Mathematics for Chemistry
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Module – 04
Lecture – 19
Spectral decomposition - normal modes, sparse matrices ill-conditioned systems

So in the last class we learnt about special matrices, we saw symmetric orthogonal hermitian and unitary matrices and we briefly talked about things called similarity transformation. Now today I am going to talk about spectral decomposition, matrix diagonalization, normal modes and then some more a few other things about matrices I will mention.

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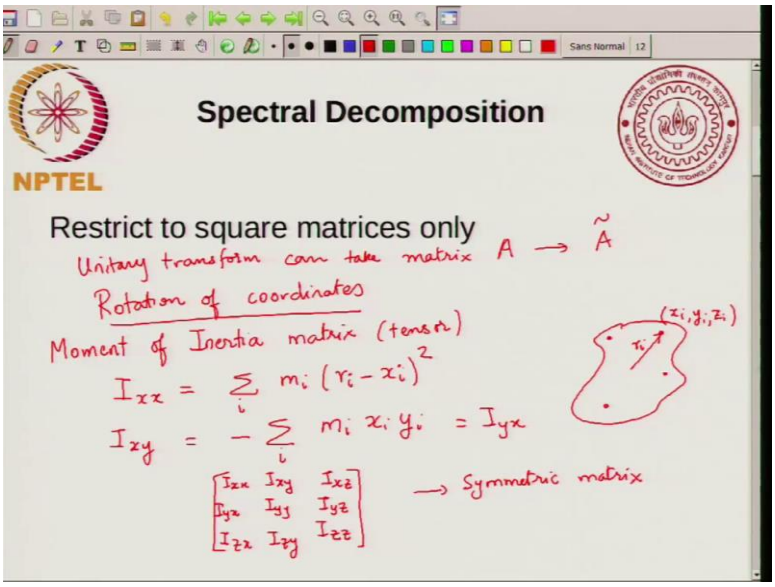

So, we will start with spectral decomposition, we will restrict the discussion to square matrices only.

And now, sometimes what happens is we saw that the unitary transformation; a unitary transformation can take matrix A to A tilde and what you say is that unitary transformations on a space preserves the norm of the vectors in that space. So, what you are doing effectively is like your rotating the coordinate system so, by rotating the coordinate system, now your matrices which become different so, it is like looking at the matrix in a rotated coordinate system.

Now, why is this useful? When would you imagine this to be useful? So, you can imagine that you take your coordinate system you rotate it to such a way. So, this is a rotation of coordinates. So, you are looking at the matrix in the new rotated coordinate system, now you can imagine that you do one particular rotation and in that rotated coordinate system your matrix becomes diagonal.

So, can you rotate the coordinate system in such a way that the matrix that was initially not diagonal becomes diagonal? Now why are we interested in diagonal matrices? Because diagonal matrices the eigenvalues are easy to calculate, so this is one example of transformations that you often do. So, one classic example from chemistry is in the moment of inertia matrix.

So, in general if you have a polyatomic molecule then it has 3 rotational degrees of freedom if you want to write those rotations as 3 independent rotations you have to find something called the principal directions. So, what do you do in calculating the principal directions? So, we look at the moment of inertia matrix or the or actually it is a tensor. So, this tensor is defined the following ways. So, you call I x x equal to sum over m i what we are thinking is that is that you have a rigid body and it has various point masses. So, these are the various point masses and these are these are located at some coordinate r r i. So, these are the coordinates and each point mass has x i y i z i then you define I x x as n i times r i which is the with respect to some point which is usually taken as the centre of mass. So, so the origin is usually taken as a centre of mass. So, you take r i which is the distance from the origin minus x i, the x coordinate of that point whole square and usually this point masses are the actual atoms. So, if you have polyatomic molecules then you do for each atom. So, you sum over all the atoms.

