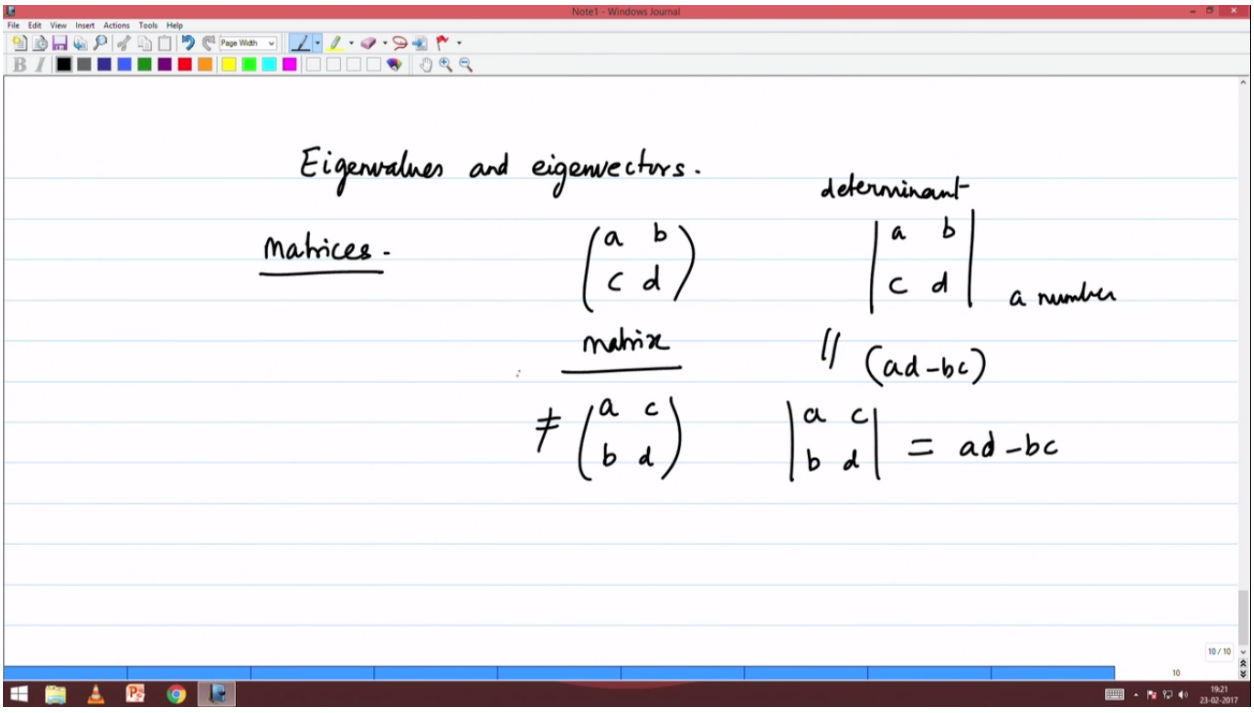
Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 27B
Operators, Commutators, Eigenvalues and Eigenvectors

Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

Welcome back to the lectures in introductory quantum and molecular spectroscopy. So let's get to the second part of the lecture 27 on operators commutator, eigenvalues and eigenvectors.

Now let's look at the eigenvalues and eigenvectors. These are associated with matrices. We are all familiar with the operations of matrices. I believe you know how to multiply matrices and you know how to add and how to those simple operations on matrices and if you have a square matrix for example given by the elements a, b, c, d then this is not the same thing as the determinant a, b, c, d this is determinant, this is a matrix. The matrix is a specific ordering or an array and that's unique to this. This is not the same as the array a, c, b, d. On the other hand a determinant like this is a number given by ad minus bc. Therefore if you write this determinant a, c, b, d this is also ad minus bc.



