Introductory Quantum Chemistry
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Lecture - 39
Variation Theorem – Proof and Illustration

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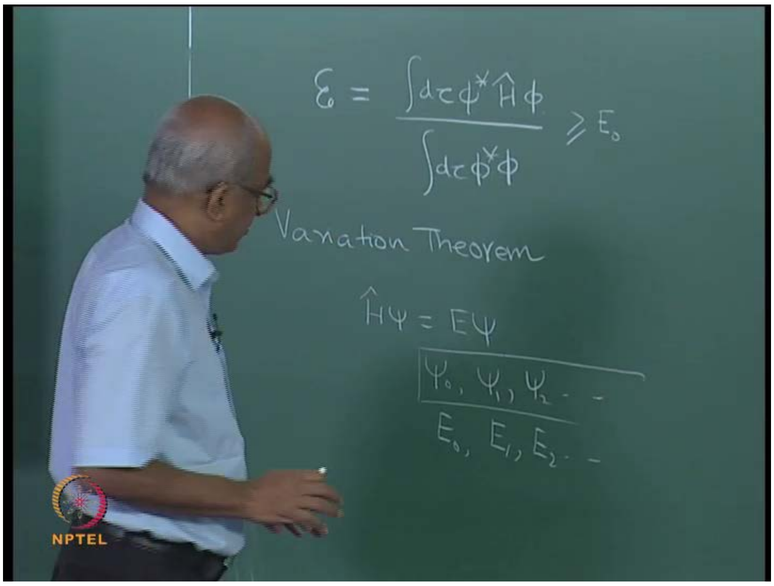

So, we were discussing the variation method. And specifically we were talking about the variation theorem, which says that script E, which is defined to be equal to integral d tau phi star H hat phi by integral d tau phi star phi, for any acceptable state function phi. This quantity is guaranteed to be greater than or at the most equal to the ground state energy of the system. And therefore, if you have a system for which you want to calculate the ground state energy, all that you have to do is you have to guess an approximate wave function; put it in there into the expression; calculate it.

The answer that you get will be greater than; that is guaranteed. It will be greater than. It may happen to be equal to, but that will happen only rarely. It will be greater than the actual ground state energy. And also, it gives us a criterion to judge wave functions. If I have a wave function and if you have a wave function, the one that is better is the one that will give a lower value for script E. So, the question is now, how does one prove this? So, the way to prove this is quite simple actually.

You know that, there is a Schrodinger equation H psi is equal to E psi. And you also know that, there are infinite number of eigenfunctions. So far, the Hamiltonian operator having their own eigenvalues, their own energies; it is just that you are not able to find what they are. But, we know that it is there. So, let me denote the eigenfunctions and the corresponding eigenvalues by the symbol psi 0, psi 1, psi 2, etcetera. And this have the energies E 0, E 1, E 2, etcetera. This we know; but unfortunately, mathematically, it is very difficult for me to find these functions and the corresponding energies. But, as I said, we know that they are there. And I also know that, these functions are actually orthogonal to one another. We have proved that, if we have a Hermitian operator, then the eigenfunctions have to be orthogonal. And I can also take them to be normalized each one of them. And further, they form what is referred to as a complete set; which means that, any arbitrary function, which is an acceptable wave function can be expanded in terms of these functions.

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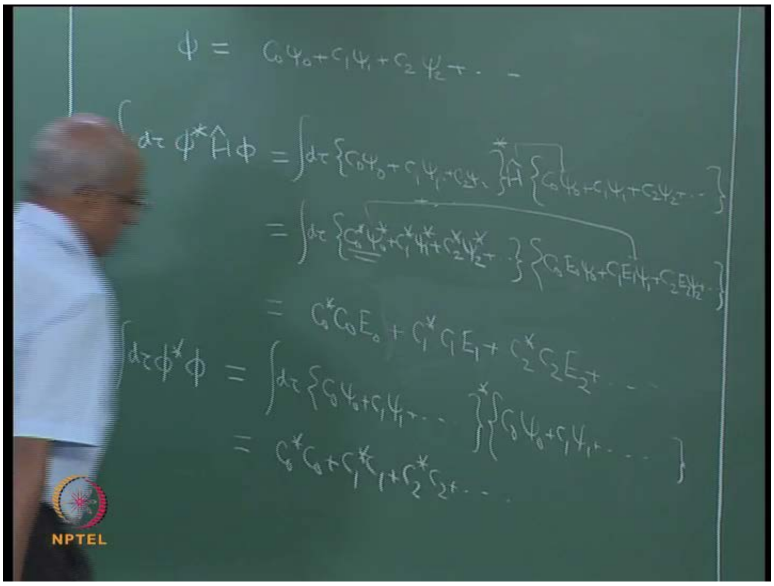

$$\phi = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \ldots$$

$$\int d\tau\, \phi^* \hat{H} \phi = \int d\tau \{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 \ldots\}^* \hat{H} \{c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + \ldots\}$$

$$= \int d\tau \{c_0^*\psi_0^* + c_1^*\psi_1^* + c_2^*\psi_2^* + \ldots\} \{c_0 E_0 \psi_0 + c_1 E_1 \psi_1 + c_2 E_2 \psi_2 \ldots\}$$

$$= c_0^* c_0 E_0 + c_1^* c_1 E_1 + c_2^* c_2 E_2 + \ldots$$

$$\int d\tau\, \phi^* \phi = \int d\tau \{c_0\psi_0 + c_1\psi_1 + \ldots\}^* \{c_0\psi_0 + c_1\psi_1 + \ldots\}$$

$$= c_0^* c_0 + c_1^* c_1 + c_2^* c_2 + \ldots$$

Therefore, I can definitely say that, phi may be written as c 0 psi 0 plus c 1 psi 1 plus c 2 psi 2. This is definitely possible even though I do not really know what the values of c 0, c 1, c 2, c 3, etcetera are. But, this is possible. And if that is possible, let me evaluate the numerator of this expression. What is the numerator? This is actually integral d tau phi star H phi. And that will be equal to… What is going to happen? You would have integral d tau c 1 psi 1 plus c 2 psi 2 plus etcetera; I forgot to put c 0; let me modify this; c 0 psi 0 plus c 1 psi 1 plus c 2 psi 2 plus etcetera. Then you will have H. And then you will have – of course, I should not forget the star. So, there is a star on top of this. Then c 0 psi 0 plus c 1 psi 1 plus c 2 psi 2 plus etcetera.

