Advanced Mathematical Methods for Chemistry

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Module - 04
Lecture - 05
Recap of Module 4, Practice Problems

So, in module 4 we have learnt about ordinary differential equations, we have learnt about the different types of ordinary differential equations and we learnt a little bit about first order differential equations. So, this is the fifth lecture of module 4 and in this lecture I will recap some of the things you have already learnt in this module and then work out a few practice problems. So, let us start with the recap.

So, in module 5 in the first lecture you learnt the types of differential equations and the types of solutions, we learnt about linear, non-linear, homogeneous, non-homogeneous. We learnt about the order and degree of differential equations.

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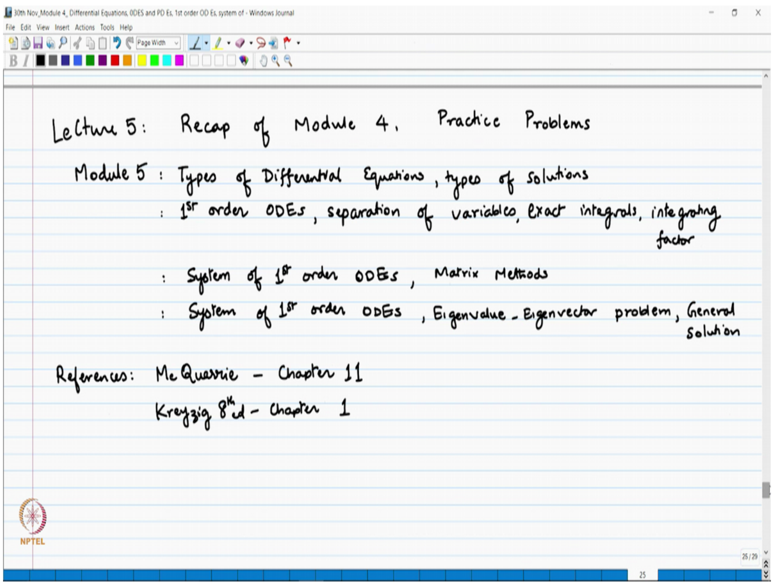

Then in the second lecture we learnt about first order ODEs and how you can solve them using separation of variables exact integrals and integrating factors. Then in the third lecture we learnt how to deal with a system of first order ODEs and how matrix methods can be used and in the 4th lecture we explicitly solve the system of first order ODEs you by solving the Eigen value eigenvector problem and the writing the general solution.

Now, this material is you can find in the reference book. So, Mc Quarrie has it in chapter 11, Kreyzig has it in chapter 1, but once again let me emphasize that I am not exactly following these books I am taking some content from this and, so you really have to follow the lectures and then try to follow the similar material in the books. Let us work out a few practice problems and let me emphasize right here that differential equations are a part and parcel of all modern science in engineering. So, you can find them almost anywhere you look. So, the in chemistry you see them explicitly in areas like quantum mechanics and then or in chemical kinetics or spectroscopy and so on or any rate process will have a rate equation which will be in the form of a time derivative.

So, it is not uncommon to find it, but also you might, you might find that if you are if you are trying to solve any mechanical problem, any problem in mechanics like a ball falling that will have differential equations. I do not need to explicitly say where you use differential equations since they are so widely used, but during the examples I will try to take certain examples which will be familiar to you from your various courses.

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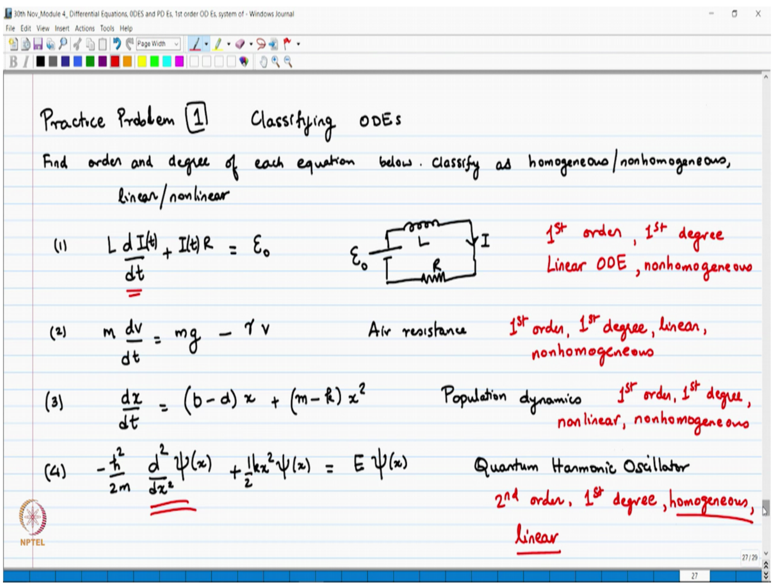

