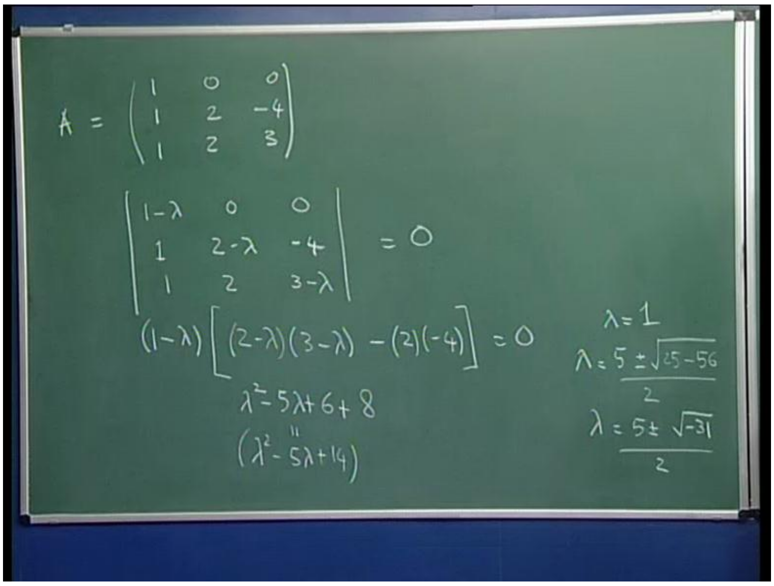
Mathematics for Chemistry
Prof. Dr M. Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 12

(Refer Slide Time: 00:22)

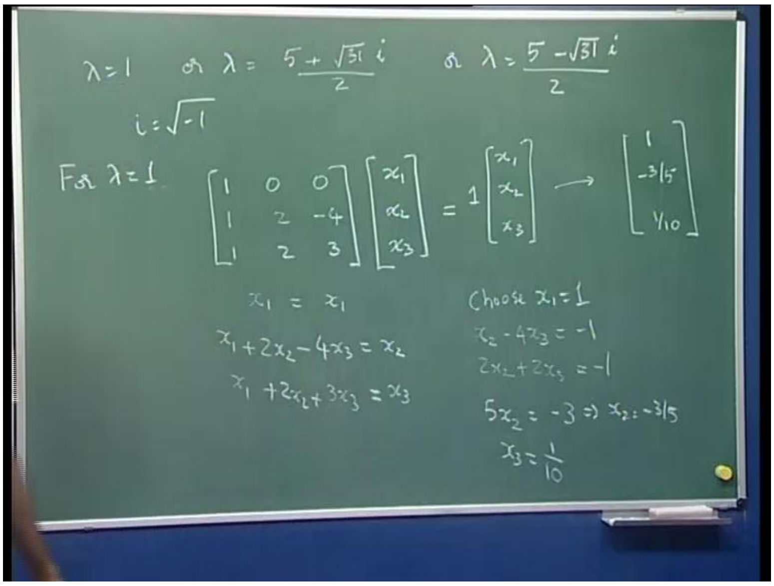


Let us look at an example of calculating the Eigen values in vectors of a matrix. Let us say you are given the matrix 1 0 0 1 2 minus 4 2, if you had given this matrix A is equal to this matrix let us see how we will calculate the Eigen values and Eigen vectors. So, in order to calculate the Eigen values, what we said is that we replace the diagonal elements by 1 minus lambda leave the of diagonal as they of 1 2 and we take the determinant of this matrix and we set it equal to 0.

So, when you solve this you will get a cubic equation and lambda and when you solve this you will get three roots corresponding to the 3 Eigen values of lambda. So, you work this out a cubic equation has roots, so the determinant will have only one term only one row contributes 2 minus lambda into 3 minus lambda minus 2 into minus 4 into 0. And straight away you can see that lambda equal to 1 is 1 Eigen value, so lambda equal to 1 and the other two Eigen values are given by the solutions of this equation. So, when you set this term to 0 you will get 2 more Eigen values.

So, let us work that out, so this gives you lambda square minus 5 lambda plus 6 plus 8. And this you can show that this is equal to lambda square minus 5 lambda plus 14. And when you solve this you will get lambda equal to 5 plus or minus square root of 25 minus 14 into 4 is 56 divided by 2 A, A in this case is just 2. So, we get one we get the second and we get the third Eigen value. So, if you work this out this comes to 25 minus 56 is minus 31, so 31 I, so lambda equal to 5 plus minus root minus 31 by 2.

(Refer Slide Time: 03:33)



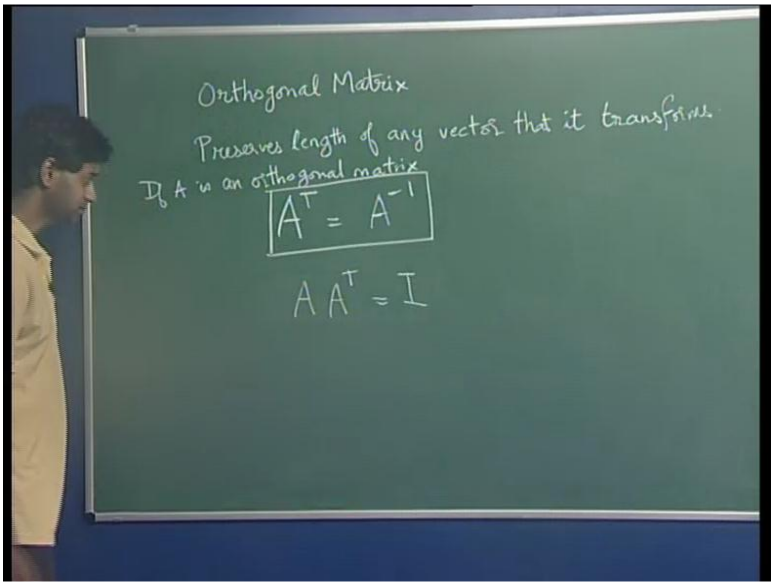
So, this root is an imaginary root, so lambda equal to 1 or lambda equal to 5 plus root 31 into i by 2 or so, this root is an imaginary root so, lambda equal to 1 or lambda equal to 5 plus root 31 into i by 2 or lambda equal to 5 minus root 31 i by 2, where is square root of minus 1. So, this gives a 3 Eigen values and given this three Eigen we can work out the three Eigen vectors, in order to solve for this Eigen vectors I will solve for the Eigen vector when lambda equal to 1. So, for lambda equal to 1 the Eigen vector is given by, so you substitute 1 0 0 1 2 minus 4 1 2 3 this is A.

