Time dependent Quantum chemistry

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Module 05 Lecture 32

Time Evolution Operator

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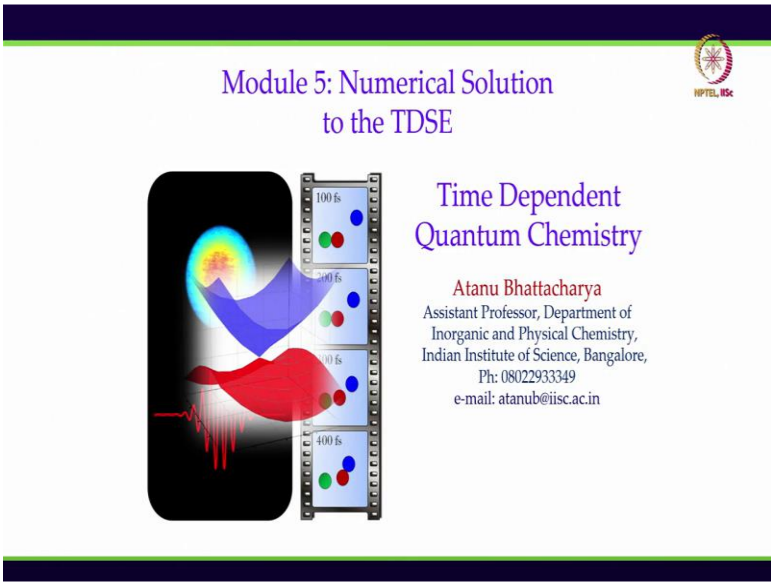

Welcome to Module 5 of the course Time Dependent Quantum Chemistry. In this module, we will go over the numerical approach to solve TDSE, that is the practical thing, which we are going to learn for the first time in this course.

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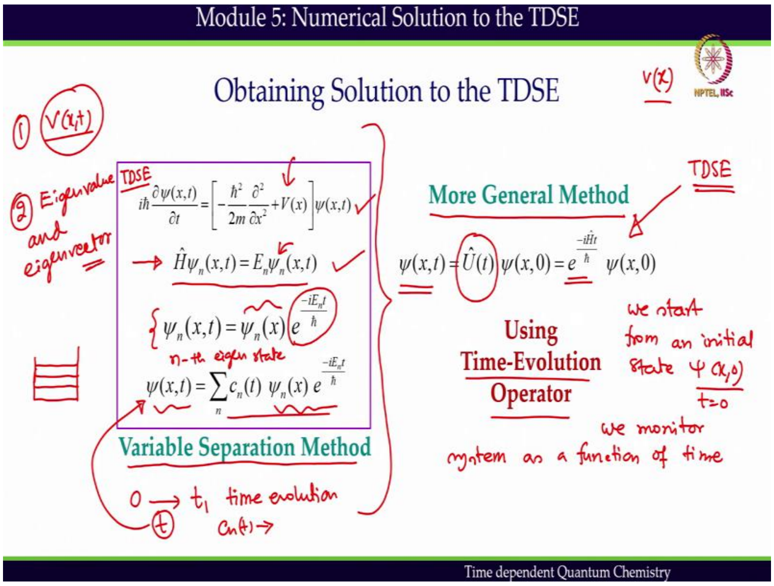

Now, we have already understood in the first module, that when a potential does not have any explicit dependence on time. So, potential does not depend and that is the way we have been assuming. There are problems in time dependent quantum chemistry, where potential will be dependent on time, but that part will be discussed later. So, far, we are saying that the potential does not depend on time, if it does not have dependency on time, then one-dimensional Schrodinger equation should look like this, this is we are quite familiar with this form.

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

And we can solve this equation with the help of variable separation method, we have used this variable separation method before. And in this method, the eigenvector and corresponding eigenvalues of the quantum system before the onset of time evolution, they are called stationary states. We can get those eigenstates and eigenvectors from this time-independent Schrodinger equation.

$$H\Psi_n(x,t) = E_n\Psi_n(x,t)$$

So, the basic idea is that to in order to solve this TDSE we have to first get the stationary states and stationary state wave function and stationary state energies from the time-independent Schrodinger equation and that is the state before the onset of the time evolution. In this, and we get a set of solutions, we have understood that think about particle in one-dimensional box when you have solved the time independent Schrodinger equation, you have got multiple solutions like this way.

