Introductory Quantum Chemistry

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Lecture - 40
He Atom Wave Function with Spin Included – Pauli's Principle

So, it is a good thing that I have still those equations on the black board, and as I told you if u like you can say I will forget this time temporarily, then the motions of the two electrons can be separated using the method of separation of variables.

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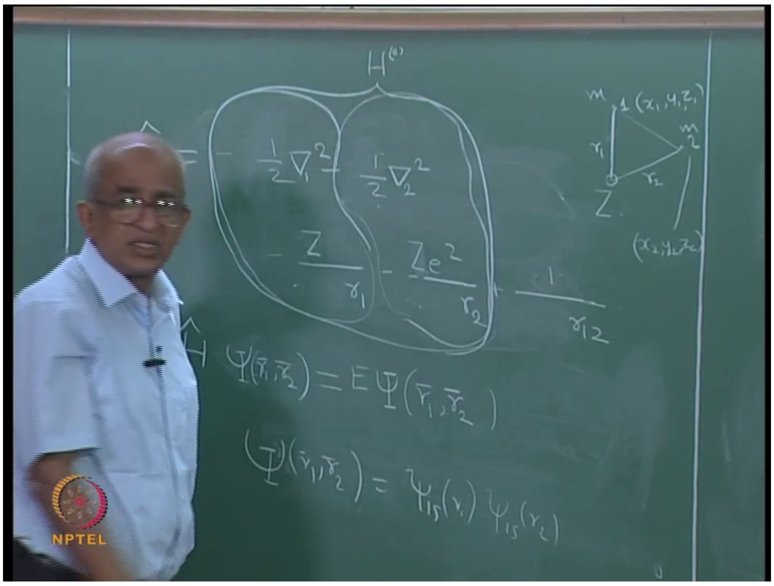

And if u did that what will happen to psi capital psi r 1, r 2 would be actually given by psi 1 s that we are only interested in the ground state; that is why we write it like this, psi 1 s at r 1 multiplied by psi 1 s at r 2. So, they are sitting in identical atomic orbitals having the same shape; this is the ground state of the system. But this is not the exact wave function; why is not exact wave function? The reason is that I have decided to neglect this 1 by r 12. If you did that this is the exact wave function.

So, therefore, I can now say that ok, this is my H 0 unperturbed Hamiltonian, and then I have a perturbation added to the Hamiltonian, what would that be? It will be this 1 by r 1 2 times. So, this is my perturbation, and I can straight away use perturbation theory to calculate the energy correction to the energy of the system. Before I do that let me tell you I mean I did not actually tell you why this term makes it difficult, why is it that this 1 by r 12 makes things or so it makes life so difficult.

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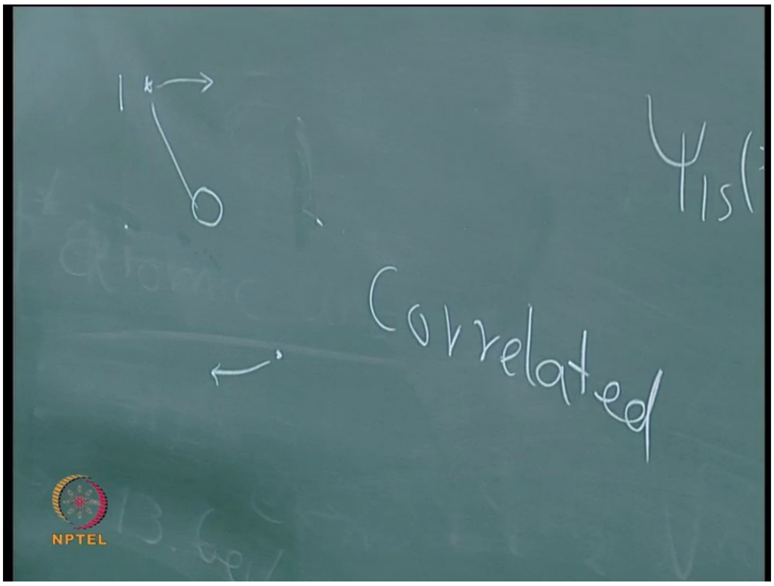

You have the nucleus that is one electron here that is another electron there; both are moving around the nucleus. Both the electrons are attracted towards the nucleus. So, they want to be near the nucleus, correct, but they do not like each other, what to say, because they repel each other; they have the same charge. So, therefore, they do not want to be near one and other, right. Now the analogy that I gave usually is imagine you have a beautiful girl and two boys. The boys both of them are in love with the girl. So, they would hopefully be would like to be near but then of course, they do not like each other. So, therefore, the dynamics of the system is extremely complex.

Now you again if you think of this, this is electron 1, that is electron 2. Suppose the electron 1 is on this side then in all likelihood what will happen is that the most probably the electron will be on the other side. So, as to minimize the repulsion between the two electrons, and further if this electron moves perhaps in this direction ideally what the other electron would do is it would move in that direction. So, that it can avoid this electron. So, that is how describing the motion of two electrons is extremely difficult. One says that the motions of the two electrons are correlated.

The motion of the second electron will depend upon the instantaneous position of the first electron. That is the reason why things are difficult. Now imagine this is the case for helium, and suppose I had uranium you have a nucleus 92 positive charges in the nucleus 92 electrons, right, all trying to avoid each other, but all at the same time trying to be as near to the nucleus as is possible, very difficult thing to treat and that is why quantum chemical calculations are difficult. But in spite of that these days actually we can do calculations using quantum chemistry and get fairly descent agreement with experiments, and as I had been saying again and again variation method is the basis for most of the calculations, ok. So, now let me tell you how to do this calculation. I say I have h 0.

