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

Module - 07
Lecture - 35
Practice Problems

So today we will end this module with some practice problems and I will just say a few things, that in this module you have learnt about technique for solving differential equations, which is called the power series method. And we have used it mainly to solve homogeneous second order differential equations, it is actually a fairly general method and we will see some conditions in the next module how when you can use it and how you what are the modifications of the method you can do.

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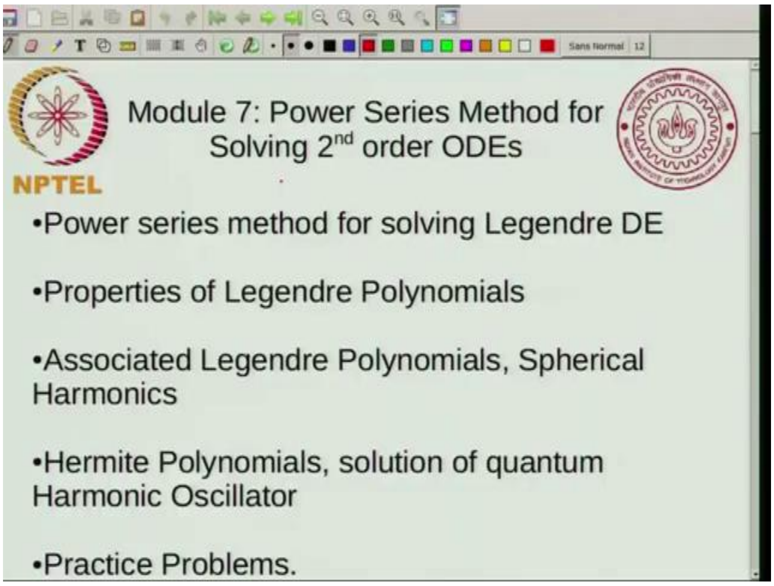

But we have in this module we are mainly focused on trying to illustrate the use of the power series method, we solve the legendre differential equation, we saw the what a call the polynomial solutions and these occur very naturally when you are dealing with many problems, we saw something called an associated legendre polynomial which we used to describe the rotational states, the hermite polynomials which are used to describe the vibrational states.

So, what I want to emphasize is that now the power series method there are lot of steps you have to work out things and finally, you get various interesting relations. And what is what is happened is that there are whole number of differential equations which are solved using the power series method, and these have been worked out in the past. So, people have worked them out. So, we have a very large number of these special polynomials. So, there is Legendre we have already talked about Legendre Hermite, but there are many other polynomials we will look at some of those in the next module.

So, let us work out a few practice problems. So, what I want to emphasize is there are 2 things to emphasize one is how you use the power series method and the second part second thing that I want to show is how you use properties of say Hermite polynomials or spherical harmonics. So, let us go and let us start with the first practice problem which essentially asked to use the power series. So, use power series method to solve y double prime plus 3 x y prime plus 3 y equal to 0.

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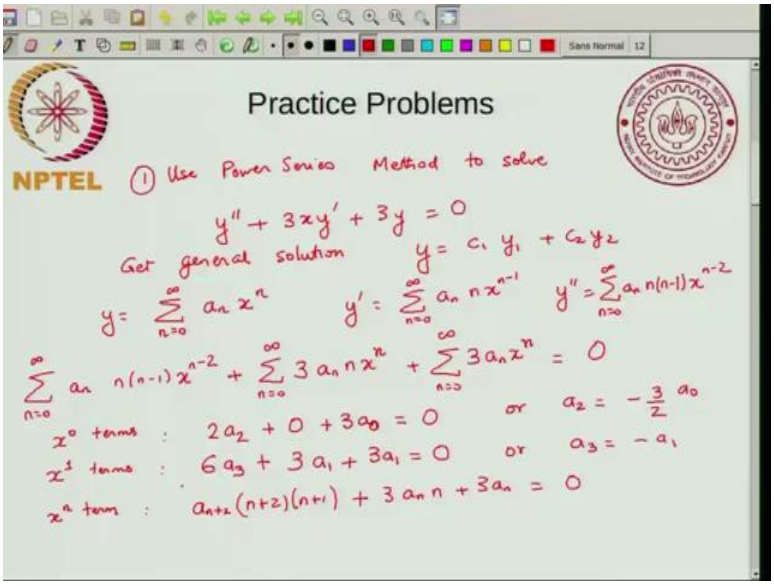

So, when I say solve you mean you would this is a homogeneous second order differential equation. So, you can write the solution as a so get general solution y is equal to c 1, y 1 plus c 2, y 2.

