Time Dependent Quantum Chemistry
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Module 03 - Lecture 17
Wavepacket

Welcome back to module 3, we are discussing how to create Wavepacket, because Wavepacket is the actual representation of a particle in quantum mechanics. And to represent an Wavepacket, we need at least two plane waves. Here we have taken two plane waves with slightly different energies.

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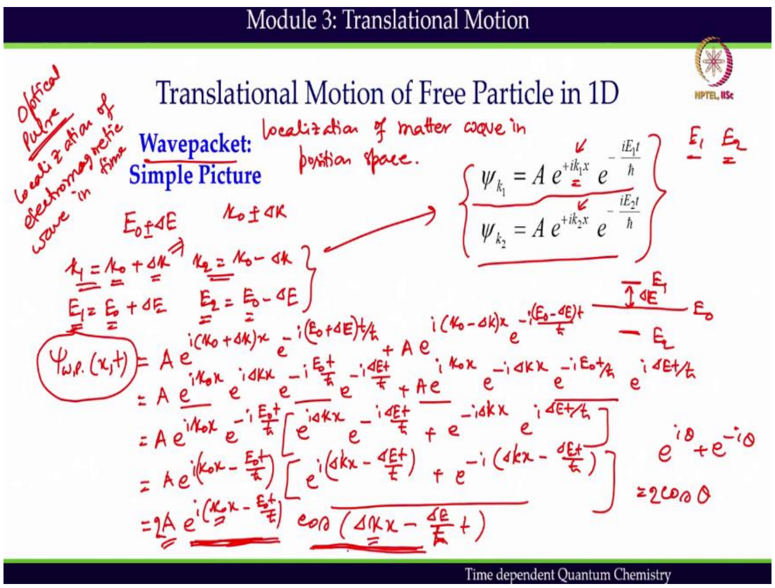

And we will write down explicitly the linear combination of these two

$$\psi_{w.p.}(x,t) = Ae^{i(k_0+\Delta k)x} e^{-i\frac{(E_0+\Delta E)}{\hbar}t} + Ae^{i(k_0-\Delta k)x} e^{-i\frac{(E_0-\Delta E)}{\hbar}t}$$

So, this is the expression we have for the wavepacket, because we have to linearly combine them and one can for the simplify this as

$$= Ae^{ik_0x}e^{i\Delta kx}e^{-i\frac{E_0}{\hbar}t}e^{-i\frac{\Delta E}{\hbar}t} + Ae^{ik_0x}e^{-i\Delta kx}e^{-i\frac{E_0}{\hbar}t}e^{i\frac{\Delta E}{\hbar}t}$$

$$= Ae^{ik_0x}e^{-i\frac{E_0}{\hbar}t}\left(e^{i\Delta kx}e^{-i\frac{\Delta E}{\hbar}t} + e^{-i\Delta kx}e^{i\frac{\Delta E}{\hbar}t}\right)$$

$$= Ae^{i(k_0x-\frac{E_0}{\hbar}t)}\left(e^{i(\Delta kx-\frac{\Delta E}{\hbar}t)} + e^{-i(\Delta kx-\frac{\Delta E}{\hbar}t)}\right)$$

$$= 2Ae^{i(k_0x-\frac{E_0}{\hbar}t)}\cos(\Delta kx-\frac{\Delta E}{\hbar}t)$$

So, if I write it down like that way then this wavepacket the final form of the wavepacket I get

$$\psi_{w.p.}(x,t) = 2Ae^{i(k_0x-\frac{E_0}{\hbar}t)}\cos(\Delta kx-\frac{\Delta E}{\hbar}t)$$

This form has two components, this is just a constant, it has this component it has this component.

This both components if we compare these two components with the planewave both components are representing a planewave, but there is a difference this difference, the difference is that here the variation depends on k0 here the variation depends on the difference. So, one is slowly varying and other one is fast varying components.

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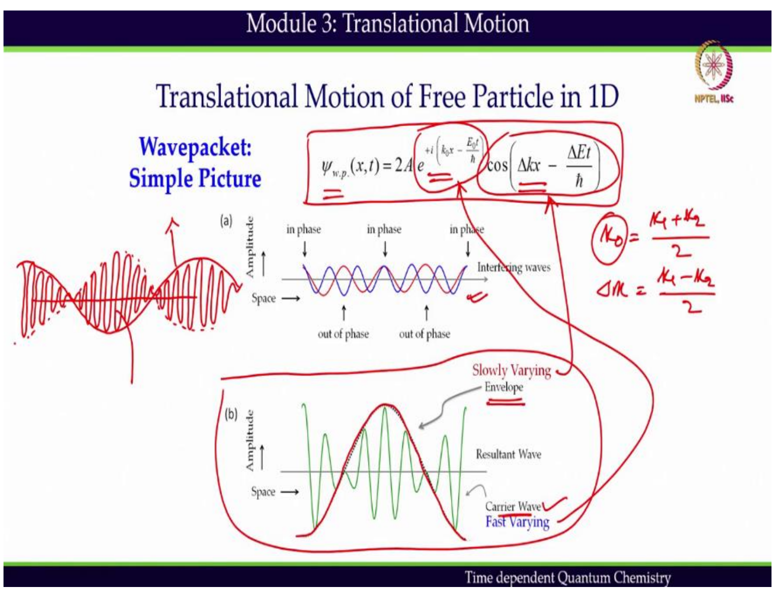

So, this is the final form of the wavepacket, a simple form of the wavepacket and if we look at that, as I mentioned that two slightly different energies which means slightly different k and slightly different k means slightly different. So, $k = \frac{2\pi}{\lambda}$, So, they are matter wavelength is different, which is shown here by this red and blue lines.

So, with two different energies, two matter waves are interfering with each other to manifest one particle in quantum mechanics, and we see that

$$k_0 = \frac{k_1 + k_2}{2}$$
$$\Delta k = \frac{k_1 - k_2}{2}$$

It is the difference between these two. So, this variation would be slow than this variation.

So, what does it mean I have two different plane wave components presenting the wavepacket it means that here we have to see this figure, this slowly varying component is this one which is giving me then envelope function, this envelope function and fast varying component is there which is giving me carrier wave.

