Free Particle

A free particle does not have any force acting on it, i.e we take the potential $V(x) = 0$.
This seems simple enough at first glance, in classical mechanics such a particle would either stay at rest if it was at rest in $t=0$, or would continue at constant velocity if it was at that velocity at $t=0$.

So we need to find a solution to the TISE when $V(x) = 0$
The TISE for this V is:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi \Rightarrow \frac{\partial^2\psi}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi \qquad \text{let } k^2 = \frac{2mE}{\hbar^2}$$

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

which is a pretty standard diff equation with ansatz: $\psi(x) = Ae^{ikx} + Be^{-ikx}$

We don't have any boundary conditions to constrain this wavefunction like we did for the infinite square well. But we can reintroduce the time-dependent term to see how this stationary state $\psi(x)$ varies in time:

$$\begin{aligned}\Psi(x,t) &= Ae^{ikx}e^{-iEt/\hbar} + Be^{-ikx}e^{-iEt/\hbar} \\ &= Ae^{ikx}e^{-ik^2\hbar t/2m} + Be^{-ikx}e^{-ik^2\hbar t/2m} \\ &= \underbrace{A\exp\left[i\left(kx - \frac{k^2\hbar t}{2m}\right)\right]}_{\text{right moving wave}} + \underbrace{B\exp\left[i\left(-kx - \frac{k^2\hbar t}{2m}\right)\right]}_{\text{left moving wave}}\end{aligned}$$

So we find that the solution contains two terms, one that corresponds to a wave moving right and the other corresponds to a wave moving left. The only difference between the two is the sign of k so we can use the more compact ansatz:

$$\Psi_k(x,t) = A\exp\left[i\left(kx - \frac{k^2\hbar t}{2m}\right)\right]$$

$$\Psi_k(x,t) = A\exp\left[i\left(k^2 x - \frac{\hbar k^2 t}{2m}\right)\right]$$

This is the solution for the free particle in quantum mechanics. That was simple, right? For $k > 0$, we have a right-travelling wave and for $k < 0$, we have a left travelling wave.

Using the definition of wave number $k = \frac{2\pi}{\lambda} \Rightarrow \lambda = \frac{2\pi}{|k|}$

we can relate this to de Broglie's wavelength $\lambda = \frac{h}{p}$, we get:

$$\lambda = \frac{h}{mv} = \frac{2\pi}{|k|} \Rightarrow \frac{h|k|}{2\pi m} = v$$

$$\therefore \quad \underline{\underline{v_{quantum} = \frac{\hbar|k|}{2m}}} \qquad \text{but } |k| = \frac{\sqrt{2mE}}{\hbar}$$

so $\underline{\underline{v_{quantum} = \sqrt{\frac{E}{2m}}}}$ if we compare this to the velocity we get in classical physics from $E = \frac{1}{2}mv^2$

$$v_{classical} = \sqrt{\frac{2E}{m}} = 2\sqrt{\frac{E}{2m}}$$

$$= 2\, v_{quantum}$$

Hmm, why is the velocity of a particle calculated using quantum theory half the velocity calculated using classical mechanics? Something isn't quite right...

Let's try and normalise our wavefunction:

$$\int \Psi_k^* \Psi_k \, dx = |A|^2 \int_{-\infty}^{\infty} \left(e^{i\left(kx - \frac{k^2\hbar t}{2m}\right)}\right)^* \left(e^{i\left(kx - \frac{k^2\hbar t}{2m}\right)}\right) dx = |A|^2 \int_{-\infty}^{\infty} dx$$

$$= |A|^2 \left[x\right]_{-\infty}^{\infty} = \underline{\infty}$$

So the wavefunction is not normaliseable! It's starting to look like the free particle is not so simple after all!

If the wavefunction is not normaliseable, then the free particle stationary state <u>cannot</u> be physical. Therefore, there cannot exist a free particle with finite energy!

It would seem no free particles exist in quantum mechanics, but we know from experiments that they do. So how do we fix this?

Consider what we learned from the infinite square well. Here we said that a general solution can be constructed as a linear combination of stationary states:

$$\Psi(x, t=0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \Leftrightarrow c_n = \int_{-\infty}^{\infty} \psi_n^*(x)\, \Psi(x, t=0)\, dx$$

where c_n gave the admixture of a given stationary state to the wave function $\Psi(x, t=0)$. Since the allowed energies for the infinite square well and the simple harmonic oscillator were discrete, the general solution was a discrete sum.

In the case of the free particle, the allowed energies are continuous as far as we know, so we need to use an integral instead of a discrete sum. Just using intuition, we can say something like:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\, e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)}\, dk$$

This seems like a little more than just intuition but don't worry!

The $\phi(k)$ function here seems to do what c_n did in the discrete case. It determines how much a stationary state for a particular momentum range $[k, k+dk]$ contributes to $\Psi(x,t)$. If we choose $\phi(k)$ smartly, we will be able to construct a normaliseable $\Psi(x,t)$ from the superposition of non-normaliseable wavefunctions $\psi_k(x,t)$. Wave functions constructed this way are called wave packets.

