Time Dependent Quantum Chemistry
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Module 04
Lecture 27
Eigen Value and Eigen Function

Welcome back to module 4, we are discussing we are briefly reviewing matrix algebra and next we will understand complex conjugate of a matrix.

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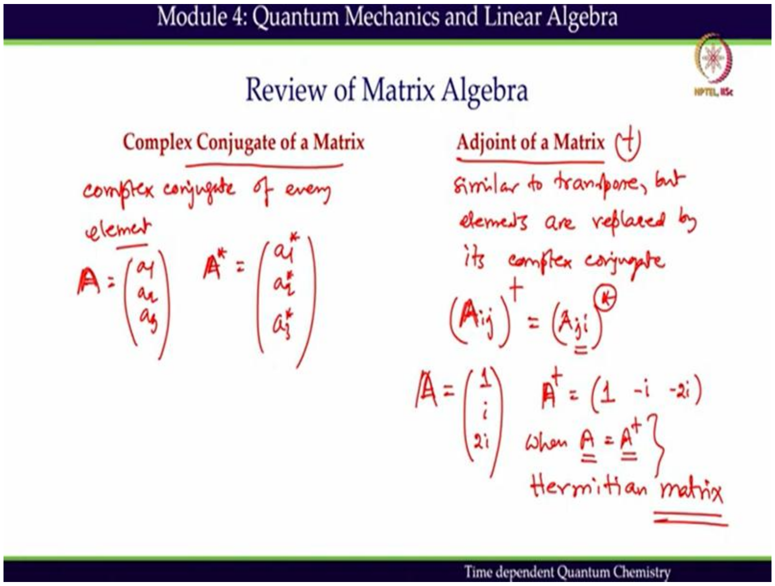

Complex conjugate of a matrix will be given by taking the complex conjugate of every element. Which means that if I have a matrix like this a $A = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$ this is a column matrix which is a vector then A^* is going to be making complex conjugate of each element $A^* = \begin{pmatrix} a_1^* \\ a_2^* \\ a_3^* \end{pmatrix}$. Adjoint of a matrix it is similar to transpose but elements are replaced by its complex conjugate. Which means that I have $\left(A_{ij}\right)^{\dagger}=\left(A_{ji}\right)^{*}$. So I am interchanging the row and column at the same time each element will be taken to be complex conjugate.

So let us say I have a function of a matrix like this $A=\begin{pmatrix}1\\ i\\ 2i\end{pmatrix}$ then adjoint of that matrix would be first of all we will change the row and column and then we will take the complex conjugate, 1 is real so there is no difference i would be minus -i and 2i would be -2i. When $A=A^{\dagger}$ that we have already seen, when an operator is equal to its own adjoint, it is called Hermitian operator or Hermitian matrix. In this case an operator will be expressed in terms of matrix so the name can be interchanged depending on the usage.

So, we will have Hermitian, this is called Hermitian operator, Hermitian matrix right now we will call it matrix. Hermitian matrix is defined when when it becomes self adjoined.

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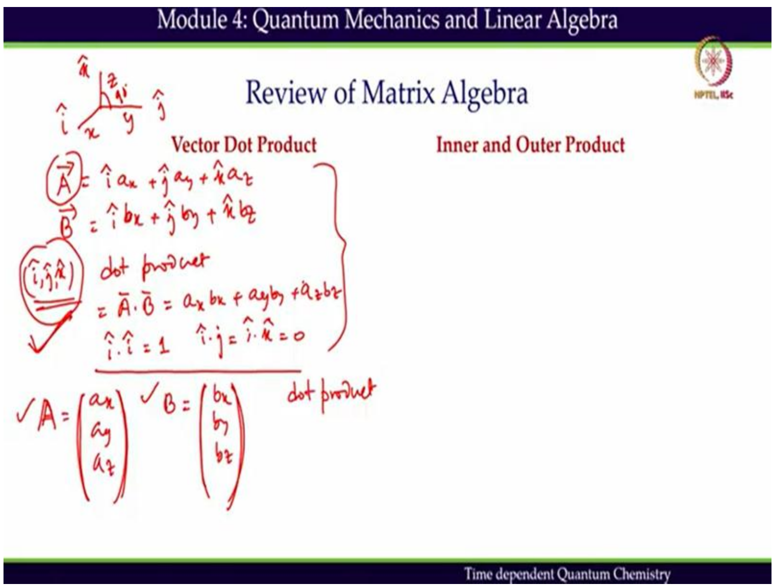

