Quantum Chemistry of Atoms and Molecules
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Lecture-15
Harmonic Oscillators: Wave Functions and Recursion Formulae

In the next couple of modules we are going to complete our discussion of harmonic oscillators. In these modules were going to talk about wave functions to a little greater extent and we will discuss and interesting recursive formula that relates the wave functions with each other. And very briefly will mention why that is important. Before we begin let us recapitulate what we are studied so far in this topic.

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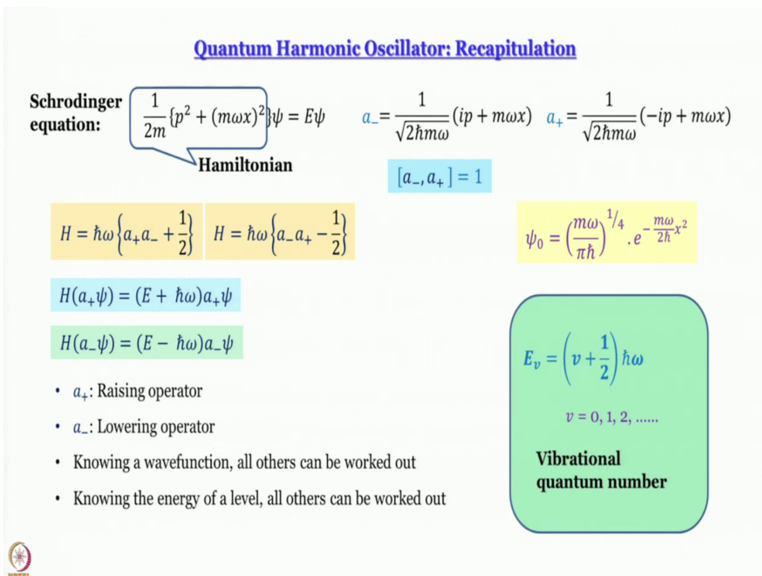

We have studied the Schrodinger equation for the quantum harmonic oscillator and starting from the elementary form we have rewritten it slightly in terms of momentum 1 by 2 m multiplied by p square + m Omega X whole square this is a Hamiltonian it operates on Psi to give us E Psi. Then we are introduced and we are talked at length about this over the last two or three modules we introduced two operators as a minus and a plus. These are called ladder operators.

And we have studied various aspects of ladder operators first of which is that the commutator between a minus and a plus is one hence we have learnt how we can rewrite the Hamiltonian this time in terms of the ladder operator. There are two ways in which we can write it because the operators do not commute with each other. It is H can be written as h cross Omega multiplied by a plus a minus plus half or you can write h cross omega a minus a plus minus half.

Remember a plus a minus and a minus a plus are not one and the same because the commutator is one and not 0. Which one do you use? We use any one of these forms whichever is convenient for the particular problem we are trying to solve. So, what we have done is we have learnt that this are called ladder operator for a reason. If a plus operates on Psi, for example, it produces a new wave function which is an eigenfunction of the same Hamiltonian operator.

Interesting a phenomenon that the eigenvalue of energy is more than the eigenvalue of the original wave function Psi by h cross Omega which is 1 quantum of vibrational energy. So, H operates on a plus Psi to give us E + h omega multiplied by a + Psi. Now a + Psi is not necessarily the actual wave function, which is one step higher in the ladder. It could be actual wave function multiplied by a factor.

So, later on when we do a little bit of treatment with this we will see we are going to write it as a 1 multiplied by the function. It was remembered always functions have to be normalised anyway. There is no guarantee that when ladder operator operates on a wave function. It gives us a new wave function, which is normalized. But the good thing is even if a wave function is not normalised Hamiltonian can still operate on it and give us the correct value of energy.

Why? Because if you look at Schrodinger equation in this form any form, the normalisation constant would come on left side as well as right so it does not matter this is one important thing that we should note in quantum mechanics that it does not matter really just find the eigenfunction and it does not matter whether the wave function is normalised or not. Of course it does matter when you want to work out the average quantity as we have seen earlier.

So a plus is called a raising operator because its action on Psi is to take us one step higher in the vibrational energy ladder ahead and a minus take us one step down so it is called a lowering operator. Now this is something I said earlier going knowing a wave function in principle using a ladder operator we should be able to work out all other wave functions by going up or down the ladder one step at a time. And knowing the energy of one level we should be able to work out the other energy as well.

