Quantum Chemistry of Atoms and Molecules
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Lecture-16
Harmonic Oscillators: Wave Functions and Recursion formulae…..Continued

So, here we had stopped in the last module we are discussing the analytic method by which we are going to say obtain a general expression for the wave function for harmonic oscillator this is where we have gone so far.

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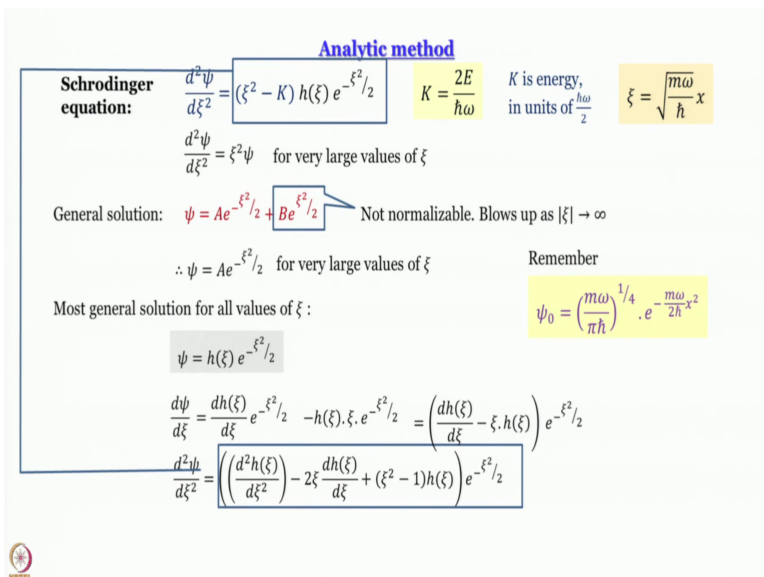

We have written Schrodinger equation in terms of this variable Xi which is proportional to x and 2E by h cross omega. So, the Schrodinger equation has become d 2 psi d Xi 2 is equal to Xi square - k multiplied by psi remember it is still Schrodinger equation and then what we have been able to do is we have been we have been able to work out the left hand side d 2 psi d psi 2 we have obtained an expression for it.

So the next step is quite obvious we are going to take this expression and we are going to substitute in Schrodinger equation ok. Let us do that but before doing that let us rewrite Psi as h of Xi multiplied by e to the power minus Xi square by 2 right. Once we have done that now we are ready to put them together and write Schrodinger equation.

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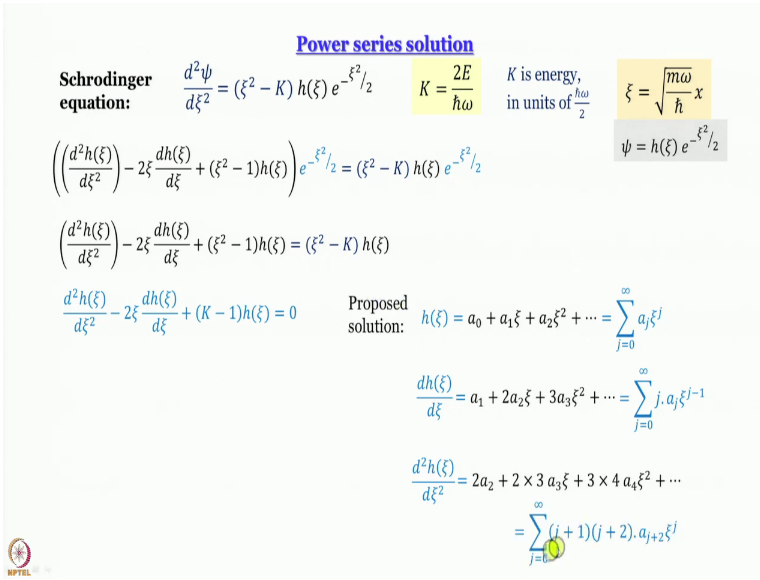

d 2 d psi 2 of h minus 2 Xi multiplied by first derivative of h with respect to Xi + Xi square - 1 multiplied by h multiplied by this Gaussian function in Xi is equal to Xi square - k multiplied by h multiplied by the same Gaussian function. The Gaussian functions are shown in blue because it is obvious that they occur on both the sides as factors so they are going to cancel each other. And this is what we are left with. And now we can think of simplifying a little further.

Look at the third term on the left hand side and look at the term on the right hand side both are in h and both contain Xi square. So, we can easily combine these 2 terms and get rid of Xi square. When we take the right hand side Xi square - k multiplied by h to the left hand side then we already have h multiplied by Xi square minus one subtract this from here Xi square and Xi square cancel sine of k becomes positive and we get this equation d 2 d Xi 2 of h - 2 Xi multiplied by d d Xi of h + k - 1 multiplied by h equal to 0.