If this Eigen value have so, let the Eigen value be x 1 x 2 x 3 and this has to be equal to 1 so, 1 times x 1 x 2 x 3. So, that implies so, the first equation will give you x 1 equal to x 1, second equation will give you x 1 plus 2 x 2 minus 4 x 3 is equal to x 2. And the third equation will give you x 1 plus 2 x 2 plus 3 x 3 equal to x 3. Now, turns out that you can not determine x 1 uniquely so, the Eigen values, the Eigen vectors we had already said that they can be determined only up to a constant.

So, let us choose x 1 equal to 1 for convenience will just choose x 1 equal to 1 and then what we have left it is two equations. The first equation if I rearrange it I will get x 2 minus 4 x 3 is equal to minus 1 and the next equation will give me 2 x 2 plus 2 x 3 equal to minus 1. So, these are the two equations and you can solve this for x 2 and x 3 and you can easily see that 5 x 2 is equal to minus 3 implies x 2 equal to the minus 3 by 5. And if x 2 is minus 3 by 5 then you show that minus 6 by 5 so, this is 1 by 10.

So, x 3 has to be 1 by 10 then this minus 3 by 5 and 1 by 10 into minus 4 will give you minus 4 by 10 that is minus 2 by 5 so, the they add up to give you minus 5. So, the Eigen vector is 1 minus 3 by 5 and 1 by 10 so, corresponding to Eigen value 1 your Eigen vector is 1 minus 3 by 5 and 1 by 10, and in this way can calculate the remaining 2 Eigen values also. Next now in the last part of discussion on matrices we will discuss, few special kinds of matrices and the kinds of special matrices will be talking about are they have special properties.

(Refer Slide Time: 07:41)

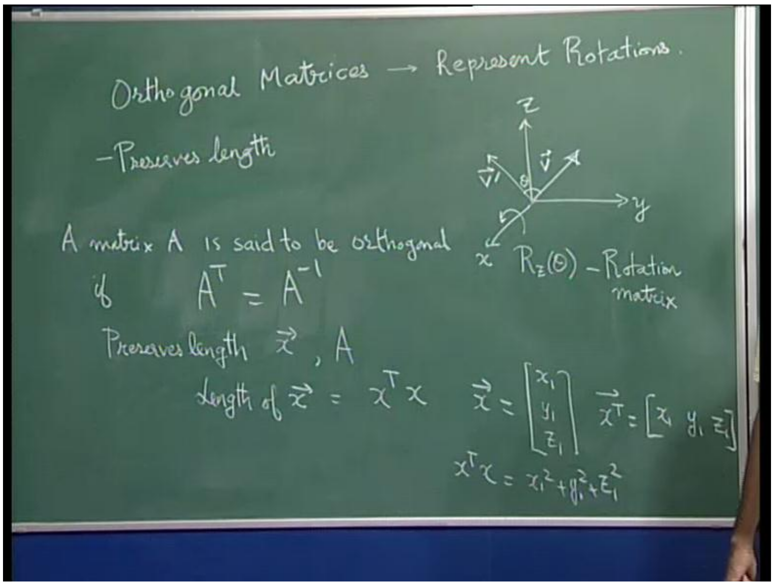


So, the first kind of matrix is for this called an orthogonal matrix, this is related to what we had talked about earlier about the rotation matrices. If you remember at that time we had said that the matrix of rotations, we had described matrix which describes rotation of a vector in three dimensions, and rotation is an operation that preserves the length of the vector. So, an orthogonal matrix is a matrix that preserves length of any vector that it transforms.

Now, we can think of length for a three dimensional vector but, however if we go to higher dimensions then the meaning of length of a vector might not always be clear, so will look at the mathematical definition of an orthogonal matrix. So, an orthogonal matrix is a matrix, so A if a is orthogonal matrix then the transpose of A is equal to it is inverse. So, this is the definition of the orthogonal matrix, so you take the transpose of A it is the same as the inverse of A.

In other words if you take A and multiplied by A transpose, you will get the identity matrix. So, if you multiply A by A transpose you will get nothing but, the identity matrix. So, next will discuss a few special matrices and this special matrices are matrices that are often used in many applications and they are special, because the matrix satisfies certain properties.

(Refer Slide Time: 10:10)



So, the first kind of special matrix, that we will be talking about are, what are called as orthogonal matrices. Now, orthogonal matrices can be thought of as matrices that represent rotations and this is in the following sense when we, has discussed the matrix of rotations what we had said is that if you had a vector in one coordinate frame. Now, if this vector was v when you rotated it by some angle about, some axis let us say you rotated by theta about the z axis and you got the vector v prime.

