Quantum Chemistry of Atoms and Molecules
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Lecture-45
Variational calculations for Harmonic Oscillator and Particle in a Box

Welcome back, let us see how far we can get in our discussion of variation calculation today. Today what we will do is we are going to sort of show you the result will run you through the procedure will not solve everything will not work out everything but we will just give you hints on how to do it and we will discuss what kind of results we get for 2 systems that are very familiar with us.

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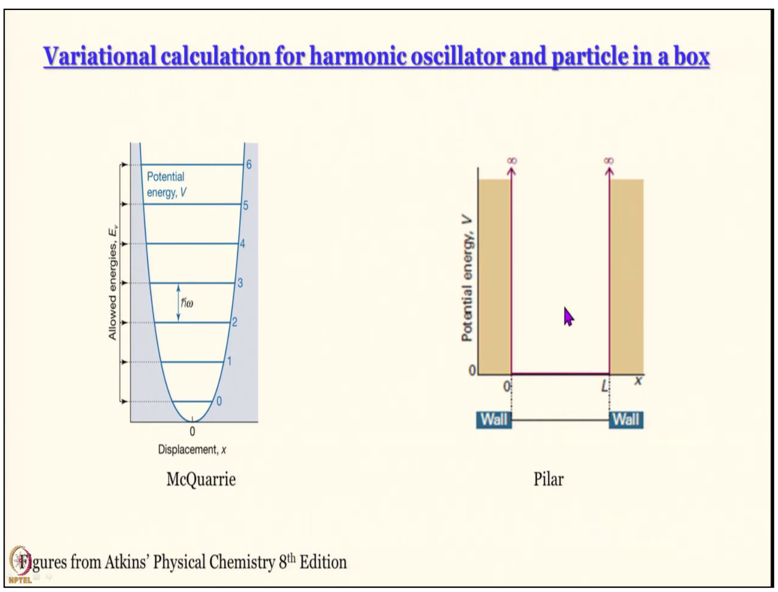

The first 1 is a harmonic oscillator the second 1 is particle in a box of course you can have exact solutions we have learnt that we know the exact solutions for your harmonic oscillator and particle in a box. We can solve Schrodinger equation we do not need any approximation methods but then that is exactly why these systems for which exact solutions are available are excellent benchmarks for testing any new theory any new approximation.

And that is what we are going to do with variational calculations. We are going to see how we can treat these 2 problems and whether we can get anywhere close to the exact solution of energy that we have got earlier. So, what I will do is you can study from any books you are comfortable with no problem and in fact there are many books like those of Prasad and A. K. Chandra which are excellent and easily available; study them by all means it is just that I like the treatment of my query the most as far as variational calculation for harmonic oscillator.

I like the treatment of Pillar the most while talking about variational calculation for particle in a box, so I am sort of going to follow their books but Prasad's book or A.K. Chandra's book or there are many other books you might want to study a little higher level Sabo's book everything is fine whatever you understand as far as that material is not less than what we are discussing here that is enough great.

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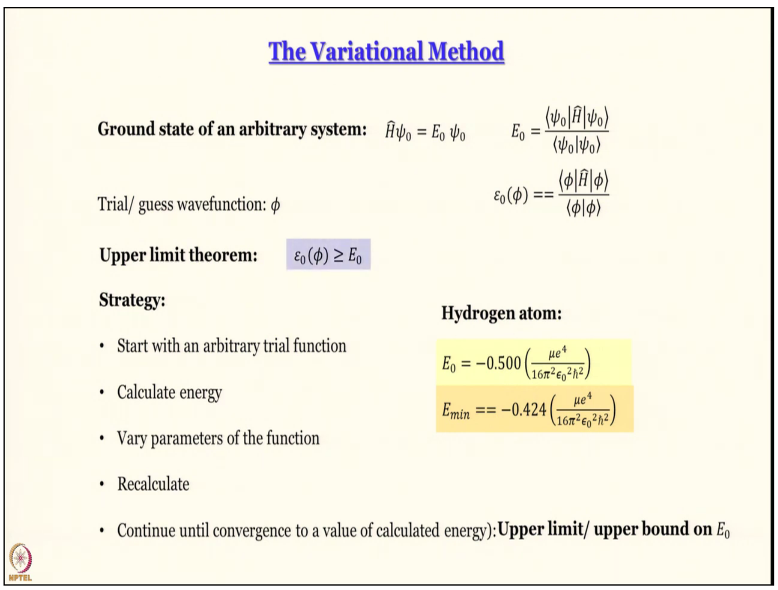

