Introductory Quantum Chemistry

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Lecture - 18
Harmonic Oscillator - The Series Solution

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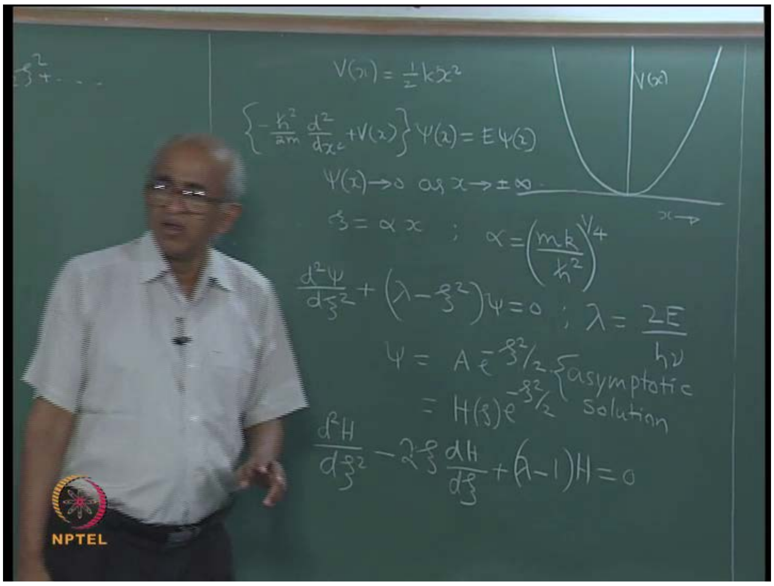

So, we here talking about the harmonic oscillator; it may just remind you of things that we did. For the harmonic oscillator potential energy is given by half k x square; the shape of the potential energy curve would be something like that and the Schrodinger equation itself would be this. And we want to solve this equation subject to the condition that as x tends to either plus infinity or minus infinity the wave function should approach zero, and the first thing that we did was we made a change of variable. We said that xi is equal to alpha times x; we determine the value of alpha. Well I will write it from my memory, but I hope you can verify this; it is correct, right. Alpha is equal to so much, and then what will happen? This differential equation becomes another one which may be written as d square psi by d xi square as lambda minus xi square into psi is equal to 0 where lambda was defined to be 2E divided by H nu where nu is the classical frequency vibration of the ammonic oscillator, right.

And then we argued that this equation has asymptotic solutions which are of the form psi is equal to some constant into e to the power of minus xi square by 2. It had also another asymptotic solution in which instead of the negative sign you would had a plus sign, but there we did not want, because that will go to infinity as xi tends to infinity, and it is not acceptable. But this is only an asymptotic solution which means that this is valid only in the region where xi is very large. It is not valid for small values of xi, but we wanted a full solution which is valid everywhere and therefore, what we did was we said let this I mean this is an asymptotic solution. So, what we do is we just modify this equation, and we say that okay, let us write the solution as H of xi e to the power of minus xi square by 2.

This is the way we will write the solution, and then our problem is to determine the function H of xi, and for that what we did was we took this functional form; substitute it that back into this equation and we arrived at an equation for H, and that equation is d square H by d xi square minus 2 xi d H by d xi plus lambda minus 1, correct me again I mean if I make a mistake; this is the equation. Please check this, and now the problem is I should solve this equation, and the question is how will I solve this equation? It is not only enough to solve the equation, but I have to ensure that the boundary conditions are satisfied; that means this function psi is equal to so how much should approach 0 as xi approaches either plus infinity or minus infinity. So, how will I solve this equation? The answer is that this is the way this equation can be solved is to just assume that H may be written.

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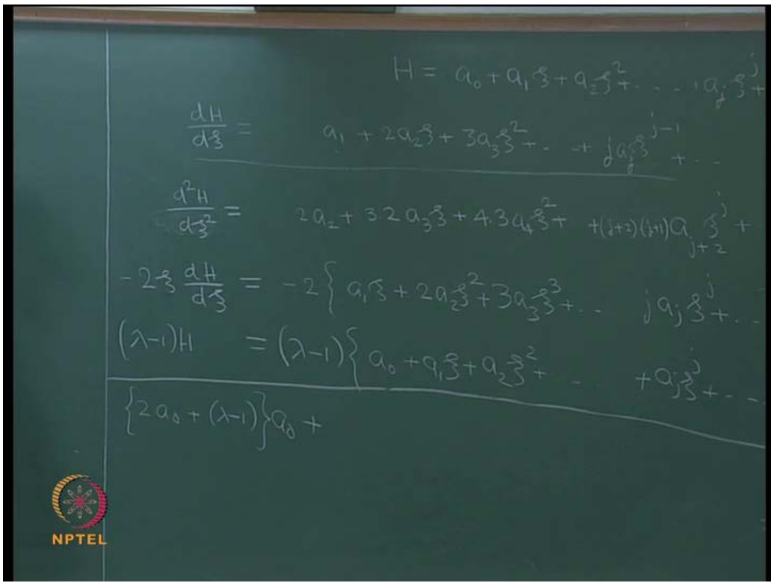

