $B = \sqrt{\frac{1}{L}}$)

6. Show that the probability of finding a particle trapped in an infinite potential well between x and x+Δx is approx Δx/L and is independent of x.

7. Find the probability that a particle in a box of width L can be found between 0 and L/n when the particle is in the nth state

8. A particle in an infinite potential well of width a. Find the probability of finding the particle between a/3 and 2a/3 in the ground and third excited states. **(Ans:)**

9. What is the minimum energy of an electron trapped in a one dimensional region the size of an atomic nucleus (1 x 10^{-14} m)? (**Ans 3.77 Gev**)

10. Find the energy required to excite a particle in a box of width '**a**' from the second excited state to the fifth state. **()**