Time Dependent Quant Chemistry
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Mod 05 Lecture 37
Wavepacket Dynamics under Linear Interaction Potential

Well come back to Python tutorial 5 of the course Time Dependent Quant Chemistry. So far we have seen how to propagate a wavepacket in the zero interaction potential when the particle is not experiencing at all the interaction potential, which means the particle is not experiencing the force acting on it. So, we have seen that the particle is traveling with a constant velocity. And also we have seen that the particle distribution, the distribution function is spreading out slowly.

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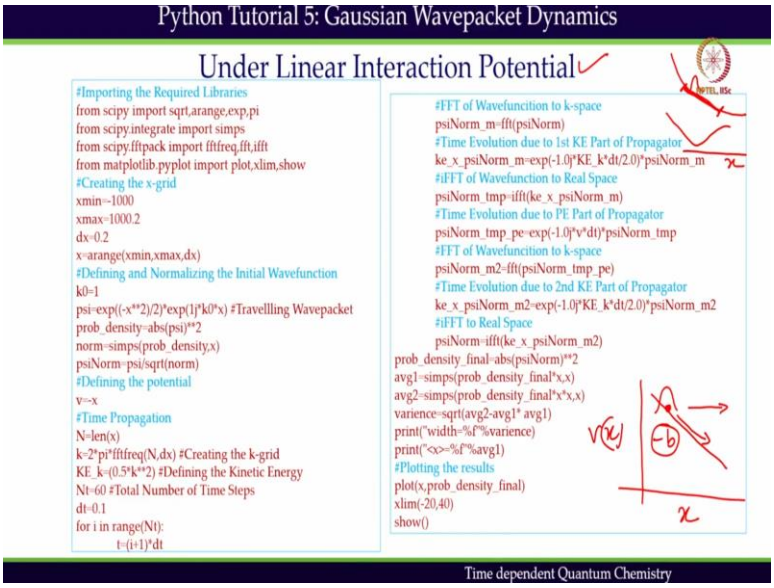