So I hope we are now all very familiar with the variational method what we do here is that we try to develop a description of the ground state of an arbitrary system and for the nth time let me remind you that arbitrary system means a system for which Schrodinger equation cannot have cannot be solved exactly but you can write the Schrodinger equation. You might not be able to write the wave function but you can usually work out the Hamiltonian and you can write Schrodinger equation H psi 0 equal to E psi 0.

And you can say that if we could somehow solve it then we will get an expectation value of energy ground state energy that would be like this integral psi 0 star H psi 0 over all function space divided by integral psi 0 star psi 0 over all function space. The denominator once again for the nth time is going to be 1; if you use normalized wave functions, so, the way to treat this is to start with a trial wave function and that is what we are going to do today and in the next module.

So we start with some trial wave function and we will see how 1 can make a guess of that wave function for that we will work out this functional epsilon 0. So, the form of epsilon 0 is exactly the same as that of E 0 the only difference is that E 0 is in terms of psi 0 epsilon 0 is in terms of phi. So, we start with the trial wave function and does it depend does it makes any difference does it make any difference.

On what kind of function I choose can I choose a polynomial can I choose Gaussian exponential what we will discuss all these questions today. But what we have learnt so far is something called upper limit theorem which says that no matter what trial or guess wave function that you get you cannot do better than the best you can never reach the actual value of energy of the ground state and you approach it from the top remember what we are interested in stabilization that means this energy is going to be negative E 0.

So you start from a 0 energy you know interaction and then you start going towards it that is why you are going from top to bottom you are not going from bottom to top. You cannot have so many parameters or you cannot somehow synthesize a wave function in such a way that the energy that you get from this expression is lesser than the actual exact solution for the ground state energy this is upper limit theorem.

And what we have done is we have said that this is a strategy you calculate energy the last part actually you have not really done vary parameters of the function recalculate we have not done all this but this is sort of a preview of what is going to come in future. What we have done is that we have just minimized this in with respect to the variation parameter and we have obtained the upper limit or upper bound on the ground state energy E 0.

And we have got results for hydrogen atom and the results is something like this the exact solution is – 0.500 multiplied by this quantity and E min means the minimum value of epsilon 0 that is the convention we will use that turns out to be you can neglect the second equal to sign here I mean here I mean no function is more equal than the others those of you who have read anomaly form will understand what I am talking about here.

But this equal sign is just a typo please ignore it. But what we see is that we get – 0.424 into something and the exact solution is –0.50 in something so we have gone close we have not got -0.1 multiplied by the same con same constant we have got –0.424 which is very close to – 0.500 well let us not say very close which is close to – 0.500 but is more than it so we have demonstrated this hydrogen atom using this hydrogen atom problem we have demonstrated the upper limit theorem.

And if you remember the wave function we took in that case was a Gaussian function which is different from the actual exact wave function which is an exponential decay in r. So, this is what we did as a demonstration and then we went ahead and we proved upper limit theorem as well the proof is really not very difficult.

