Wave Nature of Particle & Schrodinger Wave Equation

Wave Nature of Particles →

Quantum Mechanics →

Quantum Mechanics is the branch of physics which deals with the microscopic particles.

De-broglie proposed that a material particle such as electron, proton, etc is associated with the wave if m is the mass of the material particle moving with velocity v then the wavelength of the ~~velocity~~ wave associated with it is given by →

$$\lambda = \frac{h}{mv} = \frac{\lambda}{p}$$

where, p = momentum of particle

This is called De-broglie wavelength. The wave associated with the material particle is called Matter wave OR De-broglie wave. Hence, the material particle has dual nature.

Free Particle →

A particle which is not acted upon by any force is called Free particle.

According to Newton 2nd Law of motion →

$$F = \frac{dp}{dt}$$

For Free particle, F = 0

$$\frac{dp}{dt} = 0$$

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p = constant

This means that the free particle has a constant momentum. The total energy of free particle is only kinetic energy and is given by

$$E = \frac{1}{2} m v^2$$

$$E = \frac{1}{2} m v^2 \times \frac{m}{m}$$

$$E = \frac{1}{2} \frac{m^2 v^2}{m}$$

$$E = \frac{p^2}{2m}$$

Since, p is a constant. Therefore, the energy of the free particle is also constant. Hence, a free particle is characterised by definite momentum & energy.

Wave Function for a Free Particle →

Wave function is a function which describes the matter wave associated with the material particle and is represented by →

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

k = Propogation constant = $\frac{2\pi}{T}$

t = Time

A = Amplitude of wave

ω = Angular frequency

x = location of particle

This wave function describes the matter wave associated with free particle and moving along the x-axis.

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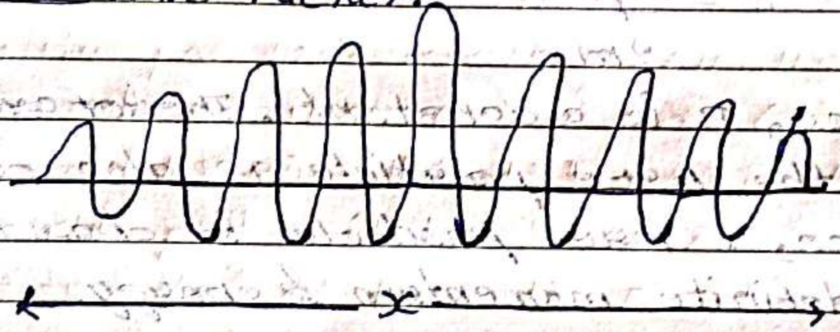
Wave Packet →

The material particle is represented by wave function $\psi(x,t) = Ae^{i(kx-\omega t)}$.

This wave spreads out over the infinite extent in one dimensional space. In order to describe the particle localised in a certain region (Δx). It is necessary that the wave function should be zero everywhere except in the region (Δx) where the particle is located.

A wave of finite extent is shown in the fig. ~~is called wave packet.~~



In order to obtain a wave packet. It is necessary to modulate the amplitude of the wave in such a way that it is non-zero in the region (Δx) and zero outside. This can be done by adding the no. of waves of slightly different frequencies & amplitude. If we suppose (N) no. of waves then the function can be written as

$$\psi(x;t) = \sum_{i=1}^{N} A_i e^{i(k_i x - \omega_i t)}$$

OR

$$\psi(x,t) = \int_{-\infty}^{+\infty} A(k) e^{i(kx-\omega t)} dx$$

This wave function represents a wave packet which describes a localised particle. Hence, we conclude that a localised particle is always associated with the wave packet.

