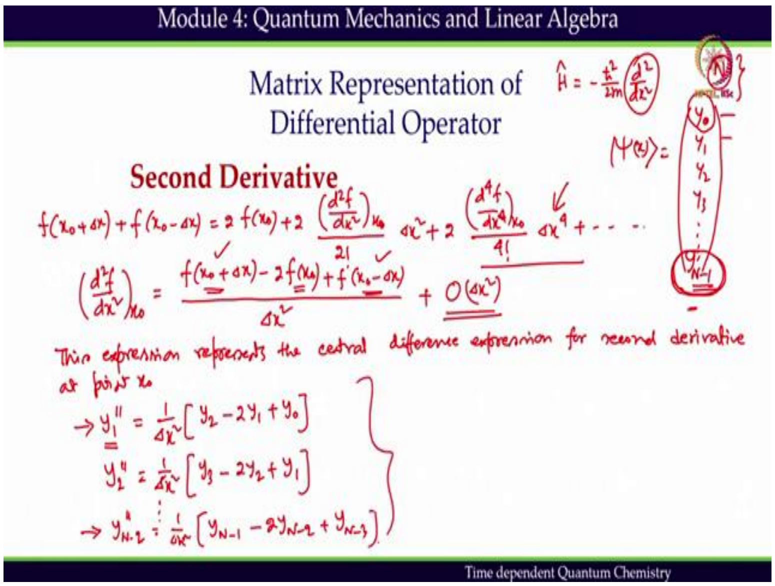
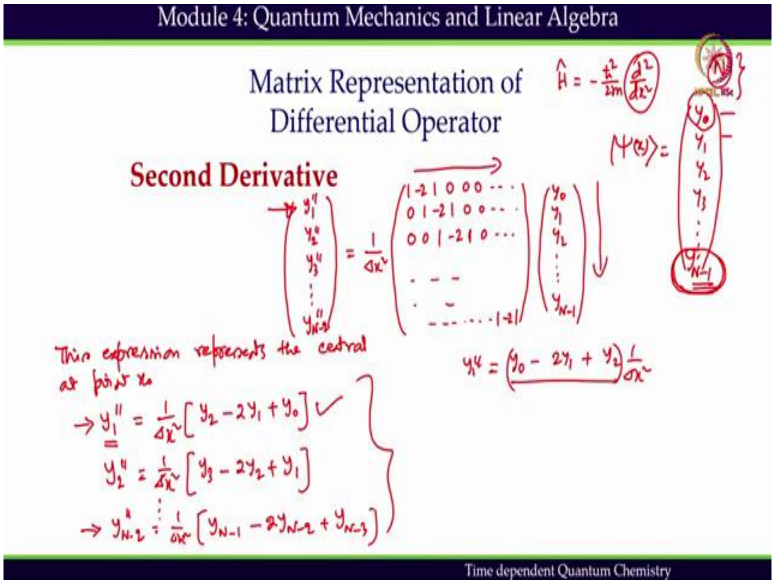
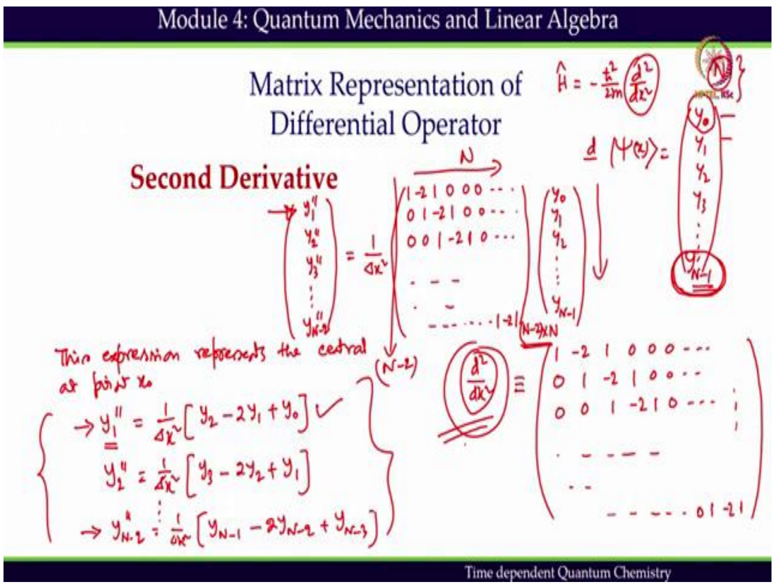
Time Dependent Quantum Chemistry
Professor Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Lecture 28
Matrix Representation of Operators