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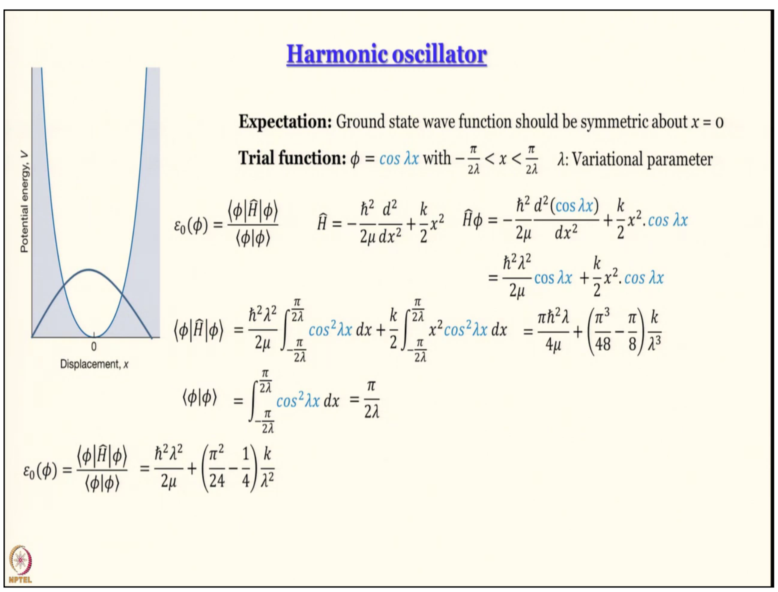

So, today with this prior knowledge we try to tackle the problem of harmonic oscillator first. For harmonic oscillator we know that this here is the potential energy a parabolic potential half k x square kind of potential. So, the first expectation is that this ground state wave function has to be symmetric about x equal to 0. Since the potential itself is symmetric with respect to x equal to 0 if the wave function is not symmetric then we got a problem yeah I mean actually psi psi star should be symmetric.

But when you are talking about ground state that is the lowest energy that would better be symmetric about x equal to 0 so what kind of a function can we think of? You can think of many things we can think of a Gaussian function so like your hydrogen atom ground state problem if you want to start with the Gaussian function I do not want to stop you in fact I would like to encourage you to do it and see what kind of answer you get but what we will do is that we will choose a trigonometric function a cosine function.

Because what is the value of say cosine x at x equal to 0 that is 1 and then as you go towards +x or -x values would fall. So, what we do is we take this this kind of a symmetric cosine function as our initial guess function and this is what we write and we set the limits to be x between minus and plus pi divided by 2 lambda of course that would bring in a relationship between say lambda and a but then see lambda here is really a variational constant parameter.

So we will play around with lambda little bit great. Well it does not really there is no not necessarily relationship between lambda a you can ignore that. So lambda is a variational parameter, so what we want to do is we want to work out the expression of this functional epsilon 0 and we want to find E min which is the minimum value of this functional with respect to lambda. So, to do that we remember that the Hamiltonian here is - h cross square by 2 mu d 2 dx2 + k by 2x square I will not discuss this further because we know it.

In case of any difficulty please go back and consult the lecture on harmonic oscillator. So, what is H phi I want to I am trying to evaluate the numerator so H phi is going to be – h cross by 2 mu d2 dx 2 of cos lambda x + k by 2x square multiplied by cos lambda x simple as that. So, this turns out to be without much hassle h cross square lambda square by 2 mu cos lambda x is that differentiate cos lambda x.

Once you get a minus sign function multiplied by lambda and then differentiate that once again you get a + cos function again multiplied by lambda that gives you lambda square and the mius sign that came out in the first differentiation process that and this minus take care of each other and it becomes plus so h cross square by 2 mu that remains the constant that comes out is lambda square and you get back cos cosine x plus you get k by 2 x square we are just multiplying it by cosine x.

So what is comforting is that this function that we have chosen is an eigen function of the Hamiltonian. So, the choice may not be all that bad great. Now what do we do we have to evaluate this integral which I am not going to do step by step because it is very, very long I am not about to do it I encourage you to try and do it out yourself hopefully your mathematical skills at this point of time is much better than mine since I do not work out maths anymore.