So, general solution has these 2 arbitrary constants c 1 and c 2. So, this is what you have to get from this by this method. So, let us go and start working of the method. So, if you want to solve this then you will say you will start with the trial form. So, y is equal to sum over n equal to 0 to infinity, a n x raise to n and then after that what you will say is that y prime is equal to sum over n equal to 0 to infinity, a n n x raise to n minus 1 and y double prime equal to sum over n equal to 0 to infinity, a n n n minus 1 x raise to n minus 2 ok.

So, this is how you start the power series method these the first step in the power series method, is to write power series and write the derivatives. Then you substitute in this equation now when you substitute in this equation, so the y double prime term will be as it is. So, I will write it sum over n equal to 0 to infinity, a n n n minus 1, and you have x raise to n minus 2, and then I can have plus sum over n equal to 0 to infinity 3; now x into a into y prime. So, I can write it as 3 a n n x raise to n with a plus sin and then you have plus sum over n equal to 0 to infinity 3, a n x raise to n that is for y equal to 0 ok.

Now, we can look at if you want you can look at x raise to 0 term. So, if you look at terms of power x raise to 0, what you get is in this case you cannot have any power of x raise to 0, in this case again you cannot have any power of x raise to 0 in this case you can have x raise to power 0. So, what I want to say is if you put x if you want x raise to 0 in the first term you have to have n equal to 2; now, n equal to if n equal to 2 yes. So, yeah in this case you can have n equal to 2. So, what you will get is n equal to 2 into 1 is 2 a 2. 2 a 2 in this case if you have term n equal to 0, but n equal to 0 term is 0. So, you get plus 0 in this case n equal to 0 now you have 3 a n, or a 0 n equal to 0. So, a 0, so you have this equal to 0 or a 2 in equal to minus 3 a 0 by 2.

Let us do x raise to 1 terms. So, if you have x raise to 1 then n has to be 3. So, 3 into 2 is 6. So, you get 6 and a 3 plus now in this case you will get (Refer Time: 06:51) x raise to 1. So, you get plus 3 into one. So, 3 a 1 and you get again 3 a 1 equal to 0. So, or what you will get a 3 equal to minus a 1, these are some of the relations you can do now you can ask in general x raise to n term. So, what is the recursion relation for x raise to n? So, if you want to have x raise to n then what you should have is a n plus 2, n plus 2 n plus 1. So, will have a n plus 2, n plus 2 n plus 1 plus.

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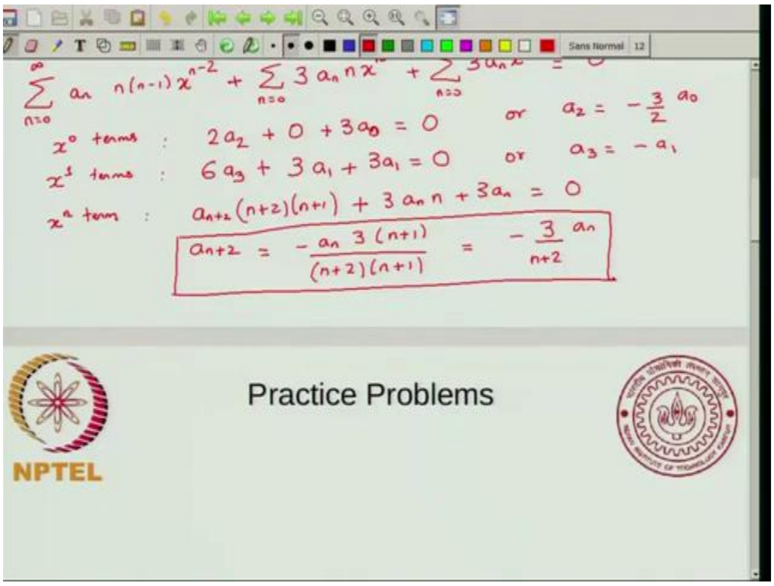

Now, if you want to have x raise to n then you will have 3 a n, n. So, 3 a n,.n and you have plus 3 a n equal to 0 or you can write you can write a recursion relation, now using this you can write the recursion relation a n plus 2 is equal to. Now this is 3 n plus 1 right or n plus. So, what I can write this as minus a n and I have a 3 and I have n plus 1 divided by n plus 2 n plus 1. So, I can write it as minus 3 a n divided by n plus 2. So, this is my recursion relation, and you can and you know incidentally you can just put a if you put n equal to 0 then you recover the a 2 and a 0 relation, if you put n equal to 1 you will recover the a 3 and a 1 relation. So, this is a general recursion relation from which you can get all the terms.

