**Time Dependent Quantum Chemistry**
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**Module 04**
**Lecture 26**
**Matrix Algebra**

Welcome back to module 4. In this module we have been presenting the connection between quantum mechanics and linear algebra. And just now we have presented the basis set approach to quantum chemistry.

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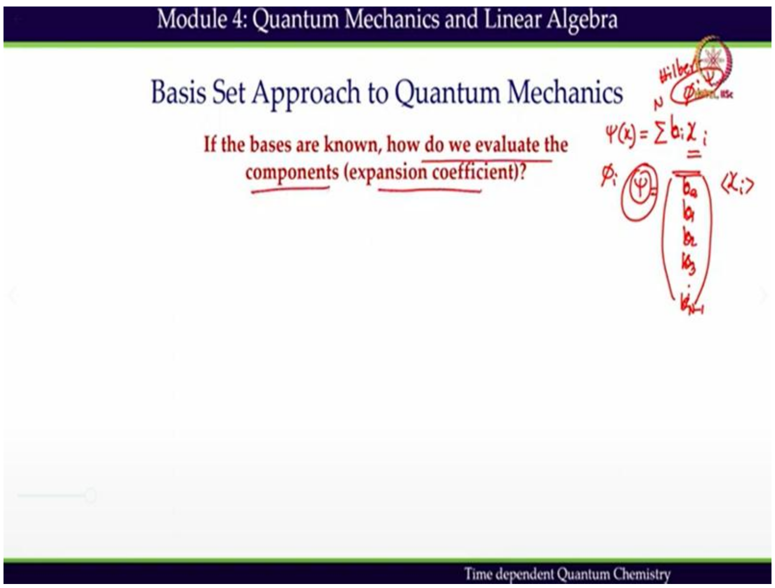


In basis set approach to quantum chemistry we have presented that $\psi(x)$ can be expanded in the basis of $\phi_i, \psi(x) = \sum_{i=0}^{\infty} c_i \phi_i(x)$. And the reason why we can write down this because we have pointed out that if $\phi_i$ living in the Hilbert space, in the same Hilbert space $\psi(x)$ will also leave. Because the linear combination of the wave functions, living in the Hilbert space will also live in the same Hilbert space. So that is the basic idea behind the basic mathematical idea behind the behind this linear combination. Now when you do this linear combination with respect to this $\phi_i$ basis one can present this $\psi(x)$ as a column matrix with its component $c_1$ ,$c_2$, $c_3$. $\psi(x) = \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \\ c_{N-1} \end{pmatrix}$

And we have said that this is going to be for the reduced Hilbert space where we have truncated this infinite summation to some certain number N and that is the way we can represent. So when we represent this is basis set representation of the wave function wave function can be represented in terms of a column matrix. Now when we represent it implicitly we assume that we it is with respect to $\phi_i$ basis if I do not if I change the basis to something else let us say $\chi_i$ then this coefficient will also change. $\psi(x) = \begin{pmatrix} b_0 \\ b_1 \\ b_2 \\ \vdots \\ b_{N-1} \end{pmatrix}$

So this is going to be then let us say $b_0$ ….and then all this coefficient will also change however wave function is remaining to be the same. So which way we represent the wave function with respect to what basis we represent wave function it really does not matter all we need to think about is that what kind of coefficient I get and the question is how do we evaluate the components expansion coefficient if the basis is known. So that is the point we are going to address here.

