Introductory Quantum Chemistry
Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 17
Schrodinger Equation for the Harmonic Oscillator

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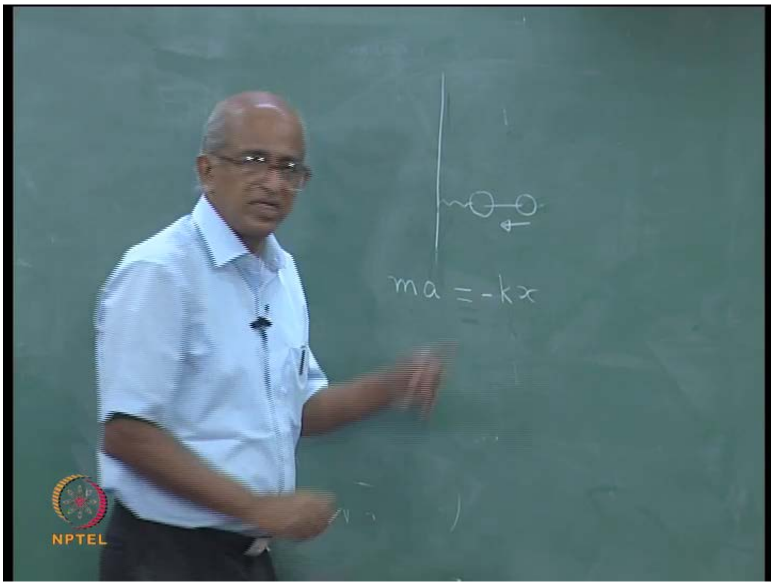

Let us look at the problem of a harmonic oscillator. So, what is a harmonic oscillator? I have discussed it several times, but today now we are going to discuss it in great amount of detail. The simplest example that I can think off is a hydrogen atom attach to the surface of tungsten by a chemical bond of course. And if you as I have been repeatedly saying, if you displace it in one direction, in that direction and release it, it will execute vibrational motion. Why does it execute vibrational motion, because when I have displaced it with this position, the bond between the hydrogen and the tungsten has been stretched. And. So, there will be a restoring force trying to bring the atom back to the equilibrium position, and the simplest thing is to say that that restoring force is proportional to the amount by which I have displace the atom.

So, if x is the displacement of the atom from the equilibrium position, the restoring force trying to bring it back to the original equilibrium position will be equal to k times x with a negative sign; the negative sign is put, because it is in the opposite direction. So, this will be the restoring force, and you know that in such a problem what will happen this is the restoring force, so therefore, if I am using Newton equations of motion what I will have to say is mass into acceleration would be equal to see the particular subjected to this restoring force. So, therefore, what will happen, it will move it will get accelerated because the force is acting on the particle under the Newton's equation will simply tell me that mass into acceleration must be equal to that force minus k x.

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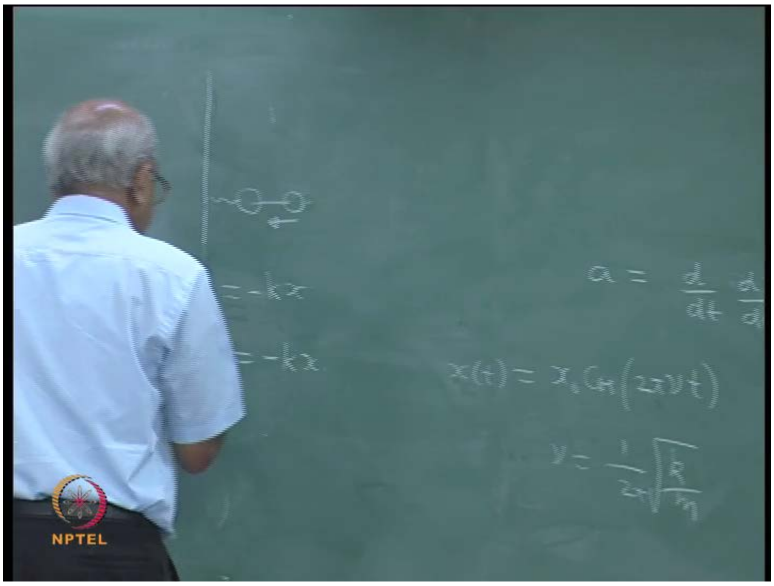

But acceleration is what, acceleration is rate of change of velocity. So, it is rate of change of velocity, so I naturally have to have dv by dt, but v itself is nothing but rate of change of position. So, therefore, acceleration is nothing but the second derivative of the position of the particle. And hence what happens to this equation, this equation becomes m into d square x by dt square is equal to minus k x, a simple differential equation very easy to solve. I shall just say that that the solution of this equation may be written as x of t equal to a some x zero cosine of 2 pi nu t this is the solution.

