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

Lecture - 38
Variation Method – Introduction

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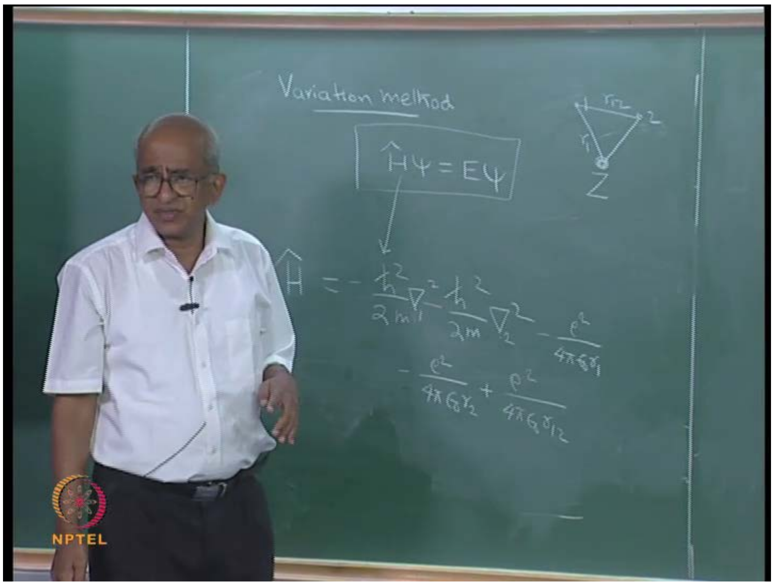

We will now discuss the variation methods, and this is extremely useful. And in fact, this is method that is used in all the calculations that or all most all the calculations that people have been doing. If you go to the computer center they would have packages which will enable you to calculate electronic structure of molecules. A program like if for your Gaussian or Gammons or other packages are there. They are all based upon this method - the variation method. Now, the most of the time what happens is that you see we are not interested in all the solutions of the Schrodinger equation, I mean of course, getting all the solutions would be very nice, but the thing is most of the time we are interested in the ground state of the system.

For example, suppose I have two hydrogen atoms I bring together these hydrogen atoms, they are in the ground state and I bring them slowly, so they will interact, but I move them, so slowly that they interact into, they are still in the ground state. And I want to calculate what happens to the energy of the system as I bring the two hydrogen atoms together would the energy decrease if it decrease that there will be the formation of a bond or would the energy increase in which case that there will not be the formation of any bond. So, this is the particularly in the ground state, of course, I mean I can say one of the hydrogen’s is existed and then I would bring them together, but that is not what you normally have in you can make in problems. Normally things are in the ground state and they interact.

The lowest possible electronic state I should very clear about this. So, therefore, what is the thing I mean I have this equation H psi is equal to E psi. And this H well one purpose we have been looking at systems for which H is sufficiently simple. If you had an atom like helium atom, if you should remember that there are three particles in helium atom - the nucleus and the two electrons, but maybe I can get rid of centre of mass motion of the system as I hold this is we have already discussed. So, therefore, it is effectively the relative motion of the two electrons with respect to the nucleus that is of great interest if you are a chemist. A helium like atom means that it has two electrons and a nuclear charge of plus Z e.

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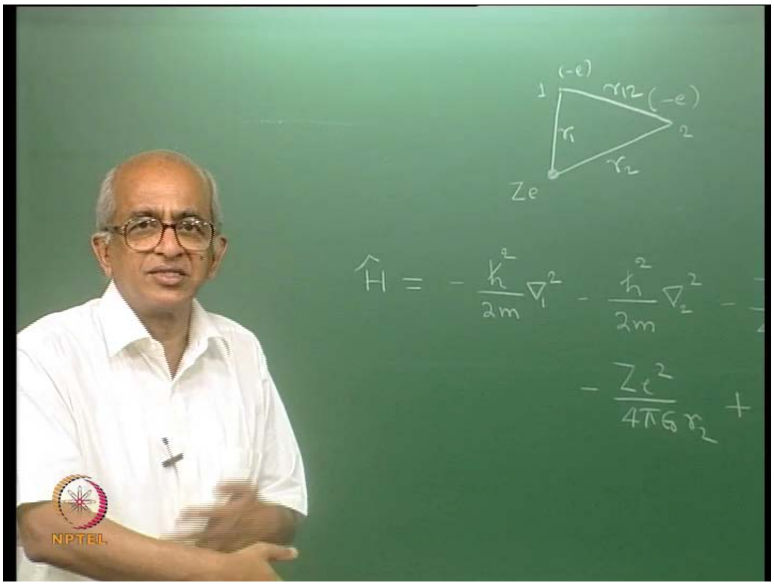