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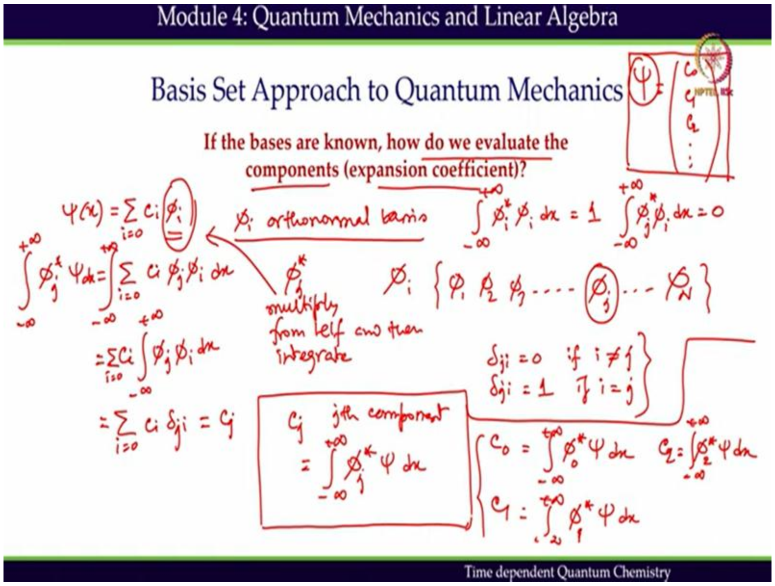


If I have the known basis then as usual we will expand $\psi(x)$ as linear combination , I am not writing here something N or infinity, $\psi(x)=\sum_{i=0}^{\infty}c_i\phi_i(x)$ and $\sum_{i=0}^{N}c_i\phi_i(x)$ because it is all equivalent. Because we have said that Hilbert space infinite Hilbert space and reduce Hilbert space will give me the same properties. And rigorous mathematics can be used to prove that and we will not get into those detail mathematics will just move forward with this demonstration. How do I get this $c_i$ , if the basis is known and we can get it done and we have to remember that this this basis $\phi_i$ this basis are orthonormal basis, what does it mean?

It means that if I do this integration $\int_{-\infty}^{+\infty}\phi_i^*\phi_i dx = 1$, but if I do this integration $\int_{-\infty}^{+\infty}\phi_j^*\phi_i dx = 0$. So what we are assuming that we are expanding total wave function in the basis of orthonormal wave function. And if we do that then we can use a trick to find out $c_i$, how do I do that I will first multiply this equation this expression by $\phi_j^*$.

And then I will integrate it from $\int_{-\infty}^{+\infty}\phi_j^*\psi dx = \int_{-\infty}^{+\infty}\sum_{i=0}c_i\phi_j\phi_i dx =$. We are continuing with one dimensional problem one can understand one can develop the understanding with the help of one dimension and then we can translate that idea to three dimensional problem as well and will do it at a later stage of this course. So we have we are using this trick and this is a trick which will be using in many occasions. So we have picked up so we had a basis $\phi_i$,which means $\{\phi_1, \phi_2, \phi_{3,} .......\phi_j ...\phi_N\}$ all this basis functions we have.

What we have done we have selected particularly 1 $\phi_j$ and then multiplied $\phi_j$ star from the left so we are multiplying from left this is a multiplication left and then integrate,

$$\sum_{i=0} c_i \int_{-\infty}^{+\infty} \phi_j \phi_i dx = \sum_{i=0} c_i \delta_{ji} , \delta_{ji} = 0 \text{ if } i \neq j \text{ and } \delta_{ji} = 1 \text{ if } i = j$$

that is the orthonormal basis the property of the orthonormal basis. And this property exactly coming from the property of the Hilbert space, property of the Hilbert space suggests that its inner product should exist. And so what we get is that the entire summation will be 0 except for this $c_j$ term because delta function will take the one value so I get this $c_j$ value. So jth component so from this exercise what I have learned is that $c_j$ jth component is given by this integration $c_j = \int_{-\infty}^{+\infty} \phi_j^* \psi dx$

So one can say it is instead of j th component one can generalize it for ith component also it does not matter or first component second component everything. So $c_0 = \int_{-\infty}^{+\infty} \phi_0^* \psi dx$. $c_1 = \int_{-\infty}^{+\infty} \phi_1^* \psi dx, c_2 = \int_{-\infty}^{+\infty} \phi_2^* \psi dx$. So this is the way expansion coefficient so all once we get this expansion coefficient I can express $\psi(x) = \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \\ c_{N-1} \end{pmatrix}$ in the matrix form, this matrix form I will repeat one more time, this matrix form is obtained with respect to certain basis basis is $\phi_i$.

