Time dependent Quantum chemistry
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Module 04
Lecture 25
Basis Set Approach to Quantum Mechanics

Welcome back to Module 4. In this module we have presented Hilbert space, which is a mathematical space and we have said that all quantum mechanically acceptable wave function must live in the Hilbert space. And any operator we select to perform anything in quantum mechanics that should not take the wave function out of Hilbert space it should keep things in the Hilbert space.

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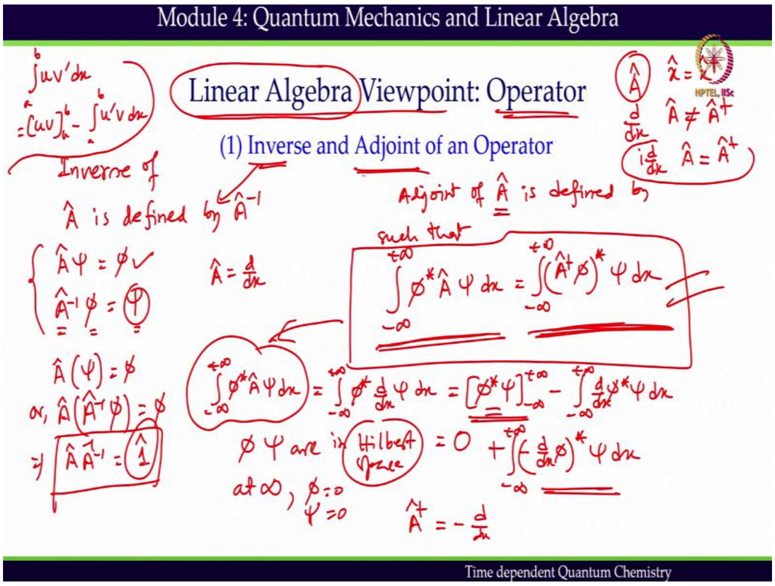

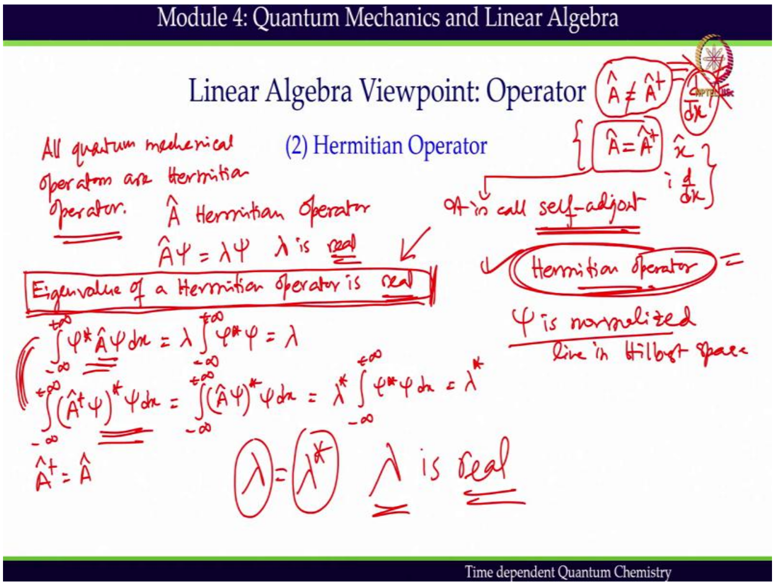

So, this criteria we have presented and we have shown the meaning of adjoint of an operator and we have seen that sometimes for an operator A in many operations we have seen that A is not equal to its adjoint, $A \neq A^{\dagger}$ such as $\frac{d}{dx}$ derivative operator they are not equal, but sometimes A can be equal to its own adjoint, $A = A^{\dagger}$ such as x operator x, such as $i\frac{d}{dx}$ operator for these two operators this is valid.