So, let us go the first practice problem that I want to do; has to do with classifying ODEs. Now this, this is a fairly useful skill to have I mean many times it is not done explicitly, but I like to emphasize this part a little bit, so that you actually think before you rush to solving a differential equation. What I have asked you to do is to find the order and degree of each of the each equation below each ODE when I say equation I mean ODE classify as homogeneous non homogeneous linear or non-linear.

So, the first equation you written the differential equation L times d I by dt plus I times R is E 0. This is an equation that comes when you are dealing with inductor register circuit, a very basic inductor register circuit a battery inductor and resistor and the current when you, when you just connect this battery then the current follows a certain follows this law the current builds up over time and it follows this equation.

Now, if you just look at this equation the highest derivative that appears is the first derivative. So, it is a 1st order ODE, now the power the power of the highest derivative is 1, so it is 1st degree. Now this has the each of the terms contains I or its derivatives to the first power or 0 th power. So, it is a linear ODE and we notice that the term on the right does not contain any I. So, the first term contains d I by dt, second term contains I, third term on the right does not contain I or d I by dt or d square I by dt or any derivative of I. So, it is a non homogeneous equation. So, these are the characteristics of this equation and you can solve this using the usual method of integrating factors.

The next equation this m times dv by dt equal to m times g minus gamma times v. So, v is the dependent variable v is variable that depends on t and this is the equation for some mass falling under gravity, but it also experiences some air resistance. So, this gamma is the constant which tells you how much air resistance it feels and the air resistance is proportional to the velocity.

So, now, clearly this is again a 1st order, 1st degree it is linear non homogeneous which 1 is ODE. So, just like the previous equation. In fact, these 2 equations are essentially identical. So, it is just different names for the constants, but essentially they are identical. Again this is a very important a skill to have we will see that the same form of the equation appears in many different areas. So, the first order differential equation linear homogeneous first order differential equations again that appears in several different contexts. In fact, in both these cases we had constant coefficients. So, the solution will be related to exponential and again we see exponentials appear in different areas.

Now, the next equation this I have written as dx by dt is b minus d b and d are constants x and m minus k x square. Now I wrote this explicitly in terms of b minus d I could combine b minus d into a single constant and m minus k into a single constant. So, I can just write this as a x plus b x square, but I would explicitly wrote it in this way because such equations appear in population dynamics. So, for example, if x is the population of some of some species then the dx by dt has a birth rate, now the birth rate depends on the population that is there and a death rate again that is also a proportional to the population that is there.

So, that this is like the net birth rate of the species both of these are proportional to x. So, you cannot have a species born unless there is some species to give birth. Then there are other things that affect this is I wrote it as m minus k. So, it could be that 2 species meet each other and they mate. So, m would be that would lead to increase in population, but that requires 2 species to mates to meet, it is a x square term, but it could also be that 2 species could meet and just kill each other. So, there would be, that would lead to decrease in population.

So, now such equations appear very often in you will see them in population dynamics and this is a fairly active area of research and you know it is I mean even though even though we have written it like a population dynamics it is such equations are often used even to model chemical equations. So, now, what would this equation be? Clearly this is 1st order, 1st degree and it is non-linear because there is an x square term and it is non homogeneous. So, this is an example of a non-linear equation. We will actually explicitly discuss non-linear equations in more detail.

Next is another the 4th equation that I have given is minus h bar square by 2 m, d square by dx square of psi of x is half k x square psi of x plus e know plus half k x square psi of x is equal to e times psi of x. Now this is the equation for a quantum harmonic oscillator you see it very often in, I mean you will see it in your quantum mechanics course if you have not already seen it you will definitely see it.

Now, this I have written it as an ordinary differential equation with a single variable, now the independent variable is x and the dependent variable is psi, is denoted by psi - psi is the symbol that is used for the wave function, and so now what we have here is as you can see there is a term that involves the second derivative. So, this term involves the second derivative. So, it is a second order and the second derivative is to first power. So, it is a first degree.

