Time Dependent Quantum Chemistry
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Lecture 28
Matrix Representation of Operators

Welcome back, we are discussing how to get the eigenvalues and eigenvectors of a square matrix which will be useful for exploring available quantum states, if the Hamiltonian is known as long as we can convert the Hamiltonian in the matrix presentation and we have seen that there is a characteristic equation which I which one can use to get the eigenvalue and eigenvector of a square matrix.

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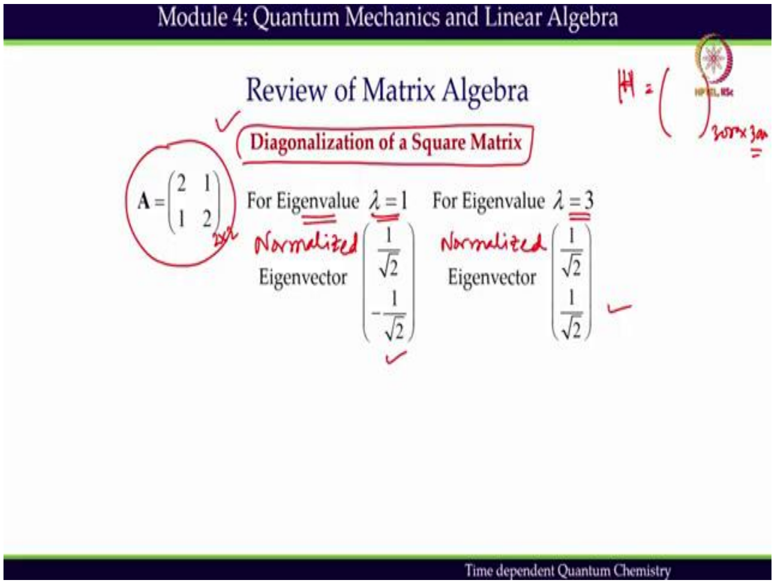


Review of Matrix Algebra

Diagonalization of a Square Matrix

$$\mathbf{A} = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}_{2\times 2}$$

For Eigenvalue $\lambda = 1$ — Normalized Eigenvector $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$

For Eigenvalue $\lambda = 3$ — Normalized Eigenvector $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

Defining:

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}_{2\times 2}$$

U^{-1}

$$UU^{-1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} \frac{a}{\sqrt{2}} + \frac{c}{\sqrt{2}} & \frac{b}{\sqrt{2}} + \frac{d}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \Rightarrow$$

$$a + c = \sqrt{2}$$
$$b + d = 0$$
$$-a + c = 0$$
$$-b + d = \sqrt{2}$$

Review of Matrix Algebra

Diagonalization of a Square Matrix

$U^{\dagger} = U^{-1}$

U unitary matrix

$$\mathbf{A} = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}_{2\times 2}$$

For Eigenvalue $\lambda = 1$ — Normalized Eigenvector $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$

For Eigenvalue $\lambda = 3$ — Normalized Eigenvector $\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