Where I have assumed that the particle has been initially displaced to a position which I denote as x zero. What I am saying is I have my particle at the equilibrium position, initially what I have done is, I have moved it and put it in to a new position such that the displacement is x zero, then this is the solution. And this nu, you can actually substitute this into that differential equation and get an expression for nu, what you will find is that this nu must be equal to 1 by two pi into square root of k by, a very easy to do that is why I am not doing it. You can take the solution substitute into the differential equation and you will see that the differential equation is satisfied by that solution provided, I take nu to be equal to 1 by 2 pi into square root of k by m. And what it means is basically simple because it must be very very familiar to all of you, I am not say describing this in detailed, but what it means is that the particle will actually execute oscillations, classical mechanical particle will execute oscillations. It will oscillate that many number of times per unit time and hence this is known as the frequency of vibration of the oscillator.

And further, if I was using classical mechanics, you see I can actually displace it by any amount. This spring is assumed to be completely elastic, even if I stressed it by a large amount, it will not break that is the assumption in this model. So, therefore, I can displace it by any arbitrary amount, and the depending upon how much I have displace the energy of the system will be different. By displace it by a small amount and they will be small device displace it by large amount energy will be large, and therefore, a classical mechanically speaking the system can have any energy starting from zero to infinity, continuously energy can be varied if you want, you can give it any energy. So, there is no quantization at the classical level, all energies are permissible.

And one more I think that I want to say is you see if you have such a restoring force what is the potential energy that is characteristic of the system. The answer is that the potential energy must be defined by v of x equal to half k x square. This essentially means that the amount of what that you have to do, in order to displace the particle from the equilibrium position to a new position goes quadratically with that position. If you want to displace the particle by an x, the amount of energy or amount of work that you have to do amount of energy that you have to supply or the amount of work that you have to will go like x square that is the meaning of saying that the potential energy of the system is quadratic in x. So, therefore, you have v of x equal to half k x square this also can be derived, but I am not going to do it. Starting from this force, it is easy to to show that this must be the expression for the potential energy. So, what is of interest to us, it is not the classical mechanics of the system, but the quantum mechanics of the system.

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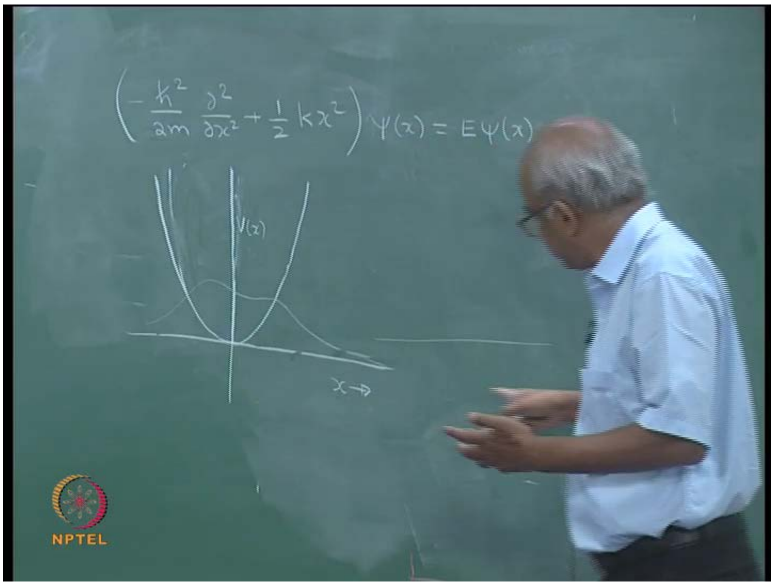

So, we will worry about the Schrodinger equation for the system. What is the Schrodinger equation, the Schrodinger equation is minus h cross square by two m dou square upon dou x square plus half a x square, remember that is the potential energy of the system operating upon the psi x must be equal to E times psi of x. Now, this potential energy, I would like to represent it in a figure. So, how will it look like, along the horizontal axis is the displacement from equilibrium position. The displacement can be in the positive direction or it can be in the negative direction right. So, what will happen the potential energy is just assumed to be half k x square. So, it is natural that the plat of potential energy against the x will resemble a parabola looking like that that is probably is the best parabola that I can draw. So, as this appearance this v of x plotted as a function of x actually strictly if you think about these this as model is not. So, very good description the reason is that see even if you supply large amount of energy what will happen is that the distance will only increase right.

