PH-107

Free Particle

Time-Dependent Schrodinger Equation

We are now convinced that we need to solve the TDSE to learn about the state of the particle, i.e.,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \qquad \text{in 3D}$$

or

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \qquad \text{in 1D}$$

Time-Independent Schrodinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\phi + V\phi = E\phi \qquad\qquad -\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V\phi = E\phi$$

Time-independent Schrödinger Equation (TISE)

We cannot go any further with solving the TISE, unless we are given the form of $V = V(x)$.

We will spend a lot of time in solving TISE for different types of $V = V(x)$ with different kinds of the boundary conditions.

Acceptable solution $\phi(x)$ must be continuous, single valued and its derivative must be continuous.

Free Particle

Free particle: *No force is acting on the particle*

$V(x) = V_0$ Particle moving in a constant potential

$V_0 = 0$ is a special case

Let us write TISE as

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} + V_0\phi(x) = E\phi(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} = (E - V_0)\phi(x) \implies \frac{d^2\phi(x)}{dx^2} = -\overbrace{\frac{2m(E-V_0)}{\hbar^2}}^{k^2}\phi(x)$$

$$\implies \frac{d^2\phi(x)}{dx^2} = -k^2\phi(x)$$

Free Particle

$$\frac{d^2\phi(x)}{dx^2} = -k^2\phi(x)$$

Let us guess a solution $\phi(x) = Ae^{\lambda x}$

After substituting the guessed solution

$$\frac{d^2\phi(x)}{dx^2} = -k^2\phi(x) \Longrightarrow \lambda^2 Ae^{\lambda x} = -k^2 Ae^{\lambda x} \Longrightarrow \lambda = \pm ik$$

Case I: $E > V_0 \Longrightarrow k^2 > 0 \Longrightarrow \lambda = \pm ik$

$$\phi(x) = Ae^{ikx} \text{ and/or } Ae^{-ikx}$$

In general, $\phi(x) = Ae^{ikx} + Be^{-ikx}$

Free Particle

$$\phi(x) = Ae^{ikx} + Be^{-ikx}$$

Show that this solution also satisfies TISE.

As we have seen in the previous slides:

$$k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \quad \Longrightarrow E = \frac{\hbar^2 k^2}{2m} + V_0$$

In the case of free particle, $V_0 = 0$ $\quad E = \frac{\hbar^2 k^2}{2m}$

Free Particle

Is free particle wavefunction is an eigen function of momentum operator ?

$$\phi(x) = Ae^{ikx}$$

momentum operator $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$

$$\hat{p}_x\phi(x) = -i\hbar\frac{\partial}{\partial x}Ae^{ikx} = -i\hbar(ik)Ae^{ikx} = \hbar k\ \phi(x)$$

momentum p_x

$$\hat{p}_x\phi(x) = p_x\phi(x)$$

Similarly $\phi(x) = Be^{-ikx}$

$$\hat{p}_x\phi(x) = -\hbar k\phi(x) = p_x\phi(x)$$

Expectation values

Let us evaluate the expectation value of momentum operator as

$$\langle p_x \rangle = \frac{\int_{-\infty}^{\infty} \phi^*(x)\left(-i\hbar\frac{\partial}{\partial x}\right)\phi(x)dx}{\int_{-\infty}^{\infty} \phi^*(x)\phi(x)dx}$$

For $\phi(x) = Ae^{ikx}$ **Travelling right**

$$\langle p_x \rangle = \hbar k \frac{\int_{-\infty}^{\infty} \phi^*(x)\phi(x)dx}{\int_{-\infty}^{\infty} \phi^*(x)\phi(x)dx} = \hbar k$$

For $\phi(x) = Be^{-ikx}$ **Travelling left**

$$\langle p_x \rangle = -\hbar k$$

Uncertainty

For $\phi(x) = Ae^{ikx}$ we know $\langle p_x \rangle = \hbar k$

Now

$$\langle p_x^2 \rangle == \frac{\int_{-\infty}^{\infty} \phi^*(x) \left(-i\hbar \frac{\partial}{\partial x}\right)^2 \phi(x) dx}{\int_{-\infty}^{\infty} \phi^*(x)\phi(x) dx} = (\hbar k)^2$$

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} = 0 \qquad \Longrightarrow \Delta x = \frac{\hbar}{2\Delta p_x} \to \infty$$

Estimate the speed of free particle based on present quantum mechanical analysis and compare it with the one obtained using classical description of free particle.

