Notes

One-dimensional Problems

We know that microscopic particles always manifest themselves in the form of waves: depending upon the situation, the wave could be an extended plane wave or could be in the form of a wave packet. The form of these waves may be obtained by solving the corresponding Schrodinger equation of the particle under the given conditions. Now we will discuss the dynamics of a particle in one-dimensional space under a given potential field, that is, we will find out energy eigenvalues and eigenfunctions of the Hamiltonian operator $\hat{H}$. Before that we will discuss some of the general features of the eigenfunctions.

Time-Independent Schrodinger Equation And Stationary States :-

Let us consider one-dimensional version of time-dependent Schrodinger eqn.

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) \quad \text{--- (1)}$$

Let us consider the special case of a closed system in which energy is conserved and potential energy $V(x)$ is independent of time i.e Hamiltonian (total energy) of the system is independent of time. In this case we can write the wave func^n. $\Psi(x,t)$ in the following form

$$\Psi(x,t) = \psi(x)\,\phi(t) \quad \text{—— (2)}$$

Then putting eq^n. (2) in eq^n. (1) we get

$$i\hbar\,\psi(x)\frac{d\phi(t)}{dt} = \left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right]\phi(t)$$

Dividing by $\psi(x)\phi(t)$ on both sides

$$\frac{i\hbar}{\phi(t)}\frac{d\phi(t)}{dt} = \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\right] \quad \text{—— (3)}$$

The L.H.S. of eq^n. (3) is a func^n. of 't' alone and R.H.S. is a func^n. of space alone and so both sides must be equal to a constant, which we call E. Thus we get two eq^{n}s:

$$i\hbar\frac{d\phi(t)}{dt} = E\,\phi(t) \quad \text{—— (4a)}$$

and $$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\,\psi(x) \quad \text{—— (4b)}$$

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Eq^n (4a) is the time-dependent S.E and (4b) is time independent S.E. The solution to the TDSE is of simple harmonic form

$$\phi(t) = e^{-\frac{i}{\hbar}Et} = e^{-i\omega t} \quad \text{--- (5)}$$

$$\therefore \Psi(x,t) = \psi(x)\, e^{-i\omega t} \quad \text{--- (6)}$$

It is obvious that the time-dependence of the wave func^n is through the exponential factor $e^{-i\omega t}$. For example in case of free particle propagating in x-direc^n the time independent wave func^n is

$$\psi(x) = e^{ikx}$$

$\therefore$ The total wave func^n $\Psi(x,t) = e^{ikx} e^{-i\omega t}$

$$= e^{i(kx - \omega t)} \quad \text{--- (7)}$$

Now the probability density $|\Psi(x,t)|^2$

$= |\psi(x)|^2$ is really independent of time.

So the wave func^n $\Psi(x,t) = \psi(x)\phi(t)$ is called a ~~stionar~~ stationary state.

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The TISE ~~Φ~~ S.E. (4b) may be written as eigenvalue eq^n

$$\hat{H}\,\psi(x) = E\,\psi(x) \quad \text{--- (8)}$$

Where $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$ is the Hamiltonian operator and E is a no, giving the energy eigenvalue. For general the eigenvalues have a discrete set with corresponding eigenfunctional

$\therefore$ We can rewrite (8) as

$$\hat{H}\,\psi_n(x) = E_n\,\psi_n(x) \quad \text{--- (9)}$$

So for a particle in a given potential $V(x)$, the solution of S.E gives a no. of stationary states (ie eigenstates) in which the particle may stay.

Some Characteristics of Wave Functions

$\psi(x)$ which is interpreted as probability amplitude is in general a complex. However the prob. density $|\psi(x)|^2$ is real and $|\psi(x)|^2 dx$ gives information about the probability of particle being found in between x and $x+dx$. If a particle is confined within a region x_1 to x_2 with wave func^n $\psi(x)$ then the total probability of the particle being found anywhere within the region of x_1 to x_2 has to be unity i.e,

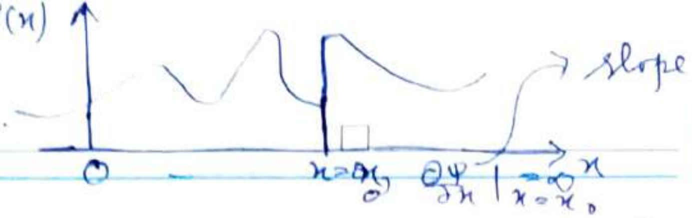
$$\int_{a_1}^{x_2} |\psi(x)|^2 dx = 1 \quad \text{—— (10)}$$