So, this is the x x component of the moment of inertia matrix and similarly you can do for y y and z z. So, and then you have the x y component which is defined as minus sum over i m i x i y i. So, what this moment of inertia matrix looks like? It looks like this. So, you have I x x, I y y, I z z along the diagonals and then you have I x y, I x z, I y x, I y z, I z x, I z y. So, this is what your moment of inertia matrix looks like and clearly you can see that I x y equal to I y x. So, therefore, the matrix is symmetric. So, it is a symmetric matrix. Now this matrix appears very naturally when you are when you are describing the rotational when you are writing of the rotational Hamiltonian for a polyatomic system. So, this moment of inertia tensor appears naturally.

Now, the main issue is that if you just use any if you just use some arbitrary coordinates then this moment of inertia matrix is not diagonal if it is not diagonal then it becomes very difficult to write to actually calculate the rotational energy.

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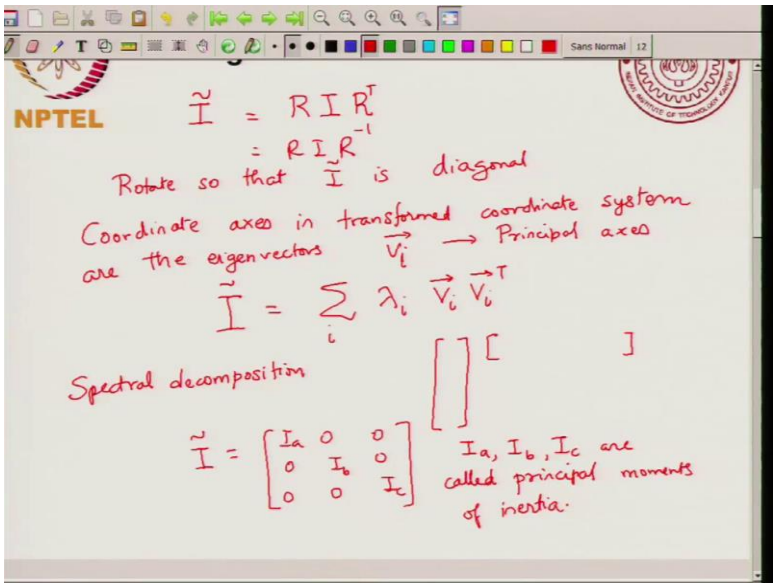

So, what is done is that you do; you transform the coordinates. So, you transform the coordinates till this matrix becomes diagonal. So, what is done is you go from; you go to some coordinate ith I some coordinate which I represent by I tilde is a moment of inertia and the transformed coordinate and this is done by using by using some sort of some sort of similarity transformation.

So, I will just put R I R transpose. So, this is a rotational matrix and if you if you do this remember for rotational matrix is orthogonal. So, this is nothing but R I R inverse. So, what you are doing is you are rotating the coordinate system and in this coordinate system, so rotate. So, that I tilde is diagonal. So, what are we done? We have taken this initial matrix which was not diagonal and essentially rotated the coordinate system. So, that it became diagonal.

Now, in this coordinate system, you will have 3 directions you will have the coordinate axis. So, the coordinate axis are basically the eigenvectors axis in transformed coordinate system are the eigenvectors just call them V i eigenvectors V i.

So, what we have done is we have rotated them and when you find that it becomes diagonal then the axis that you have in this rotated coordinate system is nothing, but the, but the axis points along the eigenvectors. So, instead of what you can write you can write this I tilde, once you have this and you can write it as sum over all the eigenvectors you can write it as lambda I V i; V i transpose. So, if you take a vector and multiplied by it is transpose then you will get a matrix. So, it is like taking one vector that looks like this and multiplying it by it is transpose that looks like this. So, you will get a matrix and so I tilde you can write as lambda I V i V i transpose and so this procedure of writing a matrix in terms of it is eigenvalues and eigenvectors is a very general procedure and this is called spectral this is either referred to as diagonalization or spectral decomposition.

So, you write this matrix in this form and this is called a spectral decomposition again this is a very commonly used technique. So, what we say is that when you do a spectral decomposition of a matrix you are basically finding out it is eigenvalues and eigenvectors.

