Time dependent Quantum chemistry

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Module 05 Lecture 33

Split Operator Method

Welcome back to Module 5. So far what we have discussed, we have shown general properties of time evolution operator. And we have shown that because it is a unitary operator its time its norm is preserved. That is why normalization constant does not change over the time during the time of evolution of this system. Next. We will go over the numerical implementation and what are the complications associated with numerical implementation.

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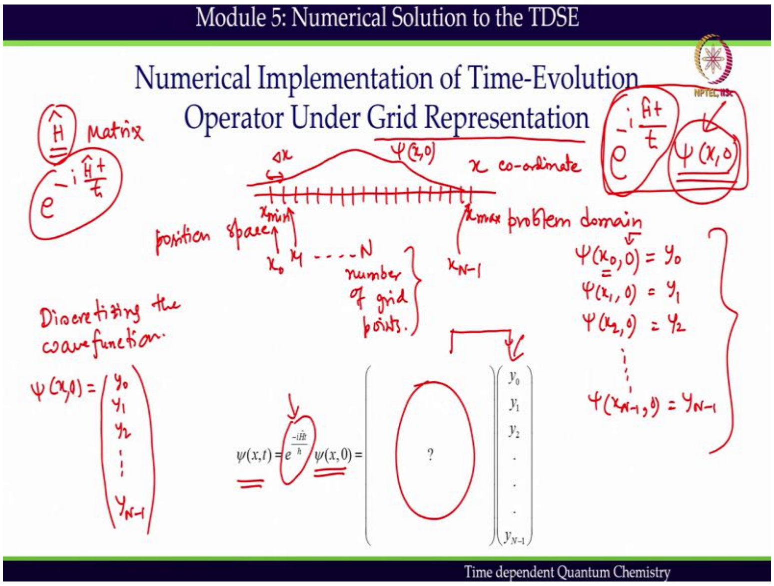

So, what we have shown so far is that mathematical strategy to obtain solution to the time-dependence Schrodinger equation, time time-dependence Schrodinger equation,

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}\Psi(x,t) = [\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)]\Psi(x,t)$$

so this solution to the TDSE can be very easily obtained by taking this form

$$\Psi\ \ (x,t) = e^{-i\frac{2\pi Ht}{h}}\Psi(x,0)$$

We can we can obtain that and then we have seen that this procedure to find out this mathematical solution was very simple and it is very straightforward. But it is numerical implementation is not an easy task, and we will rebuild why it is not an easy task. So, I have

$$\Psi\ \ (x,t) = e^{-i\frac{2\pi Ht}{h}}\boldsymbol{\Psi}(\boldsymbol{x},\mathbf{0})$$

As the time evolution operator is an exponential operator, its numerical implementation requires some method of calculating the matrix exponential. So, one of the procedures which we have already seen in Python tutorial 2 that we can represent a wave function, this kind of wave function under grid representation and we know how to represent a wave function on a grid.

And the moment we represent a wave function on a grid we have to find out how to represent this operator on the grid. And in order to get that idea, we have already mentioned that this operator will be expressed in terms of matrix on the grid and if this is a matrix, then ultimately, we have to find out this operator, we have to find out matrix exponential because H is a matrix in the grid presentation.

Almost all currently prevailing numerical methods which is used to solve TDSE make use of grid representation of a continuous wave function that we have seen. So, grid representation it means that the problem domain, if this is called problem domain which means the position space, this is called position space, this position space is divided into uniform grids. And this is something which we have already understood in Python chapter. In Python tutorial 2, we have shown how to represent our function on a grid.

So, basically, we have to take some kind of x maximum, sorry minimum and some kind of x maximum and this range will be divided into small interval. And this edge point is going to be the grid. So, this is called x grid. So, because I have the x coordinate here, as a position space, we are using this, we are dividing the entire x coordinate into very small interval.

And if we do that, then if I have an wave function, let us say something like this, this is your wave function, this kind of wave function, let us say at t equals 0 time. I have this wave function $\boldsymbol{\Psi}(x,0)$ then I will be able to write down this $\boldsymbol{\Psi}(x_0\ ,0)$. So, when I say x_o it means that this one is x_o, the next one is x_1, so on like this way, and this is going to be x_{N-1}, if I have N number of grid points.