Now, with this expression, I can do two things. First of all, I can take this star operation inside; that means everything which is inside will be affected. Each one of them is going to get a star; which means that, I am just calculating the complex conjugate. That is the first thing. Not only that; I can take H inside and allow H to operate upon this sum; c 0 is just a parameter or a constant; expansion coefficient actually strictly speaking. So, this H can go and operate upon psi 0. Then if it comes here, it will go operate upon psi 1; here it will operate upon psi 2 and so on. Therefore, this is actually integral d tau c 0 star psi 0 plus c 1 star psi 1 plus c 2 star psi 2. I should also put star on this psi's. And when H goes inside, you are going to get c 0 E 0 psi 0 plus c 1 E 1 psi 1 plus etcetera. That is what is going to happen.

And now, suppose I multiplied things out and did the integrations; so what is going to happen? Let me demonstrate you this term. This term I can multiply with that. What will be the result? The result will be c 0 star from here; there will be a c 0 from there; there will be E 0 from here; and I will have integral psi 0 star psi 0 d tau. That will be the first step. Correct? And I can simplify this, because I know that, psi 0 is a normalized function. So, that integral function that is occurring there – this must be equal to unity. Then the next term will be actually – I mean I could write it as integral d tau; c 0 star let me put first. Then I am going to take this and combining it with that. c 0 star c 1 E 1 – these are all position-independent. So, I can take it out of the integral sign. And what will I have? Psi 0 star psi 1 d tau. There are other terms, but you can easily see what is going to happen. This term is 1, while that term is 0.

And similarly, if we have taken this psi 0 star multiplied with any other psi; answer is going to be 0. Therefore, from this multiplying all those terms there, you are going to get only one term. And what is that one term? Maybe I can just remove these things that I have to written and just write that one term alone. This is that one term. Then similar thing is going to happen with c 1 star psi 1 star. So, it again multiplying all these terms, you see almost every term is 0 except the one that will involve psi 1 star psi 1. And what will that term be? That is going to be equal to c 1 star c 1 E 1.

And then you will have c 2 star; it is very obvious – c 2 star c 2 E 2 plus etcetera. This is what is going to happen. And now, look at the numerator. What is the numerator? Integral d tau phi star phi. It is going to be integral d tau c 0 psi 0 plus c 1 psi 1 plus etcetera with a star multiplied by c 0 psi 0 plus c 1 psi 1 plus etcetera. This is what is going to happen. But, in fact, this term is even simpler than the previous one, because see all that is happening is that, there is no H in between; the previous term had an H in between. And that H gave you this E 0, E 1, E 2, etcetera. But, now, you see H is not there. So, you are not going to have E 0, E 1, E 2, etcetera. Other than that, things are the same. Therefore, what will happen; I can just take this result; remove E 0, E 1, E 2, E 3, etcetera. That is the answer. Therefore, this is going to be c 0 star c 0 plus c 1 star c 1 plus c 2 star c 2 plus etcetera. And therefore, script E.

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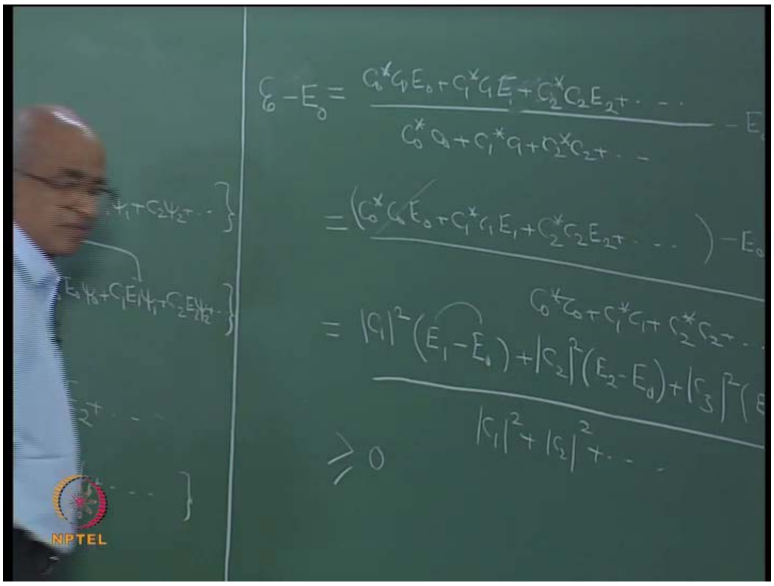

$$\mathcal{E}_0 - E_0 = \frac{c_0^* c_0 E_0 + c_1^* c_1 E_1 + c_2^* c_2 E_2 + \cdots}{c_0^* c_0 + c_1^* c_1 + c_2^* c_2 + \cdots} - E$$

$$= \frac{(\cancel{c_0^* c_0} E_0 + c_1^* c_1 E_1 + c_2^* c_2 E_2 + \cdots) - E_0}{c_0^* c_0 + c_1^* c_1 + c_2^* c_2 + \cdots}$$

$$= \frac{|c_1|^2 (E_1 - E_0) + |c_2|^2 (E_2 - E_0) + |c_3|^2 (E}{|c_1|^2 + |c_2|^2 + \cdots}$$

$$\geq 0$$

What is the expression for script E? We have evaluated both the numerator and the denominator. The numerator is this – c 0 star c 0 E 0 plus c 1 star c 1 E 1 plus c 2 star c 2 E 2 plus etcetera; divided by c 0 star c 0 plus c 1 star c 1 plus c 2 star c 2 plus etcetera. This is what it is. So, what I want to do is; you see I am going to subtract an E 0 from here. Let me remove this E and say that, I will have a script E minus E 0. All that I need to do is I will add another E 0 here – not add, but subtract an E 0 from the right-hand side. That is what that I need to do.

