Time Dependent Quantum Chemistry

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Module: 03 Lecture: 20

General Form of the Gaussian Wavepacket

Welcome back to module 3, we have just discussed how our traveling Gaussian would propagate and we have seen that the free particle, because we are discussing free particle without any potentiality it is not experiencing any potential, so, there is no potential it means there is no force acting on the particle classically we understand that the particle would be all the traveling with a constant velocity, the similar thing we have seen in quantum mechanics particle in quantum mechanics would be represented by a localized matter wave we should not view as a ball or a small dot in quantum mechanics it should be a localized Wavepacket.

And what we have seen that Wavepacket for the free particle is traveling with a constant velocity, that is a group velocity, the center of the envelope how it is moving. And so, this is very nice, intellectually stimulating discussion we had for them with an analytical solution for the Wavepacket dynamics. Next, what we will do.

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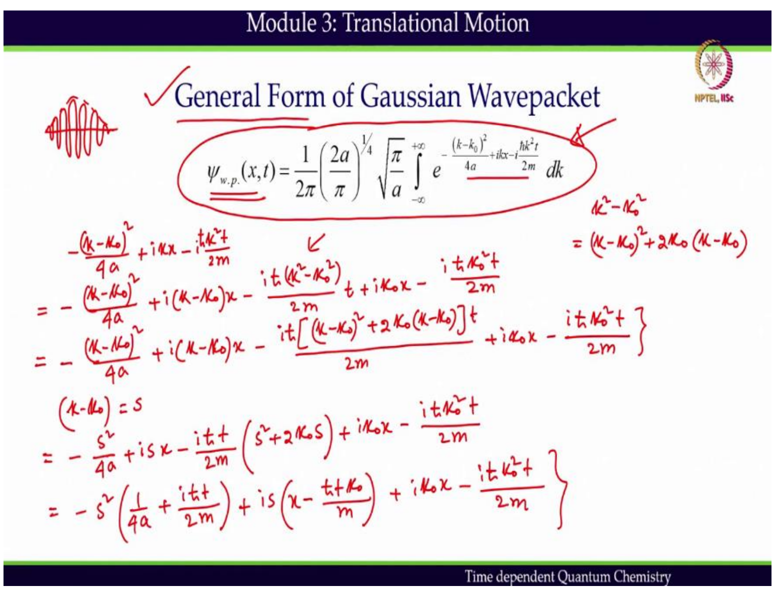

We have been seeing that this is the form which we have got for the Gaussian wave packet and the particle. So, the particle represented by this, so, I had the wave function this is the particle and at different time, I have this expression for the Wavepacket represented by the particle. Now, this expression, we will modify to a particular kind of expression, so that we can very conveniently use that for other problem. So, that is why we are calling it is a general form of the Gaussian Wavepacket, we do not want to keep it in this complicated form, we will modify it to a form given by Eric Heller who has worked significantly on this Gaussian Wavepacket dynamics, and we will reach that form to use it for our subsequent analysis. So, we will just modify this, this is just a rigorous mathematical derivation we will be getting involved right now. So, first will look at this exponentiation part. This exponentiation part can be written as

$$\psi_{w.p.}(x,t) = \frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}}\sqrt{\frac{\pi}{a}}\int_{-\infty}^{\infty} e^{-\frac{(k-k_0)^2}{4a}+ikx-i\frac{\hbar k^2 t}{2m}}\,dk$$

$$\begin{aligned}&-\frac{(k-k_0)^2}{4a}+ikx-i\frac{\hbar k^2 t}{2m}\\&=-\frac{(k-k_0)^2}{4a}+i(k-k_0)x-i\frac{\hbar(k^2-k^2{}_0)t}{2m}+ik_0x-i\frac{\hbar k_0{}^2 t}{2m}\end{aligned}$$

It is just rigorous mathematical derivation that solved, but we need this derivation to reach that final form the general form of a Gaussian Wavepacket which we will be using for subsequent analysis. So, what will do right now?