My son who is in class 12 often takes upper hand on me because he can ask me to work out mathematical problems and I cannot I am sure you are much better in maths than I am at this point of time so I encourage you to work this out. I just tell you the answer well this is how you formulate it and the answer that you get is pi h cross square lambda divided by 4 mu + pi cube by 48 - pi by 8 k by lambda cube.

Of course you can simplify it further bring it to 1 numerator 1 denominator will not do it you will see why? Now what is the denominator integral phi star phi dx here it you do not have to set it out 1 dimensional system so dx. So, integral phi star phi dx what will it be? That will be something like this now the limit is - pi by 2 lambda 2 + pi by 2 lambda remember that is the range of x you do not go from 0 to a here.

So, cos square lambda x dx yeah if you go beyond this then again you will get some other kind of I mean you will get the opposite phase as well so you do not want to do that you just stop there. So, integrate this again see these are exact these are definite integrals so there is a compendium as you know you can see the value it comes out to simply to be pi by lambda, pi by 2 lambda. So, what is the value of the functional this is what it is h cross square lambda square by 2 mu + pi square by 24 - 1 by 4 multiplied by k y lambda square.

You have definitely not worked it out I am showing you the final answer you are more than welcome to work it out by yourself.

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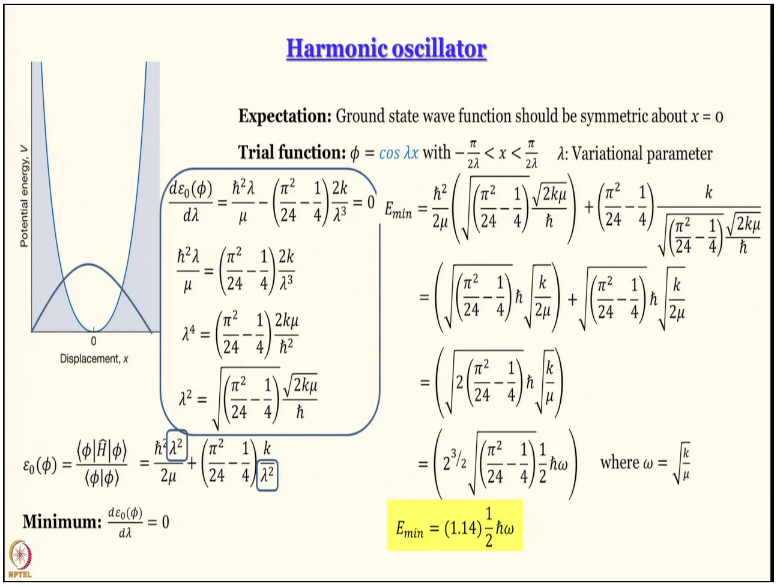

Now to find the minimum of it we differentiate with respect with respect to lambda and equate it to 0 and then when you do that this is the derivative with respect to lambda h cross square lambda by mu yeah because I have differentiated lambda square so 2 has come out 2 in the numerator 2 in the denominator would cancel you are left with h cross square by mu multiplied by lambda minus why minus? Because I have lambda to the power - 2 here so differential of that will be -2 multiplied by this I think I have no its ok its fine.

So this is what we get and finally when you work it out you get an expression for lambda square I am not going to the steps because well they are easy it is very possible that I have made some mistake while writing this equations please work it out yourself if there is any typo here correct it and you can always refer to the textbook this is I think from Macquarie's book. So, we get an expression for lambda square which we are going to substitute in the expression for epsilon 0 phi to get E min.

Remember we have equated this first derivative to 0 that means whatever we get by substituting this value of lambda, lambda is a variational parameter remember we are actually varying it. For different values of lambda you are going to get different values of epsilon 0 and remember what we have we had said about getting the surface and reaching the minimum. Here we are finding the minimum just by differentiating and equating to 0.