So, if I have, so then function value

$$\Psi(x_0,0) = y_0$$

$$\Psi(x_1,0) = y_1$$

$$\Psi(x_2,0) = y_2$$

and so on like this way. So then in the end, I get

$$\Psi(x_{N-1},0) = y_{N-1}$$

So, these are the discrete values we get. So basically, what we are doing, a continuous wave function, which is supposed to be continuous, but on the grid, we are discretizing the wave function.

And this discretized wave function can be very conveniently represented as a column matrix that we have seen. So, the initial wave function will be represented as a column matrix like this. That is going to be

And the moment we represent the column matrix here, so this part has been represented by this column matrix.

$$\begin{bmatrix} y_0 \\ y_1 \\ y_2 \\ . \\ . \\ . \\ . \\ y_{N-1} \end{bmatrix}$$

Question is how do I represent this exponential operator in terms of a matrix, because in the end, if I multiply this matrix by the wave function, I get back the wave function at a particular time and that is the motivation of doing this exercise. What would be the matrix presentation of this exponential operator?

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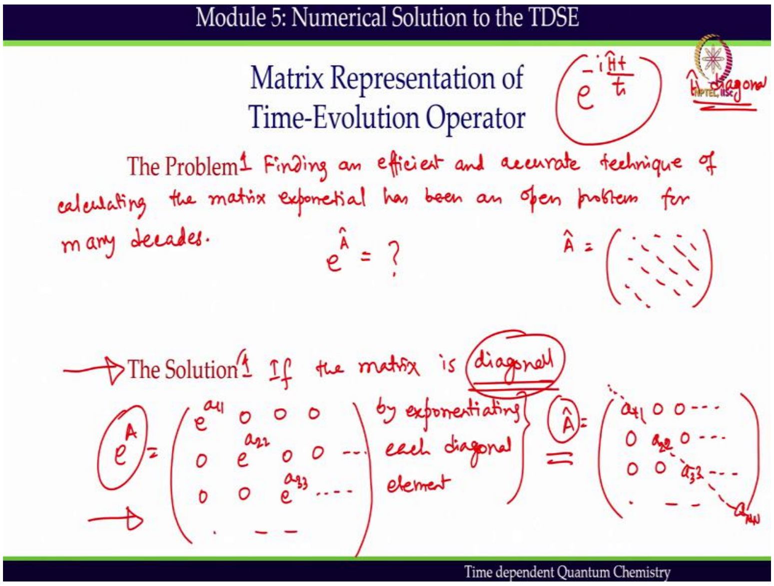

Now, there are problems and there are solutions to it. The first problem is that finding an efficient and an accurate technique of calculating the matrix exponential has been an open problem for many decades. What do I mean? It is not an easy task to find out if A is a matrix and A operator is represented by a matrix let us say, then exponential of that matrix is not an easy task to find out this exponential, but there is a quick solution.

The method of getting exponential of a matrix is heavily simplified if the matrix is diagonal. So, if A is a diagonal matrix which means that

$$\hat{A} = \begin{bmatrix} a_{11} & 0 & 0 & . & . & & & \\ 0 & a_{22} & 0 & . & . & & & \\ 0 & 0 & a_{33} & . & . & & & \\ . & . & . & . & . & & & \\ . & . & . & & . & & & \\ & & & & & . & & \\ & & & & & . & . & . \\ & & & & & . & . & a_{NN} \end{bmatrix}$$

So, if I have only diagonal elements present in a square matrix, then it is called a diagonal matrix.

And if I have a diagonal matrix, then e to the power A exponential of that matrix can be calculated as by exponentiating each diagonal element as follows, is going to

$$e^{A}=\begin{bmatrix} e^{a_{11}} & 0 & 0 & . & . & & & \\ 0 & e^{a_{22}} & 0 & . & . & & & \\ 0 & 0 & e^{a_{33}} & . & . & & & \\ . & . & . & . & . & & & \\ . & . & . & & . & & & \\ & & & & & . & & \\ & & & & & . & . & . \\ & & & & & . & . & e^{a_{NN}} \end{bmatrix}$$

So, if A is diagonal, then exponential of that matrix can be obtained by exponentiating each diagonal element. This is not true for any matrix it is true only for diagonal matrix.

So, what is our task? Our task could be, if we would like to use this trick, the simple solution to get the, so our unitary operator, what is the time evolution operator is following, this is the time evolution operator and we have to find out the matrix representation of this time evolution operator, what we need to do is that we have to convert this to be a diagonal form, in a diagonal form. The moment we get that, then we will be able to use this trick to get a time evolution operator. So, that is going to be our target. But that target cannot be -- This is problem 1 solution 1.