And when this is valid, it is called self-adjoint. And a self-adjoint operator is called Hermitian operator. And we will see that already we have noticed that this operator $\frac{d}{dx}$ operator has taken our function out of the Hilbert space and here we are seeing that their adjoint is not equal to its own operator. So, this kind of operator cannot be acceptable in the quantum mechanics.

In order to use an operator in quantum mechanics, it has to be Hermitian operator, which means that its adjoint would be always equal to its own operator. So, this is something which is a requirement for quantum mechanics, all quantum mechanical operators are Hermitian operators, which means that it is self-adjoint, it is equal to its own adjoint.

And what will prove here now, then if A is an Hermitian operator then A acting on ψ giving me $A\psi = \lambda\psi$, this is called Eigen value equation, then λ is going to be always real. What it suggests that an important property of Hermitian operator is that the Eigen value of a Hermitian operator is real, this is another property of the Hermitian operator.

So, I have mentioned that in quantum mechanics any operator cannot be used, this kind of operator cannot be used, only self-adjoint operators can be used which is Hermitian operator. The moment I use Hermitian operator in quantum mechanics, it gives me a direct consequence that Eigen value of that operator is going to be always real. So, let us prove that Eigen value of Hermitian operator would be real minus infinity to plus infinity.

I am going to find out this integration this is nothing but $\int_{-\infty}^{+\infty} \psi^* A\psi dx = \lambda \int_{-\infty}^{+\infty} \psi^*\psi dx = \lambda$. And I have to find out now $\int_{-\infty}^{+\infty} (A^{\dagger}\psi)^*\psi dx = \int_{-\infty}^{+\infty} (A\psi)^*\psi dx = \lambda^* \int_{-\infty}^{+\infty} \psi^*\psi dx = \lambda^*$ as $A = A^{\dagger}$

we are assuming that ψ is normalized which means it is living in Hilbert space, it is normalized and that is why we can write down this ψ^*. So, we have seen that in order to be an Hermitian operator itself, it has to be self-adjoint which means that these two integral would be equal, $\int_{-\infty}^{+\infty} \psi^* A\psi dx = \int_{-\infty}^{+\infty} (A^\dagger \psi)^* \psi dx$ these two integral.

And in order to be equal I need to have $\lambda = \lambda^*$ and this is possible only when λ is real. A physical quantity can only be equal to its complex conjugate when λ is real. For complex value, let us say ib is a complex value can never be equal to its complex conjugate, $ib \neq -ib$ because complex conjugate is going to be -ib.

So, λ cannot be a complex number lambda has to be a real number which proves the fact that Eigen value of Hermitian operator is going to be always real. So, in quantum mechanics, all the acceptable operators which I will use they are going to be Hermitian operator. And whenever that Hermitian operator, acceptable operator in quantum mechanics is going to be acting on the wave function I will get the real Eigen value, that is the bottom line of this analysis.

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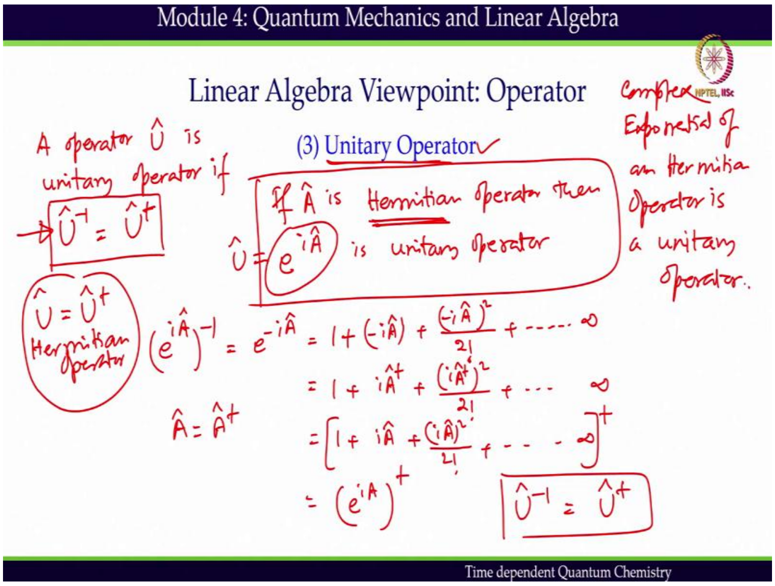

