Time dependent Quantum chemistry
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Module 04
Lecture 24
Hilbert Space and Its Properties

Welcome to Module 4 of this course Time Dependent Quantum Chemistry. In this module, we will try to find out the connection between quantum mechanics and linear algebra. And realisation of that connection will help us build the platform to obtain numerical solution to the time dependent Schrödinger TDSE.

Why we need numerical solution? Because I have been telling you Since last module that always you may not get the analytical solution. For free particle wave packet dynamics, we have been able to get the analytical solution and we have got the general solution also for that wave packet. But let us say the wave packet does not have a Gaussian form, it has entirely different very complicated form, how do you deal with those kinds of form, let us say I have a Gaussian form, but the particle is experiencing very complicated potential.

So, in that case, we will not be able to get them analytical solution, we need to rely on the numerical solution and to reach there, to understand how numerical implement implementation will be done of TDSE we need to understand the basic connection between quantum mechanics and linear algebra. So, that is exactly what we are going to do in this module.

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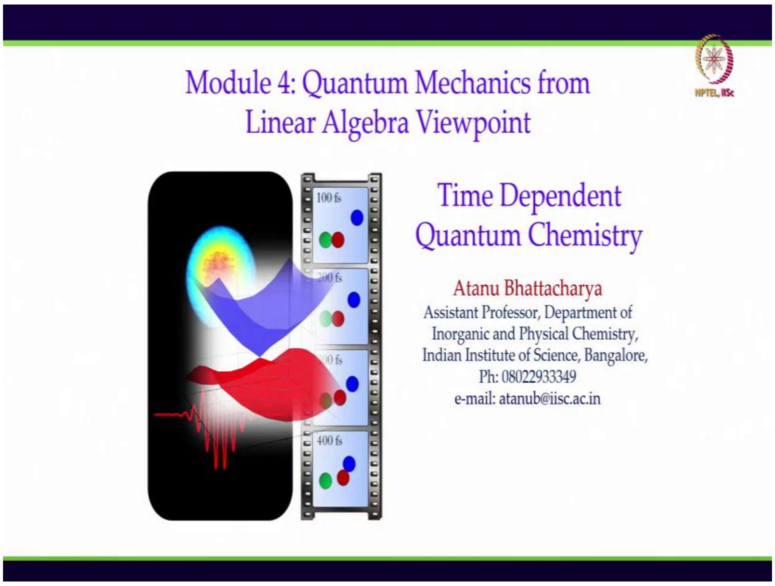

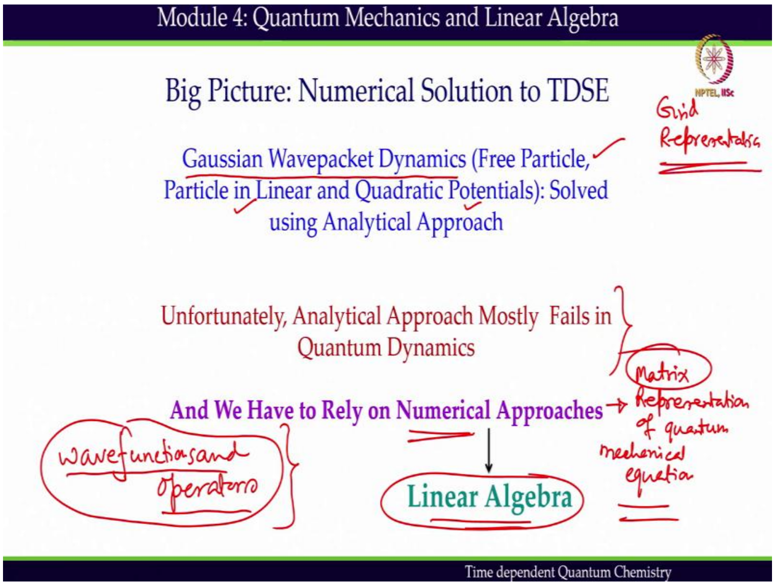

In the previous module, where we have discussed this wave packet dynamics, we have analytically solved dynamics of a free particle. And in the tutorial, we will see that the Gaussian wave packet dynamics can also be solved with linear and quadratic potential as well. So, for many aspects of Gaussian wave packet dynamics, one can use analytical approach to solve the problem.

But for any arbitrary potential this analytical approach will fail and we have to rely on numerical approaches. In fact, a number of quantum dynamics problem that can be solved analytically is very limited. Therefore, it is quite instructive that we begin a discussion on the numerical approaches, which will enable us to explore quantum dynamics for any arbitrary potential. So, that is the motivation here.