If I change the basis immediately this components will change but it does not change the wave function just like the vectorial example we have given. But our next question is from this exercise we have understood that we can find out the expansion coefficient but what kind of basis we should select.

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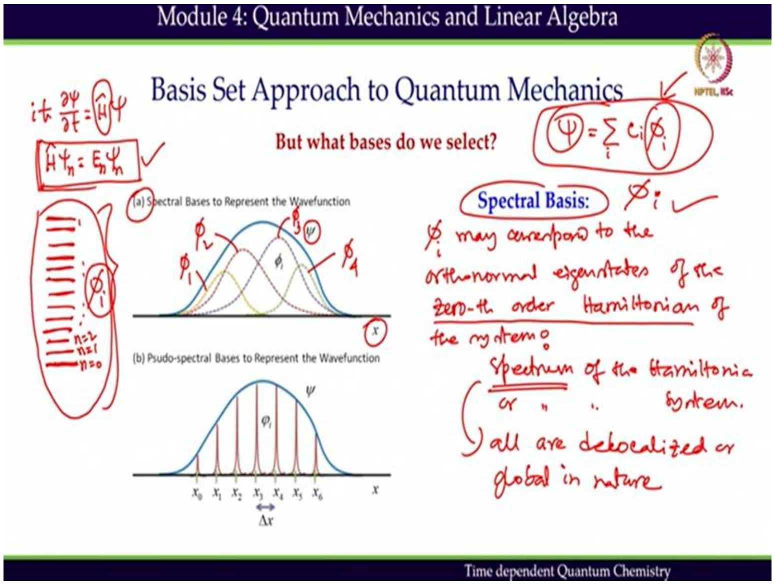


And this has two answers actually what kind of bases we should select for our work. $\psi = \sum_i c_i \phi_i$ .

So this is the basis function and we question is what kind of basis we should we should select, $\phi_i$ this basis function may correspond to the orthonormal Eigen states of the zeroth order Hamiltonian of the system. And how do you get that? Before I have been mentioning this one from the beginning that I have this time dependent Schrodinger equation $i\hbar \frac{\partial \psi(x,t)}{\partial t} = H\psi(x,t)$ .

And under variable separation method we immediately get this time independent Schrodinger equation, $H\psi = E\psi$ . But when we get this time independent Schrodinger equation, we get a solution associated with a particular state. So, this equation gives me a set of solutions these are the Eigen states of the system this is just like if you think about particularly in one dimensional box we solve this time independent Schrodinger equation and we have got n = 0 state, n = 1 state n = 2 state like this way we have got this (see slide).

Each one is representing the Eigen state of this time dependent Schrodinger equation and that is what we call zeroth order Hamiltonian. The Hamiltonian which does not include any external potential it is just we have considered the Hamiltonian of the system. So, for one dimensional particle in one dimensional box it should be then just a kinetic energy operator. And so this each state is the Eigen state and because we get a entire state, a set of states these are called the spectrum of the system, this is called spectrum of the Hamiltonian or spectrum of the quantum system.

So why it is spectrum because based on this Eigen state we find out what kind of transition I can have from one state to the another state generally we use this kind of transition in chemistry to explain the spectroscopy so that is why it is called spectrum. Now one can use those Eigen states to expand the total wave function and if we do that then it is called spectral basis then I help this $\phi_i$.

So, if I take the $\phi_i$, the basis if I use this Eigen states or the spectrum of the Hamiltonian as the basis to expand my total wave function then it is called spectral basis. what is the property of the spectral basis we have? we know that each function is representing the Eigen state or Eigen state of the Hamiltonian and each function by its own nature is delocalized.

So, for an example I have shown it here as a schematic representation of the spectral basis. I have total a function $\psi$ here but $\psi$ has been represented by different wave function obtained from this $\phi_i$. Let us say this is this yellow one is $\phi_1$ this brown color one is $\phi_2$ ,then bluish color one is $\phi_3$ this green color one is $\phi_4$. And one thing is quite clear, they are all delocalized in space. So spectral basis by its own nature, all are delocalized or global in nature. This is the property of the spectral basis if I take that respect spectral basis.