So we get a little more complicated differential equation. Now the thing is in mathematics solutions how to solve this kind of differential equations is known already. And one very powerful method by which these equations can be solved is to use a solution that is a power series right that is known already. So, we are taking known mathematics and we are applying it in our problem. So, the proposed solution for this kind of equation would be h Xi written in terms of; well written as a series or you can say a polynomial in Xi a 0 +a 1 Xi + a 2 Xi square + 1so on and so forth.

In principle this can go all the way up to infinity. So, we can simply write it as a summation sum over j equal to 0 to infinity multiplied by a j multiplied by Xi to the power j does that make sense the first term for example is a 0 for that j equal to 0 so a 0 and Xi to the power 0 is 1. For the second term j equal to 1 so a 1 and Xi to the power 1 is Xi and so on and so forth right. So, that is what we have got we have propose the solution.

Now how do we go about it simple we are going to differentiate h Xi not once but twice with respect to Xi and we are going to take those derivatives first derivative and second derivatives plug them back into this equation not only that h Xi is itself written as a summation we are going to plug that as well and then we will use another property of power series to get the solution. Here goes what is d h d Xi am not saying d h or Xi all the time right the weight is written it means that h is a function of Xi so what is d h d Xi differentiate a 0 you get 0 differentiate a one Xi you get a 1 differentiate a 2 Xi square you get 2 a 2 and so on and so forth.

So the derivative of the series for series is also another power series a 1 + 2a 2 the same how we get 2a 2 Xi square differentiate what you get you get 2 Xi right so 2a 2. Similarly well 2a 2 Xi + 3a 3 Xi square + 1 so on and so forth. We can write that as a summation as well and what we will do is since we are going to combine the summations at the end we will keep the limits the same. We will sum from j equal to 0 to infinity. So, if we do that sum over j equal to 0 to infinity then what do I get.

I get j multiplied by a j multiplied by Xi to the power j - 1 let us see first term what the first term would be is j multiplied by whatever j equal to 0. So, it does not matter what is multiplied by it is going to be 0 unless its multiplied by 1 by 0 then it could be a problem ok. So, this is the summation sum over j equal to 0 to infinity j multiplied by a j multiplied by Xi to the power j -1 ok what is Xi? The independent variable.

What is a j? a j is the coefficient of the jth power of i in the power series expansion of h okay I repeat that j is essentially the coefficient for well sorry a j is the coefficient for the term in jth power of Xi in the power series expansion of h. So, h is written as a power series we get another summation for d h Xi d Xi as well and by now it should not be very difficult for us to understand that if we differentiate once again then we end up getting another power series.

What is d 2 d Xi 2 of h, d 2 h of Xi d psi 2 what will that be well differentiate this thing with respect to Xi first term will give you 0 second term will give you 2a 2 third term will give you 3 into 2 into a 3 Xi and so on and so forth. So, what will do is we will write it in this form 2a 2 is essentially 1 into 2a 2 + 2 is already there well sorry 3 is already there and 2 comes from the differentiation of Xi square. So, we will just write will not write 6 right now we will write 2 into 3a 3 Xi.

So next one again will be 4a 4 was already there and the term that was there you differentiate once more so you get Xi square and this is 3 okay remember we had Xi to the power 3 after differentiating once. So, we will write this as summation once again. And once again we want to sum from 0 to infinity. So, what should the summation be I will give you a second to write it down yourself without looking and then let us see whether you have got the right answer.

Please write down on the notebook what the summation would be for the second derivative of h with respect to Xi ok. Now I give you the answer this is the answer j equal to 0 to infinity j + 1 multiplied by j + 2 multiplied by a j + 2 multiplied by Xi to the power j is that right what would the first term be then j equal to 0 right so first term would be 0 + 1 is 1, 0 + 2 is 2, so 2 from here a j + 2 that means a 2 see that is what we have got and Xi to the power j is Xi to the power 0 is 1.

So the first term is 2a 2 which is in line with this. Let us go to the third term third term is for third term j equal to 0 1 2 right so 2 +1, 3 multiplied by 2 + 2, 4 multiplied by a j and a j + 2 right a j + 2 j equal to 2 here. So, a 4 multiplied by Xi to the power j, j equal to 2 ok please satisfy yourself that this is really the expression for the second derivative ok. So, now we have expressed our solution as a power series and we have expressed the first and second derivatives of it as a series as well.