Next, we will move to unitary operator. How do we define a unitary operator? An operator U is unitary if inverse of that operator is equal to its adjoint $U^{-1} = U^\dagger$,so, when inverse is equal to adjoint. $U = U^\dagger$ if this is equal, we call it Hermitian operator,. But when its inverse is equal to its adjoint, then it is called unitary operator. An important property of unitary operator is that, if A is Hermitian operator, then e^{iA}, is an unitary operator. This is the property.

We can prove that

$$\left(e^{iA}\right)^{-1} = e^{-iA} = 1 + (-iA) + \frac{(-iA)^2}{2!} + ...\infty$$

This is Taylor series expansion we are using, which is nothing but

$$\left(e^{iA}\right)^{-1} = e^{-iA} = 1 + (-iA) + \frac{(-iA)^2}{2!} + ...\infty = 1 + (iA^{\dagger}) + \frac{(iA^{\dagger})^2}{2!} + ...\infty$$

And because A is Hermitian operator, because this is true for, this is Hermitian operator, A is Hermitian operator, I can write down this is nothing but

$$\left(e^{iA}\right)^{-1} = e^{-iA} = 1 + (-iA) + \frac{(-iA)^2}{2!} + ...\infty = 1 + (iA^{\dagger}) + \frac{(iA^{\dagger})^2}{2!} + ...\infty = 1 + (iA) + \frac{(iA)^2}{2!} + ...\infty$$

Because it is Hermitian operator, $A = A^{\dagger}$ in order to be Hermitian operator, this would be equal which means that this one is nothing $\left(e^{iA}\right)^{-1} = \left(e^{iA}\right)^{\dagger}$.

So, we have proved that unitary operator inverse is equal to its dagger, $U^{-1} = U^{\dagger}$. That is why this is unitary operator. So, it is an interesting property, if A is Hermitian operator, so , complex exponential of an Hermitian operator is unitary operator.

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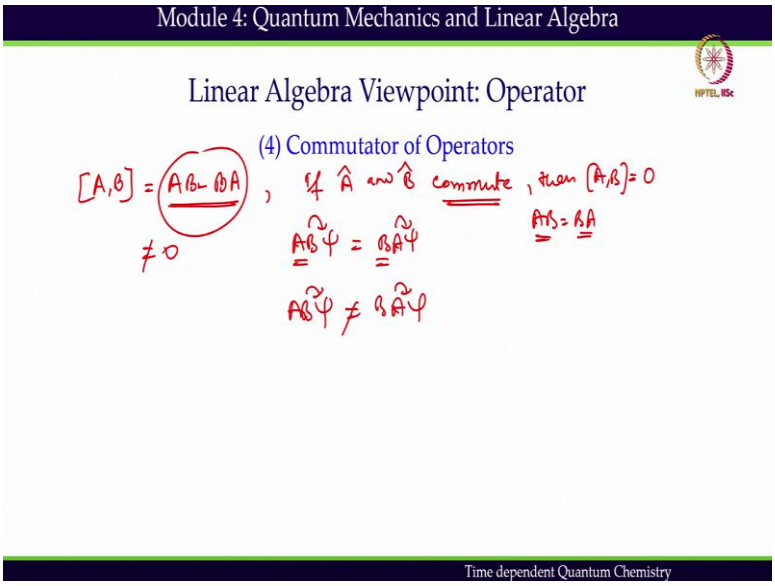

We will move forward there are many properties of the operators and the common algebra of operators we are going over. Commutators of two operators are defined by the $[A,B]=AB-BA$, this difference is called the commutator. And if A and B commute then $[A,B]=0, AB=BA$, does not matter which way it is acting.