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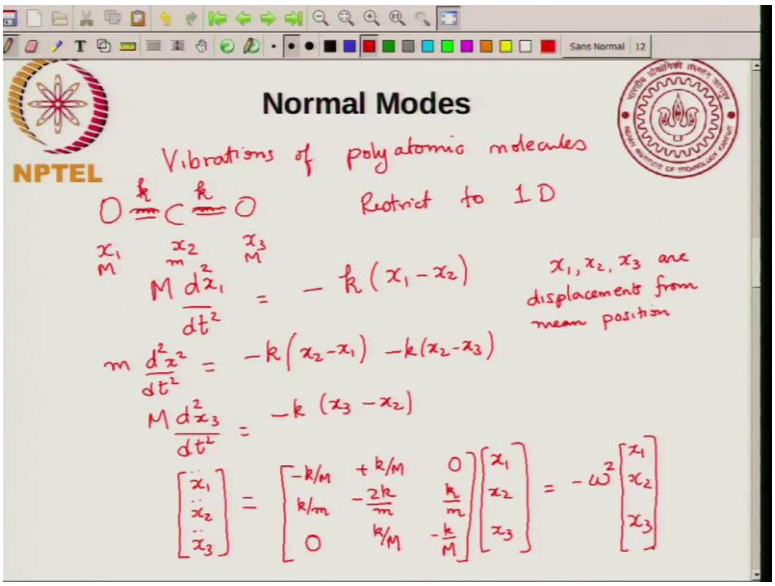

Now, we look at one very practical application of eigenvalues and eigenvectors this is what is called the normal mode. So, far we talked about rotations, now if we talk about vibrations of molecules of polyatomic molecules these are expressed in what are called as normal mode. So, in some sense, the eigenvectors for vibrations of polyatomic molecules are exactly the normal modes just as what we saw in this case that that when

you transform your more your moment of inertia into a diagonal matrix then the rotational matrix becomes diagonal I forgot to mention, but these directions are referred to as principal axis and so your I tilde; I should mention that looks like I a, I b, I c. So, in this transformed coordinate system it just looks like this it looks like diagonal in the with the I a, I b, I c are called the principal moments of inertia.

So, I a, I b, I c are called principal moments of inertia. So, when you convert it into a diagonal matrix these axis the a b c directions are called principal axis, now what we are doing is a very similar thing, but you are doing for vibrations. So, for rotations you have these principal axis and principal moments of inertia for vibrations of polyatomic molecules what you have is what are called normal modes. So, what are the normal modes?

So, let us take a very simple example this can be you can think of it as a CO 2 molecules. So, if you take a CO 2 molecule. So, it is a linear molecule and we will just restrict to one dimension 1 D so; that means, you just have you just have this has coordinate x 1 this has coordinate x 2 this has coordinate x 3. So, you just have 3 coordinates. Now what you will do if you want to express these vibrations, what you will say is that you will write the equations of motion for the first particle. So, the first particle the equations of motion will be M, let me take the mass of this as M mass of this as a little M mass of this as M.

So, by equation of motion will be M d 2 x 1 by d t square is equal to minus k; minus k and the let me take for convenience that this has a spring constant k and this is k. So, when you are modelling vibrations you think of this bond as having some spring with spring constant k. So, if I write it as minus k x 1 minus x 2. So, this is the equation of motion for this mass and you can see that. So, x 1 is in some sense, it really reflects the displacement from the mean position. So, you can think of x 1 as a displacement from the mean position.

So, x 1 x 2 x 3 are displacements from mean position. So, what I mean is if you are at the mean position then basically x 1 will be 0, x 2 will be 0, x 3 will be 0. So, when x 1 equal to x 2 equal to x 3 equal to 0, you will all the atoms will be in their mean positions.

Now I can write for x 2, I will have something like this x 2 minus x 3 and I can write for the for the x 3 particle for the third oxygen atom I can write M d 2 x 3 by d t square this

is equal to minus k x 3 minus x 2. So, these are my 3 equations of motion and I can write these equations of motion in matrix form and what I will what I will write are. So, I can write this as, instead of instead of writing this second derivative with time I will just use x 1 double dot x 2 double dot x 3 double dot and this I can write as a as the following matrix. So, I can write it as, now x double dot is minus k by M x 1. So, minus k by M and then it has plus k by M x 2 and it has 0 and then and then here it is you have plus k by M k by little M and you have for x to you have minus 2 k by little M and for x 3 I have k by M multiplied by x 1 x 2 x 3.

