

QUANTUM MECHANICS

Heisenberg's Uncertainty principle:

Statement: It is not possible to determine both the position and momentum of a particle simultaneously and accurately or It can also be stated as “the product of uncertainties inherently in measuring simultaneously position and momentum of a particle is equal or greater than $(h/4\pi)$ ”

$$\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$$

where Δp denotes the uncertainty (error) in the measurement of momentum and Δx is the uncertainty (error) involved in the measurement of position of the particle along x-axis, h is the Planck's constant.

Heisenberg Uncertainty relationships

$$(i) \Delta p \cdot \Delta x \geq \frac{h}{4\pi}$$

$$(ii) \Delta \theta \cdot \Delta L \geq \frac{h}{4\pi}$$

$$(iii) \Delta t \cdot \Delta E \geq \frac{h}{4\pi}$$

Explanation:

Heisenberg's uncertainty principle is natural consequence of wave nature of matter. When we consider the particle as a wave group, there are fundamental limits to the accuracy with which we can determine the particle properties like position and momentum.

Let us consider an individual

Since moving material particle is regarded as de Broglie wave group, there is a limit to the accuracy with which we can measure its particle properties such as position and momentum. According to Born's probability theory the particle may be found anywhere within the wave packet. This means that position of the particle is uncertain within the limits (Δx) of the of the wave packet.

The narrower the wave group, the more precisely the particle's position can be specified. However the wavelength of the waves in narrow wave packet is not well defined; there are not enough waves to measure the ' λ ' accurately. This means that the particle momentum is not a precise quantity (because $\lambda = h/p$).

On the other hand, a wide wave group clearly defines the wavelength. Therefore the momentum corresponding to that wavelength will be a precise quantity but there is large indefiniteness in the position of the particle.

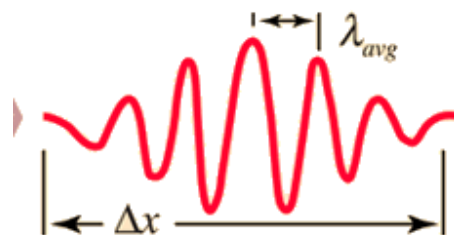
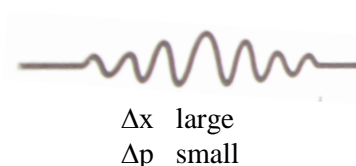
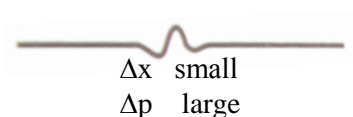


Fig. 1 wave packet



This shows that it is impossible to know where within the packet the particle is located and what its exact momentum is. That is to say there is uncertainty in the measurement of position of a particle and also its momentum.

Uncertainties involved in the measurements are inherent in nature and not due to inaccuracy of the measuring instruments. This arises from wave properties of the material particles.

Physical significance of Heisenberg's uncertainty principle:

Uncertainty principle places a limit on the accuracy with which the momentum and position (pair of physical variables, in general) of a particle can be measured simultaneously. The Physical significance of this principle is that one should not think of exact position, or an accurate value for momentum of a particle. Instead one should think of the probability of finding the particle at a certain position, or of the probable value for the momentum of the particle. The estimation of such probabilities is made by means of certain mathematical function called wave function in quantum mechanics.

Application of uncertainty principle:

(i) The non-existence of electron in the nucleus:

We can use the uncertainty principle to place a lower limit on the energy of an electron must have, if it is to be part of the nucleus.

We know by theory of relativity, the energy of body of mass m moving with velocity v is expressed as

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}} \text{ where } m_0 \text{ is rest mass of body}$$

Taking square on both sides

$$E^2 = \frac{m_0^2 c^4}{\left(1 - \frac{v^2}{c^2}\right)}$$

$$E^2 = \frac{m_0^2 c^6}{(c^2 - v^2)} \quad (1)$$

Momentum of body is $p = mv = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}}$

$$p^2 = \frac{m_0^2 v^2}{\left(1 - \frac{v^2}{c^2}\right)} = \frac{m_0^2 v^2 c^2}{(c^2 - v^2)}$$