Let me write it like this. I am going to assume that H may be written as some a 0 plus a 1 xi plus a 2 xi square plus etcetera up to infinity where a 0, a 1, a 2, a 3; these are constants, okay. I just assume a solution which is a series, and what I will do is I will try to adjust the values of the constants a 0, a 1, a 2, a 3, etcetera, in such a fashion that H is going to satisfy this equation. But then if it goes to an infinite series perhaps I may run into problem, right, if the series is infinite. Why may I run into a problem? The answer is that the boundary condition, where is the boundary condition? This is the condition. I have to ensure I mean even if it is an infinite series I have to ensure that this series is such that this condition is satisfied. Then only I will have an acceptable solution, okay.

So, what is going to happen is that you see here I will have attempt like a j xi to the power of j and then of course, it goes to infinity; that is the way the series is. So, what I am going to do is I am going to substitute this here, correct, and see what the result is. So, in order to substitute that I should first evaluate d H by d xi; what will it be? I mean you have the series; it is fairly easy to differentiate it. Derivative of the first time will be zero, the second time will give me a 1, next time will give me 2 a 2 xi plus 3 a 3 xi square plus etcetera. In general what will be the general term? You will have xi to the power of j multiplied by what will be the coefficient? a j plus 1, or maybe I will write it in this fashion. If you differentiate this term what will be the answer? You are going to get j times a j xi to the power of j minus 1 plus etcetera, okay, because the derivative of this time, what is it? It is going to be j times a j times xi to the power of j minus 1.

So, let us now calculate the second derivative while when you calculate the second derivative this time actually it goes. So, therefore, you are going to have the first time as that that one you are going to get 2 a 2 plus 3 into 2 a 3 xi plus, what will be the next time? It is going to be 4 into 3 a 4 xi square plus etcetera, okay. This is how the series is, but I want to write down the term that contains let this is xi to the power of j unlike what we did here; I want to write down xi to the power of j j time; what will that can be? You can guess what that time is going to be by just looking at this expression. If you have xi to the power of two then you have a 4 multiplied by 4 into 3.

So, therefore, if I had xi to the power of j what I will have is a j plus 2 multiplied by j plus 2 into j plus 1. So, this will be the general time, correct, and now I also need I mean if I look at the differential equation I have d square H by d xi square, but I also need minus two xi times d H by d xi; so, that means I shall multiply this by minus 2 xi. So, minus two xi times d H upon d xi would be equal to, what will be the expression? Well, you have minus 2. I am not going to take the minus 2 inside. So, I will put a bracket but the xi; see this is my expression for d H by d xi. So, I have to multiply this expression by minus 2 xi; that is what I will do, but minus two I am not going to multiply it, I mean I am going to leave it as a common factor, but xi I am going to take inside. So, the first time that I will get will be a 1 xi, next time will be 2 a 2 xi square, 3 a 3 xi cube plus etcetera.

And this time will actually give me j a j xi to the power of j plus etcetera, and I have to close the bracket, right, and then the last time in the differential equation is lambda minus 1 h. So, I will just write lambda minus 1 into H which will be equal to lambda minus 1 which I will leave outside a bracket, and then simply write H, what is H? a 0 plus a 1 xi plus a 2 xi square plus etcetera and till a j xi to the power of j plus etcetera goes to infinity. And now I can just add these things, right, because I want to say that the sum of these three things is equal to 0. So, let me just add up everything, and then what will I do? I will put the result equal to 0, right. Why do I do this? Answer is very simple. I just want to determine the constants a 0, a 1, a 2, a 3, etcetera, right; that is the reason why I do this. So, I want to find a 0, a 1, a 2, a 3, etcetera. So, you just add this up.