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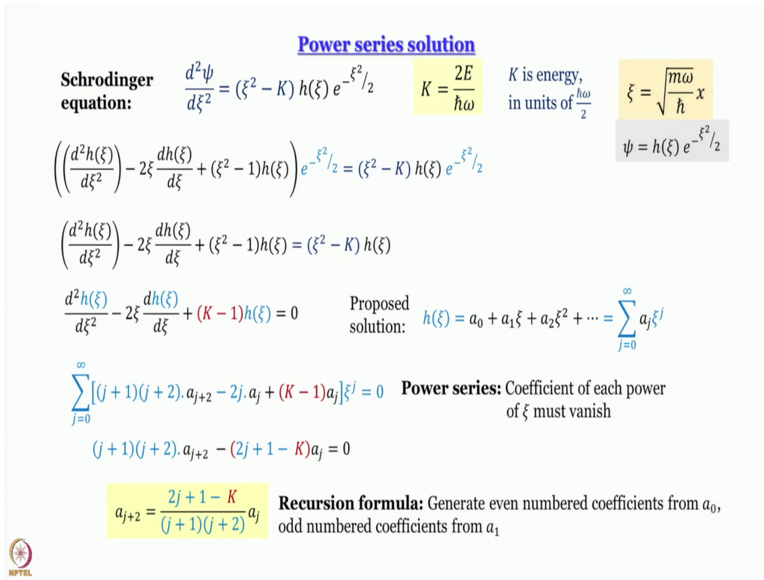

What should we do? Take this first derivative plug it in take the second derivative plug it in and in fact take the original power series and plug it in as well. When we do that we get an expression in terms of summation ok. The first one the second derivative that is summed over Xi to the power j. The third one h Xi itself is sum over Xi to the power j what about the second term here the summation is for Xi to the power j -1.

But do not forget that it is being multiplied by minus 2 Xi so psi multiplied by z to the power j -1 is essentially Xi to the power j. So, we end up in this left hand side getting summations in Xi to the power j for all the terms write it down sum over j equal to infinity sorry j equal to 0 to infinity j + 1 into j + 2 multiplied by a j + 2 that comes from here the second derivative plus well minus 2 j into a j this comes from here.

Do not forget we have taken epsilon j epsilon to the power j what am I saying Xi to the power j common outside the bracket plus we get k - 1 multiplied by a j right. So, this is the expression that we get and now we will use the property of a power series when we have a summation like this where we use the jth power of the variable. And we sum from 0 to infinity it is imperative that coefficient of each power of Xi has to vanish.

Sometimes I say epsilon instead of Xi I am sorry about that but in case I do please understand what I mean, I mean Xi. So, the property of power series tells us and this for this you need to read a book on some book on mathematics but right now we will take it axiomatically. Coefficient of each power of Xi must vanish what does that mean that means? That I can just write this we do not have to worry about the summation.

Let us take each for each value of j we can write j + 1 multiplied by j + 2 multiplied by a j + 2 - 2 j +1 - k multiplied by a j equal to 0 ok. So, we have got a relationship between the jth coefficient in this power series for h and the j + 2th coefficient so what we see is that in this series the coefficients alternate coefficients can be expressed in terms of each other. So, let us go ahead and write it first a j + 2 turns out to be 2 j + 1 - k divided by j + 1 multiplied by j + 2 multiplied by a j.

So if you know a j you can work out a j + 2 this is called a recursion formula and what it allows you to do is suppose you know a 0 then you can work out all the even number coefficient. Suppose you know a 1 you can work out all the even number sorry odd number coefficients from there so this is how recursion formulae allow us to work out the coefficients and express the coefficients in terms of each other all right.

With this will go a little further ahead and will try to find what the wave function actually looks like ok.

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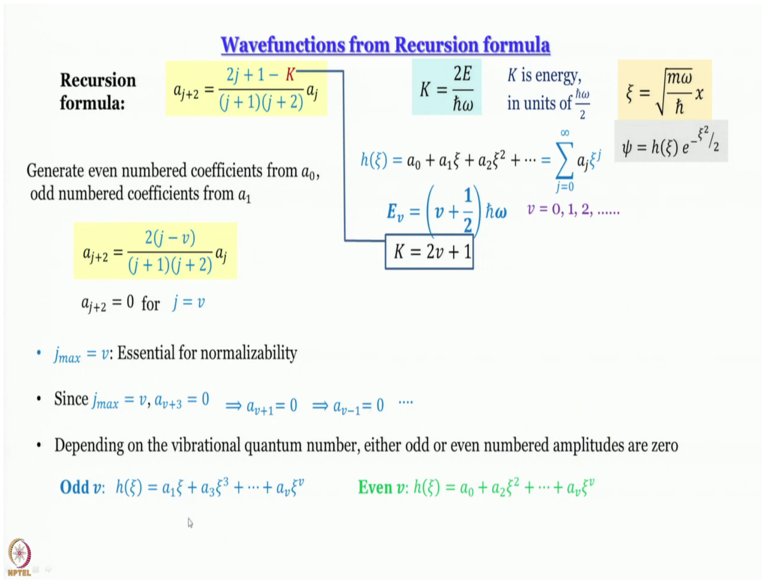

So, again we have just brought everything together this is the recursion formula that we had just written and we have said that one can generate even number coefficients from a 0 and odd number coefficients from a 1 ok. Whatever we need in the subsequent discussion is actually summarized in this slide ok. Now we will remember something else what is k? k is 2 E divided by h cross and we already know the expression for E v this is where our treatment deviates from the treatment of Griffiths.