So, in a wave packet there are two components I have. How do I draw the components one component is very slowly varying another component this is just to draw this is still a slowly varying component. Another fast-varying component I have which is very quickly varying within this envelope very quickly varying like this way.

So, this part is slowly varying and this part is fast varying component of the wave packet and this is called in the envelope slowly varying component and fast varying component is the carrier wave. So, this is the terms which will be using to represent the wavepacket the particle in quantum mechanics.

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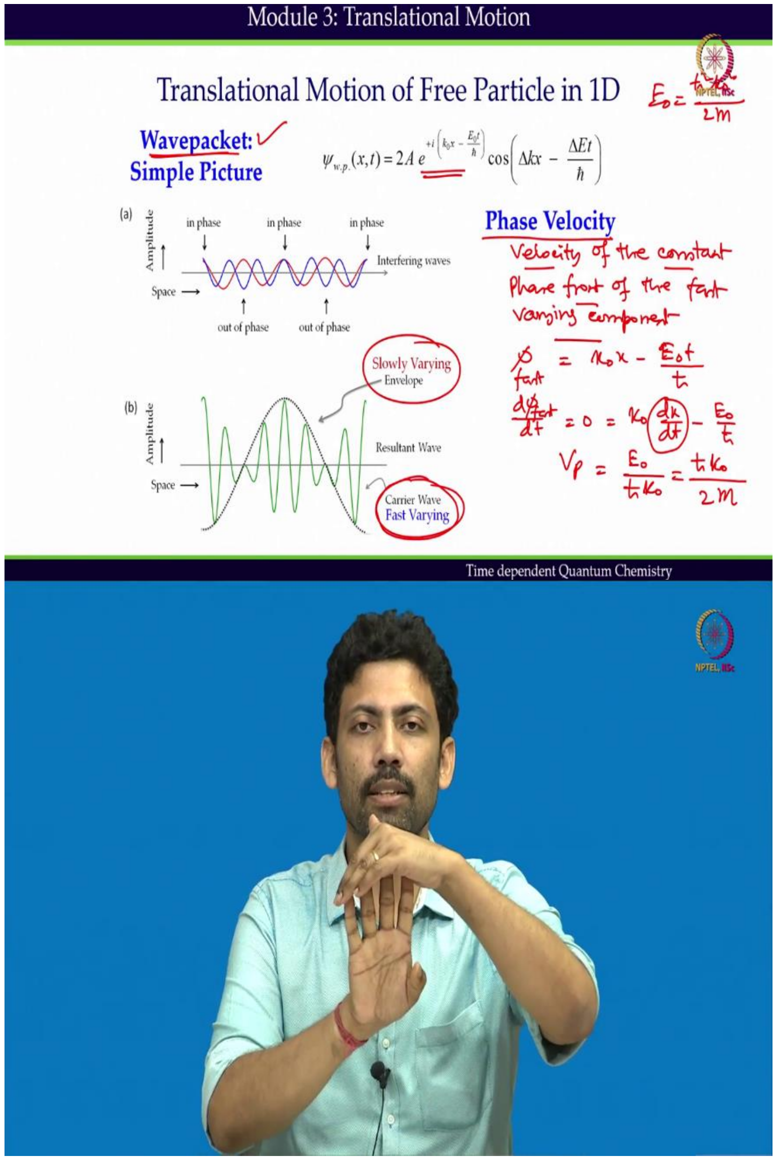