$$k^2-k_0^2=(k-k_0)^2+2k_0(k-k_0)$$

$$-\frac{(k-k_0)^2}{4a}+ikx-i\frac{\hbar k^2 t}{2m}=-\frac{(k-k_0)^2}{4a}+i(k-k_0)x-i\frac{\hbar\left[(k-k_0)^2+2k_0(k-k_0)\right]t}{2m}+ik_0x-i\frac{\hbar k_0{}^2 t}{2m}$$

$$(k-k_0)=s$$

$$\begin{aligned}-\frac{(k-k_0)^2}{4a}+ikx-i\frac{\hbar k^2 t}{2m}&=-\frac{s^2}{4a}+isx-i\frac{\hbar t}{2m}\left(s^2+2k_0s\right)+ik_0x-i\frac{\hbar k_0{}^2 t}{2m}\\&=-s^2\left(\frac{1}{4a}+i\frac{\hbar t}{2m}\right)+is\left(x-\frac{\hbar k_0 t}{2m}\right)+ik_0x-i\frac{\hbar k_0{}^2 t}{2m}\end{aligned}$$

So, this is the form we have got and the reason why we have we are using this kind of form it will be revealed very soon. So, now, we will move forward.

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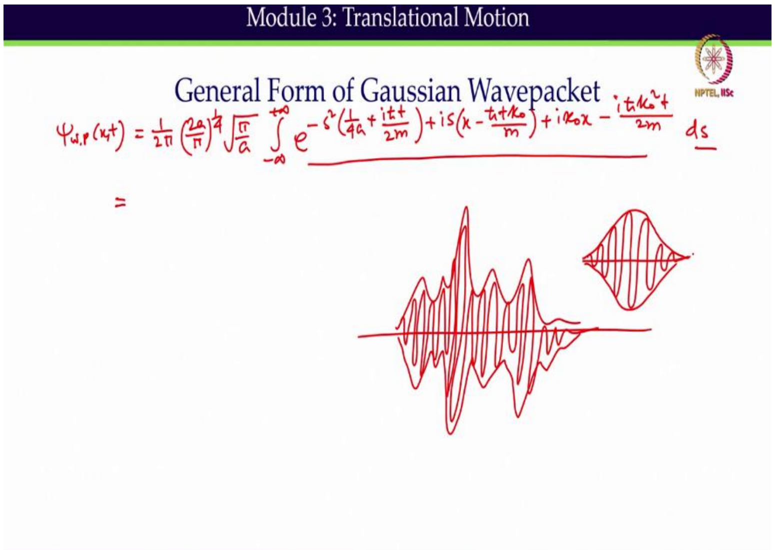