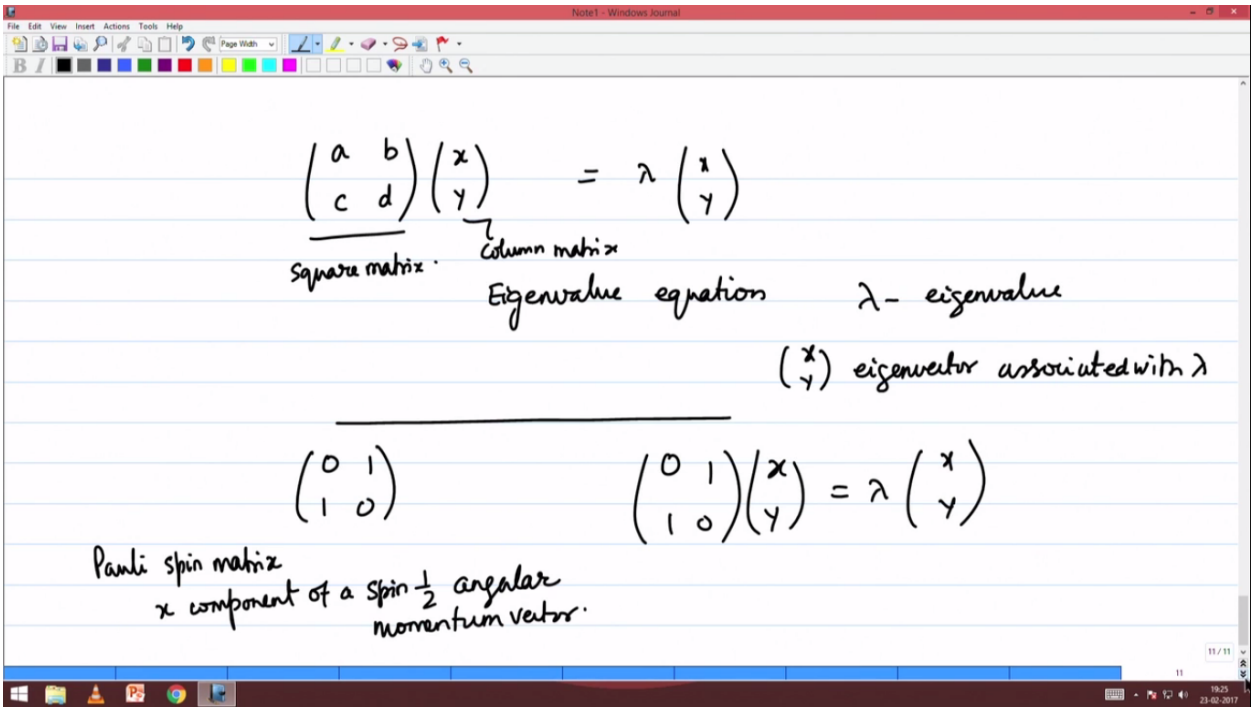
The determinants are equal but the matrices are not equal. So matrix represents specific arrays and therefore we have your whole algebra, linear algebra associated with matrices and the quantum mechanics has in the early days being developed by two different groups of researchers. The group following Schrodinger developed quantum mechanics as the solutions of differential equations and the mathematics associated with differential equations. That's what you saw. The group associated with Heisenberg, Max Born, and others developed quantum mechanics as a linear algebra problem as a problem of the matrices representing these operators as matrices and then worrying about the eigenvalues and eigenvectors of matrices. Today when you do quantum chemistry calculations on the computer 90-95% of the time you would be solving the molecular Schrodinger equation or the quantum chemistry problem as a matrix eigenvalue problem. Therefore in this brief lecture let me introduce what are called the matrix eigenvalues and eigenvectors.

This is the last segment of the quantum chemistry lecture that we have. The rest of the three weeks lectures would be on the molecular spectroscopy that we already started. However, let's look at eigenvalues.

So we'd start with a simple matrix a, b, c, d. If this is multiplied by a column or a vector this is a square matrix. This is a column matrix or a column vector. If we can find an xy such that when it multiplies a, b, c, d it gives you a constant times x and y that is the action of the matrix on the column x and y is the same as multiplying the column with a constant lambda. This equation is called the eigenvalue equation first in fact finding out lambda and xy such that this condition is satisfied is called the eigenvalue eigenvector problem and the lambda is called the eigenvalue and the column vector xy is called the eigenvector associated with lambda. Let's do that for two elementary matrices 0 1 1 0. This is a famous matrix.

It's also known as the Pauli Spin matrix in honor of Wolfgang Pauli contributed to the understanding of spins in quantum mechanics and later the general principle known as the