Multiplying on both sides by c^2

$$p^2 c^2 = \frac{m_0^2 v^2 c^4}{(c^2 - v^2)} \quad (2)$$

Subtracting eqn (2) from (1)

$$E^2 - p^2 c^2 = \frac{m_0^2 c^4 (c^2 - v^2)}{(c^2 - v^2)}$$

$$E = (p^2 c^2 + m_0^2 c^4)^{1/2} \quad (3)$$

Let us consider a typical atomic nucleus with diameter of the order of 10^{-14} m. If the electron is confined in the nucleus, then the uncertainty in the position is of the order of diameter.

$$\text{i.e } \Delta x \leq 10^{-14} \text{ m}$$

Using Heisenberg Uncertainty Principle

$$\Delta p \geq \frac{h}{4\pi\Delta x}$$

using Δx in this eqn, we get

$$\Delta p \geq \frac{6.6 \times 10^{-34}}{4\pi (10^{-14})}$$

$$\Delta p \geq 5.26 \times 10^{-21} \text{ kgm/s}$$

If this is the minimum uncertainty in the momentum, then momentum p must be at least comparable to Δp .

$$\therefore p = 5.26 \times 10^{-21} \text{ kgm/s}$$

The energy of electron with such a momentum we can find using eqn. (3)

$$E = (p^2 c^2 + m_0^2 c^4)^{1/2}$$

$$= ((5.26 \times 10^{-21})^2 \times (3 \times 10^8)^2 + (9.1 \times 10^{-31})^2 \times (3 \times 10^8)^4)^{1/2}$$

$$= (2.49 \times 10^{-24})^{1/2} \text{ J}$$

$$= 9.8 \text{ MeV}$$

This shows that K.E of the electron must exceed 9.8 MeV, if it is to be part of the nucleus. But if an electron has energy 9.8 MeV, it will escape from the nucleus since the maximum binding energy of a nucleon is about 8 MeV. So an electron cannot be confined within the atomic nucleus. Also experiments on beta decay show that even the electrons associated with unstable atom have energy of the order of 3-4 MeV and hence we conclude that nuclei do not contain the electrons.

(ii) Broadening of the spectral line:

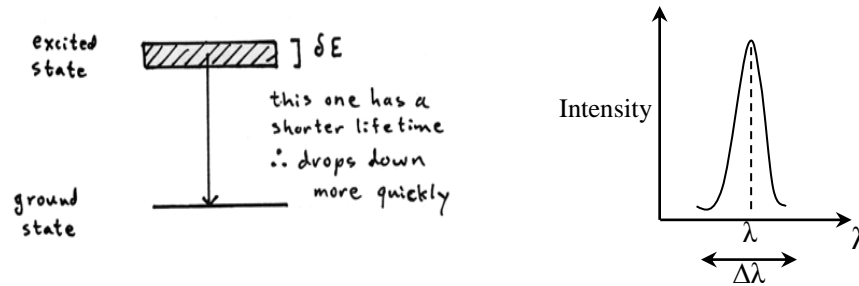
When an atom makes a transition from higher to lower energy level, the difference in energy is emitted as a spectral line.

The life time of an atom in the ground state is ∞ . Hence uncertainty in its time measurement

$\Delta t = \infty$. Substituting this value for Δt in Heisenberg's uncertainty relation, $\Delta E \Delta t \geq \frac{h}{4\pi}$, we get

for ground state, $\Delta E = \frac{h}{4\pi \times \infty} = 0$. Hence the ground state energy can be precisely measured.

Life time of an atom in the excited state is very short but finite. So for an excited state Δt is small and finite and hence ΔE is large which means that the excited state has an energy broadening. The intrinsic line width of spectral lines is due to this spread in the excited energy (i.e. band of energies).



$E = hc/\lambda$ is the energy of emitted photon.

The variation in the energy of emitted photon can be obtained by differentiating the above expression.

$$\Delta E = -hc \left(\frac{\Delta \lambda}{\lambda^2} \right) \quad (i)$$

$$\text{Also } \Delta E = \frac{h}{4\pi \Delta t} \quad (ii)$$

From equations (i) and (ii), we can obtain, $\Delta \lambda = \frac{\lambda^2}{4\pi c \Delta t}$

Here $\Delta \lambda$ is the intrinsic line width of the spectral lines.

Wave function:

In the case of electromagnetic waves, the electric and magnetic fields vary with space and time. In case of sound waves, it describes pressure variation in space and time. In analogy with these, to describe the matter waves associated with the particle motion, one requires a quantity which varies with space and time, this variable quantity is called as wave function $\psi(x, t)$.