And, now, you see this also – this E 0 also can be incorporated into the numerator. So, what you have to do is you will have c 0 star c 0 E 0 plus c 1 star c 1 E 1 plus c 2 star c 2 E 2 plus etcetera minus E 0 c 0 star c 0 plus c 1 star c 1 plus etcetera divided by c 0 star c 0 plus c 1 star c 1 plus c 2 star c 2 plus etcetera. So, actually, it is very clear that, this term and that term will cancel each other. One term actually cancels and you are left with the remaining terms. And the remaining terms I am going to write in this fashion. I would have…

If you think of c 1 star c 1, you are taking the number c 1, multiplying it by its own complex conjugate that is actually equivalent to calculating the magnitude of c 1 and squaring it. So, this is nothing but magnitude of c 1 square. And what are you going to have? You are going to have E 1 minus E 0, because here there is a term involving c 1 star c 1; there also there is a term involving c 1 star c 1; and I can combine both the terms. And the next term is going to be c 2 magnitude square E 2 minus E 0 plus c 3 magnitude square E 3 minus E 0 plus etcetera divided by magnitude of c 1 square magnitude of c 2 square plus etcetera. This is what happens.

Now, if you look at this, you see these numbers magnitude of c 1 square magnitude of c 2 square – they are all positive; absolutely no doubt; magnitude square. What about E 1 minus E 0? E 0 is the energy of the lowest possible state; E 1 is the energy of the next possible state. So, E 1 minus E 0 has to be positive; there is no other way. E 2 minus E 0 – again positive; E 3 minus E 0… Therefore, you realize that, all the terms on this side are positive. That is all that I need.

And therefore, I can say that, this has to be greater than or equal to 0, because everything on the right-hand side is positive. In the case, where it so… Suppose it so happened that, c 1, c 2, c 3, etcetera are all 0; then it is theoretically possible that, it may be equal to 0. But, then what would happen; the c 1, c 2, c 3, etcetera are all equal to 0. Therefore, phi will be equal to psi 0. So, you have somehow managed to choose the actual ground state wave function. As I said, that is not very likely. And therefore, this equal sign will be valid only rarely. It is always the case that, it is greater than 0. But, theoretically, this is possible. And therefore, we have to put greater than or equal to sign.

So, now, you see I want to develop a practical procedure for calculating energies of system and actually use it in real problems that are of chemical interest. So, how am I going to do that? Let again let me tell you how it may be done. And then I shall demonstrate it by applying it to some problems that are of great interest to the chemist.

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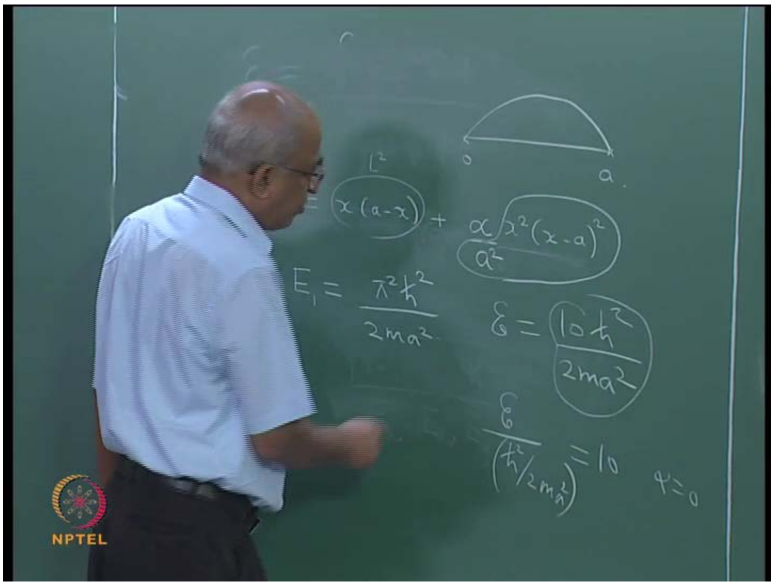

See for the case of a particle in a 1 dimensional box extending from 0 to a; we said that, an appropriate wave function would have to have its value there – 0; and its value on the other side also equal to 0. So, we decided to try phi equal to x into a minus x. Correct? This is a problem for which we know the lowest possible states energy, which is one 1 and that is equal to pi square h cross square divided to 2ma square. This is the correct answer – exact answer. And we evaluated script E; and what happened was actually you got 10 h cross square divided by 2ma square. This is what you got. So, instead of pi square, you had a number 10 sitting there; and pi square is about 9.84. So, I side the other is about 1.6 percent.

But, suppose you are not happy with that; suppose I want to improve this function; I want to do a better calculation for some reason; I am not happy with this 1.6 percent error; I want to make it a better calculation. So, how can I do that? To do that, you see I will have to somehow think of a better wave function. Correct? That is what I have to do. How can I think of a better wave function? Any function that I would choose would have to have a vanishing value at this point as well as at that point.

So, what I will do is, I will think of another possible function, which I will write as x square into x minus a the whole square. This also will satisfy the condition that, it will varnish at the origin; it will also varnish at a now. So, you can actually try calculating with this function alone; you will find that, it does not improve the energy; it does not give you a better energy. I am not going to do the exercise. But, it is possible to do the calculation. So, if that is the case, what you can do is, you can say… What I will do is, I will take a combination of this and that with some coefficient here. And that coefficient is my choice; I can choose any value for the coefficient. I will definitely have an acceptable wave function.

Now, for dimensional reasons, what I will do is, I will just take that coefficient to be alpha by a square. This is only for dimensional reasons; I mean if you are puzzled by this; you see you think of the dimension of this, this is having the dimension of length square. And I want this other function also. This is the other function – this whole thing also to have the dimensions of length square, so that alpha will be a dimensionless parameter. It is not really necessary to include this a square here; you can say you will not include that. Then what will happen is that, alpha would have the dimensions of length square.