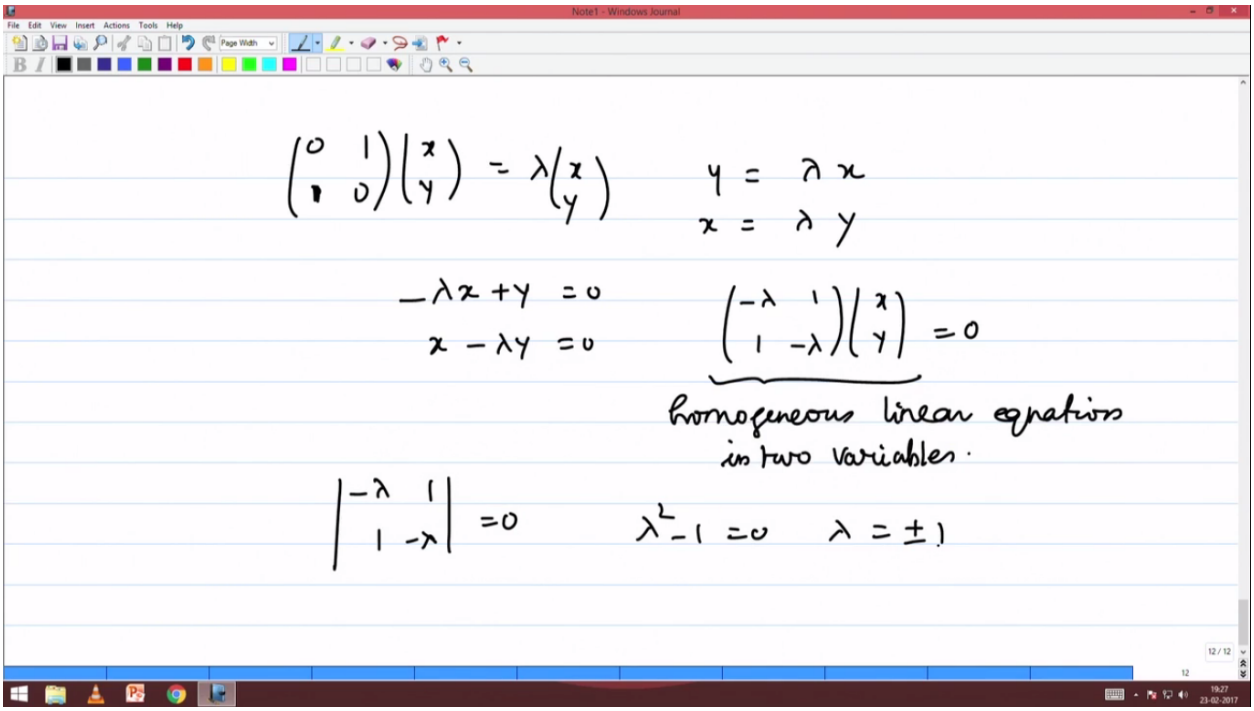
exclusion Pauli's exclusion principle and so on. Pauli Spin matrix the x component of spin 1/2 vector spin 1/2 angular momentum vector. Let's find out the eigenvalues for this matrix. It's very simple one so we will find out a column xy such that it gives you lambda times xy.



So the solution for this is very simple 0 1 1 0 xy if you expand this it is equal to lambda xy gives you 0 into x1 times y is equal to lambda x and then you get x is equal to lambda y.

So if you were to write this as an equation you have minus lambda x plus y is equal to 0. x minus lambda y is equal to 0 and that's writing this as a minus lambda 1 1 minus lambda xy is equal to 0. This is a homogeneous linear equation in two variables.

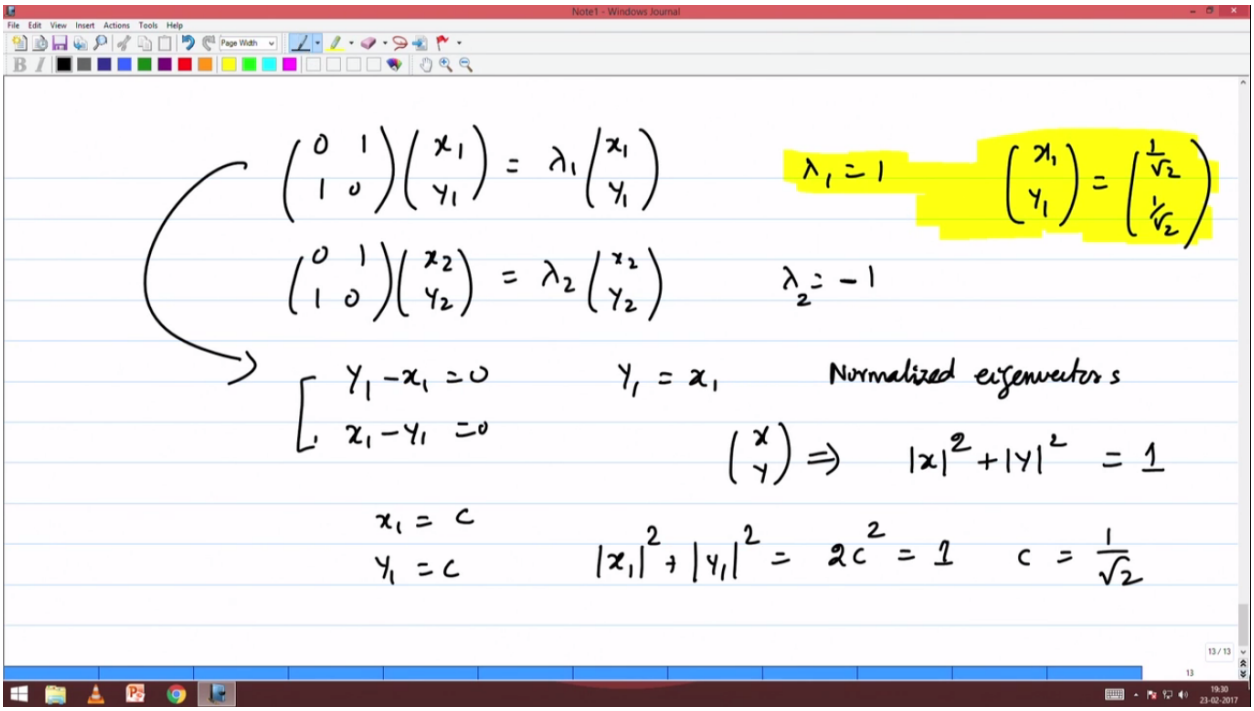
Therefore the solution for this equation exists only if the determinant minus lambda 1 1 minus lambda is 0 because the variables are now linearly dependent. There's no constant associated with them therefore x and y you need to know only one of them in order to get the other. Therefore they are linearly dependent and a linearly dependent coefficient matrix must have its determinant 0. So what's the determinant? It's lambda squared minus 1 that's equal to 0 or lambda is equal to plus or minus 1.