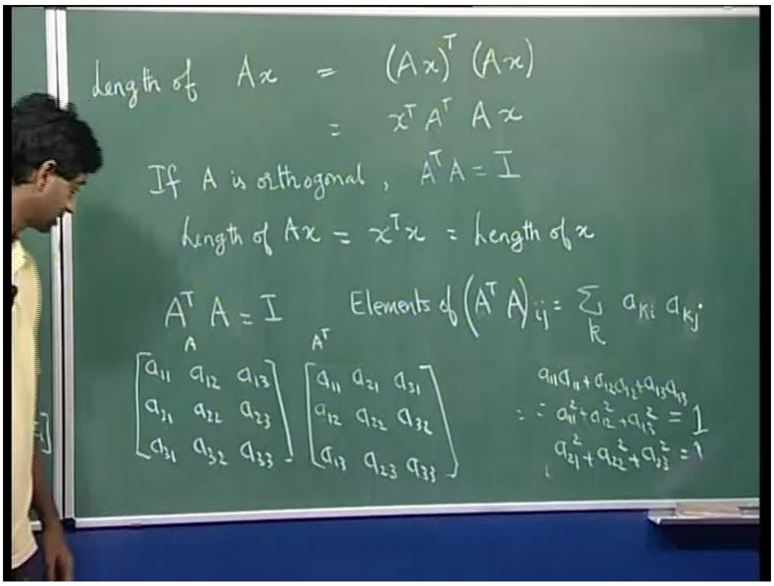
Then you could represent v prime as a matrix multiplying v and that matrix was called the rotation matrix. So, we had a matrix which you called R z the theta was the rotation matrix. And the rotation matrix has a property that any that the rotation operation preserves the length of the vector. So, then length of the vector was unchanged even though the components of the vector changed after rotation, so an orthogonal matrix is a general matrix, that preserves the length of the vector.

So, it preserves length, so the way now we are mainly thinking in terms of a matrix as an object that transforms a vector into another vector and an orthogonal matrix is matrix that preserves the length of the vector before and after the transformation. Now, the ideal of length is something that make sense when we are talking about vectors pointing in space. So, for two dimensions or three dimensions we can talk about length of vectors.

But, if we have vectors staying in other dimensions then we need a more general definition of the term orthogonal. So, the general definition of orthogonal is the following A matrix A is said to be orthogonal if A transpose equal to A inverse. So, the inverse of A is same as a transpose of A and if a, matrix satisfies this property then you can easily show that when a transforms a vector it will preserve the length of the vector.

So, will show that in a minute let us, so this preserves the length and the way to see that is the following, suppose you had a vector A, a vector x and you had this matrix A then the length of x is given by x transpose x. So, you pre multiply by the transpose so, if x is a vector that has various components x 1 y 1 z 1. So, if x vector is this, then x transpose is equal to x 1 y 1 z 1, and if you do x transpose x you get nothing but, the dot product. So, x transpose x 1 square plus y 1 square plus z 1 square. So, the length of x is x transpose x.

(Refer Slide Time: 15:15)



Now, when you transform the vector you will get A times x and the length of A times x is equal to A x transpose A x. And this is same as, A x transpose is x transpose A transpose. So, the transpose of a product of two matrices, is the product of the transpose in the opposite direction. And A x. So, I write A x in this form and now if the matrix is orthogonal a transpose a equal to identity. So, A transpose equal to A inverse and therefore, A transpose multiplies by A is nothing but, the identity matrix.

So, then the length of A x is equal to x transpose identity x, so x transpose x, so equal to length of x. So, we showed that the matrix A if it is orthogonal it will preserve the length of the vector and vice versa if it preserve length of the vector then the matrix a is called an orthogonal matrix. Now, we notice that A transpose A is identity, so A transpose A equal to identity so, now A transpose into A is a matrix the elements of A transpose A are. So, the elements of A transpose A, so these elements are given by some over k so, a k i a k j.

So, if you take A transpose A if I had if a times a then it would be a i k a k j but, now instead of a I have A transpose. So, have to take a k i times a k j so,; that means, if the i j th element is equal to this. So, the i j th element of this A transpose A is given by a k i a k j some over k. Now, it is instructive to look at what this means so, this a 1 and a trans, so this is A and A transpose is given by, and now if you take the elements of this product what it means is you take one row if you want to calculate this element.

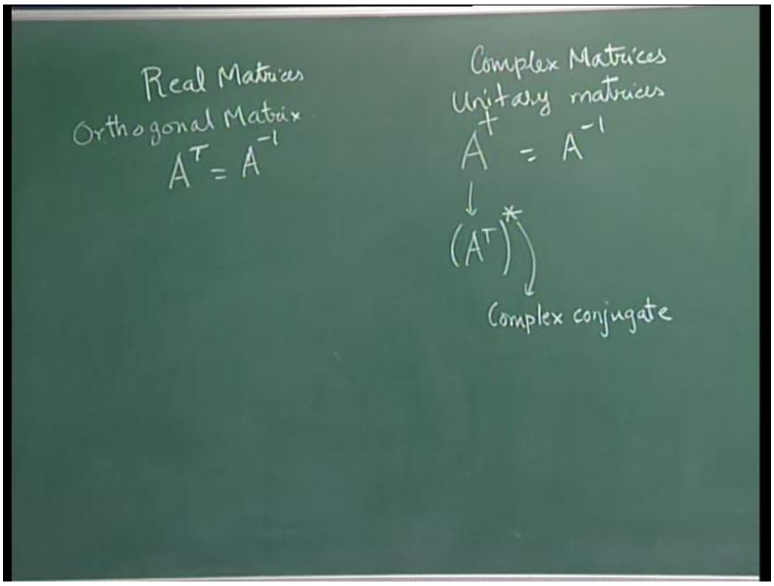
If you want to calculate 1 1 th element then you take the first and multiplied by the first column. So, that is a 1 1 a 1 1 plus a 1 2 a 1 2 plus a 1 3 a 1 3 so, what this means is that it means so, the first element is given by a 1 1 a 1 1 plus a 1 2 a 1 2 plus a 1 3 a 1 3 and this is equal to a 1 1 square plus a 1 2 square plus A 1 3 square. And so, the sum of squares of elements of any row this has to be this is diagonal element and this has to be equal to 1.

So, the first element of this product is a 1 1 into a 1 1 plus a 1 2 into a 1 2 plus a 1 3 into a 1 3. So, a 1 1 square plus a 1 2 square plus a 1 3 square it has to be equal to 1 similarly, if I take the two, two element of that I will get a 2 1 a 2 1 a 2 2 a 2 2 a 2 3 a 2 3. So, similarly, a 2 1 square plus a 2 2 square plus a 2 3 square is equal to 1 and you can also show the same for a 3 1 square plus a 3 2 square plus a 3 3 square has to be equal to 1.