But that target cannot be solved, the target cannot be achieved very quickly. It is because this Hamiltonian operator, I will show why it is difficult, because the requirement for, using this technique we have to use, we have to get the Hamiltonian operator in the diagonal form. So, in order to get the Hamiltonian in the diagonal form, it is not an easy task we need to use different tricks to use that. We all know that Hamiltonian is a sum of kinetic energy and potential energy terms.

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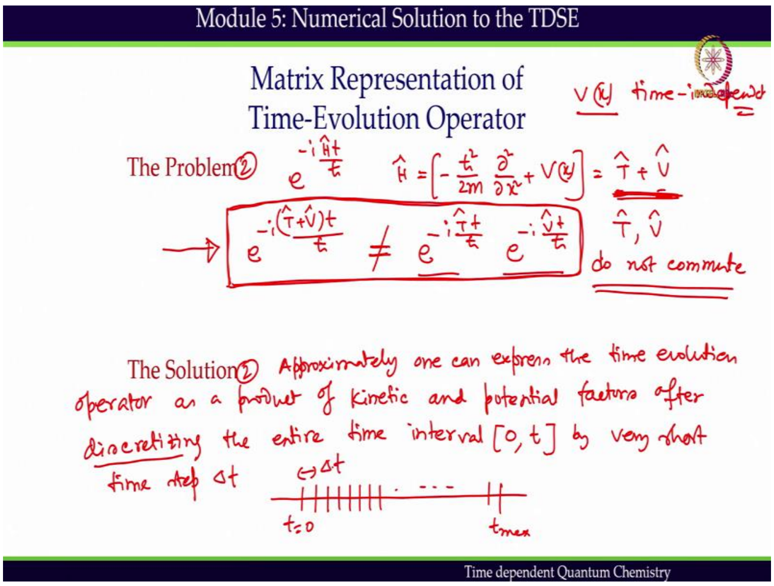

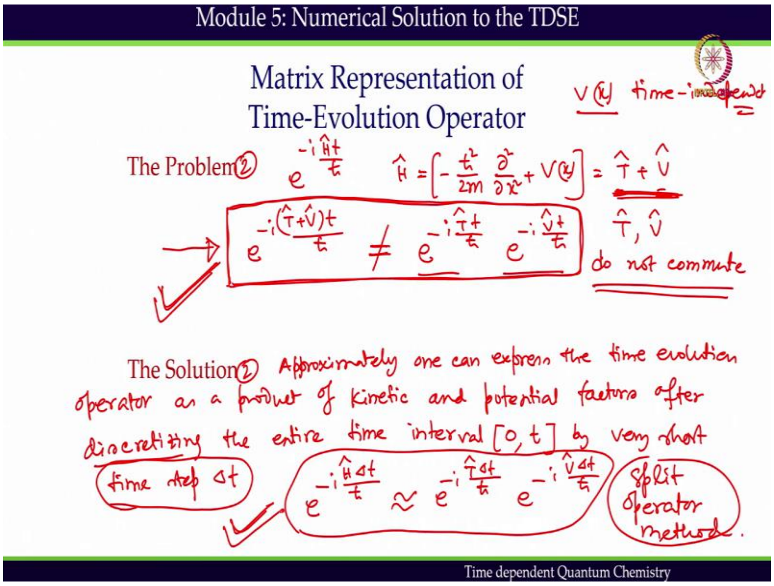

So, we have to individually check weather -- So, problem number 2 is that as the time evolution operator contents Hamiltonian operator

$$\hat{U}(t) = e^{-i\frac{2\pi Ht}{h}}$$

Hamiltonian operator is nothing but the summation of kinetic energy part which is given for single particle one-dimensional problem.

$$\hat{H} = \frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)$$

Still, we are dealing with single particle one dimensional problem plus V(x) that has the Hamiltonian we have which means I have kinetic energy operator plus potential energy operator, there are two operators which are clubbed together to form this Hamiltonian operator. And we are still assuming that V(x) is time independent. We will come to the problem later, where we will be dealing with time dependent V.

So, because this is a summation of these two operators. So, one can write down here

$$\hat{U}(t) = e^{-i\frac{2\pi Ht}{h}} = e^{-i\frac{2\pi(T+V)t}{h}} = e^{-i\frac{2\pi Tt}{h}}e^{-i\frac{2\pi Vt}{h}}$$

We may assume that this is true, but this is absolutely not true, we can write it like this way. So, you cannot separate these two operators as a product of individual operators like this.