The distance will increase some of the amplitude of vibrations will increase, and it will vibrate with the larger and larger amplitude. But if I had an actual hydrogen atom attached to tungsten and the if I went on supplying energy to the bond, what will happen is that the bond eventually break and once the bond is broken the atom will go away. So, the process of dissociation will take place, but this model has the defect at the atom will never detach from the surface, it will just go on vibrating. So, therefore, this is defective, but then if you are interested in vibrations which are not very large amplitudes then this is not a bad model.

So we think of this a very idealized model, and the model is very useful, because the quantum mechanics for it can be exactly solved. So, what we want to do is, we want solve this equation and the potential energy behaves like this, and of course, you see your wave function, you will want it to be a continues, you will want it to be single valued and and also you will want it to be normalizable. All these things have to satisfied in particular, I can say the following things physically, suppose I am the way function looks maybe something like that.

Now, I can definitely say that see if you are going in the for large values of x where the probability of finding the particle has to be decreasing why because when the value of x is very large the potential energy is getting very large. So, this in this region the potential is extremely large and my particle has only a finite amount of energy and therefore, I would not expect this particle to penetrate far into this region we have seen in the morning that if you had a potential which was like that the particle actually does penetrate a little bit into the by the region, but was rather small similarly here also I would expect that the wave function will penetrate into the into this region, but I would expect that at infinity, Infinitely far away from the equilibrium position. I would expect that the probably will defiantly vanish and therefore, I will have to solve this equation subject to the condition that is psi of x I will impose the condition that it has to approach zero. When x approaches infinity not only plus infinity, but also when x approach is minus infinity.

So, this is something that I will have to impose if I find a solution which does not obey this is then I am not going to accept that that is not basically sensible in a basically sensible solution has to satisfy the condition that when x approaches plus infinity over minus infinity the solution should approach zero. So, now, why I am going to worry about this equation I want to solve this equation, but the way this equation is written you have minus h cross square then there is a two m there is a k there is also energy and you would agree with me when I say that there are many constants there are many constants say m h cross k and d and I want to have only the minimum number of constants.

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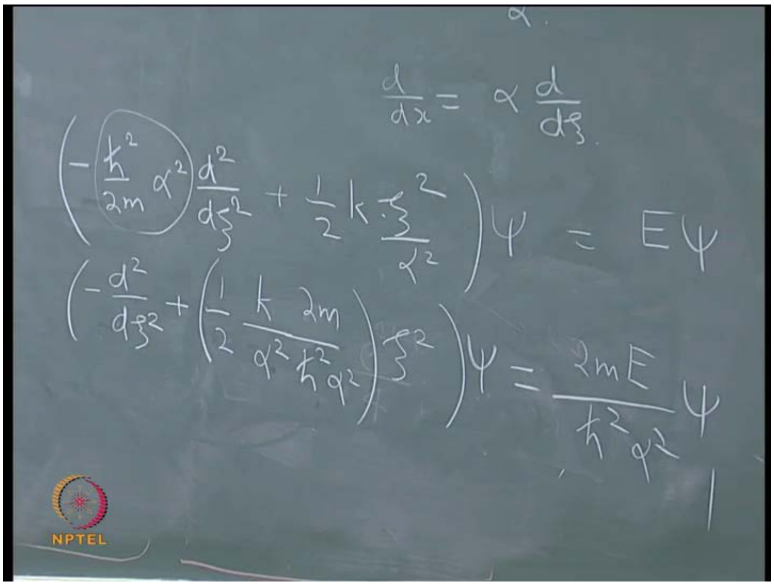

So, what I am going to do well I am going to introduce one more constant, I want to get rid of all this constants, but that I do by introducing one more constants. So, what I will do is I will define a new variable which I will denote is c this symbol is c x I and I will say that it is equal to a constant alpha times x alpha is a constant aim going to determinate right and I will determinate in such a fashion that the equation has the nicest possible appearance that is way in which I will do it. So, if you introduce such a variable what will happen you can say this means that x is equals to c divided by alpha and further you can also say that d x alpha is a constant.