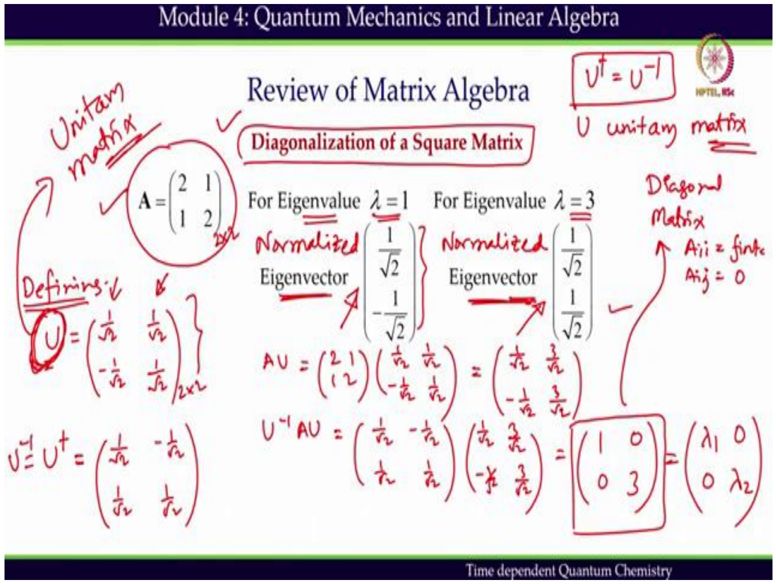
Unitary matrix

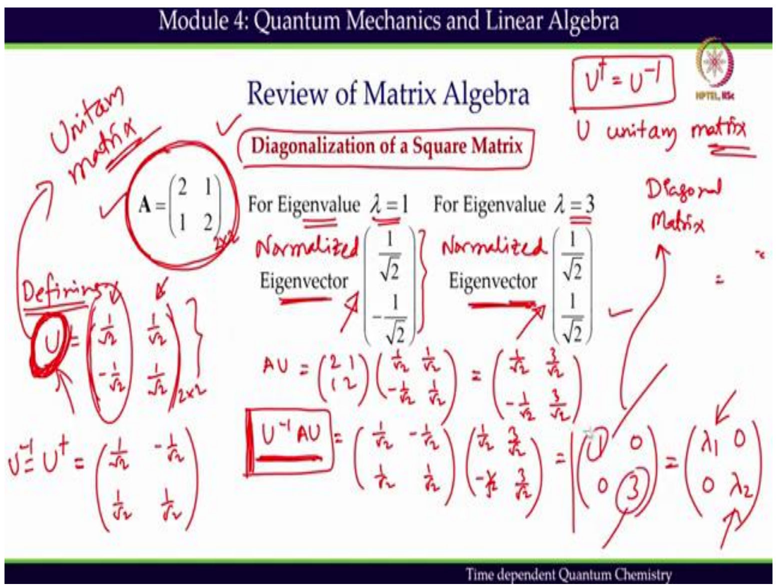
Defining:

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}_{2\times 2}$$

$$U^{-1} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

$$U^{\dagger} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$





But that using a characteristic equation it becomes little difficult when we have large matrix and usually all the under grid presentation, the matrix is can be of the order of let us say a Hamiltonian matrix would be of the order of 3000 by 3000, which is a very large matrix this here we are using only 2 by 2. So, for such a large matrix, it is not possible to do use this characteristic equation method.

What we need to do is that we have to use this diagonalization method and what is it mean by diagonalization? What is the basic idea behind it, what is the origin of this idea, we will discuss right now. We have already seen that this for this matrix, we have two normalized Eigen vectors.

And if we have these two normal normalized Eigen vectors, what we will do, I will now define a matrix like this

$$U = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$$

So, I am defining a matrix now, new matrix why I am defining this new matrix, I will reveal very soon. Let us say I have this matrix where the first column I have taken from this normalized Eigen vector, and the second column I have taken I have represented by this Eigen vector I have just defined a new matrix.

And after the definition, I will try to find out U inverse, inverse of the matrix of that matrix. So, I have now defined 2 by 2 matrix I have defined and I would like to find out inverse of that matrix, and inverse of the matrix can be found only by this equation,

$$UU^{-1} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

So, how can I get that I have to just multiply.

So, which means that let us say

$$\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

this is the form. So, I have again matrix multiplication and if we have the matrix multiplication, this multiplication can be done by

$$\begin{bmatrix} \frac{a+c}{\sqrt{2}} & \frac{b+d}{\sqrt{2}} \\ -\frac{a-c}{\sqrt{2}} & \frac{-b+d}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

And if we simplify, I jumped a step. I am not showing this elements you can do it as an home assignment. And if I do that, and then finally what we need to do is that we have to equate elements, this element should be equal to this element, this element should be equal to this element, we have to equate elements of left hand side and right hand sides.

If we do that, then finally, we will be able to get, we will be able to get a equals, in fact, a few equations will get first, such as

$$a + c = \sqrt{2}$$

$$b + d = 0$$

$$-a + c = 0$$

$$-b + d = \sqrt{2}$$

and we can solve this finally, and if we solve it, we will get this U inverse. So, finally what we get is U inverse would be of this form. I have shown the procedure already.