Welcome back to module 4, where we are trying to find out the connection between the linear algebra and quantum mechanics. And under grid representation, we have understood how to represent a wave function and then we are trying to represent the operator. And in order to represent the operator we have used a finite difference method to represent the derivative operator.

(Refer Slide Time: 01:07)







So, so far we have seen the first derivative how to represent, but we have to remember that first derivative is not present in the Hamiltonian operator. So, Hamiltonian operator has second derivative,

$$H = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$$

his is the second derivative. So, we have to get the second derivative expression for the, with the help of finite difference method. So, for that what we need to do is that we have seen the Taylor series expansion for the forward and backward expressions.

And previously we have taken subtraction now, we will take the addition so, we will add them together. So, if we add them together we get

$$f(x_0+\Delta x)+f(x_0-\Delta x)=2f(x_0)+2\frac{(\frac{d^2f}{dx^2})_0}{2!}\Delta x^2+2\frac{(\frac{d^4f}{dx^4})_{x_0}}{4!}\Delta x^4+\cdots\ldots\ldots\ldots\ldots\ldots$$

So, we get this expression adding forward and backward difference expression.

And then we will rearrange this equation a bit to find out this second derivative. So, second derivative is going to be then

$$(\frac{d^2f}{dx^2})_0=\frac{f(x_0+\Delta x)-2f(x_0)+f(x_0-\Delta x)}{\Delta x^2}$$

plus the remaining part is going to be this one. And because it is, it depends on x^4 but I have to divide x^4 delta x^4 by delta x^2.

$$(\frac{d^2f}{dx^2})_0=\frac{f(x_0+\Delta x)-2f(x_0)+f(x_0-\Delta x)}{\Delta x^2}+O(\Delta x^2)$$

that is going to be the error. So, this expression, this expression represents the central difference expression for second derivative at point x_0. And this exhibits an error which is Δx^2quadratically it will scale with Δx^2 by Δx. And so, based on this one can now construct what will happen for different points.

So, we can write down that I can have this y_1'' double dash, that is the second derivative at y_1 point. So, I started with my wave function was something like this,

$$|\Psi(x)>=\begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \\ - \\ - \\ - \\ \end{pmatrix}$$

like this. And I am trying to find out the derivative at each point and if I want to find out the derivative at each point, how do I get that? I can get this by delta x square, then doing it in order to find out the derivative at y_1 point,

$$y_1'' = \frac{1}{\Delta x^2}[y_2 - 2y_1 + y_0]$$

So, this is the expression for the derivative at y_1 point. Similarly derivative at y_2 point is going to be

$$y_2'' = \frac{1}{\Delta x^2}[y_3 - 2y_2 + y_1]$$

And this is the way we can go ahead. Finally, I can have (y_n-2) position where I have because here we have (n-1) total number is in n, n number of points we have is starting with 0 that is why it is ending at n-1, if I have total n number of points. And that is why I will not be able to get the derivative at this point, because I do not have any point one step backward. Similarly, I cannot get the derivative, second derivative particularly second derivative with central difference method.

I cannot get the derivative at this point also, because I do not have any points one step forward, because I need one step forward and one step backward values also for the function. So, I have started with, that is the way we will get this.

$$y_{N-2}'' = \frac{1}{\Delta x^2}[y_{N-1} - 2y_{N-2} + y_{N-3}]$$

Now, this set of expressions, set of equations can be very easily represented with the help of, with the help of matrix representation, and how we know matrix multiplication very nicely, and we will use that matrix multiplication method to represent this the set of equations. So, we will we have this f, the wave function, which is represented on the x grid already. And we have this x grid presentation. So, I will write down the grid the presentation as is like this.