So, spectral basis is directly coming from its own spectrum, its own the systems, its own Eigen states and based on that Eigen states also we can we can represent this. So this is one way to represent the total wave function.

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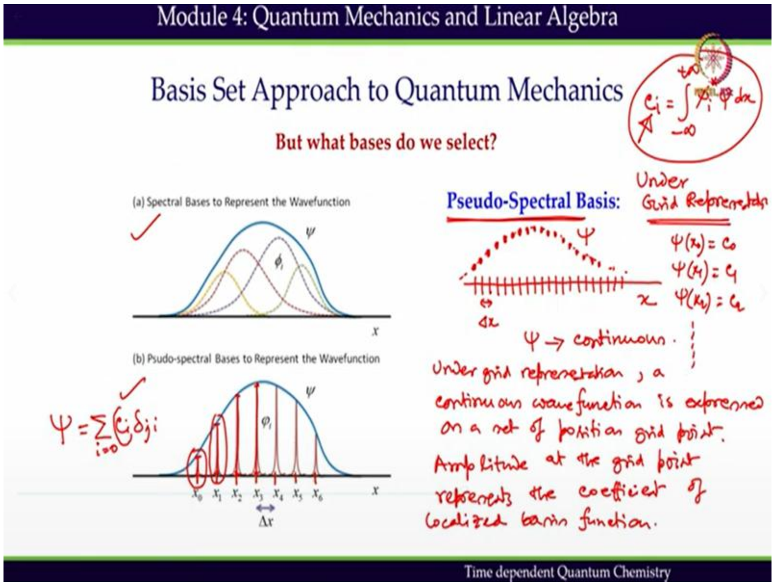


However, the spectral basis approach requires a very large number of Eigen states $\phi_i$ and integration over the Eigen states. Because finally I have to find out $c_1 = \int_{-\infty}^{+\infty} \phi_1^* \psi dx$, so I have to integrate a particular thing to get my coefficient. So, to represent the spectral basis it becomes little difficult particularly when it comes to the numerical implementation. So direct numerical implementation of spectral basis is far from straightforward, this is why almost all currently available numerical methods for solving TDSE do not make use of spectral basis.

Spectral basis is avoided generally, we do not try to solve the Schrodinger equation time independence Schrodinger equation and get that function and then use it for the for getting the solution. Rather, pseudo-spectral basis is used under the grid representation so this these are the two important concept we have given. Pseudo-spectral basis, what does it mean? It looks like a spectral basis but only difference between a spectral basis and a pseudo-spectral basis is that all pseudo-spectral bases are localized.

You see this one more like a delta function this one at a different position so and pseudo-spectral basis is used under grid representation. Now we have already shown grid representation in one of the python tutorials in this course. I will just one more time repeat. What we would like to do I have the problem domain this is the x axis that is called problem domain or the position space in one dimension (see slide figure). This position space I will just divide into a small segment, on small grids this kind of grids I will divide it each grid is separated by $\Delta x$ difference. (see slide figure).

And now I have the total wave function which is $\psi$ so what I will do right now? I will represent the entire $\psi$ which is a continuous function by its nature a wave function is going to be continuous. But under grid representation a continuous wave function is expressed on a set of position grid points. So, what I have instead of this continuous wave function which is represented by these dot lines (see slide figure). I will have certain values of the wave function on these grids. And that is the way I am going to represent the total wave function, it will be like this (see slide figure).. And amplitude of the grid points represents the coefficient of localized basis function.

So, what we are doing here is that I have this now $\psi$ under grid representation, $\psi$ would be represented as $\psi = \sum_{i=0} c_i \delta_{ji}$ . So, at each grid point I have now delta functions assigned and the coefficient $c_i$ is the amplitude. So in the end what I get is that I will get $\psi(x_0)$ point at $c_0$ point, at $\psi(x_1)$ point I will get the coefficient $c_1$, at $\psi(x_2)$ point I will get $c_2$ and so on.

So, in the end I will be able to represent the wave function in the matrix form and it is going to be similar to the spectral basis form but only difference is the nature.