Now, each term contains psi to 1 power, it contains either psi to 1 power or a derivative of psi to 1 power. So, it is a homogeneous and it is linear and, in fact the linearity of the quantum mechanical equations are very essential for the very foundations of quantum mechanics. So, the fact that your Schrodinger equation is a linear equation is a very important aspect of quantum mechanics and this equation is homogeneous so there is no term that is independent of psi and that is also another feature of quantum mechanics and, in fact the fact that it is homogeneous and linear allows us to use matrix methods in quantum mechanics. So, that was about classifying.

Now let us go to the next problem. So, this is the problem that is often discussed in certain textbooks and I just wanted to take an equation.

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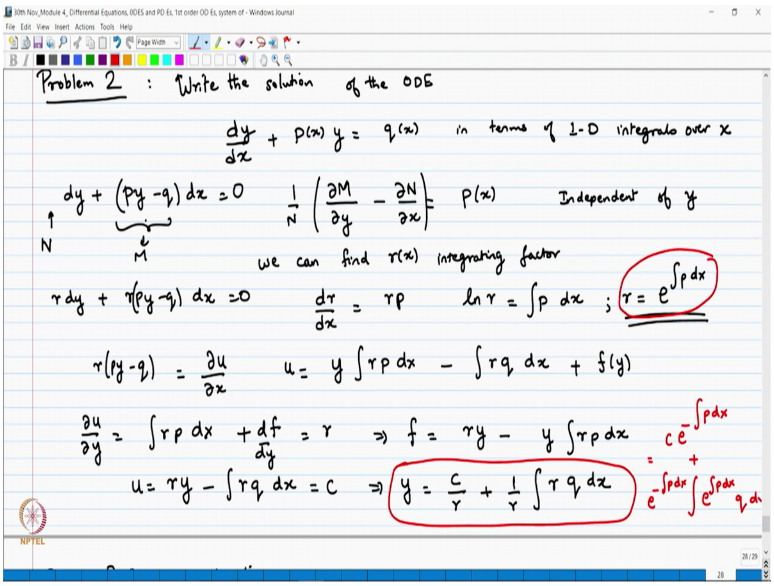

I have written this equation in this form dy by dx is some function of x p of x times y plus sorry d y by dx plus p of x times y is equal to q of x and you have to and I am asking you to write the solution of this ODE in terms of 1 dimensional integrals over x. The reason the reason the solution appears in terms of integrals is because I want to do it for an arbitrary p of x and q of x.

Now, now many textbooks do this as part of the solutions of differential equations and so, but since we did not explicitly do this I thought you can we can work this out. Now what we will do is we will write this in a familiar form. So, we will write dy plus p times y minus q dx equal to 0. So, I just rewrote this I am not writing the dependence on x explicitly. So, now, this is, this you can do the derivatives. So, if you take, so this is N this is M, N is equal to 1, M is this whole thing. So, you can clearly see that dou M by dou y minus dou N by dou x dou N by dou x is 0 dou M by dou y is not 0 is equal to p of x.

So, we can we can see that that if I take this and I divide by N, 1 over N dou N by dou x N is just 1. So, this equal to p of x this is independent of y. So, it is a function only of x. So, we can find, we can find r of x that is integrating factor depending only on x. So, we can find an integrating factor that depends only on x and let us write this. So, we will get r d y plus r py minus q dx equal to 0 and what are the conditions. So, we should have, we should have this condition that when I take the derivative with respect to x. So, I get dou r by dou x it should be equal to derivative with respect to y of this that is r times p or get I should write partial derivative I should write dr by dx equal to r p because r is the function only of x.

So, this is an ordinary differential equation in x and so what I can do is I can take the r to the left I will get natural log of r is equal to p is integral p dx or r is equal to e raise to integral p d x I am not writing p of x this is integral p dx. So, I did not write the constant of integration, I do not need to write it when I am doing this when I am I will put the constants right at the end of the when we finally, solve the differential equation. So, we got our integrating factor and it comes as a 1 dimensional integral if you know if you know p of x you can evaluate this r.

So, now, once we have the integrating factor we have to still solve the equation. So, now, our equation has this form where we know the value of r so. So, now, let us, so what we have is dou by dou x of this quantity r times p y minus q should be equal to or rather this should be equal to dou u by dou x where this whole thing is d u it is an exact differential. So, we call this d u.

