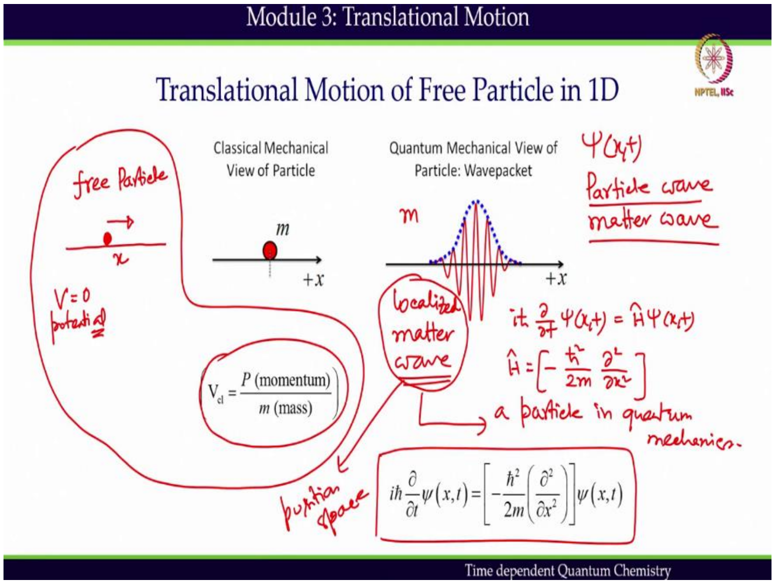
Time Dependent Quantum Chemistry
Professor Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Module: 03 Lecture: 16
Plane Matter Wave and Wavepacket

Welcome to module 3 of the course time dependent quantum chemistry. In this module, we will go over translational motion of free particle moving in 1-dimensional space and how to represent the quantum dynamics of a free particle.

(Refer Slide Time: 00:44)



One of the simplest form of motion is perhaps a free particle traveling in 1-dimensional space. And classical picture of such particle moving in 1-dimensional space is given here I have a space 1-dimensional space and generally we represent a particle by a ball like this and it is moving it is translating the potential experienced by the particle is 0.

Because it is free particle that is why V potential is 0 everywhere in in space, and classically this particle moves at constant velocity because there is no potential that is why it will just move without any restriction and we will have a constant velocity and classical velocity is given by momentum by mass.

$$V_{cl} = \frac{P(momentum)}{m(mass)}$$

That we are familiar with, but if I want to represent this classical idea, free particle moving in 1-dimensional space quantum mechanics this problem needs to be described using the time dependent Schrodinger equation and we can write down TDSE

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

Where Hamiltonian operator will be given for the free particle it is going to be only kinetic energy part potential part is 0.

$$\hat{H}=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]$$

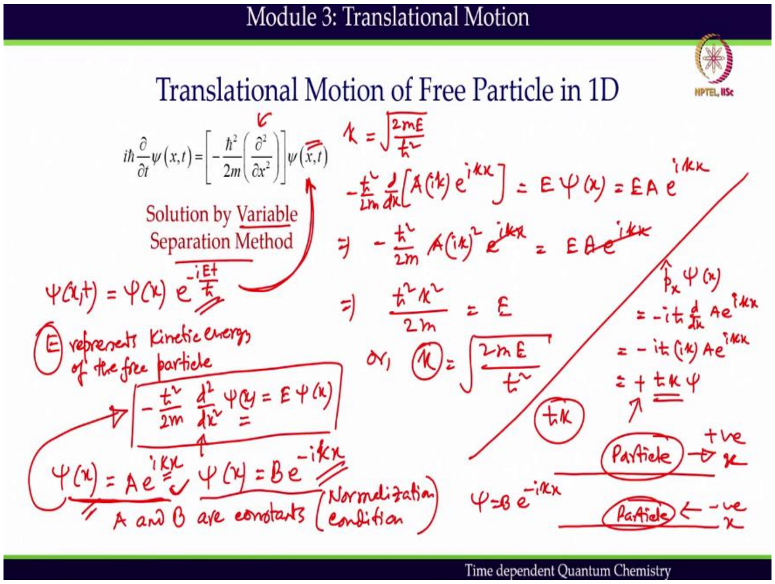
That is where you have this is 0 that is where we have removed potential part for the free particle and we have this TDSE. So, this is the TDSE which needs to be solved for free particle where this wave function is called particle wave or matter wave.