So, I do not want that; I want it to be dimensionless; I include this. Now, I know that, if I did a calculation with alpha equal to 0, what will happen? I am going to get this as the answer. If I did a calculation with alpha equal to 0, this is the answer; which means that, script E divided by h cross square 2ma square will actually be equal to 10 when alpha is equal to 0. Correct? Now, what I am going to do is, I am going to use other values of alpha. So, what will happen? Something is going to happen to the value of script E. So, script E will now depend upon the value of alpha.

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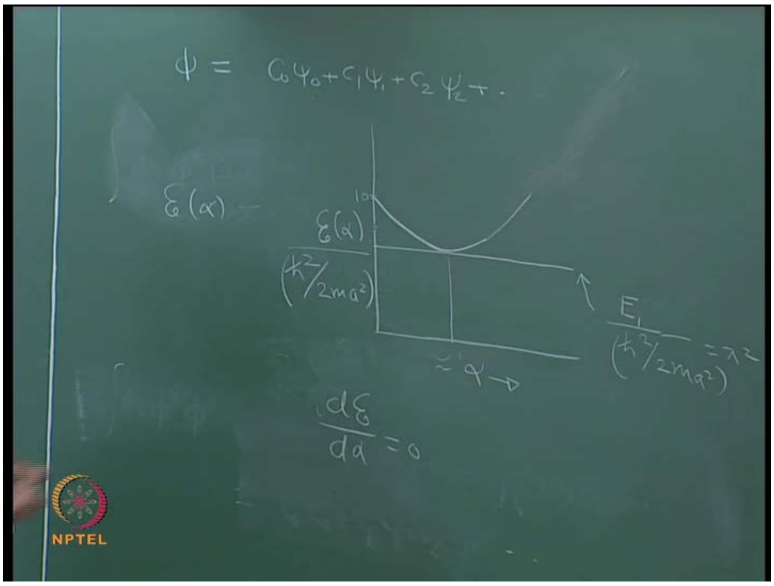

So, you can think of script E. This is now a function of alpha. What we can do is, these days, you see this kind of calculations are extremely… You see particularly if you use this software Mathematica, you can do it in a second; otherwise, you will have to do the calculations anyway. They are not very difficult calculations, but you can do it. And what you do is; I am not going to give you any expression, but what is interesting is to make a plot of E alpha against alpha. And in the same plot… I will not plot E alpha, but I will plot this divided by h cross square divided to 2ma square. This is the number that I am going to plot.

And, I know that, when alpha is equal to 0, it has the value 10. And I will also plot the actual ground state energy. How much is the actual ground state energy? The expression is written there. So, you can say in the same figure, I am also going to represent the E 1 divided by the same object h cross square divided to 2ma square, which I know is pi square. So, in the same figure, I can represent that. Maybe what will happen is that… That does not depend upon alpha. So, if you plotted it as a function of alpha, all that you are going to get is a horizontal line. This is that number.

And now, if you plotted this object as a function of alpha, what are you going to get? You will get a curve. But, the variation theorem ensures that, this curve that I get will always be above E 0 – not E 0, but the ground state energy, which in this case is E 1. Therefore, actually, if we did this calculation, you will find that, the curve that you get gets very close to E 0 – again I say E 0, because it is the ground state energy, but in this particular case, it is E 1. So, it does this. And then it goes and becomes large. Something like that. And in fact, the energy that you get is very close to the actual ground state energy. It happens; I do not remember now. But, about 1 alpha is approximately 1 or some such number. That is not very important. But, in the important thing is that, as you change the value of alpha, the curve gives a minimum and then increases. And what is the best possible value for alpha? The best possible value for alpha will be the one that minimizes script E. It has to… This E is a function of alpha. All that I should do is I should find that value of alpha, which minimizes this. In fact, if you know what this function is, this is a very simple exercise in calculus. What is the exercise? You will say the derivative of script E with respect to alpha should be equal to 0. You find that and that will give me the best possible value for this parameter alpha.

Now, this gives me an idea. What is idea? You see if I have a wave function – a trial wave function, which contains some parameters like alpha here; or, in a different problem, it may be different parameter; then what will happen? Script E is going to depend upon that parameter. And what will be the best possible value for that parameter? You have to find that value in such a fashion that script E has the least possible value; script E has to be a minimum. That will be the best possible value that you can choose for alpha. And therefore, we have a very rigorous way of making the wave function better and better if you want. What you should do is, you should write wave functions, which have maybe several parameters and then find the optimum values of these parameters by minimizing the expectation value of energy. And as I told you, this is the procedure that is adapted in all the molecular orbital – most of the molecular orbital calculations that are being performed. So, let us now think of real chemical example, which will be the case of helium atom.

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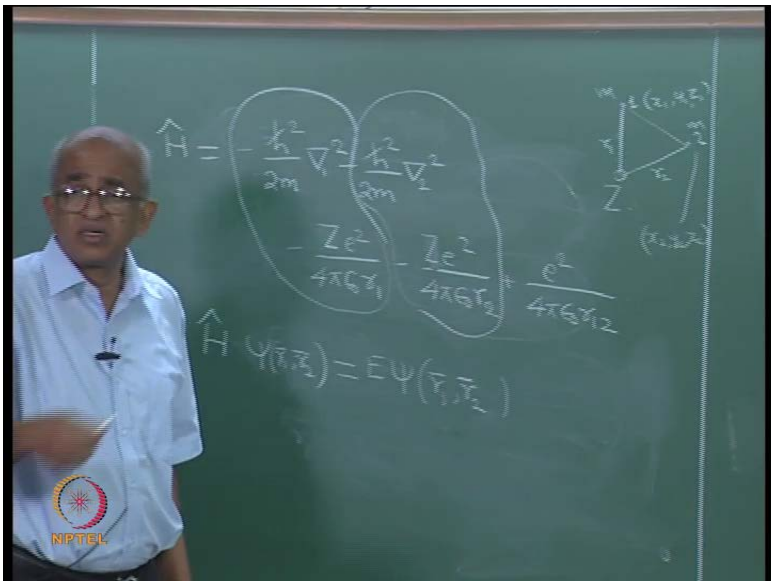

So, what is the helium atom? I have the nucleus; I have two electrons: 1 and 2. And the electron 1 would be at a distance, which I denote as r 1; electron 2 would be at a distance, which I denote as r 2. Electron 1 has the coordinates x 1, y 1, z 1. This has the coordinates – x 2, y 2, z 2. Strictly speaking, I should think of the motion of the system as a whole; that is, translational motion. But, as I have demonstrated to you in the case of hydrogen atom, we can get rid of translational motion. And then there will be some effective masses coming into the description of the problem. But, from now on, we are not going to use any… When I say effective, what I mean is actually this reduced mass that was there in the case of the hydrogen atom. So, from now on… This is a minor correction from now on. I am not going to use the reduced masses or anything; I am just going to use the masses of these electrons. So, let me just put m here and m.