This is not true, just because T and V they do not commute, T and V these two operators generally they do not commute. And because they do not commute, we cannot write down, why? I will explain it very soon. But there is a solution. Solution is that approximately one can express the time evolution operator as a product of kinetic and potential factors after discretising the entire time interval. So, two comments I have already made, I will prove it very soon.

First comment is that this is not true, always they are not equal, they are always, they are not always equal, because these two operators do not commute. And the solution can come, approximately one can express the time evolution operator as a product of kinetic and potential factors by discretizing the entire time interval. Let us say the time interval for which we are looking at the dynamics of the quantum system is 0 to t. It is starting at t equals 0 and is ending at t equals t time at an anytime t.

But this interval has to be discretized by a very short time step Δt

. If I do that, so if I do that, which means that I have a time starting at t equals 0 ending at t that is the max and each time step is discretized now, and time interval is delta t. If we do that, then I can approximately write

$$e^{-i\frac{2\pi H\Delta t}{h}} \approx e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}}$$

This is just an approximation and we are splitting these operators that is called that is why it is called split operator method. This is called split operator method. So, we have to now prove, first of all, we have to show that this is true, this inequality is true. And then if I consider very small-time step in the time evolution, then this equality may hold. I have to first prove this one, then I have to go for a proof for this one.

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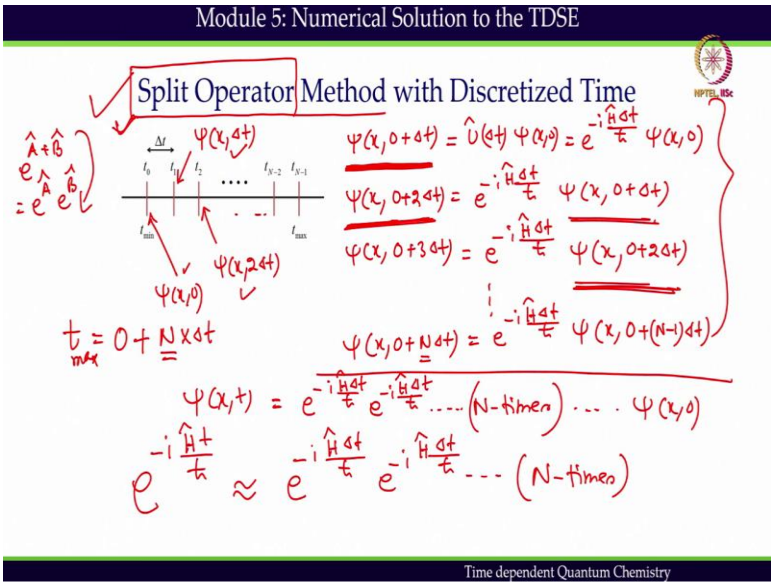

So, we will move on, and we will see how to prove this. So, let us look at the split operator with discretize time. So, here what we will do, we will elaborate them the argument which we had given that we can split, we can use the Split operator approach. The split operator approach we can use if I am discretizing the entire time interval.

And the way we can do that is following, let us

So, at this point I have been able to get the wave function that is the initial wave function. Then at this point, I have the wave function which is x, Δt

$$\Psi(x, 0+\Delta t) = \widehat{U}(\Delta t)\boldsymbol{\Psi}(\boldsymbol{x},\boldsymbol{0}) = e^{-i\frac{2\pi H\Delta t}{h}}\boldsymbol{\Psi}(\boldsymbol{x},\boldsymbol{0})$$

At this point now, I have (x,2Δt) And like this way, I am just propagating the wave function. The wave function was initially was here, then it is like this, then this like this and so on, it will keep propagating in time, and that is what we are writing here. So, this is going to be

$$\Psi(x, 0+2\Delta t) = e^{-i\frac{2\pi H\Delta t}{h}}\boldsymbol{\Psi}(\boldsymbol{x},\boldsymbol{0}+\boldsymbol{\Delta t})$$

this has become now initial wave function for this propagation, propagation for the next step. Similarly, I will be able to write down

$$\Psi(x, 0+3\Delta t) = e^{-i\frac{2\pi H\Delta t}{h}}\boldsymbol{\Psi}(\boldsymbol{x},\boldsymbol{0}+\boldsymbol{2\Delta t})$$