So, d x must be equal to d c divided by alpha agreed and therefore, d by d x would be equal to much will you can use this you will say it is actually alpha d by d xi correct. So, I am going to use that in here and if I use that in here what will happen my h minus h cross square upon two m Ihave second derivative with respect to x here this is actually the first derivative, but it is very easy to calculate the second derivative from here right because alpha is it just a constant. So, therefore, what will happen is that d square upon d x square will be nothing, but alpha square d square upon d c square notice also that you see here I was using partial derivative notation which really is not did that is why I am writing it any more why because this operator is going to operate only upon psi which is a function of x alone only one variable is there in psi.

So, this is that equation and what will happen I have plus one by two k I have decided that I do not want x, but I want ctherefore, that is going to be c square by alpha square and the whole thing is going to operate upon psi psi will now be considered as a function of the new variable xi right it is going to be considered as a function of new variable it was a function of x, but now it is a function c and this is equal to e psi that is the equation.

Now, still you see I have simply introduce an additional constant they which I do not even know, but what I will do is I will divide throughout by this factor. So, if I divided throughout by that factor what will happen I will get minus d square upon d xi square plus one by two k divided by alpha square into two m divided by h cross square alpha square into xi square and the right hand side you're going to have two m e divided h cross square alpha square into psi now will see at this point I do not seem to have a attained anything by introducing this additional constant alpha, but what I will do is I will say is I am going to choose alpha in such a fashion that the this is equal to one that I can always do right alpha is undefined.

Now, I say let me choose alpha in such a fashion that is equal to one. If we look at that expression actually there is a half here, but this half and that two can be removed. So, essentially I can attained that by defining what should be my definition of alpha if I define alpha to be k into m divided h cross square to the power of how much see I want this to be equal to one. So, what should I choose alpha to be it has to be k into m by h cross square to the power of one by four. If I choose that then I am happy, because this is equal to one and at least my left hand side looks very nice because it is minus d square upon d c square plus c square.

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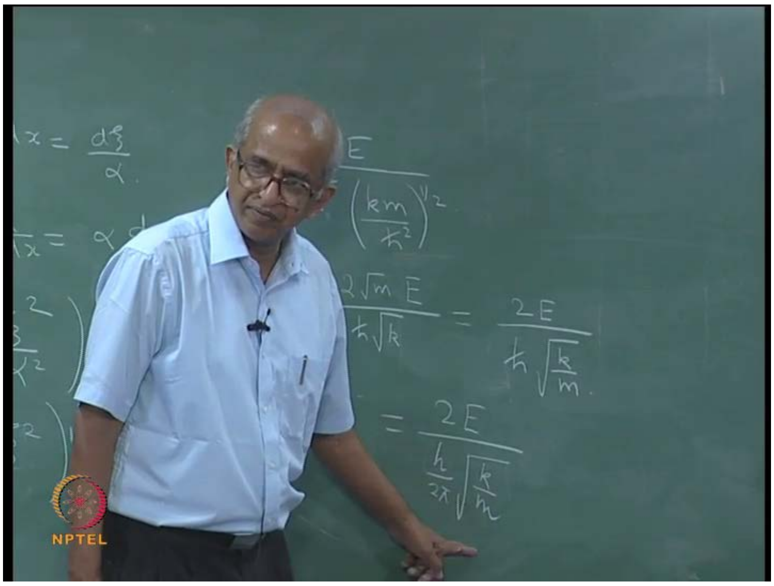

What about my right hand side I am going to evaluate this objects two m e by h cross square alpha square where will I evaluate it may be here two m e divided by h cross square alpha square, but alpha is. So, much. So, this is going to be actually k m divided by h cross square to the power of half this is that object, now you can simplify this well you can very easily work it out what is going to happen is you will have is that canceling out see this you took the square root this h cross square will become h cross and that will cancel one of the h crosses because there are two h crosses here. So, that is why you get h cross then there is an m here there is a square root of m here. So, naturally you will get square root of m in the numerator and the if you would like you can write this as two e divided by h cross square root of k by m and that you can write as two e divided by h divided by two pi into square root h cross after all is just h divided by two pi right and that again is nice because you have one by two pi into square root of k by m that is nothing, but your classical frequency of vibration of the ammonic oscillator and hence you can say this is nothing, but two e.