Are both the speed are same, if not then what is the reason behind it.

Normalisation

$$\phi(x) = Ae^{ikx} \implies \phi^*(x) = A^*e^{-ikx} \implies \phi^*(x)\phi(x) = |A|^2$$

Probability of finding a particle is constant everywhere!

$$\int_{-\infty}^{\infty} \phi^*(x)\phi(x)dx = |A|^2 \int_{-\infty}^{\infty} dx$$

Wavefunction can't be normalised.

Wavefunction is an eigen function of momentum operator, so position is delocalised.

As we have seen that the wavefunction of a free particle is not normalisable. How to overcome this issue?

Electrons in solids are routinely represented by free-particle wave function to describe several properties of solids. So the plane wave form of free-electron wave function is very useful.

Time-dependent Wavefunction

We know the general solution:

$$\phi(x) = Ae^{ikx} + Be^{-ikx}$$

$$\phi(x,t) = \phi(x)\ e^{-iEt/\hbar}$$

$$\phi(x,t) = (Ae^{ikx} + Be^{-ikx})e^{-iEt/\hbar}$$

$$\phi(x,t) = Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)} \qquad \omega = \frac{E}{\hbar}$$

Travelling right

Travelling left

Average value of Momentum

For $\phi(x) = Ae^{ikx} + Be^{-ikx}$

Let us calculate average value of momentum as

$$\langle p \rangle = \frac{\int_{-\infty}^{\infty} \phi^*(x) \left(-i\hbar \frac{\partial}{\partial x}\right) \phi(x) dx}{\int_{-\infty}^{\infty} \phi^*(x)\phi(x) dx}$$

$$= (-i\hbar) \frac{\int_{-\infty}^{\infty} (A^* e^{-ikx} + B^* e^{ikx}) \left(\frac{\partial}{\partial x}\right) (Ae^{ikx} + Be^{-ikx}) dx}{\int_{-\infty}^{\infty} (A^* e^{-ikx} + B^* e^{ikx})(Ae^{ikx} + Be^{-ikx}) dx}$$

$$= (-i\hbar)(ik) \frac{\int_{-\infty}^{\infty} (A^* e^{-ikx} + B^* e^{ikx})(Ae^{ikx} - Be^{-ikx}) dx}{\int_{-\infty}^{\infty} (A^* e^{-ikx} + B^* e^{ikx})(Ae^{ikx} + Be^{-ikx}) dx}$$

Average-value of Momentum

$$= (-i\hbar)(ik)\frac{\int_{-\infty}^{\infty}(A^*e^{-ikx}+B^*e^{ikx})(Ae^{ikx}-Be^{-ikx})dx}{\int_{-\infty}^{\infty}(A^*e^{-ikx}+B^*e^{ikx})(Ae^{ikx}+Be^{-ikx})dx}$$

$$= (\hbar k)\frac{\int_{-\infty}^{\infty}(|A|^2-|B|^2+AB^*e^{2ikx}-A^*Be^{-2ikx})dx}{\int_{-\infty}^{\infty}(|A|^2+|B|^2+AB^*e^{2ikx}+A^*Be^{-2ikx})dx}$$

Terms $\exp(\pm 2ikx)$ integrate out to zero.