In this case now, this part this wave function would be my initial wave function for the third step propagation. And so on like this way, we can propagate. The final step let us

$$\Psi(x, 0+N\Delta t) = e^{-i\frac{2\pi H\Delta t}{h}}\boldsymbol{\Psi}(\boldsymbol{x},\boldsymbol{0}+(\boldsymbol{N}-\boldsymbol{1})\boldsymbol{\Delta t})$$

And that is the way we can get this. So, this is nothing but, so t total time t, t max that is maximum time I am going there that is nothing but initial time plus. So, this is going to be

$$t_{max} = 0 + N\Delta t$$

So, N times we are doing. So, collectively this entire set of time evolution discretized time evolutions can be written and like this

$$\Psi(x,t) = e^{-i\frac{2\pi H\Delta t}{h}}e^{-i\frac{2\pi H\Delta t}{h}}e^{-i\frac{2\pi H\Delta t}{h}}\ldots\ldots\ldots\ldots(\boldsymbol{N\,times})\ldots\ldots\ldots\ \boldsymbol{\Psi}(\boldsymbol{x},\boldsymbol{0})$$

So, finally, I am getting a way out, a way out for split operator method. I can use the split operator method where I will be writing

$$e^{-i\frac{2\pi Ht}{h}} \approx e^{-i\frac{2\pi H\Delta t}{h}}e^{-i\frac{2\pi H\Delta t}{h}}e^{-i\frac{2\pi H\Delta t}{h}}\ldots\ldots\ldots\ldots(\boldsymbol{N\,times})\ldots\ldots\ldots$$

then I can use the split operator approach.

Split operator approach, what does it mean? I have already mentioned that I will be able to write down

$$e^{A+B} = e^{A}e^{B}$$

In simple algebra we do this very frequently, but when A and B are operator, we cannot directly use that, but we can use it under split operator approach within this approximation that is has to be divided into many short time propagator.

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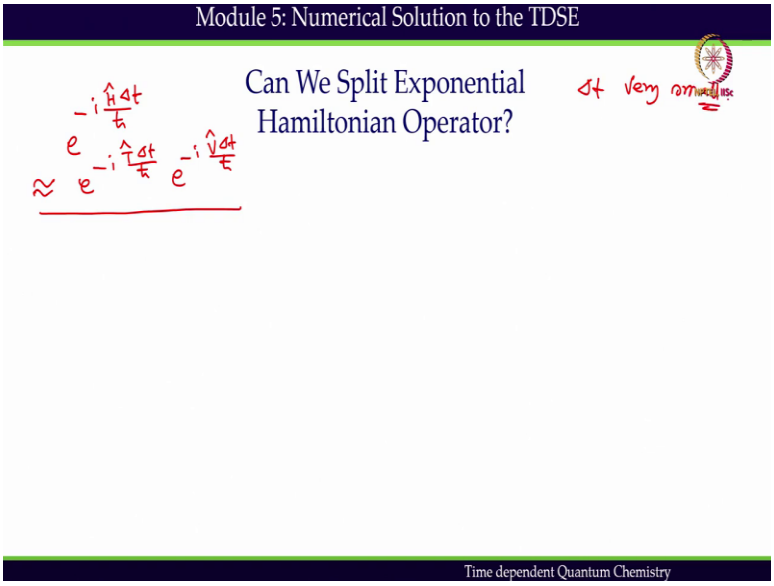