We know that matter exhibits wave like behavior under certain conditions. When the momentum of the particle is well defined, the wave can be of infinite extent. Therefore a particle moving along x-axis with well-defined momentum is described by an infinite plane wave $\psi(x, t)$ and is given by

$$\psi(x, t) = Ae^{i(kx - \omega t)}$$

It is a function of space variables (x, y, z) and time 't', where ω is angular velocity and k is wave vector.

Physical significance of wave function:

1. The wave function Ψ provides all possible information about the particle which is associated with wave-character. The state of the system is described or represented by Ψ which is a function of space and time coordinates.
2. It is a complex quantity representing the matter wave associated with moving particle.
3. It is large in magnitude where the particle is likely to be located and small in other places.
4. It connects the particle nature and its associated wave nature.
5. The wave function Ψ has no direct physical meaning. But square of absolute value of wave function $|\Psi|^2$ has physical significance. According to Max Born interpretation, square of the wave function represents probability of finding the particle in a given region. It does not give the exact location of the particle.

Probability density:

The probability density of a particle associated with de-Broglie waves can be represented as $P = \Psi\Psi^* = |\Psi|^2$ where Ψ is wave function & Ψ^* is the complex conjugate of Ψ . $|\Psi|^2 = \Psi^*\Psi$ is real and positive and has physical meaning.

(Probability of occurrence of an event is a real and positive quantity but wave function may be complex. Hence in order to get a real and +ve value while evaluating $|\Psi|^2$, the wave function is Ψ is multiplied with its complex conjugate Ψ^)

Consider a particle is in a volume V inside which particle is known to be present in a volume element dV . Let Ψ be the wave function associated with the particle then the square of the wave function associated with the particle is interpreted as measure of probability density. That is $|\Psi|^2$ is the probability density per volume element and the particle will be found in that volume element

Normalization of wave function:

Let V be a volume inside which a particle is known to be present, but where exactly the particle is situated in V is not known. Then the probability of finding the particle in a volume element dV is expressed as

$$P dV = |\Psi|^2 dV$$

Since $|\Psi|^2 dV$ is the probability that the particle will be found in a volume element dV , the total probability that the particle will be somewhere in the space must be equal to unity. Thus we have

$$P = \int_{-\infty}^{\infty} |\Psi|^2 dV = 1$$

The normalizing condition for the wave function for the motion of a particle in one dimension is

$$P = \int_{-\infty}^{\infty} |\Psi|^2 dx = 1$$

The above condition is called **normalization condition**. A wave function which satisfies above equation is said to be normalized.

Normalization is simply a statement that the particle exists at some point at all the times. Therefore, although it is not possible to specify the position of the particle with complete certainty. It is possible to specify only the probability of observing it. Thus it turns out that the waves have no real material characteristics, but are purely measure of probability.

Properties of wave function:

Besides being normalizable the wave function Ψ must satisfy the following properties

1. Ψ must be single valued.
2. Ψ must be finite everywhere.
3. Ψ and its first derivatives $d\Psi/dx$, $d\Psi/dy$ and $d\Psi/dz$ must be continuous.

The wave functions which are finite, continuous, single valued and normalized are called acceptable wave functions.

Equation of motion for de-Broglie waves:

Schrodinger in the year 1925 formulated the wave equation which is known as the Schrödinger equation of motion to describe the wave nature of a particle based on de Broglie's ideas of matter waves. This equation cannot be derived from any fundamental laws. It is the fundamental equation of quantum mechanics in the same sense that the second law of motion ($F = m d^2x/dt^2$) is the fundamental equation of Newtonian mechanics. It is the wave equation in the variable Ψ called wave function. There are two wave equations namely

1. Schrodinger time independent wave equation
2. Schrodinger time dependent wave equation

These equations are used to determine the electron energy levels in atoms and molecules. They also enable to find the location or state of the electron in a material.

Schrödinger time independent wave equation:

In many cases the potential energy V of the particle does not depend on the time t explicitly. The forces that act on the particle and hence potential energy vary with the position of the particle only. The wave equation describing only the position of the particle is called time independent Schrodinger wave equation.