Similarly, for any quantum system, its time-independent Schrodinger equation will give you a set of solutions. And here, n denotes the nth eigenstate. So, n is the nth eigenstate and once we get that solutions from here we can get the time dependent eigenstates which is nothing but multiplying the stationary states with the help of by this time dependent phase factor that we have understood.

$$\Psi_n(x,t) = \Psi_n(x)e^{-i\frac{2\pi E_n t}{h}}$$

And as a general solution, which means that if the time evolution is going on between 0 to t time. So, at any time t, let us t_1 time. Within this timescale, within this time interval, let us say time evolution is going on. Within this time at any time t if I have to present the wave function that will be presented by the linear combination of these states

$$\Psi\ \ (x,t) = \sum_n c_n(t)\Psi_n(x)e^{-i\frac{2\pi E_n t}{h}}$$

and where c_n is the time dependent expansion coefficient which will control what is the contribution of each of these functions to the total wave function, time evolving wave function.

So, that is the way we have seen variable separation method and its usage in time dependent in solving TDSE. But we have to remember that if the potential has an explicit dependence on time, if the potential is let us say V(x,t) here and instead of V(x), we have let us say V(x,t). In that case, variable separation method cannot be used anymore. In addition to that, so this is one concern we have, second concern we have is that obtaining the solution to the TDSE via eigenvalues and eigenvectors may not be always practical.

So, because, so if I want to get a solution of TDSE with the help of eigenvalues and eigenvector in terms of that, it may not be practical because a very large number of states are needed or because calculation of these states are too expensive. And in that case, it is convenient to compute the time evolution of a given initial state directly without making use of a large number of eigenstates.

So, variable separation method is a good idea, but it may not be practical all the time. So, we need more general approach to solve this TDSE. And the general approach to solve this TDSE is to use the time evolution operator,

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

this is called time evolution operator, this U(T) is representing the time evolution operator. What it does? It is actually, we start from an initial state which is **Ψ**(x,0), that is at t equals 0. What is the state is? This is t equals 0 state, at the initial state.

And then we monitored the system as a function of time with the help of this time evolution operator, which is an exponential operator. And in this module, we will find out what are the properties of this time evolution operator and how numerically one can implement this idea so that using Python programming one can find out at different time how the wave function is evolving.

Once we know the wave function at a particular time, we will be able to find out its average position and many experimental observables. We remind here that this form this time evolution operator, this form that this is a general solution of TDSE actually. In the last module in module 4, we have seen that how we have got this expression for the time evolution operator. So, let us proceed.

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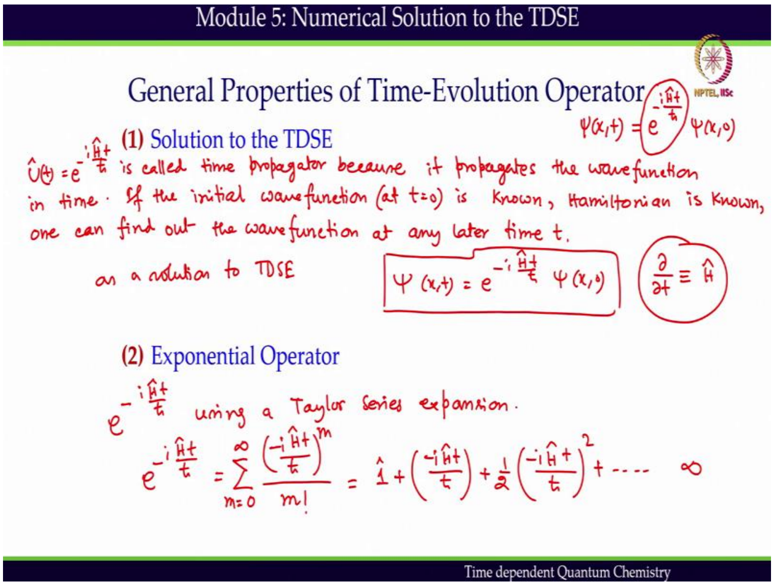

And before we represent the numerical implementation of time evolution operator, we will go over the general property, some of the general properties of time evolution operator, because that will help us understand the meaning of this time evolution operator, different properties will help us understand or numerical implementation also will be much easier to do once we understand the meaning of this expression.

So, this expression following, I have **Ψ**(x,t) anytime I would like to find out the wave function that can be done, if I know the initial wave function and then employ one time evolution operator on it.

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

This is the time evolution operator. So, the first property of time evolution operator is that this

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

is called time propagator because it propagates the wave function in time.

So, if I know the wave function, if the initial wave function that is at t equals 0, if initial function is known and its Hamiltonian is also known, if both are known, then one can find out the wave function at any later time, so that is what it means. This is an exponential operator and we have already seen that in chapter in the previous module 4, we have seen that this equation

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

This equation comes from as a solution to the TDSE. Because, remember at some point, we said that

$$\frac{\partial}{\partial t} \equiv \hat{H}$$

And this part came from TDSE in the derivation and that has been explicitly shown in module 4. This is an exponential operator and because it is an exponential operator it has to be expressed using a Taylor series expansion, which we have used already in module 4, but here we are just mentioning to collect all the general property.