And, I will assume that, the nucleus may be ((Refer Time: 26:53)) fixed at the origin. So, we are not actually worried about the translational motion of the system, because you see in chemistry, most of the time, we are interested in the electronic structure. Of course, there are any number of problems in which you have to worry about translational motion, but that is not what we do now. So, what will be the Hamiltonian for the system? The way we are operating, nucleus is taken to be fixed at the origin; and therefore, we are not worried about the nuclear kinetic energy; we are worried about the kinetic energy of electron 1, kinetic energy of electron 2. So, what will happen? Minus h cross square divided to 2m del 1 square minus h cross square by 2m del 2 square. These are kinetic energies of the two electrons.

Then, I would have minus 2 e square divided by 4 pi epsilon 0 r 1 minus 2 e square divided by 4 pi epsilon 0 r 2. And there is repulsion between the two – e square by 4 pi epsilon 0 r 1 2. You have a 2 here you have a 2 there; the reason is that, I am thinking of a helium nucleus. I can immediately generalize this and say let us not worry about helium atom, but let us think of a general situation, where the nuclear charge may be taken to be capital Z, so that this treatment that I am going to give you may be applicable for all values of nuclear charges. The only thing is that, there should only be two electrons. If you are thinking of helium atom, the value of capital Z will be equal to 2. But, if you are thinking of lithium ion – Li plus, the same Hamiltonian would be valid. But, the value of Z will then b equal to 3. So, we can have a general treatment ((Refer Time: 29:19)). You can say even it will be applicable to h minus if the species existed, because h minus would have a minus capital Z equal to 1. So, let me keep this general and say that, this charge – instead of 2, you are going to have a capital Z. Do not confuse it with the z coordinate; I am using a capital Z and here also a capital Z.

And so what is the problem now? I have H psi equal to E psi. This is the equation that I want to solve. But, in this case, what is going to happen is that, psi is going to depend upon the position coordinates of the two particles. So, how many position coordinates? Actually 6 of them: x 1, y 1, z 1, x 2, y 2, z 2. But, it is tedious to write x 1, y 1, z 1, x 2, y 2, z 2. Therefore, what I will do is I will say position vector of the electron 1. Now, here is I have introduced r 1; this r 1 is actually the distance. But, this object is the position vector. So, this is a vector. And in fact, the magnitude of this vector will be equal to that r 1. So, if you put a line on top of it; that is the position vector. If you do not put a line on top of it, then it is just the distance of the electron from the nucleus. So, this will actually… I mean if you want to be very precise, we can say r 1 will be x 1 i plus y 1 j plus z 1 into k. And similarly, you will have another expression for position vector of the electron 2. Therefore… I mean this is very convenient, because we do not have to write x 1, y 1, z 1, x 2, y 2, z 2 and so on. And then this psi on the other side will also will be dependent upon r 1, r 2. So, that is how things are.

Now, this equation if you look at this, very very messy, because it involves 6 variables – partial differential equation holding 6 variables. As I repeatedly say, even an ordinary differential equation can be extremely difficult to solve. And so a partial differential equation involving 6 variables almost impossible to solve; and so we have to think of some approximate procedure. So, how will we go about doing it? Before I go about doing it, actually, I want to understand what is the problem, where is the problem, and why is it that I cannot solve this. There should be a physical reason. You see any tough problem, there will be a physical reason why it is not possible to solve it.

Now, for a moment, imagine that these electrons you see; they do not repel each other suppose. I mean that is not the actual physical situation, but imagine; I am going to imagine that, they do not repel each other. If they do not repel each other, what will happen? This term is not going to be there. And then what will happen? You will have sum of things that depend only upon the coordinates of electron 1. Notice these depend only upon the coordinates of electron 1; while this part depends only upon the coordinates of electron 2. Therefore, you have kinetic energy of electron 1; electron 1 is interacting with the nucleus. Then you have kinetic energy of electron 2; electron 2 is interacting with the nucleus. The two electrons do not feel the presence of one another. So, what will happen? Each electron will move independently of the other electron. See the two electrons are not repelling each other. Therefore, each electron moves independently of the other electron. Each electron feels only the nucleus. And so the motion of the electron will be similar to that in the case of the hydrogen atom. And you can actually exactly solve for motion of each electron.

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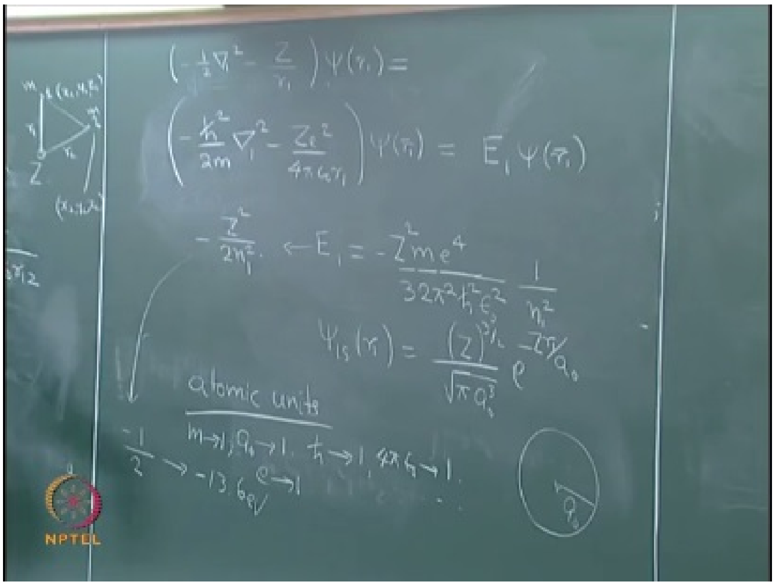