So, all I have done is are just rearrange this and return it in matrix form and then and then here I will have 0, I will have plus k by M and I have minus k by I have minus k by m. So, I wrote this these 3 equations in this form and what we want to do when you when you calculate the normal modes is this is a I mean when we do differential equations we will see this is a system of linear second order differential equation with constant coefficients and the general solution can be written as minus omega square x 3. So, it is like this is the matrix version of solving a simple harmonic oscillator one dimensional simple harmonic oscillator.

So, what does this mean? Now I wrote this in matrix form and what you can immediately tell is that omega is nothing, but an eigenvalues of this matrix. So, what we want to find out first is what are the eigenvalues and what are the eigenvectors. So, if I give you this matrix then you know that you are referring to this system. So as soon as you have the system CO 2 you can write a you can write this matrix and what we are doing is nothing, but calculating the eigenvalues and eigenvectors. So, when you calculate the eigenvalues and eigenvectors you will get what are called the normal modes.

So, these are what are these are nothing, but eigenvalues and these are the corresponding eigenvectors. So, what we did we had only this differential equation, now when you set it to minus omega square x 1 x 2 x 3, you are basically asking for the eigenvalues and eigenvectors.

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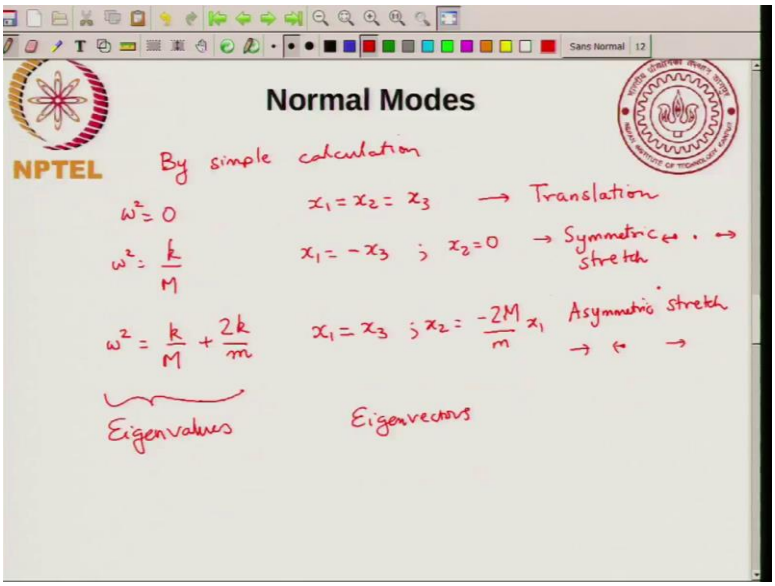

And I would not do this in detail, but you know cal by simple calculation, we can get 3 eigenvalues the 3 eigenvalues are omega square equal to 0 omega square equal to k by M and the third eigenvalues that you will get is omega square equal to k by M plus 2 k by M.

So, these are the 3 eigenvalues we will get and the corresponding eigenvector. So, so these are the; your eigenvalues and the corresponding eigenvectors are. So, for our omega square equal to 0 your eigenvector will basically have x 1 equal to x 2 equal to x 3 remember you. So, you can take any value for x 1 x 2 x 3, but basically they should be the same. So, remember eigenvectors can only be determined up to a constant they cannot be uniquely determined. So, in this case you have x 1 equal to x 2 equal to x 3 and now you can see that if x 1 equal to x 2 equal to x 3 then each of these 3 atoms is being displaced in the same direction by the same amount. So, each of these being a each of these atoms is being displaced in the same direction by the same amount.

So, this actually refers to a translation this refers to a pure translation. So, it is not actually a vibration, this is a this is one mode when all the 3 atoms are moving in the same direction in this case your eigenvector looks like x 1 should be equal to minus x 3 and x 2 equal to 0. So, when you solve for this eigenvector you will find that x 2 has to be equal to 0 and x 1 and x 2 has to be opposite signs you can take any multiple of this, but they have to be opposite signs and this is what is called a symmetric stretch. So, what

you have is that your centre carbon atom is fixed and you have these is moving in one direction this moving in the other direction the 2 the 2 oxygen atoms moving in opposite direction. So, this is a symmetric stretch.