So now that we have that let us what we can say. So, if you look at let us say you look at if a 4. So, a 4 you will say is equal to. So, using this relation a 4 is minus 3 divided by now n equal to 2.

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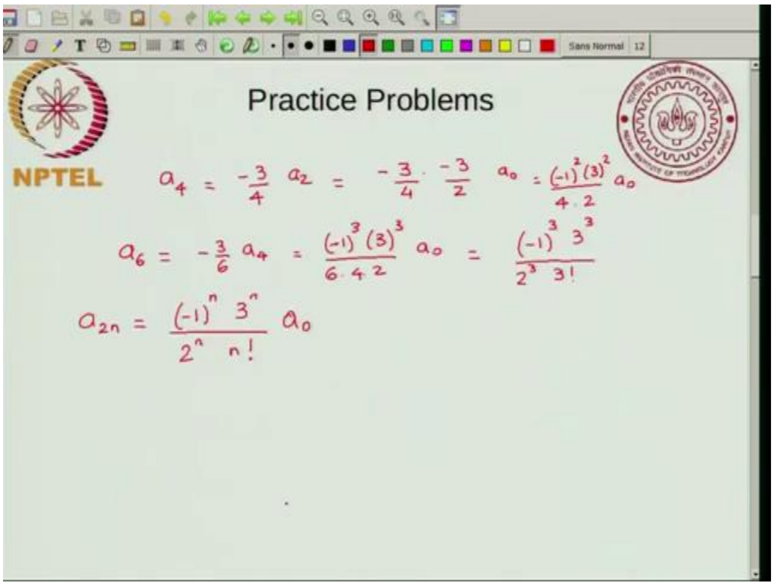

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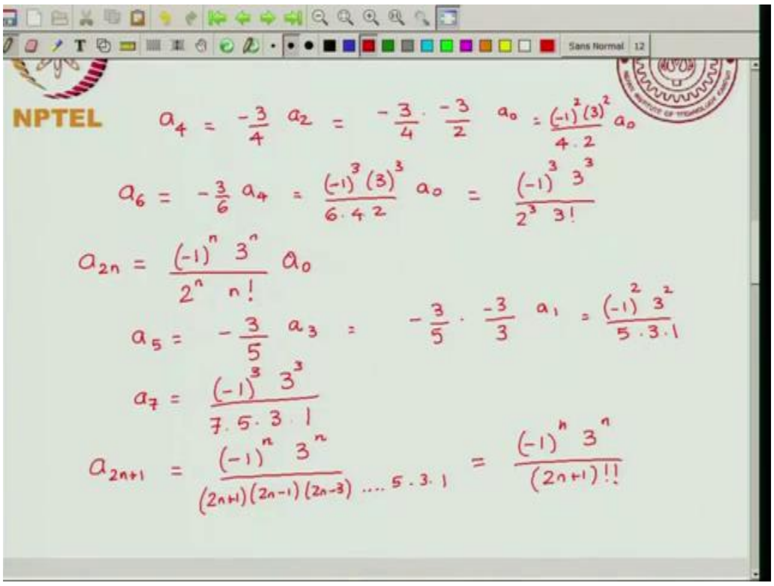

So, it is a 2 into minus 3 divided by 4; and a 2 a 2 is nothing, but minus 3 by 2 a 0. So, it is minus 3 into minus 3 divided by 4 divided by 2, a 0. So, this is equal to minus 1 square 3 square divided by 4 into 2 a 0. Similarly I can write a 6, a 6 as minus 3 by 6 a 4 and then if I use this relation what I will get is, minus 1 cube 3 cube divided by 6 4 2 a 0. So, in general you can write a 2 n as minus 1 raise to n, 3 raise to n divided by. So, now, I can write I can factor the 2 here. So, if I look at this I can just write it in a slightly different way; 3 cube divided by, now I will take a pair of I will take 2 cube into 3 factorial. So, I have 1 into 2 into 3, into 2 into 2 into 2. So, 2 cube into 3 factorial. So, I can write this as 2 raise to n, n factorial. So, this times a 0. So, I can write my a n, a 2 n in this form very very very elegant expression.