So, for example, when I am adding you see I will be little bit careful. Here I have 2 a 2 this time is independent of xi. Here there is no time that is independent of xi, but there you have a time that is independent of xi. So, just add it up; you are going to get 2 a 0 plus lambda minus 1 into a 0 as the first time, correct. Similarly you are going to get a time which will involve a 1; what will that time be? This is not there sorry.

I can now remove this; otherwise, I may take something from there. I think I have made a mistake, right, 2 a 2 I have written 2 a 0, and I have put the bracket in the wrong place. So, this is actually and please watch out, you see I do make mistakes. So, that is what it is actually 2 a 2; I have taken 2 a 2 from here and lambda minus 1 into a 0. So, therefore, that is fine. Then the time that depends upon, sorry not a 1, but the time that depends upon xi what is that? Linear in xi; well, here you will see that it is 3 into 2 a 3.

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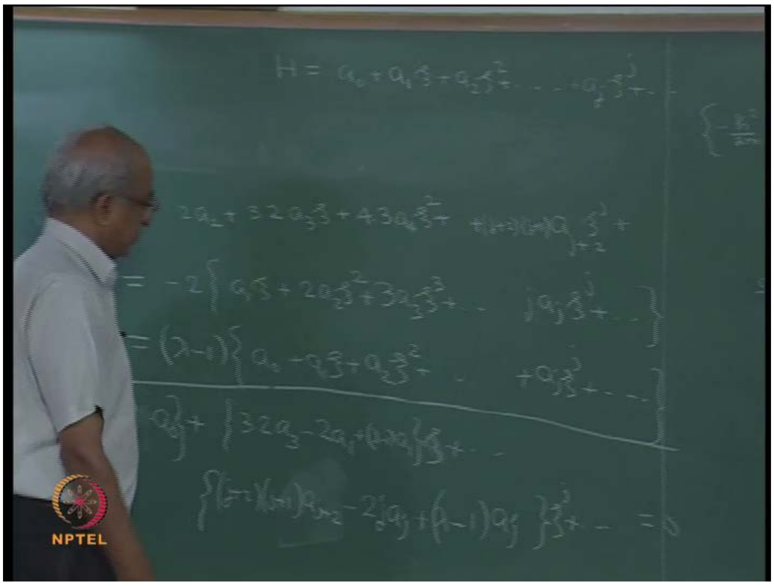

And here it is actually minus 2 a 1, and from there what will happen you will get plus lambda minus 1 into a 1, correct again I suppose I have not made any mistakes, but then you see I mean I can go on doing this, but what is of great interest is the general time where I have xi to the power of j. So, what will that term be? Let me just write that term and we are done with this, because it is the general time that is the most useful. So, what is the coefficient of xi to the power of j? Well you are going to get j plus 2 into j plus 1 into a j plus 2 that is coming from here. It is the time involving xi to the power of j; then there is a term coming from here j a j but that has a minus two associated with it. So, therefore, minus 2 into j a j, and what is the contribution from this line that is going to be plus lambda minus 1 into a j, correct. So, you have an infinite series, right, infinite series involving si.

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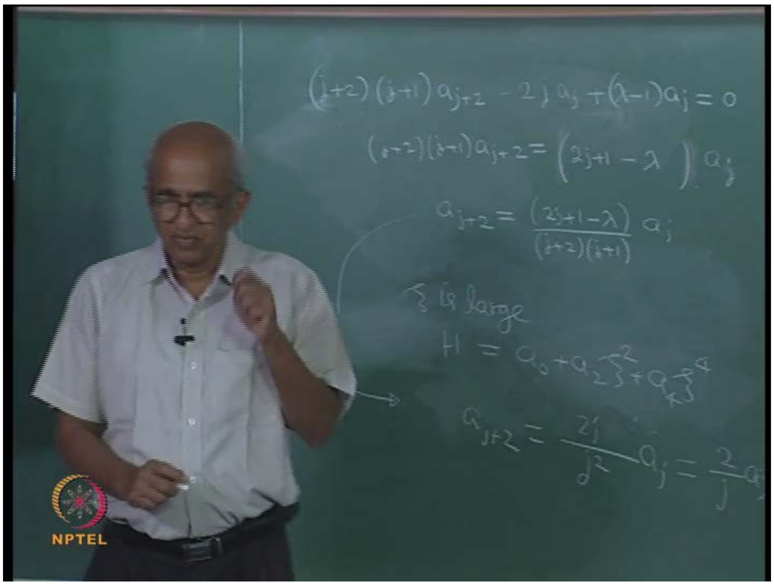