So, how do I express this exponential operator, this is going to,

$$e^{-i\frac{2\pi Ht}{h}} = \sum_{m=0}^{\infty} \frac{(-i\frac{2\pi Ht}{h})^m}{m!} = 1 + \left(-i\frac{2\pi Ht}{h}\right) + \frac{1}{2}(-i\frac{2\pi Ht}{h})^2 + \cdots \ldots\ldots\ldots\ldots\ldots.\infty$$

So, that is the way we are going to express this exponential operator.

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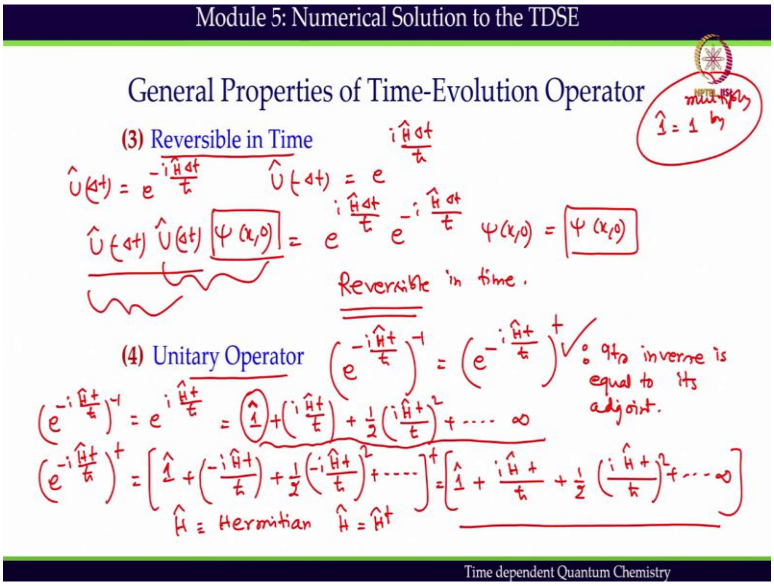

Time evolution operator is reversible in time. And this reversibility is a unique property in quantum mechanics. We will prove that how it is reversible. If I consider Δt, time advancement, then that has to be written as

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

And if I want to go back in time, then it is going to be

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

So, if I try to evaluate what will happen, if I first go back, and then come back acting on

$$\hat{U}(-\Delta t)\hat{U}(\Delta t)\Psi(x,0)=$$

So, I am just taking the product of these two time-evolution operators. If I do that, then I will be able to get

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

So, what it suggest? It suggest that first, I am making an time advancement, then what I get, I am making one backward propagation in time. So, one forward propagation one backward propagation in the end giving me back this wave function, that is why it is reversible in time.

This is quite different from our real-life experience. In real life experience, we cannot go back in time, we have to always move forward. But here, I can go back in quantum mechanics with the help of this time evolution operator, I can go back in time. So, my system will again evolve to the initial state. Time evolution operator is an unitary operator, which means that I will be able to write down, I will prove it.

But before I proved that, I will be able to write down this expression this equality, inverse is going to be equal to its adjoint. That is the definition of unitary operator which you have seen in module 4 in the previous module.

$$\left(e^{-i\frac{2\pi Ht}{h}}\right)^{-1} = \left(e^{-i\frac{2\pi Ht}{h}}\right)^{+}$$

So, what it means? Its inverse is equal to its module 4. So, we will prove that, one can prove it very easily.

If I try to find out

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

we will be able to write down, this inverse of this operator. Now, here I mentioned one important thing, this is nothing but one, but we are giving with a cap to show that the entire addition entire term is representing an operator.

So, this is not one operator, one operator is nothing but multiply by 1. And to make the notation correct here, every term we have made to be an operator. That is why we are giving this cap otherwise is just 1. So, we will now look at the adjoint, how does it look like,

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

whole square plus like this.

So, entire term, I have to consider adjoint. And we have learned from the previous module that if I make adjoint it is going to be

$$\left(e^{-i\frac{2\pi H\Delta t}{h}}\right)^{+} = \left[1 + i\frac{2\pi H^{+}t}{h} + \frac{1}{2}\left(-i\frac{2\pi H^{+}t}{h}\right)^{2} + \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\right]$$

And because H is an Hermitian operator, H is an Hermitian operator, H is actually an Hermitian operator, so I can write down it is self-adjoint which means that it will be equal.

$$H = H^{+}$$

So, this term, this adjoint sign will go away because they are equal. And the moment it goes away, this term, and what I have got here, this term are equal that is why this equality holds. So, time evolution operator is a unitary operator.

$$\left(e^{-i\frac{2\pi H\Delta t}{h}}\right)^{+} = \hat{1} + \left(e^{i\frac{2\pi H\Delta t}{h}}\right) + \frac{1}{2}(-i\frac{2\pi Ht}{h})^{2} + \cdots \ldots\ldots\ldots\ldots\ldots$$