Now let us go what happens when let us look at the odd polynomials. So, what is we already saw a 3 and a 1, now let us look at a 5. So, a 5 equal to minus 3 divided by 5, a 3 equal to minus 3 divided by 5 into minus 3 divided by 3 a 1. So, instead of minus 1 I wrote it explicitly this way, and again the reason will be clear. So, this is minus 1 into square and 3 square divided by 5 into 3, 5 into 3 and I will just put a 1 also. Just similarly I can write a 7 as I can write by the same what I will get is minus 1 cube, 3 cube divided by 7, 5, 3 1. So, you can write the general expression a of 2 n plus 1 is equal to minus 1 raise to n, 3 raise to n divided by now what I have is 1, 3, 5 7. So, what we have is 2 n plus 1, 2 n minus 1, 2 n minus 3 all the way up to 5, 3, 1. So, it is this product. So, this is the expression for a 2 an plus 1, sometimes this is called a double factorial this is sometimes you use the symbols double factorial for this. So, sometimes this denominator is conveniently denoted as 2 n plus 1 double factorial. So, that is just the notation for this.

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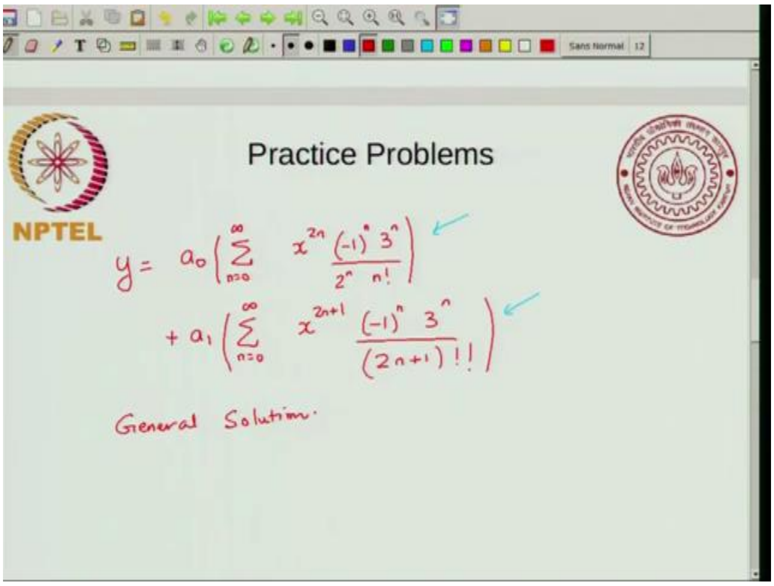

So basically now we have our general solution. So, we can write our general solution in this form. So, y is equal to you have a 0 times, what you have is sum over x raise to 2 n and what you have is n equal to 0 to infinity, and what was the coefficient of x raise to 2 n what we saw which was that minus 1 raise to n, 3 raise to n divided by 2 n, 2 raise to n n factorial; and you have the other term which is a 1 times, sum over n equal to 0 to infinity. Now I have x raise to 2 n plus 1 minus 1 raise to n, 3 raise to n divided by 2 n plus 1 double factorial. So, this is my general, and you can easily verify that each of these will actually satisfy the solution. So, each of the terms each of these terms and this term will individually satisfy the differential equation.

So, in this way the power series has given the general solution. So, this is the general solution and this completes this problem. Now the second problem that I want to do this is a very simple very nice illustration of using the recursion relation.

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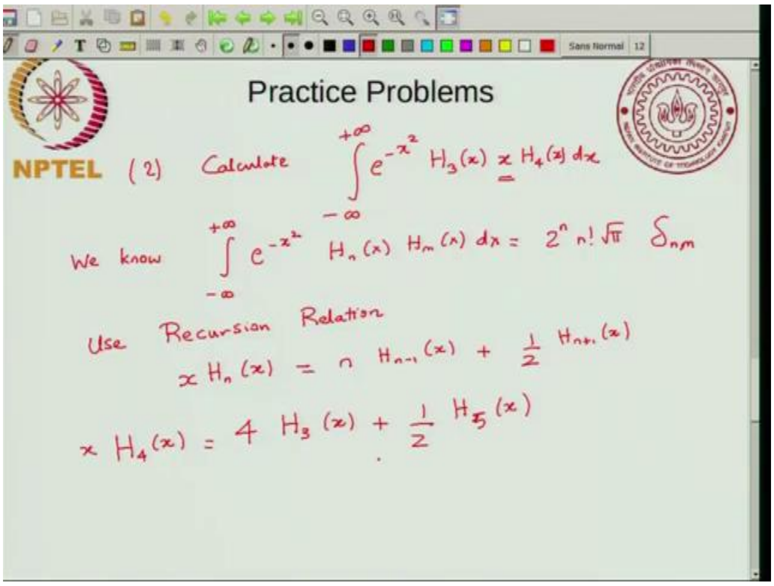