In fact we have noted that vibration quantum numbers have values of 0 1 2 3 so on and so forth and the expression for energy of vibration for a harmonic oscillator is E v equal to v plus half into h cross omega which also tells us that for the lowest value of v, v equal to 0, the energy is not 0, it is half h cross omega. But we are said it several times let us not going to that once again. And we also learnt that the lowest energy wave function is of this form m omega by Pi h Cross raise to the power 1 by 4 multiplied by e to the power minus m omega 2 h cross x square.

We have to remember this expression not really but do you have to remember we have to remember that it is a Gaussian function e to the power minus some constant into x square, if you remember that that is enough. There is no need in this course or in science in general to remember each and every expression that we come across. So, this is what I learnt so far and the question was stopped at in the previous module is what are the wave functions for v equal to 1 2 3 so on and so forth.

So, we will take two approaches first of all you are going to use a ladder operator and work out the wave function for v equal to 1 and then we want to do a more rigorous analytical approach using a power series solution to arrive at the general expression for the wave function. And we will find out their energies as well. And that is what will take us to the recursion formula. But first let us see how we can very conveniently go up the ladder using ladder operator.

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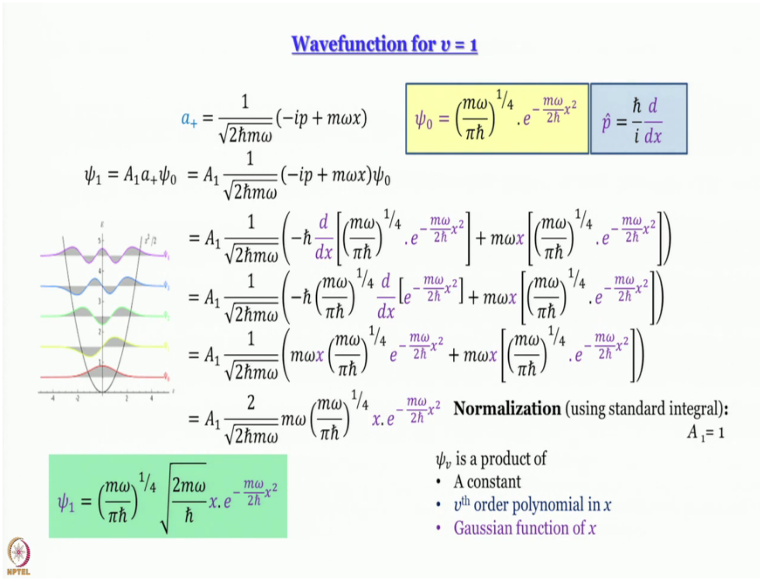

So this is what you are going to use we know Psi 0 already, and we have with us the step up ladder operator a plus what we will do is we will make a plus operate on Psi 0. So we are going to get you Psi 1 as this is what I was saying a plus Psi 0, but we should not forget the constant A1 because there is no guarantee that a plus Psi 0 is a normalised wave function. So, Psi 1 wave function for v equal to 1 is A 1 multiplied by a plus Psi 0, so far so good let us get ahead.

Now if we write like this what we do is we write the form of the a plus operator 1 by root over to h cross m omega multiplied by minus ip plus m omega x operating on Psi 0. Please remember the P here is an operator x here is an operator x is not so much of a problem because the action of x is just to multiply the wave function by the value of the position, but let us not forget what the form of the momentum operator is?

Momentum operator as you know, very well by now is h cross by i d dx or minus h cross d dx. So, in the next step you are going to substitute this expression for momentum operator in to the expression for Psi 1. So we are going to make the momentum operator plus multiplied by minus i plus m omega x operate on Psi 0. So when we do that this is what we get there. We just written it out I will give you a moment to absorb this I read it out meanwhile, but please read for yourself and you will get what I have got.

First term would be minus ip operating on Psi 0 right p is h across my i d dx so minus ip would be minus h cross d dx so minus h cross being a constant term comes out and ddx operates on the wave function 1 4th power of m omega bi Pi multiplied by e to the power minus m omega by to h cross square. In case the confused by me rattling out all these expressions, please go through this yourself and convince yourself that what we are said is correct.

