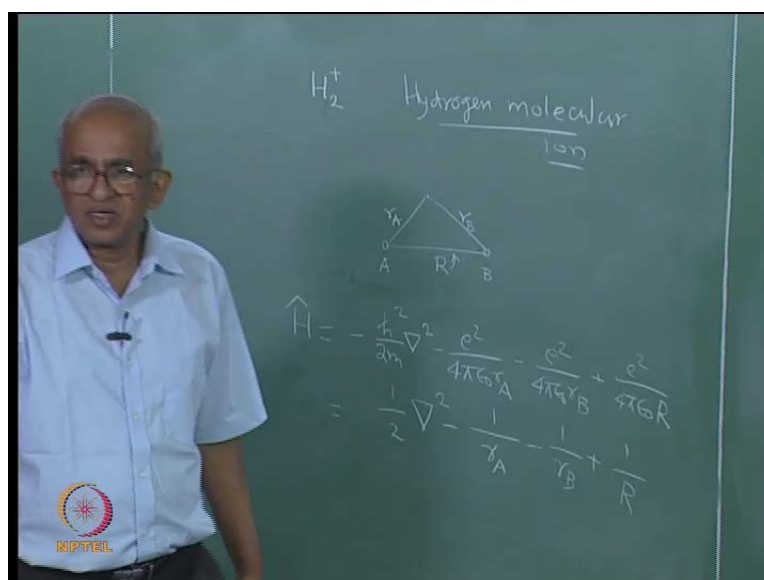


Introductory Quantum Chemistry
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Lecture - 41
Hydrogen Molecular Ion-linear Variation Method

I am going to talk about another application of the variation method. And this time, it is to a system, which has a chemical bond. As you know, chemists are most interested in chemical bond. So, we want to understand chemical bonds.

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So, the system that I am going to consider is the simplest possible system, where there is a chemical bond. And that is actually the system, which is referred to as H₂⁺ – hydrogen molecular ion. One can do experiments on this species and you can actually determine the equilibrium bond length; you can also determine the dissociation energy of molecule – the energy that is required to dissociate the molecule; which means that, you will take the two nuclei to infinity; from the equilibrium into nuclear distance. So, if I am very strict about this, what will I do; I will say that, I have two nuclei, which I will denote as A and B. These are the two nuclei. And there is one electron, which is going around it. And surprisingly, this one electron is actually able to hold together the nuclei in spite of the fact that, the two nuclei repel each other. At least in the ground state of this ion, one single electron is enough to hold the system together.

So, if I wrote the full Hamiltonian in all its glory, what is going to happen is that, you will have the kinetic energy of this nucleus, kinetic energy of that nucleus, and the kinetic energy of the electron. You will also have interactions between the charges; the two nuclei will interact; and the electron will interact with both the nuclei. So, let me denote this by r_A – this distance, because it is the distance of the electron from the nucleus a. And this one I will denote by r_B . And the distance between the two nuclei I will denote as capital R. In the actual molecule, what will happen is that, the R is changing. So, the molecule will be vibrating, and not only that; the system will execute translational motion as a whole; which is always there; I do not have to even say it.

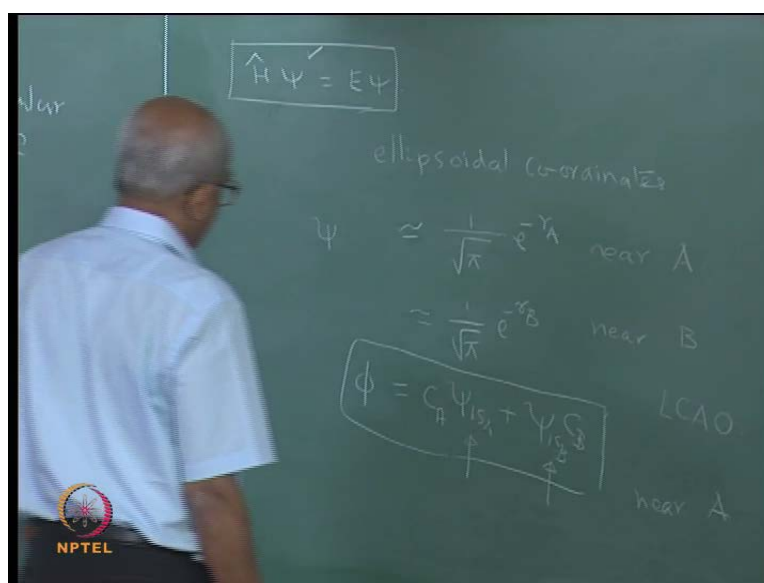
Now, what we are going to say is we are going to consider simple system; simple system in the sense that, I am going to assume that, the two nuclei are kept fixed at a particular distance. You may ask – what is the use of that? What I am going to do is I will imagine that, the two nuclei are kept fixed at a particular distance R; I will calculate the energy of system. And then I will vary the value of R and ask – is the energy decreasing when I change into the nuclear distance? If the energy is decreasing, what is going to happen is that, there will be a bond formed; correct? And if the energy is increasing no bond is going to be formed; correct?