So, I will write down the final form of the U inverse which will get the final form of the U inverse would be

$$U^{-1} = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$$

So, this is going to be the U inverse. And what we see is that if we compare now, this matrix and this matrix if we compare we see that U dagger if I try to find out U dagger, which means the adjoin of the U matrix, this is the U matrix, I have defined adjoin would be the exchange of row column, and then take the complex conjugate.

Here, all elements are real. So, we do not need to worry about complex conjugate, but we can change the position. So, this is going to be

$$U^{+} = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$$

this is going to be the U dagger, what we see here from this exercise is that U dagger is actually U inverse and whenever you have U dagger equals U inverse, we have defined that operator or here operator will be represented in terms of matrix. So, we call it U matrix is not unitary matrix that we have already presented.

U it has to be unitary matrix, because they are equal. So, the matrix which I have defined with the help of this Eigen vector individual Eigen vectors, that matrix is turned out to be an unitary matrix. That is going to be a unitary matrix always. So, the matrix which I am forming with the help of the normalized Eigen vector and eigen normalized eigenvectors of a matrix will always be an unitary matrix.

Now, I will define this AU I will, I will multiply this AU. So, this is equal. Now, I will find out AU, what is AU? A U is going to be

$$A = \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}$$

And U matrix is going

$$U = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}$$

This is the matrix I have. And if I do that, if I multiply it, I am not showing it explicitly, I will just write down the final form I, you can do it on your own once you know this matrix multiplication

$$AU = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{3}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{3}{\sqrt{2}} \end{bmatrix}$$

So, this is going to be AU and now I will multiply U inverse AU

$$U^{-1}\,AU = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{3}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{3}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 3 \end{bmatrix}$$

What I get is that

$$U^{-1}\,AU = \begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{3}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{3}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 3 \end{bmatrix} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

I get diagonalized matrix or a diagonalize matrix diagonal matrix has Aii value finite values I have but Aij all Aij is going to be 0. So, all off diagonal elements should be 0 only diagonal element will exist and those diagonal elements what we are seeing here, if I perform this operation, U inverse AU then I actually get back the Eigen values.

So, what we are learning from here is that, if I start if I have a matrix like A which can be an Hamiltonian matrix, but if I have a matrix A I have to look for this unitary matrix U if I can look for it, how can I look for it, I can look for it such a way that this U inverse AU this operation this linear transformation will finally give me the Eigen values and how can I get the Eigen vectors Eigen vectors are already given within this U matrix. So, all I have to find out is this U matrix unitary transformation and that is why it is called unitary transformation.

So, diagonalizing a matrix is nothing but finding out this unitary matrix associated with this square matrix. Because if I find out this unitary matrix immediately I will be able to get the Eigen vectors and Eigen values.

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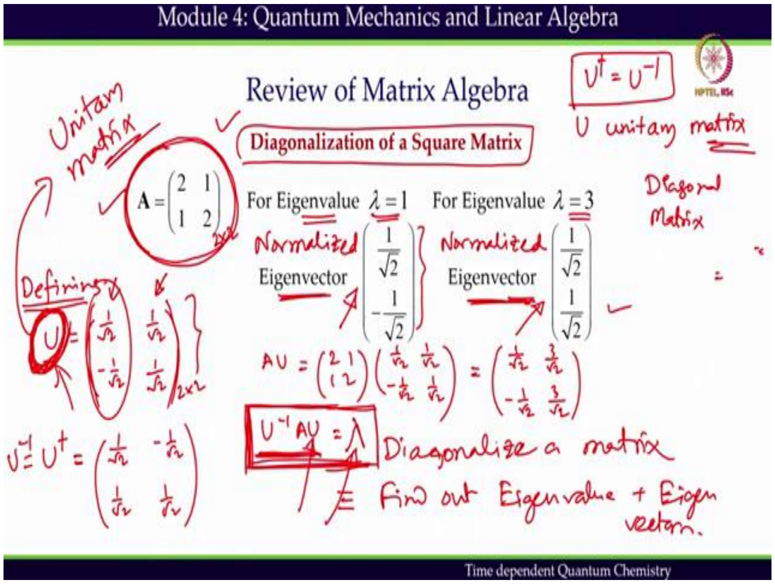

So, this is quite interesting way of interesting approach and numerical implementation is done with the help of these diagonalizing a matrix. So, if I diagonalize a matrix what I have learned here is that diagonalize a matrix is nothing but find out Eigen value and Eigen vectors.