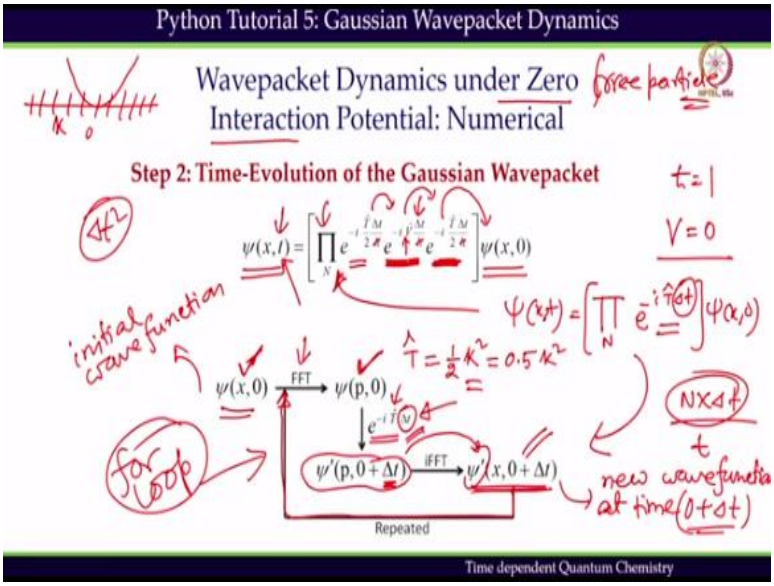

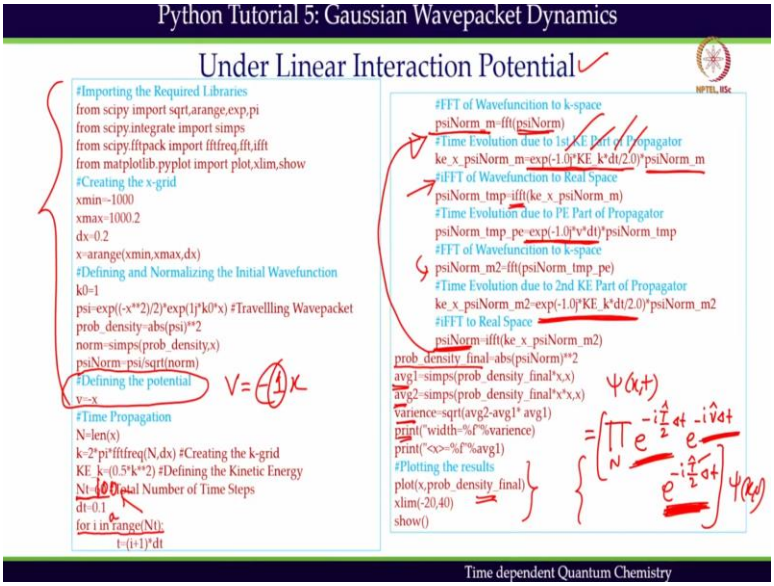

So now, the next problem we will deal with is the linear interaction potential, what will happen to the particle? What is linear interaction potential? It is a simple interaction potentially you can think about. In the x space, you have V(x) interaction potential to be like this. We have created this slope like this way, because then it is starting from here and how it is moving. Clearly, because the slope is given to be minus b, b is a constant, positive constant, it should accelerate slowly.

And classically it is also true because the, if a ball is sliding over this slope, it will be accelerating. So it will be increasing the velocity as a function of time and we will see what is going on. So, linear potential can be a model for let us say I have a potential like this, this is, this

was ground state and this is excited state and I have created a wavepacket here let us say. And for a short region of the potential, it can be considered to be linear as a function of time, as a function of space.

So, linear potential can be considered to be a dissociative potential one can in a simple form. And to understand the linear potential, remember linear potential problem can be analytically solved using the technique which we have discussed in the translational motion of quantum particle. And we will see whether we can represent the same thing numerically. And the difference between the linear potential problem and the zero interaction potential problem is that now we have to consider the V.

So previously, what we have used here, this split operator approach, we have, we did not have any potential part. Now we have the potential part and we have to construct that potential part. And we can one more time write down that equation, that split operator equation, which is high.

$$\Psi(x,t) = \left[\prod_n e^{-i\frac{T\Delta t}{2}} e^{-i\frac{V\Delta t}{}} e^{-i\frac{T\Delta t}{2}}\right]\Psi(x,0)$$

So this is what we have to implement, and we know that this product has to be implemented through a for loop. That is exactly here for i in range Nt, instead of range, we are going to use arange functionality. So, arange functionality will give me and total number of time steps I can consider to be 60 or a 100, depending on whatever we want, we want to keep it 100 because then we can compare with the a 100, at the 100 atomic unit of time what happened.

So, what happens to that wavepacket for the same time evolution, we can compare it to the free particle evolution. And we can see that this time when you are doing it, initially we have two psi norm has been converted to its moment domain. Then once we have the moment domain function, that momentum domain function, we are carrying out this kinetic energy part, the first kinetic energy part of the operator, split operator here in the momentum domain.

And that is nothing but kinetic energy that is the t multiplied with half, 1 by 2, delta t is dt and the i, i is represented by one j that is the representation in that Python programming. And after doing that, we have to convert it to a position domain, because the next two, this first part of the

kinetic energy next to this, we have this potential energy, and potential energy part of the time evolution operator needs to be carried out in the position space.

So, that is why you have again converted to inverse Fourier Transform and then get the position space part. Once we get the position space wavefunction, we employ this position potential part, the potential part of split operator, split operator. And then again, we have to carry out this kinetic energy part.

So we have to again, FFT, the Fourier Transform, Faster Fourier Transform we have done to get the wavefunction in the Fourier domain. And then employed the last part, kinetic part of the split operator. And then finally, we get this psiNorm, this psiNorm will be updated during this iteration. So, this iteration will be continued until this value or 100 minus 1 value, and it will be updated.