So, I can have AB acting on ψ equals BA acting on ψ, the order does not matter. whether B will be acting first or A will be acting first, that order does not matter if they commute, but if they are not commuting, if this is not 0, then ordered will matter. So, $AB\psi \neq BA\psi$ Who will talk to psi first? That will matter if they are not commuting.

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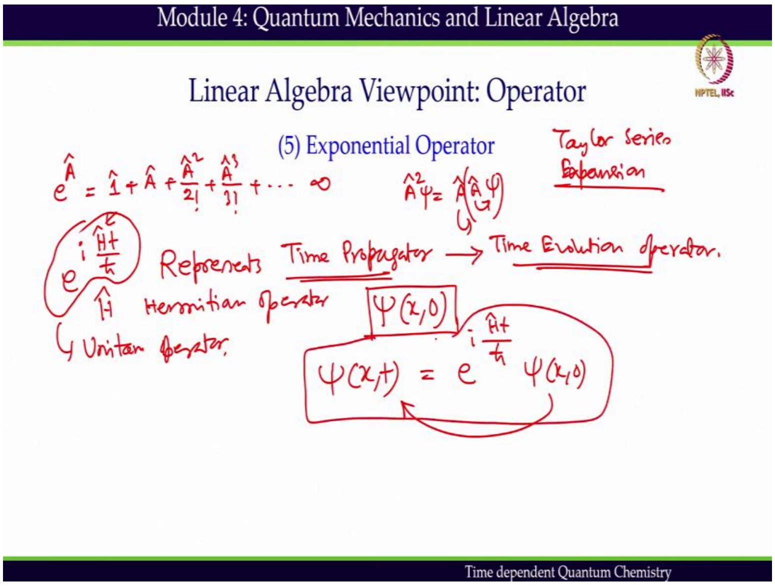

We will go to this exponential function of an operator which we have already seen how to express exponential function and operator.

$$e^A = 1 + (A) + \frac{(A)^2}{2!} + \frac{(A)^3}{3!} + ...\infty$$

$$A^2\psi = A(A\psi)$$

So, that is the way we move forward with this power law of the operator. Often in time dependent quantum mechanics, exponential operator is used to move initial wave function in time and space.

For example, $e^{i\frac{H}{\hbar}t}$ And that is why it is called time evolution operator. Why it is called time evolution operator? We will find out. But one thing is clear, because H we know that it is Hamiltonian operator.

So, in the previous slide we have seen that if H is Hermitian operator, this whole complex function $e^{i\frac{H}{\hbar}t}$ is going to be an unitary operator. So, this time propagator is an unitary operator in quantum mechanics. Now, why it is time evolution operator? We will prove this it is time evolution operator because, if we know $\psi(x,0)$, a particle represented by the wave function, initial wave function then I will be able to find out $\psi(x,t)$ at time t, what would be the function of the particle that can be found by employing this time evolution operator on it.

So, from initial wave function I can get the final wave function with the help of this time evolution operator. Now, we prove how this time evolution operator is giving us this equation $\psi(x,t) = e^{-i\frac{H}{\hbar}t}\psi(x,0)$

. This is something which will prove right now. We will use Taylor series expansion and we will check this first.