Numerical solution to the TDSE is a gigantic subject. It is a huge subject and but it is fundamentally developed based on matrix representation of quantum mechanical equation. This numerical approach we need, for this numerical approach we need matrix presentation of quantum mechanical equations. So, numerically we will be dealing with matrices.

That is why we need to represent quantum mechanical equations in the matrix form. And these numerical methodologies is developed based on the realization that mathematical language of quantum mechanics is actually linear algebra, So, in this module what we will do, we will develop a coherent sense of wave function and operator.

See these are the two key constituents of quantum mechanics. So, if I want to implement numerical, so if I want to obtain numerical solution to quantum mechanical problem, first I have to learn how do I numerically represent this wave function and operators because these are the two things, we will be dealing with in quantum mechanics.

And that is why, what we will do, we will develop a coherent sense of the meaning and the properties of the wave function and the operators from linear algebra point of view in this module. We will begin with reviewing intriguing general properties of quantum mechanically acceptable wave functions and operators from linear algebra point of view, then we will present basis set approach to quantum mechanics, which will give us a matrix representation of the wave function and the operator.

And in the end, after briefly reviewing matrix algebra, we will present methods to obtain Eigen value and Eigen functions of a quantum system making use of grid representation, we will show that also what does it mean by grid representation. So, in the end, the discussion in this module will lead us to the place where we will be able to perform numerical, we will be able to get the numerical solution to the TDSE.

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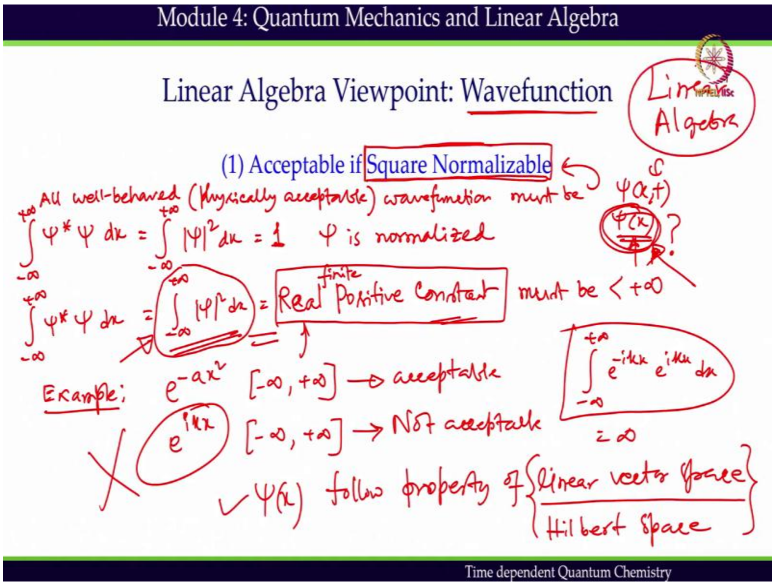

So, let us begin with the general properties of wave function from linear algebra viewpoint. All well behaved wave function which is acceptable in quantum mechanics must be Square Normalizable, this is something which we have without noticing it, we have used it, we have used normalization condition we have said that before the time evolution , we must take the normalized wave function always.

So, all well behaved or physically acceptable, any function I cannot accept physically in quantum mechanics, those functions which can be accepted in quantum mechanics is called physically acceptable wave function that must be Square Normalizable. And what does it mean by this Square Normalizable? that means that if I have the wave function to be $\psi(x)$, for the time being I can think about, okay forget about this time dependency right now, we are just thinking about the space dependency because time part comes as a phase factor, so it is not an issue.

So, if we look at this wave function, then this Square Normalizable, it has to be Square Normalizable, what does it mean? If I want to check whether this wave function is usable in quantum mechanics, then immediately I have to find out this integral $\int_{-\infty}^{+\infty} \psi^* \psi dx = \int_{-\infty}^{+\infty} |\psi|^2 dx = 1$

This is called normalization condition, but when it is 1, ψ is normalized, but always ψ may not be normalized we have to make it normalized and in that case if it is not normalized still it is acceptable in quantum mechanics as long as this integral $\int_{-\infty}^{+\infty} \psi^* \psi dx = \int_{-\infty}^{+\infty} |\psi|^2 dx$ becomes real positive constant and must be less than infinity, $< +\infty$.

So, first question is that if somebody is proposing that okay let us assume that this wave function is a solution for a particular quantum system, then immediately we have to check whether this wave function, the proposed wave function is acceptable as a solution in quantum mechanics. And how do I check that, I can check it by taking this integration and finding out whether this integration giving me a real positive constant value, if it is not giving real positive constant value, if it is becoming 0, if it is becoming let us say real constant positive, finite constant positive value. If it is becoming infinite, so, I cannot accept it, I cannot accept that wave function.