Finally, I get the probability density. Then we will calculate average values of this and variance which is the fully, the half width at the 60 percent, almost 60 percent of the maxim. And then we are going to print it. And also we can plot the final probability to check how the final probability looks like. So, that is the basic idea. Remaining part is, it remains to be the same what we have done.

Another thing is that we are now defining the potential here. So, this was not present in the zero potential problem or zero interaction potential problem. Here we are defining the potential to be minus 1x. So, the slope is going to be minus 1. So with this idea, we will now implement the entire program in our in Python.

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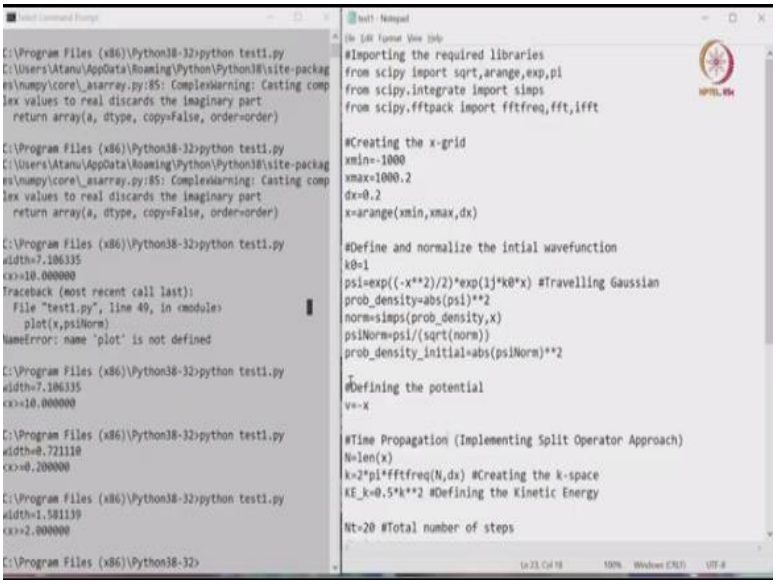

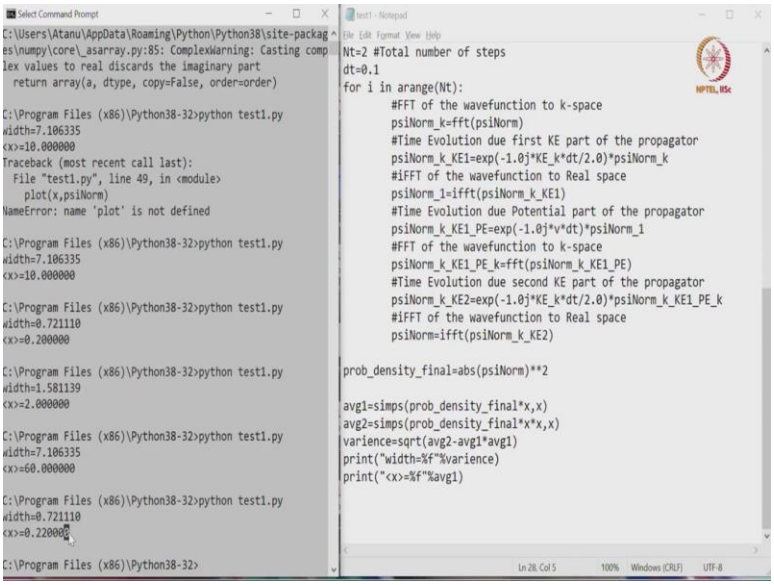

And here the, because we are going to plot it again, so we are going to use this from I can plot it later. So, we will keep all these things. Remaining part is the same. So, creating a normalizing wavefunction and then what we will do here is that we will first define the potential. So, defining the, normalizing the initial wavepacket, we have done it. And then before the time propagation, we will now define the potential.