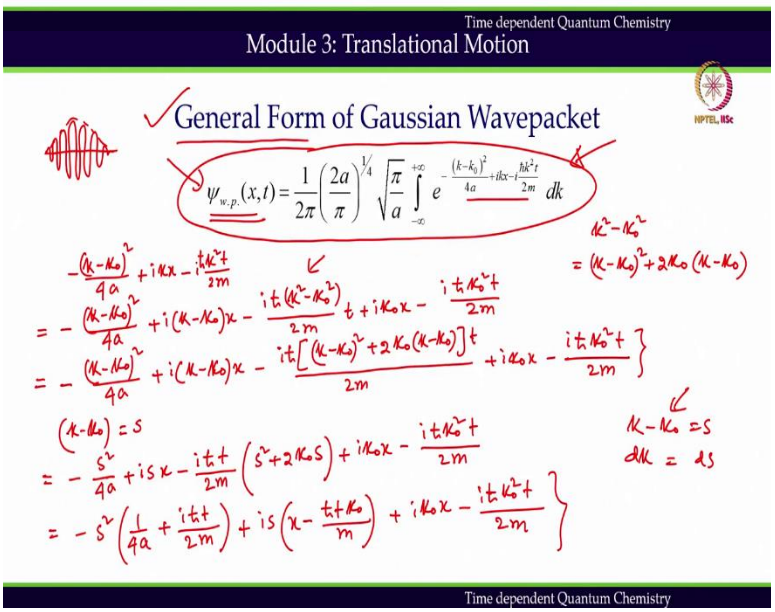

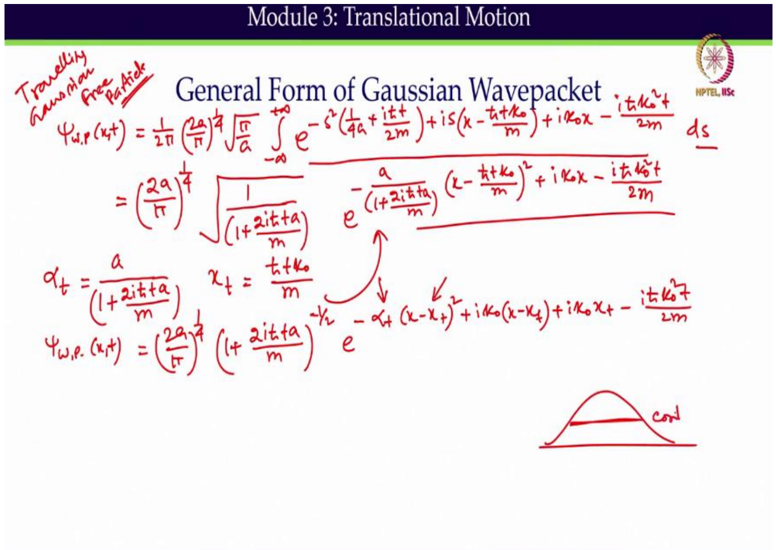

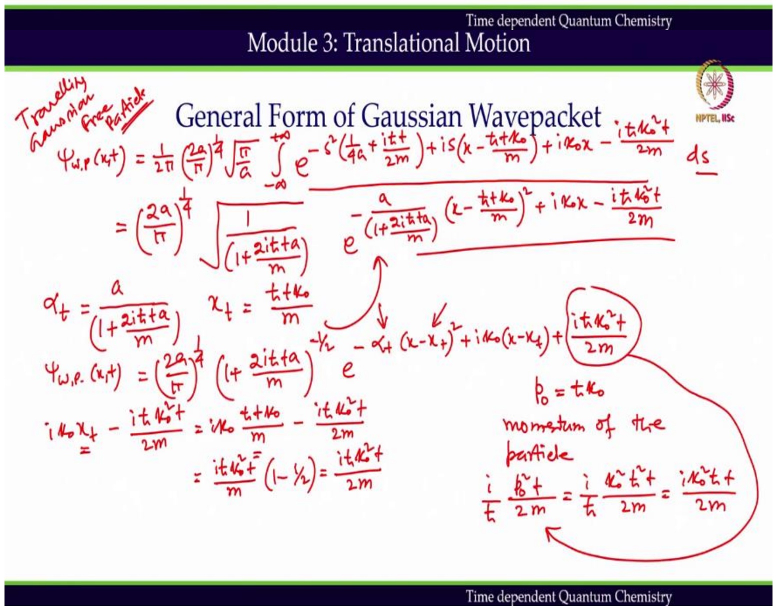

And further reduce the equation as follows. We have now,

$$\psi_{w.p.}(x,t)=\frac{1}{2\pi}\left(\frac{2a}{\pi}\right)^{\frac{1}{4}}\sqrt{\frac{\pi}{a}}\int_{-\infty}^{\infty} e^{-s^2\left(\frac{1}{4a}+i\frac{\hbar t}{2m}\right)+is\left(x-\frac{\hbar k_0 t}{2m}\right)+ik_0x-i\frac{\hbar k_0^2 t}{2m}}\,ds$$

Here integration was ober k. So, if we look at this k- k_0= S. So, I can consider dk=ds because k is actually the average wave number component which we get from the after the interference. The origin of this creation of this wave packet was the interference of many components, the matter wave components and if we take the average of all wave numbers.

That is the k_0. So, k_0 is constant for a particular Wavepacket. And because it is constant we can take this derivative. So, integration can be over ds and that is exactly what we have done here. So, the reason why we have reduced it in this form because again, we will be able to use the Standard Gaussian Integral.

We have been using it and, in many occasions, we will be using the standard Gaussian integral and that is the beauty, why we have been using this Gaussian Wavepacket, one can propose to use some other Wavepacket, some ugly looking Wavepacket like, this kind of wave packet let us him one can use that.