So, now, what do we get? So, let us do this integral and what we will find is that u is equal to. So, when you integrate this what you will get is I will in the first term I will take the y outside. So, I will get y times integral r p dx minus integral r q dx. So, this is u if I integrate it, now it is a partial derivative so I have a constant of integration that constant will be a function of y. So, I will say f of y.

Now, how do I how do I solve for f of y? I say that dou u by dou y is equal to. So, if I take the derivative with respect to y then in this term the y is there only here. So, I will get integral r p d x and then I have a minus this term is independent of y. So, that term does not have; does not contribute. So, plus dou f or df by dy. So, this is dou u by dou y and this should be equal to r.

So, now I can integrate, I can integrate and I can get f equal to r y minus y this is only a function of x. So, it is y, so when I integrate it I will get y multiplied by this whole thing y times integral r p dx that is my f. And now I can substitute in the expression for u, what I get is now when I substitute this, this y times integral r p dx will just cancel here. So, what I will get is u is equal to r y minus integral r q dx and the solution is that this equal to constant.

So, now I can write the solution I can take this to the, I can take this to the right I can write this implies y is equal to constant by r plus 1 over r integral r q dx where r itself, r itself is this integral. So, this is the final solution. So, r is this integral and your y is written in terms of r in this form.

Now, this is a very common I mean this problem is actually very very commonly seen, if I write this out, I will just write this out just to, so the first term looks like c divided by r. So, that is e to the minus integral p dx. So, this is the solution that would have been there if q was 0 if q was not there then you just get dy by y is minus p dx and so when you integrate it you will just get this term constant times e to the minus integral p dx. So, let me just write this in this form. So, the first term is constant times e to the minus integral p dx. So, that is the first term. The second term is again you have e to the minus integral p dx from the 1 by r and then you have integral of, now you have r itself is an integral; integral e raise to p r itself is e raise to integral p dx and you have q dx. So, these 2 terms look like this and sometimes many books often give this directly as an expression to solve this differential equation.

Now, what is important about this differential equation is that if q of x is not there then this will be a homogenous differential equation. So, what we did is. So, the first term is like solving the homogenous differential equation. So, first you solve the homogeneous differential equation then this is the solution due to the non homogeneous part. The last problem that I want to do is has to do with chemical kinetics and I just I just gave a very simple chemical kinetics scheme where I have A going to B with k 1 and k 2 and B going to C.

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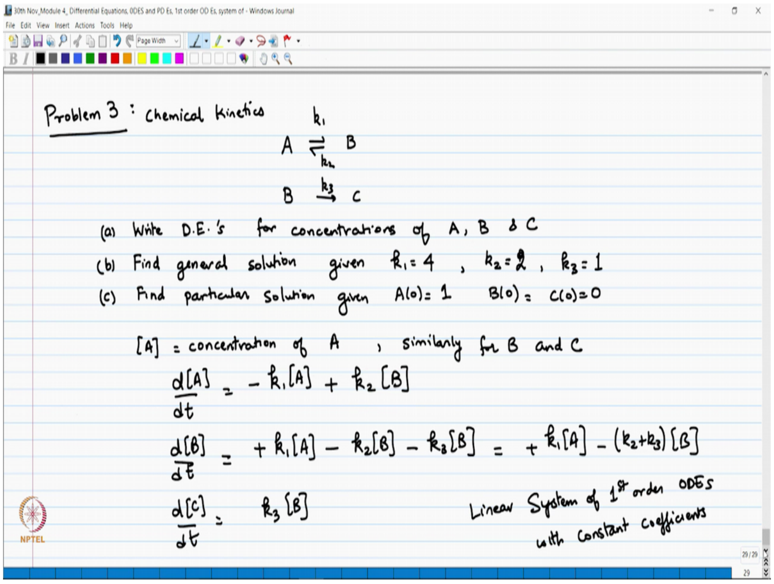

So, this problem has 3 parts. So, first you write differential equations for concentrations of A B and C. So, we can see this. So, if we call I will say instead of writing A is the concentration of A. So, this is concentration of A and similarly for B and C, so this is the usual notation. And now what we want to do is we want to write differential equations for this. So, what you will write is d A by dt is equal to minus k 1 A. So, k 1 A is the rate at which A disappears and A is formed with a rate of k 2 B.