So, I have the wave function as

$$|\Psi(x) = \begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \\ . \\ . \\ . \\ y_{N-1} \end{pmatrix}$$

this is my wave function. On this wave function, this operator is acting and if this operator can be represented as

$$\frac{1}{\Delta x^2}\begin{bmatrix} 1 & -2 & 1 & 0 & 0 & . & . & . \\ 0 & 1 & -2 & 1 & 0 & . & . & . \\ 0 & 0 & 1 & -2 & 1 & 0 & . & . \\ & & & & & & & \\ . & . & . & & & & & \\ . & . & . & & & & & \\ . & . & . & . & . & 1 & -2 & 1 \end{bmatrix}\begin{bmatrix} y_0 \\ y_1 \\ y_2 \\ . \\ . \\ . \\ . \\ y_{N-1} \end{bmatrix}$$

So, what we see here and then I have this 1 by delta x square, this is represented by the, the function after taking the derivative discretize function after taking the derivative.

$$\begin{bmatrix} y_1'' \\ y_2'' \\ y_3'' \\ . \\ . \\ . \\ . \\ y_{N-2}'' \end{bmatrix} = \frac{1}{\Delta x^2}\begin{bmatrix} 1 & -2 & 1 & 0 & 0 & . & . & . \\ 0 & 1 & -2 & 1 & 0 & . & . & . \\ 0 & 0 & 1 & -2 & 1 & 0 & . & . \\ & & & & & & & \\ . & . & . & & & & & \\ . & . & . & & & & & \\ . & . & . & . & . & 1 & -2 & 1 \end{bmatrix}\begin{bmatrix} y_0 \\ y_1 \\ y_2 \\ . \\ . \\ . \\ . \\ y_{N-1} \end{bmatrix}$$

And why this is the way it is? Because if we multiply this operator by this matrix by this matrix, then what will happen I will end up with y_1'' , I have to equate the left hand side element to the right hand side element. So, in that case I will be equaling, equating this y_1 value to the first product. So, that product is going to

$$y_1'' = \frac{1}{\Delta x^2}[y_0 - 2y_1 + y_2]$$

.Of course, we have this 1 by delta x square. So, each element we will be equating, we will be equating each element and we will get back this set of equations. So, this entire set of equations, one can represent in this matrix form. The moment I represent it in the matrix form, what I get immediately is the vectorial represent matrix representation of the derivative operator.

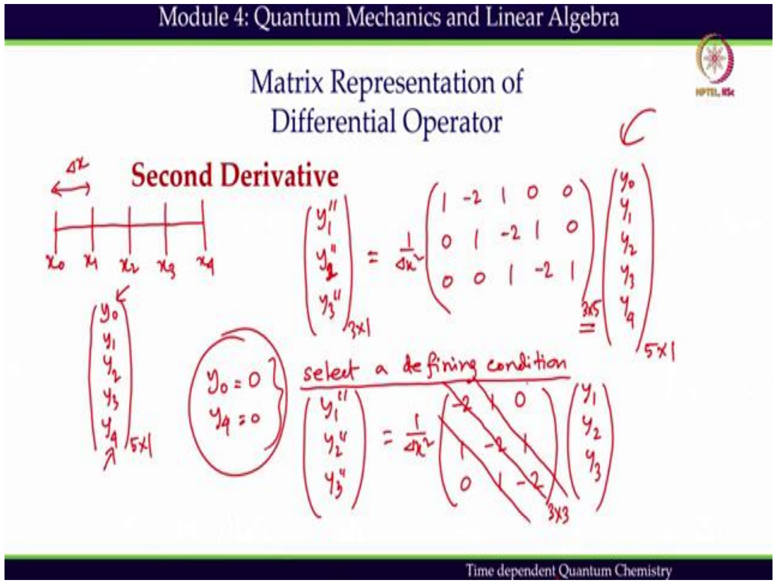
Because I started so, I started with, so basically