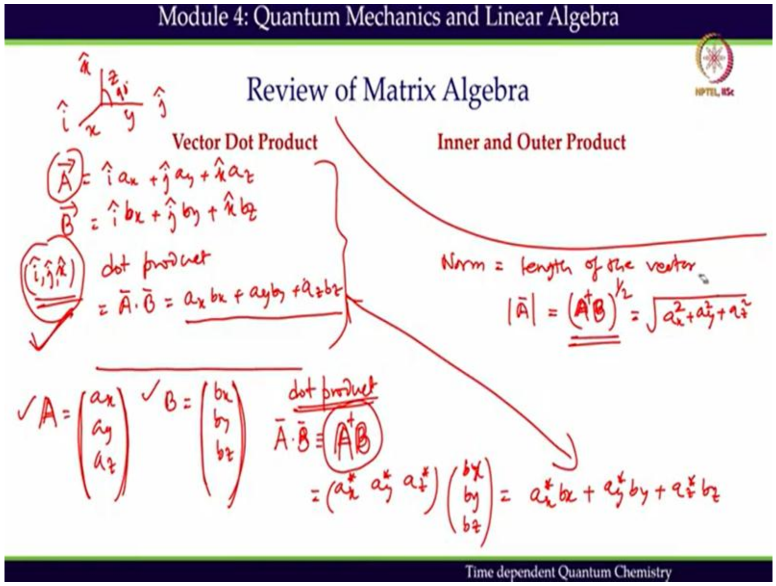

We will look at dot product, generally algebraic definition of vector, a vector is represented like this way in algebra $\vec{A} = \hat{i}a_x + ja_y + ka_z$, with cap they are representing the unit vector along that x, y, z axis. So, unit vector is going to be $\hat{i}, j, k$. So if we do that and then B vector another vector can be represented by $\vec{B} = \hat{i}b_x + jb_y + kb_z$ e we are representing the vectors with the help of $\hat{i}, j, k$ basis.

And algebraic definition of dot product, so we can take the dot product as $\vec{A}.\vec{B} = a_x b_x + a_y b_y + a_z b_z$, $\hat{i}.\hat{i} = 1$, because they are parallel but $\hat{i}.j = \hat{i}.k = 0$ because they are perpendicular, it becomes $1.1\cos\theta = 0$.

So this is the definition comes from algebra and in the matrix form if I want to represent it as I have told you before this vector can be represented in the matrix form when I represent the vector in matrix form it becomes a column matrix $A = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$ and B becomes a column matrix $B = \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix}$. These are represented with respect to this basis often we do not mention that one implicitly , we keep it hidden in when we are describing the matrix representation of a vector assuming that we know what kind of basis we are using.

But we have to remember that the actual terminology or actual construct of the statement should be following. This vector A and B has been represented with using these column matrices with respect to this particular basis. If we change the basis the value of each element will change. So let us see what does it mean by this dot product if we do the dot product it means that I have to reach this expression.

And this expression can be obtained by taking like this way $\vec{A}.\vec{B} = A^{\dagger}B$

$$\vec{A}.\vec{B} = A^{\dagger}B = \begin{pmatrix} a_x^* & a_y^* & a_z^* \end{pmatrix} \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} = a_x^* b_x + a_y^* b_y + a_z^* b_z$$

And that is the definition of the dot product of two matrices which you get here is equivalent expression. So dot product has to be done like this way in in the matrix form.