So, this is the nucleus having a charge of plus Z e and there are two electrons one and two both of each of course, are negatively charged. So, they have charges of minus e each. Now as I said we are not going worry about centre of mass motion; that means, I will take a coordinate system in such a fashion that the nucleus is sitting at the origin and then if I think of the Hamiltonian, you see you have H given by the expression which I will write now. This first electron is moving, so it has kinetic energy and therefore associated with that I shall have the operator minus h cross square by 2 m dell one square dell; one square means I am differentiating partially with respect to the coordinate of electron one, there are three coordinates. So, this involves three partial differentiations and then I would also have the kinetic energy of second electron which gives me another operator minus h cross square by 2 m dell two square. Again three partial differentiations with respect to the coordinates of the second electron, and then I have to worry about the potential energy of the system.

So, electron one will interact with the nucleus. Let me call this distance R 1 that interaction energy will be attractive and therefore I shall have a negative sign, it will be given by minus Z e square divided by 4 pi epsilon 0 r 1. Minus Z e square comes it was the nuclear charge is plus z e and the charge on the electron is minus e. So, minus e into Z e square will give me minus Z e square. Similarly electron two will interact with the nucleus, if I denote that distance as r 2 then that will give me a term which will read like minus Z e square divided by 4 pi epsilon 0 r 2.

And not only that you see the two electrons, so they have the same kind of charge as a result of which they ripple each other. So, let us denote this distance as r 1 2 and so the repulsive interaction because it is repulsive interaction it increases the energy of the system. And therefore, I have a plus sign here plus e square divided by 4 pi epsilon 0 r 1 2. So, this is the full Hamilton for the system and as I have already told you there are six partial differentiations involved in this operator.

If you look at the Schrodinger equation, which would be H psi is equal to e psi and this is a partial differential equation involving six variables extremely difficult substructure one should perhaps a impossible to solve. But as I said we would like to get some idea of the energy of the ground state if possible, the mathematical difficult is involved in solving these are enormous. People have try to solve this equation exactly I think even now there must be a few people few scientists trying to solve this equation, but I will suspect, so that nobody in the right senses would do it because this is such a difficult thing.

Of course, I mean having said that probably that is not a very careful statement, because if you can solve this equation you will become very very famous. And what I say I told should not discourage you from trying to solve it, but I doubt whether it can be solved anyway. Now the mathematical difficulties are enormous, and therefore I cannot solve it. So, then at least I mean I would like to know the ground state energy roughly at least if possible, can I have a procedure, which will enable me to estimate the ground state energy of the system, this is the question. So, what I want do is, I want to get an expression for energy. So, how am I going to get an expression for energy. I have this equation H psi is equal to e psi, this is this is not of great use because I cannot solve it, but what I am going to do is I am going to multiply both the sides by psi star.