The classical wave equation that describes any type of wave motion can be given as

$$\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y(x,t)}{\partial t^2}$$

where y is a variable quantity that propagates in 'x' direction with a velocity 'v'. Matter waves should also satisfy similar equation and we can write the equation for matter waves as:

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi(x,t)}{\partial t^2} \quad (i)$$

we can eliminate time dependence from above equation by assuming suitable form of the wave function and making appropriate substitutions.

Consider one dimensional wave function Ψ describing the de Broglie wave for a particle moving freely in the positive X-direction. Ψ be the wave function which represents the displacement of the particle moving with velocity 'v' at any time 't' with a velocity 'v'.

$$\text{Let } \psi(x,t) = \psi_x e^{-i\omega t} \quad (ii)$$

where ψ_x depends only on 'x', and $e^{-i\omega t}$ depends only on 't', ω is the angular frequency

Differentiating equation (ii) twice w. r .to 'x' we get

$$\begin{aligned} \frac{\partial \psi(x,t)}{\partial x} &= \frac{\partial \psi_x}{\partial x} e^{-i\omega t} \\ \frac{\partial^2 \psi(x,t)}{\partial x^2} &= \frac{\partial^2 \psi_x}{\partial x^2} e^{-i\omega t} \end{aligned} \quad (iii)$$

Differentiating equation (ii) twice w. r .to 't' we get

$$\begin{aligned} \frac{\partial \psi(x,t)}{\partial t} &= \psi_x e^{-i\omega t} (-i\omega) \\ \frac{\partial^2 \psi(x,t)}{\partial t^2} &= \psi_x e^{-i\omega t} (-\omega)^2 \end{aligned} \quad (iv)$$

Substitute equation (iii) and (iv) in equation (ii), we obtain

$$\frac{\partial^2 \psi_x}{\partial x^2} e^{-i\omega t} = -\frac{\omega^2}{v^2} \psi_x e^{-i\omega t}$$

we can cancel $e^{-i\omega t}$ on both sides to eliminate time dependence and get

$$\frac{\partial^2 \psi_x}{\partial x^2} = -\frac{\omega^2}{v^2} \psi_x = -k^2 \psi_x$$

$$\frac{\partial^2 \psi_x}{\partial x^2} + k^2 \psi_x = 0 \quad (\text{iv})$$

$$k = \frac{2\pi}{\lambda} \text{ and } \lambda = \frac{h}{p}, \therefore k^2 = \frac{4\pi^2 p^2}{h^2}$$

The energy of the particle, 'E' is the sum of kinetic and potential energy

$$E = \frac{p^2}{2m} + V \text{ or } p^2 = 2m(E - V)$$

$$\text{or } k^2 = 8\pi^2 m(E - V)/h^2$$

Substituting the value of k^2 in equation (iv) and replacing ψ_x by $\psi(x)$, we obtain the Schrödinger's time independent wave equation in one dimension as

$$\frac{d^2 \psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi(x) = 0$$

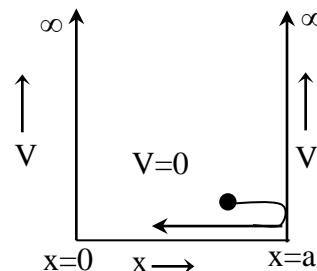
Eigen functions and Eigen values:

A system is defined by its energy, momentum, position etc. Once, the wave function and corresponding to system is known, the state of the system can be determined. In order to find Ψ , the Schrödinger equation has to be solved. But, it is second order differential equation; there are not one but several solutions. All of them may not be correct wave functions which we are looking for. We have to select those wave functions which would correspond meaningfully to a physical system. Such acceptable well behaved wave functions which are finite, continuous, single valued and normalized are called **eigen functions** while the energies corresponding to these eigen functions are called **eigen values**. (*Eigen is the German word meaning proper or characteristic*).