Also $|\psi(x)|^2 dx$ has a finite value for finite value of dx. Therefore the cond^n.

$$\lim_{dx \to 0} |\psi(x)|^2 dx = 0 \quad \text{—— (11)}$$

dictates that $\psi(x)$ has to have finite value everywhere in the region i.e the wave func^n is not divergent at any value of x i.e $\psi(x) = 0$ at $x = \pm\infty$. So $\psi(x)$ is a well behaved function.

Continuity of Wave func^n : Not only the wave func^n $\psi(x)$ should be finite everywhere in the region, $\psi(x)$ and its derivative $\left(\frac{d\psi}{dx}\right)$ should be continuous i.e it gives finite value. The discontinuity in the wave func^n $\psi(x)$ for example shown in fig. would results in a non physical situation. In fact infinite slope $\left(\frac{d\psi}{dx} = \infty\right)$ of the wave func^n at $x = x_0$ would result in infinite contribution to the expectation



Orthogonality of Wave Functions

Here we will show that all eigenfunctions of a Hermitian operator (Hamiltonian is a Hermitian operator) corresponding to different eigenvalues (which are real) are orthogonal

Consider a particle in one dimensional potential $V(x)$. The S.Es. corresponding to two eigenvalues E_{n1} and E_{n2} with corresponding eigenstates $\psi_{n1}(x)$ and $\psi_{n2}(x)$ are

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{n1}}{dx^2} + V(x)\psi_{n1} = E_{n1}\psi_{n1} \quad (12)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{n2}}{dx^2} + V(x)\psi_{n2} = E_{n2}\psi_{n2} \quad (13)$$

Let us multiply eq^n (12) by ψ_{n2}^* and multiply the complex conjugate of eq^n (13) by ψ_{n1} and subtract

$$-\frac{\hbar^2}{2m}\left[\psi_{n2}^*\frac{d^2\psi_{n1}}{dx^2} - \psi_{n1}\frac{d^2\psi_{n2}^*}{dx^2}\right] = \left[E_{n1} - E_{n2}^*\right]\psi_{n2}^*\psi_{n1}$$

Integrating b/w the limits x_1 and x_2 we get

$$-\frac{\hbar^2}{2m}\int_{x_1}^{x_2}\left[\psi_{n2}^*\frac{d^2\psi_{n1}}{dx^2} - \psi_{n1}\frac{d^2\psi_{n2}^*}{dx^2}\right]dx = \left(E_{n1} - E_{n2}^*\right)\int_{x_1}^{x_2}\psi_{n2}^*\psi_{n1}\,dx$$

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or, $$-\frac{\hbar^2}{2m}\left[\psi_{n2}^* \frac{d\psi_{n1}}{dx} - \psi_{n1}\frac{d\psi_{n2}^*}{dx}\right]_{x_1}^{x_2} = (E_{n1}-E_{n2}^*)\int_{x_1}^{x_2}\psi_{n2}^*\psi_{n1}\,dx \quad \text{—— (14)}$$

If we take $x_1=-\infty$ and $x_2=+\infty$, then L.H.S. of eq^n (14) vanishes as ψ_{n1} and ψ_{n2} are eigenfunc^{n}s. and they are zero at $\pm\infty$. So

$$(E_{n1}-E_{n2}^*)\int_{-\infty}^{\infty}\psi_{n2}^*(x)\,\psi_{n1}(x)\,dx = 0 \quad \text{—— (15)}$$

If $n_1=n_2$, the integral $\int_{-\infty}^{\infty}|\psi_n(x)|^2 dx = 1$

So $$E_{n1} = E_{n1}^* \rightarrow E_{n1} \quad \text{—— (16)}$$

clearly showing that all energy eigenvalues are real. Eq^n (15) for $E_{n1}\neq E_{n2}$ gives

$$\boxed{\int_{-\infty}^{\infty}\psi_{n2}^*(x)\,\psi_{n1}(x)\,dx = 0} \quad \text{—— (17)}$$

