Unit II- Quantum Mechanics

Matter and Radiation are both forms of energy and are inter convertible, as established by Einstein's mass energy equivalence relationship, E =mc². Electromagnetic radiation commonly exhibits wavelike properties (interference, diffraction and polarization) and in certain cases (black body radiation, photoelectric effect and Compton scattering) behaves like a stream of particles called photons. The dual nature of electromagnetic radiation has led Louis de Broglie to propose that matter should also have dual character and that particles such as electrons should also have wave like properties.

de Broglie hypothesis: A free particle moving with a linear momentum, p, is associated with a sinusoidal wave of wavelength

 $\lambda = h/p \qquad (p=mv \ , \ m \ is \ the \ mass \ and \ v \ is \ the \ velocity \ of \ the \ particle)$ The wavelength λ is called the de Broglie wavelength.

- For ordinary objects, the wave like behavior cannot be observed as Planck's constant is very small ($\approx 10^{-34}$ Js).
- ➤ In the atomic or subatomic scale, the momentum can be sufficiently small to bring the de Broglie wavelength into the observable range.
- ➤ The basic difference between a wave and a particle is that position of a particle can be localized in time and space but a wave is spread out in both these dimensions.

Distinction between the expressions for energy of a photon and a particle

Photon is a mass less particle and for a photon $E = mc^2 = pc$

$$(mc = p$$
 as the velocity is equal to c)

$$E = pc = hc/\lambda$$
 for a photon

For a matter particle, the velocity is always less than the velocity of light and as the velocity approaches the velocity of light the mass of the particle tends to∞ as seen from the relation,

Relativistic mass,
$$m = m_0 / \sqrt{1 - (v^2/c^2)}$$
 -----(i)

where m_0 is the rest mass and m is the mass corresponding to a velocity v.

Squaring the equation (i) and rearranging the terms, we obtain

$$m^2 [c^2 - v^2] = m_0 c^2$$
 -----(ii)

Multiplying on both sides with c^2 we get,

$$m^2c^4 - m^2c^2v^2 = m_0^2c^4$$

or $E^2 = E_0^2 + p^2c^2$

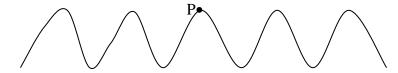
Therefore, energy of a relativistic matter particle, $E = \sqrt{E_o^2 + p^2 c^2}$

For a particle whose velocity, v << c, (non-relativistic particle), $m=m_0$

and
$$E = \frac{1}{2}mv^2 = p^2/2m$$

<u>Phase velocity:</u> Phase velocity is the velocity with which a phase point located on a progressive wave is transported.

Phase velocity is the same as the wave velocity. $V_P = v\lambda$ (v is the frequency)



Let P be a phase point located on a Travelling wave represented by the equation

$$y = Asin(kx - \omega t)$$

 $k=2\pi/\lambda$ is the wave number and $\omega=2\pi\nu$ is the angular frequency

 λ is the wavelength of the wave and ν is the frequency.

The velocity of the phase point will be the same as the wave velocity and can be given as

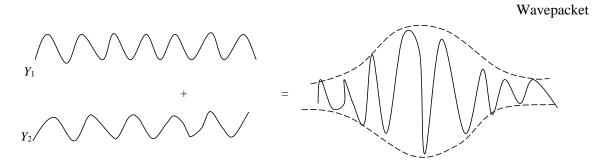
$$V_P = v \lambda = \frac{\omega}{2\pi} \cdot \frac{2\pi}{k} = \frac{\omega}{k}$$
(i)
Also, $v = E/h$ and $E = mc^2$ (ii)
 $\lambda = h/p$ and $p = mv$ (iii)

Substituting (ii) and (iii) in (i), we obtain $V_P = \frac{E}{p} = c^2/v$

v is the velocity of the particle associated with the wave. For photons (light quanta), v = c in vacuum and hence phase velocity is equal to velocity of light. Particles like electrons travel with velocities less than c and so phase velocity of matter waves $V_P > c$ which has no physical significance. For a physical representation of matter waves, we require to consider a wave packet to be associated with the moving body.