Griffith has done a more rigorous more general treatment what we will do is since we have worked out E v already we are going to use that expression and try to reach the answer in a little shorter way ok. So, for v equal to 0 1 2 and so on and so forth E v is given by v plus half into h cross omega. So, what we can do is we can just take this and we can put it in the expression for k and its very simple for you to see that k turns out to be 2v + 1 ok.

Why are we doing this just hold on a minute and we will see but first check E v equal to v plus half into h cross omega to get k first of all multiplied by h cross omega you are left with v plus half then multiply by 2 e sorry what am I saying e equal to h cross omega k divided by 2 right. So, just multiply this by h cross omega k divided by 2 this is what you will get ok. So, k turns out to be 2v + 1 ok I just give you a minute to absorb that.

Yeah instead of e let us put v plus half multiplied by h cross omega in the expression for k it easily comes out that k is equal to 2v + 1. So, of course k is quantized that is not a surprise not a surprise at all and also what we see is what we have said earlier k is a positive integer the smallest value of v is 0 so 2 into 0 is 0 + 1 is 1, so k goes 1 and then for v equal to 1 it is 1 into 2 + 1, 3 1 3 so on and so forth ok.

So what we will do is we are going to plug this into the expression for we are plugged this into the plug this into the recursion formula. So, we get a j + 2 is equal to a j multiplied by very simply 2 into j - v by j + 1 multiplied by j + 2 is that ok 2 j + 1 was already there - 2v – 1, so 1 - 1 is 0 so you get 2 j - 2 v in the numerator I have written it as 2 into j - v ok what does that mean or what is the important observation that this leads to.

It leads to an important observation that well a j + 2 if you do it very simply is equal to 0 for j equal to v is not it, just algebra put j equal to v, a j + 2 becomes 0 what is a j + 4? a j + 4 will also be equal to 0 right because whatever you get here will be multiplied by now a j + 2 what will be aj + 6 + 8 10 12 everything will be 0 which means that v equal to j is what defines the upper limit of j, j max is equal to v there is an upper limit to j it cannot keep on going ok.

And it would better be that way otherwise if it really goes to very high values of Xi square then once again the function will not be normalizable. So, it is great that we get an expression for j max right. Now let us consider something, so we are saying that it is the maximum value of j so av + 3 should also be equal to 0 is not it, which means av + 1 is also 0 you are just going down by 2 which means av - 1 will also be equal to 0 what does that mean what is the relationship between av and a v + 1 or a v - 1 if v is even then v + 1 v -1 these are odd and vice versa.

So, what we are saying is that depending on the vibration quantum number either odd or even numbered amplitudes are 0 that is we have just suddenly dropped something very profound on you let us see if we understand this. What we are saying is this we have proved that j max is determined by v now remember suppose v is equal to even then what are the coefficients we will get? The coefficients will get are a 0 a 2 a 4 so on and so forth.

From there we cannot get a 1 etcetera but then since we have determined that you cannot have a j beyond v, v + 3 will also not be there. And then you can go down from v + 3 and on so forth you can show that v equal to 1 that will also not be there. And similarly you can work it out for odd v's as well. So, either odd numbered amplitudes will be 0 or even numbered amplitudes will be 0. So, for odd v values this is what I mean the function h is going to be a 1 multiplied by Xi plus a 3 multiplied by Xi cube note there is no a 2 multiplied by Xi square.

Next term will be a Phi multiplied by i to the power Phi so on and so forth up to a v multiplied by Xi to the power v. Similarly for even v the function h is going to be a 0 plus there will not be anything in a 1 so the next term will be a 2 multiplied by Xi square plus a 4 multiplied by Xi to the power four and so on and so forth again the last one will be a v multiplied by Xi to the power v. Only difference between this and this is that here v is even here v is odd ok.

So I think it is better to break now and come back for a short third module to complete this discussion. So, what we see then is for odd v h Xi is equal to a 1 Xi + a 3 Xi cube + a 5 Xi cube and so on and so forth. Note there is no a 2 no a 4 right so these even number terms are all missing when v the vibrational quantum number is odd. Similarly for even v the order numbered coefficients are missing they are all 0 ok.

So we have worked out the expression for h of Xi for even and odd values of v we have learnt that both of them go only up to j equal to v. Now to complete this discussion and build a full description of the wave function will need to work a little more but let us break this module here. We will come back for a short module to complete this discussion.