Potential definition V equals minus x. x is an array, so V will be getting an array and array values is just multiply each element by minus 1, multiply the element of x array. And then we will look that look at the time propagation part. When you look at the time propagation part,

definitely we have to first clear the k grid that we have created here and this is the k grid preparation. We have created the k grid. Then kinetic energy has been defined for each grid point of K, we get the kinetic energy, corresponding kinetic energy. And then Nt, we keep it 100 and dt to be the same. So we will be able to compare what is going on if it is a free particle.

And then for we will start the iteration for loop to implement the short time propagator. And for that, what we will do is that we will start t equals i plus 1 multiplied by dt. So, t I am defining as i plus 1 multiplied by dt. Now this, this t definition I use in, in many occasions we might want to check what is, at what time I have this wavepacket. I may not need it immediately. We will see later.

So, what we will do is that the remaining part is the same. FFT of the wave function, first we have to do FFT of the wavefunction. And then after FFT, we will say time evolution due to first kinetic energy part of the propagator. And for that, first kinetic energy of the propagator, it will give me psiNorm, then k, kinetic energy, we call it 1. And that has to be given by exponential of, so the name, we have given the name to be exponential off minus 1 j kinetic energy dt divided by now, I have to divide by 2.0 and psiNorm K.

Then I have to do the first Fourier, inverse Fourier transform the real space, that is going to be K1. Then we have to employ time evolution due to the, time evolution due to the potential part of the propagator. And this we will name it, psiNorm, this we name it as the 1. So the kinetic energy is done, then potential energy, that is going to be psiNorm 1. So, this is the potential energy for. This is not potential energy, we have to define the potential ij multiplied by v, multiplied by dt, there is no half.

So, this is the potential part we are doing, after doing the potential part, I have to now, again, Fourier transform to k space. And for that, this is the function which I will Fourier transform. And I give the name to be k, this is the Fourier transform. After Fourier transforming, again, I have the time evolve it, and for that, we have to employ the kinetic energy part again, but this is the second kinetic energy part we will be carrying out.

And now I have, this is the function and I will name it 2. Then we have to invert Fourier transform to the real space. Here, I am going to now update this psiNorm. And this is the function which I have here. So, this time, I am going to update this. So, this psiNorm will be

used. In the next iteration in this place. So then, I can bring the probability density to be the final probability density is going to be psiNorm. It is the same thing we keep.

Then average values, we are going to calculate average 1 is going to be Simpson's method of numerical integration we are using that is the final multiplied by x, and then average 2 is going to be final multiplied by x multiplied by x. And then, variance is the same thing and print, we are going to print the width as variance and the expectation value of the average 1. So, this is what we are going to do.

So, if we do that, if we run the program, then we see that the width we have found to be 7.10. For this step, Nt equals 100. But if we make it, let us say, Nt to be 2, then the center position is now 0.22 atomic unit, previously it was 60 atomic unit for the 100 steps, but here, we have taken 2, so it is going to be 0.22. And this is the way, if we keep collecting all the values, possible values, we will go back to the slide now.

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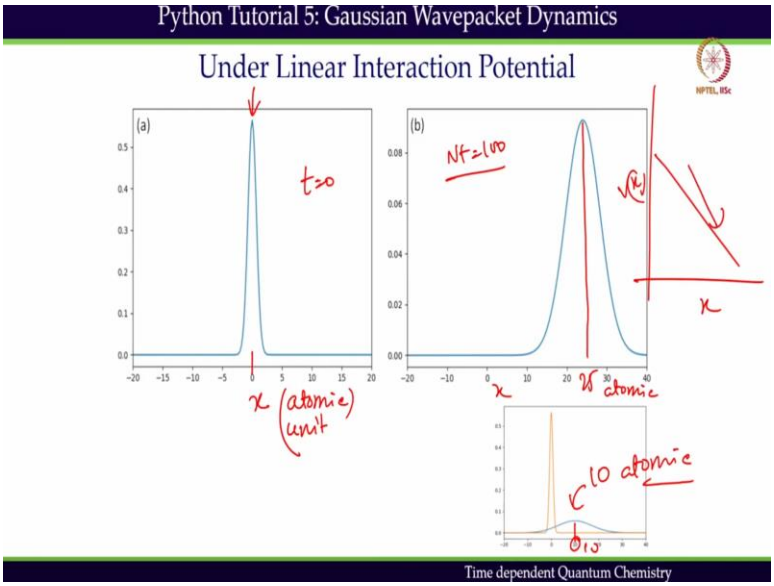