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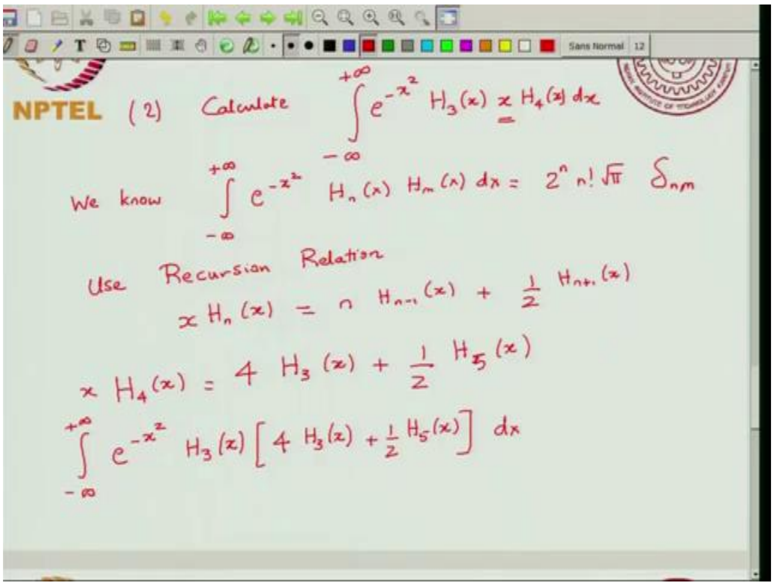

So, what you are asked to do is to calculate integral e to the minus x square H 3 of x, x H 4 of x, d x from minus infinity to plus infinity. Where h is a hermite polynomial. So, h 3 and h 4 are Hermite polynomials and you are asked to calculate this integral.

Now what you know, so we know integral minus infinity to plus infinity, e to the minus x square H n of x, H m of x, d x is equal to 2 raise to n, n factorial root pi times delta n m. So, if n is not equal to m it is 0, if n is equal to m then it is this number. So, now how will you calculate this? So, here you do not have just H 3 into H 4 you have H 3 x H 4. Now these actually such integrals appear when you are calculating the transition dipole moment for vibrational spectroscopy, and in fact though the idea the selection rules fall for vibrational spectroscopy come from calculations involving such integrals.

So, it is a actually a very relevant integral that you worry about in the that we worried about such integrals a lot. So, this x comes from the dipole moment operator, and this is something that we see a lot in spectroscopy. So, now how can you deal with H x times H 4. So, here you be use a relation we use recursion relation, what is the recursion relation I will write it in a slightly different form I will write x times H n of x equal to n times H n minus 1 of x, plus half H n plus 1 of x. So, this recursion relation is what we use and the notice that the right hand side has no x in front, it only has hermit polynomial multiplied by some constants it does not have x. So, now, once you use this in the relay in this integral then you can easily do the integral. So, what will says that H 4 x times H 4 of x is equal to now it will be 4 times H 3 of x plus half times H 5 of x.

So, what I did is a I will put n equal to 4 and I got this relation, now I will take this and substitute there and then you see orthogonality condition. So, when you substitute in the expression, what you will get is the following I will do it right here. So, you will get integral minus infinity to plus infinity, e to the minus x square now what you have is you have H 3 of x, then you have 4 H 3 of x plus half H 5 of x, d x now this has 2 terms.