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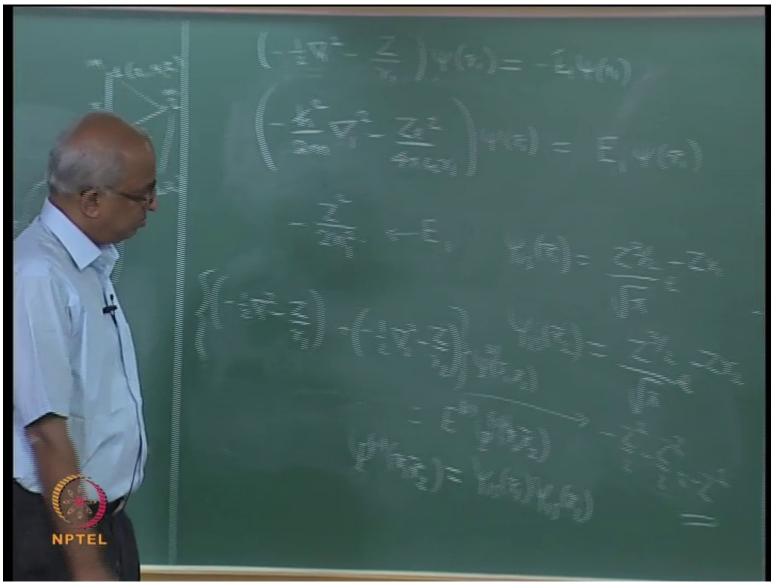

H 0 is actually the sum of these two terms; I mean sum of this set of terms and this set of terms. So, h 0 will be operating upon I mean maybe I should write it in detail minus 1 by 2 del 1 square minus z by r 1; that is electron 1 plus minus 1 by 2 del 2 square minus z by r 2, right. This is my h 0, and this h 0 operating upon the wave function psi maybe I should call it psi 0, because I have not included electron-electron repulsion, and this will be equal to what e 0, right, psi 0 r 1 r 2, and specifically I mean this can be actually separated into two separate problems, electron 1 moving in the field of the nucleus and electron 2 moving in the field of the nucleus which actually means that psi 0 may be written as a product of these two functions, and these two functions are specific.

You are interested in the ground state; if you are interested in a first excited state what will happen is that you would not have both the electrons in 1 s but one of them or may be both of them are in some other atomic orbital. So, because we have always been interested in the ground state, what will happen? We will say that psi 0 r 1 r 2 would be how much? It is equal to psi 1 s r 1 and psi 1 s r 2, fine, and what would be the energy? I mean the two electrons do not interact with each other. So, the energy of the system will be sum of the energies of the two electrons.

Each electron has how much energy? Well, we remember we are working in atomic units. This is the expression for energy in atomic units, but in this particular problem both the electrons have the quantum number n equal to 1, and therefore, energy of first electron will be minus z square by 2, energy of the second electron will also be the same. So, therefore, e 0 will be how much? Minus z square by 2 minus z square by 2 and that would be equal to minus z square. So, if you neglected the electron-electron repulsion the energy of the system is simple; it is minus z square.

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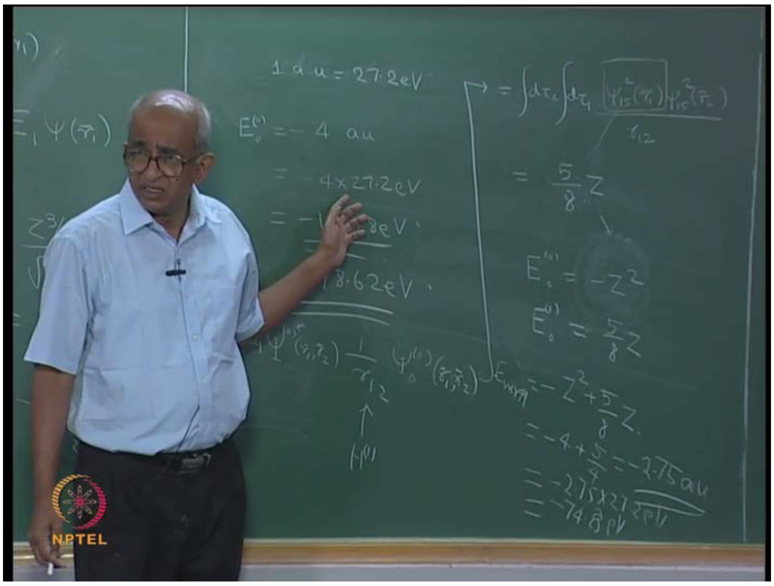

And if you are thinking of helium atom right z is actually equal to 2. So, therefore, the energy that we get e 0 because we are the thinking of the ground state may be I can add another subscript; it is not really necessary, but it is a ground state. So, minus 4 well, if you put z equal to 2 you are going to get minus 4 atomic units, ok, and minus 4 atomic units is how many in electron volts? It is going to be minus 4 into 27.2 electron volts, and this is going to be minus 108.8 electron volts. Now it is possible for you to determine the energy of the ground state of the helium atom experimentally, ok.