So how do we choose $\phi(k)$?

$$\boxed{\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)\, e^{ikx}\, dk} \Leftrightarrow \boxed{\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0)\, e^{-ikx}\, dx}$$

This relation is called the Fourier transform

Let's do an example to understand how this works.

Consider a free particle with initial condition:

$$\Psi(x,0) = \begin{cases} A & -a < x < a \\ 0 & \text{otherwise} \end{cases}$$

we can normalise this as $\int_{-\infty}^{\infty} |\Psi(x,0)|^2 \, dx = 1 \Rightarrow \int_{-a}^{a} |A|^2 \, dx$

$\Rightarrow 2a|A|^2 = 1$ so $A = \pm \frac{1}{\sqrt{2a}}$ we choose positive for convenience.

So let's determine $\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} \, dx$

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-\infty}^{\infty} e^{-ikx} \, dx = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \left[\frac{e^{-ikx}}{-ik} \right]_{-a}^{a}$$

$$= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \frac{1}{-ik} \left(e^{-ika} - e^{ika} \right) = \frac{1}{\sqrt{\pi a}} \frac{1}{k} \frac{e^{ika} - e^{-ika}}{2i}$$

$$= \underline{\frac{1}{\sqrt{\pi a}} \frac{1}{k} \sin(ka)}$$

We can thus find $\Psi(x,t)$ by using the formula but this time introducing the time dependent term $e^{-iEt/\hbar}$

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} e^{-iEt/\hbar} \, dk \quad \text{but } E = \frac{k^2 \hbar^2}{2m} \text{ so } \frac{-iEt}{\hbar} = -i \frac{\hbar k^2}{2m} t$$

$$= \underline{\underline{\frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{\pi a}} \int_{-\infty}^{\infty} \frac{1}{k} \sin(ka) \, e^{i\left(kx - \frac{\hbar k^2}{2m} t\right)} \, dk}}$$

This type of integral is called a Fresnel integral and cannot be evaluated analytically, only numerically.

So let's instead look at some special cases where the problem simplifies.

We will look at the cases of very small and very large a.

In the case of small a:

$$\phi(k) \approx \frac{1}{\sqrt{\pi a}} \frac{1}{k} ka = \sqrt{\frac{a}{\pi}}$$

so we have a very localised $\Psi(x,0)$ in position space but it is smeared out in momentum space.

In the case of large a:

$$\phi(k) = \frac{1}{\sqrt{\pi a}} \frac{a}{ka} \sin(ka) \quad \text{letting } ka = z$$

$$= \sqrt{\frac{a}{\pi}} \frac{1}{z} \sin(z)$$ This has a sharp maximum at $z=0$ that falls quickly.

So we have a very localised $\phi(k)$ but $\Psi(x,0)$ is smeared out.

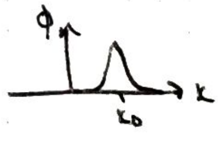
This is oddly familiar! It is just Heisenberg's uncertainty principle, that localising in one space smears out the wavefunction in the other.

So now we have shown how we can construct a physical solution to the free particle SE by superposing non-physical solutions. But we still haven't answered one of our other questions. Why is $V_{classical} = 2V_{quantum}$?

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx-\omega t)} dk \qquad \text{where } \omega = \frac{\hbar k^2}{2m}$$

We can identify two velocities, one velocity of the "envelope" and the other velocity of the individual waves. We call these group velocity and phase velocity respectively. Perhaps the $V_{quantum}$ we found earlier was for phase velocity while we should have been using group velocity?

We can test this for a momentum space wavefunction that narrowly peaks at k_0:



$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - w(k)t)} dk$$

We can expand $w(k)$ with a taylor exponsion as:

$$w(k) \simeq w(k_0) + \left[\frac{dw}{dk}\right]_{k_0} + \text{higher order values}$$

so $$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - (w_0 + w'(k-k_0))t)} dk$$

using $s = k - k_0$ $\quad \frac{ds}{dk} = 1 \Rightarrow ds = dk$:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k_0 + s) e^{i((k_0+s)x - w_0 t - w' s t)} ds$$

$$= \frac{1}{\sqrt{2\pi}} e^{i(-w_0 t + k_0 w_0' t)} \int_{-\infty}^{\infty} \phi(k_0 + s) e^{i(k_0+s)(x - w_0' t)}$$

$$= e^{i(-w_0 t + k_0 w_0' t)} \underbrace{\Psi(x - w_0' t, 0)}$$

This corresponds to a wavefunction moving with V_{group}

$$\therefore \quad \underline{\underline{V_{group} = \frac{dw}{dk}}}$$

so using $w = \frac{\hbar k^2}{2m} \Rightarrow \frac{dw}{dk} = V_{group} = \frac{\hbar k}{m} = 2 V_{quantum}$

$$\therefore \quad \underline{\underline{V_{classical} = V_{group} = 2 V_{quantum}}}$$

Bound and Scattering States

We have now studied both bound (infinite square well and harmonic oscillator) and scattering states (free particle). In bound states, the stationary states never have energy exceeding the potential, so are trapped. In scattering states, the stationary states have energy exceeding the potential.