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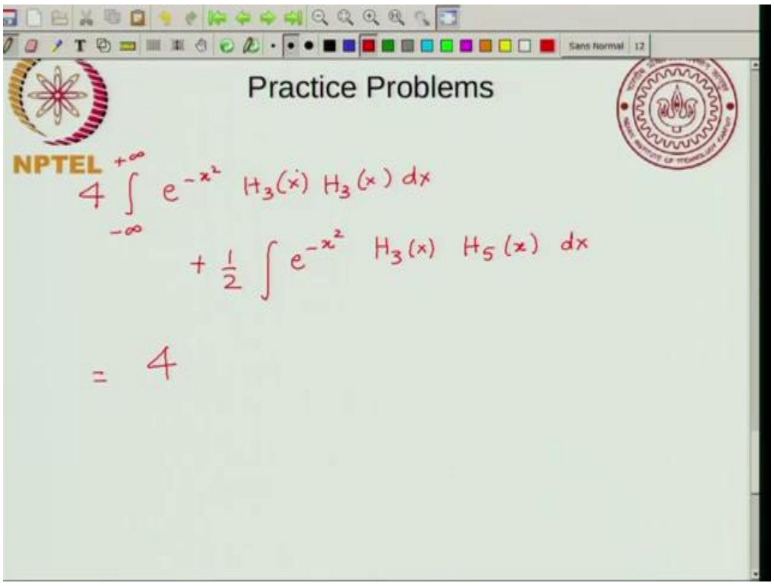

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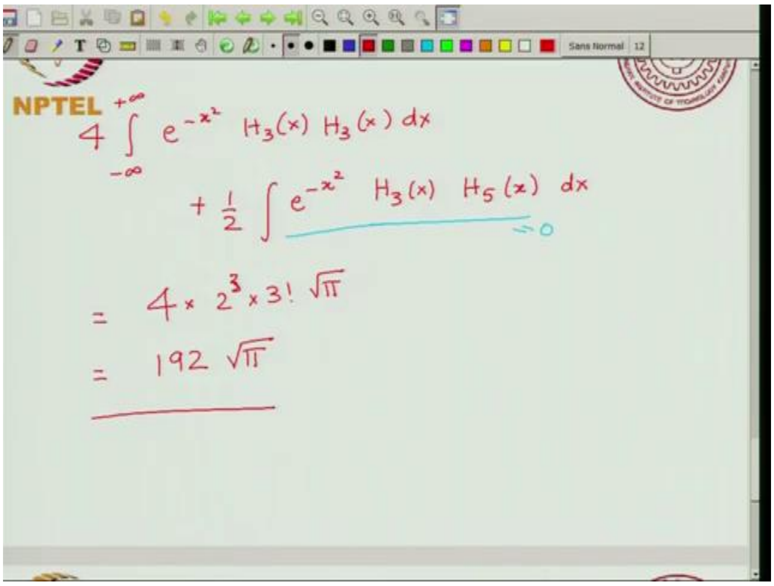

So, this has 2 terms. So, the first term first term is integral minus infinity to plus infinity, e to the minus x square, H 3 of x times H 3 of x, d x and this is multiplied by a factor of 4 and the second term is half integral e to the minus x square, H 3 of x, H 5 of x, d x.

So, now you use the orthogonality relation, so from the orthogonality relation the first term. So, here you have H 3 into H 3. So, if you go back to the orthogonality relation H n H m. So, here when n is equal to m then you will get only this part 2 raise to n, n factorial root pi because delta of n m is 1. So, what I get in this case n, n equal to m equal to 3, so you have 2 raise to 3 into 3 factorial into root pi, into 3 factorial into square root of pi 2 raise a 3, and the second case here n is not equal to m. So, this equal to 0, so the second integral is just 0 the whole term, the whole term is just 0.

So, then all you get is this and this is your answer. So, this turns out to be how much. So, you have 6 into 848 into 4, 192 square root of pi. So, what we started is with an integral that looked like this, and you got a number out of this derivation. So, you got the final expression you evaluated this integral, in order to evaluate that you have to use this orthogonality relation, now this orthogonality relation I expect you to remember this constant factor. So, I expect you to remember the orthogonality relation and the constant factor.

Similarly, I also it is also expected that you remember the recursion relation for hermit polynomials, because this is a very important relation that appears in lot of spectroscopy.