How will you do that? You can externally determine the first ionization potential, and then we can determine the second ionization potential. First ionization potential is the energy required to take the first electron out, and second ionization potential is the energy required to take the second electron out. So, by measuring ionization potentials which is quite standard you can get how much the ground state energy is, and actually if you do the experiment the value that I get is minus 78.62 electron volts and you can see that there is a huge error. When I say huge error, how much? I mean 25 or 30 electron volts is the difference; 30 electron volts will work out to be probably 40 percent of the actual value.

So, the error is huge, and therefore, what does it imply? It implies that electron-electron repulsion is very important, ok. So, then how will I do the calculation of electron-electron repulsion? The answer is actually extremely simple. My h 1 is given by this expression; first order correction to energy is nothing but the expectation value of the disturbance, expectation value of that part of the Hamiltonian which causes the problem which causes the disturbance. So, therefore, what you will have is 1 by r 12; that is the disturbance, this is your h 1, and this has to be multiplied by psi; what is my notation? Okay, psi 0 r 1 r 2 and psi 0 r 1 r 2.

You remember this is the ground state of the system. So, again I mean we have too many subscripts; otherwise, maybe I should put a 0 here also just to indicate that this is the ground state, but it is not really necessary, because repeatedly I had been telling you that that we are interested only in the ground stage. So, therefore, what will you do? You will take the ground state wave function for the unperturbed system. This is the disturbance the perturbation multiplied by the complex conjugate of this same function integrate over the entire space. And what do I mean by the integrating over the entire space? This is a problem in which there are two electrons. So, you will have to integrate over the coordinates of the first electron, and you will have to integrate over the coordinates of the second electron.

So, therefore, what I will do is I will say d tau 1 that is electron 1 d tau 2, and you can actually take this expression and put it in there. If you did that you are going to get that integral d tau 2 d tau 1; remember this is integration over six variables in total, because you have d tau 1 and d tau 2, and then what will happen? You put this wave function. So, if you think about this you are actually going to get psi 1 s r 1, where is it? Okay, r 1 square, I am already using the fact that the functions are real. So, therefore, I do not have to put star operation there, and psi 1 s r 2 square, right, both the electrons are sitting in the same orbital, and what will happen is that you will have 1 by r 12. So, this is the integral that you have to perform, correct.

Now think about the physical meaning of this; what is this? This is actually the electron density, psi square is electron density, the electron density of electron 1 sitting in the 1s atomic orbital, correct. So, therefore, let me draw a picture. This is the nucleus; this is psi 1 s r 1 square. It is actually spherically symmetric, because it is a 1 s atomic orbital, and this psi 1 s again but it is now r 2. So, this is the electron density of second electron, and why do you have this r 1? 1 by r 12 symbol because the two electrons repel each other. So, therefore, what actually happens is that you have a spherical electron density due to electron 1; you also have a spherical electron density due to electron 2, and these two spherical electron densities are actually repelling each other because of the columbic interaction; that is the physical meaning of this term.

Now evaluating this integral is actually an interesting exercise in electrostatics, because it is just electrostatic repulsion between two charged densities, and I am not going to do that because it will simply take too much time. I shall simply give you only the answer; this is the answer. I mean the integral is quite complex, but when you do the calculation eventually what happens is that the answer turns out to be such a simple number. I mean physical meaning is obvious; you have two spherically symmetric charged densities electrons are; these at due to the two electrons the two electrons repel each other. That effectively means that the two spherically symmetric charged densities repel each other. So, the energy of the system will increase because of the repulsion, and the amount by which it increases is actually 5 by 8z.

So, therefore, if you added this correction to the energy, what was our original energy? The original energy was minus z square for a general value of z. So, what is going to happen is that I will have e 00 to be equal to minus z square, and I have now calculated the correction e 1 to the lowest possible state. This means this is the correction to the first order correction, and this means that I am interested in the ground stage. What we find is that this 5 by 8 z, and remember we are using perturbation theory, right, and so the total energy of the system, how do you get that? You take e 00 which is the Eigen value of the unperturbed Hamiltonian not to it the correction. So, how much? The energy that you are going to get is minus z square plus 5 by 8z is the answer; this is valid for any z, ok.

Now you can put a value of 2 if you are interested in helium atom, and that will give you minus 4 plus how much? I mean z is 2. So, therefore, 5 by 4 which works out to be minus 2.75 atomic units; that is our better answer after using perturbation theory, ok, and minus 2.75 atomic units you can convert that into electron volts and compare with the experimental value. Well, to get the value in electron volts you will have to take minus 2.75 and multiply it by 27.2. This will be in electron volts. If you did that the answer that you will get is minus 74.8 electron volts, ok, and now you can compare this number with the experimental value. The experimental value is minus 78.62, unperturbed Hamiltonian had this Eigen value which was far away huge amount of error, but the first order correction to the energy calculated using perturbation theory, what is the answer that you get? Minus 74.8 it is not very close, but it is not bad, right.

The difference is about three, four electron volts, ok, which roughly I mean how much would it work out to be? May be about 8 percent, 6 percent of that volt; so earlier it was40 percent, but now it is only less. And now we want to do better, and to do better we can actually make use of the variation method, ok. So, the variation method how will I make use of the variation method is the question? You have to get an approximate wave function an approximate trial function. What is the wave function that we were using here, where is it sitting? I have not actually I mean the wave function that we were using here is this one. So, let me remove most of the other things, and let me now write this in a little bit more explicit fashion.