Now, the third one this has eigenvalues. So, it has x 1 equal to x 3 and x 2 equal to minus 2 capital M by small m x 1 and this is this is what is called an asymmetric stretch where your 2 oxygen atoms are moving in the same direction. So, they are moving in the same direction by the same amount and the centre atom is moving in the opposite direction by some other amount your carbon atoms. So, this is your asymmetric stretch.

So, what we can see is that just by calculating the eigenvalues and eigenvectors you can get the normal modes and you can identify what is the symmetric stretch and asymmetric stretch and what we see is that the normal modes normal modes of this linear CO 2 molecule, we restricted the CO 2 molecule to move only in one direction and we naturally find that these are the 2 normal modes. So, symmetric and asymmetric stretch are not things that we choose for convenience these are the natural normal modes of this system and you can do this for multidimensional polyatomic atoms to ok.

Now, I will just before I end this, I will just mention a couple of things there is something called an ill conditioned matrix.

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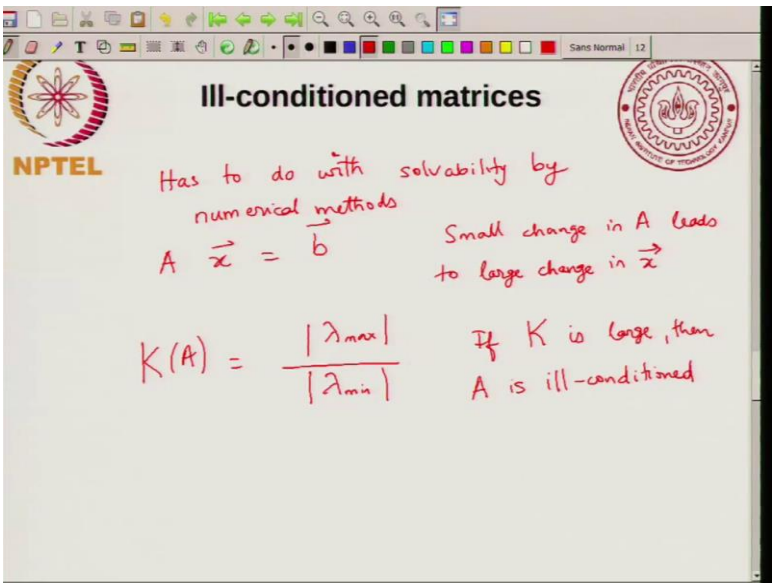

So, this has to do with do with solvability by numerical methods. So, numerical methods are a very integral part of matrices. In fact, in fact there are very large number of numerical methods that involve matrix operations and now a matrices said to be ill conditioned. So, if it is very sensitive if the results are very sensitive to the values.

So, what happens is you know you know often you are trying to solve a matrix equation. So, if you have A x equal to B, now you just make a small change in a if you get a very large change in x then you then you say that matrix is ill conditioned. So, small change in A leads to large change in x. So, x is the solution. So, you are solving for x and what you say small change in A or B, we leads to a large change in x and so this is called an ill conditioned system or an A is said to be an ill conditioned matrix.

Now, a matrix there is a there is a way to check for this ill conditioned matrix by doing something called the condition number. So, I will call this k of A, this is the absolute value of the largest eigenvalues divided by the absolute value of the smallest eigenvalues. So, if k is large then A is ill conditioned now, many times you are evaluating you are solving these matrix equations by some numerical procedure then you have to really worry about whether matrix is well conditioned or ill conditioned.

So, this is one thing about matrices that I want to mention the other kind of matrix I will mention is what is called a sparse matrix.