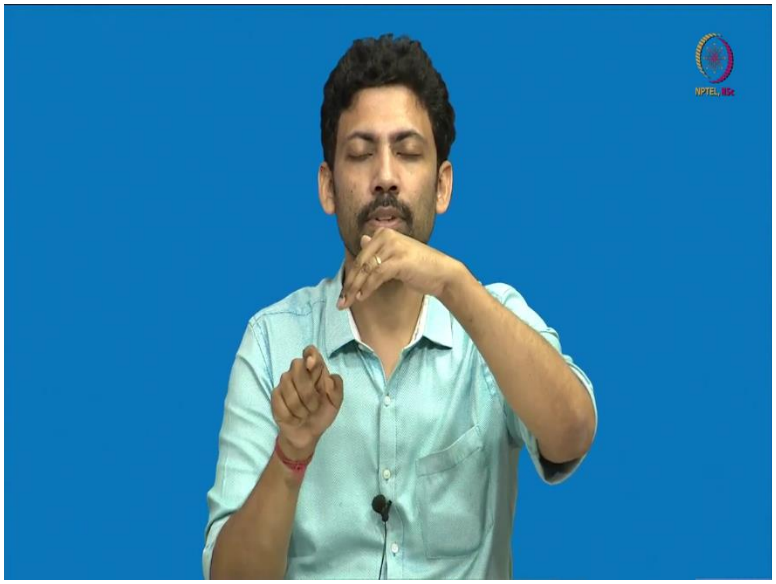

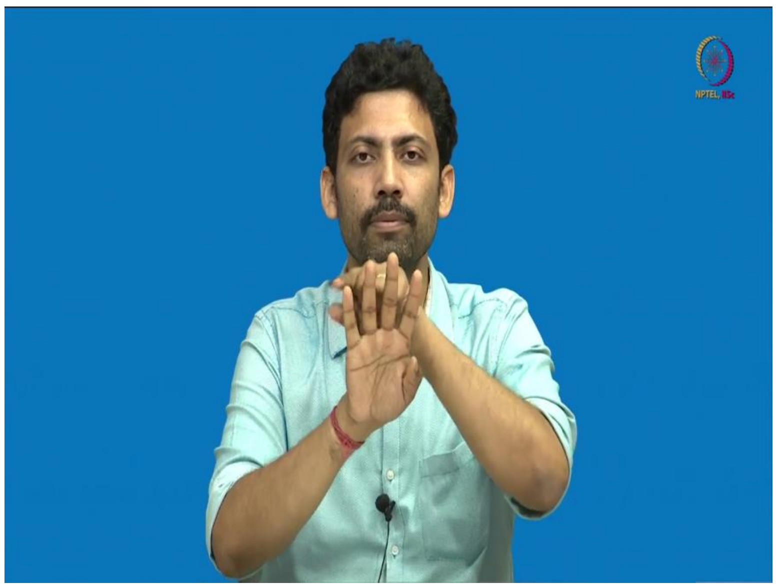

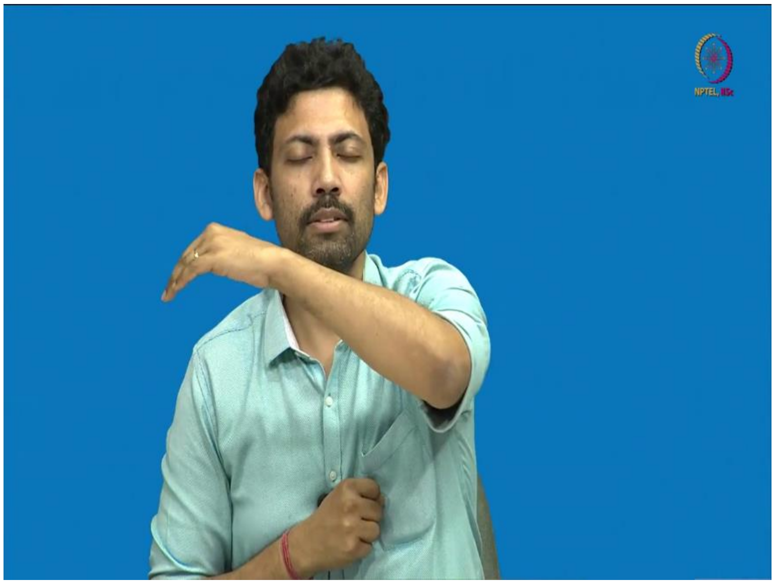

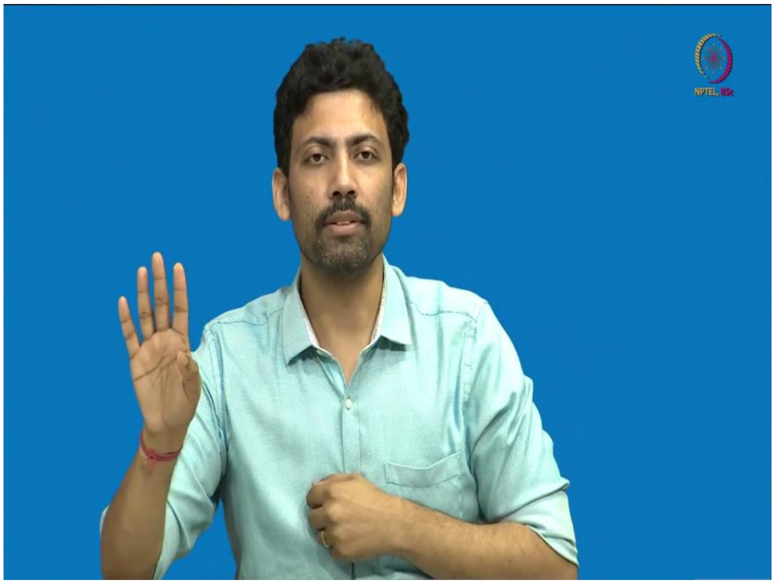

Now, the velocity of a wave packet will be defined based on these two components. First, we will go for phase velocity. Phase velocity for our wavepacket will be defined as the velocity of the constant phase front of the fast-varying component. So, this carrier wave every particle every quantum particle will be represented by wavepacket.

And in wavepacket I have two different components. One component is very slowly varying, another component is very fast varying, this fast-varying component is called the carrier wave. Question is what is the velocity with which carrier wave is propagating that is represented by the phase velocity of a wavepacket.

And that is how can I calculate that one, it is just the definition coming from the definition velocity of the constant phase front of the fast-varying component and fast varying component is here. So, all we need to do is that this fast-varying phase we have to write down and take the first derivative and make it 0.

That is the way we have been doing always. So, first derivative of this fast-varying component is going to be 0 which is nothing but

$$\phi_{fast} = k_0 x - \frac{E_0}{\hbar} t$$
$$\frac{d\phi_{fast}}{dt} = 0 = k_0 \frac{dx}{dt} - \frac{E_0}{\hbar}$$
$$V_p = \frac{E_0}{\hbar k_0} = \frac{\hbar k_0}{2m}$$

This is the phase velocity of the wavepacket. So, what does it mean? I will show one more time this is the particle which is having two components one component is the envelope component which is varying very slowly another one is fast varying component which is varying very quickly, is varying very quickly.

Now, question is how what is the velocity with which this component is propagating. And what is the velocity with which this component is propagating these two components are separately propagating independently propagating and we are trying to find out what is the velocity of individual component in the wavepacket. This phase velocity of the wavepacket is represented and is given by this value.

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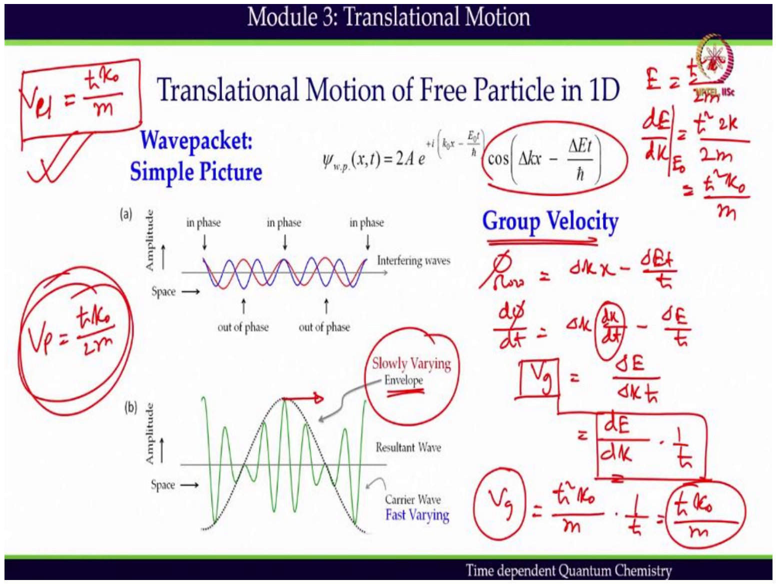