Now, d B by dt is equal to now B is, it will be plus k 1 A minus k 2 B minus k 3 B. So, I can write this as plus k 1 A minus k 2 plus k 3 B and then d C by dt equal to k 3 B. So, these are our, these are all the differential equations and you can see that each of these, each of these is a first order linear differentially. So, what we have is a system of first order ODEs with first order of linear. So, this is a linear system of first order ODEs with constant coefficients and when you have such a system you know that you can solve it using matrix methods.

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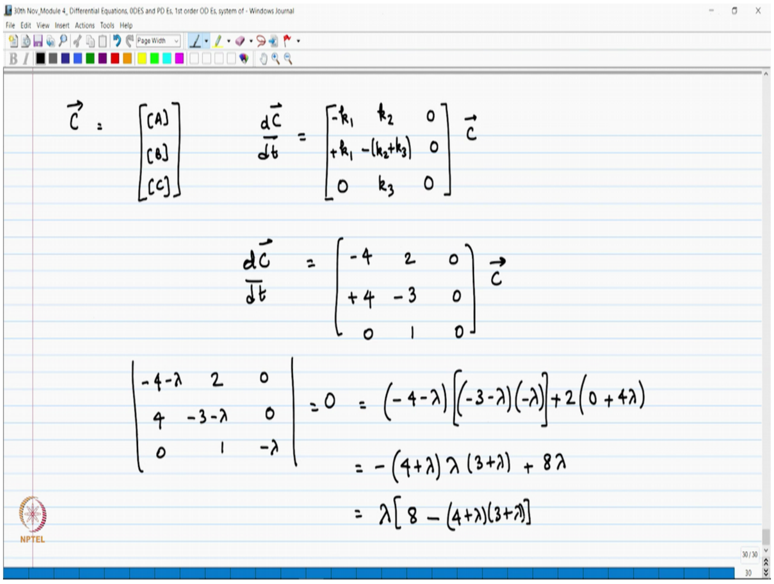

So, let us go ahead and write the matrix. So, I will call the C matrix. So, C is equal to A B C now I can write d C by dt. So, C is a vector, C vector. So, d C by dt is equal to now I will put this, I will write this matrix now what is this matrix. So, this matrix you have minus k 1 you have plus k 2 and 0, so, that that comes from this equation. So, minus k 1 A plus k 2 B and 0 times C, then you have in this case you have plus k 1. So, minus of k 2 plus k 3 and you have 0 and here you have 0 k 3 0. So, this is the, this is the matrix that you have and now you can try to calculate the Eigen values and eigenvectors of this matrix. When you try to solve it ok we are given certain values you are given k 1 equal to 4, k 2 equal to 2 and k 3 equal to 1.

So, what you get is minus 4 k 2 equal to 2 0 plus 4 minus 3 0 0 or 1 0. So, now, if you want to solve this, so we need to find the Eigen values and eigenvectors of this matrix now let us solve for the Eigen values and eigenvectors of this. Now to solve for the Eigen values what you will write is minus 4 minus lambda 2 0, 4 minus 3 minus lambda 0, 0 1 minus lambda this determinant is equal to 0.

Now, if I evaluate this determinant what I will get is this is minus 4 minus lambda times minus 3 minus lambda times minus lambda and then you have minus 1 and then you have plus 2 into 0 minus or 0 plus 4 lambda and then you have 0 for the from the third term. So, what you get is you will get 4 plus lambda into lambda into 3 plus lambda plus 8 lambda. So, what I can take lambda as constant. So, lambda outside and I can write it as 8 minus 4 plus lambda into 3 plus lambda and so you need to set this equal to 0. So, you need to solve this equation.

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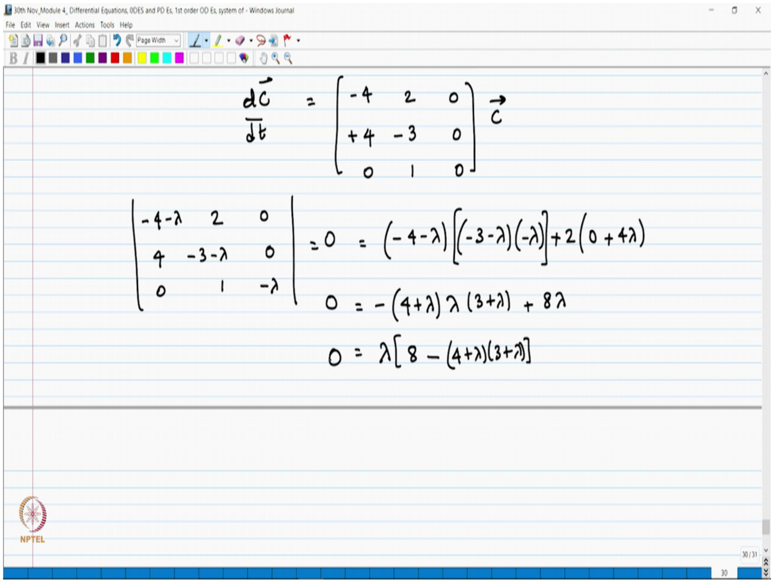