Uncertainity Principle →

According to uncertainity principle, it is impossible to measure simultaneously and precisely both the position and momentum of particle. If the (Δx) is the uncertainity in position & (ΔP) is the uncertainity in momentum. Then,

$$\Delta x \cdot \Delta P_x \geq \hbar$$

It states that, if we try to measure the position & momentum of particle simultaneously then the product of uncertainities (Δx) and (ΔP_x) cannot be less than $\hbar$.

$$\Delta P_x \geq \frac{\hbar}{\Delta x}$$

$\Delta x = 0$

$$\Delta P_x \geq \frac{\hbar}{0} \Rightarrow \Delta P_x \geq \infty$$

This means that the momentum of the particle is completely unknown.

$$\text{If } \Delta P_x = 0 \Rightarrow \Delta x \geq \infty$$

Hence, the particle is completely unlocalised & spreads out all over the space.

In 3D, the uncertainity principle becomes

$$\Delta y \cdot \Delta P_y \geq \hbar$$

$$\Delta z \cdot \Delta P_z \geq \hbar$$

The uncertainity principle indicates that we don't known the exact position and momentum of particle of atomic dimensions.

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Born Interpretation of Wave Functions →

Max Born →

Extend the concept of wave packet associated with a material particle the motion of the electron travelling (x) direction with constant momentum (P) is controlled by the matter waves associated with its. The wave function of such a wave is given by →

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

The quantity $(\psi)^2$ play the important role for the matter waves. The square of the absolute value of wave function $\psi(x,t)$ measures the probability per unit length of finding the electron at position (x) & time (t).

The product $(P) = \psi(x,t)\,\psi(x,t)$ is the probability per unit length of finding the particle at position (x) at time (t). $P(x,t)$ is the probability density. The probability of finding the particle is large whenever (ψ) is large & vice-versa.

Hence, $\psi(x,t)$ is called probability amplitude.

→ Born Interpretation of wave function mean the location of the particle cannot be defined precisely but the wave function can predict only the probability density for finding the particle.

Time Dependent Schrodinger Wave Equation →

Newton's law cannot describe the motion of the particles of atomic dimensions where behaviour is explained by De-broglie waves associated with them OR by the wave function. The knowledge of $\psi(x,t)$ at one point in space & time is not sufficient. We need to know $\psi(x,t)$ at all the times to describe the motion of the particles in space and time. For this it is necessary to find a differential equation which controls the space-time behaviour of the wave function.

→ For free particle :-

The wave function for a free particle is given by

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

The total energy of a free particle of mass 'm' is only kinetic & is given by →

$$E = \frac{1}{2}mv^2 = \frac{p^2}{mv} \rightarrow 1st$$

The momentum & the energy is related to the propagation constant & angular frequency by the relation

$$E = \hbar\omega$$

$$p = \hbar k$$

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \rightarrow 2nd$$

$\lambda = \frac{h}{p}$

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

$\therefore \frac{2\pi}{k} = \frac{h}{p} \Rightarrow p = \frac{h}{2\pi} \times k$

$p = \hbar k$

Differentiate the wave function $\psi(x,t)$ with respect to x & time. We get →

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

$$\frac{\partial^2 \psi}{\partial x^2} = -Ak^2 e^{i(kx-\omega t)}$$

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi$$

$$k^2 = -\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2} \rightarrow 3rd$$

$$\frac{\partial \psi}{\partial t} = A i \omega e^{i(kx-\omega t)}$$

$$\frac{\partial^2 \psi}{\partial t^2} = A i^2 \omega^2 e^{i(kx-\omega t)}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -A \omega^2 e^{i(kx-\omega t)}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi$$

$$\omega = -\frac{1}{i\psi}\frac{\partial \psi}{\partial t}$$

$$\omega = -\frac{i^2}{i\psi}\frac{\partial \psi}{\partial t}$$

$$\omega = \frac{i}{\psi}\frac{\partial \psi}{\partial t} \rightarrow 4th$$

From 2nd, 3rd & 4th

$$\frac{i\hbar}{\psi}\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m\psi} \cdot \frac{\partial^2 \psi}{\partial x^2}$$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} \rightarrow 5th$$

This is the time dependent wave equation for a free particle.