But the problem is that we will be facing one problem of getting an analytical solution, how do you get the analytical solution for such a Wavepacket. So, this can be represented, this can represent a particle as well. And, but for our derivation, we are considering that is a very nice looking this Gaussian type of Wavepacket, which is representing the particle.

Because the mathematics should be much easier to deal with this kind of Wavepacket, if we deal with, we have to go for numerical solution which will go over very soon in this class. Anyway, we have to use the standard integral and if we use the standard integral, finally, we get I will jump one step here, you can go ahead and try to do it on your own just one step I have jumped here.

$$\psi_{w.p,}(x,t)=\left(\frac{2a}{\pi}\right)^{\frac{1}{4}}\sqrt{\frac{1}{\left(1+\frac{2i\hbar ta}{m}\right)}}\,e^{-\frac{a}{\left(1+\frac{2i\hbar ta}{m}\right)}\left(x-\frac{\hbar tk_0}{m}\right)+ik_0x-i\frac{\hbar k_0{}^2t}{2m}}$$

So, this is the final form of the Wavepacket we have this is a different way to represent the traveling Gaussian, we are still using Traveling Gaussian.

It’s is just another way to represent it. So, if I have this now, I will assume that I will define

$$\alpha_t=\frac{a}{\left(1+\frac{2i\hbar ta}{m}\right)}$$

I will define this one and also, we have already seen that x_t that is the center of the Gaussian. The Gaussian we had this and this was the position x_t. The center of the Gaussian that is represented by we have already seen that this is going to be $x_t = \frac{\hbar t k_0}{m}$ we have already seen this.

So, if we use this to and then plug that in here, we get the expression for the Wavepacket as follows

$$\psi_{w.p,}(x,t) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \left(1 + \frac{2i\hbar ta}{m}\right)^{-\frac{1}{2}} e^{-\alpha_t (x-x_t)^2 + ik_0(x-x_t) + i\frac{\hbar k_0^2 t}{2m}}$$

This entire argument we have written in terms of α_t and x_t and if we do that alpha t what is the meaning of α_t definitely you see this e^{ax^2} this is the Gaussian form. Now, if something or in this case this is going to be $e^{a(x-b)^2}$, that is the Gaussian form we have. Now, anything here is written a it will control the width of the Gaussian.

So, it is quite clear that this α_t is going to control the width of the Gaussian and x_t is controlling the center of the Gaussian which means, I have a Gaussian this width will be controlled by α_t it will be controlled by it is not proportional to α_t. I will show how it is related it is controlled by α_t and the center position that is controlled by x_t.

So, that is the basic idea meaning of this the function. So, now we have this expression and we can further reduce this expression this argument particularly, we can reduce this part of this argument as follows

$$\begin{aligned} &ik_0 x_t - i\frac{\hbar k_0^2 t}{2m} = ik_0 \frac{\hbar t k_0}{m} - i\frac{\hbar k_0^2 t}{2m} \\ &= i\frac{\hbar k_0^2 t}{m}\left(1 - \frac{1}{2}\right) \\ &= i\frac{\hbar k_0^2 t}{2m} \end{aligned}$$

So, this can be simplified as i h cut k naught square t by m 1 minus half which is nothing but I h cut k naught squared t by 2m. So, what we get here is that I can reduce this part of the argument and I can write down as $i\frac{\hbar k_0{}^2 t}{2m}$. And we have also realized that the momentum of the particle free particle is going to be $p_0 = \hbar k_0$. That we have seen already the momentum of the particle.

So, if this is the momentum of the particle then I can write down that

$$\frac{i}{\hbar}\frac{p_0^2 t}{2m} = \frac{i}{\hbar}\frac{\hbar k_0{}^2 t}{2m} = \frac{i k_0{}^2 \hbar t}{2m}$$

So, what we see is this part can be represented as this in terms of the momentum. So, if we do that finally.