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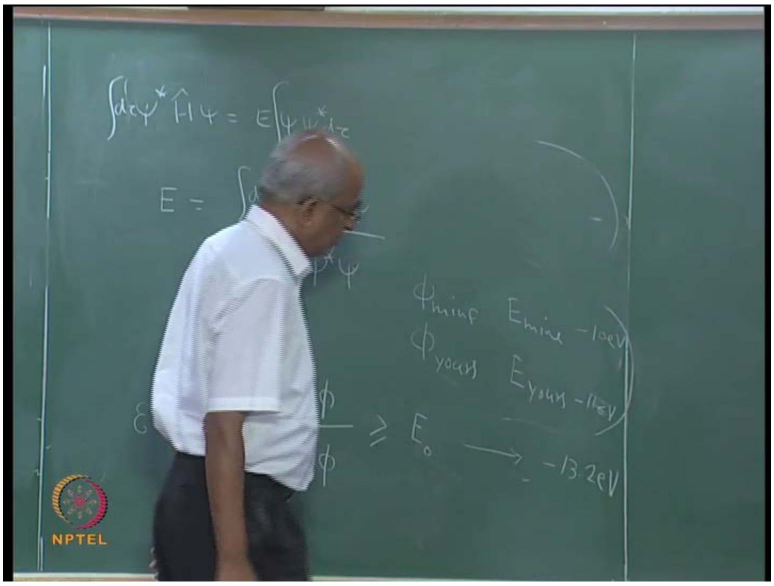

Even though I do not know what psi is I can always imagine that I multiply by psi star and that integrate over the entire space. Now what is d two well you see if you are thinking of helium atom d 2 will contain d x 1 d y 1 d z 1; d x 2 d y 2 d z 2 remember that. So, therefore, depending upon what you would problem is d 2 can be different and this expression you can take and to get another expression which looks nice. So, this is the expression that have I get for E nice to look at, but totally useless expression. Why is it useless, it is of no use simply because you see you do not know what psi is, so what is the final having such an expression for you because after all you did not know psi, you do not know psi. Even if you knew psi then why should you write this expression, because you can just you see take that psi put it put it here allow H psi to be operated upon right allow H to operate upon that psi and you will get E. So, this is straight forward.

So, therefore, as it stands this is not a useful expression that you cannot think any use for it, but there is something very interesting. Usually if you have a physical system our physical intimation will allow us to write down a wave function for the system, which we think is approximately correct, which I will show you how it can be done. So, let me say that I have an approximate wave function pi which I am just guessing and I suspect that this phi is a fairly decent approximation to psi and pi is not because I have guessed it. And then what I will do is I will take this approximate function and wherever psi locates in here I can put that phi.

So, what will I get, I will get an approximate energy. You are not going to get the exact energy that you will not get. So, you will get an energy which I will denote by this symbol, I shall refer to this as script e, it is not the normal way you write e this is little bit written differently, and therefore, I shall refer to that as script e. So, what do I expect, I expect that script e will be an approximation for the energy of the system to be specific. I would imagine probably that if I was use, if I was careful in in choosing my wave function, it will be an approximation for the ground state energy. I mean all that I need to do is I have to choose pi in such a fashion that there are no nodes, because I know the ground state wave function has no nodes.

So, I can make use of that imagine that I have chosen pi in such a fashion that there there are no nodes then probably it will turn out to be an approximation for the ground state energy of the system. If that was all then again this is not very interesting, you can actually prove that script e has to be greater than or equal to the ground state energy, this is what is very interesting. It does not matter what pi you use, I may have phi one of you may have a different phi. For both the phi’s my phi I will call phi mine and your phi I will call phi yours, it is guaranteed that this put here or this put there, both will give you answers, they are will not be the same they will be different, but both are guaranteed to be greater than the actual ground state energy.

And suppose you get two such values, well for the first one I get E mine and the second I get E yours, both are greater than E zero. So, which one among these two will you choose as the better approximation, the one that is closer to E 0 which one would that be that will be the one which is lowest or which is lower among these two. So, even see suppose this I mean as an example suppose this stands out to be I mean let us say I am doing a calculation for hydrogen atom, and suppose this I comes out to be minus ten electron volt. And this comes out to be minus eleven electron volt where as the actual ground state energy of the hydrogen atom in the ground state is minus 13.2 electron volt.

So, you can see what has happened both of them are greater than minus 13.2, but the one that is lower which is minus 11 electron volts is the better approximation. So, therefore, I have a very quantitative way of estimating the goodness of wave functions, if I have a wave function and if you have a wave function, I can easily tell you I all that I need to is I do this calculation and find out which one will gives me lower energy that is a better approximation. And this is the very useful procedure. Now if you illustrate this procedure actually I will take the example of a particle in a box, in a one-dimensional box.