So, I can find out the spectrum of the system and this diagonalization is done with the help of this linear transformation

$$U^{-1}\,AU = \Lambda$$

where you contains the Eigen vector information lambda contents the Eigen value information. So, what we have pretty much covered the kind of linear algebra we need to explore the quantum system.

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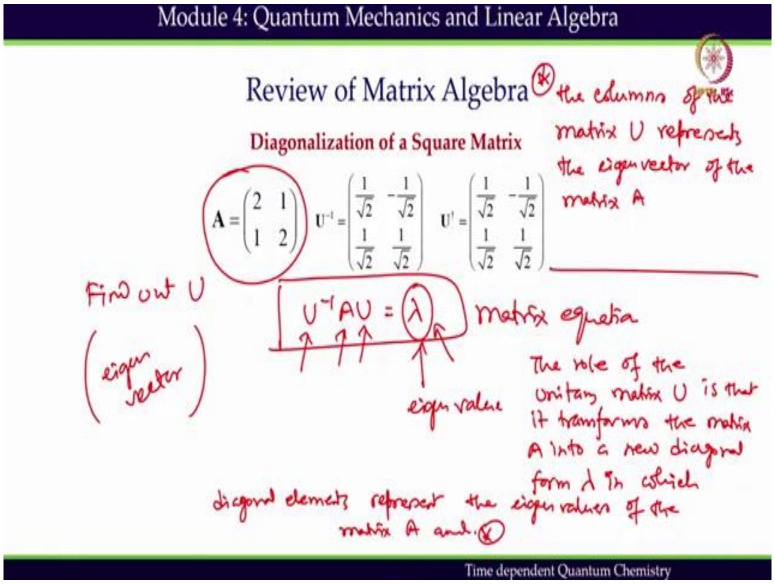

And we will ask this question what we have seen is that diagonalizing a matrix is a convenient way and we have gotten useful perspective of diagonalizing a matrix. So, if I have a matrix I have to find out then U that is going to be unitary matrix and that you will content the Eigen vector and if I do that then this linear transformation will give me associated Eigen values this is matrix equation which means that each one is actually representing a matrix this is an unitary matrix this is the matrix which I have and this is a unitary matrix and this is the matrix which is incorporating or containing that Eigen value information.

$$U^{-1} AU = \Lambda$$

So, the role of the unitary matrix U is that it transforms the matrix A into a new diagonal form lambda in which diagonal elements represent the eigenvalues of the matrix A and the columns of the matrix U represents the eigenvector of the matrix A. So, that is the meaning of this unitary transformation. So, we will move forward now, this is pretty much what we need to review for the matrix algebra.

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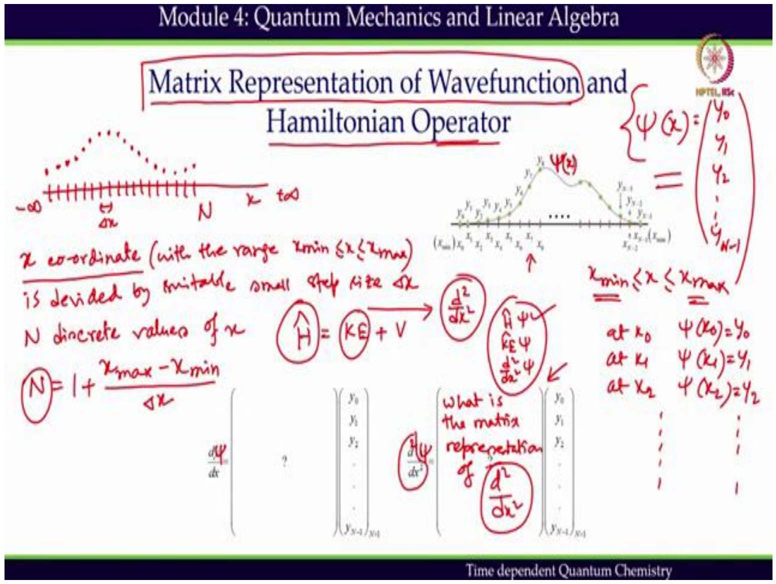

Because this similar kind of matrix algebra will be used to represent the Hamiltonian operator and we said that we have to perform this matrix representation of the wave function and the Hamiltonian operator to get the numerical solution. So, this is the final goal of this module to represent this function and Hamiltonian operator in the matrix form. So, wave function we have already shown that wave function can be represented in on the grid, and if we represent the wave function, this is a nice example, we have shown if the wave function **Ψ**(x) can be represented **Ψ**(x) is a continuous function by nature, that is the postulate of quantum mechanics.