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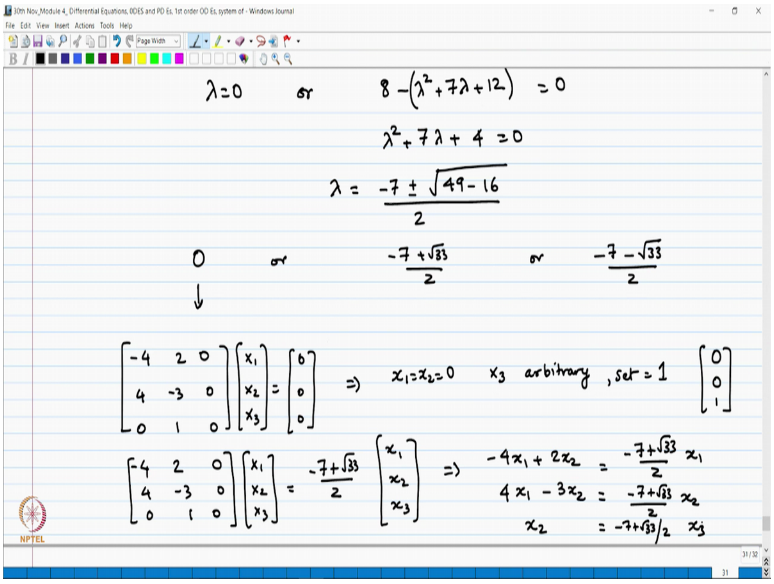

Now, so either lambda equal to 0 or 8 minus now we will expand this out, so lambda square plus 7 lambda plus 12 equal to 0. So, I can write this as, I can write this as lambda square plus 7 lambda and plus 4 equal to 0. So, what you get is lambda equal to minus 7 plus or minus square root of 49 minus 4 into 4 - 16 divided by 2. So, you get, so 49 minus 16 is 33. So, you get minus 7 plus root 33 by 2 or minus 7 minus root 33 by 2.

So, we get, we have the 3 values of lambda. So, we get lambda equal to 0, 0 or minus 7 plus root 33 by 2 or minus 7 minus root 33 by 2. Now for each of these you have to find the corresponding eigenvectors. Now if lambda equal to 0 you can just see from this expression, so if I take this and multiply it by 0 0 1. So, I will get, I will get with eigenvector. So, corresponding to this the eigenvector is. So, if you write, if you write our equation minus 4 2 0 4 minus 3 0 0 1 0 times some I will just call it x 1, x 2, x 3 equal to equal to 0 0 0 then this can only be true if, so implies x 1 equal to x 2 equal to 0 and x 3 can be arbitrary set equal to 1. So, since you can choose at arbitrary we will just set it equal to 1. So, therefore, this eigenvector is has the form 0 0 1.

Now, the next eigenvector, so suppose you have to solve for this. So, suppose you have to solve for the next equation. So, we will say minus 4 2 0 4 minus 3 0 0 1 0 times x 1 x 2 x 3 is equal to and say minus 7 plus root 33 by 2 times x 1 x 2 x 3. So, this implies minus 4 x 1 plus 2 x 2 is equal to minus 7 plus root 33 by 2 x 1. So, that is from the first row. The second, so the second 1 gives you 4 x 1 minus 3 x 2 is equal to minus 7 plus root 33 by 2 x 2 and the third one gives you x 2 is equal to minus 7 plus root 33 by 2, root 33 minus 7 plus root 33 by 2 x 3. So, these are the 3 equations that you have.

So, as you can see the first 2 equations are will end up giving you essentially the same equation. So, you can you can see that.