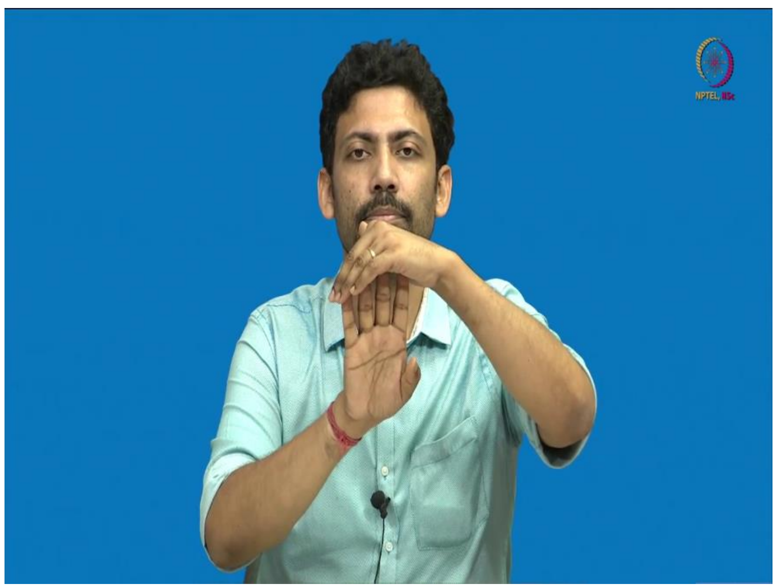

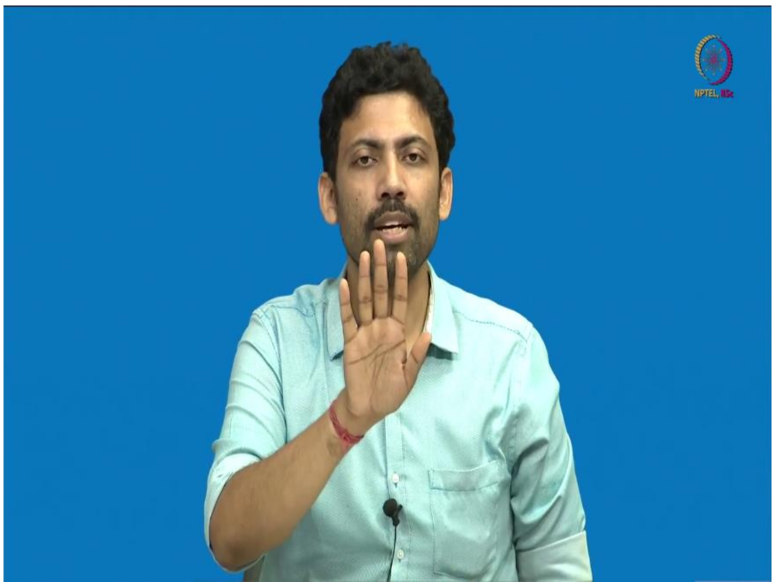

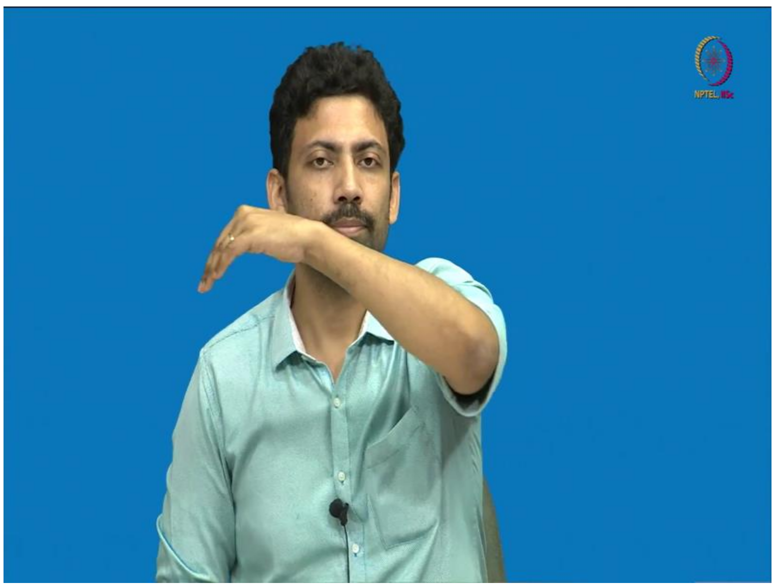

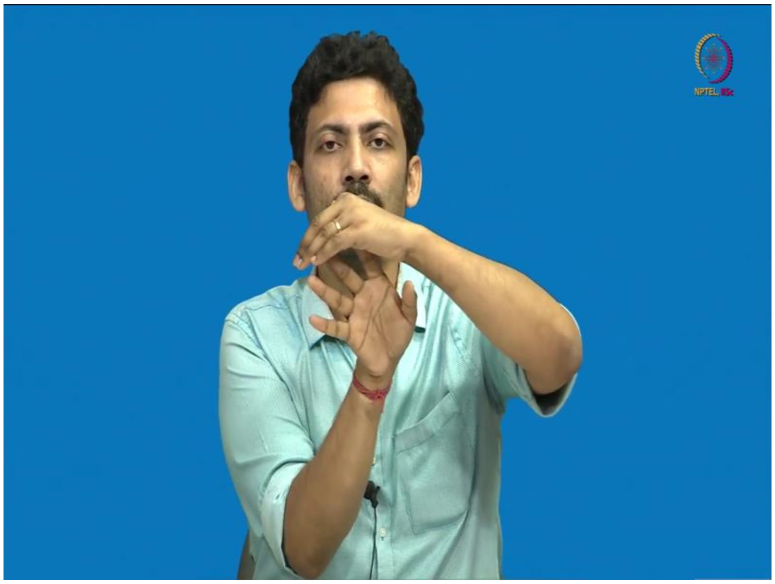

Will go for the blue group velocity. As usual, the definition of group velocity comes from the velocity of the envelope function, that is called the group velocity. So, velocity of the envelope function and envelope function is coming from this. So, total phase, it is a slow varying component total phase is going to be delta k x minus delta E t by h cut.