But, on the grid representation, we will first take the grid of the x axis the problem domain is divided. So, grid means x is not continuous anymore, certain values of x is taken with a specific separation. So, in the grid representation this entire x axis is divided into discrete grids that is shown here and on each grid that wave function value will be calculated. So, wave function is now represented as a discretized wave function.

Discretize wave function and the separation is delta x we have shown in the Python tutorial one of the Python tutorials that this if I have N number of grids if the x coordinate within this range x minimum to x maximum within the range I can use minus infinity to plus infinity it is not possible numerically I cannot implement minus infinity to plus infinity, we have to always select a range which is finite.

So, this is the finite range we have selected this finite range of x coordinate or x axis within this range, this is minimum x maximum within this range, this x coordinate is divided by suitable small step size that is delta x. So, that is the way we produce these grid and once we produce these grid, let us say I have N discrete values of x within this range. So, if we have this N discrete values n can be represented as

$$N = 1 + \frac{x_{max} - x_{min}}{\Delta x}$$

This many points will have and at each point on each grid, we will represent this continuous wave function **Ψ**(x). So, I will what I will get at x_0 , I will get **Ψ**(x_0) value at x_1 **Ψ**(x_1) value at x_2, I will get **Ψ**(x_2) value and so on. And we said that, within this grid representation what I can do this values I can call it as y_0 t y_1, y_2 like this, these values can be represented in a column matrix y_0, y_1, y_2 like this y_{N-1} column matrix.

$$\begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \\ .. \\ . \\ .. \\ y_{N-1} \end{pmatrix}$$

And the moment we represent on discretized once we have discretize the wave function, so we know the matrix representation of the wave function now, under grid representation on a grid representation matrix representation of the wave function is a column matrix. So, once we have discretized the wave function on the grid because Hamiltonian operator this operator is having kinetic energy part plus potential energy part kinetic energy part having a derivative operator.

So, first question in order to address in order to convert this Hamiltonian operator in order to represent the Hamiltonian operator in the matrix form the first thing we have to understand is that this Hamiltonian operator is going to act on the wave function. So, when H is going to act on the wave function, its kinetic energy part is going to act on wave function and kinetic energy part has this derivative on.

So, derivative will be acting on the wave function. So, question is if this is question is, how do I represent this particular derivative operator in the matrix form then only we will be able to do this operation. So, our next question is what is the matrix the presentation of this derivative operator which will be acting on this wave function? In the matrix form we will be able to do the matrix multiplication. If we know the matrix representation of the derivative operator.

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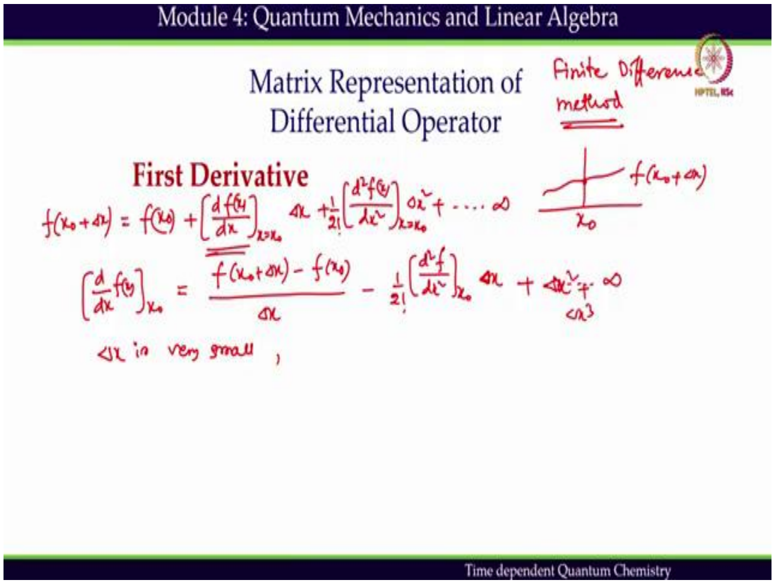