→ For a particle subjected to a force :-

When the particle is acted upon by a force then the total energy is the sum of the K.E & P.E. Hence,

$$E = \frac{1}{2} m v^2 + V(x,t)$$

Then, the wave equation becomes →

$$\frac{i\hbar}{\psi}\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m\psi}\frac{\partial^2\psi}{\partial x^2} + V(x,t) \quad \text{[From 5th]}$$

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

This is one dimensional time dependent wave equation for a particle subjected to a force.

For 3D →

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\psi + V(r,t)\,\psi(r,t)$$

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\psi + V(r,t)\,\psi(r,t)$$

Note → • $E = h\nu \times \frac{2\pi}{2\pi}$

$$E = \frac{h}{2\pi} \cdot 2\pi\nu$$

$$E = \hbar\omega$$

• ~~REMX~~ $\lambda = \frac{h}{p}$

$$p = \frac{h}{\lambda} \times \frac{2\pi}{2\pi}$$

$$p = \hbar k$$

Time Independent Schrondinger Wave Equation →

The one dimensional time independent schrodinger wave equation is =

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi$$

In quantum mechanics, the potential energy is not a function of time. In such case, it is possible to separate the space & time variable in the Schrodinger Wave equation. Let us assume that the wave Function $\psi(x,t)$ is a product of two Functions $\psi(x)\,T(t)$. Then, we can write →

$$\psi(x,t) = \psi(x)\,T(t)$$

$$i\hbar \frac{\partial \psi(x)T(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)T(t)}{\partial x^2} + V\psi(x)T(t)$$

$$i\hbar\,\psi(x)\frac{\partial T(t)}{\partial t} = -\frac{\hbar^2}{2m}T(t)\frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\,\psi(x)\,T(t)$$

Divide the above equation by $\psi(x)\,T(t)$ →

$$\frac{i\hbar}{T(t)}\frac{\partial T(t)}{\partial t} = -\frac{\hbar^2}{2m\psi(x)}\frac{\partial^2 \psi(x)}{\partial x^2} + V(x)$$

The Right Hand Side of this equation is a Function of x only. and the LHS is a Function of $T(t)$ only. The only wave in which both sides can be equal is that each expression should be equal to a constant.

Let us assume the constant be E.

$$\frac{i\hbar}{T(t)}\frac{\partial T}{\partial t} = E$$

$$-\frac{\hbar^2}{2m\psi(x)}\frac{\partial^2 \psi}{\partial x^2} + V(x) = E$$

$$-\frac{\hbar^2}{2m\psi(x)}\frac{\partial^2 \psi}{\partial x^2} = E - V(x)$$

$$-\frac{\partial^2 \psi}{\partial x^2} = \frac{2m}{\hbar^2}(E - V)\,\psi(x)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\,\psi(x) = 0$$

This equation is known as Time independent Schroding Wave equation in one dimension.

$$\nabla^2 \psi + \frac{2m}{\hbar^2}[(E-V)(\vec{r})]\,\psi(r) = 0$$

This equation is in 3-D. $[\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}]$

Expectation Value →

The average value of a function in quantum mechanics is called Expectation value. The expectation value of a function $F(x)$ is represented as $\langle F(x)\rangle$.

$$\langle F(x)\rangle = \int \psi^*(x,t)\,F(x)\,\psi(x,t)\,dx$$

Expectation Value of Momentum →

The expectation value of x component of momentum is written as →

$$\langle P_x\rangle = \int \psi^*(x,t)\,P_x\,\psi(x,t)\,dx \rightarrow 1st$$

consider a wave function of a free particle moving in x direction is given by

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

$$\frac{\partial \psi}{\partial x} = iAk\,e^{i(kx-\omega t)}$$

$$P_x = \hbar k \Rightarrow k = \frac{P_x}{\hbar} \qquad \left[\hbar = \frac{h}{2\pi}\right]$$

$$\frac{\partial \psi}{\partial x} = \frac{iP_x}{\hbar}Ae^{i(kx-\omega t)}$$

$$\frac{\hbar}{iAe^{i(kx-\omega t)}}\frac{\partial \psi}{\partial x} = P$$

$$\frac{\hbar}{i}\frac{\partial \psi}{\partial x} = P_x\,\psi(x,t)$$

Put in 1st

$$\langle P_x\rangle = \int \psi^*(x,t)\,\frac{\hbar}{i}\frac{\partial \psi}{\partial x}\,dx$$