This is actually I mean if you use that expression for psi 1 s this actually going to be z to the power of 3 divided by pi, because I am multiplying these two e to the power of minus z r 1 minus z r 2; that is what the wave function is actually, because psi 1 s is given by this expression, and you have to multiply psi 1 s with psi 1 s r 2, and you will get the wave function. So, this is the function that we have used, right.

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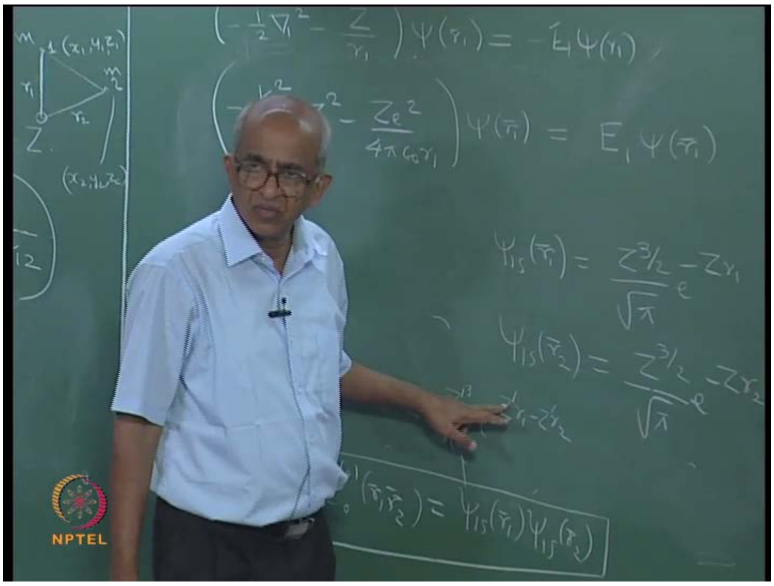

Now why do I write this? The answer is that I want to think of an approximate wave function for the system which hopefully will be better. Now when trying to guess approximate wave functions you always use physical intuition; if you want to get good answers you should always use physical intuition when you guess the wave function. So, let us look at the problem. The nucleus is here; nucleus has a charge of capital z into e that is a nuclear charge, ok.

In the case of helium z is 2 and you have two electrons. Now what this is saying; this function is saying is that the two electrons do not feel each other, right; that is what this function is saying, and each electron feels the full nuclear charge. That is why this capital z is sitting there, correct. Each electron feels the full nuclear charge, but that we do not think is likely, because what will happen is that you see the first electron, suppose it is here, here is the nucleus. It is likely that the second electron will sometimes not always, but sometimes it will come in between. So, we can say that the first electron would be if it is coming in between actually it is screening the nucleus, right. If the second electron is coming between electron 1 and the nucleus then it is screening the electron 1.

So, therefore, what will happen? The effective nuclear charge felt by electron 1 cannot be this z. It has to be less than z, ok, and similarly for the other electron also; for the other electron also it has to be it cannot be z but some number which is different from z. So, how will you account for that? Well, you are saying that effectively the nuclear charge is not z but less than that. So, therefore, I mean if the nuclear charge was less than that what would be this function? Well, the new function that I can think of is z would have an effective nuclear charge which I shall denote as z prime, and what will happen? I would have a z prime here, z prime here.

So, effective nuclear charge is now z prime, but I do not know what the value of z prime is, but it is a parameter that occurs in my wave function. So, what will I do? I will calculate the expectation value of energy, right; I will calculate the value of script e, script e is going to depend upon this parameter z prime, and then having determined the value of script e as a function of z prime, what I will do is I will have to choose the best value for z prime, and how will you do that? You will do that by minimizing the value of script e. So, this is the procedure.

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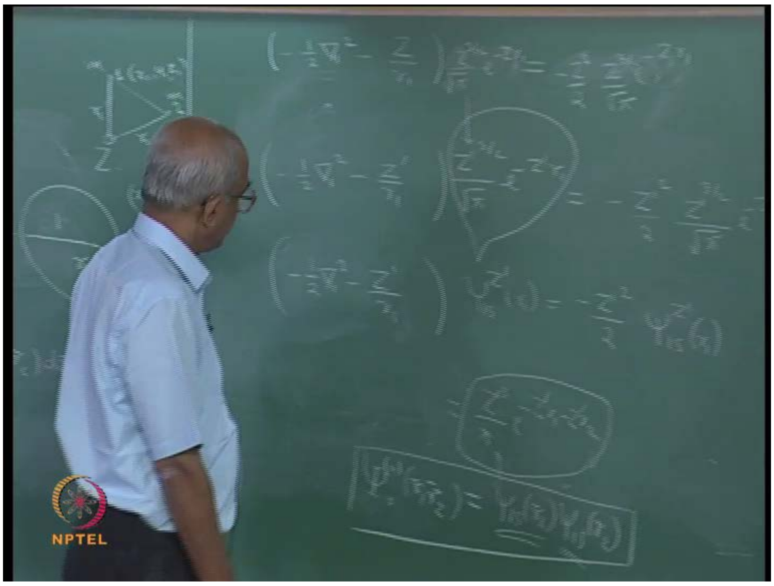

So, as I have told you what will happen is that I would have script e, what will be the definition of it? It is going to be equal to integral phi r 1 r 2 h phi r 1 r 2; I am being explicit, note to that I have used capital phi, because this is a function that depends upon r 1 and r 2. And then you will have to integrate over the entire space d tau 1 and d tau 2, and again strictly speaking what should I have? I should have the same, well; there should be a star here. I should have phi star r 1 r 2 multiplied by phi r 1 r 2 and integrated over d tau 1 d tau 2. But then you see you look at the wave function it is a product of two separate functions, each one of them is normalized.