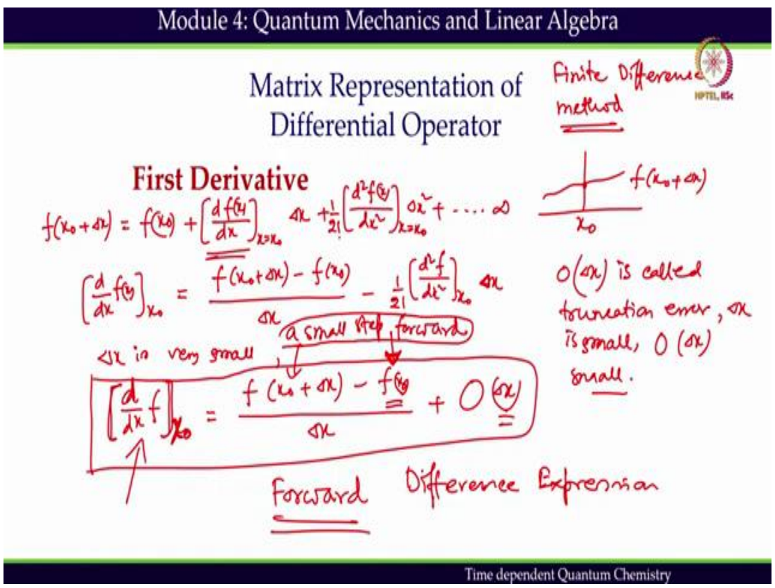

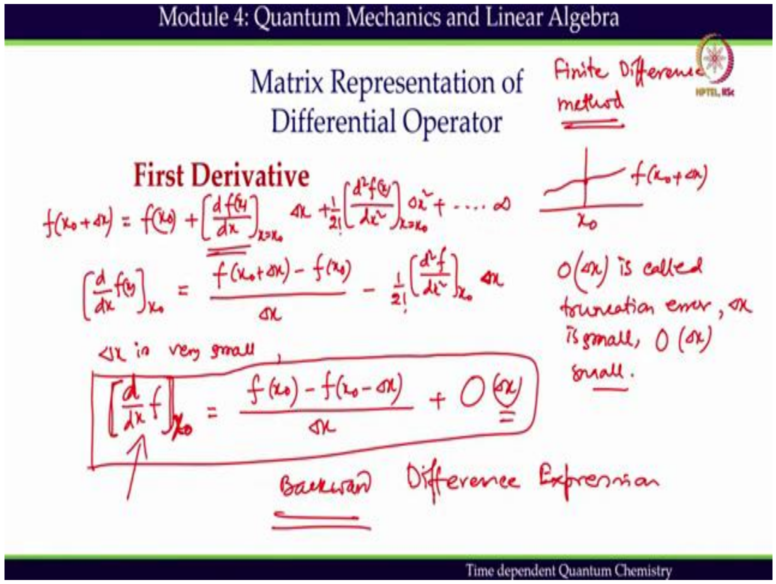

In order to find out the matrix representation of the derivative operator, we will introduce finite difference method. Under the finite difference method, what we will do, we will assume that the function of a particular function can be expressed in terms of a Taylor series expansion

$$f(x_0+\Delta x) = f(x_0) + [\frac{df(x)}{dx}]_{x=x_0}\Delta x + \frac{1}{2!}\left[\frac{d^2f(x)}{dx^2}\right]_{x=x_0}\Delta x + \ \dots\dots\dots\dots\dots..\infty$$

So, what I will do right now, I will represent this first derivative

$$[\frac{df(x)}{dx}]_{x=x_0} = \frac{f(x_0+\Delta x)-f(x_0)}{\Delta x} - \frac{1}{2!}\left[\frac{d^2f(x)}{dx^2}\right]_{x=x_0}\Delta x^2 + \ \dots\dots\dots\dots\dots.\infty$$

So, what we will do as delta x is very small I can neglect this other terms because that is going to be delta x square then delta x is cube all these terms can be neglected and I can say that approximately I can write down

$$[\frac{df(x)}{dx}]_{x=x_0} = \frac{f(x_0+\Delta x)-f(x_0)}{\Delta x} + O(\Delta x)$$

this is called truncation error.