So, each electron what will happen; it will be governed by an equation, which I may write as minus h cross square by 2m del 1 square minus is Z e square divided by 4 pi epsilon 0 r 1. This will be the kinetic energy of electron 1, potential energy of electron 1 due to its interaction with the nucleus. And you will see there is a wave function, which will depend upon the coordinates of that electron alone. And I actually have to a little bit careful, because I have introduced one psi here, another psi there; and they are not the same. This psi is a function of 6 variables; while this psi is a function of 3 variables. And so because I have used the same symbol, there is a possibility that you may get confused. And therefore, what I am going to do is I am going to denote maybe this by capital psi. If I added this, that is the minimum change that I can make. I say this is capital psi. And that also is capital psi. But, this one – the way it is written, I hope you can recognize this as small psi, not capital.

And, what will this going to happen is you see this will have its own energy, which is going to be E 1 psi r 1. And similar equation should be valid for electron 2. And there also, I will have a function. There also I am going to have a function, which will be the wave function for electron 2. And what are the solutions of this equation? Same as in the case of the hydrogen atom, but for the fact that, the nuclear charge is not equal to 1, but it is equal to Z.

Therefore, I should tell you what happens. I mean the process of solution can be carried out easily. We have already done it. So, all that will happen is that, the allowed energy levels – this E 1 for example, will be given by… I do need the expression. So, I cannot remember it; I will just copy it from my notes. You are going to get minus m e to the power of 4 divided by 32 pi square h cross square epsilon 0 square into 1 by n square. This was just the expression for the hydrogen atom except for the fact that I have not used reduced mass here, I have just put the electronic mass. But, reduced mass and the electronic mass are only slightly different. So, as I said, we are not going to worry about that difference. So, this is the expression. But, this definitely is not correct, because you see the nuclear charge is not there in the equation. So, what actually happens is extremely simple; you will have Z square sitting there.

And then you will have the wave function also. The wave function what will happen is that… I mean I am not going to worry about all the possible wave functions; just take the… As in the case of the hydrogen atom, you have all the possible wave functions.

Specifically, I am interested in the ground state of helium atom. Therefore, what will happen is that, I will have the lowest possible state, which will be psi 1 s. And psi 1 s I know it will depend only upon r 1; it depends only upon the distance of the electron from the nucleus; I know that. And what was the expression that we had? It was actually 1 by square root of pi. I think we wrote it in this fashion E 0 to the… Is this is… You can check this. Then you will have e to the power of minus r by a 0. This was the solution for the case of the hydrogen atom for the 1s orbital. This is correct.

But, of course, this is not valid for this particular problem, because nuclear charge is not unity. This would be valid if the nuclear charge was 1 unit. So, what actually happened is you will have capital Z to the power of 3 by 2 sitting here and capital Z sitting there. And not only that, this is the distance of electron 1. r is the distance of electron 1 from the nucleus. And therefore, you will have to put r 1 here. So, that will be psi 1 s. And what will be the corresponding energy? All that you need to do is you have to put… If you are thinking of this particular state, you have to put n equal 1, because you are thinking of the lowest possible state. Again strictly speaking, I should say that, there is going to be an n 1. This is the quantum number associated with electron 1; it is not just n. n would be the case if you had only one electron. But, now, here I have two electrons. Therefore, I have to distinguish between them. And therefore, it is better that, I put a subscript there and write it as n 1.

Now, you will definitely agree with me that, this is all very messy, because there are so many constants. You have m; you have e; you have h cross. What else do you have? You have epsilon 0 and so on. And usually in quantum chemistry, one therefore, changes to another system of units. This is written in SI units so to say. I mean you will have to put in the SI values for m, e and so on. So, what we will do is, we will think of changing over to another system of units, which are referred to as atomic units. See in SI, for example, you know that, meter is the unit of length; kilogram is the unit of mass. Now, these things are not very good for describing things happening at the atomic level, because atom is so small. So, it is better that we do not use this SI units, but we use something else.

And, what would that something be? The answer is that, you see in the Bohr theory, you know that, there is this first Bohr orbit; it has a radius a 0. It has a radius a 0. And that is an appropriate unit for length, because the size of the atom is roughly a 0. Therefore, I will take a 0 as the unit of length; I will take electronic mass as the unit of mass. Correct? And if you do similar things; I mean similarly, you can define a unit of time. The nice thing is that, if you did that, in this system of units, what happens is that, a 0 is 1; interestingly, h cross will have a value unity; everything actually simplifies; 4 pi epsilon 0 will have a value unity. And as I told you, mass of the electron again has a value unity. So, very very nice system of units, because if you look at this expression, you have h cross here; h cross is 1; m is the mass of the electron, that is, 1; e – e again has the value unity. So, e becomes unity. So, e has the value of unity; 4pi epsilon 0, which is occurring there – that also has the value unity. Therefore, this equation actually becomes minus half del 1 square minus Z divided by r 1.

But, now, you should remember that, r 1 is measured in atomic units. If you say r 1 has a value equal to 1; that actually means that, the electron is at a distance a 0 from the nucleus. That is the meaning. And this operating upon psi r 1 will be equal to E 1. What will be the expression for E 1? That also we can simplify; because m is 1, e is 1; in here 4 pi epsilon 0 is 1; h cross is 1. So, if you did all that, what will happen is that, this E 1 will get transformed. We can easily verify this; it will become simply minus 1 by 2 n 1 square.