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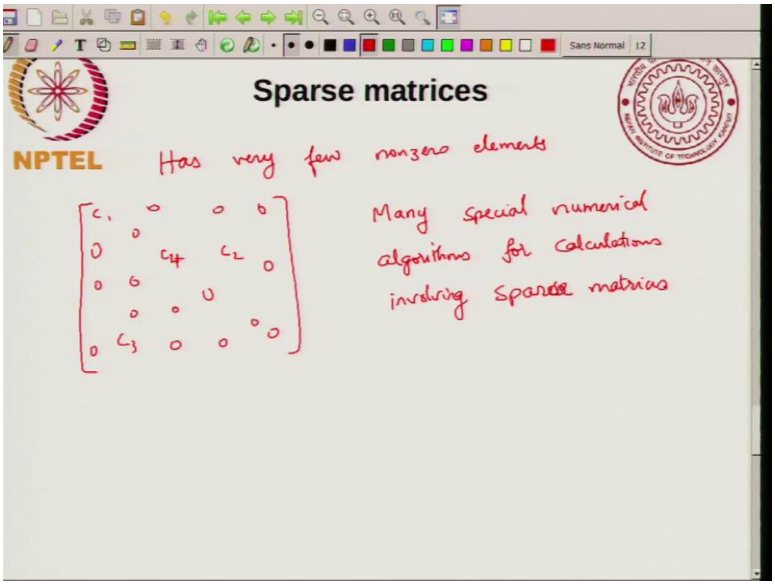

So, a sparse matrix has very few non0 elements so; that means, you have a matrix where you have basic essentially you have you have some numbers C 1 C 2 C 3 and most of it is 0. So, most of a most of the matrix is just 0 and you just have a few numbers that are non 0.

So, you might have C 4 here somewhere they are so a sparse matrix has very few non0 elements now again there are very many special numerical algorithms for calculations involving sparse matrices. So, if you know that if you know that you are the matrix at you are working with is a sparse matrix then you can come up with very nice numerical methods for these systems? So, I will just mention again that many times matrix operations are done numerically.

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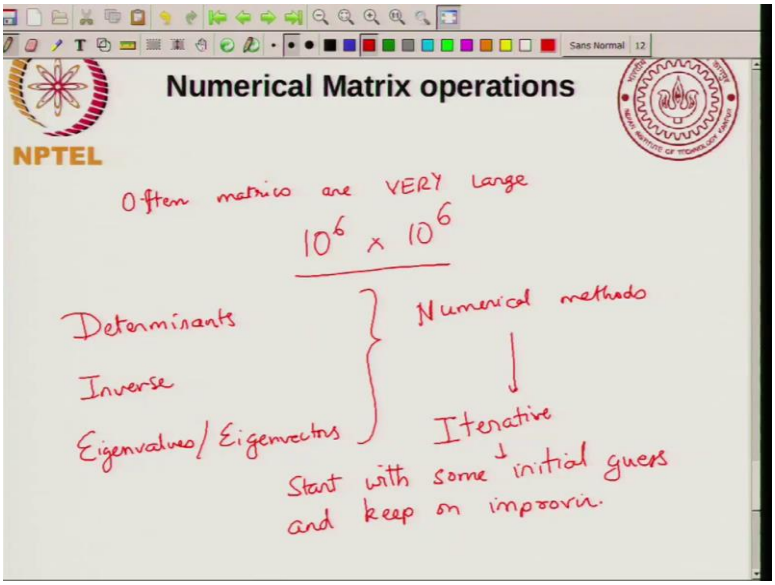

So, suppose you want to you often deal with often matrices is very large.

When I say very large you might deal with 10 raise to 6 by 10 raise to 6. So, million by billion matrices and you know you cannot calculate the determinant the usual way of the inverse the usual way. So all operations, determinants inverse etcetera these are the eigenvalues, eigenvectors all done using numerical methods and many of these numerical methods are actually iterative; that means, you start with some guess and then you keep correcting it and when you go on so many many methods are actually iterative means starts with some initial guess and keep on improving.

So, what I just wanted to tell you is that you know nu numerical methods are an integral part of matrix methods and these are some of the most important things that that people do in all branches of science and engineering and I will conclude this discussion on matrix. Now in the next lecture, I will do one illustrative problem involving rotational matrix is matrices using matrix of rotations.