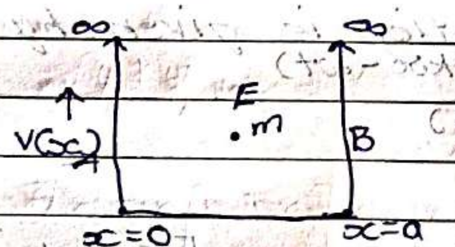
$$\langle P_x\rangle = \int \psi^*(x,t)\,\frac{\hbar}{i}\frac{\partial \psi(x,t)}{\partial x}\,dx$$

$$\langle P_x \rangle = -\int \Psi(x,t) \frac{i\hbar\, \partial \psi(x,t)}{\partial x} dx$$

$$P_x \longrightarrow -i\hbar \frac{\partial}{\partial x}, \quad P_y \rightarrow -i\hbar \frac{\partial}{\partial y}, \quad P_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

Expectation value of Energy $E \rightarrow i\hbar \frac{\partial}{\partial t}$

Solution of stationary state Schrodinger Equation
For one dimensional Problem Particle in 1-D box →
consider a one-dimensional closed box of width [a]
This box is represented by infinite square well.
It is defined as $V(x) = 0, \; 0 < x < a$
where $V(x) = \infty, \; x < 0, \; x > a$
$V(x)$ = potential difference



Suppose a particle of mass 'm' & energy 'E' is confined between the two rigid walls A & B at $x=0$ & $x=a$ respectively. The one-dimensional schrondinger wave equation is given by →

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

Inside the well $V(x) = 0$, so, equation becomes →

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2mE}{\hbar^2}\Psi = 0$$

$$\frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi = 0 \quad \rightarrow 1st$$

where $k^2 = \frac{2mE}{\hbar^2}$ $\rightarrow$ 2nd

The general solution of equation 1st is $\rightarrow$

$$\psi(x) = A\sin(kx) + B\cos(kx) \rightarrow 3rd$$

where A & B are the arbitrary constants.

At $x = 0$, $\psi(x) = 0$

Put in 3rd

$$0 = A\sin k \times 0 + B\cos k \times 0$$

$$0 = 0 + B$$

$B = 0$ Now, $\psi(x) = A\sin(kx)$

At $x = a$, $\psi(x) = 0$

$$0 = A\sin(ka)$$

$$\sin ka = 0$$

$ka = \pm n\pi$ where, n is a integer $[n = 1, 2, 3, \ldots]$

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

From eqn 2nd $\rightarrow$

$$\frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$

It is called the Ground state energy of the particle. This minimum energy of particle is called zero point energy.

For $n = 2$

$$E_2 = \frac{4\pi^2\hbar^2}{2ma^2}$$

The state of the particle corresponding to $n = 2, 3, \ldots$ are called Excited states.

$$E_3 = \frac{9\hbar^2\pi^2}{2ma^2}$$

Hence, the particle inside the potential well cannot have any arbitary energy but only discrete energy values given by $E_1, E_2, E_3, \ldots$
So, the energy of the particle in the box is quantized.

Eigen values → E_1, E_2, E_3 are the eigen values.

Eigen Function →
Put the value of K in equation $\psi(x) = A\sin(kx)$

$$\psi(x) = A\sin\left[\frac{n\pi x}{a}\right]$$

To find the value of K apply the normalization condition.

$$\int \psi_n^* \psi_n \, dx = 1$$

$$\int A\sin\left[\frac{n\pi x}{a}\right] A\sin\left[\frac{n\pi x}{a}\right] dx = 1$$

$$\int_0^a A^2 \sin^2\left[\frac{n\pi x}{a}\right] = 1$$

Using the standard ~~cond~~ integral

$$\int_0^a \sin^2\left[\frac{n\pi x}{a}\right] = \frac{a}{2}$$

Now,

$$A^2 \frac{a}{2} = 1$$

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

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

This function is known as Eigen Function.