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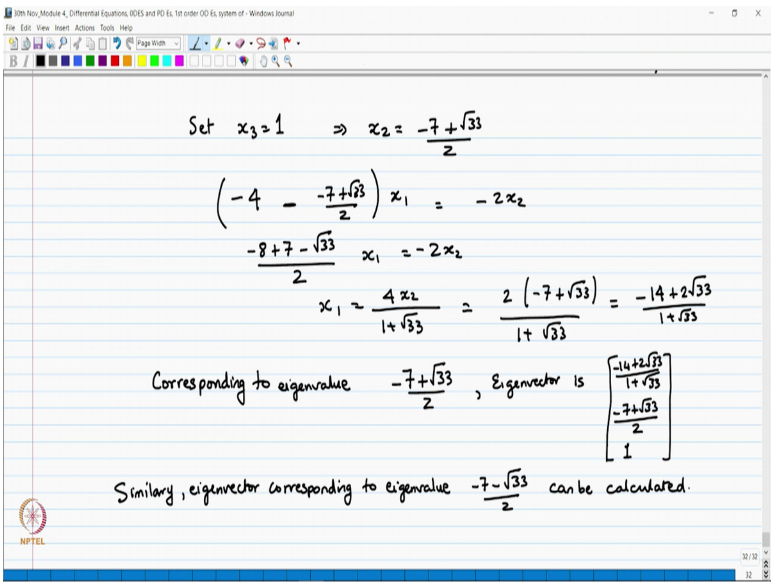

So, the first equation gives you minus 4 and the third equation connects x 2 and x 3. So, suppose you set, suppose you set x 3 equal to 1 this implies x 2 equal to minus 7 plus root 33 by 2 and once you have the value of x 2, so twice x 2 is just minus 7 plus root 33 by 2. So, you can work out this the answer to this to the value of x 1. So, suppose you use the first equation you get minus 4 x 1 plus or minus 7 plus root 33 by 2 and now x 1. So, I just took this to the to the left hand side now this will minus this equal to minus 2 x 2.

So, let us just multiply this out. So, you get minus 8 and now we will get plus 7 minus root 33 divided by 2, x 1 equal to 2 x 2 minus 2 x 2. So, this is, so I can write. So, now, now what I see is minus 1 minus root 33. So, I will just write x 1 is equal to 4 x 2 divided by 1 plus root 33 and this will give me x 1 equal to 4 times, now if I substitute this value of x 2, I will get twice minus 7 plus root 33 divided by 1 plus root 33 so.

So, this is the value of x 1. So, I have x 1 x 2 and x 3 and you can explicitly solve. So, we have the eigenvector corresponding to this to x equal to minus 7 to the Eigen value minus 7 plus root 33 by 2. So, corresponding to Eigen value minus 7 plus root 33 by 2 eigenvector is, so we set x 3 equal to 1 we got x 2 as minus 7 plus root 33 divided by 2 and this let me just write this out as minus 14 plus 2 root 33 divided by 1 plus root 33, minus 14 plus 2 root 33 divided by 1 plus root 33. So, this is the eigenvector it looks a little complicated, but really I mean you can easily put the values and you can write the numbers.

So, similarly eigenvector corresponding to Eigen value minus 7 minus root 33 by 2 can be calculated. So, this eigenvector I will just write the value, corresponding to this. So, the eigenvector will look very similar to this I will just write down the value I will write here. So, you will get 1 minus 7 minus root 33 by 2 and you will get minus 14 minus 2 root 33 divided by 1 minus root 33.

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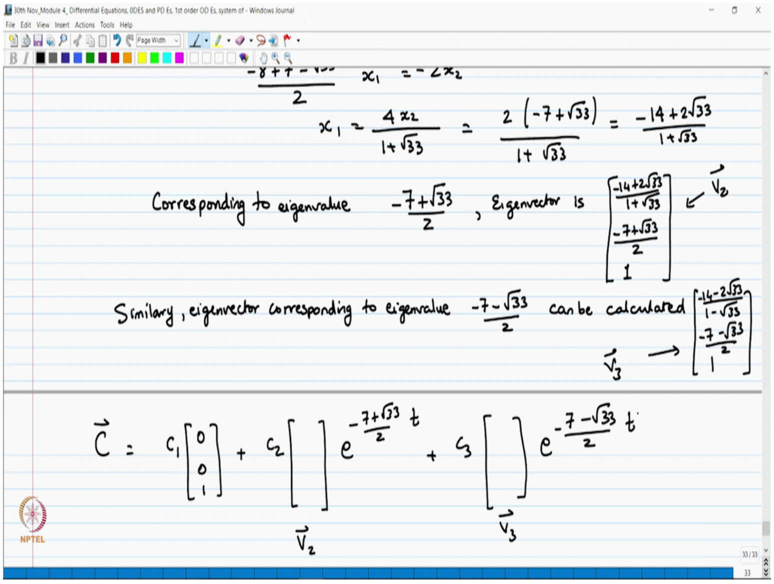