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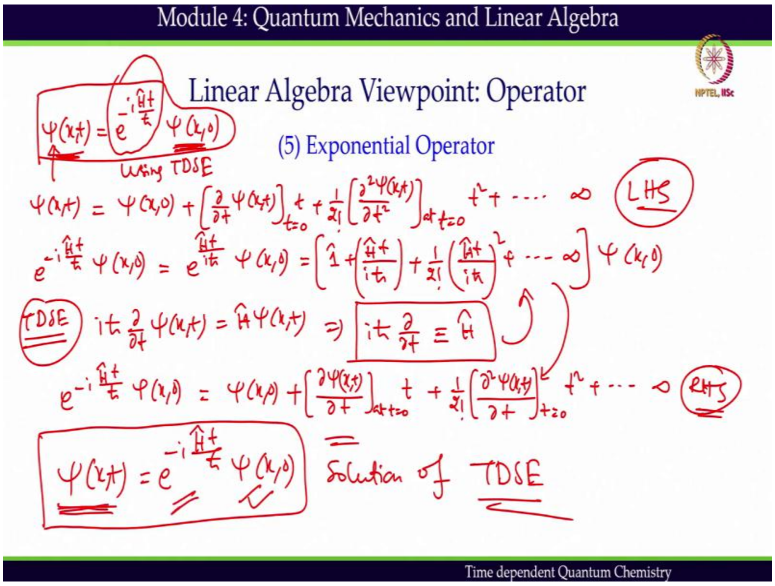

$\psi(x,t) = e^{-i\frac{H}{\hbar}t}\psi(x,0)$. So, this is something which you have to prove using time dependence-oriented equation. And if we can prove then it will show that this operator which is unitary operator, can be use to move the wave function from zero-point, zero time to other time, and we will be able to find out the wave function at time t.

$$\psi(x,t) = \psi(x,0) + \left[\frac{d\psi(x,t)}{dt}\right]_{t=0} + \frac{1}{2!}\left[\frac{d^2\psi(x,t)}{dt^2}\right]_{t=0} t^2 + ... + \infty$$

$$e^{-i\frac{H}{\hbar}t}\psi(x,0) = e^{\frac{H}{i\hbar}t}\psi(x,0) = \left[1 + (\frac{H}{i\hbar}t) + \frac{(\frac{H}{i\hbar}t)^2}{2!} + ...\infty\right]\psi(x,0)$$

TDSE, $i\hbar\frac{\partial\psi(x,t)}{\partial t} = H\psi(x,t)$, $i\hbar\frac{\partial}{\partial t} = H$

$e^{-i\frac{H}{\hbar}t}\psi(x,0) = e^{\frac{H}{i\hbar}t}\psi(x,0) = \psi(x,0) + \left[\frac{d\psi(x,t)}{dt}\right]_{t=0} + \frac{1}{2!}\left[\frac{d^2\psi(x,t)}{dt^2}\right]_{t=0} t^2 + ... + \infty$,LHS=RHS

$\psi(x,t) = e^{-i\frac{H}{\hbar}t}\psi(x,0)$, One can say that this is the solution of TDSE. If I know at 0 time, will get for time t.

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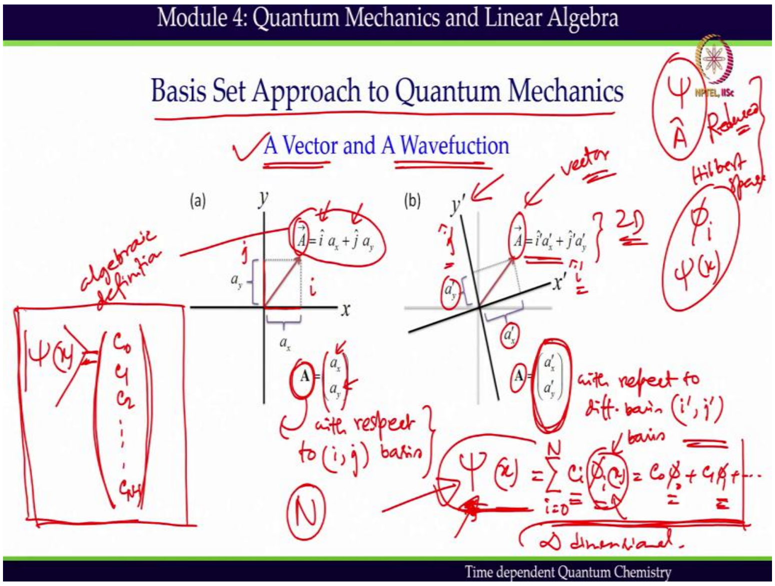