So, actually if you think about this, this is of the form some constant a 0 plus a 1 into xi plus a 2 into xi square plus etcetera; that is of the form of this equation speaking in general, right, and this has to be identically equal to 0; it has to be 0 for all values of psi, right. Whatever value of psi you put in here whatever value of psi you put in there this has to be equal to 0, correct. So, how can that be satisfied? The only possibility is that each coefficient in here; when I say each coefficient the coefficient is a 0 or a 1. Coefficient of xi to the power of j has to be equal to 0; that is the way in which this can be satisfied. I mean it is not difficult to prove this. If you want to prove it what you do is first you have to put xi equal to 0 into this equation, because this equation is valid for all values of si.

So, if we put xi is equal to 0 you will find that a 0 is equal to 0, fine. Then you differentiate this with respect to xi, because this is valid for all values of xi I can differential it. If you differential this term will go, the first term will be a 1, the next term will be 2 a 2 xi plus etcetera, and you put xi equal to 0, right, and the right hand side has to be 0 because right hand side is 0; you are differentiating 0. So, answer has to be 0. So, therefore, if you differentiated this and put the derivative equal to 0, you will find that a 1 has to be 0. Then you differentiate it once more, and put xi is equal to 0; you will find that a 2 has to be equal to 0, then a 3 has to be equal to 0 and so on. That is another way of arguing the same thing.

So, if you had such an equation where you have a power series and the power series is identically equal to 0 for all values of the variable, then the only way that can happen is that each coefficient, right. The coefficient of xi to the power of j in general has to be equal to 0. So, that means a 0, a 1, a 2, a 3, a 4, they are all equal to 0. So, therefore, if that is the way it is you can say that well if this equation has to be satisfied this equation that we have here if it is to be satisfied then this must be equal to this is the coefficient of xi to the power of zero. So, this has to be equal to 0, not only that; this also has to be equal to 0, right, for each power of xi the coefficient has to be equal to 0, right.

So, how many equations do you get? You get infinite number of equations which you need because you have infinite number of unknowns; you have a 0, a 1, a 2, a 3, a 4, etcetera, they are all unknowns' right. So, you want to determine them, and this is the way in which you can determine them. So, therefore, in general what happens is that this term which is the coefficient of xi to the power of j must be 0. So, this is the only term that I actually need; this is only condition that I need. Let me write that condition; it says that, that is what it says, and this has to be valid for all values of j. j equal to 0, 1, 2, 3, etcetera. Now we can rearrange this. You can say that this means j plus 2 into j plus 1 a j plus 2 must be equal to I will take these terms to the other side. But we can see that there is a a j that is common. So, I will take a j outside, and what I will have left is 2 j plus 1 minus lambda, right.

This is what I would have. This actually means a j plus 2 must be equal to 2 j plus 1 minus lambda into a j divided by j plus 2 into j plus 1; this is the condition. So, for any j this condition has to be satisfied. Look at this condition; it is quite interesting, because suppose I put j equal to 0, what will I get? Let me just illustrate what happens. If I put j is equal to 0 what I am going to get is 2 j will be is 0. So, 1 minus lambda divided by 2 into 1 should be equal to a 2; that is what this says, correct. And similarly if I put j is equal to 1 you will find a 1 here; I am not going to write this. You can easily write what it is, and that actually will give you the value of a 3. So, you notice that the value of a 0 determines a 2, and the value of a 1 determines a 3, but then if I know the value of a 2, I can put that value here, right; put j is equal to 2 then I would have determined the value of a 4.

So, therefore, from here I can determine a 4, right, and from a 4 I can determine a 6 from which I can determine a 8. So, once you tell me what the value of a 0 is, right, once you have a value for a 0, then that will uniquely determine a 2, a 4, a 6, etcetera. And similarly if we had a unique value if you had some value for a 1 that you can put into the equation you will get a 3, then from that you can calculate a 5, a 7, etcetera, right. So, this relationship actually determines I mean this is the general relationship; it determines a j plus 2 in terms of a j, and it is referred to as a recursion relation. So, therefore, what we can do is we can have some value for a 0 and some value for a 1; that we can choose as we like, but then a 2, a 4, a 6, etcetera has to be chosen according to the recursion relation, right.