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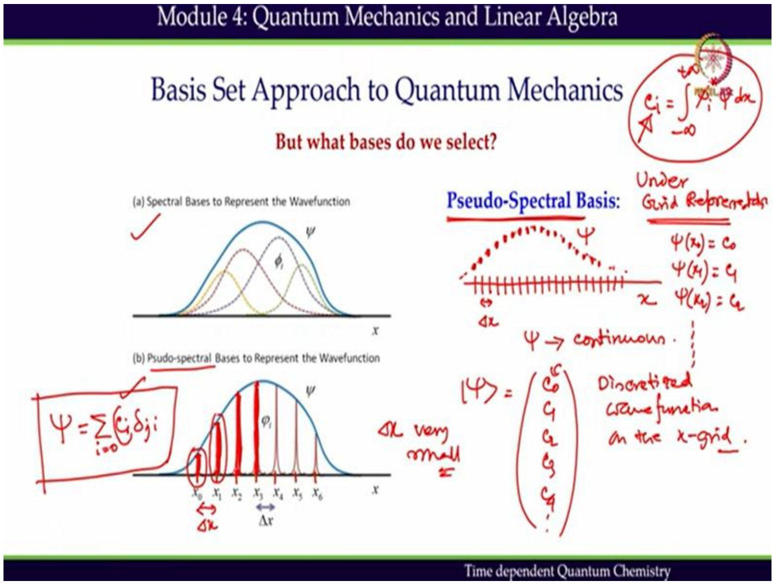


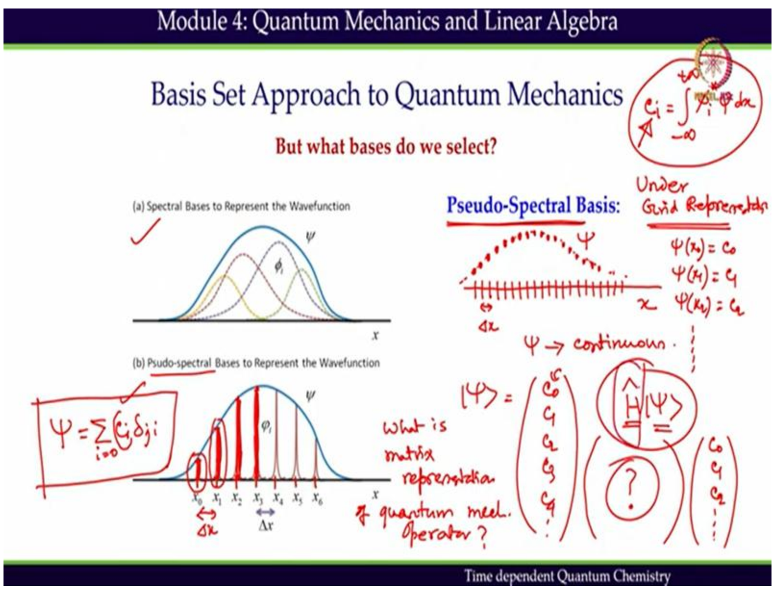


So the matrix would look like following I have this $|\psi\rangle = \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \\ c_{N-1} \end{pmatrix}$ and this is called Discretized wave function on the x grid. So, what does it mean by this? $c_0$ is this value, then $c_1$ is this value, $c_2$ is this value, $c_3$ is this value, for just pictorial representation I have made them very well separated $x_0$ to $x_1$ . It may give you an impression that we are going to separately use that. I mean we are going to use such a big separation, but remember $\Delta x$ will be selected to be very small, so they are not heavily separated they will be very close to each other so that we can use a huge, a big grid points, a large number of grid points and we can represent the wave function.

It is the value of the wave function at on those grids, so it is representing a function value on those grids and the form of the spectral basis pseudo-spectral basis is going to be like this. Delta function represented by this and then $c_i$ value. So, once a wave function is represented by a column matrix using pseudo-spectral basis approach under grid representation. Next important question is following what the matrix representation of quantum mechanical operators under grid representation .