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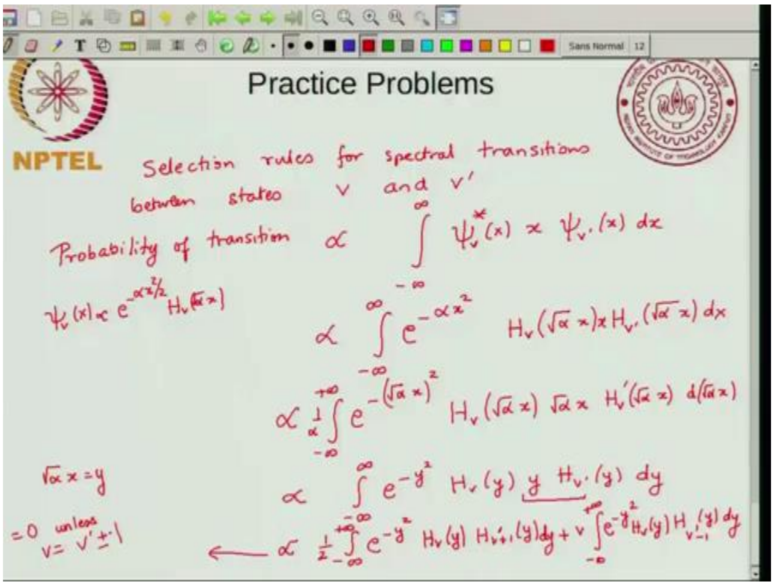

So, what is important about this about this problem is the following that suppose see when you want to do selection rules for spectral transitions between states v and v prime. So, we are going from a vibrational state v to a vibrational state v prime, then what appears in this selection transition is a quantity that looks like. So, actually you can write that the probability of transition under what is called the dipole selection rules.

So, this is proportional to something that involves an integral just like this. So, you have e to the minus x square by 2, rather what you will write it in a slightly different way. So, what appears is something that looks like this. So, you have psi v of x, x psi v prime of x, d x and if you remember the expression for psi v you had exactly an integral factors you have e to the minus alpha x square by 2, and you have another e to the minus alpha x square by 2. So, psi v I should put a complex conjugate here. So, what you get is because you had we had the expression psi v of x, has proportional to e to the minus alpha x square by 2 times some hermit polynomial of v of square root of alpha x, that was the expression.

So, now, when you substitute that you get one e to the minus alpha x square by 2 from the psi v star, one from psi v prime. So, you get e to the minus alpha x square, then you have H v of square root of alpha x, H x H v prime of square root of alpha x, d x; and now you can see this is a really amazing relation. So, basically if I multiply by square root of alpha, and let us say I divide by square root of alpha. So, if I multiply and divide by square root of alpha this will look like integral minus alpha infinity to plus infinity, e to the minus I will write it as square root of alpha x the whole square, H v of square root of alpha x, square root of alpha x, H v prime of square root of alpha x and what I will write is d of square root of alpha x and I will just take a, I will just I will just have a 1 by alpha square 1 by alpha (Refer Time: 25:05) 1 by alpha, 1 by alpha I will absorb into the constant.

So, essentially what I will get is if I say square root of alpha x equal to y, then this is basically proportional to integral minus infinity to plus infinity, e to the minus y square H v of y, y, H v prime of y, d y. So, what you get. So, this is equal to now if you use y H v as if you use a relation the recursion relation, then this becomes essentially proportional to integral minus infinity to plus infinity, e to the minus y square. Now what you will get is a H v of y, and you will get a term that looks like H v plus 1 of y, and there is a factor of 1 by 2 and you will get another term that looks like plus v times then the other integral will have exactly the same, but you have e to the minus y square H v of y, and you have h or v prime plus 1 sorry v prime minus 1 of y, d y.

What I did is I used a recursion relation to write this as a as a sum of 2 terms one involving H of v plus 1, in the other involving H of v minus 1 or v prime minus 1; and each of these there should be a d y. Each of these integrals is 0, so probability of transition, so this equal to 0 unless v equal to v prime plus or minus 1. So, either if v equal to v prime plus 1 then the first term is non zero, if v equal to v prime minus 1 then the second term is non zero.

So, if v is not equal to v prime plus or minus 1, then this term goes to 0 and this is actually the selection rule. So, in a vibrational selection rule you learn that the difference between the screws 2 states that are involved in the transition should be plus or minus 1, and here we have seen a very elegant way to arrive at that result starting from the Hermite polynomials. Starting from when we and just remind you we use 2 properties of the hermite polynomial we use the recursion relation. So, this recursion relation and we use this orthogonality. So, with just these 2 relations you can easily derive the selection rule for vibrational spectral transitions.

So, I will conclude module 7 here, so in the next week we will do some more power series method, a little more advanced power series method which is called the Frobenius method.

Thank you.