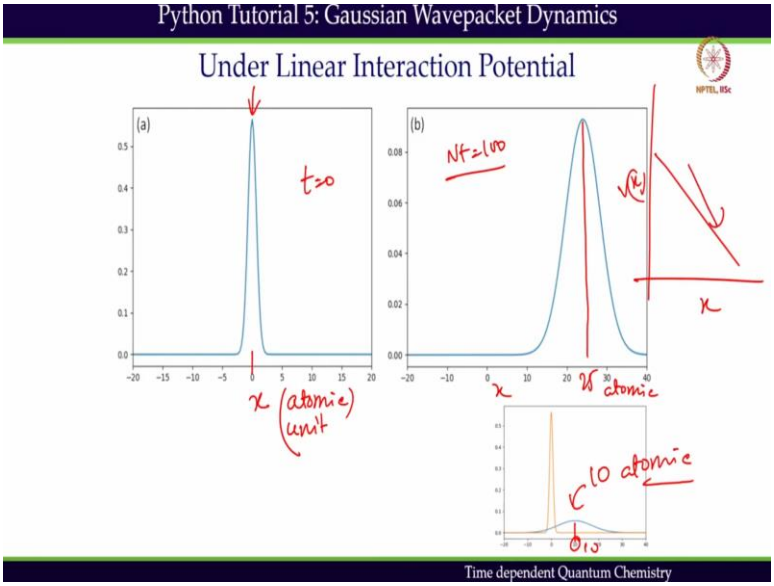

And if we, if we keep collecting it, we will be able to get it. But if we plot it, what we see here is that we started now, we started with the same initial Gaussian wavefunction which is centered at x equals 0, this is x atomic unit. And it is centered at x equals 0. This is x equals 0 and we have considered Nt to be 100 here. So, we see that Nt to be 100, we can, this centered almost at 25 atomic unit, whereas the free particle we have found it was entered at 10 atomic unit.

This was at 10 atomic unit, which shows that because of this slope in the potential, it is moving much faster and it is moving much faster, and if we keep collecting the values at different time we will see that, initially if we plot it this one, then what we can see here is that this is the average or variance plot as a function of time. This is function of time average or the variance plot. So this is variance and this is average plot.

What we see is that now, there is this striking difference between the linear potential particle, particle experiencing linear potential and the particle experiencing 0 interaction potential, this is v equals 0, this is the potential and v equals x, that is the potential is experiencing. What we see that the mean position is non-linear with respect to time. And that should be because if x is non-linear with respect to time, some kind of let us say t-square for an example, I am, I do not know, I have to check the non-linearity again, I have to fit this data with certain, function.

But if we assume that it is x equals t square, then only I get dx dt to be time dependent, which means velocity is time dependent and velocity is changing as a function of time. And that should

happen. Classically also, it should happen. If I have a ball sliding through this slope, it slowly accelerating, which means that velocity depends on time.

Similarly, if our wavepacket is created here, when the wavepacket will be propagating in space, it will be accelerating its velocity, its velocity is increasing and that is why the mean position or center of the velocity or center of the wavepacket is non-linear now with respect to timing. And the sigma also we have seen that sigma is also kind of non-linear and, is non-linear, but it is also spreading out.