$$\phi_{slow} = \Delta k x - \frac{\Delta E}{\hbar} t$$

$$\frac{d\phi_{slow}}{dt} = \Delta k \frac{dx}{dt} - \frac{\Delta E}{\hbar}$$

$$V_g = \frac{\Delta E}{\Delta k \hbar}$$

$$V_g = \frac{1}{\hbar} \frac{dE}{dk}$$

$$V_g = \frac{1}{\hbar} \frac{\hbar^2 k_0}{m} = \frac{\hbar k_0}{m}$$

This is the group velocity of the particle for infinitesimal change. So, I will remind phase velocity of the particle phase velocity. So, this is the particle in quantum mechanics the represented by the wave packet and I have a phase velocity which means that what is the velocity with which.

So, this is we represent the particle in quantum mechanics which is nothing but the wavepacket, it has two different components each component is propagating with it is own characteristic velocity and this carrier wave which is varying very fast it is moving with the phase velocity. And envelope function, which is very slowly moving, it is moving with group velocity and these are the two differences we have.

So, phase velocity expression which we have is

$$V_p = \frac{\hbar k_0}{2m}$$

this is the phase velocity we have got on the other hand group velocity, we are getting the expression

$$V_g = \frac{\hbar k_0}{m}$$

If I compare now, with the previous classical velocity which was calculated to be

$$V_{cl} = \frac{\hbar k_0}{m}$$

What we see is that now, classical velocity is actually represented by the group velocity.

So, when I say that a particle is moving in quantum mechanics it is envelope function is moving at the classical velocity. But it is carrier wave is propagating with a different velocity. That is why these two are not locked anymore. They are not like this way they are velocities are different. This carrier wave is propagating much faster velocity, and that is why when it is propagating, it is changing.

This the tip of the envelope function, they are actually changing with respect to each other. So, that is the manifestation that is the meaning of two different velocities of a particle in quantum mechanics, one velocity is represented by group velocity, which is nothing but the classical velocity another velocity phase velocity is the velocity of the constant phase front of the fast-varying component or carrier wave that is moving in a different velocity with a phase velocity. So, with this understanding.

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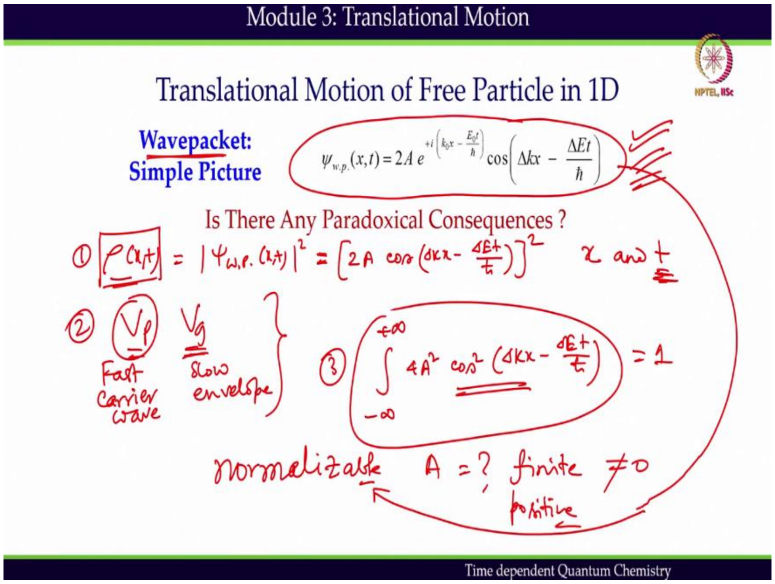

We will move forward and we will ask the same question. Remember, we started this part representing the wavepacket, because the plane wave solution failed to represent the particle in quantum mechanics. Now, after getting this new solution, we can ask the same question is there any strange consequence we get from this?

So first of all, we will check what is going on with the probability density. Probability density for this wavepacket will be given by

$$\rho(x,t) = \left|\psi_{w.p.}(x,t)\right|^2 = \left[2A\cos(\Delta kx - \frac{\Delta E}{\hbar}t)\right]^2$$

Now, $\rho(x,t)$ is a depends on x and t that was the requirement we had always the wave function cannot be observed experimentally.

I can observe only density and in quantum dynamics density should change as a function of time. This form is allowing me to see the change in density as a function of time. So, this is acceptable definitely acceptable form of the particle in quantum mechanics. Second part we had a contradiction in plan wave solution solution.

In plan wave solution solution, we could not understand why a particle should have two different velocities. We did not understand that. Two different derivation, two different ways we can think of getting the solution. And we got two different solutions. So, same particle having two different velocities in the form of plane wave is meaningless.

That is just a mathematical artifact, or we cannot accept as a physical solution. But here we have understood that Vp and Vg I can have two different solutions. I can have two different velocities of the particle. These two velocities are representing two different components of the particle.

The phase velocity is representing the fast component, which is the carrier wave and Vg is representing the slowly varying component, which is the envelope function. Because every particle has two components in quantum mechanics, because it is represented by the wavepacket and wavepacket has two different components, one component is fast varying and another one is slowly varying component.

So, this is now understandable, we have understood the meaning of it. Third one question is whether this is normalizable or not

$$\int_{-\infty}^{\infty} 4A^2 \cos^2(\Delta kx - \frac{\Delta E}{\hbar} t)dx = 1$$

I will not show this derivation. But clearly cos square function can be integrated and I can get certain value of A. This is going to be of finite value not going to be 0. So, finite positive number which means that this wave function is normalizable and requirement fulfilled for the quantum dynamics a form of the function should be normalizable for an acceptable solution to that TDSE.