So, therefore, what will happen to this integral? It is going to be equal to unity, because you see you take two functions which are normalized multiply them, first depends upon r 1, the second depends only upon r 2, and then you integrate. You are going to get the answer unity, because we have chosen this function to be normalized this also turns out to be, I mean this turns out to be normalized. Okay, this is my function. So, because I have chosen I mean these individual functions I have chosen them to be normalized, and therefore, the product is also normalized. And therefore, I need to evaluate only this, correct. Now let me remind you of this; minus half del square minus z, z is the nuclear charge divided r 1 operating upon psi 1 s. This is the unperturbed problem; if you remember this would have I mean if I wrote the wave function explicitly it will be 1 by square root of pi z to the power of 3 by 2 e to the power minus z r 1; that is the ground state wave function.

I am assuming that the electron fills the full nuclear charge, and then what will happen? I am going to get back, this is an Eigen function. So, I am going to get the same object minus z r 1 z to the power of 3 by 2 divided by root pi multiplied by if I get this function back, but it is now multiplied by the corresponding energy. How much is the energy? In this case the energy is actually minus z square by 2, right, ground state; energy is minus z square by 2, we have seen that, agreed. So, this is if the nuclear charge were z and if the electron felt the full nuclear charge then the wave function would be so much and the corresponding energy will be so much. But now suppose I say ok, I have not the full nuclear charge but the nuclear charge which I denote as z prime, ok, and then what will happen; what kind of equation will that function obey is the question that I want to answer.

So, instead of this if you say z prime to the power of 3 by 2 divided by root pi e to the power of minus z prime into r 1. Suppose you were operating upon that minus half del 1 square minus z by r 1; this obviously, you see here the electron is not feeling the nuclear charge z. The wave function is such that it is feeling a nuclear charge of z prime, correct. So, therefore, what will happen? This operator operating upon that is not going to give me an Eigen function. It is definitely is not going to give me an Eigen function. So, if that is the way it is what I can do is I can imagine that if I change this z to z prime suppose, then it is as if the nuclear charge is now z prime and therefore, what will happen

I shall get an answer which is minus z prime square divided by 2 z prime to the power of 3 by 2 divided by root 5 e to the power of minus z prime r 1 actually.

Now the notation is actually cumbersome. So, therefore, what I will do is I will just say that ok, this function I will write it as psi 1 s with an effective nuclear charge which I shall denote as z prime, because then that means I do not have to write this whole thing again and again, and it is a function of r 1. And what happens is that minus half del 1 square minus z prime divided by r 1 operating upon this will actually give me minus z prime square divided by 2 into psi 1 s z prime r 1. Now why do I do this? The answer is that this will make the calculation of script e easy; that is the reason why this is done.

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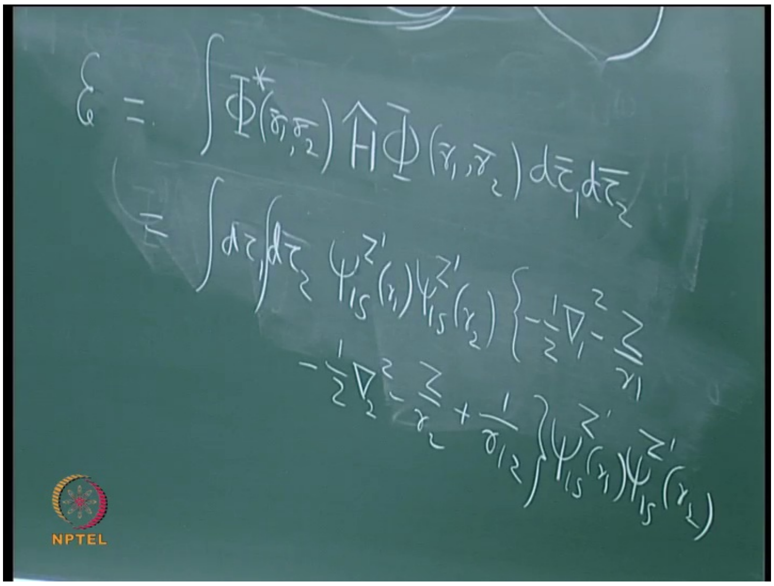

$$\mathcal{E} = \int \Phi^*(r_1, r_2)\,\hat{H}\,\Phi(r_1, r_2)\,d\tau_1\,d\tau_2$$

$$= \int d\tau_1\,d\tau_2\;\psi_{1s}^{z'}(r_1)\,\psi_{1s}^{z'}(r_2)\left\{-\frac{1}{2}\nabla_1^2 - \frac{z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{z}{r_2} + \frac{1}{r_{12}}\right\}\psi_{1s}^{z'}(r_1)\,\psi_{1s}^{z'}(r_2)$$

So, now I want to calculate script e; how will I calculate script e? And the answer is here. You look at this it is going to be integral d tau 1 d tau 2, may be it is not necessary to put that bar d tau 1 d tau 2, then psi 1 s z prime r 1 that is part of my wave function. This is multiplied by psi 1 s z prime r 2, and what do I have here minus the actual Hamiltonian minus half del 1 square minus z by r 1 minus half del 2 square minus z by r 2 plus of course, I have my troublesome term which is 1 by r 12, correct. This is the full Hamiltonian, and what does it do? It acts upon my trail function which is 1 s z prime r 1 1 s z prime r 2; that is all. This is the quantity that I want to evaluate, and you notice that this is actually dependent upon z prime.