So, it look very similar with just the minus signs and so, now we have. So, we can write the general solution in terms of Eigen values and eigenvectors.

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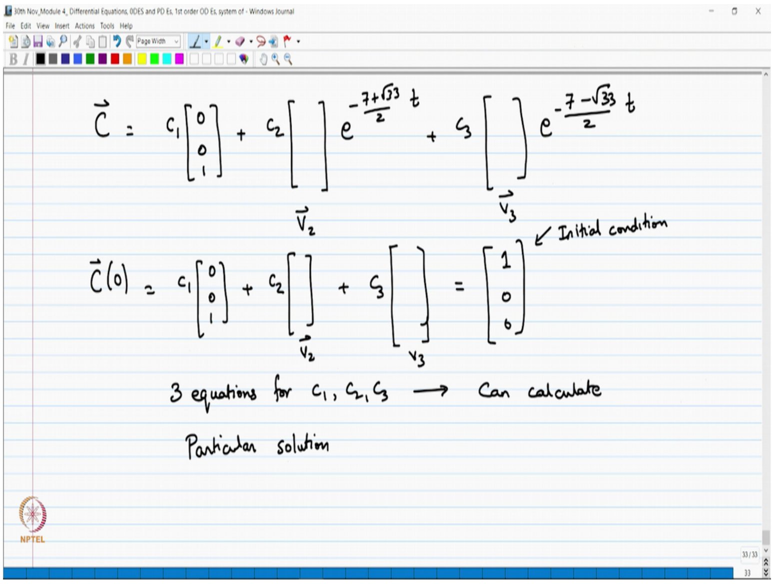

So, the general solution C is equal to. So, the first eigenvector is this constant eigenvector. So, 0 0 1, it is c 1 times 0 0 1, now you have e raised to 0 t that is not there at all and c 2 times. Now I will just call this v 1 v 2 and v 3. So, this is my v 2. So, eigenvector v 2 which is essentially this, this is v 3 and you have e raised to e raised to, so minus 7 plus root 33 by 2 t and you have c 3 times.

Now, I will have v 3 here I am not writing the values and I have e raised to minus 7 minus root 33 by 2 t and now if t equal to 0. So, each of these quantities is negative. So, each of these quantities is negative. So, when t equal to 0 this exponent will go to 0. So, what will happen is that this term will become 1, so will this. So, when t equal to 0. So, your c at 0 looks like c 1 times 0 0 1 plus c 2 times v 2 plus c 3 times v 3 and what you will get is you will get 3 equations.

So, now, this c 1 at 0 from the boundary conditions this is basically 1 0 0. So, this gives you 3 equations for c 1, c 2, c 3 and we can calculate, so can be calculated. So, finally, you can calculate c 1, c 2, c 3 and so this comes from the initial condition. So, initial condition we said that that A has 1, B and 0 are 0. So, that was this initial condition. So, c of 0 has this form 1 0 0, you can get 3 equations and you can solve for c 1 c 2 c 3. So, this gives the particular solution. And I am not actually explicitly working out these numbers, but you can substitute the values of v 1 v 2 v 3 and you can work it out, it will look a little messy because of this square root of 33, but essentially what I have shown is you can write the particular solution. So, once you have c 1 c 2 c 3 you know the solution of this kinetic equation.

So, what you got by this procedure is we did not apply any steady state approximation, we did not apply any equilibrium approximation, but we just solved the general problem of this the general chemical kinetics with these rates. So, this is a very important application and you know you can do this for any number of equations. In this case since everything was first order, so the whole system of equations was linear. Now if you add second order differential equations then you cannot do this because you will get non-linear equations, since everything was first order you could do with linear equations you could use Eigen values and eigenvectors and calculate the general solution of this equation.

So, with this I will conclude module 4 and next we will start module 5 in which we start talking about second order differential equations.

Thank you.