Two ~~wave~~ func^{n}s. $\psi_{n1}(x)$ and $\psi_{n2}(x)$ having the property in eq^n (17) are called orthogonal to each other. If each ~~ea~~ $\psi(x)$ is normalized, we may write

$$\int_{-\infty}^{\infty} \psi_{n_2}^*(x)\psi_{n_1}(x)\,dx = \delta_{n_1,n_2} \quad \text{--- (18)}$$

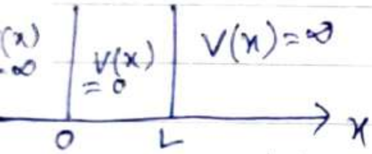
where δ_{n_1,n_2} is called the Kronecker delta funcn. defined through the eqn

$$\delta_{n_1,n_2} = \begin{cases} 1 & \text{if } n_1 = n_2 \\ 0 & \text{if } n_1 \neq n_2 \end{cases}$$

Two funcn's which satisfy eqn (18) are orthogonal and normalized and simply called orthonormal.

Particle In A One-Dimensional Potential Box

Let us consider a simple case of a particle in one-dimensional potential box. We will solve the S.E of a particle of mass m confined in a potential box of length L. The potential is expressed as



$$V(x) = 0 \quad \text{for } 0 < x < L$$
$$\quad = \infty \quad \text{for } x < 0 \text{ and } x > L \qquad -(19)$$

↳ potential well with infinitely high potential barriers on both sides.

In this case the particle might be moving along x-axis in the form of some wave packet. We have to find the form as well as the energy of the wave packet, obviously by solving S.E of the particle. Any information about the particle may only be obtained from its S.E.

Energy Eigenvalues and Eigenfunctions

The one-dimensional time independent S.E. of the particle inside the well where V=0 is

Notes $\hat{H}\Psi = E\Psi$

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$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \underset{V(x)=0}{0} = E\,\psi(x) \quad \text{—— (20)} \quad \text{Since } V=0$$

As the potential energy V(x) is infinite outside the well, that for $x<0$ and $x>L$, the probability of finding the particle outside the well is zero. Therefore the wave funcⁿ $\psi(x)$ should vanish outside the well. And, in fact, we need to solve S.E. (20) only inside the well. We know that wave funcⁿ must be continuous and therefore $\psi(x)$ must vanish at the potential well boundaries i.e.,

$$\psi(x) = 0 \text{ at } x=0 \text{ and at } x=L \quad \text{—— (21)}$$

The condition (21) are known as rigid boundary conditions. In fact, we will learn shortly that it is the boundary condⁿs, which lead to discrete values of energy of the particle.

Eqⁿ. (20) may be written as

$$\frac{d^2\psi(x)}{dx^2} + k^2\psi(x) = 0 \quad \text{—— (22)}$$

where $$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{—— (23)}$$

The general solution of 2nd order differential eqn (22) is a linear combination of two linearly independent solutions

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad \text{—— (24)}$$

Where A and B are arbitrary constants. These constants are to be fixed by the boundary conditions which give

$$\psi(0) = A + B = 0 \quad \text{—— (25a)}$$

and $$\psi(L) = Ae^{ikL} + Be^{-ikL} = 0 \quad \text{—— (25b)}$$

From these two eqns. we get

$$A = -B$$

and $$A\left(e^{ikL} - e^{-ikL}\right) = 0$$

$$A2i\left(\frac{e^{ikL} - e^{-ikL}}{2i}\right) = 0$$

or, $$2Ai \sin kL = 0$$

$$\therefore \sin kL = 0 \quad \text{—— (26)}$$

which dictates that only allowed values of k and k_n given by

$$k_n L = n\pi \quad , \quad n = 1, 2, 3 \quad \text{—— (27)}$$

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So the wave func^n given in eq^n (24) becomes

$$\psi(x) = \psi_n(x) = A\left(e^{+ikx} - e^{-ikx}\right)$$
$$= 2iA \sin k_n x \quad \text{—— (27)}$$

Now normalization of $\psi_n(x)$ means

$$\int_0^L |\psi_n(x)|^2 dx = 1$$

or, $$\int_0^L (-4A^2) \sin^2 k_n x \, dx = 1$$

$\cos 2\theta = \cos^2\theta - \sin^2\theta$
$\cos 2\theta = 1 - 2\sin^2\theta$

or, $$(-4A^2)\frac{L}{2} = 1$$

since $\cos 2\theta = 1 - 2\sin^2\theta$
$\int_0^L \sin^2 k_n x \, dx = \frac{L}{2}$
$= \frac{1}{2}\int_0^L 1 - \cos 2k_n x \, dx = \frac{L}{2} - 0 = \frac{L}{2}$

or, $$2iA = \sqrt{\frac{2}{L}} \quad \text{—— (28)}$$

Therefore we get normalized wave func^n.