So, what we are going to do here is that the moment we come to this quantum mechanics view there is nothing called particle in quantum mechanics. In quantum mechanics, although we can name it as a particle moving, but it is not exactly like a ball moving or like a point moving which we generally percept from classical viewpoint.

So, what is the picture of a particle in quantum mechanics? It has a mass definitely it has a mass, but it should look like a localized wave this is an advanced information I am giving, I am going to prove that but the reason why I am giving this advanced information immediately is because this will give you the correct picture of a particle in quantum mechanics.

So, will never imagine that in quantum mechanics I have a particle of mass m like this, this is a wrong picture because it is represented by particle wave more specifically localized matter wave, this localized matter wave is actually a particle in quantum mechanics, it is localized in position space. So, we will prove this, how do you know that, but this is your localized wave in quantum mechanics. So, let us begin.

(Refer Slide Time: 06:18)



Let us start with this solution of TDSE.

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

And, because, we have no potential, which means potential event does not depend on time. So, there is no potential I can use the variable separation method and if I use variable separation method, immediately I can write down the form of the solution would be like this

$$\psi(x,t)=\psi(x)e^{-i\frac{Et}{\hbar}}$$

E represents kinetic energy of the free particle.

And it can be anything a free particle can have any kinetic energy and depending on the kinetic energy my solution will vary. Because the phase factor will change. So, as usual what we do, we insert this solution to the TDSE, that is exactly what we have done always and if I insert it, then immediately I get time independence Schrodinger equation which will be given by

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

Note that here I have used partial derivative and here I have used total derivative because it depends on only x and here ψ depends on both x and t. So, what is the solution of this I can have a solution of following form

$$\psi(x) = Ae^{ikx}, \psi(x) = Be^{-ikx}$$

these are the two solutions I can have A and B are constants and I can get these constants from normalization condition and we can prove very easily that if I know the kinetic energy of the particle I will be able to get to know k as well. So, k is going to be

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

I can prove that if I plug this form into this equation, what I get

$$-\frac{\hbar^2}{2m}\frac{d}{dx}\left[A(ik)e^{ikx}\right] = E\psi(x) = EAe^{ikx}$$

$$-\frac{\hbar^2}{2m}\left[A(ik)^2 e^{ikx}\right] = EAe^{ikx}$$

$$\frac{\hbar^2 k^2}{2m} = E$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

So, if I know the kinetic energy of the particle, if I know the mass of the particle, I will be able to get the k this is called wave number it is related to the wave vector of the particle, because it is and when each time I am using particle.

But remember it is not like this, what is the actual form of that particle in quantum mechanics that will be presented very soon. So, I said that there are two forms I can have these two forms I can have and if I have these two forms, what does it mean by these two forms of solution, I can try to find out by taking the momentum operator acting on them.

Momentum operator, i h cut d dx A e to the power i k x I am considering the first form I get

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

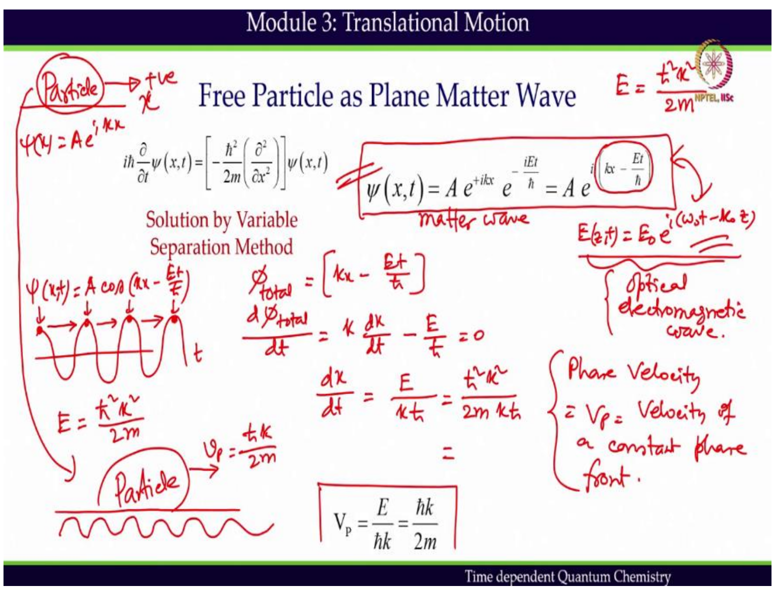
because it is positive momentum positive, which means it is representing a particle what is the form of the particle will get to know but representing a particle which is moving along positive x direction.