So, for an example, this is just an example, we have seen that a Gaussian function this is an example, we have already seen this example. A Gaussian function $e^{-ax^2}\left[-\infty, +\infty\right]$ this function within this $-\infty$ to $+\infty$ limit it is a well-behaved wave function, this is acceptable function in quantum mechanics.

But we have already seen that $e^{ikx}\left[-\infty, +\infty\right]$, when you try to normalize it, when you try to get this square normalization condition, we have found that within this limit $-\infty$ to $+\infty$, this is not acceptable because, within this limit we have got infinite value, if we take this integration $\int_{-\infty}^{+\infty} e^{-ikx} e^{ikx} dx = \infty$ is square modulus, this is going to be infinite. So, this integration becoming infinite.

So, this function cannot be used in quantum mechanics. So, one thing we have to remember that I can propose a wave function, but I have to in the end definitely need to check whether that wave function is acceptable in quantum mechanics and whether it will be acceptable or not that can be checked by taking this integration and finding out whether I am getting a real constant positive value.

One interesting mathematical fact about all Square Normalizable wave function is that they all follow property of linear vector space. And the reason why it should be this is that if we take only wavefunction which is Square Normalizable then those were functions acceptable wave functions will follow the property of linear vector space. And that is why we can use linear algebra.

So, in order to use linear algebra or this linear vector space also called sometimes called Hilbert space, both are, this is just mathematical language, we say that okay, those wave functions which can be acceptable in quantum mechanics, they live in Hilbert space. Hilbert spaces a mathematical space, is a hypothetical space, let us say where these wave functions are living, it is more like we are living in solar system and if any living being is living in solar system, they will follow the similar property.

So similarly, if the wavefunction is living in a Hilbert space or linear vector space, it means that it must be Square Normalizable. There is a consequence and that is the reason why I can use linear algebra. Otherwise, I cannot use linear algebra. So, I have to start with always Square Normalizable wave function.

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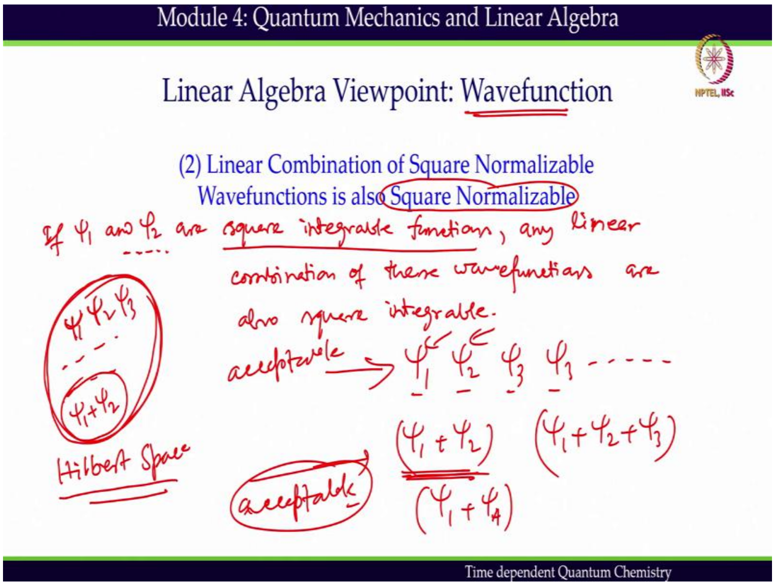

Second property of wave function from linear algebra viewpoint is that if ψ_1 and $\psi_{2,}$ are square integrable, which is Square Normalizable functions which means that I have a vector space linear vector space let us say this is a space, this is called Hilbert space let us say. And in this Hilbert spaces $\psi_1, \psi_{2,} \psi_3, ...$ all are living then we have to remember that in the same Hilbert space their linear combination any linear combination will also live in the same Hilbert space.

So, if $\psi_1, \psi_{2,} \psi_3, ...$ many other functions square integrable, all square integrable functions are living in the Hilbert space. Any linear combination of these wave functions are also square integrable, Square Normalizable. So, what it is suggesting that as long as the wave functions are sitting or living in the Hilbert space their linear combination will also live in the same Hilbert space. And we know that anything which is living in Hilbert space would be Square Normalizable, I can normalize it.

Which means I can accept it as a solutionm to the solution in quantum mechanics. Because, one defining condition of Hilbert space is that both functions and their linear combinations should be part of that Hilbert space. And, if it is so, then if I have an individual solution of $\psi_1, \psi_{2,} \psi_3, ...$ and each one is Square Normalizable then I should have another solution $(\psi_1 + \psi_2)$ that is also would be Square Normalizable.