Therefore you have two solutions for the eigenvalue lambda and if you have two solutions for them then essentially what it means is that there are two eigenvalues and two eigenvectors. So you can call this as x1 y1 as lambda 1 of x1 y1 where lambda 1 is 1 the other is 0 1 1 0 x2 y2 is equal to lambda 2 x 2 y2 where lambda 2 is equal to minus 1 which is the other eigenvalue. So what's the solution? You have this is y1 minus x1 is equal to 0 for this first set. Lambda 1 is 1 and the second one is x1 minus y1 was equal to 0. So you see that these two equations are not independent. One is the negative of the other. That's what is meant by saying that these equations are linearly – these quantities are linearly dependent.

So you have only the solution y1 is equal to x1. Therefore you have to define one of them in order to get the other. So the constant is undefined the eigenvectors are always defined with what are known as the normalized eigenvectors. We require the eigenvectors xy to satisfy this requirement namely the absolute square of x and the absolute square of y is equal to 1 I mean the square root or square. These vectors are normalized to 1 therefore if we make that requirement then the solution if you call x1 to be some number like say c then y1 is also c then the absolute square of x1 square and the absolute square y1 square is 2 c square that's equal to 1 therefore c is 1 by root 2.

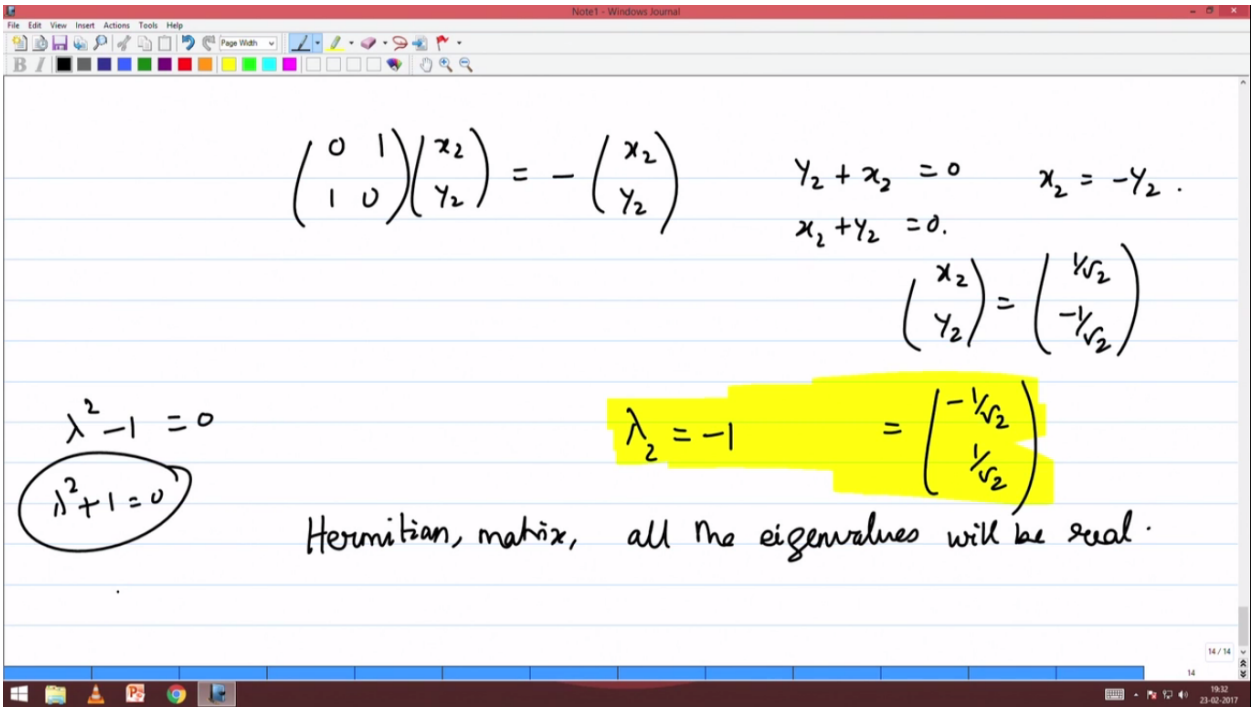
So x is equal to therefore the column vector x1 y1 or the eigenvector x1 y1 is 1 by root 2, 1 by root 2. The eigenvalue is lambda is equal to 1. So let's highlight that. So this is one solution to the eigenvalue problem that you have. It's easy to see that the second solution is in a similar way with the minus 1.