Group velocity

A wave group is formed due to superposition of waves of different wavelengths whose interference with one another results in variation of amplitude.



Expression for group velocity

Consider two waves of same amplitude A but slightly different wave numbers and angular frequencies represented by the equations,

$$y_1 = A \sin(kx - \omega t)$$
 and $y_2 = A \sin[(k + \Delta k)x - (\omega + \Delta \omega)t]$ -----(i)

The resultant of the superposition of these two waves can be written as,

$$y = y_1 + y_2 = 2Acos\left(\frac{\Delta kx}{2} - \frac{\Delta \omega t}{2}\right)sin\left[\left(\frac{2k + \Delta k}{2}\right)x - \left(\frac{2\omega + \Delta \omega}{2}\right)t\right]$$
 -----(ii)

Substituting, $2k + \Delta k \approx 2k$ and $2\omega + \Delta\omega \approx 2\omega$

$$y = 2A\cos\left(\frac{\Delta kx}{2} - \frac{\Delta \omega t}{2}\right)\sin(kx - \omega t) - (iii)$$

The above equation represents a sine wave of angular frequency ω and wave number k whose amplitude is modulated with the angular frequency $\Delta\omega/2$ and wave number $\Delta k/2$.

Group velocity is defined as the rate at which the amplitude is modulated **or** the rate at which energy is transported **or** the velocity of motion of the wave packet

From eqn. (iii) the rate of modulation of amplitude, $V_g = \Delta\omega/\Delta k = d\omega/dk$

$$d\omega = 2\pi. dv = 2\pi d(\frac{E}{h})$$
 and $dk = \frac{2\pi}{d\lambda} = 2\pi. h/p$

$$\therefore V_g = d\omega/dk = dE/dp$$

The wave packet consists of regions of constructive and destructive interference. The probability of finding the particle in a given region depends on the amplitude of the wave group in that region. The

wave group representation enables the localization of the particle. The motion of the wave group, not the motion of individual waves that make up the wave group, corresponds to the motion of the body. We can prove that group velocity of the wave packet is the same as the velocity of the particle.

To show that group velocity is equal to velocity of the particle

$$V_g = d\omega/dk = dE/dp$$
 $E = p^2/2m \text{ and } dE = 2p. dp/2m$
 $\frac{dE}{dp} = \frac{p}{m} = \frac{mv}{m} = v$
 $\therefore V_g = v$

Relationship between phase velocity and group velocity

Depending on how the phase velocity varies with wavelength, the group velocity may be less or greater than the phase velocities of the member waves. If the phase velocity is independent of wave length, it is a nondispersive medium. Variation of phase velocity with wavelength is called dispersion.

We can obtain the relationship between group and phase velocities in a dispersive medium in the following way:

$$V_P = \frac{\omega}{k} \quad or \ k. V_P = \omega$$
 -----(i)

Differentiate w.r.t.
$$k$$
 to obtain, $V_P + k \frac{dV_P}{dk} = \frac{d\omega}{dk} = V_g$ -----(ii)
$$k = \frac{2\pi}{\lambda} \qquad -----(iii)$$
 and
$$dk = -2\pi . \, d\lambda/\lambda^2 \qquad ------(iv)$$

substituting (iii) and (iv) in (ii) we obtain,

$$V_P - \lambda \frac{dV_P}{d\lambda} = V_g$$

which relates phase and group velocities in a dispersive medium.

Case 1.
$$V_g = V_{ph}/2$$

$$\frac{dV_p}{V_p} = \frac{1}{2} \frac{d\lambda}{\lambda} \quad \text{This on integration yields} \quad \ln(V_p) \propto \ln \sqrt{\lambda} \quad \text{or} \quad V_p \propto \sqrt{\lambda}$$

This implies that the phase velocity is proportional to the square root of the wavelength

Case 2.
$$V_g = 2V_{ph}$$

$$\frac{dV_p}{V_p} = -\frac{d\lambda}{\lambda}$$
 This on integration yields $\ln(V_p) \propto \ln(\frac{1}{\lambda})$ or $V_p \propto \lambda^{-1}$

This implies that the phase velocity is inversely proportional to the wavelength.