I can take different kinds of combination. $(\psi_1 + \psi_2 + \psi_3)$ ..this is also Square Normalizable. I can take $(\psi_1 + \psi_4)$, this is also Square Normalizable, all linear combination will be Square

Normalizable. So, this is also if they are acceptable in quantum mechanics then they are also acceptable in quantum mechanics. And this is something which without noticing it we have used it already.

In the first module we have checked the linear combination. In the third module where we have proposed the wave packet, we have already taken linear combination of different plane wave of solution. So, these were the plane wave solutions and we have taken linear combination to make this acceptable solution. So, this is quite common thing in quantum mechanics and the reason why we can do that is that is the property of the Hilbert space, the mathematical space we have defined.

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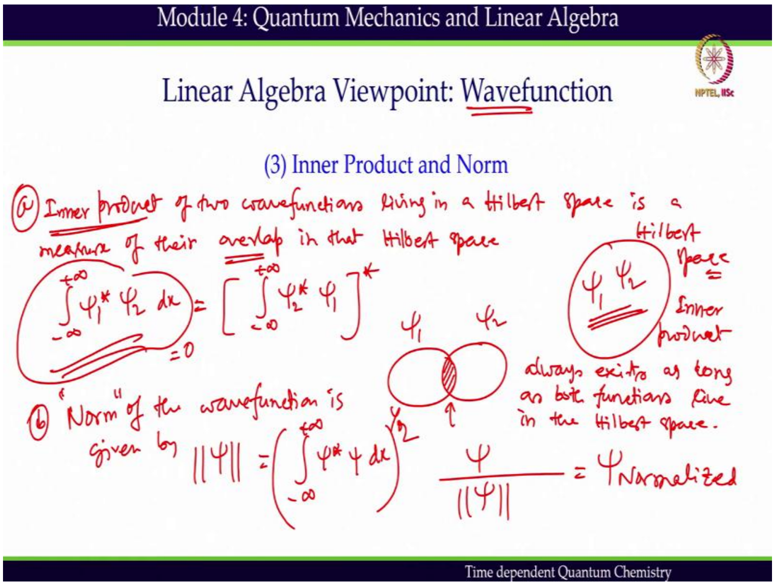

Third one, third property of the wave function is going to be inner product. What is inner product? I will just show, inner product of two wave functions living in a Hilbert space is a measure of their overlap in that Hilbert space. So, inner product is nothing but the overlap of the wave function which is given $\int_{-\infty}^{+\infty} \psi_1^* \psi_2 dx = \left[\int_{-\infty}^{+\infty} \psi_2^* \psi_1 dx \right]^*$. So, what is the meaning of it? It means that in the Hilbert space, if I have two wave functions ψ_1 and $\psi_{2,}$, and if we find out this integration, then this integration shows how much overlap they have, let us ψ_1 and $\psi_{2,}$ is represented by these two ellipse, this kind of function, ψ_1 here and $\psi_{2,}$ here, So, overlap means how much space it is occupying and sharing the space that is called overlap. This is the overlap part. And this integration will show how much overlap we have between two wave functions in the Hilbert space. What it suggests? It suggests that the inner product always exist as long as both functions live in Hilbert space, because these two functions are living in Hilbert space, their inner product will definitely exist, it will not happen that this integration will become infinite, it will not happen as long as this wave function is sitting in the Hilbert space.

So, the basic idea mathematical background for this is that the inner product always exist as long as both functions live in the Hilbert space. So, that is the property of the Hilbert space. This is inner product. And another property of the wave function is going to be the norm of the wave function is given by this integration $\|\psi\| = \left(\int_{-\infty}^{+\infty} \psi^* \psi \, dx \right)^{1/2}$, this is the normalization constant.

So, if I want to normalize a wave function, all I have to do is that $\frac{\psi}{\|\psi\|} = \psi_{Normalized}$, norm of tthis I will get the normalized wave function. This is the way one can get the normalized wave function. And if this part, this integration is $\int_{-\infty}^{+\infty} \psi_1^* \psi_2 dx = \left[\int_{-\infty}^{+\infty} \psi_2^* \psi_1 dx \right]^* = 0$ becoming 0, it means that these two functions are orthonormal.

So, these are the properties which we have already used, orthonormal wavefunction already we have used, but we have not noticed that we are using it as a consequence of the Hilbert space, the property of the Hilbert space and this is something which we are pointing out.