And length of the vector is called norm of the vector and norm is represented by following. The norm is actually length of the vector and that is represented by, this is representation of the vector representation then we will go for matrix representation. Matrix representation is going to be $|A| = \left(A^{\dagger}B\right)^{1/2} = \sqrt{a_x^2 + a_y^2 + a_z^2}$ that is the way the norm would be represented in the matrix form, this is the matrix form of the of the norm.

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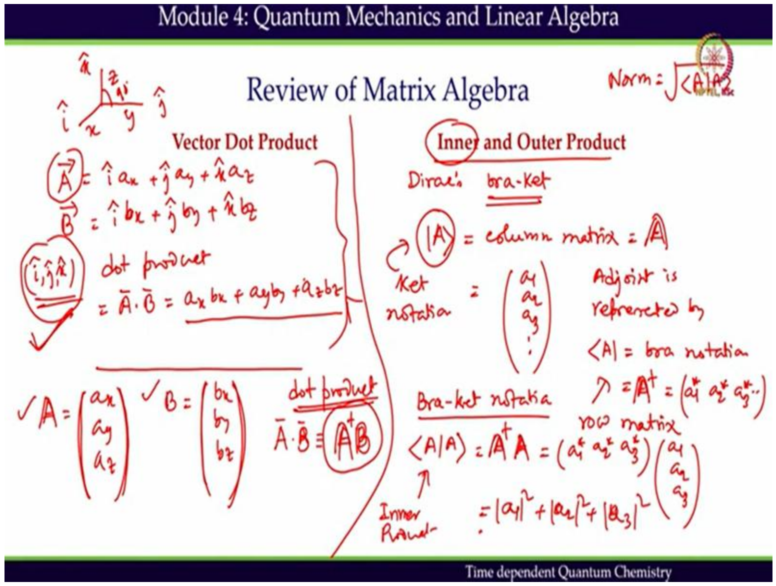

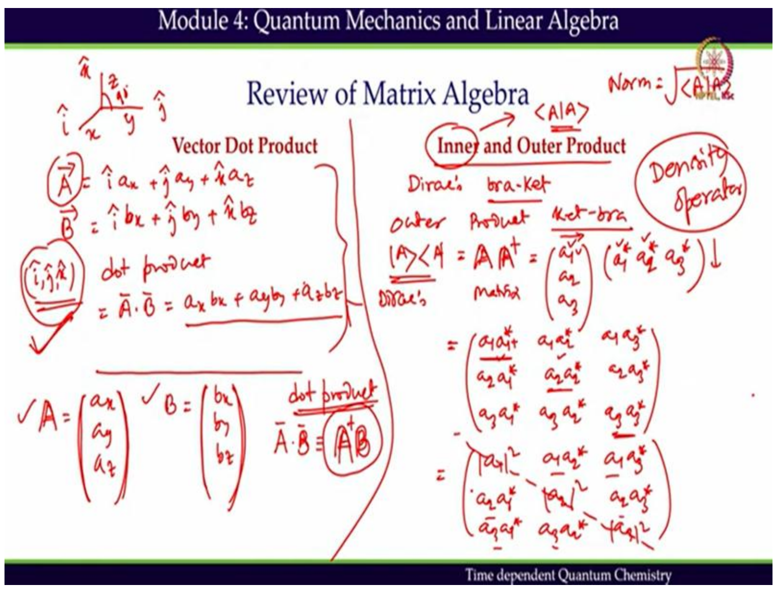

So we will now move to inner and outer product. A column matrix represents a vector I have already mentioned that one and if I use Dirac's bra-ket notation, in the bra-kat notation/Dirac notation this a the column matrix is represented by this notation it is nothing but $|A\rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}$ like this.