So, you chose any value for a 0; you will get the corresponding values of a 2, a 4, etcetera, and similarly you choose any value for a 1 you will get the corresponding values for a 3, a 5, etcetera, and therefore, how many variables do I have which are free to choose which I can choose; I can choose any value for a 0, I can choose any value for a 1. So, therefore, I have two things that can be independently chosen not surprising, why because this is a second order differential equation. Any solution would have two constants to be determine, and here the way it has happened the two constants are actually a 0 and a 1; that is why that is happening, nothing strange. But then I can use information which is already known to us; the information is that this is a potential that is symmetric, this is a potential that is symmetric. So, that means solution of the Schrodinger equation it has to be either symmetric or antisymmetric under the operation of replacing x with minus x.

So, if we change the sign of x the wave function either has to change sign, or it has to remain unchanged. So, suppose I am looking at solutions which are symmetric, then what will happen? Well, you have a power series; the power series is of this form, correct, and that power series multiplied by e to the power of minus xi square by 2 is the solution. So, whenever you place x with minus x what will happen to si? Si will get replaced with minus xi, but this term is not going to change, and this is always symmetric with respect to this interchange with respect to this replacement of x by minus x or xi by minus xi. So, what will happen is that this H may be symmetric or it may be antisymmetric, and when is that H is symmetric? If H is to be symmetric then what should happen is that I should have only the even terms in the series.

I should have a 0, then a 2 xi square; I can have a 4 and so on. Then the function will be symmetric, and if it is to be antisymmetric or an odd function then I should not have any even terms in the series, I should have only the odd times. So, therefore, what I realize is that in my power series I would have only the even terms or only the odd terms, right. So, that means I have two possibilities now; what are the two possibilities? I can put a 0 nonzero and a 1 equal to 0, right. If I put a 0 nonzero then what will happen? a 2, a 4, etcetera will all be nonzero, and I will get the even solution, or I have the possibility of putting a 0 equal to 0 then a 1 is nonzero, and what will happen? I will get the odd series and that means I will get the antisymmetric functions, correct.

So, let us say that I will think of the situation where a 0 is nonzero, but a 1 is equal to 0, why? Maybe this will give me the solution that is symmetric which means again what I mean by symmetric if you replaced xi with minus xi the solution will not change; it will remain unchanged, and therefore, it will contain only even powers of xi. So, those even powers of xi which are in the solution are actually governed by this recursion relation, correct. See you look at the recursion relation, what does it tell you? You give me the value of a 0, then I will calculate a 2, a 4, a 6, a 8, etcetera, according to this recursion relation, and what happens is that the series actually goes to infinity, because you cannot see that anything is 0 anywhere, because you give me a value I will put it there I will just calculate.

So, then the question is if it is an infinite series what is the behavior of that series? Is it a series which will guarantee that this object will tend to 0 when the value of xi tends to infinity, right. It is not enough to have any series; the series should be such that that series into e to the power of minus xi square by 2 should tend to 0 when xi tends to infinity. So, this is something that I want to analyze, and how am I going to analyze that? Well, the answer is this. Suppose the value of xi is very large, well, what we are saying is that I have an H which may be written as a 0 plus a 2 xi square plus a 4 xi 4. Notice I am writing only the symmetric case plus etcetera. This is the behavior, and I am going to analyze the behavior of the series when xi is very large.

When xi is very large, which are the times that you would expect are the most important definitely those terms with large powers of xi; that means I am interested in the situation where the value of j is very large, right because those are the ones that are important for large values of xi. So, if j is very large what will happen to this recursion relation? If j is very large you see it should possible for me to neglect this lambda or one. Let us say that a j is 1000 for example, correct. Then you can neglect the value of this lambda; you can neglect the one in comparison with 2 j, right. So, what will happen? You will have 2 j in the numerator divided by j plus 2 you can neglect that two, j plus 1 you can neglect the one.

So, therefore, j square into a j. This is the form of the recursion relation when j is very large, right, and therefore, what happens is that this recursion relation becomes 2 divided by j into a j. So, for large values of j this recursion relationship actually becomes simple. It simply says that a j plus 2 must be equal to 2 divided by j into a j. Now what I am going to say is that if a series obeys that kind of recursion relationship then the series actually behaves like the function actually will behave like e to the power of plus xi square. That is the claim; that is what I am going to claim. If I have an infinite series where for large values, let me repeat this. I have an infinite series where for large values of xi the recursion relationship is given by a j plus 2 equal to 2 by j a j. Then my claim is that the series for large values of xi will behave like e to the power of plus xi square.