E is remember the energy of the particle and this object that you have there is two e by h nu. So, this constant that is occurring on the right hand side just two e by h nu right, but then again writing two e h nu is tedious again and I have to write it again and again and again. So, what I will do is I will call this lambda that says be the trouble of writing this again and again and therefore, what is happened my differential equation my differential equation.

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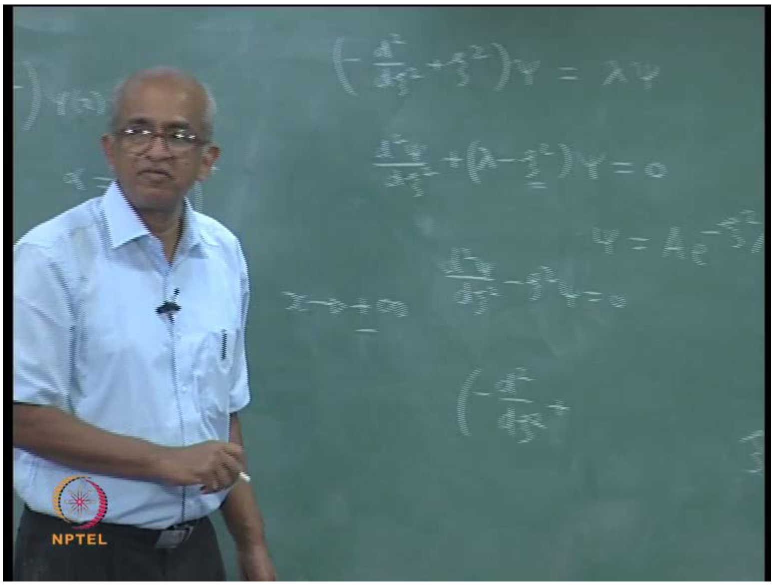

Now looks much better than earlier the way it looks is minus d square up and d xi square plus xi square operating upon psi is equal to two e by h cross square alpha square, but that is actually something that you have calculated it is equal to lambda that is the notation.

So, lambda times psi and now things are nice because I would leave one constant in my equation and that constant is lambda and that constant is related to the energy of the particle correct it is actually two e divided by h nu. So, I would now like to try and solve this equation. So, let me rearrange this equation how can you write this it may be written as d square psi by d xi square plus lambda minus xi square I think about it for a second you would realize that this is the way you can rearrange this equation. So, the only a thing that is I mean the constant here right the only unknown why should not say unknown only parameter that I have given is lambda ok.

So, we want to solve this equation and now how do we solve this equation well the way in which I am going to solve this equation is interesting the first thing that I will do is I claim that psi equal to any constant and e to the power of minus xi square by two will be what I refer to as an asymptotic solution of the differential equation. So, where do I mean by asymptotic solution the answer is that this is a solution and that is valid for large values of psi suppose xi is very large; that means, you are far away from psi equal to zero suppose your far away from psi equal to zero.

Let see is much much larger than one and so on. So, if your very far away from the origin xi will be very large and if you’re in such a region you have xi square here what you have do is you do not want to worry about this lambda it compares and with that xi square because xi square is very large. So, in that region in the asymptotic region this differential equation will become d square psi by d xi square minus xi square psi is equal to zero this is there in form of differential equation in the asymptotic region where psi is very large, but now you look at this function.

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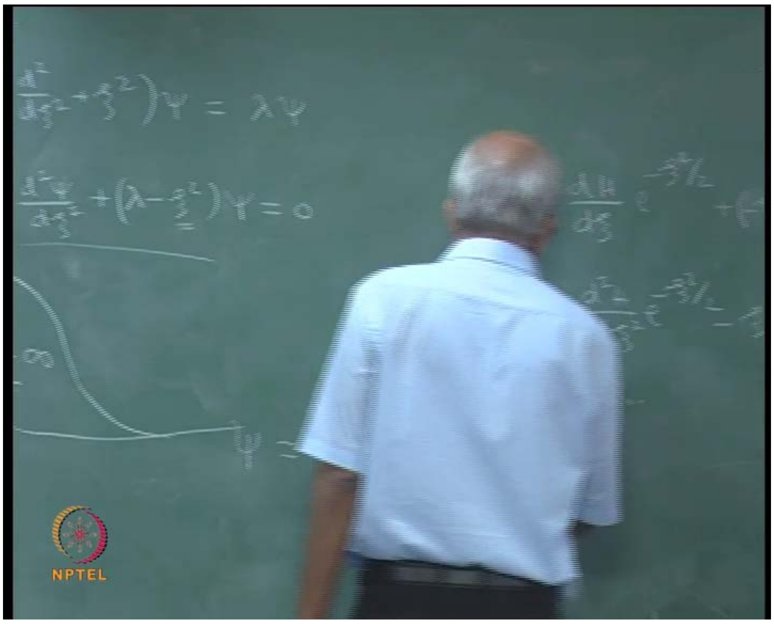