And adjoined is represented by so this is ket notation and it is the adjoint of it which means it is a $\langle A| = \left(a_1^* \quad a_2^* \quad a_3^* .... \right)$ like this it becomes a row matrix. So, this is represented by a row matrix. And when I say inner product, it is the bra-kat notation. So I use this bra-kat notation, inner product will be given by like this $\langle A|A\rangle = A^\dagger A = \left(a_1^* \quad a_2^* \quad a_2^* \right) \begin{pmatrix} a_1 \\ a_2 \\ a_2 \end{pmatrix} = a_1^2 + a_2^2 + a_3^2$

And norm is given by square root of this inner product. Similarly, I can define outer product as well and outer product is going to be following. I will have in this case I will not have bra-kat I will have kat-bra. So outer product is given by

is going to be column row matrix. So it is going to be a 1 star it a 2 star a 3 star and if I multiply matrix multiplication we have to employ and matrix multiplication can be done following way we have to always follow this way and this way. So if we do that then in the end we get this matrix a 1 a 1 star a 1 a 2 star a 1 a 3 star so we have to multiply this one first and this one then I am supposed to add this one next one next one multiplied by x one but that is 0 we do not have anything that is why we are getting only one term in this each element.

$$|A\rangle\langle A| = AA^\dagger = \begin{pmatrix} a_1 \\ a_2 \\ a_2 \end{pmatrix} \left(a_1^* \quad a_2^* \quad a_2^* \right) = \begin{pmatrix} a_1 a_1^* & a_1 a_2^* & a_1 a_3^* \\ a_2 a_1^* & a_2 a_2^* & a_2 a_3^* \\ a_3 a_1^* & a_3 a_2^* & a_3 a_3^* \end{pmatrix}$$

And after we get that we can further rewrite this matrix as this one is nothing but this one and this one all this diagonal elements can be represented by $\begin{pmatrix} |a_1|^2 & a_1 a_2^* & a_1 a_3^* \\ a_2 a_1^* & |a_2|^2 & a_2 a_3^* \\ a_3 a_1^* & a_3 a_2^* & |a_3|^2 \end{pmatrix}$. So, what we see is that in the diagonal term we get individual absolute square and in the off diagonal terms all these off diagonal terms we get the cross terms. So this kind of ket-bra notation will be used to represent the density operator we will go back we will come back to density operator later stage not right, now it is related to density operator. We will come back to this later but inner product, we have understood inner product is going to be bra-kat where I have presented like this way.

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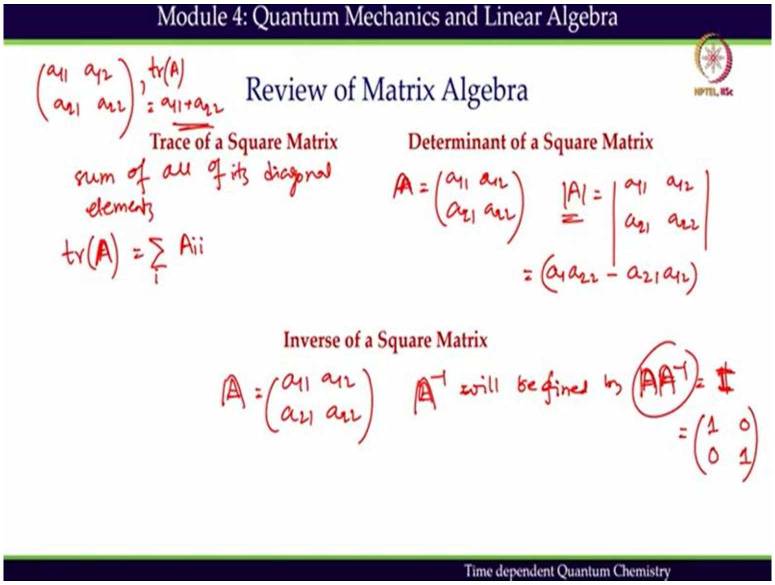

We will move on we will present the trace of a square matrix, it is the sum of all of its diagonal elements which means that I will write down, $tr(A) = \sum_i A_{ii}$, diagonal elements we have to sum.