So, if the matrix is orthogonal then the sum of elements of any row have to add up to 1. And you can also show that the sum of elements of any column have to add up to 1, so the sum of squares of elements of any row or column have to add up to 1. Secondly, now if I take the one two element so, a 1 1 into a 2 1 a 1 2 into a 2 2 a 1 3 into a 2 3 and if you notice this is a 1 1 into a 2 1 so, a 1 1 a 2 1 a 2 1 comes here. So, it is product of these two similarly, it is the product the next element is the product these two, the third element is the product these two.

So, that means, if you take a dot product of any two rows you should get 0. So, an orthogonal matrix you should get 0 because all the of diagonal elements of the product of these two matrices is 0. So, an orthogonal matrix has a property that if you take dot product of row with itself you will get one and if you take dot product of any two rows you will get 0. That is the property of the orthogonal matrix, so for we have seen that the orthogonal matrix is given by A transpose equal to A inverse.

(Refer Slide Time: 22:18)

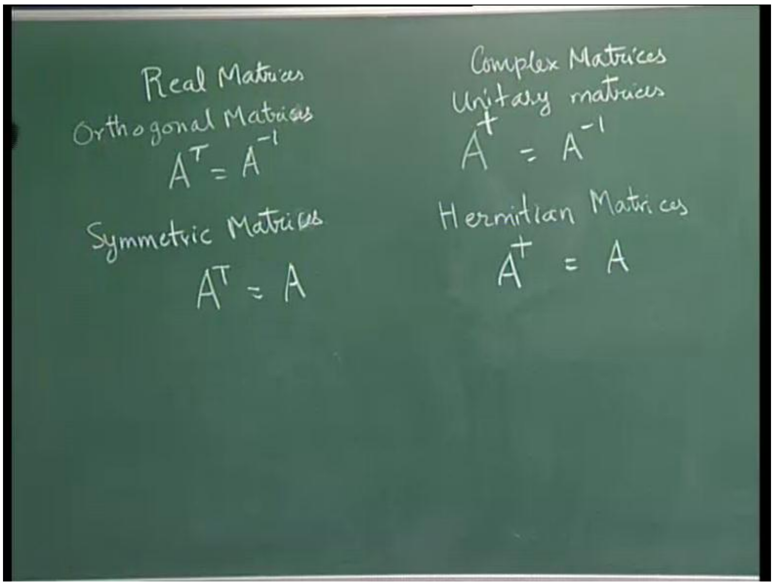


Now, if the matrix A is has complex number sum of it is elements if sum of the elements of a matrix are complex. So, this useful for real matrices for complex matrices, the useful definition it is not just transpose that useful. So, instead of transpose we use something called permission conjugate, which is represent by digger and this digger is basically transpose followed by complex conjugate, so this the complex conjugate. So, you first take the transpose of the matrix and then you take the complex conjugate of every element in the matrix.

So, for complex conjugate the equivalent of orthogonal matrices are called unitary matrices and unitary matrix has the property that the complex conjugate is equal to the to it is inverse. So, just as for real matrices the interesting matrices are the once which are orthogonal with because, they preserve the length for a complex matrix it is the unitary matrix that is interesting because in this case the length is always defined with a complex conjugate.

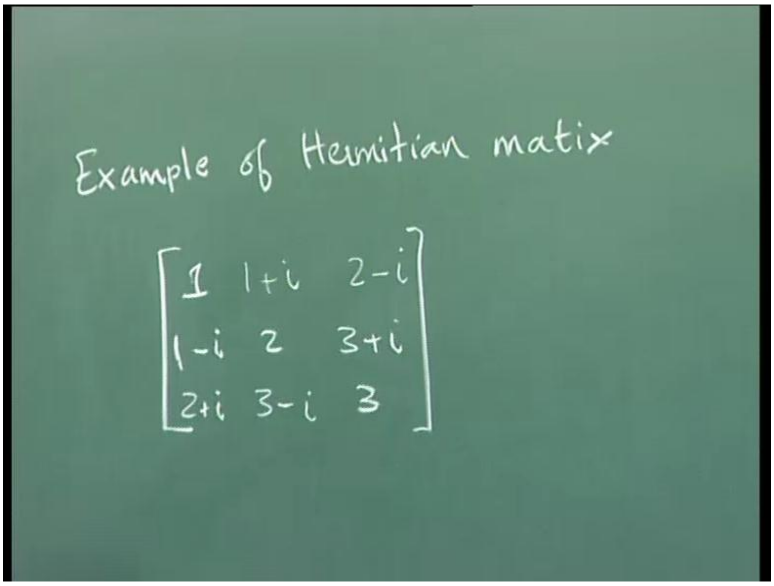
Now, there are some other special matrices that will just mention for completeness and will always mention the real matrix and the equivalent for complex matrices. So, I will just erase this here and we just note that this digger refers to complex conjugate or conjugate it is actually the commission conjugate. So, it is a transpose and a conjugate so, the next will define what is called as symmetric matrix.

(Refer Slide Time: 24:52)



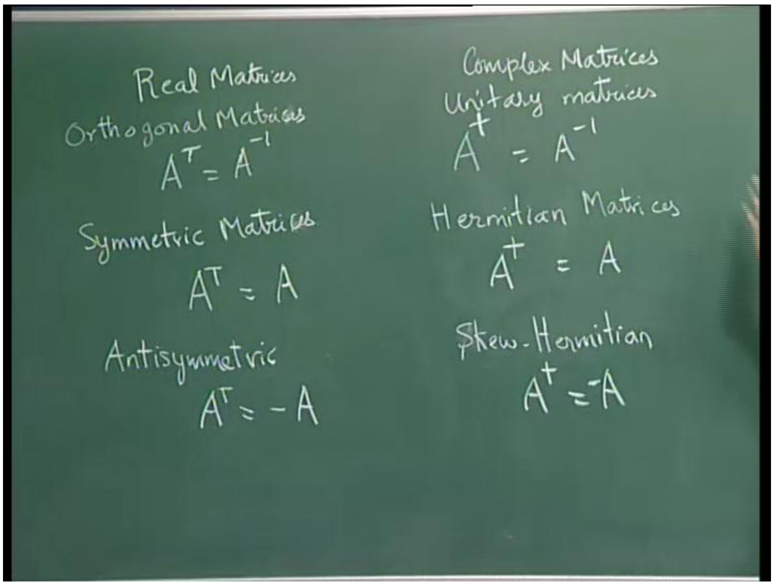
And a symmetric matrix is one for which A transpose equal to A. So, the off diagonal elements are equal to each other and for complex conjugate instead of symmetric matrices we use, hermitian matrices and for a hermitian matrix the conjugate transpose is equal to the matrix. So, the elements of the diagonal elements will be real and the off diagonal elements will be complex conjugate of each other so, an example of a hermitian matrix.