The first term here is just an expansion of minus ip Psi 0. What about the second one second one is easier m omega x Psi 0 m omega x is there you just write the expression for Psi 0 from there in this expression. So, this what you got but of course this is only the beginning and not the end what we should do next is we should differentiate this function and that is not all that difficult also. Because this m omega x by pi h cross to the power one fourth is just a constant it will come out and we have to differentiate is Gaussian function with respect to x it is not so difficult.

So that is what we need to do here I just shown every step so that in case anyone is confused, you can go through the presentation later on and you can convince yourself this can be self study material and as I said following by and large textbook on Quantum Mechanics by Griffith at the moment. So, this is what we get since we differentiate e to the power minus m Omega x 2 h cross 2x we get back the same exponential function but it has to be multiplied by 2x multiplied by m Omega by 2h Cross minus of that minus and minus becomes plus h cross in the numerator h cross in the denominator cancel each other 2x that 2 and the 2 in the denominator cancel each other and finally we are left with m Omega x, m omega by h cross e to the power 1 by 4 is from the previous line.

M omega x comes from differentiation of e to the power minus m Omega by 2 is h cross classic square and you get the same term anyway, this is what you got A 1 multiplied by 1 by root over 2h cross m omega multiplied by sum of these 2 terms. Well the first term is m omega x multiplied by 1 4th power of omega by Pi h cross then multiplied by e to the power minus m omega by 2 h cross x square 2nd term is also the same you add them up 2 comes out and this is what you get.

A1 multiplied by 2 by root over 2h cross m omega x m Omega multiplied by m omega multiplied by m omega by Pi h cross to the power 1 by 4 multiplied by x multiplied by e to the power minus m Omega to 2h cross x square and of course you have 2 m omega in the numerator root over 2h cross m omega in the denominator and you are going to simplify this and you are going to get root over 2 m omega in the numerator and h cross denominator.

That is what you will get and you have to normalize it. While normalizing you are going to use a standard integral since we have talked about standard integrals already. I am not going to it once again in any case you need to look at a companion to solve it. I am just telling you that when you standard integral A1 turns out to be 1. So, this is what you get Psi 1 is this. So essentially this is the wave function we have got.

This we have I got already Psi 0. We are got this Psi 1 which often looks like a sine function but actually is not really a sine function. It is x x multiplied by e to the power minus m omega by 2h cross x square multiplied by a constant. It is a product of vth order polynomial in x. Here I am jumping the gun a little bit but it is not very difficult for you to see that x is a force of first order polynomial in x. And I am saying vth order polynomial already because if you look at Psi 0, you see we had e to the power minus m omega by 2 h cross x square in Psi 0 as well as Psi1.

The Gaussian function is there in both the wave function some constant will be there, constant will depend will differ from function to function. But what we you see here is that here there is nothing else in x which means you x to the power 0 for Psi 0. For Psi 1 you have x to the power 1 and as we see later on as you go higher up you get terms in x to power 2 x to the power 3 so on and so forth. You are going to get polynomials in x and order of the polynomial will be the same as the vibrational quantum number .

So, this is an example of how one can use ladder operator to go up a ladder and given a wave function help you work out the wave function that is immediately next. So from Psi 0 we worked out Psi 1. So, what we can do is we can keep on doing this. We can keep on using ladder operator and finding your Psi 2, Psi 3, Psi 4 and so on and so forth one by one. One thing I should says is that you do not really need to normalize like this.

There is another way by using Hermitian conjugate by which one can do the normalization but that requires a little more of linear algebra right now we are not going to going in to it may be later on if you get time will come back and will expand will get into that as well. But what we have obtained is a way in which we can generate the wave functions, knowing one wave function one by one.

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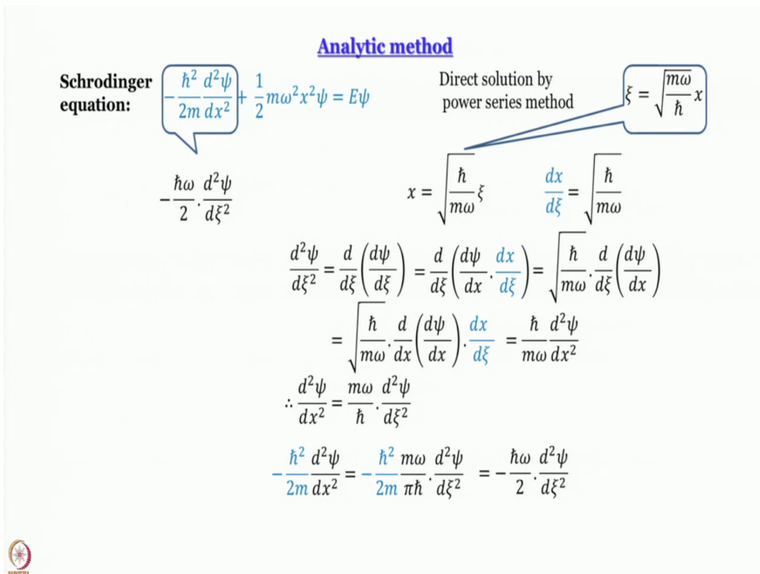