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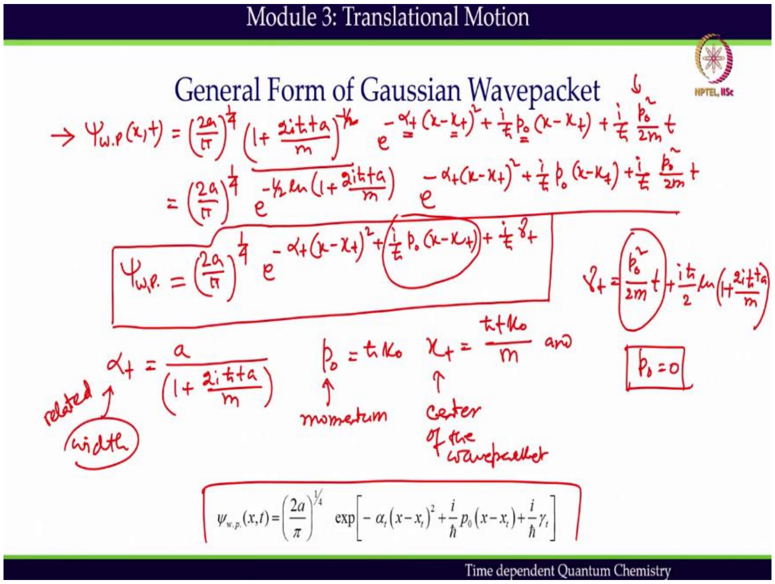

What we have is following Wavepacket

$$\psi_{w.p,}(x,t) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \left(1+\frac{2i\hbar ta}{m}\right)^{-\frac{1}{2}} e^{-\alpha_t (x-x_t)^2 + \frac{i}{\hbar} p_0 (x-x_t) + \frac{i}{\hbar}\frac{p_0{}^2 t}{2m}}$$

So, now, we have represented the free particle Gaussian Wavepacket.

In terms of α_t ,x_t and P_0 that is the momentum of the Wavepacket and we can further reduce it in the following way

$$\psi_{w.p,}(x,t) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\ln\left(1+\frac{2i\hbar ta}{m}\right)} e^{-\alpha_t (x-x_t)^2 + \frac{i}{\hbar} p_0 (x-x_t) + \frac{i}{\hbar}\frac{p_0{}^2 t}{2m}}$$

$$\psi_{w.p,}(x,t) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} e^{-\alpha_t (x-x_t)^2 + \frac{i}{\hbar} p_0 (x-x_t) + \frac{i}{\hbar}\gamma_t}$$

So, this is the final expression of the Wavepacket free particle wave packet.

The general form this general form will be used when we have α_t and this is given here where α_t is

$$\alpha_t = \frac{a}{\left(1+\frac{2i\hbar ta}{m}\right)}$$

P_0 is the momentum of the Wavepacket $p_0 = \hbar k_0$, x_t is the center of the Gaussian. So, these are related to the width. So, related to width I am not saying this is represented, representing the width it is related to width.

This is related to but this is not related this is directly representing the momentum of the Wavepacket. This is center of the Wavepacket which is nothing but $x_t = \frac{\hbar t k_0}{m}$ and finally, I have

$$\gamma_t = \frac{p_0^{\,2} t}{2m} + \frac{i\hbar}{2} \ln\left(1+\frac{2i\hbar ta}{m}\right)$$

So, this is the general form of the traveling Gaussian Wavepacket and we can see that if this is an and the same form can represent a stationary Gaussian function as well to stationary Gaussian Wave packet which we have seen previously. And in order to make it stationary, all we need to do is that P_0 should be 0.

Because it is does not have any velocity. So, it does not have any momentum it is not moving at all. So, it does not have momentum. So, in this if you use P_0 equals 0, then the term which will be eliminated from here is this term will be eliminated and this term will be eliminated because they both have P_0 term.

And remaining term will be there and if you compare remaining term with the previous results, you will see that they are matching with each other. So, this is the general form of the Gaussian will remember this and we will use very frequently. This is used in Wavepacket dynamic, Gaussian Wavepacket dynamics particularly.