So, this is represented by O, O delta x is called truncation error and as long as delta x is small this error would be also small. So, what we have just represented this equation this is representing the first derivative under finite difference method first derivative finite difference method where error is proportional to delta x. This is called the forward difference expression is called forward difference why this is forward difference expression because we need the function value in order to find out this first derivative of the function.

I need the function value where we are interested this is the function value where we are interested to find out the derivative because derivative is being calculated at x_o. So, function value I need at $x_{0.}$ In addition to that I need the function value at a small step forward this one also I need a small step forward a small step forward. So, because I would like to find out the derivative at x equals 0 I need the function value at x equals 0 plus I need in addition to that, I need the function value at a point small step forward that is why it is called forward difference expression.

Similarly, backward difference expression can be obtained and in that case the expression would be following expression would be

$$[\frac{df(x)}{dx}]_{x=x_0} = \frac{f(x_0) - f(x_0 - \Delta x)}{\Delta x} + O(\Delta x)$$

that is also possible to get that this is called backward difference expression.

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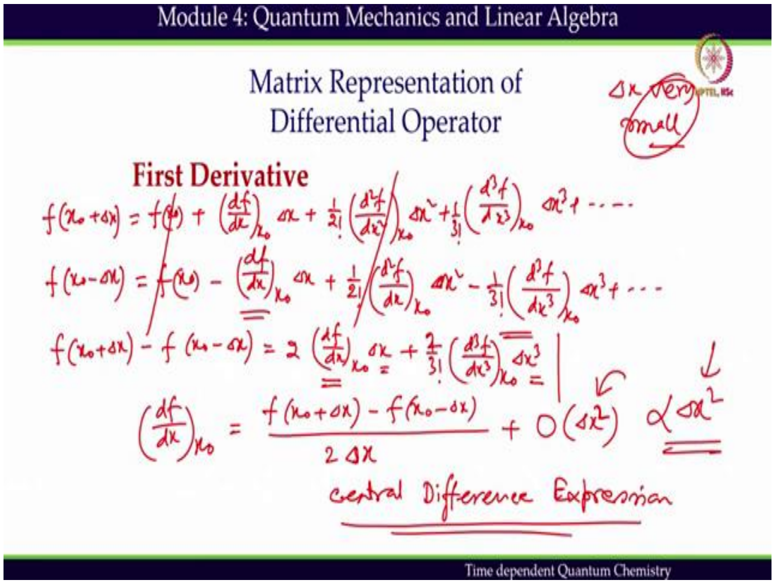

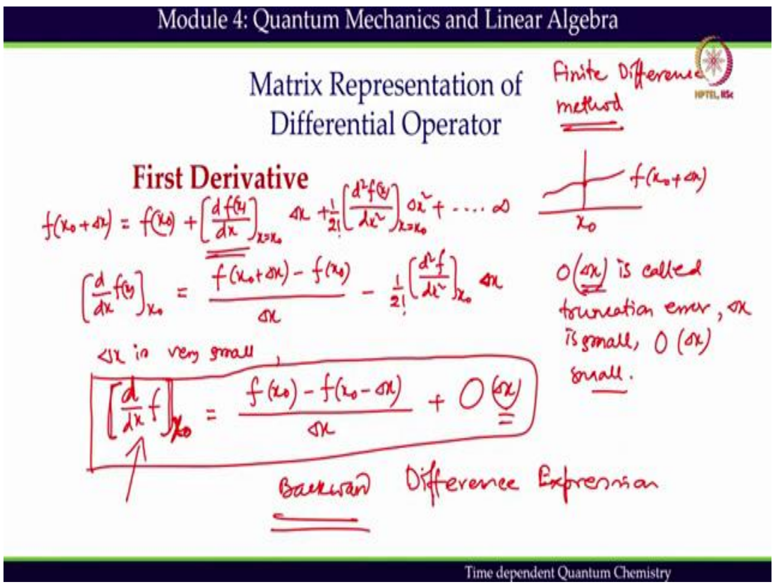

And similar way we can think about central difference as well and that can be obtained by following I will take the forward difference