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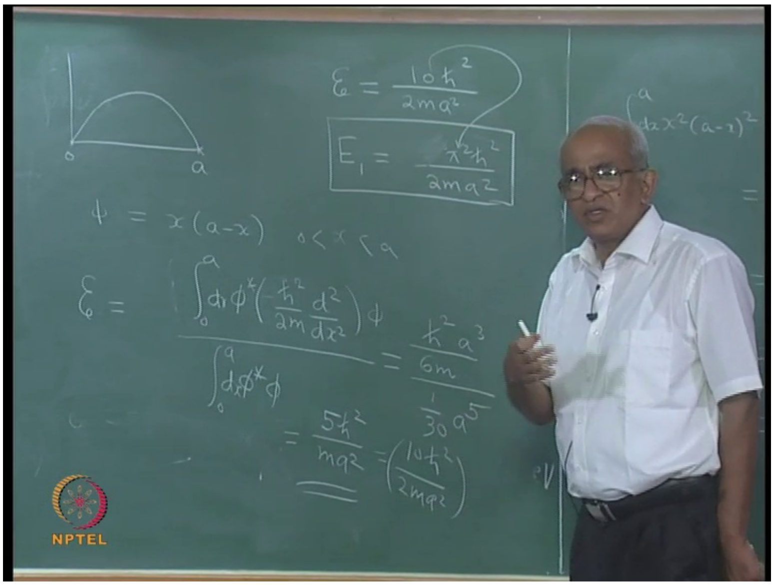

So, here is my particle in a one-dimensional box. The box goes from 0 to a, I actually know the everything regarding this problem, I know the Eigen functions, I know the Eigen values and so on. But let me not to worry, let me just say that I do not know anything about this Eigen functions and the Eigen values, I want to use an approximate wave function to calculate the energy of the ground state. But the information that we have already have means that the ground state energy is actually E one equal to n square pi square h cross square by 2 m a square with n equal to 1. So, this is the actual ground state energy of the system.

If you solve the Schrödinger equation exactly, this is what is going to happen. And now you see I do not want to follow that procedure I may essentially I want to illustrate the variational approach. So, what I wanted to do is I want to guess a wave function for the system and use that guessed wave function to calculate the value of script e. So, how will I guess the function, well it is fairly simple in this case, because I know that you say here and there what should happen the function the wave function, I know it has to vanish at the boundaries of the box. The particle does not go beyond the boundaries of the box, because at the boundaries of the box we have infinite the high potential. So, therefore, at the boundaries of the box wave function has to vanish, it has to vanish here; it also has to vanish there.

So, what is the simplest function that I can think of, what is the simplest phi if I has to be a function of x, but it has to vanish at x is equal to 0 as well as at x is equal to a. What is the simplest function that I can think of, which will satisfy this criterion or will satisfy these requirements? The answer is that I can think of a function which may be something like x into a minus x, because if you put x is equal to 0 the function will vanish; if we put x is equal to a again the function will vanish, and therefore, this is the simplest function. You can think of any number of other functions, but this is the simplest one, and in fact, if you plot at this function against x how will it look like it will be zero here, and it will increase reach a maximum and it will decrease, so that is how this function looks like. It has no nodes in between zero and a.

And now I want to calculate script e, what would script e be, well of course, you see here x is between 0 and a, remember that because in that region the function is this outside that region of course, in other particle does not goes of the wave function will be 0, even my phi will be 0 outside. So, script e will be integral what is the Hamiltonian well minus h cross square divided by 2 m d square upon dx square this is the Hamiltonian operator for a particle in a one-dimensional box. This is the Hamiltonian operator provided the particle is within the box. So, therefore, I would have my this operator operating upon my phi.

So, phi then phi star then d x integrated from 0 to a that is all that is of interest to me, because outside everything is 0 the function is 0. So, and what do you have as the denominator going into be integral 0 to a phi star phi dx this function the way it is written it is not normalized, so therefore, I have to include this. If it was normalized this would be equal to one.