(Refer Slide Time: 26:00)



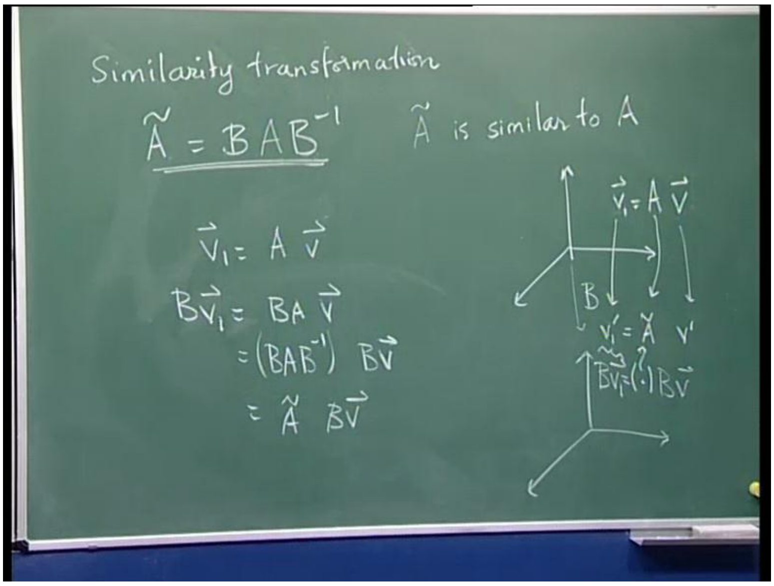
So, diagonal means have to be real then, so you notice that the diagonal elements will all be real and the off diagonal elements will be complex conjugate of each other. So, they will be complex conjugate of the corresponding of diagonal element.

(Refer Slide Time: 26:47)



Then just as your symmetric matrices you can also have an anti-symmetric matrix and in that case A transpose equal to minus A. So, the off diagonal elements are my they are related to each other by minus signs. And in this case you have an skew hermitian, so a skew hermitian matrix you digger equal to minus A. So, these are some of the special matrices that appear often in various discussions of matrices especial when we are especial in quantum chemistry we do lot of operation involving matrices and it is very important to know what these operations do. And these are various matrices that have certain special properties. Now, one application of these matrices is in what is called as similarity transformation.

(Refer Slide Time: 27:49)



So, if you have a matrix A and you define an matrix A tilde which is related to A by B A B inverse. So, if a matrix a tilde is related to a by this operation, so you first multiply by the matrix then you multiply by it is inverse. But, you do not multiply them together you multiply them on either sides. Then you say that A tilde is similar to A and this has certain implication on relation between these two matrices, what is of interest to us is that this is a way of transforming vectors from one coordinates to other.

This similarity transformation plays the role in transforming vectors from one coordinate to other. And it plays a role in the following way so, suppose you have a vector v and you operated by A and you get a vector v 1. So, in one coordinate system you operate by A on v and you get v 1 and a need not be an orthogonal matrix anything it just some operation that converts v to v 1. And these are defined in this coordinate system and now if we imagine that you transform the coordinates to some other coordinates.

So, operate by B and this transforms a vectors into a new coordinate system. So, in the new coordinate system you have B v so, v goes to b v and v 1 goes to b v 1, then what is the relation between these two how are b v 1 and b v related in the new coordinate system. So, what is this quantity that appears here. So, that is the question we will ask and what we will find is that the quantity that appears here is nothing but, a tilde.

So, in order answer this question we start with v 1 equal to A v, now, b v 1 equal to B A v and this is equal to B A v inverse in to B v. So, I put B inverse B here and so, this is equal to A tilde into B v so, the relation v 1 equal to A v becomes B v 1 equal to a tilde B v.

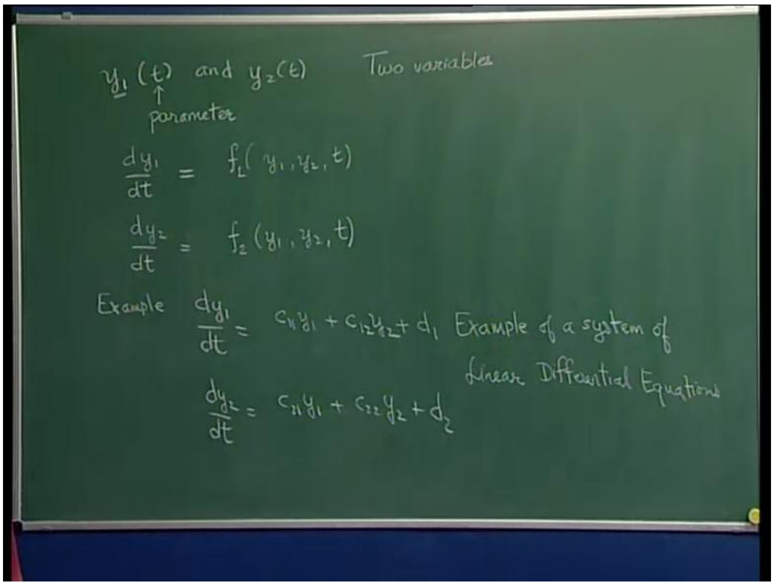
So, in the new coordinate system if I call this v 1 prime so, if v 1 goes to v 1 prime v goes to v prime then A will transform to A tilde. So, that the relation between v 1 and v is maintained so, in a way this is the way a matrix transforms when you transform the coordinates. So, just as the vectors transform when you transform the coordinates the matrix A also gets transformed in the new coordinate system. And the way it transforms is through this similarity transformation.