Now if it behaves like e to the power of plus xi square is it acceptable? Well, you look at H. See H is here; I am now saying that if I had an infinite series this is going to behave like e to the power of plus xi square and e to the power of plus xi square into e to the power of minus xi square by 2. The net result is going to be xi; one of them is e to the power of plus xi square, and the other one is only minus xi square by 2. So, therefore, the net answer will be e to the power of plus xi square by 2, and if it behaves like that it is not an acceptable solution. Because you see this function this power it is decreasing, but the increase in this is huge and is not able to compensate for the decrease caused by the other term. And therefore, what happens is that this infinite series if I had an infinite series then I will not get an acceptable solution, correct, this is with the problem.

So, the question is how will I get an acceptable solution? Answer is that I should not have an infinite series. The series has to terminate. It has to be a polynomial; the function that I am getting must be a polynomial. I have to manage things in such a fashion that the function H is a polynomial, okay. Well, before I go into that I how does one prove that if a series obeyed this recursion relationship, it behaves like e to the power of xi square. Well, very briefly let me tell you how it can be done. I do not think I need these equations anymore. So, let me remove them.

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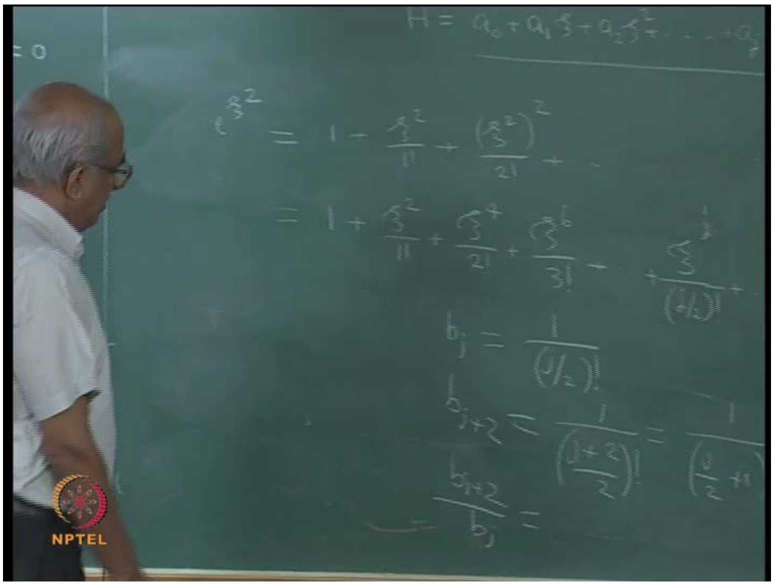

So, you see if you had e to the power of xi square you know the power series expansion for e to the power of x; e to the power of x can be written as the power series. So, similarly e to the power o f xi square can also be written. So, what will happen is you will get 1 plus xi square by 1 factorial plus xi square the whole square by 2 factorial plus etcetera, right. This is what is going to happen which may be written as 1 plus xi square by 1 factorial plus xi to the power of 4 by 2 factorial plus xi to the power of 6 by 3 factorial plus etcetera; xi to the power of nu divided by how much or may be xi to the power of j divided by how much, right? j has to be even the way it is. So, it will be j by 2 factorial, right, plus etcetera, agreed. The coefficient of xi to the power of j has to be 1 by j by 2 factorial.

So, therefore, this series you see the coefficient of xi to the power of j for this series the coefficient of xi to the power of j I will denote by b j; for notation purpose I just call it b j. So, what is b j? It is going to be 1 by 2 factorial, right. The coefficient of xi to the power of j for this series is actually b j, and it is equal to 1 by j by 2 factorial. So, what will be b j plus 2, right? The next term is going to be b j plus 2, and what will that be? It will be equal to 1 by j plus 2 by 2 factorial, agreed, and that will be equal to 1 by j by 2 plus 1 factorial, correct. I mean why do I do this, because I want find the recursion relationship that is valid for the series, and to show that that recursion relationship and this recursion relationship are the same, and because the recursion relationships are the same the behavior of this series and the behavior of that series has to be the same; that is the reason why I am doing this. So, therefore, now let me calculate b j plus 2 divided by b j, how much would it be? Well, the answer is firstly I ran out of space there difficult for me to write.