So you have 0 1 1 0 x2 y2 is minus of x2 y2 you can see that this is nothing other than y2 plus x2 is equal to 0, x2 plus y2 is equal to 0 therefore x2 is equal to minus y2 and keeping in mind the normalization constant you can immediately write x2 y2 as 1 by root 2 minus 1 by root 2. It does not matter whether you write it this way or whether you write it minus 1 by root 2, 1 by root 2.

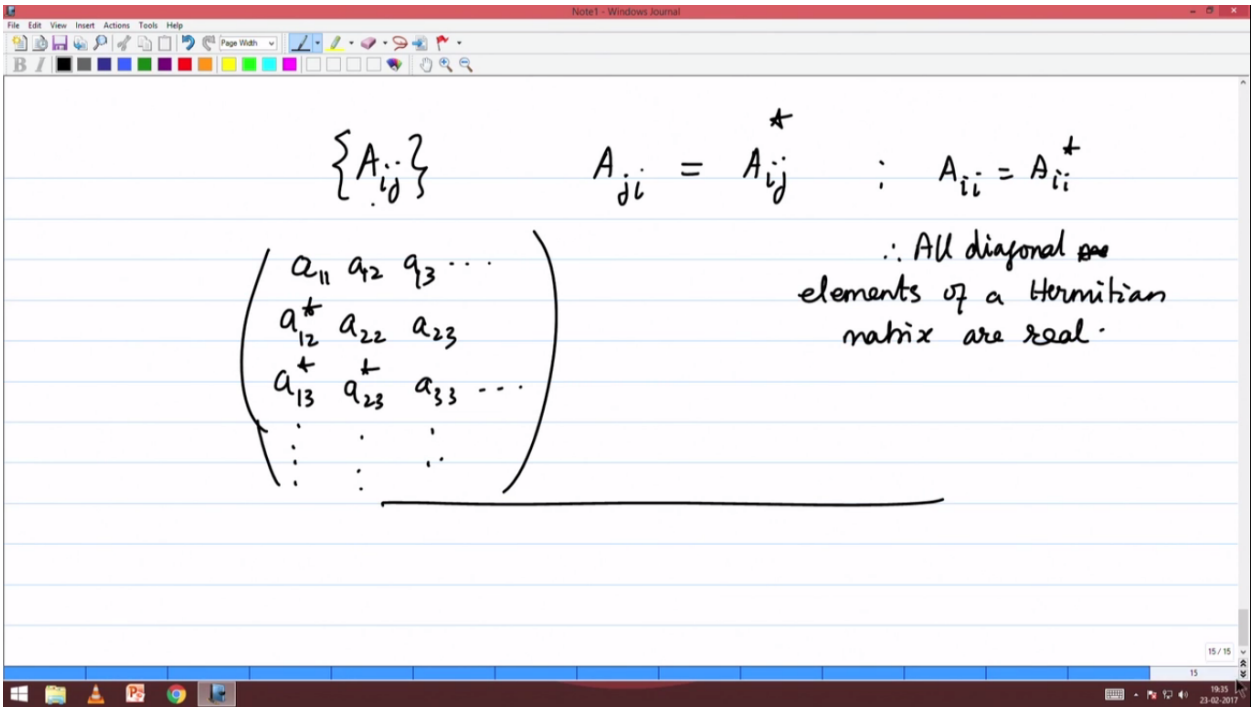
It does not matter because the overall sign is irrelevant to the conditions of the eigenvector namely y2 plus x2 is equal to 0. If both y and x are changed by a sign the equation is still valid. Therefore the eigenvectors are defined with respect to a constant arbitrary constant. They are defined with respect to an arbitrary phase or a sign and therefore we ensure that the signs are taken in a way that's convenient to us and it's consistent. So the two eigenvectors that we have with the eigenvalue lambda 2 is equal to minus 1 you can see that the second eigenvector is this and this matrix hass only two eigenvalues and two eigenvectors. In general a matrix which is n by n will have n eigenvalues and n eigenvectors. It's possible that some of the eigenvalues are the same. In such cases we say that the eigenvalues are degenerate and determination of the eigenvectors is a bit tricky.

One has to carefully go through the degeneracy requirement. Otherwise an operator if it is represented by a matrix that's a connection to this problem. If it is represented by a matrix the eigenvalue for that operator is given by all the eigenvalues that the matrix will have and we have a theorem it says that if the matrix is Hermitian matrix all the eigenvalues will be real. It's a quadratic equation that you will solve. You remember the quadratic equation you solve was lambda square minus 1 that's equal to zero.