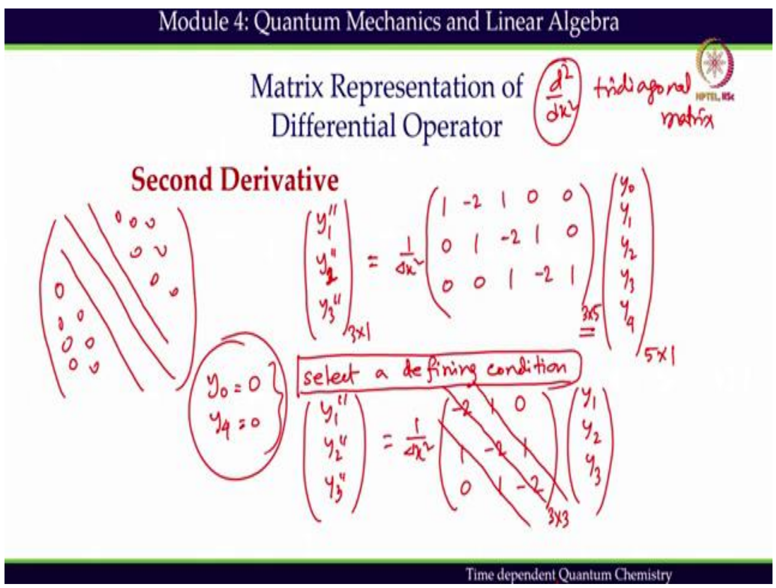
$$\frac{d^2}{dx^2} = \begin{bmatrix} 1 & -2 & 1 & 0 & 0 & . & . & . \\ 0 & 1 & -2 & 1 & 0 & . & . & . \\ 0 & 0 & 1 & -2 & 1 & 0 & . & . \\ & & & & & & & \\ . & . & . & & & & & \\ . & . & . & & & & & \\ . & . & . & . & . & 1 & -2 & 1 \end{bmatrix}$$

So, what do we get this matrix is actually in the dimension of this matrix is going to be (n-2)*n, that is the dimension.

So, I have (n-2) number of rows, and n number of column. So, I have n number of column and (n-2) number of rows I have in this, in this matrix, and that is the representation. So, matrix the presentation of this derivative operator under under this, under this grid presentation is given by this pastor where we can represent the second derivative in the matrix form.

(Refer Slide Time: 12:59)





So, we will have one example, simple example. And this example will be helping us because we are dealing with too many numbers. So, we will just reduce the dimension of the system. We have let us say the grid is following. I have this x_0, then I have this x_1, then I have this x_2 and then I have this x_3 and finally, I have x_4. So, this is the grid I have selected, a very small grid I have selected.

And obviously, the difference between each adjacent agreed points is Δx. Now, if we take this, and under this grid, if I have the wave function, the function represented

$$\begin{bmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix}$$

So, it is a 5*1 matrix, that it, that is the way the function is represented. Then, question is how do I represent the, the derivative at each point?

So, derivative can be represented by according to the previous discussion is going to be I will get only the derivative at 3 different points, y_2 y_3, only 3 different points, I will get that derivative.

$$\begin{bmatrix} y_1'' \\ y_2'' \\ y_3'' \end{bmatrix}$$

At the first point and and the last point I will get, not get that second derivative. Because I do not have the data point which is required to calculate that derivative. So, this is going to be Δx^2.

And now I will explicitly write down the full matrix

$$\begin{bmatrix} y_1'' \\ y_2'' \\ y_3'' \end{bmatrix} = \frac{1}{\Delta x^2} \begin{bmatrix} 1 & -2 & 1 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 1 & -2 & 1 \end{bmatrix} \begin{bmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix}$$

So, that is the way we have the values.