But what I really want is something that is more general. Can we do everything at one go. Can we find a general expression for all the wave functions that is what the analytic method allows us to do. It is little more vigorous so since I think most of our students of this course will be chemistry students. Some of you might not have studied too much of math. If you find this a little bit dry or a little bit intimidating. Please bear with us because the real beauty of this harmonic oscillator business will not come out unless we are a little persistent and unless we crack all these math that we want to do.

We will go step by step where we have to make a assumptions I will tell you but by and large we are going to actually work out everything. So, please bear with me and please work out yourself. You have to work this out using a pen and paper by yourself after the lecture or even during the lecture pause it and work it out so that every steps carefully ok. So, I hope everybody has a pen and paper in your hand. Let us get ahead.

Now for using the analytic method we go back to the Schrodinger equation in which we have this kinetic energy term on the left hand side. The potential energy term is half m omega square x square remember what omega is angular frequency of vibration. On the right hand side, we have E Psi. So we are going to try and obtain direct solutions of this by using a power series method. What is power series method? We will see when the time comes but first let us rewrite the variable.

The equation is an x since we are not the first working out this x equation. We know that the final result will be neater if we work this out in terms of not x but another related variable Xi this letter that you see on the left hand side here this is the Greek letters Xi sorry in English it is Xi. Xi equal to root over m omega by h cross multiplied by x. Why do we take this? Because well somebody has worked it out already and it has become clear that a making the substitution make the working easier make the answer look little neater.

So here goes epsilon is equal to root over m Omega by h cross x that is what we are going to use. Using that what will see is we are going to transform the kinetic energy term and you are going to obtain minus h cross omega by 2 d2 Psi d Psi 2 most of you might be able to work this out by yourself, but as promised we will go through this step by step. To do that since we know that Xi is equal to root over m omega by h cross multiplied by x defined it that way let us make x the subject of formula.

X is root over h cross divided by m omega multiplied by Xi. So the first thing to do would be to differentiate x with respect to Xi so dx dXi is a constant square root of h cross by m omega. That is straight forward. Now, what you want is you want to know what is d2 Xi sorry d 2 dXi 2 I said again what is d 2 Xi d Xi 2 why because d 2 Xi d Xi 2o is there in the kinetic energy of the Hamiltonian. So d2 Xi d Xi 2 is equal to derivative with respect to Xi of d Psi d Xi.

So, what is d Psi d Xi? D Psi D Xi is d Psi dx multiplied by dx dXi I hope all of us are familiar with changing the variable during differentiation. This is how we do it. So d Psi d Xi is equal to d Psi dx multiplied by dx dXi that is what we are going to use. And then we are going to differentiate with respect to a d Xi once again. So let us do that we know what d x d Xi and there is a constant we just taking the constant out and then we are left with the d dXi d Psi dXi.

So that then will be again equal to root over h cross by m omega d dx of d Psi dx multiplied by dx d Xi same thing once again, we know what is dx dXi is write it. So the roots sign goes and we get h cross by m omega multiplied by d2 Xi dx 2. So, d 2 Psi dx2 very easily is m omega by h cross d 2 Psi d Xi 2 so what we do is instead of d2 Psi dx2 to write this and then we are going to multiplied by minus h cross square by 2 m so minus h cross square by 2m multiplied by m omega by Pi h cross d Psi d Xi 2 gives us minus h cross Omega by 2 d 2 Psi d Xi 2, that is what we have written here.

So we have worked out the first term on the left hand side of Schrodinger equation in terms of naught x, but Xi.