So, therefore, script e will be a function of z prime, and what you will do is you will find the value of z prime in such a fashion that the energy is having the least value, ok. So, that is the procedure. Now how will you do the calculation? I can very quickly tell you how to do the calculation, where would I write it? Okay, I will have to remove this. See, this one if you look at this minus of del 1 square minus z by r 1, z is the actual nuclear charge, and this is going to operate upon psi 1 s z prime, correct, and if that operate upon this function you are not going to get back the same function. So, that is a minor problem, but we can solve that problem, how? I will introduce a minus z prime by r 1 right.

So, that this and that together when it operates upon that, what will you get? You will get back the same function, but then I cannot simply introduce that I have to compensate for that. So, what will happen? I will have another plus z prime by r 1, I have to do that. Similarly this del 2 square minus z by r operating upon this is not going to give me back the same function, because it is not an Eigen function, because the nuclear charge is z. So, what I will do is I will introduce another term which is minus z prime by r 2 plus z prime by r 2. So, these are the modifications that I will perform and then let us see.

In fact, it would have been better if I could write here, but that is not possible, but anyway what is going to happen is this. You look at this operator operating this; these two terms together operating upon psi 1 s z prime r 1. This operator is depended only upon r 1. So, therefore, it will not affect that. So, this operator is going to operate only upon that, and if it operate only upon that what is the answer. It is actually nothing but minus z prime square divided by times that function. So, that is where I make the simplification. So, now I hope having told you that I can remove these two equations and start writing here.

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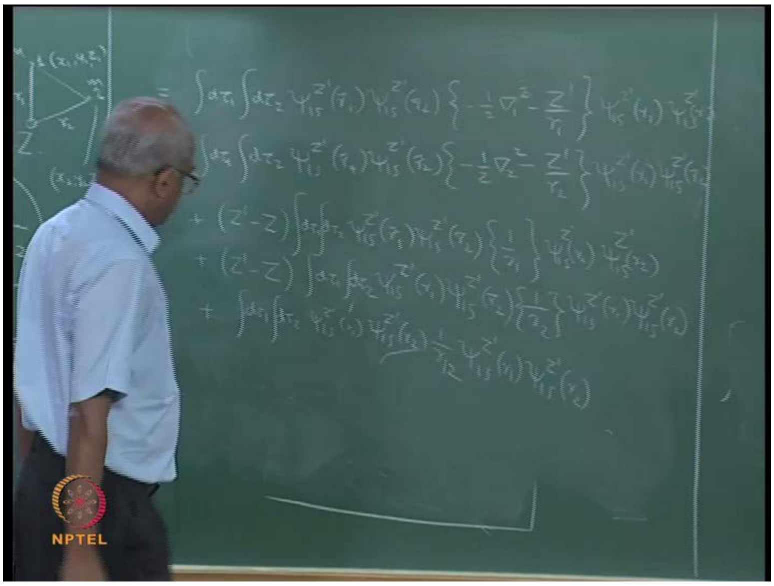

So, this will become integral d tau 1 integral d tau 2 psi 1 s z prime r 1 psi 1 s z prime r 2; we split this. I have minus half del 1 square minus z prime; I put z prime there divided by r 1 operating upon psi 1 s same function psi 1 s z prime r 1 psi 1 s z prime r 2. I have written only part of it. I have another term coming from electron 2; how would it look like? Similar kind of term psi 1 s z prime r 2 r 1 psi 1 s z prime r 2, and I will have kinetic energy of electron 2 interaction of electron 2 with the nuclear charge which I temporarily have manipulated to be equal to z prime and psi 1 s z prime r 1 psi 1 s z prime r 2. This is what happens, but I am not done, because there are other terms which I should be taking care of; which are the other terms? I have accounted for this one; I have accounted for this one.

I have also taken this and that; that is all, but there are other terms left; which are the other terms? This is going to be plus; well, the difference between these two, right, z prime minus z that is a constant then d tau 1 d tau 2 psi 1 s z prime r 1 psi 1 s z prime r 2. What we have here? You look at this expression; you have z prime with a positive sign and z with a negative sign; that is why I had z prime minus z, but both of them have a 1 by r 1. So, therefore, I should put that 1 by r 1 and psi 1 s r 1 z prime psi 1 s r 2 z prime, correct; this is from electron 1, similar term is going to come from electron two. So, what will happen the only difference will be instead of this 1 by r 1 you are going to have 1 by r 2. So, you will get plus z prime minus z integral d tau 1 d tau 2 psi 1 s z prime r 1 psi 1 s z prime r 2.

Notice also that whether I put the vector symbol here or not it does not really matter, because it actually depends only upon the distance; it does not depend upon the vectorial nature of this vector. So, 1 by r 2 psi 1 s z prime r 1 psi 1 s z prime r 2; this is what happens. I am not done yet, because there is the problematic term; what is a problematic term? The electron-electron repulsion; so I have to put that. So, what will happen? I will have plus d tau 1 d tau 2 psi 1 s z prime r 1 psi 1 s z prime r 2. Well we may need this, but I am now going to remove it. 1 by r 1 2 psi 1 s z prime r 1 psi 1 s z prime r 2; that is the way things are, but then if you look at this, ok, this operator depends only upon r 1.