And if somehow, not somehow, for some reason, if we can say that $y_0 = 0$, and $y_4 = 0$, when I'm defining the function for the first time, this function, when I am defining the function, if I if I select the defining condition, if I select a defining condition like this, so, initial value is 0 and final value is 0, then what we can do? We can eliminate these two values and we can write down another simplified form which is going to be

$$\begin{bmatrix} y_1'' \\ y_2'' \\ y_3'' \end{bmatrix} = \begin{bmatrix} -2 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -2 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix}$$

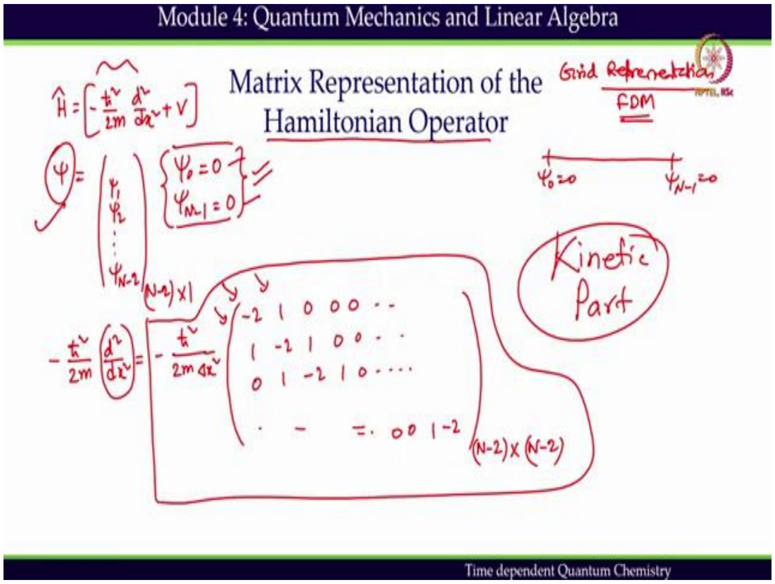
entire matrix dimension has reduced now. Because of this initial defining initial condition, and that is very important to realize. So, the moment we do that, if I, if I use this defining condition for the function, where we are saying that the initial point has to be 0 and the final point has to be 0, which means the boundary.

So, in the grid points, the boundary values are actually taken to be 0. If we do that, then this matrix which was previously 3*5 is becoming now square matrix, 3*3 square matrix. And defining it in the square form is very advantageous I will show that, why I should do that. And the moment I do this square matrix, this becomes a tri diagonal matrix, tri diagonal matrix, why tri diagonal matrix?

It is because I have now diagonal elements here then upper diagonal elements, and then lower diagonal elements. Only three components associated with the diagonal region is having the finite value. Otherwise, every other points are going to be 0. So, so, a tri diagonal matrix should look like this. A tri diagonal matrix, in general, a tri diagonal matrix should look like I have this is going to be a square matrix, I will have always diagonal values.

I will have lower diagonal values and upper diagonal values, remaining part is going to be all 0. So, this is called tri diagonal matrix. And I can represent so, so, basically, this $\frac{d^2}{dx^2}$ gives me a tri diagonal matrix, when I use this boundary condition, this defining condition for the for the initial wave function. And this kind of tri diagonal, tri diagonal matrix can be used to find out the eigenvalue and eigenvector for the operator.

(Refer Slide Time: 19:20)



So, we will move on and we will now look at the Hamiltonian operators, this is what we wanted to do under grid presentation. We have used finite difference method and under grid representation we will present that. So, one dimensional Hamiltonian as we know that Hamiltonian operator is going to be

$$H = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + V$$

This is your Hamiltonian operator, on the grid presentation we have already discretized the wave function.

So, we function is represented by this, this is going to be

$$\Psi = \begin{bmatrix} \Psi_0 \\ \Psi_1 \\ \Psi_2 \\ . \\ . \\ . \\ . \\ \Psi_{N-1} \end{bmatrix}$$

this is the grid representation. And these are the values we have, and and we are going to use that defining condition. Defining condition is that at the boundary that is going to be $\boldsymbol{\Psi}(0)$ is going to be 0 and **Ψ**(n-1) is going to be 0, this is the defining condition we are going to use for the wave function.