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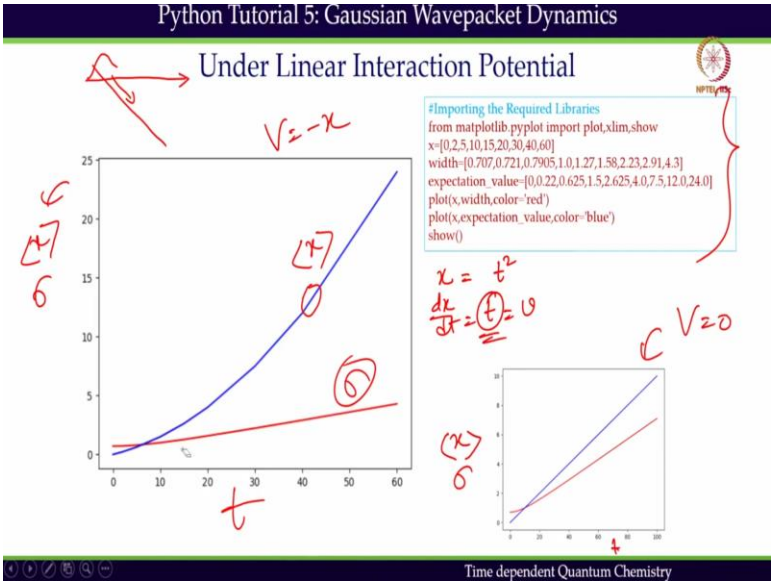

So, both of the, one similarity between the zero interaction potential and the linear potential problem is that both are spreading out. Here the width and here the width are different. Both are spreading out. But in 0 interaction potential, its velocity was constant, but in the particle, which is experiencing a linear potential of this kind, minus x kind of potential, if it is plus x kind of potential, the situation can be different, but it is minus x kind of potential, it is accelerating and that is quite expected. And it is because accelerating, it is, it is, the mean position is slowly is non-linear with respect to time.

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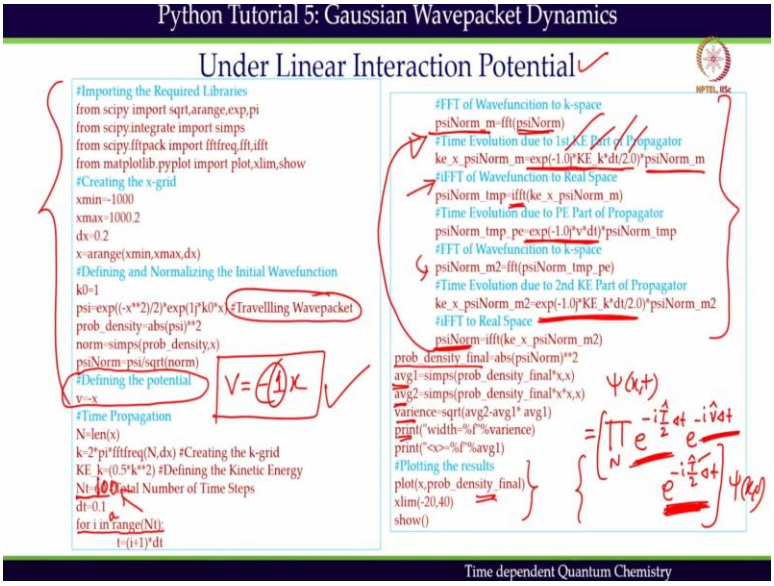

So, this entire procedure, particularly, what we have given here, this entire procedure is now can help anybody to express the wavepacket dynamics following this symmetrized split operator approach. In order to implement this split operator approach, all we need to know is that potential, what is the potential experience by the particle? As long as the potential is known by the partner, by the user or by somebody who is exploring this dynamics, 1 dimensional dynamics. And as long as the initial wavefunction is known, this is the initial wavefunction traveling Gaussian. This initial wavefunction is known, then one can time evolve the particle on that potential.