So, this particular value of lambda corresponds to the minimum value of epsilon 0 we substitute there and find the value that value we call E min and that turns out to be h cross square divided by 2 mu multiplied by root over pi square by 24 - 1 fourth multiplied by root over 2 k mu by h cross + pi square by 24. So, this is what it is I will not read it out but I think it is not very difficult to understand. But please do write out at least these steps yourselves.

Now you see when you simplify you end up getting this familiar quantity root over k by 2 mu we know what it is, is not it; it is omega the angular frequency of oscillation of the harmonic oscillator. So, what we can do is we write this expression we get this and finally it boils down to 2 to the power 3 by 2 square root of pi square by 24 - 1 fourth multiplied by half H cross omega. So, I am not going taking you through the every simplification please do it yourself.

So half H cross omega we remember what it is so E min turns out to be if I just put in this value of pi and work this out turns out to be 1.14 multiplied by half h cross omega do you remember what the exact solution was? The exact solution was half h cross omega. So, even though we have used some arbitrary wave function which sort of would have a compatible shape from common sense we have got a value of E min which first of all satisfies the variation theorem upper limit theorem.

And is higher than the exact value by 14% actually 14% is too much you do not want something that is away from the actual value by 14% in ideal scenario sometimes you have to live with it but here see what we have done we have used such a simple wave function still we get only 14% over estimation of the value of energy. So, given the level of simplification we have used here this is actually remarkable great.

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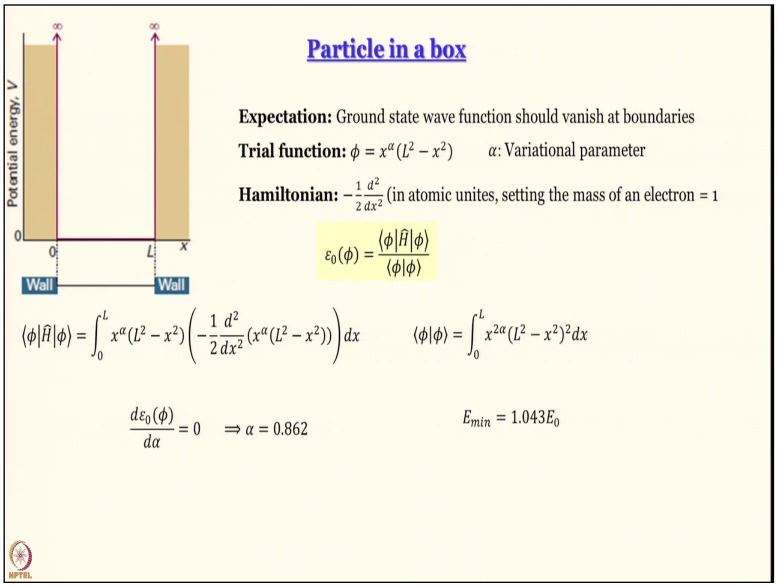

Now let us move to the other system particle in a box. Here we expect the ground state wave function to vanish at the boundaries you might remember what the boundary condition is and secondly we also expect it to be symmetric with respect to l by 2 or I do not remember whether I have used l or a in the later calculation whatever it is either capital A or capital L or small a. So, it has to be symmetric with respect to the center in this case l by 2 two conditions then ground state wave function should vanish at boundaries and any wave function should vanish at the boundaries.

And the ground state wave function like that of particle in a box should be symmetric about the midpoint which is at x equal to l by 2. So, the trial functions we use now see we can use so many functions. You remember the exact function it is a sine function. So, what we do is we deliberately move away from trigonometric function now. We want to write an algebraic function because we want to see what happens when we write a wave function that is not similar to the exact 1 can we still live with it? Can we get close that is a question we are asking.

Because eventually we want to deal with systems in which we have absolutely no idea about what the wave function should look like should it be real should it be imaginary well real imaginary is not a problem perhaps because you can take linear combinations and go from 1 to the other. But we should be trigonometric should it be exponential should it be something else so these things will not even know.