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin k_n x = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \text{—— (29)}$$

from eq^{n}s (27) & (28)

The energy of the particle $E \left(= \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}\right)$ has discrete values as wave vector k has discrete values $k_n \left(= n\pi/L\right)$

$$\therefore E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3 \cdots \qquad **$$

We see the eigen energy spectrum of the particle consists of infinite no. of discrete energy levels $E_1, E_2, \cdots$ corresponding to bound eigenstates $\psi_1, \psi_2, \cdots$. That $\psi_1, \psi_2, \psi_3 \cdots$ are called bound states, is clear, because the particle in these states is confined with the box.

Let us see how the real wave func^n $\psi_n(x)$ looks like for different values of n.

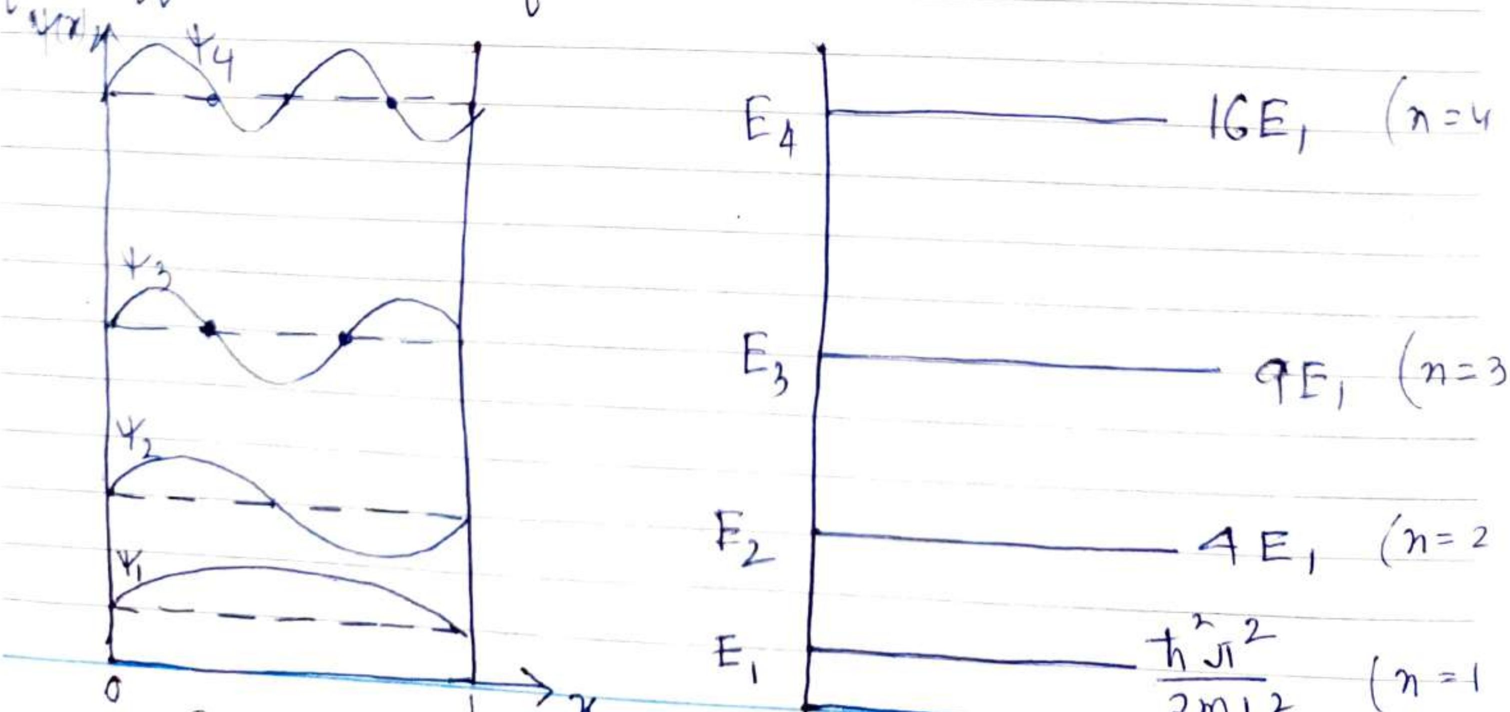

Fig (a)

Fig(b) $E_n = \frac{\hbar^2 \pi^2 n^2}{}$

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Fig(a) First four eigenfunc's of the particle in the infinite potential well. Fig(b) corresponding four eigenvalues.