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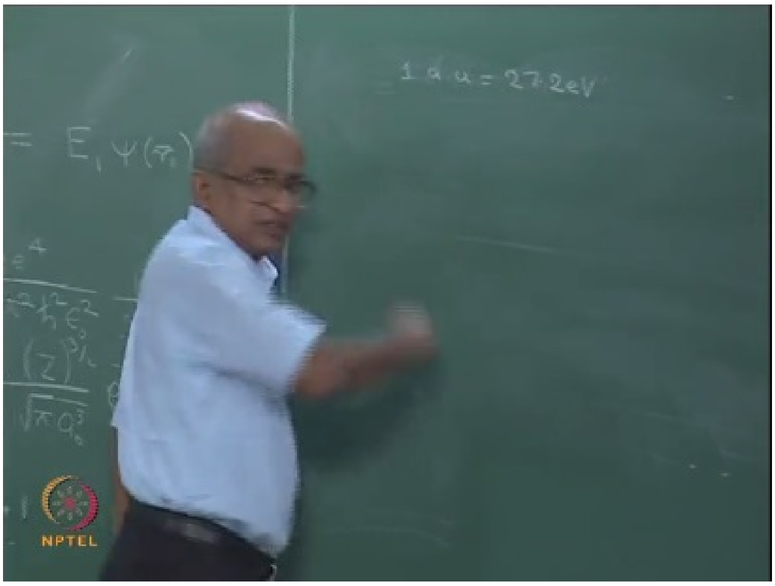

So, again, in this system of units, you see energy has a very simple appearance. All these constants we can get rid off; and you will say it is actually minus 1 by 2 n 1 square, is the expression for the allowed energy levels of the system. And this is in atomic units. Now, you would already know that, the unessential potential of… I should not forget this Z, because I mean Z is – you are not saying it is 1, because it is not the hydrogen atom; it is general. So, then this is energy. Remember this is energy. And this is energy expressed in atomic units of energy.

And, what is the atomic unit of energy? I can… I mean you can find that by using calculations. But, we will not do that; we will say that, 1 atomic unit of energy is equal to 27.2 electron volts. This is all that we need. Now, if you want to just check this, what we can do is you think of the ground state of hydrogen atom; for hydrogen atom, Z is 1. Ground state means the quantum number n is 1. Therefore, what will happen; you will get a simple answer – minus half. So, this is in atomic units, but you know that, the energy of an electron in the hydrogen atom expressed in terms of electron volts is minus 13.6. So, this is in atomic units.

In our other calculations, you would know that, this is actually minus 13.6, which immediately tells you that, 1 atomic unit of energy is nothing but 27.2 electron volts. So, that is convenient. I mean this is very nice, because you see if you look at this Hamiltonian, what is going to happen? You will see that, it simplifies enormously. Even the Hamiltonian for the helium atom – this will just half; this will be just half; this will be Z by r 1; that will be Z by r 1.

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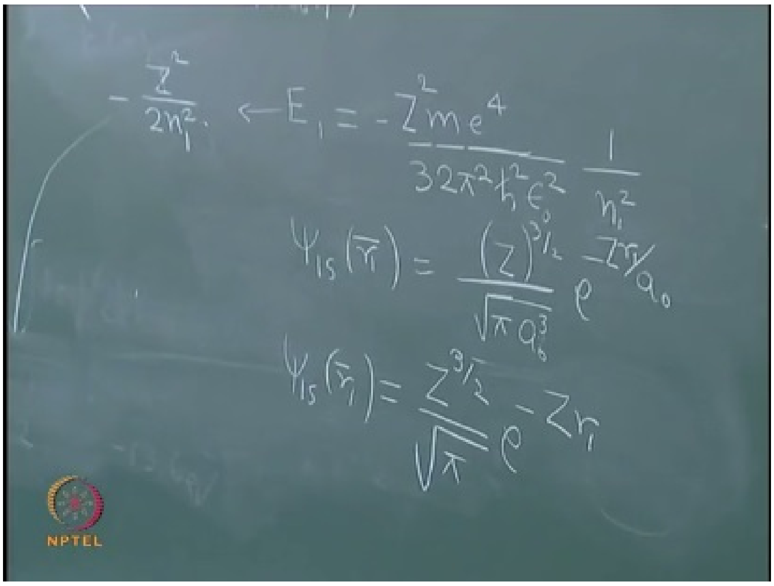

And what will happen to this? This will be just 1 by r 1 2. Therefore, the Hamiltonians appearance is very nice and simplified. And therefore, atomic units are very convenient; you do not have… Even writing is very easy. And, what will happen to the wave function? Wave function also gets very simplified, because this a 0 is now 1. In atomic units, a 0 is 1. So, you can remove that; you can remove this a 0. And therefore, the wave function will become… That is all. So, from this point onwards, we decided we do not want to use the usual system of units, but we will stick to atomic units and because it is extremely convenient.

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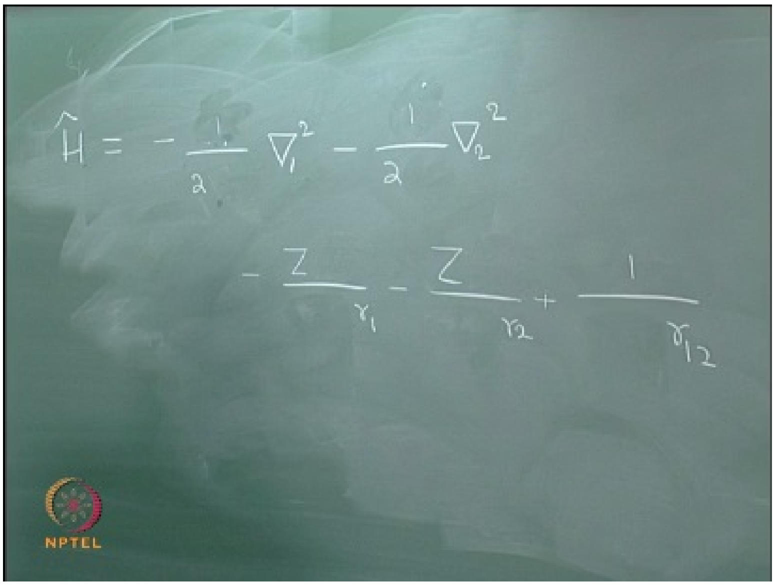

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

And so let us do that here with this Hamiltonian. So, here is the Hamiltonian for the helium like atom. And let us see what happens to this atom when we write it in atomic units. Remember in atomic units, h cross will be equal to 1; mass of the electron will be 1. So, h cross by… This h cross will become unity; that will become unity; 4 pi epsilon 0 is unity. So, e is unity. So, let me just modify the Hamiltonian on the board itself. m is 1. So, that goes. h cross square is 1. So, you will get that. Here again the same thing happens. You get 1 here; m is 1. Z e square – the electronic charge is taken to be unity. So, this is 1. 4 pi epsilon 0 is unity; 4 pi epsilon 0 here; 4 pi epsilon 0 there. They are all unity. e square here is unity; e square there will become unity. And you can see that, now, the Hamiltonian actually looks very nice.