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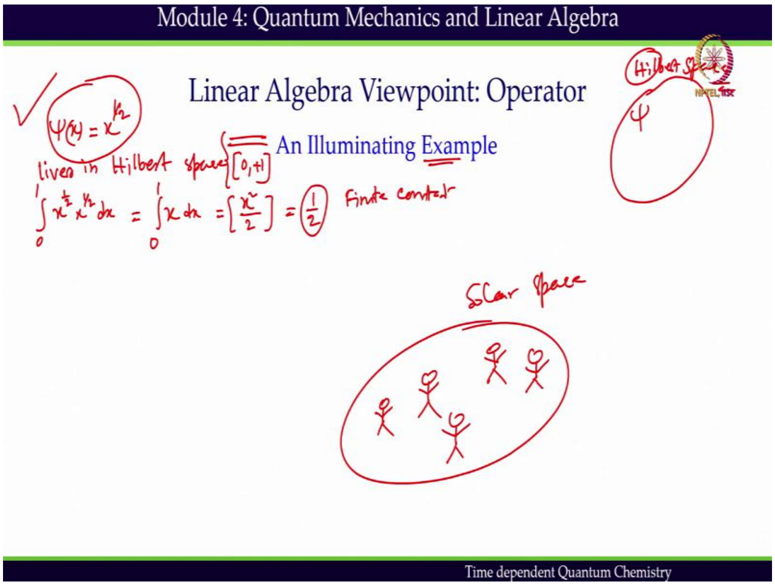

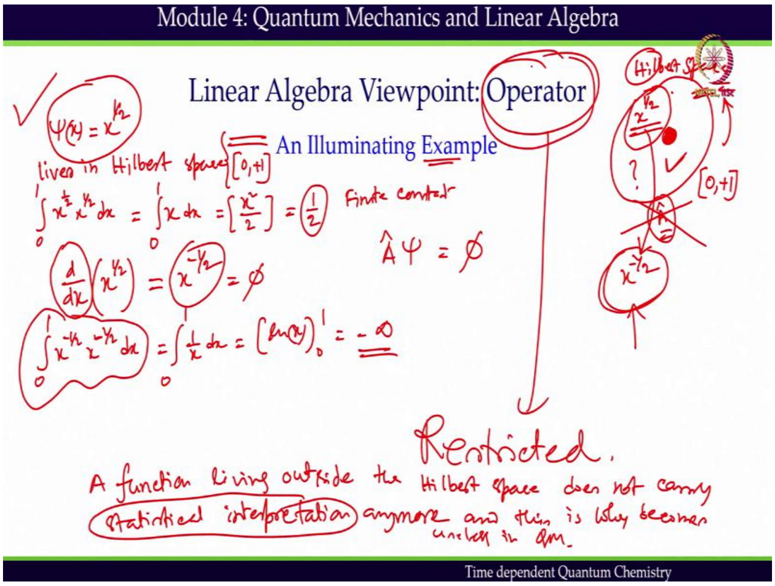

Now, we will move forward to the operator, but before we move forward to the operator, one interesting point will be raising here. Let us assume that I have a function $\psi(x) = x^{1/2}$ to, this is a wave function. And question is whether this wave function lives in Hilbert space.

Because, if it is living in Hilbert space, it will be useful in quantum mechanics whether it can leave in Hilbert space for the interval $[0,+1]$. So, all we need to do, we need to check that what we need to do we have to find out this integration $\int_0^1 x^{1/2} x^{1/2} dx = \int_0^1 x dx = \left[\frac{x^2}{2}\right]_0^1 = \frac{1}{2}$

Different limit may have a different Hilbert space. So, within this limit, I would like to check whether I can construct the quantum mechanics within this limit. So, limit is not minus infinity to plus infinity here, we are considering 0 to 1 limit. And we see that this value is going to be half, this is a finite constan,t positive constant. So, this function can live in Hilbert space and if it is living in Hilbert space for this limit, I can use it in quantum mechanics only for this limit, I did not take for other limit.

So, I will construct the Hilbert space, this is my Hilbert space. It is more like, I told you, more like a solar system let us say, all human are living in solar system. This is your solar space, let us say. So, no matter which human you pick up, they will have similar kind of property they have two hands, two legs, one head, similar kind of property.

Similarly, in this mathematical space, Hilbert space, if one wavefunction is sitting here, then that will follow the property of the Hilbert space and the property of the Hilbert space suggest something and that suggestions we are actually using in quantum mechanics. So, that is the connection between quantum mechanics and linear algebra. So, we have already seen that this within this limit, this wave function, $x^{1/2}$ is living in Hilbert space, so it will be useful in quantum mechanics. Very nice.

Now in quantum mechanics, we know that some operator will be acting on it, let us assume that my operator is $\frac{d}{dx}$, derivative operator, very simple derivative operator, which will act on this $x^{1/2}$, let us say. When operator acting on the derivative operator, $x^{1/2}$ what will happen? Immediately I will get $x^{-1/2}$,

And the limit is to define this Hilbert space I have considered the limit is going to be 0 to +1. That is the defining condition for the Hilbert space, for this particular Hilbert space not for all Hilbert space, I can define another Hilbert space for a different limit. But within this limit, I am defining this Hilbert space. What I see is now I have got another wave function, so an operator acting on wave function, and I am getting another wave function.