Heisenberg's Uncertainty Principle

Statement: It is not possible to determine simultaneously and with unlimited precision, a pair of conjugate variables like position and momentum of a particle.

Heisenberg's uncertainty relationships:

$$\Delta x. \Delta p \ge h/4\pi$$

 $\Delta \theta. \Delta L \ge h/4\pi$
 $\Delta t. \Delta E > h/4\pi$

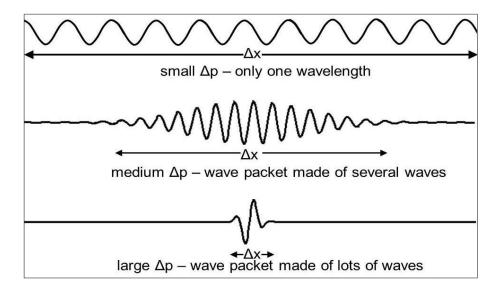
Heisenberg's uncertainty principle is a natural consequence of wave nature of matter.

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 wave which can extend from $x=-\infty$ to $x=+\infty$. This wave has a precisely defined wavelength and consequently, a precisely determined wave number and momentum. So, the uncertainty in the momentum $\Delta p=0$ which implies that the momentum can be precisely determined in case of a single wave. However, the amplitude of the wave is the same at all points from $x=-\infty$ to $x=+\infty$. and the uncertainty in determining the position $\Delta x=\infty$.

In order to localize the particle and reduce the uncertainty Δx from ∞ to a finite value we have to consider a wave group of different wavelengths and this introduces uncertainty in wave number and

hence the momentum. A large number of waves will result in lesser Δx and higher value of Δp and vice versa.



A more rigorous Fourier analysis of the waves will give us the relationship

$$\Delta x. \Delta p \ge h/4\pi$$

Applications of Heisenberg's uncertainty principle

(i) Applying the uncertainty principle, we can show that electrons cannot exist within the atomic nucleus

Proof:

The diameter of an atomic nucleus is $\approx 5 \text{ x} 10^{-15} \text{m}$. If an electron is inside the atomic nucleus, the uncertainty in determining its position, $\Delta x = 5 \text{ x} 10^{-15} \text{m}$.

The uncertainty in determining its momentum, $\Delta p = h/4\pi$. Δx

=6.6 ×
$$10^{-34}/4$$
 × 3.14 × 5 × 10^{-15}
= 1.05 × 10^{-20} kg m s⁻¹

But, the momentum must be greater than the uncertainty in it

ie.,
$$p \ge \Delta p$$
, or, $p = 1.05 \times 10^{-20} \text{ kg m s}^{-1}$

The energy of the electron can be calculated from the expression, $E = \sqrt{E_0^2 + p^2 c^2}$

$$E = \sqrt{\{9.1 \times 10^{-31} \times (3 \times 10^{8})^{2}\}^{2} + \{(1.05 \times 10^{-20})^{2} \times (3 \times 10^{8})^{2}\}}$$
=20 MeV

5×10⁻¹⁵m

If an electron has an energy of 20 MeV, it will escape from the nucleus since the binding energy of a nucleon is approximately 3 or 4 MeV. Hence an electron cannot be confined within the atomic nucleus.