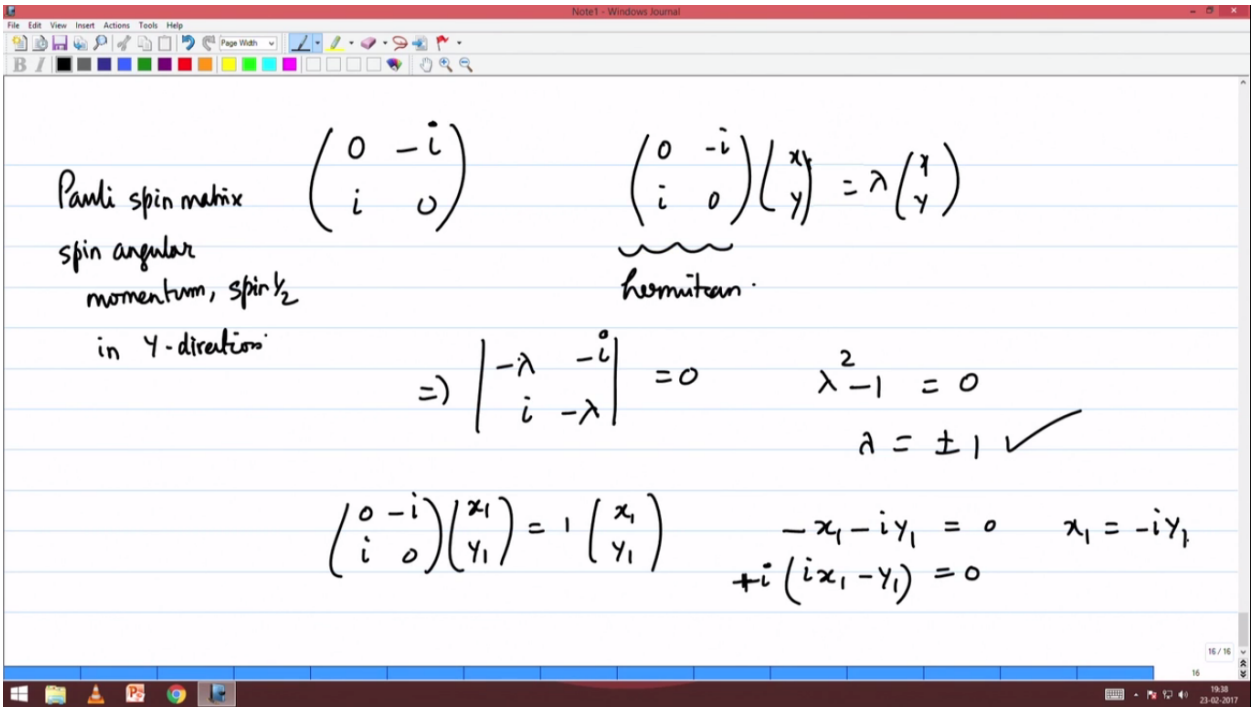
If you have another matrix in which the solution is to be solved by lambda square equal plus one is equal to zero if that's the quadratic equation you know that lambda is nothing but plus or minus i which is square root of minus one. That's a complex eigenvalue or imaginary eigenvalue. Therefore the fact that we have real eigenvalues for this particular matrix is associated with the fact that the matrix is a Hermitian matrix. What's a Hermitian matrix? I think all of you know that if I have a matrix and its elements are written as Aij, ith row and jth column for a Hermitian matrix Aji is equal to Aij star if the elements are complex. Therefore you have to have something like this. If you have a1, a2, a3 then the row must have a11, a12, a13 to indicate that these are the rows and columns write this as a12 star, a13 star this is the requirement for a Hermitian matrix and a22, a23 this will be a23 star, a33 and so on. Therefore the matrix element must satisfy this relation.

By this requirement you know that Aii is equal to Aii star, therefore all diagonal matrix elements – all diagonal elements of the Hermitian matrix are real. Let's see one example of that for getting the eigenvalues and eigenvectors.



Let's consider the matrix 0 minus i i 0 this is again Pauli Spin matrix for the spin angular momentum of a spin 1/2 in the Y-direction. So if you have to look at the eigenvalues of this it's a zero minus i i 0 xy is equal to 0 you know that this is a Hermitian matrix because the A12 is the complex conjugate of A21. Therefore we hope – we get only real eigenvalues. So if you have to write this the eigenvalue equation that's lambda times x,y and the eigenvalue equation is lambda square i into minus i is plus 1 therefore lambda square minus 1 is equal to 1 lambda is equal to plus or minus 1.