$$f(x_0 + \Delta x) = f(x_0) + [\frac{df(x)}{dx}]_{x=x_0} \Delta x + \frac{1}{2!}\left[\frac{d^2 f(x)}{dx^2}\right]_{x=x_0} \Delta x^2 + \frac{1}{3!}(\frac{d^3 f}{dx^3})_{x=x_0} \Delta x^3 \ldots\ldots\ldots\ldots\ldots..\infty$$

this way I have one forward difference and then I have backward difference as well. Backward difference can be obtained by this

$$f(x_0 - \Delta x) = f(x_0) - [\frac{df(x)}{dx}]_{x=x_0} \Delta x + \frac{1}{2!}\left[\frac{d^2 f(x)}{dx^2}\right]_{x=x_0} \Delta x^2 - \frac{1}{3!}(\frac{d^3 f}{dx^3})_{x=x_0} \Delta x^3 \ldots\ldots\ldots\ldots\ldots..\infty$$

$$f(x_0 + \Delta x) - f(x_0 - \Delta x) = 2[\frac{df(x)}{dx}]_{x=x_0} \Delta x + \frac{2}{3!}(\frac{d^3 f}{dx^3})_{x=x_0} \ \Delta x^3 \ldots\ldots\ldots\ldots\ldots\ldots\infty$$

and because delta x is assumed to be very small I can neglect other terms also because they are too small.

I will neglect other terms here and I truncate it here. So, in the end what I get is that the first derivative can be represented in following

$$[\frac{df(x)}{dx}]_{x=x_0} \frac{f(x_0 + \Delta x) - f(x_0 - \Delta x)}{2\Delta x} + O(\Delta x^2)$$

This is cube but I have to divide by delta x and that is why I get an expression with delta x square.

So, what we see is that this is called central difference expression, central difference this is called central difference expression. And in the central difference expression, what we see is that this is a better way of finding first derivative because this error is now proportional to delta x square. So, by selecting a very small delta x, I will be able to reduce the error quadratically previously in the forward difference and backward difference, both error were linear.

So, it will drop down linearly, but here dropped down quadratically it will drop down drastically, that is why it is better if approximation so, central difference expression is a better approximation for doing this derivative.

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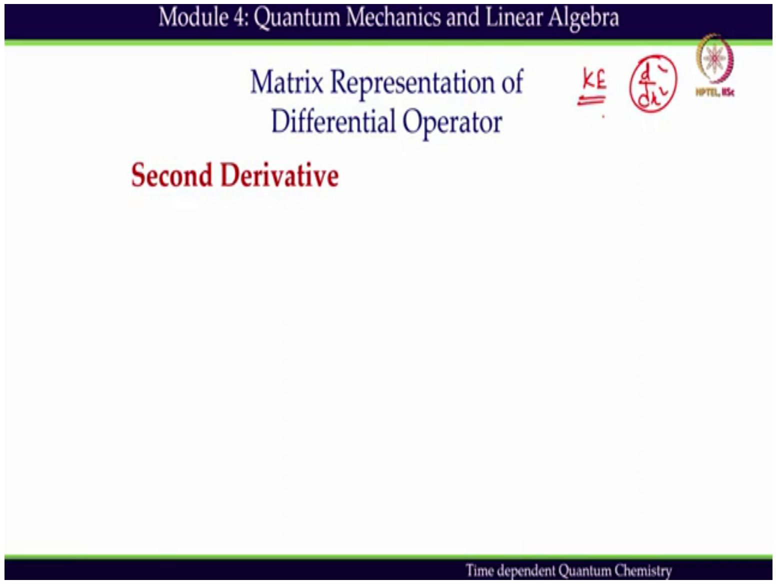

And so, after learning remember we have to go for the second derivative it is not the first derivative we are interested in it is the second derivative we are interested in because kinetic energy operator has second derivative in it. So, we have to get the second derivative I represented the first derivative to get the idea of finite difference method and three different expressions we can get one is called the central difference and another one is called forward difference. So, these are the expressions we need to get. I will continue this module in the next session.