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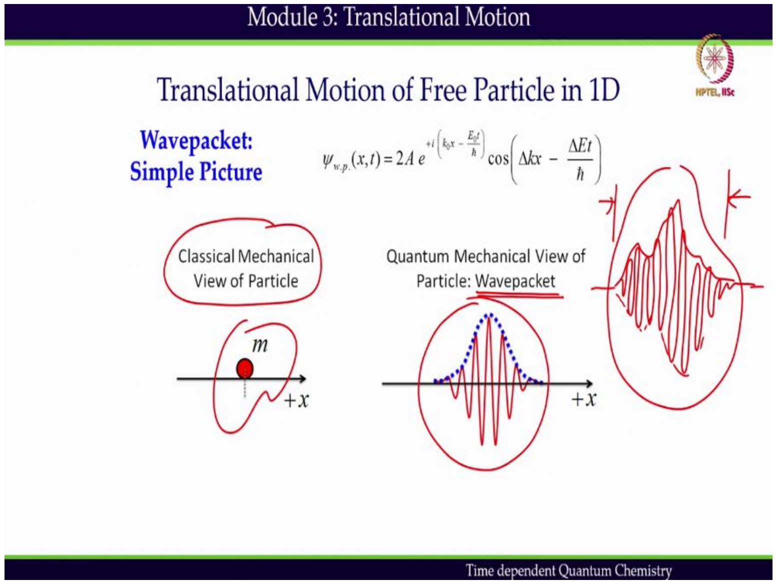

So, based on this analysis now, I go back to the first slide I started with this slide classical mechanics when in the classical mechanics or in our daily life, when I say particle, I represent like a ball moving along the direction x, but in the quantum mechanics, I can have a particle, but the particle cannot be represented with the ball I have to represent with a localized matter wave.

And localized matter wave is a consequence of the interference of multiple matter waves which will allow the localization of the matter wave in position space and the correct terminology for particle in quantum mechanics is the wavepacket. So, this is the picture which is a valid picture for the let us say, free particle in quantum mechanics.

But it does not need to be always very nice-looking Gaussian shape here, I can have a particle like this also. It is just for the representation we have made this to be like this. So, I can have as long as it is a localized matter wave, it can be present the particle and actual shape of the particle what kind of particle I will have the actual shape of the particle or actual shape of the wave function of the particle I should say or the wave function of the wave packet, it depends on the potential it will experience during the motion.

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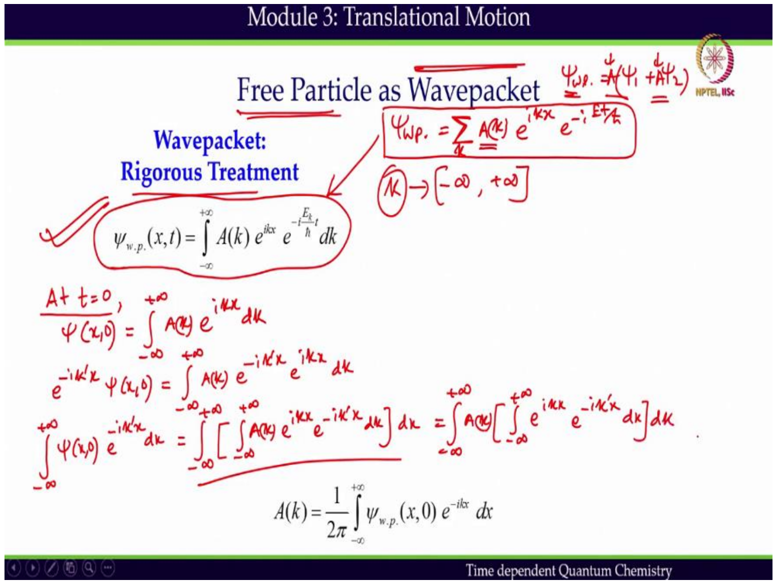

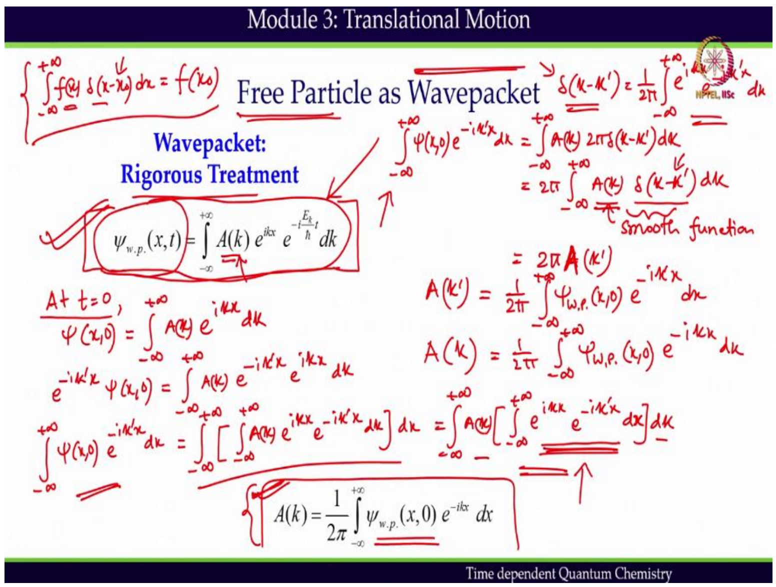

So, with this preliminary idea, we will move to more rigorous treatment of the free particle as wavepacket previously what we did we have prepared wavepacket with the help of adding two matter waves. But free particle can have any energy and that is why one can propose that more rigorous treatment.

Mathematical treatment for wavepacket should be represented as summation of A, I am now making it k dependent the amplitude may vary depending on thing here, when I presented to interference of two matter waves to represent the wave packet they are I have made A to be independent of k I did not select different k different A for two different waves.

But, to make it a general I can have A to be dependent on k and then I have the same thing

$$\psi_{w.p.} = \sum_k A(k) e^{ikx} e^{-i\frac{E}{\hbar}t}$$

The summation can be over all possible k that can be the correct representation of the wave packet more mathematically appropriate or I mean correct representation of the wave packet.

And because k may adopt any value from minus infinity to plus infinity and it can be continuously varying. So, k can be minus in from minus infinity to plus infinity, any value it can take up because free particle it can have any kinetic energy and those kinetic energies a particle in quantum mechanics can travel with any kinetic energy if it is a free particle.