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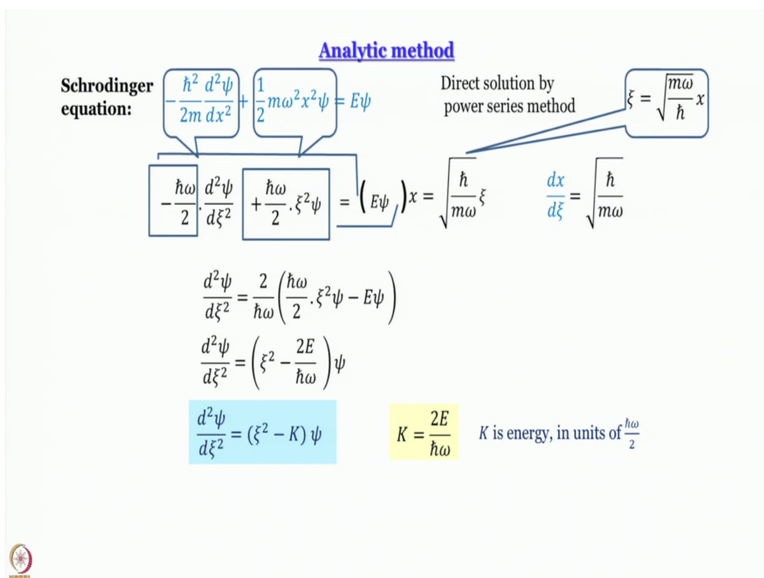

Now let us workout the second term this is a much more straight forward because all you have to do here is that instead of x square we have to write the term in Xi square that is very easy square of this what will it be, x square is equal to h by m omega h cross by m omega square multiplied by Xi square as simple as that is what we will use x square equal to h cross by m Xi square so half m omega square x square will be equal to half m omega square multiplied by h cross by m omega Xi square m and m cancel one of the omega get cancel you are left with a h cross omega by 2 Xi square.

Write that left hand Psi now is written in terms of Xi minus h cross m omega by 2 d2 Psi d Xi 2 plus h cross omega by 2 Xi square Psi that of course it is equal to E Psi. Now what we can do is we can take this whole thing on the right hand side because we want to write a differential equation in any form that is why we are doing this. So we can take the second term to the right hand side. And then what will do is entire right hand side is multiplied by -2 by h cross omega then on the left hand side we will be left with d 2 Psi d Xi 2 this is what we get.

D 2 Psi d Xi 2 is equal to 2 by h cross Omega multiplied by h cross omega by 2 Xi square Psi – E Psi so you have think that we actually taken the first term to the right hand side or you can just well, you can see it is just a algebraic manipulation not very difficult to understand. So from the right hand side we have 2 by h cross omega multiplied by h cross omega by 2 Xi square Psi – E Psi. Ok. So in the right hand side we have 2 terms both of them are Psi multiplied by some constant of the other.

So you can take Psi common outside the bracket and also the nice thing is your h cross omega in the numerator here and h cross omega in the denominator here 2 in the numerator here 2 in the denominator here they are going to all cancel if you open the bracket. So, the first term will become Xi square 2nd term will become – E well -2E divided by h cross omega right this is what will get, d 2 Psi d Xi 2 is equal to Xi square – 2E by h cross omega multiplied by sin.

Ok again this is an eigenvalue equation and the differential equation which we can solve without much hassle, but I would like to draw your attention to this E by h cross omega once again, what is this? E by h cross omega is essentially E is energy h cross omega is energy of each quantum. So it is a number of quantized energy is not it. So, we are going to write it as K, K equal to 2E divided by h cross omega.

So K essentially is the twice the number of point quanta of energy that is there. Ok so depending on which vibrational levels were talking about this number will be 1 2 3 4 something like that, 10, 20 whatever it is. So, the differential equation we get finally is d2 Psi d Xi 2 is equal to Xi square - K multiplied by Psi. What is the next step? The next step obviously is to try to solve it?