In the above figure we plot $\psi_1, \psi_2, \psi_3, \psi_4 \ldots$ and show corresponding energies $E_1, E_2, E_3, E_4 \ldots$ We know that the wave vector k_n is ~~those~~ quantized $\left(k_n = \frac{n\pi}{L}\right)$. The corresponding de Broglie wave lengths are $k_n = \frac{2\pi}{\lambda_n} \Rightarrow \lambda_n = \frac{2\pi}{k_n} = \frac{2L}{n}$.

So only those states are allowed in which either half an odd integral or integral no. of de Broglie wavelengths fit into the box of length L, like

$$L = \frac{\lambda_1}{2}, \quad L = \lambda_2, \quad L = \frac{3\lambda_3}{2}, \quad L = 2\lambda_4 \text{ etc}$$

Also we note that as energy increases, no. of nodes in that state increases

Precisely, the eigenstate $\psi_n(x)$ with energy E_n has $(n-1)$ nodes within the potential well (leaving the nodes at the boundaries).

*** The energy level increases with n^2 meaning that high energy levels are separated from each by greater amount then low energy levels. The lowest possible energy of the particle (its zero pt energy) is found when it is in state 1 ($\psi_1, n=1$) which is given by $E_1 = \frac{\hbar^2\pi^2}{2mL^2}$. The particle therefore always has a +ve energy. This contrast with classical system where the particle can have zero energy by resting motionlessly. This can be explained in terms of the uncertainty principle which states that $\Delta x \Delta p_x \geq \hbar/2$.

→ It can be shown that the uncertainty in posⁿ of the particle is proportional to the width of the box. Thus the uncertainty in momentum is roughly inversely proportional to the width of the box. The K.E of the particle is $E = \frac{p_x^2}{2m}$ and hence the

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Orthogonality of Wave Functions

We may easily check that different wave functions are orthogonal to each other

We have got the wave funcⁿ

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$$

$$\therefore \int_0^L \psi_n^*(x)\,\psi_m(x)\,dx = \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\sin\frac{m\pi x}{L}\,dx$$

$$= \frac{1}{L}\int_0^L \left\{\cos\frac{(n-m)\pi x}{L} - \cos\frac{(n+m)\pi x}{L}\right\}dx$$

$$= \frac{\sin(n-m)\pi}{(n-m)\pi} - \frac{\sin(n+m)\pi}{(n+m)\pi} = 0 \quad \text{for } n \neq m$$

$= \delta_{n,m}$ When $\delta_{n,m}$ is Kronecker delta

$$\delta_{n,m} = 1 \quad \text{for } n = m$$
$$= 0 \quad \text{for } n \neq m$$

$\sin(A+B) = \sin A\cos B + \cos A\sin B$
$\sin(A-B) = \sin A\cos B - \cos A\sin B$
$\cos(A+B) = \cos A\cos B - \sin A\sin B$
$\cos(A-B) = \cos A\cos B + \sin A\sin B$
$\therefore \cos(A-B) - \cos(A+B) = 2\sin A\sin B$

When $n = m$

$$\int_0^L |\psi_n|^2 dx = \frac{2}{L}\int_0^L \sin^2\frac{n\pi x}{L}\,dx$$

$$= \frac{2}{L}\times\frac{1}{2}\times\int_0^L \left(1 - \cos\frac{2n\pi x}{L}\right)dx = \frac{1}{L}\times L - 0$$