Determinant of a square matrix if I have a matrix like this $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$, $tr(A) = a_{11} + a_{12}$,

If I have a matrix $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$ then determinant is given by this $|A| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{21}a_{12}$. This is called determinant of the square matrix.

Inverse of s square matrix if matrix looks like this $A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$, then inverse of the matrix A^{-1} would be given by, will be defined as $AA^{-1} = I$, if I matrix multiply a inverse that will give me an identity matrixm what is identity matrix? Identity matrix is nothing but the diagonal element is one, that is the way inverse of the matrix will be defined.

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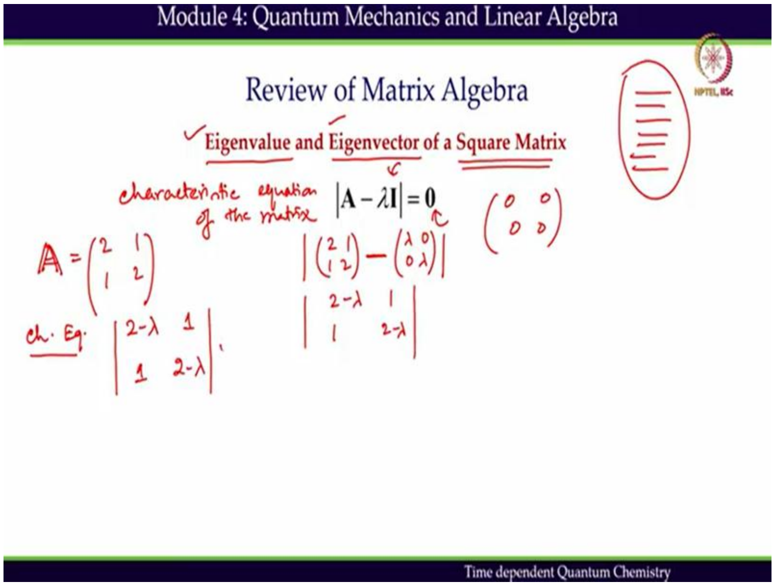

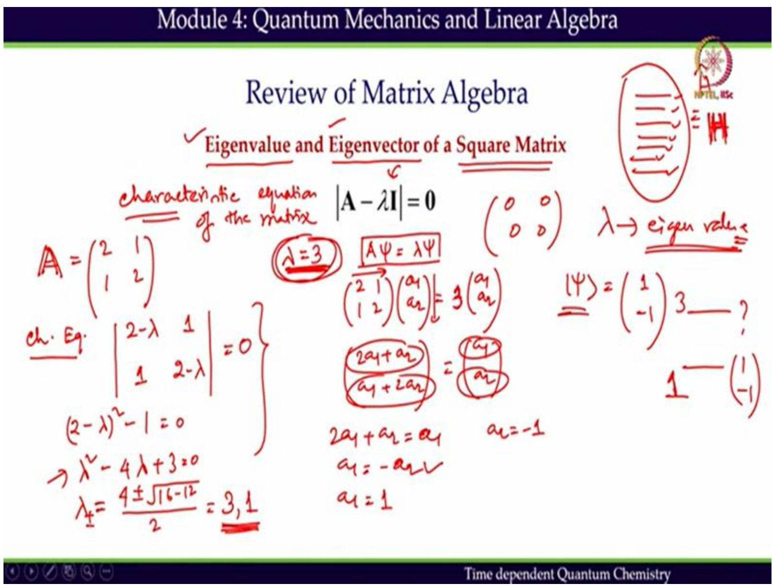

We will move on and we will explore now the Eigen value and Eigen vector of a square matrix. This is an important subject and in linear algebra and this is used very frequently to find out the eigenvalue and Eigen vector of the Hamiltonian operator. And Hamiltonian operator will be represented in terms of square matrix and the moment we represent it in terms of square matrix will be able to find out Eigen value and Eigen vector. Eigen vectors are Eigen states so which means that I will be able to get the different Eigen states or the spectrum of the system.