So, it is not going to affect the second function; it is not going to affect the second electron wave function. So, therefore, I can just move it here. What will you get? You will get psi 1 s z prime square r 2 that I can again move here. I can do this integration, the function is normalized. So, you will psi 1 s r 2 square integrated over the entire space for this second electron; answer is 1. So, therefore, immediately I can remove this; I can remove that, and I can remove that. That is a nice simplification, and I am sure you would realize that the same thing can be done with the second term, because the second term only depends upon electron 2. It will not affect this term. So, you can move this outside, this r 1, this term and that term can be combined.

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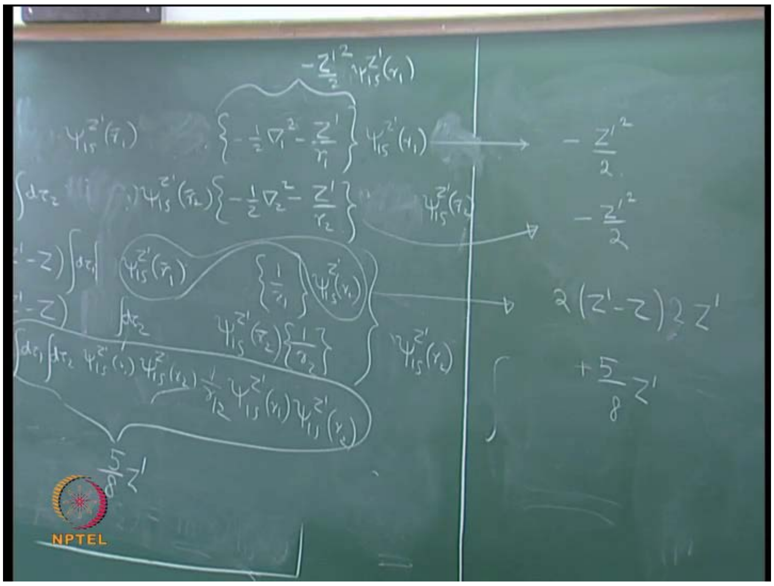

You can take it out do the integration over tau 1; answer will be unity. So, this also goes, correct, and if you look at this term, what will happen? You see there is 1 by r 1 here, right; that is the operator that is occurring. It is not going to affect that term. So, again you can move it out; this term and that term may be combined. You will get the square of the wave function for electron 2, integrate over the entire space again it will give you unity. So, that also I am going to remove. This goes and what about that term? You can do exactly the same thing, right, but this term this is you have 1 by r 2.

So, therefore, you will have to remove this one, right, and unfortunately the last term you cannot remove anything. It remains as it is, but if you look at the last term what will happen is that you have psi 1 s psi 1 s r 1 into psi 1 s r 1. So, it is actually psi square. What is psi square? It is the electron density of electron 1, right. This into that is nothing but the electron density of electron 1. This into that will be the electron density of electron 2, and what is happening? These two electrons are actually interacting with an electrostatic interaction, right, and these orbitals. So, they have effective nuclear charge as z prime. If the charge was z we know how much the value of this integral is the electrostatic repulsion; if the value was z then the answer is 5 by 8z.

So, therefore, I can generalize that and immediately say as far as this is concerned it is nothing but 5 by 8z prime. So, this is actually 5 by 8z prime, and then if you looked at the first term, what is going to happen? You have minus half del 1 square minus z prime by r 1 operating upon psi 1 s which fills the nuclear charge z prime. So, what will happen is that this operator will simply give me minus; this is an Eigen function of that operator. So, therefore, minus z prime square by 2 into psi 1 s r 1 is the result, correct, because this is an Eigen function of that. So, you can put that value here. Then you will realize psi 1 s and psi 1 s can be multiplied, you will get psi 1 s square; this is a constant minus square.

So, you can take it out of the integral sign, and therefore, you can do the integral over d tau because it is just the integral of psi 1 s square, and what is the answer? It is just unity and therefore, this integral you will evaluate to be minus z prime square divided by 2, right, and what about this integral? Same argument because you have this operator operating upon psi 1 s z prime; it is just that it is electron 2, but it does not matter. It is filling the nuclear charge z prime. So, this will again give me the same. If you allowed this operator to operate upon psi 1 s you are going to get minus z prime square by 2, and then you can take that out and so effectively this will give you minus z prime square by 2, another minus z prime by 2, and then these integrals are not very difficult to perform these two together.

Well, if you think about this actually you will realize that they have to be equal; why do I say that? You look at this; you see you have this psi 1 s into that psi 1 s; that means psi 1 s square electron density of electron 1, and you have 1 by r 1; that means that electron is interacting with the nucleus; electron 1 having an electron density which is equal to so much is interacting with the electron with the nucleus if you looked at this 1, right. Electron 2 has the electron density which is the product of these two, and that is interacting with the nucleus, but both the electrons are sitting in the same orbital. So, therefore, their interaction with the nucleus has to be the same, and therefore, these two integrals must be the same. So, therefore, I am going to get 2 times z prime minus z and the integral that is left.