Let me denote this function temporarily by the symbol of f which is a function of xi it is equal to a e to the power of minus xi square by two right the function is defined to be this suppose you take it is a first derivative d f by d xi will be how much where it is valid simple and straight forward it is going to be equal to minus c times a e to the power of minus xi square by two correct if we skip this function took its first derivative that is the answer if we took its second derivative what will be the answer that you are going to get well second derivative means you have to actually differentiate this ten. So, you will get minus a e to the power minus xi square by two plus xi square a e to the power minus xi square by two this is what you will get the second derivative is is equal to that which actually says that the second derivative is equal to minus of the function f of xi plus xi square into the f of xi.

So, this is the deferential equation that f of c obeys, but then if you're in the largest c region right you have c square here you have instead of c square you have one there here if you want you can say there is a one there and there is a c square here. So, if you c is very large this one and that c square you can compare and you can defiantly neglect this one in comparison with xi square. So, simply what I am saying is you look at this this may be written as xi square minus one into f of xi this equation as it is may be written as xi square minus one into xi and if xi is very large defiantly this one can be neglected in comparison with xi square and. So, let me neglect that and then what happens this.

Equation by d square f by d xi square is equal to xi square times of f of xi which is exactly the same deferential equation as the one obeyed by psi and therefore, what is the conclusion in the large its xi region psi a possible solution of this equation is psi is equal to that function f and. So, what I have proved is that psi equal to a e to the power of minus xi square by two is an asymptotic solution it is valid only in the largest xi region it is not valid near xi equal to zero, but it is valid when xi is very very large this is a solution, but then you may say well, you can also think of it another solution which is of the form be to the power of plus xi square the same procedure you can try the same procedure differentiate in two times, you will find that this also satisfies the same deferential equation not surplice m because this is a second order deferential equation there should two independent solutions.

So, the most general solution in the asymptotic region will be a combination of these two a into e to the power of minus xi square by two plus b into e to the power of plus xi square by two, but then having seen that what will you say are this an acceptable solution while you have problems with this if you say this is the solution the problem is that as the value of xi becomes very large this time becomes extremely large it actually goes to infinity in the limit xi to goes to infinity and therefore, you will have to say that b has to be zero there is no other way.

So, therefore, the only possibility is that you have this as the asymptotic solution not the other one in order that the solution is acceptable asymptotically the solution must resembled some constant into e to the power of minus xi square, but this is valid this solution is correct only for large values of xi it is not valid for small values of se. So, what I am going to do is I am going to take this solution what is a solution the solution is actually psi equal to some constant into e to the power minus xi square by two that is what it is right there is a constant there, but I want make this function a solution even for small values of xi definitely it is not a solution, but may be what I can do is I can replace this constant by a function of xi what will this function do it will adjust thinks in such a fashion that this product will become a solution everywhere not only when xi is infinity xi is very large not infinity, but very large even when xi is very small this h will see to it that is a solution right.

So, if that is the way it is what can I do well I will now have to find h. So, how will I find h is the next question well the way to find the function h is I will take this I will assume that this is a solution and take that solution and put it into the original differential equation that I want to be satisfied I want this equation to be satisfied. So, let me take this h this psi and put it into that deferential equation which psi has to obey right. So, we will have to find h that is what we will do for that we will take this and put it here and find the equation for h, but of course, any h that I find has to be satisfying this condition what is the condition as the value of x becomes very large which actually means where is the value of xi becomes very large any x that you find has to satisfies the condition that h into e to the power of minus e square by two has to approach zero that has to be satisfied any solution that I find for h anything that I have for h has to satisfies the condition that this will approach zero as xi approaches infinity otherwise I am not going to have an acceptable wave function. So, let me now take this and put it in here and see what happens to this deferential equation.