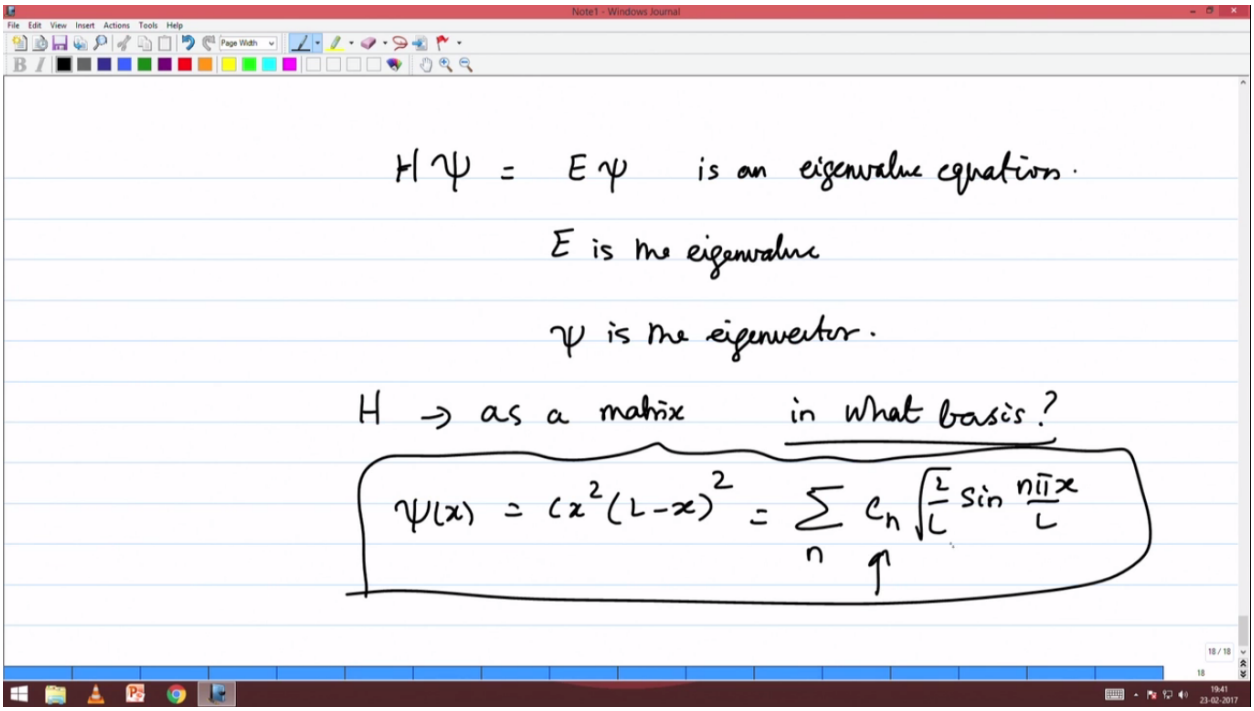
Therefore again the eigenvalues are plus or minus 1 for this matrix and the eigenvectors in a similar way can be obtained. Let's do that now. 0 minus i i 0 x1 y1 is equal to plus 1 x1 y1 so this gives you the equation minus x1 minus iy1 is equal to 0 if you bring that here and likewise this gives you ix1 minus y1 is equal to 0. Remember this is the same as this equation because if you multiply this by minus i you get this equation. You get this minus i no plus i. If you multiply this way plus i you get minus and you get a minus i; so these two are linearly independent. So you have x1 is equal to minus iy1.



And now you see why the absolute squares are important in the definition of the normalization. So you can see that that will give you still 1 plus 1 times c squared that's equal to 1 which means c is equal to plus or minus sorry c is equal to 1by root 2, 1 by root 2. So the eigenvector is x1 is minus iy1 therefore if we choose x1 to be y1 to be 1 by root 2 then x1 is minus i by root 2. If you multiply both of them by i you get i by root 2 and 1 by root 2. So the column vector x1 y1 can be written as 1 by root 2 i by root 2.

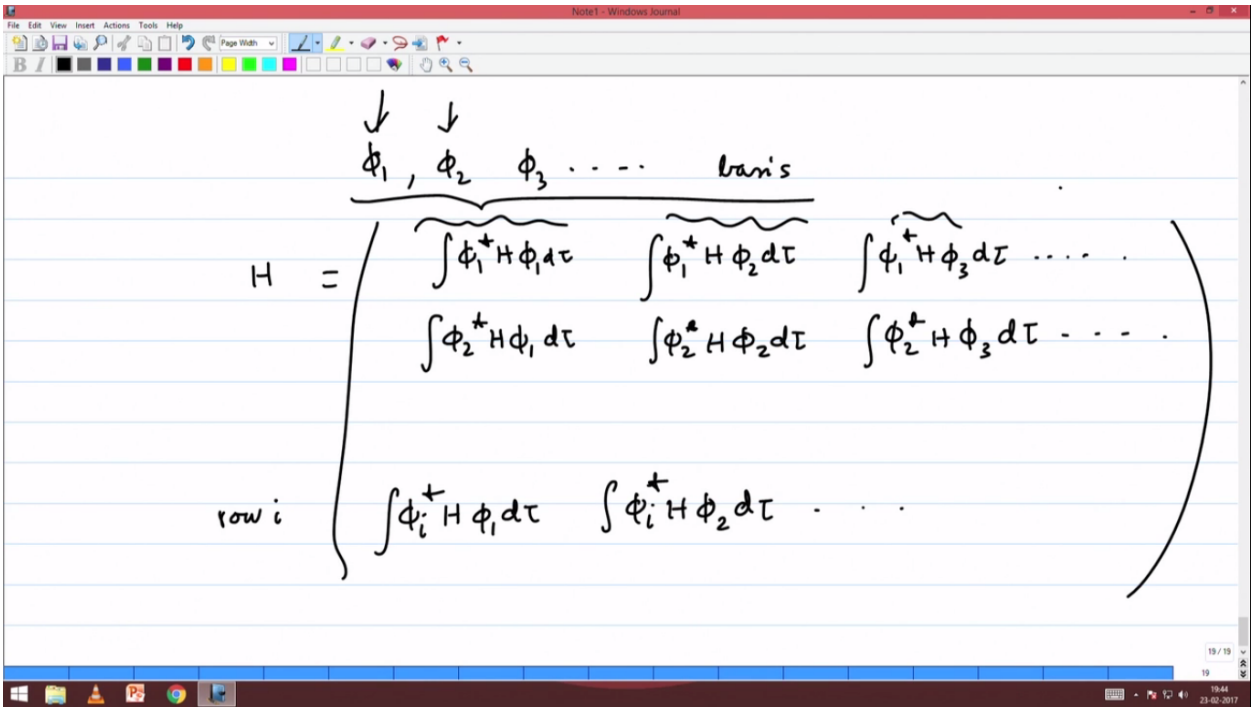
In a similar way you can find out the second column x2 y2 for the eigenvalue lambda is equal to minus 1 as 1 by root 2 minus i by root 2 or if you want to keep the --- I mean this is fine. This is the eigenvector. This is the eigenvector. So these are the eigenvalue, eigenvectors associated with a simple 2 by 2 matrix. What's the quantum mechanics? The quantum mechanics is that h Ψ is equal to E Ψ is an eigenvalue equation. E is the eigenvalue. Ψ is the eigenvector.