So in the grid representation if wave function should look like this, then we have to remember that in the end I have to employ Hamiltonian operator on the $\psi$. So, what would be the matrix representation under grid representation of this Hamiltonian operator which will be acting on this wave function $\psi$. So, that is the next question we have. What is the matrix representation of quantum mechanical operator? Because I have to operate this Hamilton operator on this wave function, so I need to find out the matrix representation of the Hamiltonian operator.

But before we go ahead and find out what is the matrix representation of Hamiltonian operator because will be using the lot of matrix algebra to find out the ultimate form of a matrix representation of the Hamiltonian operator.

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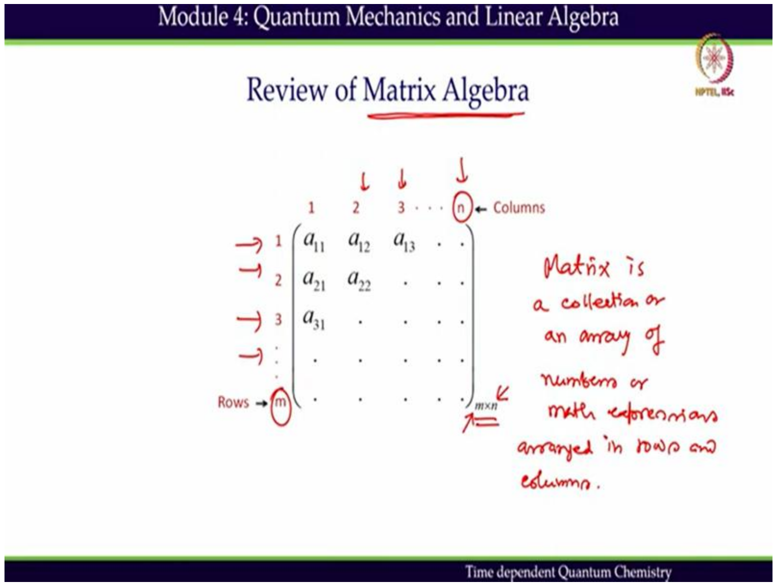


We will briefly go over the matrix algebra first because we will be using matrix algebra to find that out. In linear algebra a matrix represents, an array of numbers, a collection of numbers or mathematical expressions arranged in rows and columns like this. $\begin{pmatrix} a_{11} & a_{12} & a_{13} & . & . \\ a_{21} & a_{22} & . & . & . \\ a_{31} & . & . & . & . \\ . & . & . & . & . \\ . & . & . & . & . \end{pmatrix}$

Most of us are quite familiar with this matrix representation just to remind what does it mean by this, these are the columns we have and these are the rows we have and these are the columns we have and matrix can be of the order of mxn. And when we represent the matrix certain rules are followed to carry out algebraic operation with matrices.

So, what are the rules we have? Matrix is nothing but is a collection or array of numbers or mathematical expressions arranged in rows and columns. So, m representing the row and n representing the column. So, first we will write down the row and then cross n row cross column. i.e., mxn.

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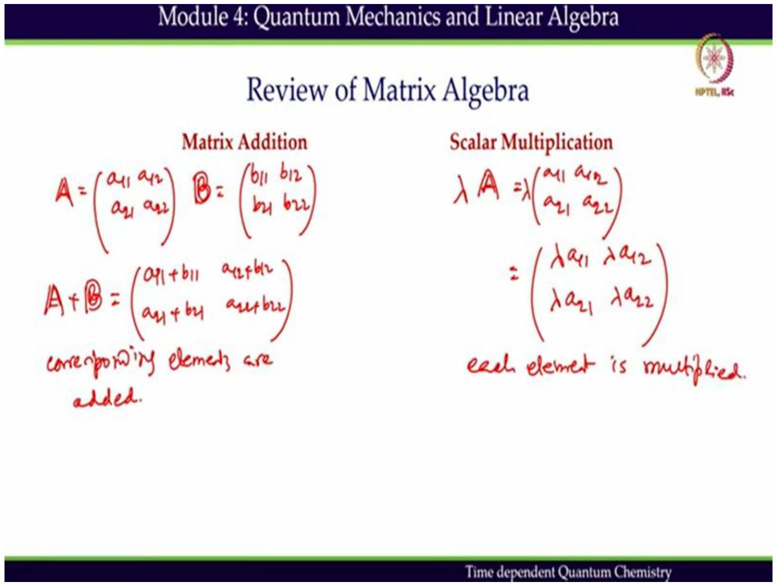