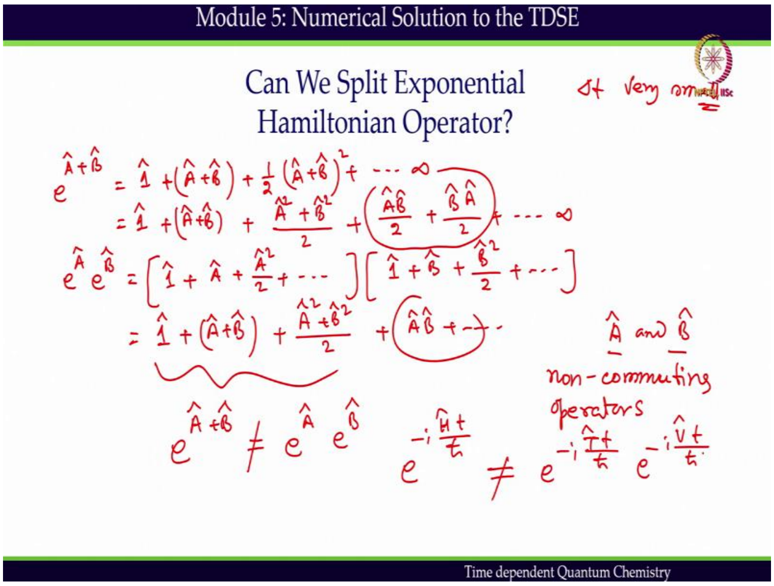

So, question is what about the Hamiltonian operator. Hamiltonian operator, if we consider Hamiltonian operator, we will be able to show here. I have the requirement is that I should be able to write down this. So, I will be able to right down this as a split operator

$$e^{-i\frac{2\pi H\Delta t}{h}} \approx e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}}$$

And we will just prove that, in general this does not work unless delta t is very small. And this is what we are going to prove it first.

So, first let us prove this one. And what will happen if I split it directly? If we split it directly, I have two operators let us say A and B I will be able to write down

$$e^{A+B} = \hat{1} + (\hat{A} + \hat{B}) + \frac{1}{2!}(\hat{A} + \hat{B})^2 + \ldots\ldots\ldots\ldots\infty$$

which is nothing but

$$e^{A+B} = \hat{1} + (\hat{A} + \hat{B}) + \frac{\hat{A}^2 + \hat{B}^2}{2!} + \frac{\widehat{AB}}{2} + \frac{\widehat{BA}}{2} \ldots\ldots\ldots\ldots\infty$$

So, this is the form of e to the power A plus B.

On the other hand, I would like to check what is the form of A and what is the form of the product of this exponential of these individual operators. So, that is nothing but I have to expand each one as Taylor series expansion. So, I will do it

$$e^{\hat{A}}e^{\hat{B}} = \left[\hat{1} + \hat{A} + \frac{1}{2}\hat{A}^2 + \ldots\ldots\ldots\ldots\infty\right][\hat{1} + (\hat{B}) + \frac{1}{2!}\hat{B}^2 + \ldots\ldots\ldots\ldots\infty]$$

$$e^{A+B} = \hat{1} + (\hat{A} + \hat{B}) + \frac{\hat{A}^2 + \hat{B}^2}{2!} + \hat{A}\hat{B} \ldots\ldots\ldots\ldots\infty$$

So, what we see here already there is a mismatch between the terms, we have been able to reproduce this part, but then this part is now mismatching.

So, it is quite clear that as long as A and B non-commuting operators the definition of commuters have a pair of operators, we have shown that in the previous module, so we are using that definition. So, if A and B are non-commuting operator then we cannot write down this equality, they are actually inequal they are not equal.

$$e^{A+B} \neq e^{\hat{A}}e^{\hat{B}}$$

And that is the reason why we cannot directly write down

$$e^{-i\frac{2\pi Ht}{h}} \neq e^{-i\frac{2\pi Tt}{h}} e^{-i\frac{2\pi Vt}{h}}$$

So, they are not equal.

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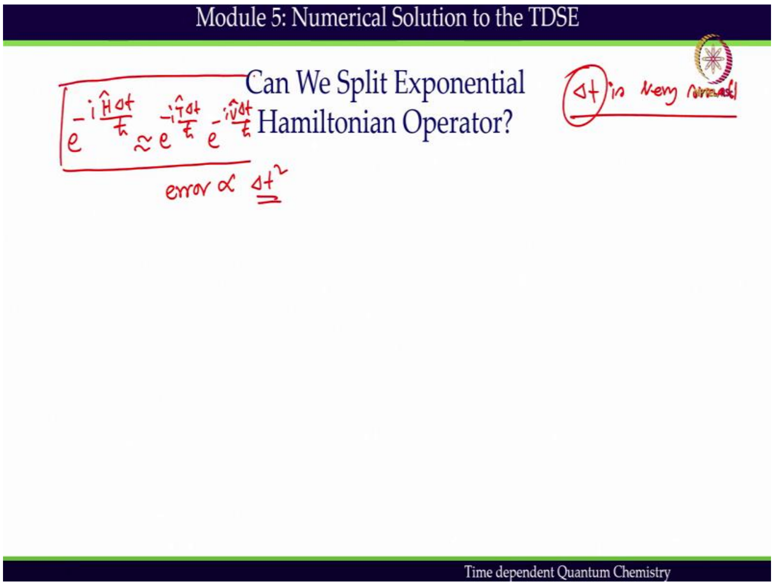