Wave function

Matter waves are represented by a complex function, Ψ (x,t), which is called wave function. The wave function is not directly associated with any physical quantity but the square of the wave function represents the probability density in a given region. The wave function should satisfy the following conditions:

- (i) Ψ should be finite
- (ii)Ψ should be single valued
- (iii) Ψ and its first derivative should be continuous
- (iv) Ψ should be normalizable.

$$\int_{x=-\infty}^{x=+\infty} \Psi(x)^* \Psi(x) dx = 1$$
, in one dimension or

 $\iiint \Psi(r)^* \Psi(r) dr = 1 \text{ where } r = xi + yj + zk \text{ represents the position r in three dimensions.}$

Born's Interpretation

In 1926, Max Born attempted to relate the properties of the wave function $\Psi(x,t)$ and the behavior of the associated particle which is expressed in terms of the probability density P(x,t). This quantity specifies the probability per unit length of the x axis, of finding the particle near the coordinate x at time t. According to this postulate, $P(x,t) = \Psi^*(x,t)\Psi(x,t)$

Where $\Psi^*(x)$ is the complex conjugate of $\Psi(x,t)$

If, at the instant t, a measurement is made to locate the particle associated with the wave function $\Psi(x,t)$, then the probability P(x,t) dx that the particle will be found at a coordinate between x and x + dx is equal to $\Psi^*(x,t)\Psi(x,t)dx$.

Observables

The physical parameters associated with the particle such as energy, momentum, kinetic energy, spin, etc are observables of the state of a system. Experimental results can give us values of observables, and multiple measurements on the system at the same state should result in the same value or average

values for the observables, if the state of the system is not modified by the measurement. Observables have real values and their accurate measurements would be limited by the principles of uncertainty.

The wave function carries information about the state of the system or the observables can be extracted from the wave functions with the help of appropriate operators.

Operators

Generally, operators tell us, what operation to carry out on the quantity that follows. Let us consider a system described by the wave function $\psi(x,t)=Ae^{\frac{i}{\hbar}(px-Et)}$. This function contains information about the observables of the system. The values of the observables can be inferred using a mathematical operator operating on the wave function.

Differentiating ψ with respect to x, $\frac{d\psi}{dx} = (\frac{ip}{\hbar})\psi$

Or the operation $\left\{-i\hbar\frac{d}{dx}\right\}$ on ψ yields the momentum of the system.

 $\hat{p} = \left\{-i\hbar \frac{d}{dx}\right\}$ is the momentum operator.

Differentiating the above yields $\frac{d^2\psi}{dx^2} = (\frac{ip}{\hbar})^2\psi$

Rearranging the terms and dividing by 2m we get $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \frac{p^2}{2m}\psi = KE\psi$

Thus the operation $\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\}$ on ψ yields the kinetic energy.

 $\widehat{KE} = \{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\}$ is the kinetic energy operator

Differentiating ψ with respect to time yields $\frac{d\psi}{dt} = (-\frac{iE}{\hbar})\psi$

Or the operation $\left\{i\hbar\frac{d}{dt}\right\}$ on ψ yields the total energy of the system

 $\widehat{E} = \left\{ i\hbar \frac{d}{dt} \right\}$ is the total energy operator.

The position operator $\hat{x} = x$.

The potential energy operator is not explicitly defined as the potential energy can be inferred if the total energy and the kinetic energy of the system is known.

Momentum operator	$\hat{p} = \left\{ -i\hbar \frac{d}{dx} \right\}$
Kinetic energy operator	$\widehat{KE} = \{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\}$
Total energy operator	$\widehat{E} = \left\{ i\hbar \frac{d}{dt} \right\}$
Position operator	$\hat{\mathbf{x}} = \mathbf{x}$.
Hamiltonian operator	$\widehat{H} = \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right\} + V$

Expectation values

Quantum mechanics deals with probabilities and hence predicts only the most probable values of the observables of a physical system which are called the expectation values. These expectation values could be the average of repeated measurements on the system. The method of evaluating the expectation values is outlined as below.

Let \hat{p} be an operator that gives the value of the momentum p when it operates on the wave function ψ .

The operation $\psi^*\hat{p}\psi = \psi^*p\psi = p\psi^*\psi$ where p is the value of the observable extracted from ψ . If the many values of p are extracted from the wave function has to be averaged for the wave packet. The same can be obtained by integrating the expression $\psi^*\hat{p}\psi$ which gives

 $\int \psi^* \hat{p} \psi \, dV = \int \psi^* p \psi \, dV = \langle p \rangle \int \psi^* \psi \, dV \text{ where } \langle p \rangle \text{ is the most probable value of the momentum.}$

Thus, the expectation value of the momentum is written as $\langle p \rangle = \frac{\int \psi^* \hat{p} \psi dV}{\int \psi^* \psi dV}$.