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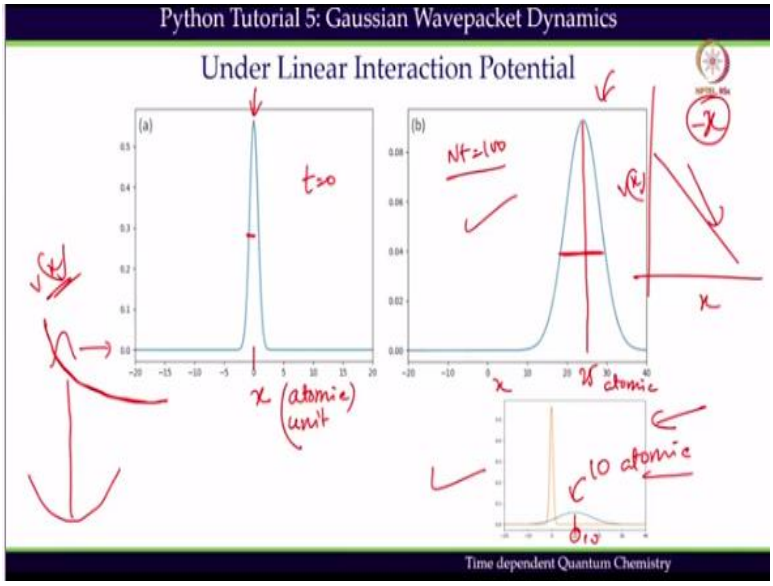

One of the simple problem can be, one can think of a dissociative potential like this, and one can create the wavepacket here and check what is the dynamics of the wavepacket on this kind of dissociative potential. Now, this kind of dissociative potential can be found or can be calculated with the ab initio calculations, one can use Gaussian calculations, small group calculations, and find out the potential and that potential can be used to check the, how the particle is actually moving on that kind of potential. And that is, that is presenting the dissociation of a, of a chemical bond.

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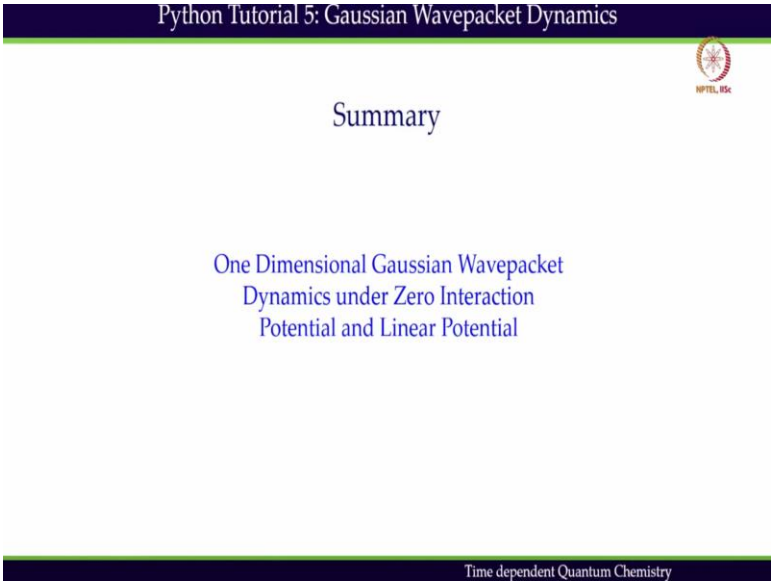

So, we have almost come to the, we have come to the end of this present tutorial, Python tutorial. What we have seen is that we have numerically solved or numerically time evolved the wavepacket starting from Gaussian wavepacket as an initial Gaussian wavepacket. We have used this technique the, we have implemented this split operator approach in Python programming for zero interaction, potential and linear potential.

And we have seen how to plot the mean position and the width of the wavepacket as a function of time. This procedure is general procedure, one can use it for any unknown potential, but it has to be one dimensional in nature. That is the way we have studied so far multidimensional, wavepacket dynamics is little more complicated. If time permits, we will definitely think about it and we will present it. So, we will stop here. We will meet again for the next module.