Similarly, one can show that this form

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

This form is representing a particle, actual shape of the particle is still unknown, but we are just encircling the whole ward and then showing it. It is moving in negative x-direction. So, these are the two different form of the particles. Either way it is moving and that is the representation of these two solutions.

(Refer Slide Time: 13:42)



Let us assume that our particle the particle is moving along positive x-direction. In that case, I will be able to consider

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

And as a result, I will be able to write down the total wave function space and time dependent wave function to be like this

$$\psi(x,t) = Ae^{ikx}e^{-i\frac{Et}{\hbar}} = Ae^{i(kx-\frac{Et}{\hbar})}$$

That is the kinetic energy of the particle. And if we look at if we recall our we represented the plane wave electric field of the plane wave we represent it like this way

$$E(z,t) = E_0 e^{i(\omega_0 t - k_0 z)}$$

That is the way we have the represented in the first module we have represented an optical wave a plane wave and note the similarity between these two.

So, this is your Matter Wave, and this is your optical electromagnetic wave. Eventually, they are showing the plane wave form of the wave function for the particles so, the particle is represented by the plane wave for the time being, and will see whether this is possible or not. But one thing we have already learned from when we have presented electromagnetic wave that everything within this exponential part is called the phase function.

And the phase is important because if I get to know the phase I will be able to get the velocity phase will give me the velocity information. So, how can I get that

$$\phi_{total} = \left[kx - \frac{Et}{\hbar}\right]$$

and the definition of phase velocity, what is the definition of phase velocity? Phase velocity is defined as the velocity of a constant phase front.

That is the definition of phase velocity constant phase front. And how do I plot this is an complex form of the real part. So, this real part will be given like this way

$$\psi(x,t) = A\cos(kx - \frac{Et}{\hbar})$$

This is like this. And we see that this is a time after each particular time, this particular phase is repeating and that is called Constant Face Front.

So, if I ask this question with what velocity it is repeating or with what velocity it is propagating, that is the constant face front propagation and for that, I need to make the first derivative to be 0 constant face front, it is going to be for the constant face front, the first derivative is going to be

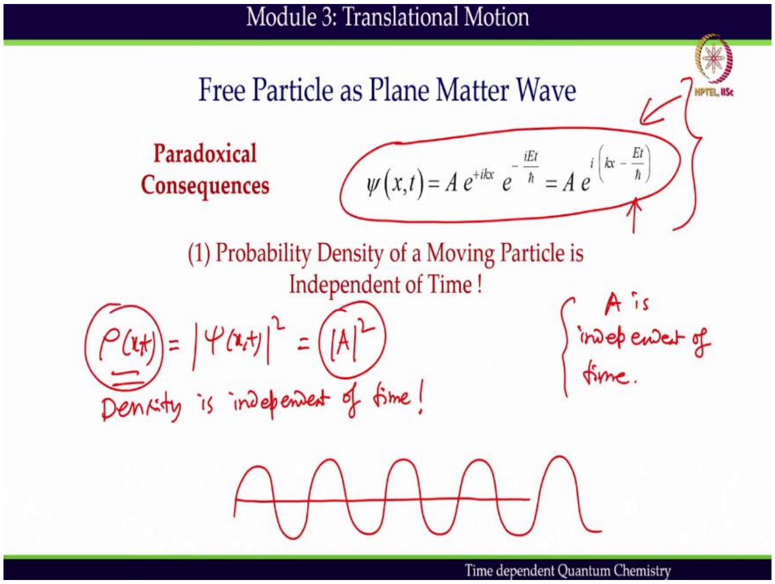
$$\frac{d\phi_{total}}{dt} = k\frac{dx}{dt} - \frac{E}{\hbar} = 0$$

$$\frac{dx}{dt} = \frac{E}{k\hbar} = \frac{\hbar^2 k^2}{2mk\hbar}$$

$$\frac{dx}{dt} = V_p = \frac{\hbar k}{2m}$$

So, we get the phase velocity of the particle, particle velocity I can get from this wave function. So, this particle which is moving as a velocity, which is called phase velocity $V_p = \frac{\hbar k}{2m}$ and so far, the particle, how does it look like? It looks like a plane wave, a wave propagating through space. Now, if this is the picture of the quantum particle.