Hence,

$$\boxed{\langle p\rangle = \hbar k\frac{|A|^2-|B|^2}{|A|^2+|B|^2}}$$

$\dfrac{|A|^2}{|A|^2+|B|^2}$ is the fraction which has positive momentum

$\dfrac{|B|^2}{|A|^2+|B|^2}$ is the fraction which has negative momentum

So far

$$\frac{d^2\phi(x)}{dx^2} = -k^2\phi(x) \qquad\qquad k = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$$

Assuming trial solution $\phi(x) = Ae^{\lambda x}$

For $E > V_0 \implies k^2 > 0 \implies \lambda = \pm ik$

We obtain $\phi(x) = Ae^{ikx} + Be^{-ikx}$

If $E < V_0 \implies k^2 < 0$ $\implies k = \sqrt{-\frac{2m|E - V_0|}{\hbar^2}} = i\kappa$

$$\kappa = \sqrt{\frac{2m|E - V_0|}{\hbar^2}}$$

In this case, $\lambda = \pm\kappa$

$$\phi(x) = Ce^{\kappa x} + De^{-\kappa x}$$

Also, if we recall earlier solution

$$\phi(x) = Ae^{ikx} + Be^{-ikx}$$

On substituting $k = i\kappa$, above equation is written as

$$\phi(x) = Ae^{-\kappa x} + Be^{\kappa x}$$

So, let us write

$$\phi(x) = Ce^{\kappa x} + De^{-\kappa x}$$

For $x > 0, x \to \infty, e^{\kappa x} \to \infty, e^{-\kappa x} \to 0$

Therefore, $\phi(x) = De^{-\kappa x}$ for $x > 0$

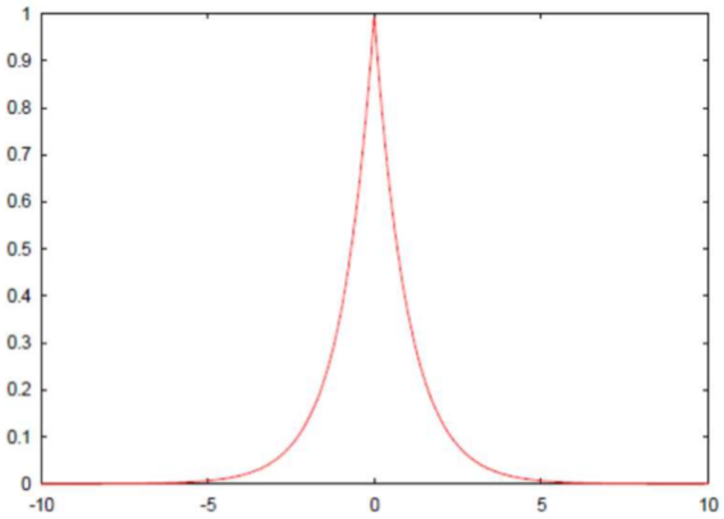
and $x < 0, x \to -\infty, e^{\kappa x} \to 0, e^{-\kappa x} \to \infty$

Therefore, $\phi(x) = Ce^{\kappa x}$ for $x < 0$

The wave function must be continuous and single valued

Therefore, $C = D$ and $\phi(x) = Ce^{-\kappa |x|}$

$$\phi(x) = Ce^{-\kappa|x|}$$



The wave function is continuous at x=0,

but the derivative of the function is not continuous at x = 0

$$\phi(x) = Ce^{\kappa x} \qquad \left.\frac{\partial\phi(x)}{\partial x}\right|_{x=0} = \kappa Ce^{\kappa x}|_{x=0} = \kappa C$$

$$\phi(x) = Ce^{-\kappa x} \qquad \left.\frac{\partial\phi(x)}{\partial x}\right|_{x=0} = -\kappa Ce^{-\kappa x}|_{x=0} = -\kappa C$$

For the derivative to be continuous, $\kappa C = -\kappa C \implies C = 0$

No physical solution exists for the case $E < V_0$ everywhere.

This does not mean that a solution does not exist if there are finite regions where $E < V_0$ and other regions where $E > V_0$

We shall revisit this problem later !