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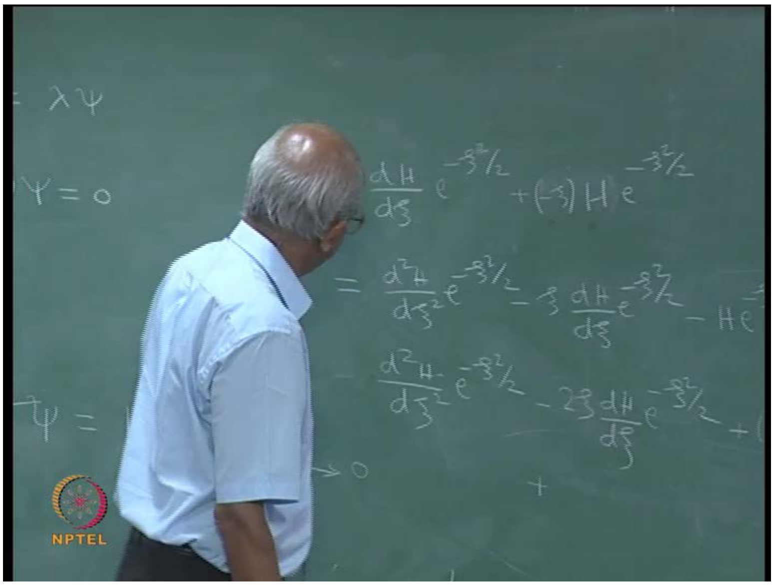

So, to that let me first evaluate d psi by d xi it is going to be d h by d xi h actually depends upon se, but let be save some trouble by not writing that xi within the brackets into e to the power of minus xi square by two plus h into minus xi e to the power of minus xi square by two ok.

This can be confusing because you may think that this is a function xi what I will do is I will put minus xi on this side that is what it is. So, that is the first derivative how about the second derivative well let me just go ahead on differentiate I will get d square h by d xi square e to the power of minus xi square by two when if you just carry out the differentiation you have to differentiate this let me give me a minus xi d h by d xi e to the power of minus xi square by two then from here I will get a minus h e to the power of minus xi square by two that is only time, but I have additional times I will also have minus xi d h by d xi e to the power minus xi square, but two and note down because there is one more time and what is that m that is going to be plus xi square h e to the power of minus xi square by two.

So, this is the full set of time that result that when you carry out this differentiation. In fact, if you look at this expression you will notice that the second and the fourth time they are the same they may be added up this time and that time you will find they are the same. So, you can say this is actually d square h by d xi square e to the power of minus xi square by two minus two xi d h by d xi e to the power of minus xi square by two these two times I have added up plus what will happen I will get xi square minus one this time and that time I am combining h e to the power of minus xi square by two this is what happens.

So, the next thing that I should do is I should take this expression put it here and add lambda minus xi square into psi to each. So, is that taking it there what I will do is to this right hand side that I have here which is you think here I am going to add that a m will let me remove this equal sign because this is the second derivative I have determined it this is the second derivative of psi to that all that I need to do is I have to add lambda minus xi square into psi into psi here, but psi is e to the power of minus xi square by two into h and this should be equal to zero that is the differential equation, but once you look at that equation you would see that it can be simplified because e to the power of minus xi square is sitting everywhere just divide throughout by that that makes it look nicer this goes this also goes, but that is not all there is a plus xi square minus sorry plus xi square here and there is a minus xi square there. So, this time and that time will cancel and I will be left with d square h by d xi square minus two xi d h by d.

Se plus what happens what is what do I have left this and that will cancel. So, I would have to lambda minus one h is equal to zero well when you look at it you really wonder because this was your original equation and I have arrived at another equation and it does not appear much simpler right this equation ant that equation if we compare they do not appear when want does not appear to be might simpler that the other, but they interesting thing is that it is actually easy to solve this equation it is quite easy to solve this equation we will discuss that in the next lecture and just we solved subject to the condition that psi equal to e to the power of minus xi square by two into h should approach zero as xi approaches is there plus infinity or minus infinity just we solved subject to that condition and that is what we will do in the next lecture.

Thank you for listening.