(Refer Slide Time: 19:35)



We have many issues many strange behavior, we will be able to find out immediately if I consider this to be a solution for the free particle. And what are the strange behavior we have already let us understand the meaning of this wave function. And how does it really reflect the nature of the particle if this is the solution for the free particle, if this is what free particle which is moving, if this is the wave function, which is representing the free particle which is moving, then let us find out the density for this wave function, what is the density of the particle would be that is going to be

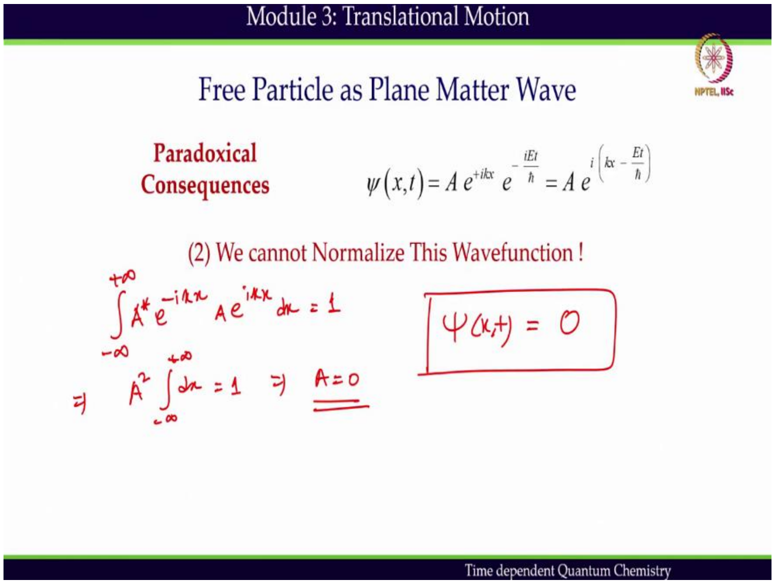
$$\rho(x,t) = |\psi(x,t)|^2 = |A|^2$$

A is independent of time. So, density is becoming independent of time and this is a big problem a strange consequence.

Why it is strange consequence we have been saying that in quantum dynamics if anything moving in quantum mechanics, its density should change as a function of time. And if density is not changing as a function of time, then there is no effective motion which you should observe. So, in order to observe any evolution time evolution or dynamics or motion of a particle in quantum mechanics, it is density should change as a function of time.

On the other hand, what we see here, if I consider this as a solution of the particle, how does that particle look like then a particle look like this, this is the particle in quantum mechanics and this particle does not have change in density. So, we are saying that is a particle which is moving in 1-dimensional space, which is moving with a particular momentum velocity, but on the other hand, we are saying the density is not changing is totally contradicting. So, it is a strange consequence we cannot accept this.

(Refer Slide Time: 22:34)



Seconds strange consequence is following let us normalize this wave function for quantum dynamics to explore quantum dynamics, the first step is to use a normalized wave function that we have been saying for in the last module. So, this is the normalization condition, if we try to normalize it, what I get