And if k can have any value, then instead of summation I can represent it in terms of this integration, it is just the integral form of the same idea.

$$\psi_{w.p.}(x,t) = \int_{-\infty}^{\infty} A(k) e^{ikx} e^{-i\frac{E_k}{\hbar}t} dk$$

Superposition of many matter waves as a result of interference among the component plane waves at one instant the wave packet exhibits large amplitude at one region of space due to constructive interference.

And the region of constructive interference changes with time because of presence of the time dependent phase factor. So, question is, can I have one analytical solution for the free particle wave packet, if I consider this rigorous expression for the wave packet. So, what will happen? Let us see, at t equals 0 initial time, when the evolution did not start.

$$\psi(x,0)=\int_{-\infty}^{\infty} A(k)e^{ikx}dk$$

$$e^{-ik'x}\psi(x,0)=\int_{-\infty}^{\infty} A(k)e^{-ik'x}e^{ikx}dk$$

$$\int_{-\infty}^{\infty} e^{-ik'x}\psi(x,0)dk=\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} A(k)e^{-ik'x}e^{ikx}dk\right]dk$$

$$\int_{-\infty}^{\infty} e^{-ik'x}\psi(x,0)dk=\int_{-\infty}^{\infty} A(k)\left[\int_{-\infty}^{\infty} e^{-ik'x}e^{ikx}dk\right]dk$$

I can do that because this integration is over x and this integration is over k. And if we do that, then we can use one property of Dirac delta function.

And, the property is following delta function of

$$\delta(k-k')=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik'x}e^{ikx}dk$$

So, this integration here is related to Dirac delta function or so, I can write down minus infinity to plus infinity. So, this part I will be right down in following way.

$$\int_{-\infty}^{\infty} e^{-ik'x}\psi(x,0)dk=\int_{-\infty}^{\infty} A(k)2\pi\delta(k-k')dk$$

$$=2\pi\int_{-\infty}^{\infty} A(k)\delta(k-k')dk$$

$$=2\pi A(k')$$

So, when a delta function appears inside an integral as one component of the product with a smooth function, this one will consider a smooth function the value of the integral becomes simply the value of the integrand at the position of the delta function.

$$\int_{-\infty}^{\infty} f(x)\delta(x-x_0)dx=f(x_0)$$

Is another property of delta function and if I use that delta function property, I can write down this one to be 2 Pi A(k’) just like here, if it is a product of delta function and a continuous function fx.

Then this integration will give me the value of the function at x naught. Similarly, this integration will give me the value of A(k) at k'. And that is what we have written here.

So, A(k') is represented by

$$A(k^{'}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi_{w.p,}(x,0) e^{-ik^{'}x} dx$$

So, k' was selected arbitrarily it can be anything. So, I can represent I can rewrite this equation as A in terms of k also make it a general. In that case it will be it will look like this

$$A(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \psi_{w.p,}(x,0) e^{-ikx} dx$$

That is exactly what we have written here. So, with the help of this analytical approach with the help of this Dirac delta function property of the Dirac delta function.

What we have got is that this is the general form of wavepacket. But in the general form, one thing was unknown, the unknown part was Ak, and what we see here Ak, can be calculated from the initial wave packet. So, if I know the initial wave packet, I will be able to get the A k, once I know Ak, I can plug that in here and I can get the final wavepacket at different time. So, this is giving me.

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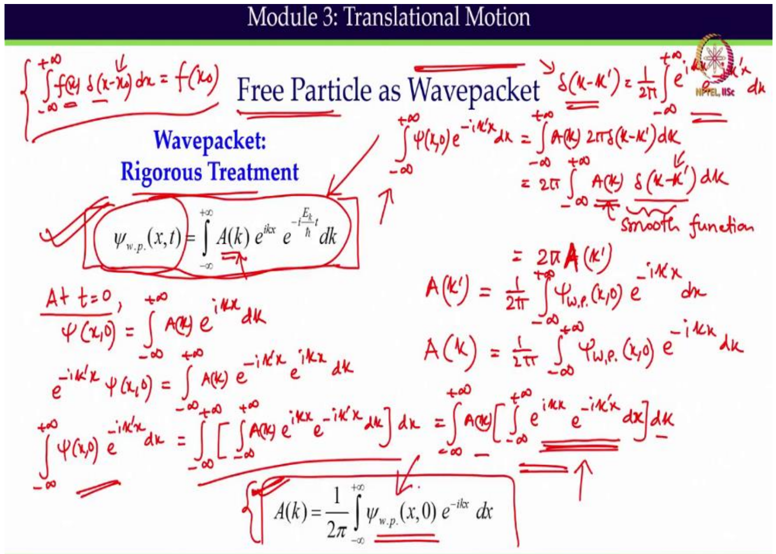