Now, if B is an orthogonal matrix then you can then B inverse can be replaced by B transpose and you have the corresponding similarity transformation. Similarly, if you are dealing with complex matrices you can define transformation by unitary matrix and so, on. And these are various tools that are used in the many areas of matrix of matrix algebra they are often useful ways to diagonalise matrices that is in other words to calculate it is Eigen values and Eigen vectors.

So, you can use the similarity transformation are often use we want go in to that in too much detail in the next class we will discuss and application of all the matrix methods. That the application that will discuss is related to molecular orbital theory and in particular a kind of molecular orbital theory called the hocl molecular obituary theory. We seen so, far how to solve first order differential equations and the strategy that we set is to first try to separate variables.

Then if you are not able to separate the variables then, you try to see if this can be formulated as an exact differential. And then if you not able to formulate it is as on exact differential then you try to look for integration factors and typically integration factors that depend only on one variable which can be either x the independent variable or y the dependent variable. And then using all this techniques you can get you can solve a large number of first order differential equation.

(Refer Slide Time: 34:37)



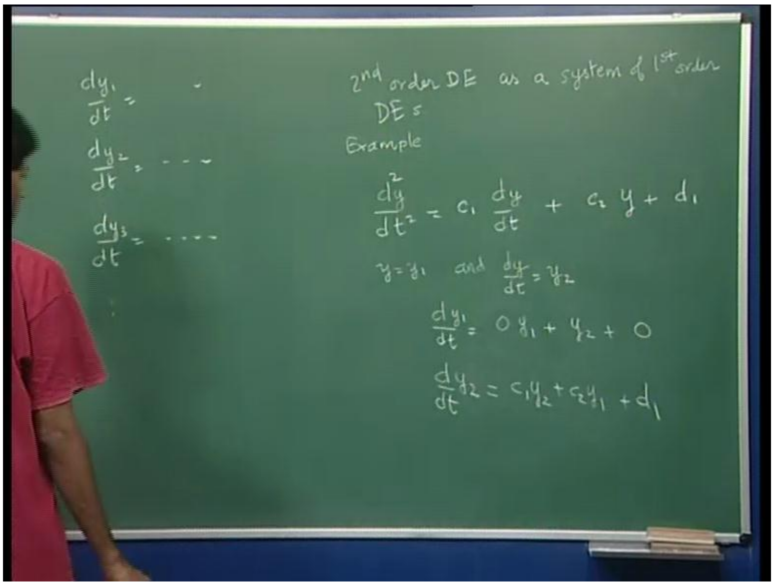
Now, sometimes times in many real problems you have not a single differential equation but, you have a whole set of differential equations involving different variables. For example suppose you have the variables y 1 which is the function of time and y 2 which is function of time. So, these are two variables both of them are functions of some parameter t i said time but, this is just a parameter. It could have been x i could call it x or anything else.

But essentially the physical problem consists of two variables that have functions of one variable. So, in such a case you might have differential equations for each of these variables so, you could have d y 1 by d t is equal to some function of y 1 y 2 and t. And some function of so, both y 1 both d y 1 by d t is some function of y 1 y 2 t and this is some other function of y 1 y 2 t. So, these are two different functions and such situations are very commonly encountered.

And if this function of y 1 y 2 t contains y 2 in it then you say that the two equations are coupled to each other. So, for example, this is one simple example where, d y 1 by d t has two terms one is proportional to y 1 and the other is proportional to y 2. So, c 1 1 c 1 2 c 2 1 and c 2 2 are constant. And this is one example of a system of differential equations so, this is an a system of I would say linear differential equations. And I say linear because the terms y 1 are proportional to y 1 or y 2. So, you only have linear terms.

You could have constant also in addition to this you could also have a constants. So, for example, you could also have plus d 1 so, this is an example of a system of linear differential equations. It is a and I showed only two equations but, you could have a whole you could have a very large system of linear differential equation. For example, you could have y 1 by d t is equal to something and so, on could have a whole set differential equations and. They could either be linear as in this case or they could be some other more complicated functions.

(Refer Slide Time: 38:05)



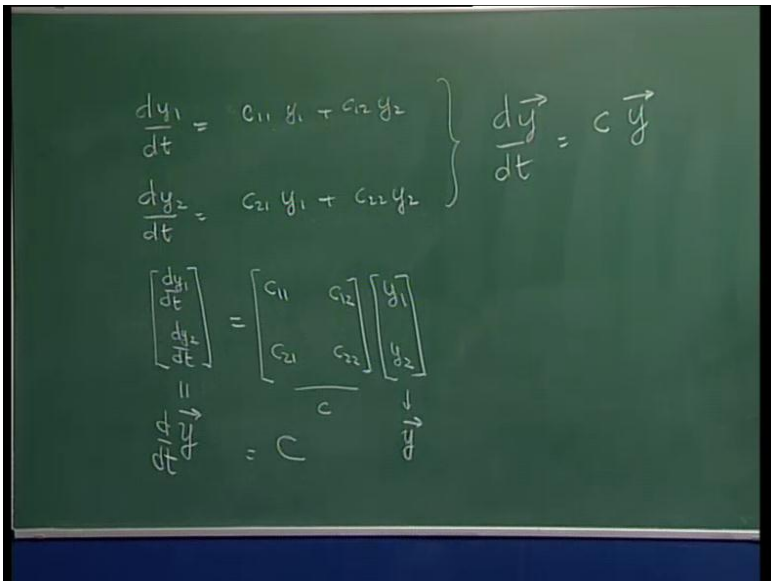
And these are commonly encountered in many physical problems. Now, one thing to note is the following that it is possible to write a second order differential equation as system of first order differential equations. So, the ideas is the following suppose I had a second order let us take an example suppose I had d square by 2 by d t square is equal to and say c 1 divide by d t c 2 y plus d 1. Suppose I had i had a second order this is a second order differential equation it involves second derivative of y first derivative y, y and a constant term.