So, we have, we have to select the grid such a way that in the end here at the beginning of the grid and at the end of the grid, the **Ψ** values should take 0. This is, this is, this is, this is something which we have to do. So, that I can represent the derivative operator in the tridiagonal square matrix form. And, and question is I cannot just represent like this way I have to check whether I am supporting or or I, am I supported by the, the property of the Hilbert space.

Because I am dealing with in the end wave function. So, any wave function which is living in the Hilbert space must be square normalizable. And if it is square normalizable at the boundary it has to be 0. So, this is the basic idea. So, in the reduced Hilbert space when we will be presenting in this finite grid presentation, it is quite clear that this initial defining condition is spontaneously supported or naturally supported by the reduce Hilbert space, the property of the reduced Hilbert space.

So, you are good to go with this kind of wave function where the initial and the final values should is taken to be 0. And if we have taken 0 then this matrix has reduced to this form,

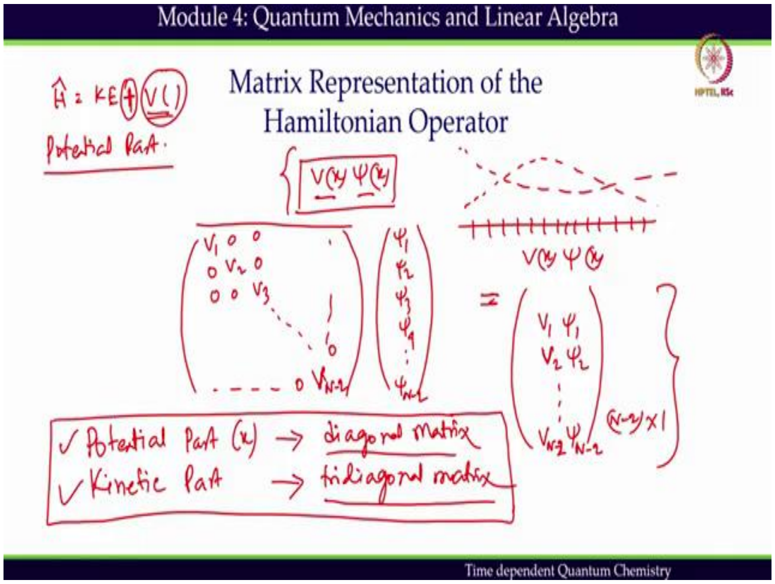
$$\Psi = \begin{bmatrix} \Psi_0 \\ \Psi_1 \\ \Psi_2 \\ . \\ . \\ . \\ . \\ \Psi_{N-2} \end{bmatrix}$$

So, this is now (n-2)*1 matrix under this representation. Now, we will use the central difference method to calculate the second derivative. So,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} = \frac{h^2}{8\pi^2 m}\frac{1}{\Delta x^2}\begin{bmatrix} -2 & 1 & 0 & 0 & 0 & . & . & . \\ 1 & -2 & 1 & 0 & 0 & . & . & . \\ 0 & 1 & -2 & 1 & 0 & 0 & . & . \\ & & & & & & & \\ . & . & . & & & & & \\ . & . & . & & & & & \\ . & . & . & . & . & 0 & 1 & -2 \end{bmatrix}$$

So, I get a square matrix, but it is a tri diagonal matrix it has diagonal, upper diagonal and lower diagonal finite values. So, all other values are 0. So, I have this (n-2)*(n -2) matrix represented by this. So, what I get is that the kinetic part, the kinetic part, the kinetic part is represented by this matrix under under grid representation with the help of this finite difference method.

(Refer Slide Time: 24:05)



On the other hand, if I look at the potential part in the Hamiltonian I had kinetic energy part plus potential energy part. And if this potential energy part has to be now expressed, so, potential part is going to be, how do I get that? Now potential we have to have one realization here, potential is nothing but a multiplication function. So, I have V(x)**Ψ**(x). So, **Ψ** has been already represented by grid, under grid representation discretized **Ψ** has been represented. So, this is let us say, **Ψ** and V(x) let us say V(x) has a form of like this, let us say V(x).