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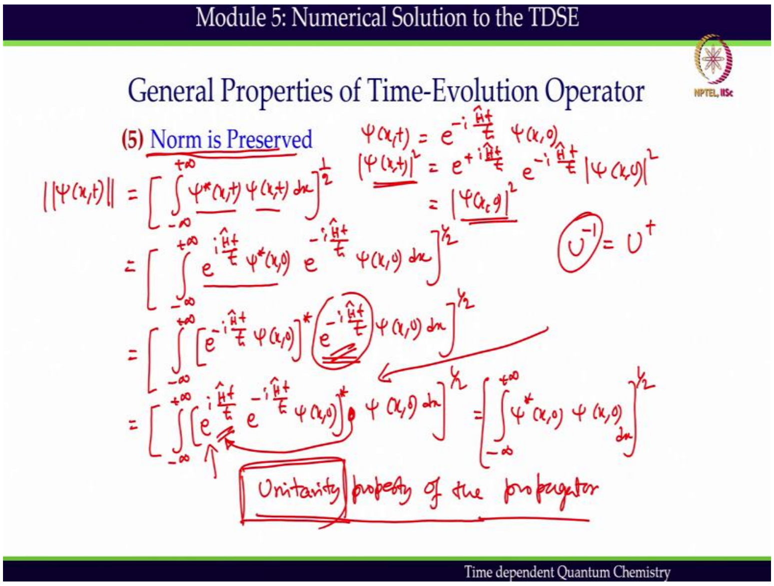

We will see that, we have been seeing in many occasions in this course that to explore quantum dynamics, we need to have wave function which is normalised initially, and it will remain normalised over all the time when we are exploring the quantum dynamics and that is called norm preserving.

So, first thing we have to check, because we are evolving time, we are evolving, we are monitoring the evolution of wave function in time we have to understand that whether when I employ this unitary operator on this function, whether I am preserving the norm or not, that is the most important part of quantum dynamics before exploring quantum dynamics. So, we will check it first.

So, we will see that if

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

then I can consider its absolute value square, square of its absolute value

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

So, what we see is that it is at t equals 0 its norm and at t equals t time anytime t any arbitrary time t during the time evolution its norm is going to be equal.

So, that is why we can say this a norm preserving, we can explicitly prove it as follows

$$\|\ \Psi\ (x,t)\ \| = \left[\int_{-\infty}^{+\infty}\Psi\ *(x,t)\Psi\ (x,t)dx\right]^{1/2}$$

that is the norm, definition of the norm. Now, I employ time evolution here. So, that is going to be

$$\parallel \Psi \ (x,t) \parallel = \left[\int_{-\infty}^{+\infty} e^{i\frac{2\pi Ht}{h}} \Psi \ * (x,0) e^{-i\frac{2\pi Ht}{h}} \Psi \ (x,0) dx \right]^{1/2}$$

Here, I have removed this negative sign because this is of complex conjugate part of the wave function. So, this part is represented here So, I will rewrite, a little bit mathematical trick will have help me get to the point we are trying to make here,

The entire thing I have clubbed them together and then placed it under this star, which means that entire thing has to be complex conjugate of this term

$$\parallel \Psi \ (x,t) \parallel = \left[\int_{-\infty}^{+\infty} [e^{-i\frac{2\pi Ht}{h}} \Psi \ (x,0)]^* e^{-i\frac{2\pi Ht}{h}} \Psi \ (x,0) dx \right]^{1/2}$$

So, this is I can write down because I can take the adjoint. So, if I take the adjoint of this

$$\parallel \Psi \ (x,t) \parallel = \left[\int_{-\infty}^{+\infty} [e^{i\frac{2\pi Ht}{h}} e^{-i\frac{2\pi Ht}{h}} \Psi \ (x,0)]^* \Psi \ (x,0) dx \right]^{1/2}$$

So, this is nothing but I have now

$$\parallel \Psi \ (x,t) \parallel = \left[\int_{-\infty}^{+\infty} \Psi^* (x,0) \Psi \ (x,0) dx \right]^{1/2}$$

So, we are using, making use of unitary property, unitarity property of the propagator. So, what is going on, its norm is preserved, because it is an unitary operator. And which step we have used this unitary property, in this step. You see this term has been taken here, how did we get that, because we said that this we have proved that this time evolution operator, inverse of the time evolution operator is actually its adjoint.

And adjoint, the definition of adjoint being an adjoint, I can take this operator from here to the other side. And if we did that, then that is going to be inverse of that operator. And that is exactly we have taken this part and this part is inverse of one another. And so, because it is an unitary operator, its norm is preserving. So, that is something which we should remember.

So, as a result, normalisation constant does not change during dynamical evolution of the quantum system. So, these are the 5 properties we have shown so far. And we will stop here and we will present the numerical implementation of time evolution operator in the next session.