So this subject is very important, the Eigen values of a matrix can be computed from using this characteristic equation of the matrix, $|A-\lambda I|=0$ this is called characteristic equation. And this I is identity matrix or unit matrix I and this is 0 matrix or null matrix where all elements are 0. So, we will do one thing, we will take one example here to find out Eigen value, Eigen vector. So, let us say I have the matrix $A = \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$ a simple 2x2 matrix I have.

So $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{vmatrix} 2-\lambda & 1 \\ 1 & 2-\lambda \end{vmatrix} = 0$ this is the characteristic equation. So addition or subtraction, so first of all this is the scalar multiplication so will be able to multiply each element with this scalar once we are done then we can use this subtraction, subtraction is equivalent to the addition procedure where each element will be subtracted which means that I will be able to get $\begin{vmatrix} 2-\lambda & 1 \\ 1 & 2-\lambda \end{vmatrix}$. From the characteristic equation, $(2-\lambda)^2 - 1 = 0$ $\lambda^2 - 4\lambda + 3 = 0$.

$\lambda_{\pm} = \frac{4 \pm \sqrt{16-12}}{2}$ This is the root finding we are trying to find out the root with the general expression and I get finally the value is going to be 3 and 1, $_{\pm} = \frac{4 \pm \sqrt{16-12}}{2} = 3,1$. So λ has now 3 and 1 and what is λ, λ is the Eigen value which means that if I have an Hamiltonian operator which is represented now in terms of Hamiltonian matrix, once we represent it in in terms of Hamiltonian matrix, then I can find out just like this way will not follow this procedure there are other more convenient procedures are available not using this characteristic equation I will present it what kind of convenient procedures are available.

But let us say I have certain convenient procedure to get the Eigen values, once I get the Eigen values it means that I am getting all the energy levels. Here because it is 2x2 , I get only two Eigen values. Next would like to find out , λ and what is the associated with particular state λ equals one Eigen value, what is the Eigen vector or the wave function should look like? That can be represented by following we have this Eigen value equation $A\psi = \lambda\psi$ which is a wave function equals lambda wave function that is the Eigen value equation and in the matrix form.

How do I represent it in the matrix form will represent it a has been represented in terms of matrix 2x2 then psi is going to be unknown, it is unknown to me that is why I will write down a one a two remember I am now representing ψ in the basis of something and that basis is giving me this coefficient just like the way we have presented previously. So, this coefficients are with respect to certain basis, let us say the coefficients are a_1 and a_2 and which means that λ equals one and then a_1 and a_2 are unknown. $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 1\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$

So $|\psi\rangle = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$, and we get from the previous expression that $\begin{pmatrix} 2a_1 + a_2 \\ a_1 + 2a_2 \end{pmatrix} = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$

So now what will do we will equate the components of the vector on the left and right hand side if we equate it , $2a_1 + a_2 = a_1, a_1 + 2a_2 = a_2$

So, if I have $a_1 = -a_2$, because does not matter what basis we take finally we need the relative components. So, for a particular basis I may get $a_1=1$ and I get $a_2 = -1$, which means I have the wave function associated with this state that particular Eigen state will be represented by $|\psi\rangle = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$. One can suggest I do not want to use 1, I want to use 2 and then I can get $|\psi\rangle = \begin{pmatrix} 2 \\ -2 \end{pmatrix}$ that is also fine one can use that.

It does not matter what we use because depending on the moment we take 2 it means that I am changing the basis, depending on the basis I may get different coefficient. So, I am selecting one basis for which I should get 1 for a_1 and the moment I get 1 for a_1 , I get -1 for a_2 immediately. And we can represent that wave function by this way $|\psi\rangle = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ is go is going to be the representation and I have two states. So I have two states like this one state, I have given is $\lambda = 1$ another one is $\lambda = 3$ and it is this wave function will be represented $|\psi\rangle = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ for $\lambda = 1$ and we will see what is the representation for this $\lambda = 3$.