So, if I multiply these two functions, multiplication of these two functions, this is scalar multiplication. So, scalar multiplication is nothing but the multiplication of individual elements of their respective matrix. So, what we have is that v can be represented diagonally because it is just a scalar multiplication. So, so, in the end.

$$\begin{bmatrix} V_1\Psi_1 \\ V_2\Psi_2 \\ V_3\Psi_3 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ V_{N-2}\Psi_{N-2} \end{bmatrix}$$

So, this is going to be now (n-2)*1 (n-2)*1 matrix column matrix. Now, this column matrix can be very conveniently represented by following form.

We get this column matrix with the help of this.

$$\begin{bmatrix} V_1 & 0 & 0 & . & . & & \\ 0 & V_2 & 0 & . & . & & \\ 0 & 0 & V_3 & & & & \\ . & . & . & . & & & \\ . & . & . & . & & & \\ & & & & & . & . \\ & & & & & . & V_{N-2} \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \\ .. \\ .. \\ .. \\ \Psi_{N-2} \end{bmatrix} = \begin{bmatrix} V_1\Psi_1 \\ V_2\Psi_2 \\ V_3\Psi_3 \\ . \\ . \\ . \\ . \\ V_{N-2}\Psi_{N-2} \end{bmatrix}$$

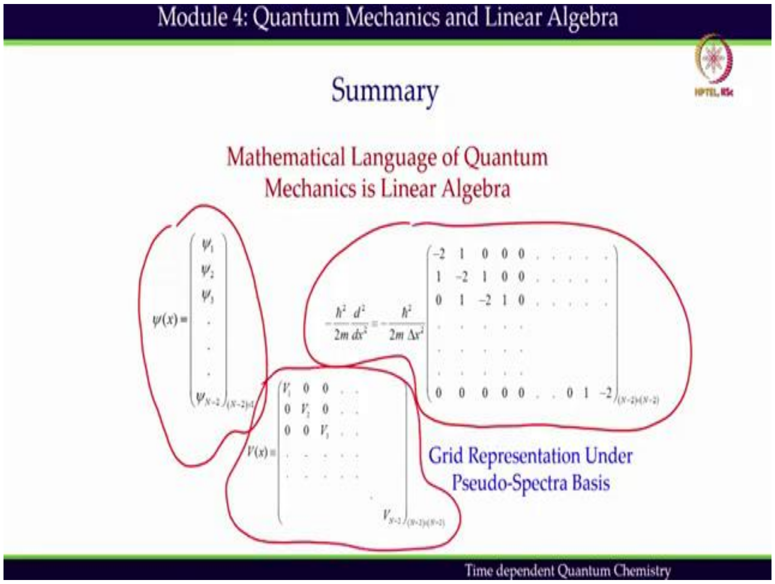
So, basically we get back this element by element multiplication to get this scalar multiplication with the help of our father's potential operator the potential operator in the end can be represented as a diagonal form.

So, so, the conclusions we have is that potential part which is only x dependent we have to remember that we have not included any time dependency so far, just we have we have kept the entire derivation very simple. And we have maintained that one dimension so, that we can understand the basic idea behind it. And so, potential part is giving me a diagonal matrix and kinetic part is giving me 1 tri diagonal matrix.

So, these are the two things and once we get potential part, potential matrix and kinetic part both part it is just a matrix addition in the end we have to do to get them the TDSE because and matrix addition we know when to matrix addition is done by adding individual element, corresponding elements.

So, this is something which you should remember that in the end that under grid representation with the help of pseudo spectral basis and using finite difference method one can represent kinetic energy part of the Hamiltonian in tridiagonal matrix and potential part as diagonal matrix.

(Refer Slide Time: 28:51)



So, we have with this, we have come to the end of this module where we have discussed quantum mechanics the connection between quantum mechanics and linear algebra. We have shown different linear algebra terminologies and also we have shown the analytical approach using matrix algebra, how can I represent different operators. So, this is the general form of the wave function under grid representation.

Then this is the general form of the kinetic energy part and this is the general form of the potential energy part under grid representation. So, we will stop here and we will meet again for the next module.