Now the solution of this therefore requires h to be expressed as a matrix. In what form? In what basis? There has to be a basis in which h has to be written as a matrix. Now remember the particle in a box problem in which we had Ψ of x written as cx square into L minus x square we had given that and expressed to this sum over n cn root 2 by L sine n pi x pi by L.



Therefore for any arbitrary eigenfunction it's possible for us to express this in terms of unknown coefficients and some basis functions which have very specific properties like the orthogonality and the normalization. If we have such a set then the Hamiltonian can be expressed as a matrix in that basis. So the general form of the Hamiltonian matrix would be write it in terms of functions if he used phi 1, Phi 2, Phi 3, etc. as the basis then the Hamiltonian matrix would be integral Phi 1 star H Phi 1 d tau that will be the 11 element H11 let me write that later. The element Phi 1 star H Phi 2 d tau as a second element. Phi 1 star H phi 3 d tau this is the matrix representation for the Hamiltonian in the basis chosen as the basis with the requirement that Phi 1 star Phi 1 is equal to d tau is equal to 1 for all the other you can call it as i and i is 1 to n and if i is not equal to j then the integral Phi i star Phi j d tau is zero like the particle in one dimensional box where if this is n and this is m the n wave function and this is the m wave function then they are 0 if n is not equal to m. So there are examples that you have studied but this is a general formalism for quantum mechanics.

The Hamiltonian matrix can be expressed in this form. The second row will be Phi 2 star H Phi 1 d tau, Phi 2 star H Phi 2 d tau, Phi 2 star H phi 3 d tau and so on and therefore if you have row i if you have row i then the elements will be Phi i star H Phi 1 d tau, Phi i star H Phi 2 d tau and so on.



So this is the matrix representation for the Hamiltonian. The choice of the matrix representation is decided by the ease with which we can calculate these integrals all these quantities and then if the matrix is very large and if the basis function set is very large quantum chemistry tells us that we can -- there are procedures for calculating the eigenvalues and eigenvectors of such large matrices through numerical methods and by using computational chemistry and using high speed computers and so on. Therefore the mechanics that you have studied with the help of the basic differential equations for the particle in the 1-D box 2-D box and so on when you want to study them for more complex problems it's always easier to find a matrix representation for the Hamiltonian operator whose eigenvalues we are after and then use that matrix representation also to write all the operators as matrices and then look for eigenvalues and eigenvectors of these operators the Hamiltonian and other operators and so on.

Therefore, the process is of a differential equation turned over into a solution of the linear algebra and the basic ideas were explained here with the help of a two-by-two matrix where you spin a half system which has only two states plus and minus states as you would have studied in your school. The two states are represented in the operator form for the spin 1/2 as a 2 by 2 matrix. We used two of them but in general the algebra is very similar. It can be extended to n dimensions and many dimensions and today's computational chemistry programs basically use a program called the Gaussian which does this calculation very very efficiently and it has been developed by thousands of scientists working collaboratively and it's a commercial program also. Many many computational chemists use that to solve the eigenvalues and eigenvector problems of quantum chemistry.

Therefore this is the starting point for understanding quantum chemistry in a much more detailed way and we will relate that to a next course at some other time when I again give lectures on the advanced slightly more advanced methods but at this point we will stop with the quantum chemistry methods and from the next lecture onwards we will continue to the spectroscopy and I

request you to review lectures number. In the first week there were three lectures on spectroscopy please quickly review them and then continue with the next week's lectures on spectroscopy.

We will start with some of the elementary concepts in molecular spectroscopy in the next lecture. Until then thank you very much.