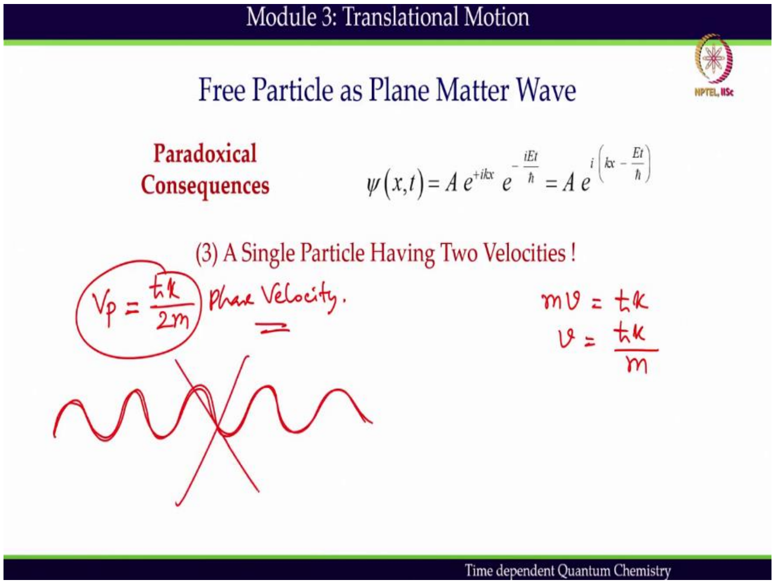
$$\int_{-\infty}^{\infty} A^* e^{-ikx} A e^{ikx} dx = 1$$

$$A^2 \int_{-\infty}^{\infty} dx = 1$$

$$A = 0$$

So, the moment I tried to normalize the wave function, the wave function will vanish $\psi(x,t) = 0$ as A = 0 everything is 0, how come a wave function would be 0 and which will represent a particle in quantum mechanics. So, this is another problem with the solution.

(Refer Slide Time: 23:49)



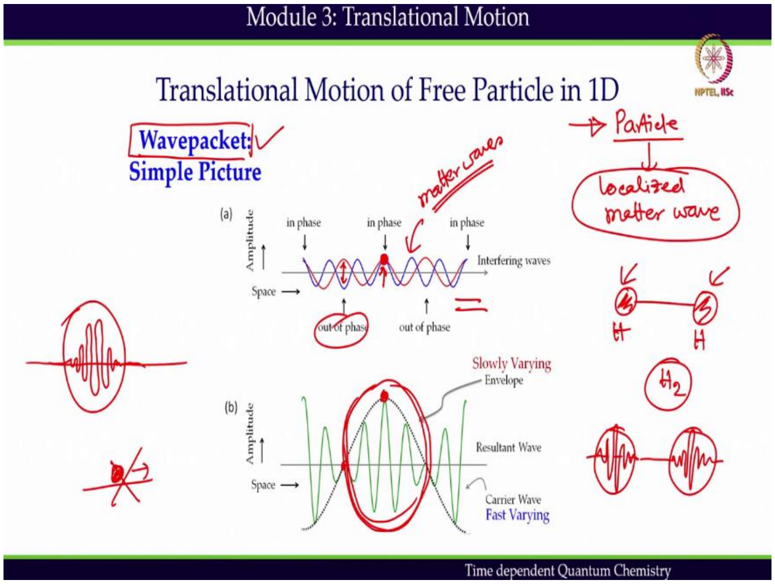
The third problem with the solution is following we have already explored that Vp velocity of the particle we said that the quantum particle is traveling with this velocity Vp which looks like this, this is my quantum particle or wave nothing but wave, matter wave and it is velocity is

$$V_p = \frac{\hbar k}{2m}$$

That is called phase velocity.

So, this is the velocity of the particle we are saying on the other hand, we can calculate the momentum and momentum we have already calculated to $mv = \hbar k$ or velocity is going to be then $v = \frac{\hbar k}{m}$. So, two different calculations of the velocity is giving me entirely two different results a single particle traveling on 1-dimensional space with two different velocities, how come it is possible. So, these are the three consequences which we have they are strange and cannot be accepted as the free particle. So, whatever I have presented that a particle in quantum mechanics should look like this a plane wave is still not correct.

(Refer Slide Time: 25:21)



In order to realize the particle in quantum mechanics, I said that the particle in quantum mechanics is going to be a localized matter wave this is called particle. So, localized matter wave there will be a wave but it has to be localized which means that there will be wave nothing nothing, nothing then something localized this is quantum particle.

This is the way we have to represent a quantum particle and this is called nothing but Waveppacket. So, in quantum mechanics, whenever I want to say particle just like let us say two hydrogen atoms are bonded through chemical bond and forming H_2 hydrogen gas, each one can behave as a particle and should we draw like a dumbbell like this no.

In quantum mechanics, we have to draw like this way. Each particle is a localized wave and what kind of wave they are, they are actually matter wave, the localized matter wave, one matter wave localized here and other matter wave localized here. So, Wavepacket is the correct terminology for the particle in quantum mechanics and how do you create the Wavepacket.