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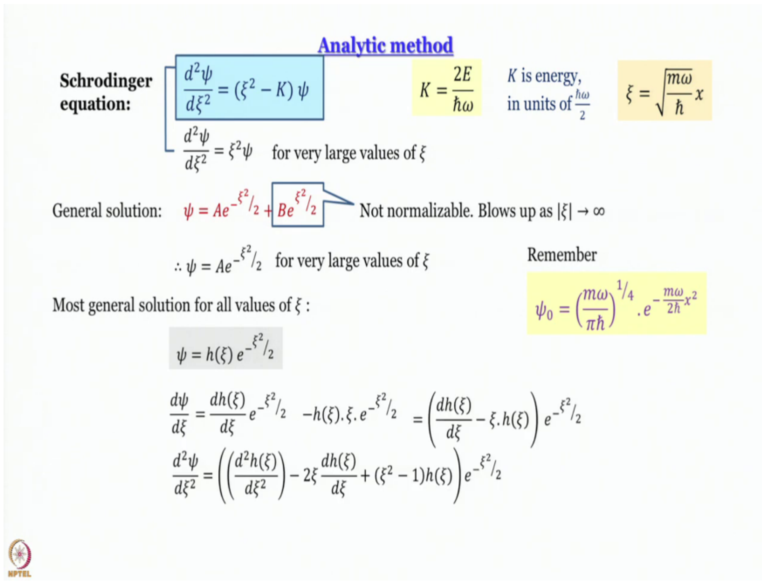

Let us tid y the board a little bit is what we are saying we have rewtitten Schrodinger equation in terms of Xi square and K where K is 2 E by h cross omega and Xi that we forget is x multiplied by square root of m omega divided by h cross. So now let us understand something we have said that K is just a number like 1, 2, 3, 4 so on and so forth. So, what happens if Xi is very large, then you can neglect K with respect to Xi square.

Then d 2 Psi d Xi 2 become Xi squares Psi. So what will do is first we are going to work this out. What is the solution for very large value of Xi? And then will go to the general solution. So, first of all general solution here would be A e to the power minus Xi square by 2 + B e to the power Xi square by 2 you just work it out by yourself differentiate twice you get back the same equation. One thing to remember is that mathematics is not the be all and end of us.

Mathematics is only the tool that helps us get to the Physics. So, we must remember that the second term is problematic e to power Xi square by 2 so as Xi increases either in positive direction or in negative direction this e to the power Xi square by 2 going to increase which means that it is not a normalisable function. That means that this part of the wave function should not be there, remember we will looking for acceptable wave functions only.

And wave function that is not normalizable is not really acceptable. So, we can simply write Psi equal to A e to the power minus Xi square by 2 for very large values of Xi. That should remind us of the wave function that we got already using ladder operator. That is also A multiplied by e to the power some constant multiplied by well instead of x you can write in terms of Xi square. So this is what it is.

So what will the general solution, if you think of small values of Xi as well we can restore generality by remembering that we need this e to the power minus x square by 2 function exponential factor, which becomes 0 at plus minus infinity that will be required. Whatever we have as to be multiplied by it but there is no guarantee that the pre exponential factor well we should not call it pre exponential factor because it is Gaussian term. Pre Gaussian factor what is the guarantee that it is a constant and it is a constant for the large of Xi but not necessarily for all value of Xi.

So to keep it very general we write it as h function of Xi will not consider as constant it is a variable something what it is? We will see. So what is the d Psi d Xi? So let us work it our first, d Psi d Xi as you can see very clearly is a product of two functions. One function is h of Psi h of Xi and other function is e to the power minus Xi square by 2. So, we know what will be the derivative of a product is, let us do that the first one, what we do is keep e to the power minus Xi square by 2 as it is.

And we differentiate h and since do not really know what it is. Just write d h d Psi multiplied by e to the power minus epsilon square by 2. What will be the second term h is the function of Xi will remain intact and it will multiplied by the derivative of e to the power minus Xi square by 2 which will be -2Xi multiplied by e to the power minus Xi square by 2 this is what you get minus h of Xi multiplied by Xi e to the power minus epsilon square by 2.

This are the two term that we have got for d Psi d Xi what is the next step? The next step is to first write it little cleanly. Let us take e to the power minus Xi square by 2 common and then we differentiate once again. I am not doing this step explicitly. I leave it for you to do. So we get the d 2 Psi d Xi 2 is equal to just the Gaussian factor multiplied by d 2 d Xi 2 of h minus 2 Xi multiplied by first derivative of h with respect to Xi + Xi square - 1 multiplied by the function h of Xi.

So, we have obtained this expression for d 2 Psi d Xi 2 which we can now replace in this expression of Schrodinger equation and then we can go for the head that is what will do in the next module.