Now, you can write this as a system of differential equations if you use the following idea. So, you use y is equal to y 1 and d y by d t is equal to y 2. So, now instead of y you use y 1 and y 2 and you use it in the following way you say the first equation you will say d y 1 by d t is equal to 0 times y 1 plus y 2 plus 0. I am just putting the 0 just to make connection with this sort of expression. So, d y 1 by according to these d y by d t is y 2 in other words since y is y 1 you write d y 1 by d t is equal to y 2.

The second equation is you have d square y by d t square. That is same as d by d t of d y by d t d y by d t of y 2 so, I write this as d by d t of y 2 and this is equal to now you had c 1 now d y by d t I write as y 2 plus c 2 y I write as y 1 plus d 1. Now, you can see that this is clearly in the form of two coupled first order differential equations. So, we wrote a second order differential equation in the form of two coupled first order differential equations or you wrote it as a system of two first order differential equations.

So, what is the advantage of doing this and the advantage of doing this will be particularly seen when we look at linear first order differential equations. So, when we look at linear differential equations, so will take the example of a set of linear coupled first order differential equations. So, let us look at a set of linear coupled first order differential equations will start with the simple example just to illustrate the use of this technique. But, you can extend this to various other systems also, let us take the example of and I will just for illustration I will just take a two coupled differential equation.

(Refer Slide Time: 42:47)



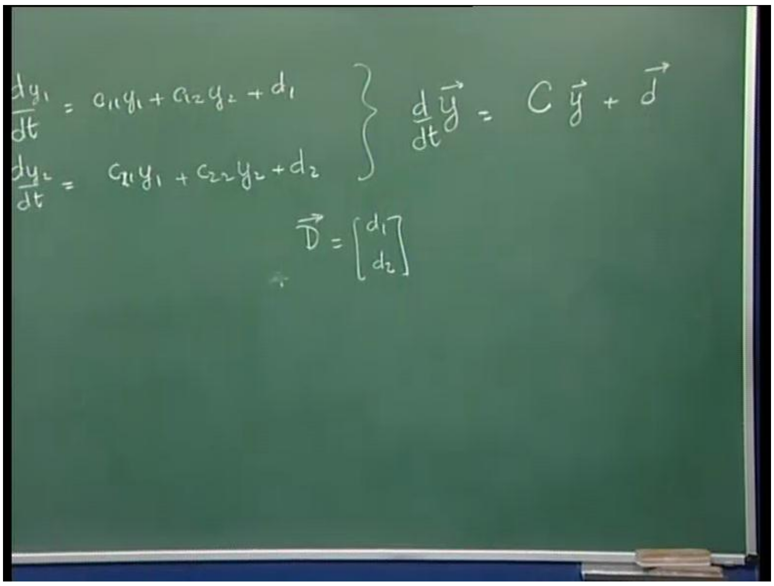
But, you can extent this to as many variable as necessary to solve your problem. So, let us take the example, you have d y 1 by d t is equal to c 1 1 y 1 y 2 and d y 2 by d t is equal to c 2 1 y 1 c 2 2 y 2. So, I deliberately wrote the variables in this form so, that you might be able to see some connection. Now, if we look at the right hand side c 1 1 y 1 plus c 1 2 y 2 and c 2 1 y 1 plus c 2 2 y 2, so what will do is will write this set of coupled equations in the following form the left hand side will write it as.

So, will write it as a two component vector the first component is d y 1 by d t the second component d y 2 by d t and then the right hand side is also, a two component vector these are the two components. But, instead of writing it in this form will write it as c 1 1 so, we write it as a matrix multiplying y 1 and y 2. So, the advantage of writing in this form will become clear in a few minutes. So, we wrote this set of two equations we wrote it in this matrix this vector form.

Now, I can call this vector y or other I will start by calling this as y then this vector is d by d t of y so, this vector is d by d t of y and I will call this matrix as c. So, then you can write your you can write your set of equations in the form c y so, you have set of two differential equations we wrote in this form as d in vector notation. So, d y by d t is c times y where y is a vector that has two components.

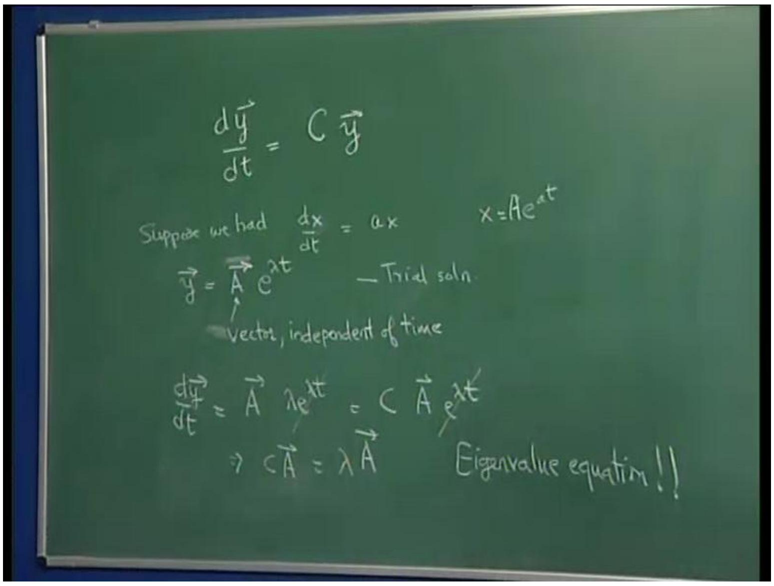
Now, you can you can extend this to any number of different equations the import thing is that each term should be linear in one of the coefficients. You can also extend this to the case where in addition to the terms that are linear in the coefficient you also have a constant and will see that in a minute. So, suppose you had d y 1 by d t is equal to c 1 1 y 1 c 1 2 y 2 plus d 1 and you had c 2 1 y 1 plus d 2 if you had these two equations then you write this as you would call this you would say that d is equal to d 1 d 2.