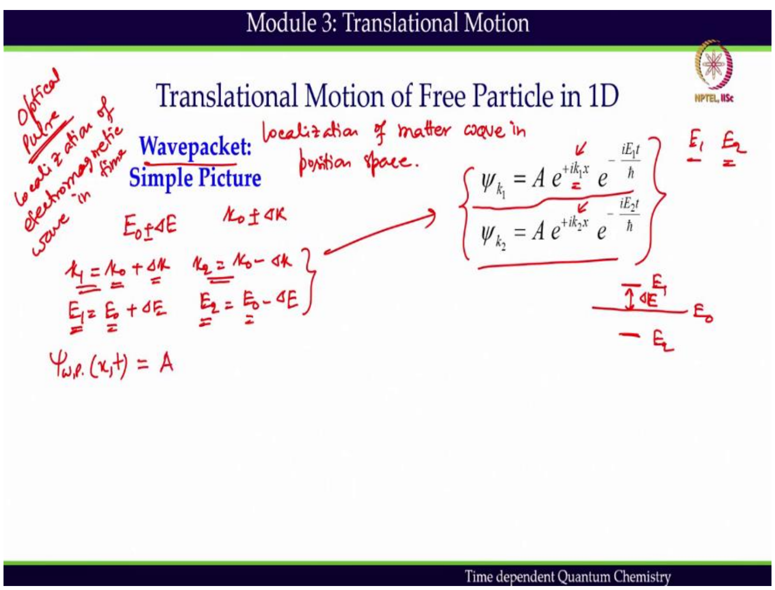
It is just like the optical paths which we have created previously in the first module. And the same figure I used to represent the optical paths, I can use the same figure to represent the Wavepacket as well. So, let us find out the meaning of this Wavepacket to eliminate all the strange consequences of the previous analysis, the general solution to the time dependence Schrodinger equation of a free particle. So, should be given by a linear combination of the plane wave solutions.

And so, I should have at least two matter waves interacting because without this interaction without this interaction, I cannot localize a wave. So, this localization of the matter wave occurs due to the interference of more than one matter waves. And when they interfere, there will be a position where they will magnify it is strength, there will be a position where they will destroy it is strength they are pulling out in opposite direction.

And here, they are actually magnifying and that is why out of phase part will have no contribution in phase part will have a maximum contribution. And that is the way we can localize the matter wave in space. And this is the correct representation of a particle in quantum mechanics. It is not like a ball moving in 1-dimensional space, it is not like that it is a classical picture this ball moving is a classical picture Wavepacket is the quantum mechanical picture.

In the Wavepacket this kind of superposition of matter wave is called Wavepacket and which exhibits nonzero amplitude in small region like this region and, close to 0 elsewhere. And that is the way Wavepacket is localizing the matter wave. So, we will try to understand mathematically.

(Refer Slide Time: 29:37)



And what we will do exactly will follow the same thing. Here I will write down that optical pulse what is optical pulse we have presented in the first module optical pulse is localization of electromagnetic wave in time that is called optical pulse. On the other hand, this Wavepacket is localization of matter wave in position space and such a localization can be realized with the help of interference of at least two waves. So, we have taken these two waves, slightly different energies, E1 and E2, they are propagating along the same direction because E1,E2 are different little bit. That is why k1 and k2 are different, because k depends on its kinetic energy. And we will say that, due to this interference, there is an average value I am getting that is $E_0 \pm \Delta E, k_0 \pm \Delta k$.

So, what we have here is this k1 I will assume that

$$k_1 = k_0 + \Delta k, k_2 = k_0 - \Delta k$$
$$E_1 = E_0 + \Delta E, E_2 = E_0 - \Delta E$$

In the end, what we are showing here is that these two plane waves having slightly different energies, that is all. And we are now representing those energies with respect to some average values. So, this is let us say average value of E naught the resultant value E1 was here, and this is E2. And this difference is delta E.

That is the basic idea with respect to certain average value we are presenting it. So, if we have that and if we plug that in here, then Wavepacket actual Wavepacket superposition of those two functions, which will be represented by a linear combination of these two-wave function. We will look at this linear combination of this wave function in the next session.