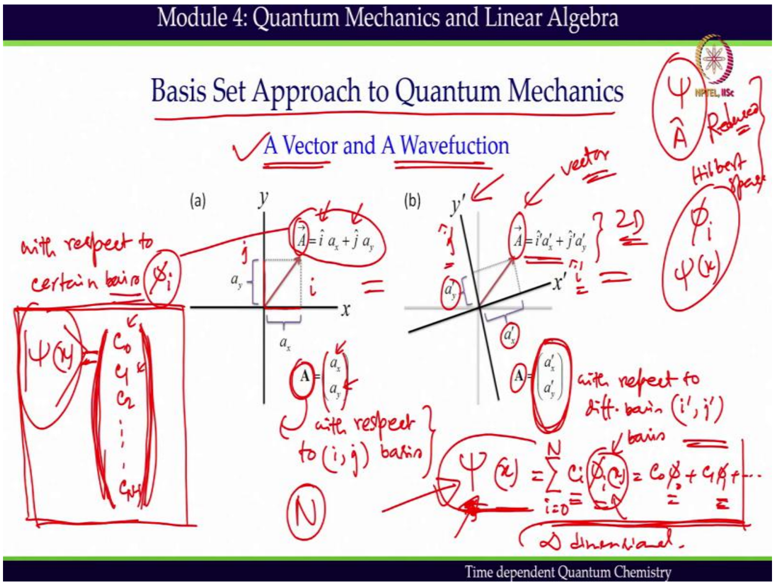

So, with this idea, so far, we have described different properties of the wave function and the operator which can be used in quantum mechanics. And we have reviewed several general properties of the quantum mechanically acceptable wave function and operators, which are two key constituents of quantum mechanics.

And we have defined necessary linear algebra terminologies using simple analytical mathematics, such as integration, differentiation, exponentiation, all this we have used, Taylor series expansion. So, we have used simple analytical mathematics such as integration, all these thingsm, integration, differentiation, and we have defined the properties of the wave function and the operator.

While this analytical approach helps develop the basic theoretical framework needed to understand the quantum mechanically acceptable wave function space and operator space in details, I have already pointed out earlier that our ultimate target in this module is to prepare the platform for numerical implementation of the wave function and the operator and that will give birth to this basic set approach to quantum mechanics.

And we will look at how this can be done. So, so far whatever we have studied has prepared the linear algebra connection, the background or the realization of the connection between linear algebra and quantum mechanics. Now, we are going to represent the key constituents of quantum mechanics which is wave function and operator ψ and A both needs to be represented in the matrix form with the help of all the properties of linear algebra, and we will see how to do that.

So, here first we will do one comparison between a vector and a wave function what is the connection between them. In three-dimensional space, a vector is often represented by its components with respect to the xyz-axis. For simplicity, here considered a vector, two-dimensional space you consider and the consider this vector, this vector is represented by this a_x is the component along the x-axis, a_y is the component along the y-axis and these are the unit vectors along the respective axis.

This vector in linear algebra, this same vector, this is called algebraic definition and this is matrix representation same vector (see slide) $A = \begin{pmatrix} a_x \\ a_y \end{pmatrix}, \vec{A} = \hat{i}a_x + ja_y$. So, in the matrix representation I can represent the vector in terms of its components, what is the components I have, a_x component and a_y components I have for this vector. So, the same vector can be represented in a different way in a matrix form.

Now, but when we have represented this, implicitly we are saying that with respect to (i, j) basis, with respect to i, j basis, why we have to say it explicitly i, j basis because if I can change the basis in the following way, I can change the axis given like this, I just rotate it the axis. Vector does not change, vector remains to be same in the space in the position space on the problem domain. But I have just rotated the axis, my representation.

And if I rotate that then what will happen, my i would be different this is now i', my j would be different j'in a different direction and their components will also be different. $\vec{A} = i'a_x + j'a_y$ But the same vector would be represented by different components with respect to different basis. Right now, i', j', basis is not the same for these two representations, all of the vector is the same, the same vector I am representing with two different bases.