Well, this d tau 2 actually goes because we have used normalization; this d tau 1 also goes because we have used normalization. So, that is the way the integrals are, and if you actually perform this what happens is I am not going to do it out to be 2 z prime both of them together these two together. Their values are same; I have told you are the same. So, if you evaluated them and added up; you will have this z prime minus z sitting outside, and then each one of them is actually equal to 2z prime. So, therefore, you have a two there, and the last term is how much? It is actually 5 by 8z prime; ok, that is a lot of work. Now why did we do all this work? We wanted to get script e, and we now have script e as a function of z prime. So, what is the expression for script e? The answer it is going to be the sum of all those terms.

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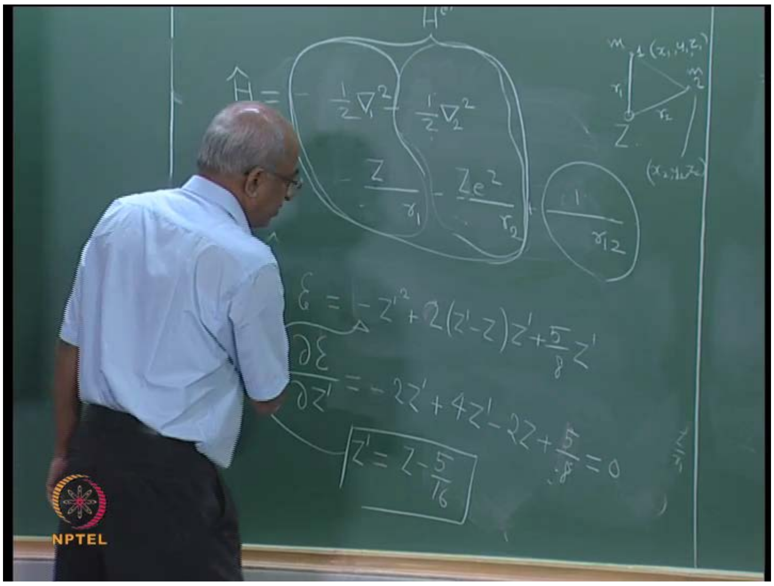

So, it is going to be minus z prime square plus 4 z prime minus z into z prime. I hope I have not made any mistake plus 5 by 8 z prime, because I have not evaluated all the integrals; I have to be careful, ok, relay is that there is a minor mistake. There is an extra 2 that I have put; this is not there if you evaluate, because you see I did not evaluate the integral. So, I had to copy and in copying I have made this minor mistake. So, all that happens is you have a 2 here instead of the 4, and so what will you do now? You will take the derivative of script e with respect to z prime, because that is our variational parameter, and put the derivative equal to 0. What is the answer that I am going to get? Minus 2 z prime; still I am little bit worried about this.

It seems to be ok, dou e by dou e z prime will be minus 2 z prime plus 4 z prime, right; that will come from here, minus 2 z plus 5 by 8 is equal to 0. This is the answer that you will get. So, what happens; what is the value of z prime? This has to be equal to 0. This means that z prime should be; you can rearrange and get this answer z minus 5 by 16, right. You put it equal to 0, solve for z prime. You get the answer z prime is equal to z minus 5 by 16, and what does this mean physically? The effective nuclear charge that the electron fills is actually less than z by how much; it is less by 5 by 16.

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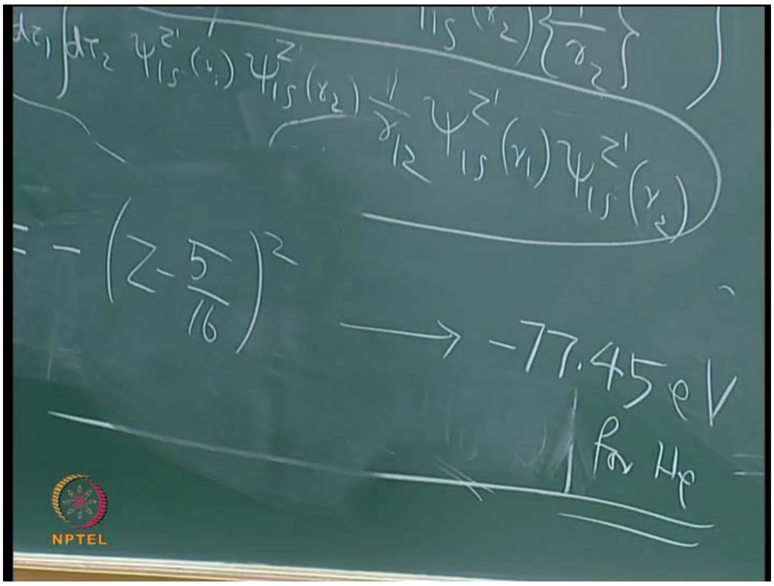

So, therefore, you can refer to this as a screening factor. The electron 1 is screened by electron 2 to the extent of 5 by 16, right. This may be referred to as a screening factor, and then you can take this expression. This is our z prime. You can take that and put it in here, and evaluate the value of script e, the best possible value for script e. If you did that you will find that script e is given by this expression; they are fairly simple exercise.

So, let me just quickly finish this. The best possible value of script e you can calculate, and you will find that it is nothing but minus z minus 5 by 16 the whole square. This is the answer that you will get provided you took this value of z prime and put it in here. That is the answer that you will get, and specifically in the case of helium you can put z is equal to 2, and get the best value for script e, correct, and that turns out to be minus 77.45. This stands out to be minus 77.45 electron volts for helium whereas the actual energy I have told you it is about minus 78.62. So, you can see that you are getting close. Okay, I think I will continue in the afternoon.

Thank you for listening.