And I have to check whether this new wave function which we call ϕ, whether that also live in the same Hilbert space or not, that is the first thing we will check and in order to check that what we need to do, we have to again carry out this integration,

$$\int_0^1 x^{-1/2} x^{-1/2} dx = \int_0^1 \frac{1}{x} dx = \left[\ln(x)\right]_0^1 = -\infty$$

Whenever I have this integration to be infinite, then we cannot say that this wave function is living in Hilbert space. So, what is going on, I had a wave function which was happily living in Hilbert space and operator acting, acted on it and it made the function to be out of Hilbert space, that function cannot stay in the same Hilbert space anymore, it is going out of the Hilbert space.

This causes a problem because if a function is going out of the Hilbert space due to an action of an operator, then I cannot use it in the same quantum mechanics. In order to use the wave function in quantum mechanics, I need to have the wave function living in the Hilbert space all the time, does not matter whether any operator acting on it, it can act, an operator can act on it.

The defining condition of using that Hilbert space is that anytime the function which I am using as a solution of the quantum system, that should stay in the Hilbert space. In addition to that, if an operator acting on that wave function, the new wave function should also stay in the same Hilbert space that is the defining condition.

So, what we see that there are certain kinds of mathematical operators such as derivative operator which use can actually take an operator and wave function living in Hilbert space out of the Hilbert space and that is not acceptable. So, this kind of operator cannot be used. So, there are restriction in what kind of operated I should use in quantum mechanics, it should be restricted. It should not be a function living outside the Hilbert space does not carry statistical interpretation anymore and this is why it becomes useless in quantum mechanics.

So, the basic idea is that when I am selecting a wave function that should stay in the Hilbert space, because it will then carry statistical interpretation and that is the only interpretation I have for the wave function in the standard interpretation in quantum mechanics, statistical interpretation. If the statistical interpretation is gone. So, then there is no wave function, meaning of the wave function, and if there is no meaning of the wave function, there is no quantum mechanics anymore.

So, that is why the wave function has to be living, has to live in the Hilbert space. And if an operator acting on that wave function living in the Hilbert space, if it is taking out of the Hilbert space, then that is also a problem then we have lost the interpretation of the quantum mechanics again. So, everything has to be in the Hilbert space and that is why operator space needs to be restricted, we cannot use any operator to control to work in quantum mechanics.

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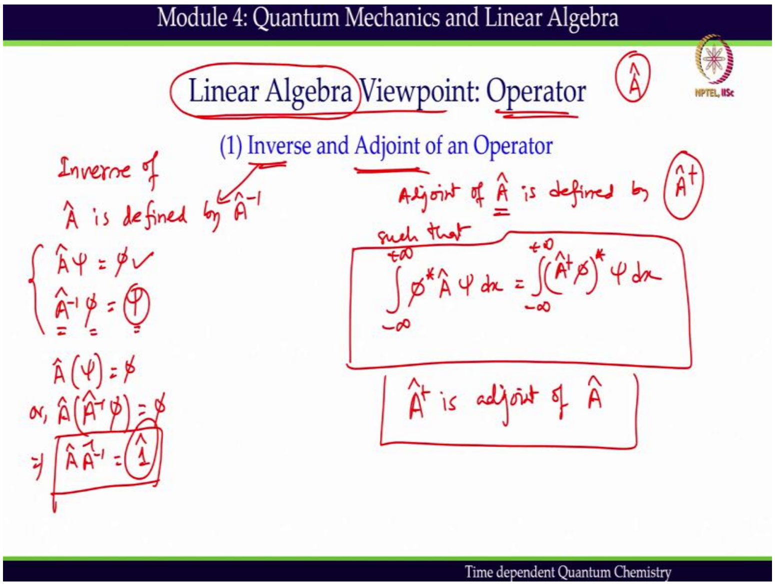