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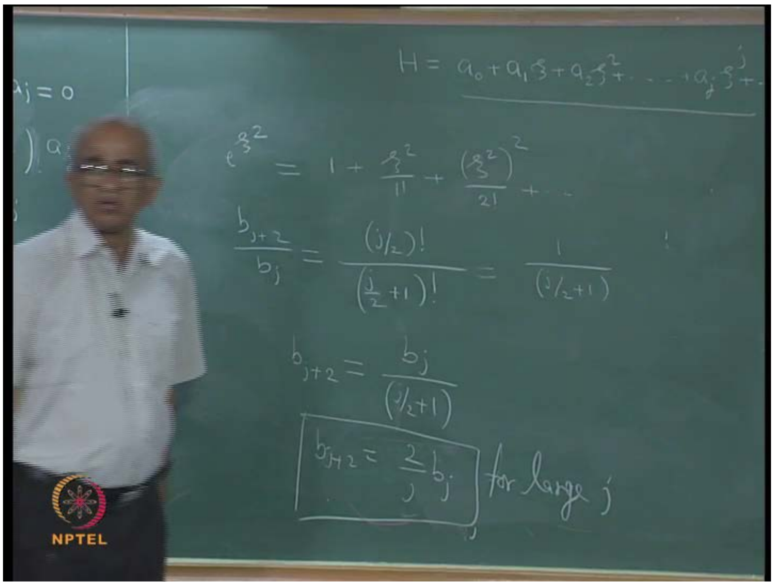

b j plus 2 divided by b j will be equal to j by 2 factorial in the numerator divided by j by 2 plus 1 factorial in the numerator; that is all and to this I mean this is a very easy to simplify. It is of the form you see some number n factorial divided by n plus 1 factorial; that is all, right. This is of the form some number n factorial divided by n plus 1 factorial. Well, the answer is 1 by n plus 1. So, therefore, what will happen is that this will just become 1 by j by 2 plus 1; that is all, very, very simple, and therefore, what happens? I find the recursion relationship for this series. It simply says that b j plus 2 must be equal to b j divided by j by 2 plus 1; that is the recursion relation for this series. And if the value of j is very large, what will happen to this recursion relationship? The value of j is very large; you can neglect that one.

And then what will you find? You will find that b j plus 2 must be equal to 2 divided by j b j, and therefore, I have actually proved what I wanted to prove namely this recursion and that recursion are the same, and therefore, the behavior of the series is just the same as the behavior of that series, and therefore, this series will behave like e to the power of xi square for large values of xi, and hence is not an acceptable solution. Well, you see I seem to be arguing against myself. I found the solution, and then I am arguing that this is not a valid solution. Well, it is not a valid solution if it has infinite number of terms.

So, what is the way out? It should not have infinite number of terms. I should be able to terminate the series at some power of psi, how will I do that? Well, there is a very easy way out; see you look at the lambda, what is lambda? Lambda is given here; lambda is this is given here. So, if you give me some arbitrary value of energy, the value of lambda is something, and the series will actually go on to infinity, and you will not get an acceptable solution. But suppose it so happens that lambda is equal to let us say 11, suppose just to illustrate, suppose lambda is actually a number like 11.

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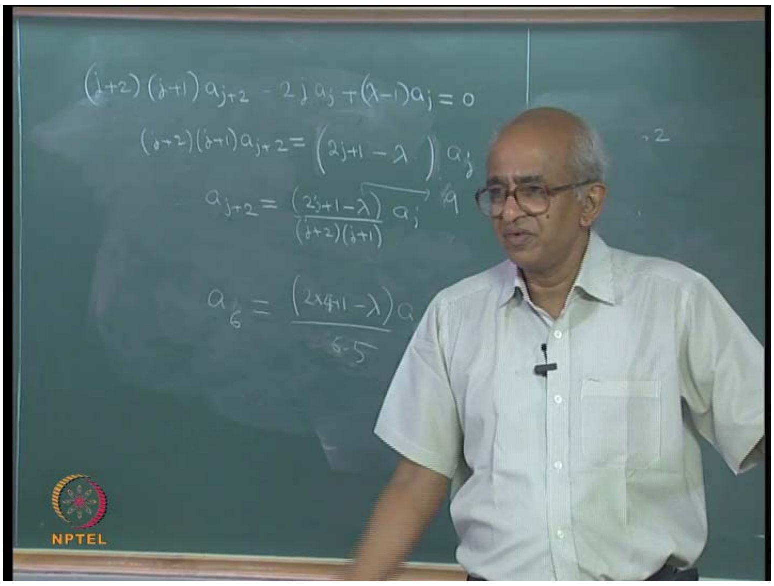

So, if lambda is equal to 11, what will happen? Suppose if lambda is equal to 11 and suppose I put j is equal to 5; suppose I put j equal to 5 on the right hand side I will have a 5, on the left hand I would have a 7. But then I will have 2 into 5 plus 1 minus lambda divided by 7 into 6, right; this is there, okay. I was actually saying that I am concerned with the even series, and now suddenly I switched over to the odd series. It is better that I say lambda is equal to 9 suppose, then what will happen is that I will have 2 into 4 here, and I am thinking of a 4 and 6 into 5, and this will be a 6; I mean just to be consistent with what I was saying. Earlier I was saying okay, I am only concerned about the even series not about the odd.