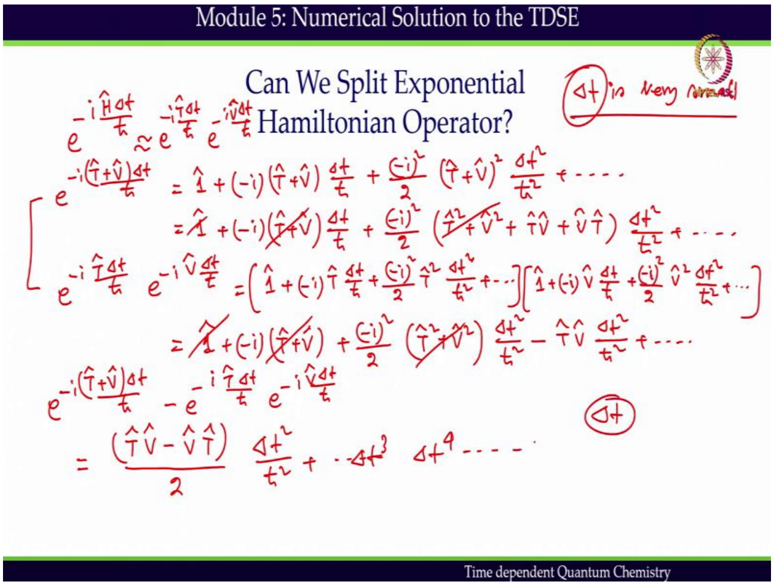

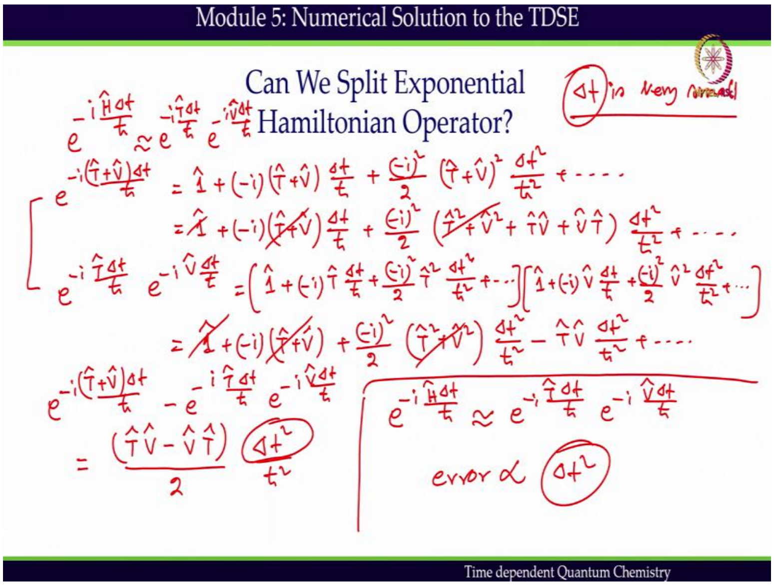

However, we have shown that if Δt is very small then approximately one can write down

$$e^{-i\frac{2\pi H\Delta t}{h}} \approx e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}}$$

This is called split operator. And if we do that, this is definitely an approximation then the error in this approximation, error would be proportional to Δt^{2}.

So, as long as Δt is small the error would be small and that we are going to prove right now, that if we express this the split operator approach then the error is going to be Δt^{2}. So, for that we will start with

$$e^{-i\frac{2\pi(T+V)t}{h}} = 1 + \left(-i\frac{2\pi(T+V)\Delta t}{h}\right) + \frac{1}{2}(-i\frac{2\pi(T+V)\Delta t}{h})^2 + \cdots \ldots\ldots\ldots\ldots\ldots.\infty$$

We just reorganized little bit,

$$e^{-i\frac{2\pi(T+V)\Delta t}{h}} = 1 + \left(-i\frac{2\pi(T+V)\Delta t}{h}\right) + \frac{1}{2}(-i\frac{2\pi(\Delta t)}{h})^2(T^2+V^2+TV+VT) + \cdots \ldots\ldots\ldots\ldots\ldots.\infty$$