Applications of Schrödinger wave equation:

1. Particle in a one dimensional potential well of infinite height (or particle in a box):

The simplest quantum mechanical problem is that of the particle trapped in a box of infinitely hard walls. Consider a particle of mass m is free to move in x -direction only. We may specify a particle motion by saying that it is restricted to travel along the x -axis between $x=0$ to $x=a$ by infinitely hard walls. The particle makes elastic collisions with walls so its total energy remains constant. From a formal point of view consider



potential $V = \infty$ on the both the side of the box and say $V = 0$ inside the box. Because the particle can't have infinite energy it can't exist outside the box, so $\psi = 0$ for $x \leq 0$ and $x \geq a$

$$\begin{aligned} \text{i.e. } V(x) &= \infty & \text{for } x \leq 0 \text{ and } x \geq a \\ \text{and } V(x) &= 0 & \text{for } 0 < x < a \end{aligned}$$

The Schrödinger wave equation for wave like particle is given by

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi(x) = 0$$

Out side the box (for $V = \infty$), the Schrödinger equation becomes

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2}(E - \infty)\psi(x) = 0$$

This equation holds good only if $\psi = 0$ for all points outside the box i.e., $|\psi|^2 = 0$, probability of finding the particle outside the box is zero. (or electron can not be found at all outside the box)

Inside the box ($V = 0$), the Schrödinger equation

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2}E\psi(x) &= 0 \\ \text{or } \frac{d^2\psi(x)}{dx^2} + k^2\psi(x) &= 0 \end{aligned} \quad (1)$$

$$\text{where } k = \sqrt{\frac{8\pi^2m}{h^2}E}$$

The solution of equation (1) takes the form

$$\psi(x) = A \sin kx + B \cos kx \quad (2)$$

Where A and B are constants which can be evaluated by applying boundary conditions

(i) But $\psi = 0$ at $x = 0$, $\psi = 0$ as per condition I

\therefore equation (2) becomes

$$\begin{aligned} \psi(0) &= A \sin k0 + B \cos k0 \\ \text{or } B &= 0 \end{aligned} \quad (3)$$

(ii) at $x = a$, $\psi = 0$ equation (2) becomes

$$\begin{aligned} \psi(a) &= A \sin ka + B \cos ka \\ \text{But } B &= 0 \text{ from equation (3)} \\ \psi(a) = 0 &= A \sin ka + 0 \cos ka \end{aligned} \quad (4)$$

Here either $A = 0$ or $\sin ka = 0$; but $A \neq 0$ because if $A = 0$ the entire function given by equation (2) will be zero as $B = 0$. $\psi = 0$ leads to no probability of finding the particle, but we are dealing with the particle present in the potential well. thus equation (4) is satisfied only when

$$ka = n\pi$$

$$\ominus \sin n\pi = 0 \text{ for } n = 0, 1, 2, 3, \dots$$

n is called quantum number.

$$\therefore k = \frac{n\pi}{a}$$

\therefore substituting for k and B , equation (2) can be written as

$$\psi_n(x) = A \sin \frac{n\pi}{a} x \quad (5)$$

Our solution $\psi(x)$ is yet not complete since we have not yet determined the constant A . To do this, we use the normalization condition,

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1,$$

Since $\Psi = 0$ except for $0 < x < a$, the integral vanishes except inside that region, so that

$$\int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1,$$

but $\sin^2 \theta = \frac{1}{2} (1 - \cos 2\theta)$

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

$$\therefore \frac{A^2}{2} \left[x - \frac{a}{2n\pi} \sin \left(\frac{2n\pi x}{a} \right) \right]_0^a = 1$$

$$\Rightarrow \frac{A^2}{2} \left[a - \frac{a}{2n\pi} \sin \left(\frac{2n\pi a}{a} \right) - 0 \right] = 1$$

$$\Rightarrow \frac{A^2}{2} [a] = 1 \quad (\ominus \sin 2n\pi = 0)$$

$$\therefore A = \sqrt{\frac{2}{a}}$$

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

which represents the permitted solution.

Eigen value:

Using equation $k = \sqrt{\frac{8\pi^2 m}{h^2} E}$ and $k = \frac{n\pi}{a}$

$$\frac{n\pi}{a} = \sqrt{\frac{8\pi^2 m}{h^2} E}$$

$$\left(\frac{n\pi}{a} \right)^2 \times \frac{h^2}{8\pi^2 m} = E$$

$$E_n = \frac{n^2 h^2}{8ma^2} = n^2 E_0$$

Where $n=1,2,3,\dots$

and $E_0 = \frac{h^2}{8ma^2}$ is called **zero point energy**.

From above equation it is clear that the energy of the particle can have only certain values i.e., energy of the particle is quantized.

Below is represented a schematic diagram of wave functions energy values and probability density Ψ^2 for the first three permitted states.