If the integral is over all of space then the integrals could be evaluated between limits of $\pm \infty$. In this case it is observed that the denominator would be the total probability and can be written as 1. However, it is customary to write the expectation values in the standard form.

In the general case for an operator \widehat{A} the expectation value of the parameter A can be written as $\langle A \rangle = \frac{\int \psi^* \widehat{A} \psi dV}{\int \psi^* \psi dV} \,.$

Schrodinger's time independent wave equation in one dimension

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 a similar equation and we can write the equation for matter waves as

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

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

Let
$$\Psi(x,t) = \Psi_0(x)e^{-i\omega t} \cdots (ii)$$

where, $\Psi_0(x)$ depends only on 'x,' and $e^{-i\omega t}$ depends only on 't'.

Differentiate eqn. (ii) w.r.t. 'x' successively to obtain

$$\frac{\partial \Psi(x,t)}{\partial x} = \frac{d\Psi_0(x)}{dx} e^{-i\omega t} \quad \text{and} \quad$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{d^2 \Psi_0(x)}{\partial x^2} e^{-i\omega t} \cdots \cdots (iii)$$

Differentiate eqn.(ii) w.r.t. 't' to obtain

$$\frac{\partial \Psi(x,t)}{\partial t} = (-i\omega)\Psi_0(x)e^{-i\omega t}$$

$$\frac{\partial^2 \Psi(x,t)}{\partial t^2} = (-i\omega)^2 \Psi_0(x) e^{-i\omega t} \cdots (iv)$$

Substituting (iii) and (iv) in eqn. (i), we obtain

$$\frac{d^2\Psi_0(x)}{\partial x^2} e^{-i\omega t} = -\frac{\omega^2}{v^2} \Psi_0(x) e^{-i\omega t} \cdots (v)$$

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

$$\frac{d^2\Psi_0(x)}{\partial x^2} = -\frac{\omega^2}{v^2} \Psi_0(x) = -k^2\Psi_0(x) \cdots (vi)$$

or
$$\frac{d^2\Psi_0(x)}{\partial x^2} + k^2\Psi_0(x) = 0 \qquad \cdots \cdots (vii)$$

$$k = \frac{2\pi}{\lambda}$$
 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

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

Substituting the value of k^2 and replacing $\Psi_0(x)$ by $\Psi(x)$ in eqn.(vii), we obtain the Schrodinger's time independent wave equation in one dimension as:

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

The above equation can be solved for different cases to obtain the allowed values of energy and the allowed wave functions.

Eigen values and Eigen functions

Upon solving the Schrodinger wave equation, the values of energy E_n is called Eigen values and the corresponding wave functions as Eigen functions. Eigen functions are exact solutions of the Schrodinger's wave equation.

Example: Discrete energy levels of Hydrogen atom $E_n=\frac{me^4}{32\pi^2\epsilon_0^2h^2}\frac{1}{n^2}$, which is called the Eigen values.

In general, Eigen value equation is written as $\widehat{G}\Psi(x) = G\Psi(x)$.

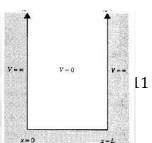
Similarly, energy eigen value equation is $\widehat{E}\Psi(x) = E\Psi(x)$.

where, \widehat{G} and \widehat{E} are operators when operated on ψ , gives eigen values G and E.

Particle in an infinite one-dimensional potential well

Consider a particle of mass 'm' confined to a one-dimensional potential well of dimension 'L'. The potential energy, $V = \infty$ at x=0 and x=L and V=0 for $0 \le x \le L$. The walls are perfectly rigid and the probability of finding the particle is zero at the walls.