And if I change the basis, I will change the components as well and that is why matrix representation will change, but each representation is representing the same vector. Therefore, one can represent the same vector using different basis as long as basis and corresponding components are known. As a physical state in quantum mechanics is represented by a wave function, which can be expanded with respect to certain orthonormal basis.

The above vectorial argument the argument which we have given here applies to quantum mechanical state of a system and this is called basis set expansion of the wave function. So, a wave function we have seen that in quantum mechanics, a wave function can be represented by a linear combination of certain function this is called basis function,

$$\psi(x) = \sum_{i=0}^{\infty} c_i \phi_i(x) = c_0 \phi_0(x) + c_1 \phi_1(x) + \ldots \infty$$

What is the difference between these two? Here, we have two-dimensional but here we have infinite dimensional because I have infinite number of basis set. So, that is the only difference, it is a dimensionality difference, but is the same idea, I am just, with respect to basis I am representing the wave function and if I do that, then one can say that this $\psi(x)$ can have a matrix representation following matrix representation , $\psi(x) = \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \\ \infty \end{pmatrix}$ and this is called the column matrix which is called vector in linear algebra.

We will understand more about it, but the basic connection should be clarified here a vector and the wave function both would be equivalent in linear algebra in the context of basis set expansion, here also we have a basis of i and j and I have expanded this vector and I have got this column matrix. Here, I have used different basis i', j', and I am getting a different representation of the same vector.

Similarly, here I have components c_i and this is the basis and that is why all the components can be collected in a column. And in this column matrix we can represent the wave function. This is the bracket notation we are using we will be using. But one thing we have to remember here, the reason why we can use this basis set expansion is quite clear because in Hilbert space we said that if in a Hilbert space, if ϕ are living in Hilbert space, then their linear combination will also stay in Hilbert space.

And that is exactly that is why we can write it. So, this representation, basis representation is directly coming from the property of the Hilbert space as long as ϕ the basis are living in Hilbert space, we can use this kind of linear combination because linear combination of them would also live in the same Hilbert space. But one thing is clear from this discussion is that the formal mathematical framework of quantum mechanics in the basis set approach represents an infinite dimensional Hilbert space. I told you that this summation $\psi(x) = \sum_{i=0}^{\infty} c_i \phi_i(x) = c_0 \phi_0(x) + c_1 \phi_1(x) + ...\infty$ is infinite.

So, dimensionality is going to be infinite dimension. However, no numerical calculation of quantum mechanics can deal with infinite dimensional space, it can only deal with finite dimension of the basis. Therefore, the sum in equation in this equation must we have to truncate it to some finite number, let us say N number of basis we would consider instead of infinite we consider N number.

And we have to truncate it for the numerical implementation. And this requirement can be fulfilled by making use of reduced Hilbert space. In that case, one would assume that all the general properties of wave functions and operators which we have discussed so far must be valid in the reduced Hilbert space, then only we will be able to use linear algebra.

So, even if I truncate it to some finite value N number of basis if I use then we have to assume that even after truncation the reduced Hilbert space I prepared, this reduced Hilbert space, in this reduced Hilbert space all the properties which we have seen previously are valid and there are basically rigorous mathematical support for that, it remains valid. So, it is not an issue for the numerical solution to get the numerical solution.

So, finally, the wave function can be represented in this. And generally, we do not mention very frequently, but we should remember that, when you say that a function is represented by this column matrix with these components, this can be represented with respect to certain basis because, if the basis is changing, this coefficient will also change.

As we have seen here two vectors, if the basis is changing coefficient will change. Similarly, if the basis are changing coefficient will change, but in the end the wave function will not change, it is just different representation. So, when you say that, this is the representation of the wave function, we implicitly say that it is with respect to certain basis ϕ_i. We will stop here and we will continue this module in the next session.