On the other hand, if I try to express this product form

$$e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}} = (\ 1 + \left(-i\frac{2\pi T\Delta t}{h}\right) + \frac{1}{2}\left(-i\frac{2\pi T\Delta t}{h}\right)^2 + \cdots \ldots\ldots\ldots\ldots\ldots.\infty)(= 1 + \left(-i\frac{2\pi V\Delta t}{h}\right) + \frac{1}{2}(-i\frac{2\pi V\Delta t}{h})^2 + \cdots \ldots\ldots\ldots\ldots\ldots.\infty)$$

$$e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}} = 1 + \left(-i\frac{2\pi(T+V)\Delta t}{h}\right) + \frac{1}{2}(-i\frac{2\pi(\Delta t)}{h})^2(T^2+V^2) + (-i\frac{2\pi(\Delta t)}{h})^2 TV + \cdots \ldots\ldots\ldots\ldots\ldots.\infty$$

So, in order to find out the error, if I make a subtraction between these two, then what would be the error, I will find out the error by subtracting these two expressions. So, why we will be able to get

$$e^{-i\frac{2\pi(T+V)\Delta t}{h}} - e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}}$$

So, that is the difference I take. If I take the difference, then in the end, what we will get this part will be cancelling out, this part will cancel out, these two parts will cancel out.

So, I will have the difference between the remaining parts. And difference between remaining parts is going to be, one can show it very easily, -1/2, a little bit of simple algebra

$$e^{-i\frac{2\pi(T+V)\Delta t}{h}} - e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}} = \frac{(TV-VT)}{2}\left(\frac{2\pi\Delta t}{h}\right)^2 + O(\Delta t)^3 + O(\Delta t)^4$$

So, what we will do, we will take because delta t is already very small, we have considered.

In that case, we can neglect all other higher terms and we can say that the error, if I do that, then error is going to be proportional to

$$\Delta t^{2}$$

So, this approximation that

$$e^{-i\frac{2\pi H\Delta t}{h}} \approx e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}}$$

this approximation will give me an error off which is proportional to Δt^{2}. So, as long as Δt is very small, we will be able to neglect this error and we can write down this the split operator part.

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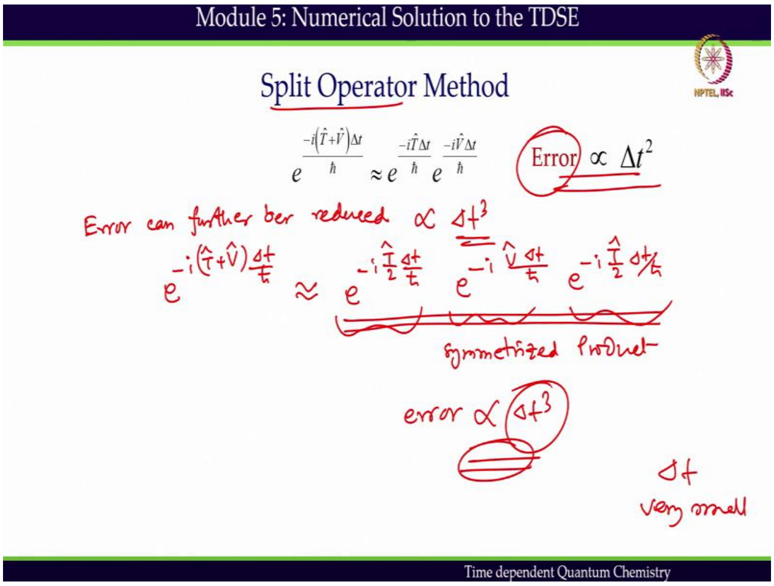

This error which we have mentioned in the split operated approach can further be reduced. So, error can reduced and it will be then proportional to Δt^{3}. If we take this symmetrized product of the split operator method, which means that

$$e^{-i\frac{2\pi H\Delta t}{h}} \approx e^{-i\frac{2\pi T\Delta t}{h}} e^{-i\frac{2\pi V\Delta t}{h}} e^{-i\frac{2\pi T\Delta t}{2h}}$$

This is a symmetrize product, why do symmetries product, we see that here I have kinetic energy part, here I have kinetic energy part, here I have potential energy part, if I take this kind of product the symmetrize product, then error one can use the same technique through Taylor series expansion, one can prove that, then if I do that then error would be proportional to Δt ^{2}, sorry Δt^3

.

So, this is better approximation because if I take Δt to be very small then error will be much smaller here than this one. And we will show the numerical implementation of time propagator with this symmetrize product in the next session.