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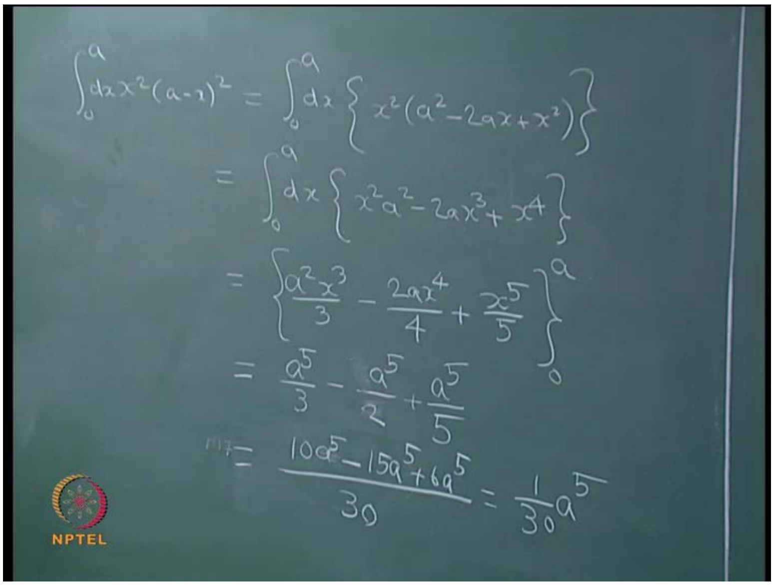

$$\int_0^a dx\, x^2(a-x)^2 = \int_0^a dx \left\{ x^2(a^2-2ax+x^2) \right\}$$

$$= \int_0^a dx \left\{ x^2a^2 - 2ax^3 + x^4 \right\}$$

$$= \left\{ \frac{a^2x^3}{3} - \frac{2ax^4}{4} + \frac{x^5}{5} \right\}_0^a$$

$$= \frac{a^5}{3} - \frac{a^5}{2} + \frac{a^5}{5}$$

$$= \frac{10a^5 - 15a^5 + 6a^5}{30} = \frac{1}{30}a^5$$

So, now fairly simple and straightforward to evaluate this, let me first evaluate this part integral 0 to a phi star phi after all you see a phi is a simple thing phi star is phi itself. So, therefore, it is nothing but x square into a minus x the whole square into dx that is how this is the denominator. And this will be equal to I mean integral 0 to a dx quickly simple, if I do the integral and get the answer. Well, please follow carefully, because I do not want to be making a mistake I think this is ok, so we have evaluated that part.

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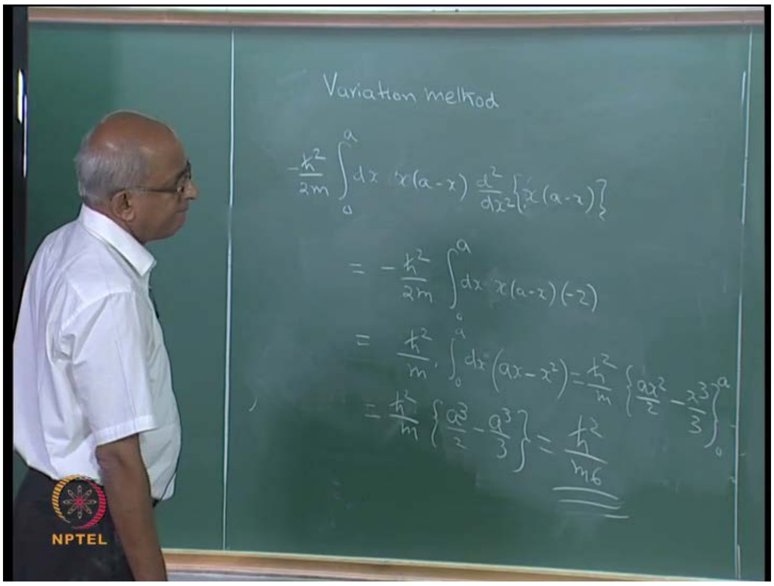