(Refer Slide Time: 46:05)



Then you can write this whole thing as d y by d t is equal to c times y plus d. This is the most general way of writing a system of linear differential equations. So, system of linear differential equations system of linear first order differential equations is written in this form, and this is probably one of the most used problems in many engineering and scientific applications I will just mention briefly how you can use some techniques from matrix algebra to solve the system of linear first order differential equations.

(Refer Slide Time: 47:43)



So, let us start with our set of linear first order differential equations of the form d y by d t is equal to c y. I will just start with c y but, to illustrate what we are going to show but, you can extend it to other problems. Now, in order to motivate the solution I will say that suppose y was just a scalar and c was just a constant, so suppose y was a scalar and c was a constant then you would immediately say that the solution of this differential equation is y is some constant times e to the minus c t so, that would be your answer.

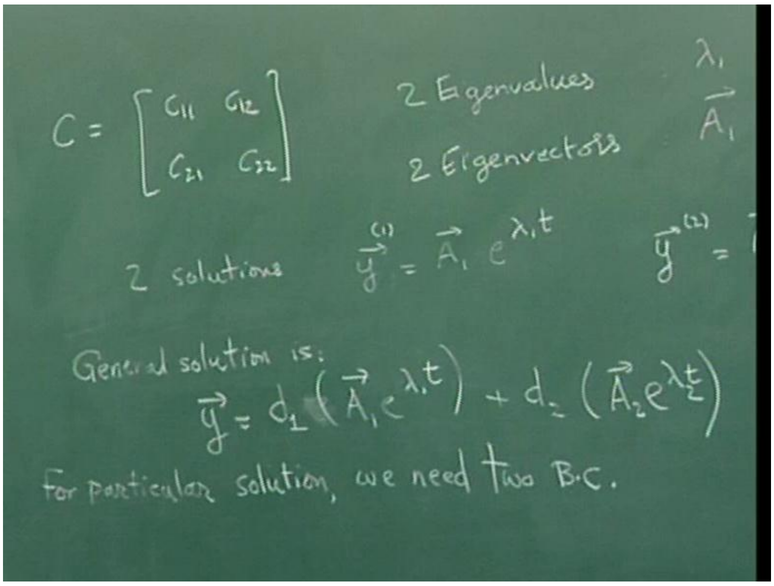
So, if this was the scalar this was the constant. So, suppose we had d y by d t or I will say just to differentiate with that way I will say d x by d t is equal to a x. Then to solve this you will get x is equal to e to the a t sometimes, some constant so, I will just say a e to the a t that could be the solution. Now, here you do not have the luxury of having these scalar, these are vectors and you do not know and. So, this is the two dimensional vector.

Now, we cannot use this technique but, there is a way of but, what will say is that will guess that y is equal to some matrix. I will just call it a matrix that is independent of time. So, y is a matrix depends on time e to the lambda t. So, this is the matrix or sorry this should be a vector a e to the lambda t vector and it is independent of time. So, lets uses as a trial solution and what will do is try to find out what is what does a what do a and lambda represent with respect to this matrix c.

So, suppose I that take this and substitute it here, then d y by d t is equal to now A is independent of time. So, I can just write this as A lambda e to the lambda t and if I substitute here for y then I will get this should be equal to c A e to the lambda t. So, then that since lambda is just a scalar I can bring it in front e to the lambda t is a is a scalar which can cancel on both sides. So, I will get c this implies c times A is equal to lambda times A, c is a matrix, A is a vector, lambda is a scalar.

So, this is an Eigen value equation. So, when you make this trial solution what you find is that lambda should be an Eigen value of c and the Eigen vector should be A. So, suppose you know the Eigen values and Eigen vectors of this matrix c, then you know the solutions c was our matrix.

(Refer Slide Time: 52:03)



So, if you know the Eigen values and Eigen vectors of this matrix then you can write the solution. Now, this will have 2 Eigen values and 2 Eigen vectors in general two by two matrix will have 2 Eigen values and 2 Eigen vectors. And so, what you get is you will get two solutions so, result is two solutions, so we call them 2 Eigen values if you call then if you denote them as lambda 1 and lambda 2 and this as A 1 and A 2. Then the two solutions will have the form y 1 is equal to A 1or I will just say y 1 is A 1 A 2 the lambda 1 t and y the second solution of y is A 2 e to the lambda 2 t.

So, now, the question is which of these is the solution is one or should we do something else. The answer lies that in the fact that your general solution is y is equal to some constant I will call it d 1 times the first solution. So, d 1 times A 1 A 2 the lambda 1 t so, some constant multiplied by the first solution plus some other constant multiplied by the second solution. So, it is the general solution so, it has two undermined constants d 1 and d 2.

And this is the way you write the general solution and if you want for particular solution we need two boundary conditions. So, you need two boundary conditions because your y was a 2 by 2 matrix. Since y was a two by two matrix you need two boundary conditions and that will give you the particular solution. So, by finding the Eigen values and Eigen vector of this matrix you can solve this differential equation. So, the way to solve this differential equation is to find the Eigen values and Eigen vectors of this matrix.

Once you have the Eigen values and Eigen vectors then you can write down a general solution. And we had two undermined constant because you had two coupled first order differential equations. If you had more differential equations you would have had this should have been a larger matrix and you would had more undermined constants. So, in the in the next class we will see an application of this method this system of first order differential equations.

The application is something many of you will be familiar with but, will just cost it in the form of this differential equations and solution. And that and the application will be talking will be taken from reaction kinetics, a when you have in any reactor system you have many reactions taking place and the product of one reaction will be relate to the reactant of the next reaction and. So, you have a set of coupled reactions and each of them has it is own differential equations and under certain conditions you get a set of coupled first order differential equations, so will look at an example of how to solve that using this technique.