Hence, the boundary conditions are, $\Psi(x) = 0$ at x=0 and x=L. $V = \infty$ The one-dimensional time independent wave equation is



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

We can substitute V=0 since the particle is free to move inside the potential well.

we obtain ,
$$\frac{d^2\Psi(x)}{dx^2} + \frac{8\pi^2 mE}{h^2} \Psi(x) = 0$$
Let
$$\frac{8\pi^2 mE}{h^2} = k^2 \text{ and the wave equation is,}$$

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

The above equation represents simple harmonic motion and the general solution is

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

Applying the condition, $\Psi(x) = 0$ at x = 0, we get

$$0 = A.0 + B$$
 which implies that B = 0

Substituting the condition $\Psi(x) = 0$ at x = L, we get, $A \sin kL = 0$

$$A \neq 0$$
 which implies that $\sin kL = 0$

The quantization condition is

$$kL = n\pi$$

or, $k = n\pi/L$ where $n = 1,2,3 \cdots$ is a positive integer.

Eigen values of energy:

$$E_n = \frac{k^2 h^2}{8\pi^2 m} = \frac{n^2 \pi^2 h^2}{8\pi^2 m L^2}$$
$$E_n = \frac{n^2 h^2}{8m L^2}$$

n' is the quantum number corresponding to a given energy level.

n=1 corresponds to the ground state, n=2 corresponds to the first excited state and so on.

Eigen functions: The allowed wavefunctions are

$$\Psi_n(x) = A \sin(n\pi x/L)$$

The constant A can be evaluated from normalization condition,

$$\int_{r=0}^{x=L} A^2 \sin^2(n\pi x/L) = 1$$

using the trigonometric identity $sin^2\theta = (1 - cos2\theta)/2$

we get
$$A^2 \int_0^L \left(\frac{1 - \cos(\frac{2\pi nx}{L})}{2} \right) dx = 1$$

after integration we obtain, $\frac{A^2}{2} \left[x - \frac{L}{2n\pi} \sin(2n\pi x/L) \right]_0^L = 1$

or
$$\frac{A^2L}{2} = 1$$
 or $A = \sqrt{\frac{2}{L}}$

hence, the eigen functions are $\Psi_n(x) = \sqrt{\frac{2}{L}}$ $Sin(n\pi x/L)$

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

$$P_{n}(x) = \frac{2}{L} \sin^{2}(n\pi x/L) dx$$
or,
$$\int_{x_{1}}^{x_{2}} P_{n}(x) dx = \int_{x_{1}}^{x_{2}} \frac{2}{L} \sin^{2}(n\pi x/L) dx$$

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

Eigen values

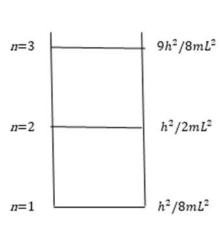
Eigen functions

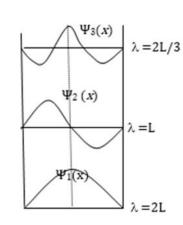
Probability densities $P_n(x)$

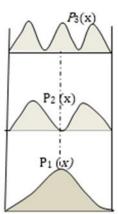
$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$\Psi_n(x) = \sqrt{2/L} \sin(n\pi x/L) \qquad P_n(x) = \frac{2}{L} \sin^2(n\pi x/L) dx$$

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







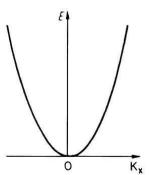
The wave length ' λ ' of the matter waves satisfies the condition for stationary waves.

$$k = n\pi/L = \frac{2\pi}{\lambda}$$
 or $\frac{n\lambda}{2} = L$

Free Particle

An ideal free particle does not have any constraints on its motion and can be found anywhere in space with equal probability. The potential energy V(x) = 0 between the limits, $-\infty \le x \le +\infty$. The Schrodinger's wave equation for a free particle is

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



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

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

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

The energy is not quantized and is given by the equation

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

E vs k curve for a free particle is a parabola