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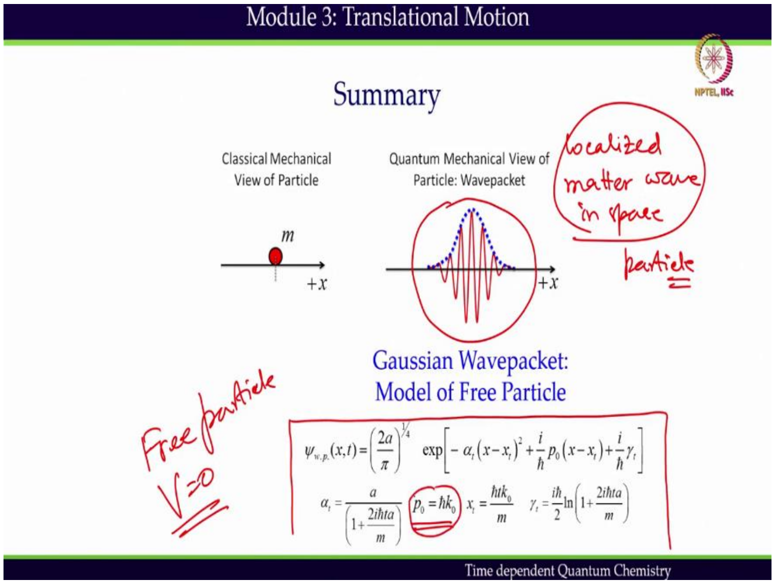

So, we have come to a conclusion or come to the end of this module 3, in this module what we have studied the first take home message should be from this module is that when I think of particle immediately I get an impression that I am seeing a ball and that should be avoided in quantum mechanics.

There is nothing called particle like ball in quantum mechanics. In quantum mechanics, particle would be represented by this shape can be different shape can be Gaussian, shape can be different else. Something else, but what does it mean by particle in quantum mechanics particle is actually a localized matter wave in space, this is called particle.

And this is something which we should practice it does not come immediately. Because we have so, much familiar with our daily experience that immediately once we think of particle immediately think of the ball and that should be avoided it is in quantum mechanics, there is nothing like ball it has to be like a localized matter wave.

So, this is one important point which we have clarified and then what we have done is that we have shown different rigorous mathematical derivation and in the derivation we have shown how Gaussian Wavepacket would propagate in time and then finally, we have got this general expression for this Wavepacket.

General expression of those Wavepacket would be very useful for and this is for free particle this, I will keep some reservation this is a general expression for free particle. So, far we are calling it free particle because we are using P_0 and question is, it is for free particle. Free particle which means potential experienced by the particle is 0 there is no force acting on the particle. So, if the force is not acting on the particle quantum particle, it will just move with the same velocity it will not change the velocity at all. And that is where momentum is constant. This is the momentum which is constant. Now, question is.

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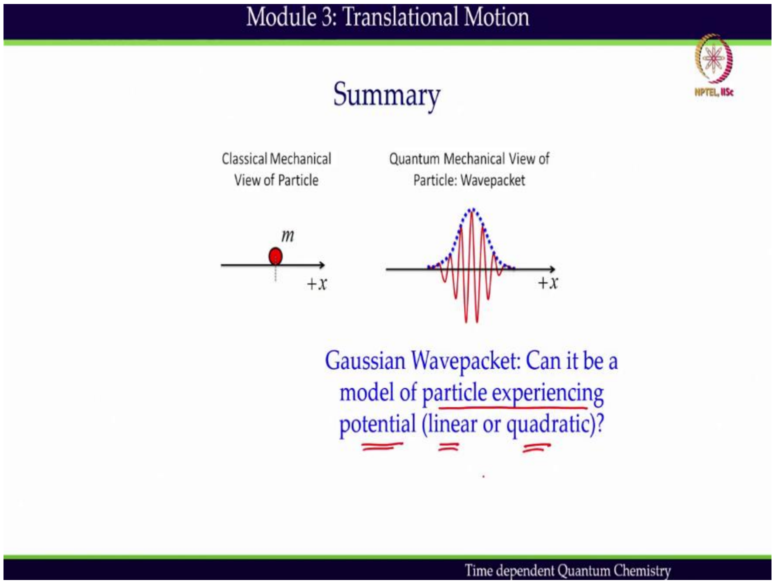

Can I use similar kind of form for a particle experiencing potential such as linear potential or quadratic potential? I will keep this question open and I will end this session. I will meet again in the next module.