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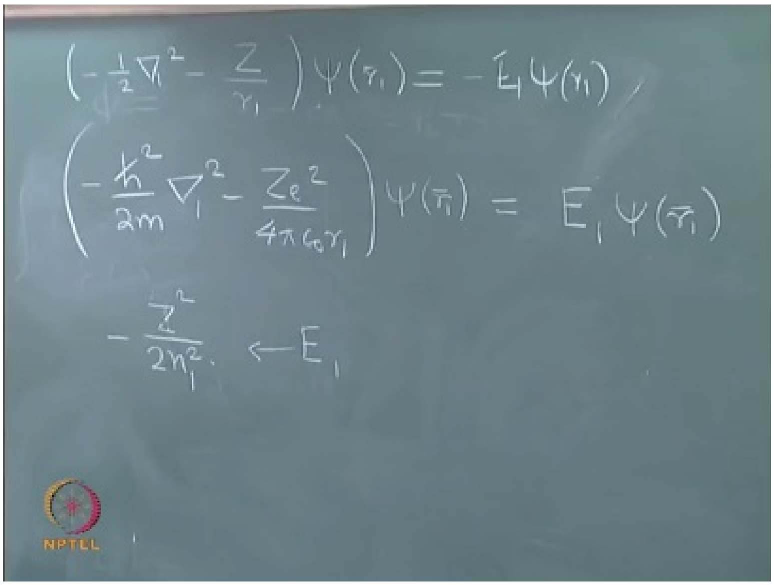

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right)\psi(r_1) = -E_1\psi(r_1)$$

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}\right)\psi(\bar{r}_1) = E_1\psi(\bar{r}_1)$$

$$-\frac{Z^2}{2n_1^2} \leftarrow E_1$$

And, even here it gets modified. In fact, you are going to get minus E 1 psi of r 1. And E 1 has a simple expression; E 1 is actually given by this. So, this is for the first electron. What will happen to the second electron? It is way exactly the same kind of equation. And if I am interested in the ground state of the hydrogen – not hydrogen, but helium atom, what will happen?

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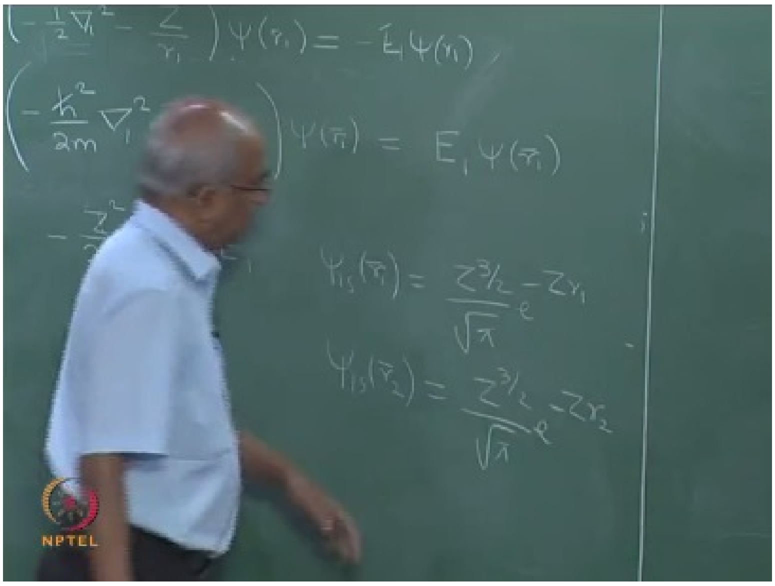

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right)\psi(r_1) = -E_1\psi(r_1)$$

$$\psi(\bar{r}_1) = E_1\psi(\bar{r}_1)$$

$$\psi_{1s}(\bar{r}_1) = \frac{Z^{3/2}}{\sqrt{\pi}}e^{-Zr_1}$$

$$\psi_{1s}(\bar{r}_2) = \frac{Z^{3/2}}{\sqrt{\pi}}e^{-Zr_2}$$

If there is no electron-electron repulsion, the wave function for the first electron will be given by this 1 s atomic orbital, which unfortunately I have rubbed off. Therefore, let me write it once more; psi 1 s r 1 is equal to how much? Z to the power of 3 by 2 divided by root pi e to the power of minus Z r 1. This is the wave function. See if we think of the first electron, it will be sitting in the 1 s atomic orbital. This will be the wave function. If you think of the second electron; if there is no electron-electron repulsion, we can say that, it is going to sit in the same orbital and its wave function will be given by precisely the same expression. So, you are going to have psi 1 s r 2, because I am thinking of the second electron; that is going to be Z to the power of 3 by 2 divided by root pi e to the power of minus Z r 2.

So, electron 1 has this wave function; electron 2 has that wave function. And therefore, the entire system, you see the two are moving independently of each other. And so what will happen? The total wave function will turn out to be simply a product. In a sense, you can say the system is separable. Remember we had method of separation of variables. So, if I wanted to be rigorous, what I can do is, I can neglect this electron-electron repulsion; then use the method of separation of variables to get the solution. And in the method of separation of variables, what will you do? You will say that, the total wave function is a product of two parts: one depending only upon electron 1; other depending only upon electron 2. And then you are going to get all these equations, which may be solved. We will continue in the next lecture. Thank you for listening.