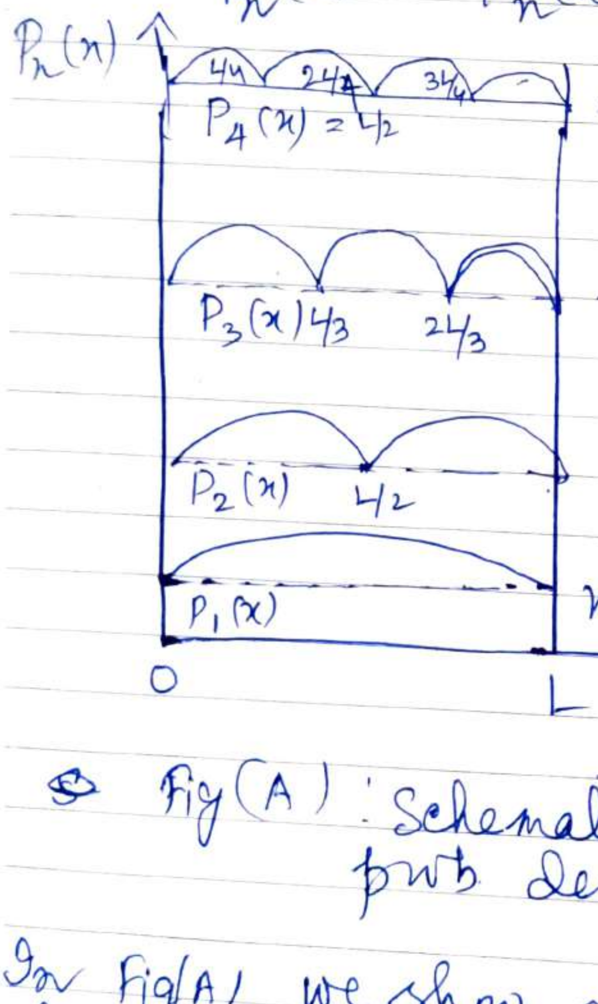
$$\therefore \int_0^L \psi_n^*(x)\,\psi_m(x)\,dx = \delta_{m,n}$$

→ minimum K.E. of the particle in the box is inversely proportional to mass and square of the well width, in qualitative agreement with the calculation above.

Position Probability Density

For n^{th} state, the pos^n probability density $P_n(x)$ is given by

$$P_n(x) = \psi_n^*(x)\,\psi_n(x) = \frac{2}{L}\sin^2\frac{n\pi x}{L}$$



$n=4$ when $x=0$, $P_n(x)=0$, $x=\frac{L}{4}$, $P_n(x)=0$
$x=\frac{L}{2}$, $P_n(x)=0$, $x=\frac{3L}{4}$, $P_n(x)=0$
$x=L$, $P_n(x)=0$

$n=3$ When $x=0$, $P_3(x)=0$
$x=\frac{L}{3}$, $P_3(x)=0$, $x=\frac{2L}{3}$, $P_3(x)=0$
$x=L$, $P_3(x)=0$

$n=2$ → when $x=0$, $P_2(x)=0$
$x=\frac{L}{2}$, $P_2(x)=0$
$x=L$, $P_2(x)=0$

$n=1$ when $x=0$, $P_1(x)=0$
$x=L$, $P_1(x)=0$

Fig (A): Schematic plot of first four pos^n prob densities.

In Fig(A) we show schematic plot of pos^n prob. density $P_1(x)$, $P_2(x)$, $P_3(x)$ and $P_4(x)$. From the above figure it is obvious when the particle is in $\psi_1(x)$ state ($i=n$), the particle prob. density at $x=0$ and $x=L$ are zero ie no observer will find the particle at pos^n $x=0$ and $x=L$ when it is in $\psi_1(x)$ state

Similarly when the particle is in $\psi_2(x)$ state, no observer will find the particle at position $x=0$, $x=L/2$ and $x=L$. Similarly when the particle is in $\psi_3(x)$ state, no observer will find the particle at pos^{n}s $x=0$ $x=\frac{L}{3}$, $x=\frac{2L}{3}$, $x=L$ because at these pos^n prob. density is zero. In this way we can see when the particle is in $\psi_4(x)$ state the prob. of finding the particle at pos^{n}s, $x=0$, $x=\frac{L}{4}$, $x=\frac{2L}{4}=\frac{L}{2}$, $x=\frac{3L}{4}$, $x=L$ are zero because at those pos^n ~~positions of a~~ values of x the pos^n prob. density of the particle are zero.