So for that we have to take lambda λ =3 so here we have to take λ =3 and if we take λ =3 then this is going to be 3.

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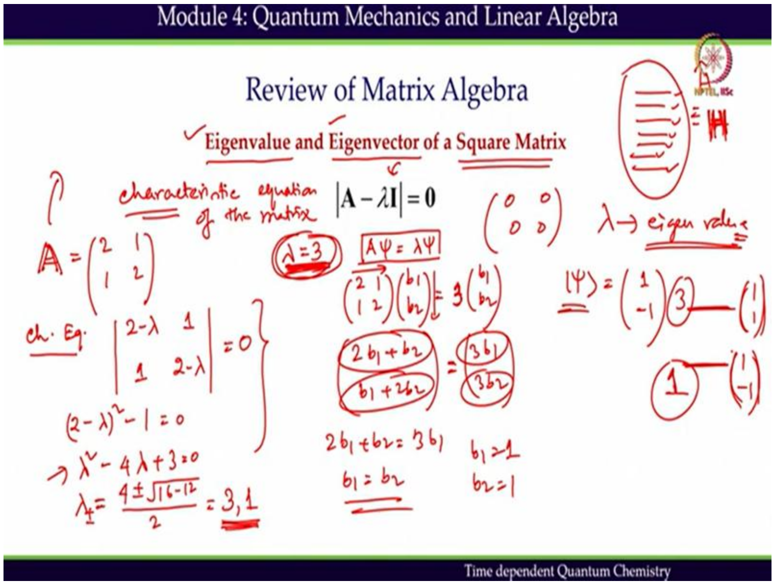

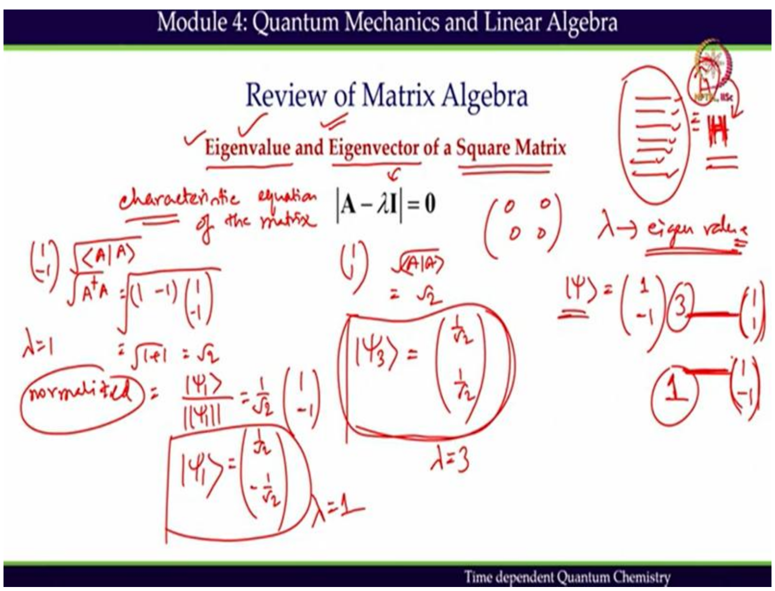

And if it is 3, then again we can use the matrix multiplication rule it takes a while to be familiar with this matrix multiplication part. So I suggest you to practice a lot. $\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = 3\begin{pmatrix} b_1 \\ b_2 \end{pmatrix}$.

$\begin{pmatrix} 2b_1 + b_2 \\ b_1 + 2b_2 \end{pmatrix} = \begin{pmatrix} 3b_1 \\ 3b_2 \end{pmatrix}$, $2b_1 + b_2 = 3b_1, b_1 + 2b_2 = 3b_2, b_1 = b_2$, If $b_1 = 1$, then $b_2 = 1$

.

$$|\psi\rangle = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

So, if a is represented by the Hamiltonian then I have two states and for these two states the first energy is going to be 1 second energy is going to be 3 with some unit. And each wave function associated with these states will be represented by this column matrix $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ and $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$. We will use heavily use this kind of matrix representation in this course, so going over this exercise would help to adapt the procedure.