Linear Harmonic Oscillator →

A system on which the force is directly proportional to the displacement from equilibrium position & [x] in a direction opposite to the displacement is called a Harmonic Oscillator.

If $x=0$ is the equilibrium position then the force is $F \propto -x$.

$$F = -kx$$

where, k is the constant of proportionality. The relation b/w force & the potential energy is given by

$$F = -\frac{dV}{dx}$$

$$+Kx = +\frac{dV}{dx}$$

$$Kx = \frac{dV}{dx}$$

$$kx\,dx = dV$$

Integrating both sides →

$$V = \frac{1}{2}Kx^2$$

This gives the potential energy of harmonic oscillator. We know that the time independent schrondinger wave equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

For harmonic oscillator $V = \frac{1}{2}kx^2$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}kx^2\right]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE\psi}{\hbar^2} - \frac{kmx^2\psi}{\hbar^2} = 0$$

We know that $k = \omega^2 m$. So, eqn becomes

$$\frac{d^2\psi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \frac{\omega^2 m^2 x^2}{\hbar^2}\right]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + (\beta^2 - \alpha^2 x^2)\psi = 0$$

where, $\beta^2 = \frac{2mE}{\hbar^2}$ & $\alpha^2 = \frac{\omega^2 m^2}{\hbar^2}$

On solving the above equation we obtain

$$\frac{\beta}{\alpha} = 2n+1$$

Now,

$$\frac{\sqrt{2mE}/\hbar}{\omega m/\hbar} = 2n+1$$

$$\frac{2mE}{\omega^2 m^2} = (2n+1)^2$$

$$E = \frac{1}{2}\omega^2 m(2n+1)^2$$

$$\frac{2mE/\hbar^2}{\omega^2 m/\hbar} = (2n+1)$$

$$\frac{2E}{\omega\hbar} = (2n+1)$$

$$E = \frac{1}{2}\omega\hbar(2n+1)$$

$$E = \hbar\omega\left[n + \frac{1}{2}\right]$$

where $n = 0, 1, 2, 3, 4, \ldots$

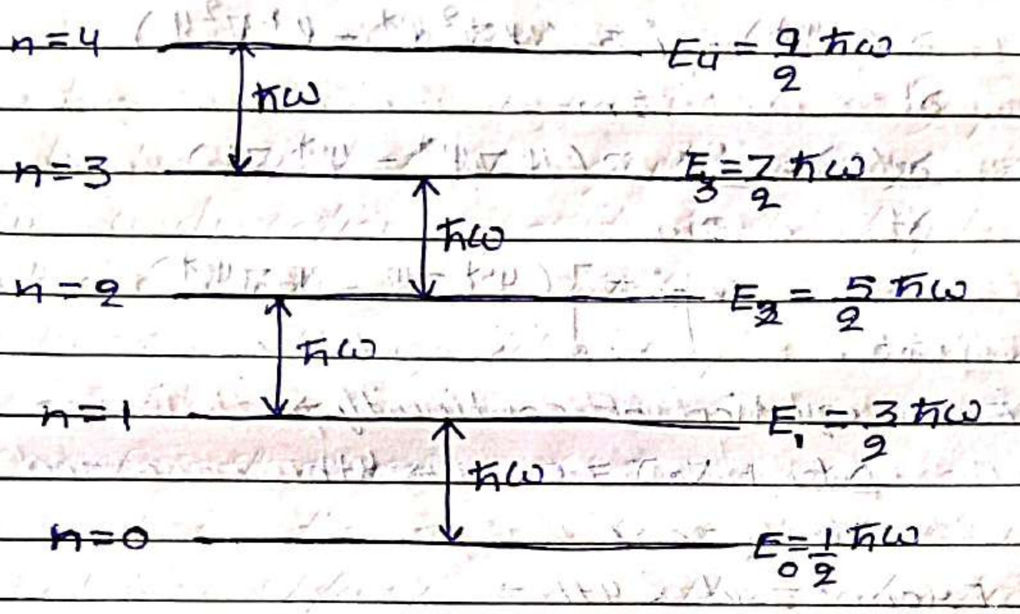
Since, the energy depends on n:

$$E_n = \left[n + \frac{1}{2}\right]\hbar\omega$$

when $n = 0$

The oscillator have minimum $E_0 = \frac{1}{2}\hbar\omega$

This energy is called zero point energy. Hence, the particle executing simple harmonic motion can only have discrete energies, i.e, $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega$



Probability current →

consider a plane wave is represented by a wave function $\Psi(x,t) = Ae^{i(kx-\omega t)}$. The time dependent Schrondinger wave equation is →

$$i\hbar\frac{\partial\Psi}{\partial t} = \frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

Multiply by Ψ^* on both sides →

$$i\hbar\Psi^*\frac{\partial\Psi}{\partial t} = \frac{\hbar^2}{2m}\Psi^*\nabla^2\Psi + V\Psi\Psi^* \rightarrow 1st$$

Taking the complex conjugate of equation 1st

$$-i\hbar\Psi\frac{\partial\Psi^*}{\partial t} = \frac{\hbar^2}{2m}\Psi\nabla^2\Psi^* + V\Psi\Psi^* \rightarrow 2nd$$

Subtract eqn 2nd from 1st →

$$i\hbar\Psi^*\frac{\partial\Psi}{\partial t} + i\hbar\Psi\frac{\partial\Psi^*}{\partial t} = \frac{\hbar^2}{2m}\Psi^*\nabla^2\Psi + \cancel{V\Psi\Psi^*} - \frac{\hbar^2}{2m}\Psi\nabla^2\Psi^* - \cancel{V\Psi\Psi^*}$$

$$i\hbar\left[\Psi^*\frac{\partial\Psi}{\partial t} + \Psi\frac{\partial\Psi^*}{\partial t}\right] = \frac{\hbar^2}{2m}\left[\Psi^*\nabla^2\Psi - \Psi\nabla^2\Psi^*\right]$$

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$$i\hbar \frac{\partial (\psi\psi^*)}{\partial t} = -\frac{\hbar^2}{2m}(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi)$$

$$i\frac{\partial (\psi\psi^*)}{\partial t} = \frac{i^2\hbar}{2m}(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi)$$

$$\frac{\partial (\psi\psi^*)}{\partial t} = \frac{i\hbar}{2m}(\psi\nabla^2\psi^* - \psi^*\nabla^2\psi)$$

$$\frac{\partial (P)}{\partial t} = \frac{i\hbar}{2m}\nabla(\psi\nabla\psi^* - \psi^*\nabla\psi)$$

$$\frac{\partial P}{\partial t} = -\nabla\left[\frac{i\hbar}{2m}\right](\psi^*\nabla\psi - \psi\nabla\psi^*) \rightarrow 3rd$$

From equation of continuity →

$$\frac{\partial \rho}{\partial t} + \nabla\cdot J = 0 \rightarrow 4th$$

From 3rd & 4th →

$$J = \frac{i\hbar}{2m}(\psi^*\nabla\psi - \psi\nabla\psi^*)$$

This gives you the probability current for a plane wave.

Properties of the Wave Function →

The wave function $\psi(x)$ & $\partial\psi/\partial x$ must satisfy the following conditions →

- The wave function $\psi(x,t)$ & $\partial\psi/\partial x$ must be finite everywhere.
- The wave function $\psi(x,t)$ & $\partial\psi/\partial x$ must be a single value.
- The wave function $\psi(x)$ must be continuous everywhere & its $\partial\psi/\partial x$ must be continuous everywhere.
- The $\psi(x)$ must be ~~ban~~ vanish at infinity.

$$\psi(x) = 0 \text{ at } x \rightarrow \infty$$