So while we have some control over the system while we are talking about a system in which exact solution is known we want to go far away from what we know to be the correct solution and see if we can get anywhere close to the actual solution. So, what we do is we use an algebraic function x to the power alpha multiplied by l square - x square let us say where alpha is the variation parameter you can use many other things you can use l - x whole square or you can use just l - x or you can use l - x to the power alpha you may not use alpha here.

There are so many combinations I am just choosing 1, the 1 chosen by Pillar. Does it satisfy the expectation at x equal to 0 this x to the power alpha equal to 0 so the wave function is 0 at x equal to l l square - x square will be equal to 0, so again wave function is 0. So, at least that is satisfied and is it symmetric with respect to this l by 2 yeah x to the power alpha is an increasing function l square - x square is a decreasing function. The product has to go through a maximum which is going to have occur at l by 2. So, our expectations the written 1 and the unwritten 1 are both match.

We got a trial wave function which has a variational parameter great. So, now this is the Hamiltonian of course you know what the Hamiltonian is - h cross square by m into d2 dx 2, h cross y by 2 m into d2 dx 2 here I have deliberately eliminated the m like what Pillar has done because I also want to just start sensitizing you to what is called atomic units you not unites we all unite in using atomic units this is units.

So in atomic units what happens is the most fundamental quantities like electronic mass electronic charge these are set to 1 and all the quantities we get are in terms of these we are going to use them excess extensively when we talk about multi electron atoms. So, I just wanted to be faithful to Pillar and keep their convention. So, this is the Hamiltonian we use this is your epsilon 0 we know that by heart by now.

So this is the integral you want to evaluate you want to do it be my guest I am not about to do it because it takes so much of time. See it is not difficult it is a highly doable problem and we have much more difficult problems that we said in say JE advance or JE mains but it is a lot of work, it is tedious if I may use a term that is not so pleasant it is a lot of donkey work. So, the only problem with this approach is that you have to do tedious calculations otherwise concept and all if you are careful it is not difficult.

So if you do that tds calculation and then if you equate this d epsilon 0 d alpha to 0 then it turns out that we the value of parameter alpha is 0.862 when the minimum in epsilon 0 is obtained with respect to alpha. So, the wave function finally becomes phi equal to x to the power 0.862 multiplied by l square - x square. So, I got the animation wrong but that does not matter now E min turns out to be; so if you put this value and if you work out the expression of epsilon 0 it turns out to be 1.043 multiplied by E 0.

So I have jumped perhaps 45th steps here I am just showing you the final answer E 0 is the exact value of energy that we have got earlier when we talked about particle in a box solution of Schrodinger equation what we see is that we are away from it by only 4% in your simple in your how many oscillator we were away by 14%. Here we are away only by 4% even though we have used such a strange weird trial function which looks nothing like the actual exact wave function that we know what it is.

So as long as the shape matches and as long as you have a parameter that you can play around with you can it seems you can get close to the exact solutions and if you think 4% is close just wait and see what happens in the next module when we try and increase the number of parameters we will keep getting closer and closer. So, that is what we wanted to discuss in this module 2 simple systems for which the exact solutions are known they serve as excellent testing pads for this variational calculation.

We have seen that in 1 case we can get close by 14% in the other case we can get close by 4% and what we have done is that we have used very simple easy wave functions. Now that we are more or less convinced that we can use whatever wave function we like I mean at most will have to do a bigger calculation. But will never get an energy that is lower than the actual energy what we will do now is we are going to see what happens when we use wave functions trial wave functions that are actually linear combinations of some functions that is what we will discuss in the next module.

Then later on we will go on to the discussion that we said sum function what happens if you use orthonormal functions to and we express this trial wave function as a linear combination of these orthonormal functions and use the coefficients of this functions as variational parameters what happens then. So, that is the path ahead and in the next module we come back and we pick it up from here.