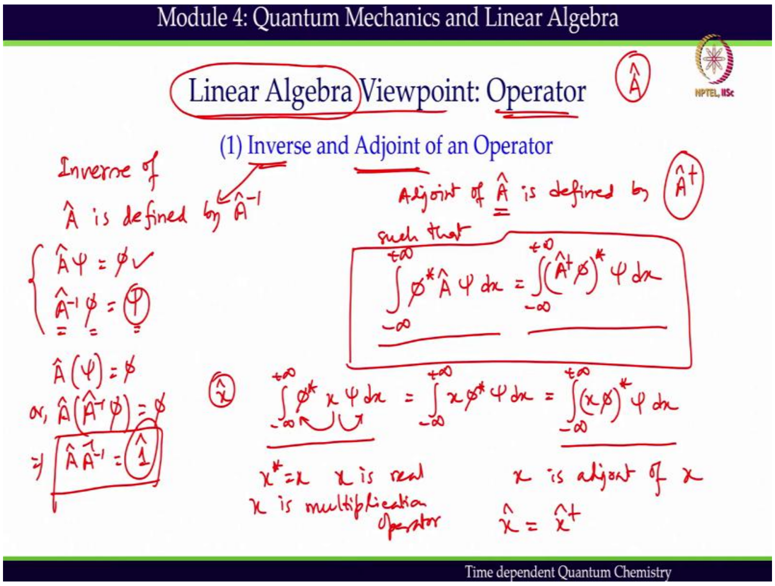

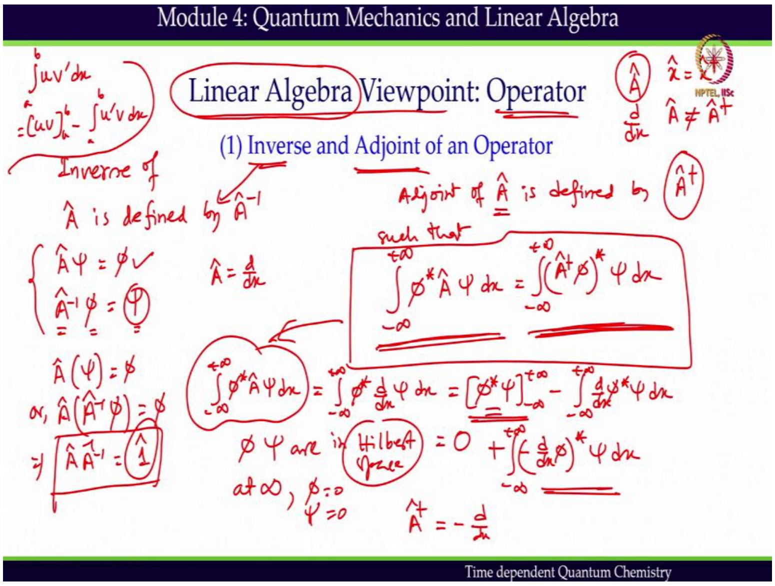

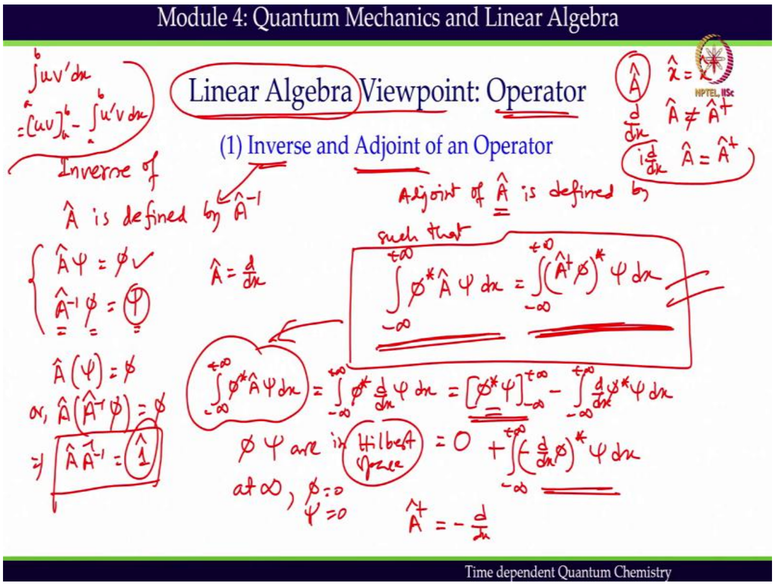

So, let us find out what kind of operators we can use and what are the operations of operators we can think of from linear algebra viewpoint. Inverse of an operator will be given by let us say A, inverse of A is defined by A inverse, A^{-1}. So, what happens A acting on ψ giving me another wave function, $A\psi = \phi$. In that case, inverse of A on ϕ is giving me ψ, this is more like a reversible process, $A^{-1}\phi = \psi$.

From this point of view, quantum mechanics is reversible. If this operator is acting on ψ and giving me ϕ, then inverse of this operator can act on ϕ and I can get ψ. So, this is one property of the operator which will be using in quantum mechanics and that is directly coming from the property of linear vector space, linear algebra or Hilbert space.