So, now what will do we will find out the norm of the Eigen vectors. So, we have two states right now and we would like to normalize both states so that we can get the normalized wave functions. And associated with this $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$ we will get the norm how do we get the norm? Norm is given by inner product, $\sqrt{\langle A|A\rangle} = \sqrt{A^{\dagger}A} = \sqrt{\begin{pmatrix} 1 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ -1 \end{pmatrix}} = \sqrt{1+1} = \sqrt{2}$

Normalized wave function is given by $\frac{\psi}{\|\psi\|} = \psi_{Normalized}$, we have shown already. So this is nothing but $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$,. So this is the normalized wave function we have associated with λ =1.

Next, we will normalize the second state and the second state can be normalized in following way. We can again take the inner product which is second state is for $\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \sqrt{\langle A|A\rangle} = \sqrt{A^{\dagger}A} = \sqrt{\begin{pmatrix} 1 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \end{pmatrix}} = \sqrt{1+1} = \sqrt{2}, \frac{\psi}{\|\psi\|} = \psi_{Normalized}, \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$.

For λ =1, $|\psi_1\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$, For λ =3, $|\psi_3\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

So this is the two states we can represent with the help of matrix representation. So one thing is clear from this entire exercise that as long as we know Hamiltonian operator and as long as we can convert it to its matrix form the moment we get the matrix form, I can immediately calculate or find out its Eigen value and Eigen vectors and we can get normalized wave functions associated with that Hamiltonian. So normalized wave functions and Eigen states are giving the quantum states for the for the system.

So, finding out this Eigen value Eigen vector procedure is very important but often we will avoid this using characteristic equation of the matrix this procedure is rigorous procedure and it may not be useful for bigger metrics.

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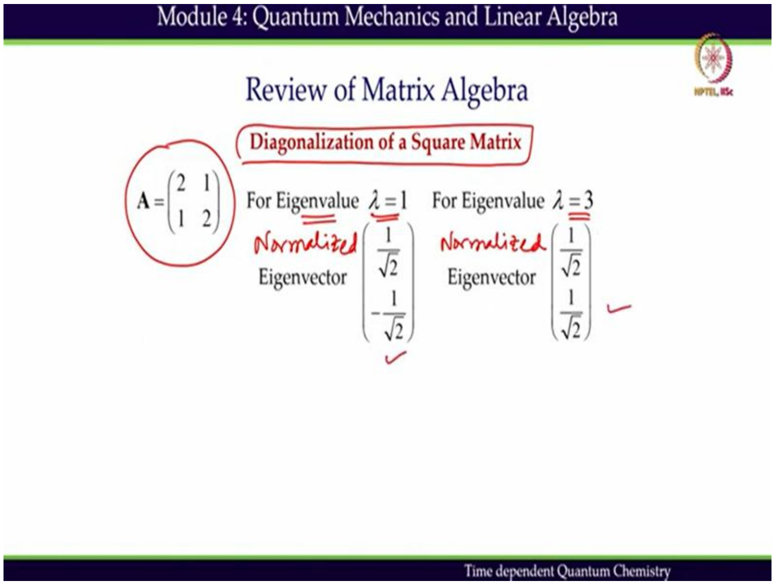

The more convenient way of doing is diagonalization of a normalized matrix. So, it is a diagonalizing diagonalization of a square matrix this is what we do and what is diagonalization I will explain it right now. We have seen that if I take this matrix this is just an example we are illustrating this example so that we can understand it for this matrix we have seen that the Eigen value is 1 and 3 and corresponding normalized vectors are like this.

For λ =1, $|\psi_1\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}$, For λ =3, $|\psi_3\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$

We will stop here and we will continue the discussion of diagonalizing of square matrix in the in the next session