So, imagine that I have a value of lambda which is 9, and imagine that I calculate a 6 from a 4. Then what will happen is that you will have 2 into 4 plus 1 minus lambda divided by 6 into 5. And if I say lambda is equal to 9, you can see what is going to happen? a 4 is not zero, but a 6 is 0, and if a 6 is 0, what about a 8? a 8 is determined in terms of a 6. So, if I have lambda equal to 9 then what will happen is that I will have a 0, a 2, a 4, and starting from a 6 all the terms are 0, and therefore, I have successfully terminated the series at a finite power of psi, and I will have an acceptable situation. That is absolutely no problem, because this H is a polynomial, and any polynomial multiplied by e to the power of minus e square by 2 will tend to 0 as xi tends to infinity, and therefore, everything is fine.

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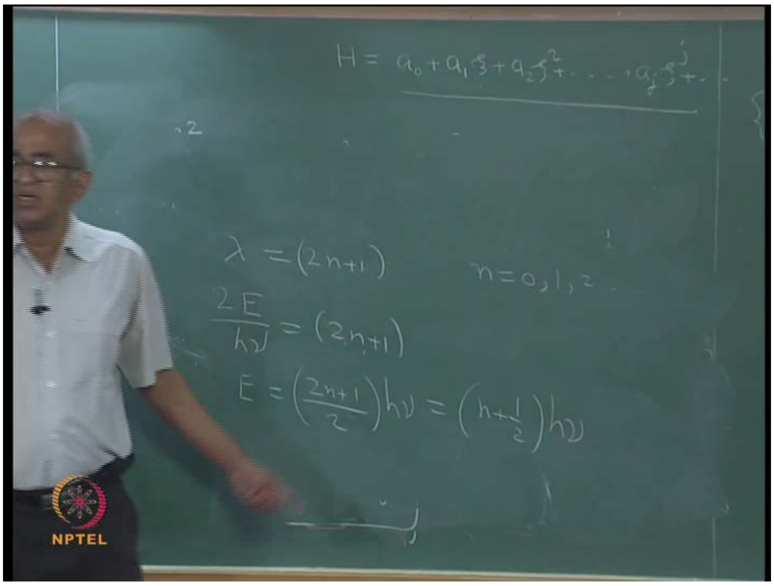

So, therefore, what is the solution? The solution is very simple. I should have lambda equal to what? If I had lambda is equal to 2 n plus 1 where n is an integer, right, then what will happen is that a n can be nonzero, but a n plus 2 will be 0, and if n plus 2 is 0 everything higher will also be 0. So, therefore, in order to get acceptable solutions I should have lambda is equal to 2 n plus 1. If I have lambda equal to 2 n plus 1 guarantee I can have acceptable solutions, right, and what are the values that I can have for n? n may be 0 perhaps it may be 2, it may be 4, it may be 6 and so on, right. Why these even numbers? Because I am only thinking of the even solution; if I had thought of the odd solution exactly the same thing is going to happen and then n can have the values 1, 3, 5, etcetera.

So, therefore, the final result is that n can have the values 0, 1, 2, 3, etcetera and further lambda should be equal to 2 n plus 1; if that is the way it is I will get an acceptable solution, and what does it mean in terms of energy? Lambda is related with the energy by this relationship. So, 2 e divided by H nu must be equal to 2 n plus 1 or that means e must be equal to 2 n plus 1 divided by 2 H nu or that means e must be equal to n plus half H nu; e must be equal to n plus half H nu. Then only you will have acceptable solutions; otherwise, you are not going to get acceptable solutions, fine, and further this lambda is equal 2 n plus 1 can be put here, right, and therefore, what we are actually looking for the solutions that we are looking for have instead of lambda minus 1 we would have the number 2 n here where n is an integer, right, we will stop here.

Thank you for listening.