Or in other words, I can write down A acting on ψ is ϕ, $A(\psi) = \phi$ or $A(A^{-1}\phi) = \phi$ and this is only possible when this $AA^{-1} = 1$. So, this is an operator which is suggesting that we multiply by 1. So, this is another property of the inverse of an operator. Adjoint of an operator, what does it mean? Adjoint is defined, adjoint of A is defined by $A^{\dagger}$ such that $A^{\dagger}$ will be considered to be adjoint of A when this will hold $\int_{-\infty}^{+\infty} \phi^* A\psi \, dx = \int_{-\infty}^{+\infty} (A^{\dagger}\phi)^* \psi \, dx$,

When this relation will be satisfied, then we can say that $A^{\dagger}$ is adjoint of A. So, we have to take few examples to show that adjoint of an operator and we will take one example. Let us say we find out adjoint of an operator x, $x^{\dagger}$. If we take x operator, x, then what will happen? So, let us say I start with x operator, x operator, x is nothing but multiply by x.

$\int_{-\infty}^{+\infty} \phi^* x\psi dx$. Now, x is a multiplication operator. So, I can place x anywhere. Remember when you are dealing with an operator, let us say I am dealing with this differential operator acting on ψ. And on this side, I have ϕ. If I am dealing with this kind of operator, derivative operator, this derivative operator means it is operating only on ψ, it cannot be just, the position cannot be changed without any constraint, I cannot write down this ,$\phi \frac{d}{dx}\psi \neq \phi\psi \frac{d}{dx}$, it is not possible, operator acting on this.

But if it is a multiplication operator then I can replace it anywhere it is just multiply. So, I can place this conveniently, here x it is the same value, because it is a multiplication operator. So, I can, and x is real, so I can also write down $\int_{-\infty}^{+\infty} \phi^* x\psi dx = \int_{-\infty}^{+\infty} x\phi^* \psi dx = \int_{-\infty}^{+\infty} (x\phi)^* \psi dx$. We have now, this is fulfilled. This form is equal to this form because it is fulfilled, I can see that $x = x^{\dagger}$.

Now, we will check our derivative operator, let us stick with the derivative operator whether we get what kind of results we get for derivative operator. So, we have already, I will write it down, $x = x^{\dagger}$. For the derivative operator, let us say I have an operator which is d/dx, $A = \frac{d}{dx}$ if this is the operator then I can try to find out $\int_{-\infty}^{+\infty} \phi^* A\psi dx = \int_{-\infty}^{+\infty} (A^{\dagger}\phi)^* \psi dx$.

Now, I cannot just position this operator anywhere without any constraint, it is not possible. This operator only acting on this. So, I have to go for integration by parts and integration by parts if I do that, then

$$\int_{-\infty}^{+\infty} (A^{\dagger}\phi)^* \psi dx, \int_{-\infty}^{+\infty} \phi^* A\psi dx = \int_{-\infty}^{+\infty} \phi^* \frac{d}{dx}\psi dx = \left[\phi^*\psi\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{d}{dx}\phi^*\psi dx = 0 + \int_{-\infty}^{+\infty} \left(-\frac{d}{dx}\phi\right)^* \psi dx,$$

this is integration by parts. And the general formula of integration by parts I will just remind it is $\int_a^b uv' dx = \left[uv\right]_a^b - \int_a^b u'v dx$, that is the general formula of integration by parts and that is exactly what we have done here.

And so, what I can write and now $\left[\phi^*\psi\right]_{-\infty}^{+\infty}$ this part is going to be 0, why? Because I said that ϕ and ψ are in Hilbert space and if they are in Hilbert space, there has to be Square Normalizable in order to be Square Normalizable, at infinite their values should be 0, at $\infty, \psi = 0, \phi = 0$. This is all coming from the property of the Hilbert space.

So, this part, this integration will be, this part $\left[\phi^*\psi\right]_{-\infty}^{+\infty}$ will be 0, then I have $\int_{-\infty}^{+\infty}\left(-\frac{d}{dx}\phi\right)^*\psi dx$, , I have now, the relation fulfilled. This one, this part is here and this part is here. But what is the difference right now, I have now, $A^\dagger = -\frac{d}{dx}$

So, what we see here is that if it is derivative operator d/dx, $A = \frac{d}{dx}$, then $A \neq A^\dagger$. So, it is not necessary that adjoint would be the same as the operator always, it depends on the operator, what kind of operator I have, one can very easily prove that if the operator, $A = i\frac{d}{dx}, A = A^\dagger$,one can prove this.

So, with this idea what we are seeing is that adjoint can be found analytically with this expression with this integration and one can find out different operators whether that will be adjoint, what would be the adjoint and sometimes I may have a situation where its adjoint would be equivalent to its own operator form. We will stop here and we will continue this session in the next class.