Matrix addition is one simple algebra we do with the matrices how do we add two matrices. Let us say I have first matrix is $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$, and another matrix is $, B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$ we can add them as corresponding elements are added. So, I can add $A + B = \begin{pmatrix} a_{11} + b_{11} & a_{12} + b_{12} \\ a_{21} + b_{21} & a_{22} + b_{22} \end{pmatrix}$ corresponding elements are added. Scalar multiplication if I have a matrix like this $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$, and if I multiply by $\lambda$, some scalar value then it is actually each element is multiplied. So,

$$\lambda A = \begin{pmatrix} \lambda a_{11} & \lambda a_{12} \\ \lambda a_{21} & \lambda a_{22} \end{pmatrix}$$

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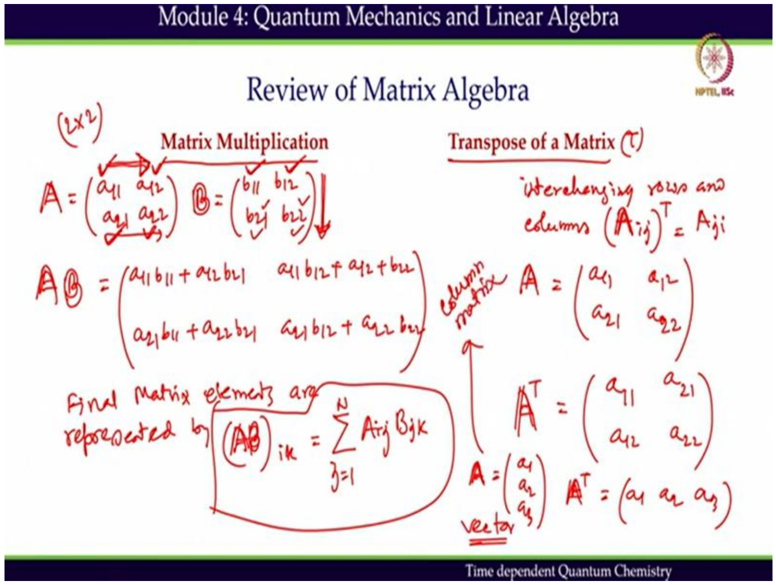


Matrix multiplication and scalar multiplication these are the two concepts we have to distinguish these two concepts. Previously we have shown scalar multiplication here will show matrix multiplication I have again two matrices a simple matrix 2x2 we are considering because that will give us a direct visualization what might happen. Matrix are represented if it is A, then we just cover it like this way we are representing like this way $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$. So B matrix is $B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$. So if I multiply these two matrices, matrix multiplication will give me in a following way little complicated we will go this way and will go this way so what does it mean.

$$AB = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{pmatrix}.$$

Matrix multiplication is little complicated but if we understand the order we have to follow always this order and we multiply and add them. So final matrix elements matrix multiplication requires little bit more practice to do it quickly. Final matrix elements are represented by

$(AB)_{ik} = \sum_{j=1}^{N} A_{ij} B_{jk}$ that is the rule, one should follow for the matrix multiplication. Transpose of a matrix obtained by interchanging rows and columns. So, I have to do $(A_{ij})^T = A_{ji}$.

So if I have a matrix like this $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$. If this is the matrix then transpose of the matrix will be given by this I just change the row and column interchange the row and column. So this is remaining to be the same but this one will change, this is going to be $A^T = \begin{pmatrix} a_{11} & a_{21} \\ a_{12} & a_{22} \end{pmatrix}$ that is called transpose of a matrix. Therefore, transpose of a column matrix is a row matrix so if I have a column matrix like this $A = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$ then transpose would be $A^T = \begin{pmatrix} a_1 & a_2 & a_3 \end{pmatrix}$, column matrix will be converted to row matrix. And this kind of column matrix are called vector in linear algebra. We will stop here and we will continue this discussion of this module in the next session