Probability densities:

The probability of finding the particle in a small region 'dx' in a given quantum state 'n' is

$$P_n(x) = \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\text{or } \int_{x_1}^{x_2} P_n(x) dx = \int_{x_1}^{x_2} \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) dx$$

Graphical representation of $\psi_n(x)$ and $P_n(x)$ for $n=1,2$ and 3 quantum states.

Eigen values

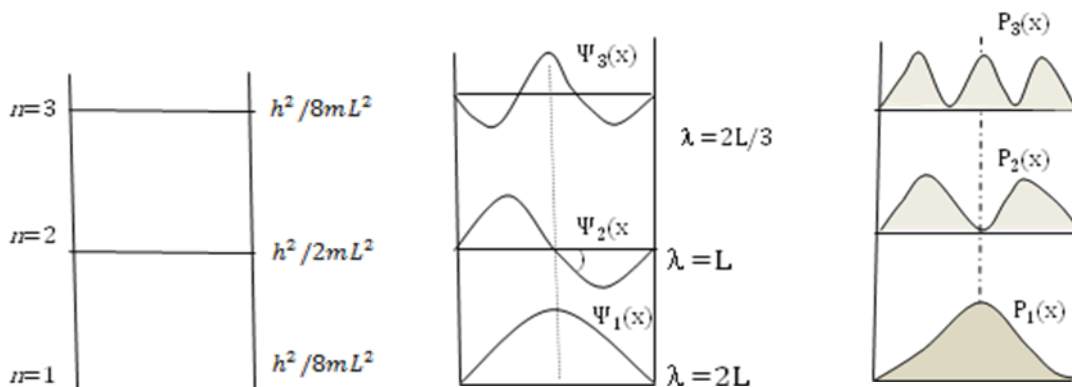
$$E_n = \frac{n^2 h^2}{8ma^2}$$

Eigen functions

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

Probability densities

$$P_n(x) = \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) dx$$



Case (i) : For $n=1$

This is the ground state and normally particle is found in this state.

$$E_1 = h^2/8ma^2$$

$$\text{And } \psi_1 = (2/a)^{1/2} \sin(\pi x/a)$$

with $\psi_1 = 0$ at $x = 0$ and $x = a$

But ψ_1 is maximum at $x=a/2$.

Case (ii) : For $n=2$

This is the first excited state.

$$E = 4h^2/8ma^2 = 4 E_0$$

And $\psi_2 = (2/a)^{1/2} \sin(2\pi x/a)$
 with $\psi_2 = 0$ at $x = 0, a/2$ and a
 and ψ_2 reaches maximum values for $x=a/4$ and $3a/4$.

Case (iii): For $n=3$

This is the second excited state.

$$E = 9h^2/8ma^2 = 9 E_0$$

And $\psi_3 = (2/a)^{1/2} \sin(3\pi x/a)$
 with $\psi_3 = 0$ at $x = 0, a/3, 2a/3$ and a
 and ψ_3 reaches maximum values for $x=a/6, a/2$ and $5a/6$.

The wavelength of matter waves satisfies the condition for stationary waves.

$$k = \frac{n\pi}{a} = \frac{2\pi}{\lambda} \quad \text{or} \quad L = \frac{n\lambda}{2}$$

Energy Eigen values for a free particle

An ideal free particle does not have any constraint on its motion and can be found anywhere in space with equal probability. The potential energy $V(x) = 0$ between the limits, $-\infty \leq x \leq +\infty$.

Then the Schrodinger time independent equation for a free particle is

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2} E \psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} + k^2 \psi(x) = 0, \text{ where } \frac{8\pi^2m}{h^2} E = k^2$$

The equation for free particle is similar to that of a particle in an infinite potential well and the general solution is a travelling wave of form

$$\psi(x) = A \sin kx + B \cos kx$$

A and B cannot be evaluated as there are no boundary conditions.

The above eqn. holds good for a particle for which the potential $V=0$ over the entire space (no boundaries at all).

In the case of particle in an infinite potential well, the $V=0$ holds good only over a finite width 'a' and outside this region $V=\infty$.

The energy is not quantized and is given by the equation

$$E = \frac{k^2 h^2}{8\pi^2 m} = \frac{4\pi^2 h^2}{8\pi^2 m \lambda} = \frac{p^2}{2m}$$

The E vs k curve for a free particle is a parabola.