Variation method

$$-\frac{\hbar^2}{2m}\int_0^a dx\; x(a-x)\,\frac{d^2}{dx^2}\{x(a-x)\}$$

$$= -\frac{\hbar^2}{2m}\int_0^a dx\; x(a-x)(-2)$$

$$= \frac{\hbar^2}{m}\int_0^a dx\,(ax-x^2) = \frac{\hbar^2}{m}\left\{\frac{ax^2}{2}-\frac{x^3}{3}\right\}_0^a$$

$$= \frac{\hbar^2}{m}\left\{\frac{a^3}{2}-\frac{a^3}{3}\right\} = \frac{\hbar^2}{m6}$$

So, the what is left is the other part integral of 0 to a dx into x a minus x minus h cross square by 2 m, I will take it outside d square upon d x square x into a minus x is equal to minus h cross square by 2 m integral 0 to a dx x into a minus x. We have to evaluate the second derivative of this of object very simple, because the first time is a x second derivative is 0, the second time minus x square second derivative is minus two. So, therefore, this minus two can be taken in outside you will get h cross square divided by m integral 0 to a d x in to a x minus x square that is equal to h cross square by m a x square by 2 minus , this is the final answer. Therefore, what is happened is script e will be equal to tell me if there is any mistake h cross square divided by 6 m a is cube is missing as I told is happens with me. So, a cube divided by 1 by 30 a to the power of 5. So, what is the answer that I get, this is the final answer. You can verify this, because I want to finish in a few minutes.

So, this I may write as 10 h cross square divided by 2 m a square. So, the result about these calculations, which are not difficult, but it may be perhaps tedious what was stand out is that script e. Script e is how much 10 h cross square divided by 2 m a square, this is your value of script e, using this we approximate wave function which we just guessed. All that we used was that the function should vanish at the boundaries of the box and so on. And if you look at the actual expression, what happens instead of this 10 you have pi square that is all. So, pi you know is 3.14, 15 etcetera.

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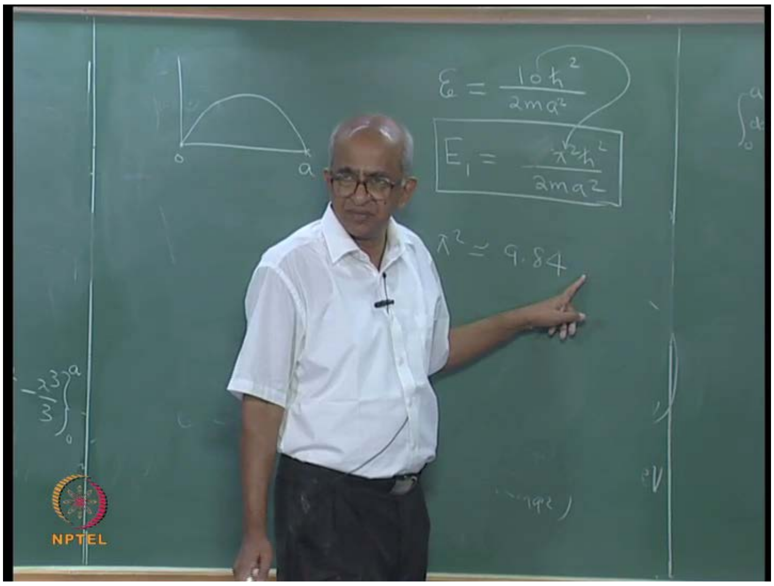

So, if you calculated the value of pi square, pi square will be approximately nine point how much eight four, I mean there are approximate that may it be 9.85, do the calculation you will find it. So, instead of the actual 9.84 what did I obtain I have obtained 10. What is the percentage of error I have got in this calculation is only 1.6 or 1.5 percent, because 10 and 9.84. The percentage of error is only 1.5 percent. So, even this rather crude calculation gives me a fairly decent value for the energy, and not only that this energy that we obtain it is ten, it is greater than the actual energy which a substantiates the variation theorem.

So, in my next lecture, what I will do is I will prove the variation theorem, which says that script e is greater than or equal to the actual ground state energy, this is known as the variation theorem script e. I will prove that it has to be greater than or equal to the actual ground state energy, and then discuss some applications of the variation methods.

Thank you.