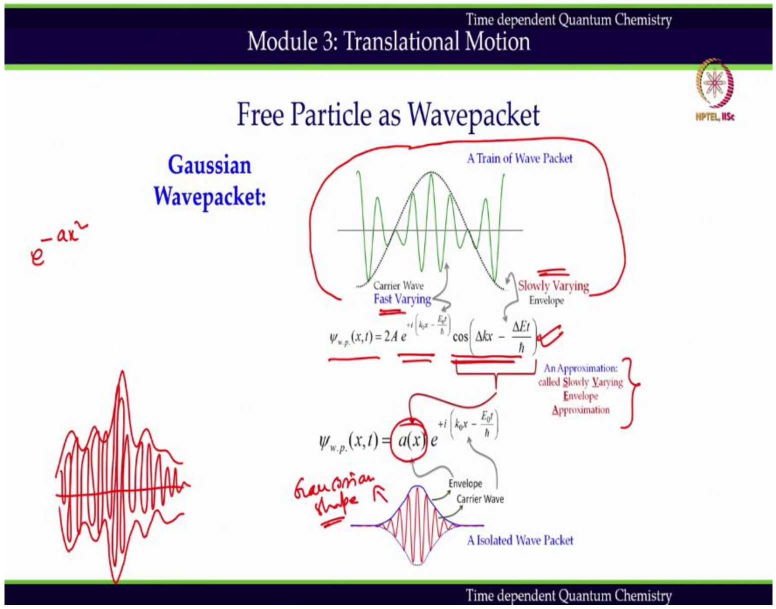

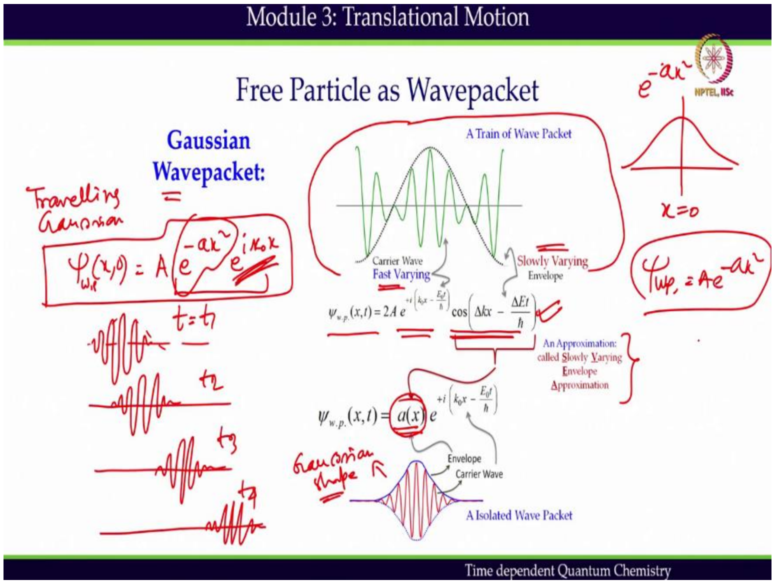

An analytical approach of the describing the particle, describing the motion of wavepacket when it is freely moving, and that is why we can use that equation, we will use that equation, but before we do so, as I have shown here, I need to know the initial wave packet. So, I have to start with a particular kind of particle, it can be nice looking Gaussian.

So, if it is nice looking Gaussian, then I will be able to plug that in here, that is my initial packet and how this initial packet is propagating, this is at t equals 0, and then at different time, how the particle would be look like that I can calculate with the help of this equation with this analytical approach.

So, first thing I have to start with the starting point for this wavepacket dynamics is going to be the assumption of the initial wavepacket. How does it look like? This is the form of the, the train of wavepacket we have shown previously, it comes directly from the simple interference of two different matter waves.

And we have seen that it has two different components fast varying components slowly varying components, all you are trying to do here now. Every wavepacket will have these two components slowly varying component and fast varying component what we are doing here now, we are using a slowly reading in envelope approximation under this approximation. We can say that the slowly varying component can be used as a envelope function.

It is actually an envelope function, but instead of considering a plane wave form, I can assume a certain shape of that envelope function. In this case, I have considered a Gaussian shape why I am interested in Gaussian shape, because if I consider Gaussian, which is represented by e^{-ax^2}.

A simple equation e^{-ax^2}, if I use that Gaussian, then I can do many analytical integration without any difficulties. Integration that minus infinity to plus infinity Gaussian integrals are very well known and standard integral, if I take different shape, some other shape some ugly shape, let us say like this. So, in that case, the fast-varying component like this, in that case, I cannot get the analytical solution, I have to go for the numerical solution. So, in this module, we are trying to present the analytical form of the how the wavepacket should move. And I have to start with a against an initial wavepacket.

The initial wavepacket I can make it as a Gaussian form, Ae^{-ax^2} is the Gaussian function which is centered at x equals 0. So, this is a Gaussian function, but this will not move this will move only when I include this plane wave part also

$$\psi_{w.p,}(x,0) = Ae^{-ax^2} e^{ik_0 x}$$

So, if I have a moving Gaussian wavepacket traveling Gaussian wave packet. This is traveling also Gaussian Wavepacket, then I have to use this initial wavepacket to be like this. Where this is the Gaussian function and this is the plane wave part and then it is actually moving. So, how it is moving it will show like this way, at a particular time is like this.

After a particular time, it will be like this. After a particular time it will be like this. So, it is different moving it is time because t1, this is t2, this is t3, this is t4 like this way it is moving. So, traveling Gaussian has to be represented by this way, and if I start with a stationary Gaussian, then I do not need this plane wave part, I can use only Ae^{-ax^2}. So, this functional realization is very important to begin with the analytical solution of the Gaussian wavepacket dynamics.

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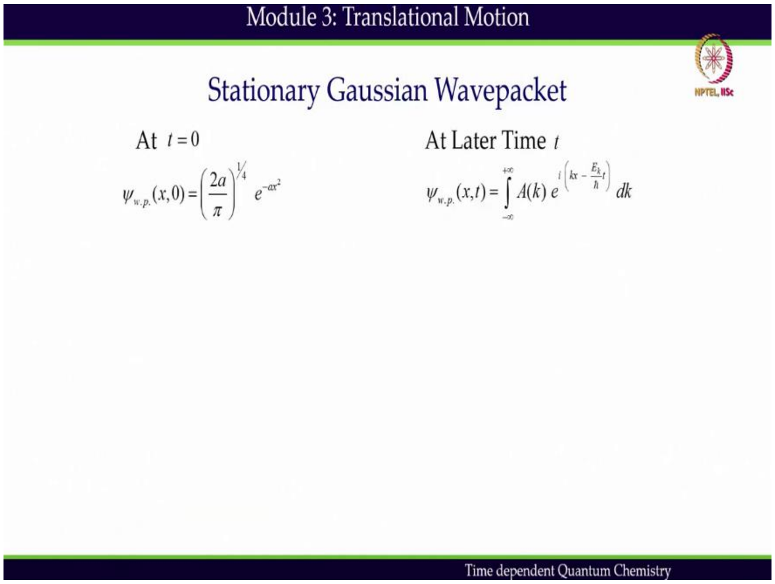

We will now move forward in the next session, we will continue this and we will try to find out if I start with an initial Gaussian and if it is freely propagating, freely moving, what will happen to the shape of that Gaussian, whether is broadening or compressed. We will find out in the next session