Expectation Values of Linear Momentum and Kinetic Energy Operators

We know that in quantum mechanics a physical quantity is obtained by finding the expectation value of the corresponding operator. We also know that the operator $\left(-i\hbar\frac{\partial}{\partial x}\right)$ corresponding to the physical quantity p_x, the x component of the linear momentum. So let us find the expectation of the operator $\left(-i\hbar\frac{d}{dx}\right)$ in state $\psi_n(x)$

$$\langle \hat{p}_x\rangle_n = \int_0^L \psi_n^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_n(x)\,dx$$

$$= \frac{2}{L}\int_0^L (-i\hbar)\sin\frac{n\pi x}{L}\frac{d}{dx}\left(\sin\frac{n\pi x}{L}\right)dx$$

$$= \frac{2}{L}\int_0^L (-i\hbar)\left(\frac{n\pi}{L}\right)\sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L}\,dx$$

$$= \frac{-i\hbar\, 2n\pi}{L^2}\int_0^L \sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L}\,dx$$

$$= 0$$

Let $\sin\frac{n\pi x}{L} = p$ $\therefore$ $\frac{n\pi}{L}\cos\frac{n\pi x}{L}\,dx = dp$

$$\frac{n\pi}{L}\int_0^L p\,dp = \frac{n\pi}{L}\frac{p^2}{2}\Big|_0^L = \frac{n\pi}{2}\left[\sin^2\frac{n\pi x}{L}\right]_0^L$$

$$= \frac{n\pi}{2}\left[\underbrace{\sin^2\frac{n\pi L}{L}}_{0} - \underbrace{\sin^2\frac{n\pi 0}{L}}_{0 \text{ for any value of } n}\right]$$

$$= 0$$

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However, the expectation value of $\hat{p}_x^2$ is

$$\langle \hat{p}_x^2 \rangle_n = -\hbar^2 \frac{2}{L} \int_0^L \sin\frac{n\pi x}{L} \frac{d^2}{dx^2}\left(\sin\frac{n\pi x}{L} dx\right)$$

$$= \hbar^2 \frac{n^2\pi^2}{L^2} \frac{2}{L} \int_0^L \sin^2 \frac{n\pi x}{L} dx$$

$$= \frac{\hbar^2 n^2 \pi^2}{L^3} \int_0^L \left(1 - \cos\frac{2n\pi x}{L}\right) dx$$

$$= \frac{\hbar^2 n^2 \pi^2}{L^3} L - 0 = \frac{\hbar^2 n^2 \pi^2}{L^2}$$

$\hat{p}_x^2 \to \left(i\hbar \frac{\partial}{\partial x}\right)^2 \to -\hbar^2 \frac{\partial^2}{\partial x^2}$

∴ The expectation value (or average value) of the K.E. operator is

$$\langle \hat{T} \rangle_n = \frac{\langle \hat{p}_x^2 \rangle_n}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \quad \text{—— (1)}$$

It may seem to be surprising to see that the value of $\langle \hat{p}_x \rangle$ is zero, whereas that of $\langle \hat{p}_x^2 \rangle$ is non zero. But one may understand it as the eigenstate $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$ is really representing a ~~standing~~ standing wave (not a running wave).

In fact, we should write time-dependent

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eigenstate to see what type of the wave the eigenstate represent.

$$\psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \exp\left(-i\frac{E_n}{\hbar}t\right) \quad \boxed{e^{i(kx-\omega t)} \quad \omega = \frac{E}{\hbar}}$$

$$= \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \exp\left(-i\frac{\hbar n^2\pi^2}{2mL^2}t\right) \rightarrow \text{from eq}^n\ (1)$$

$$\text{——— (2)}$$

Now it can be easily checked that $\psi_n(x,t)$ is representing a standing wave and not a running wave. For example at $x = \frac{L}{n}$, the wave func^n $\psi_n(x)$ is zero at all times, a node there which is the characteristic of standing wave in classical physics. So just like in classical mechanics, exp^n (2) may be thought of superposition of two propagating wave of equal wavelength and freq (i) one propagating in +ve x direc^n and (ii) the (after reflected at $x = L$) propagating in –ve x direc^n. Each of these two constituent waves (i) and (ii) carry equal and opposite linear momentum and therefore the net linear momentum carried is zero. So the average $\langle \hat{p}_x \rangle_n = 0$ where as $\langle \hat{p}_x^2 \rangle \neq 0$.