And, not only that; I expect that, the energy will decrease; perhaps reach a minimum that value of R at which energy is a minimum; must be the equilibrium bond length of the molecule. And then as you push it further, the energy I would expect will increase. Therefore, the calculation should give me the equilibrium into nuclear distance; it should also... As we will see, it should also give me the dissociation energy of the molecule. And these are things that we can determine experimentally. And therefore, if I have a procedure for calculating these things; that should be nice, because that is, I can say almost the check of quantum mechanics as applied to molecules.

Now... Then you will ask – what about nuclear kinetic energy because they are also moving well. We will come to that later. At the moment, let us think of a simple system. And this is what always our policy; whenever we have a tough problem, we will divide it into smaller problems and try to understand the smaller problems and then understand the bigger problem. So, at the moment, I will say that, the two nuclei are kept fixed; the distance between them is equal to capital R. Therefore, if I was going to write the Hamiltonian, how would it look like? See I am not thinking of nuclear motion. So, I

would have only minus \hbar^2 divided by $2m$ times the Laplacian. This is the kinetic energy of electron – minus e^2 divided by $4\pi\epsilon_0 r_A$ – interaction of the electron with nucleus A minus e^2 divided by $4\pi\epsilon_0 r_B$ plus e^2 divided by $4\pi\epsilon_0 R$; where, R is the distance between the two nuclei. This leads to the repulsion. When you push the two nuclei together, they repel each other. And that is what is accounted for in this time. But, of course, you see here I have the constant – e , ϵ_0 and so on; but we decided that, we do not want them. So, what do we do? We change to atomic units. And in atomic units, what will happen? This actually becomes a very nice looking Hamiltonian; very nice looking, but difficult to solve. Now, let me repeat. This does not have the kinetic energy of the nuclei in it. We will have to worry about that and we will do that later. So, this is the Hamiltonian.

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And, what is the equation that I should solve? I should solve the equation $\hat{H}\psi = E\psi$. And the way I have been approaching this problem, ψ will be a function of just this one electron; only one electron is moving. Therefore, ψ has to be a function of just the coordinates of that one electron. So, it is a function of three coordinates. Any particle will need three coordinates to specify it. Now, incidentally, I should also tell you for your knowledge that, this equation can be solved exactly... This is possible to solve it exactly by changing over to what are known as ellipsoidal coordinates. It is just like parabolic coordinates. There is another coordinate system, which is referred to as ellipsoidal.

Now, that solution is nice and in fact, it agrees with the experiment – experimental values if we actually solved it. But, then the problem is that, this change to ellipsoidal coordinates cannot be done for any other molecule; it can be done only for H₂ plus. For any other system, it is very very difficult. And therefore, we are not going to study this method; but we will study a method, which is of general applicable, so that even if I had a more complicated molecule, I would be able to solve that also. But, if you would like to have a look at it, you can look into any one of the standard quantum chemistry books. One of the books that I like the most is the book by Pauling and Wilson. I think I mentioned this. This is an old book, but still it has one of the best treatments of quantum chemistry.

So, now, you see what I am going to do is I am going to try to solve this equation. And what I am going to do? I am going to try to use the variation methods. So, how will I use the variation method? I need an approximate wave function; then only I can use the variation method. So, what would be a suitable approximation for the wave function? This is the question that I would like to answer. Now, this is the system. Imagine that, this electron is in the vicinity of this nucleus suppose. Then what will happen is that, the distance of the electron from this nucleus is much smaller than the distance of the electron from the other nucleus.

And therefore, what will happen is that, at least close to this nucleus, only the term r_A is important. This other term is of less important; r_B is of less importance because r_B is much larger than r_A . The influence in the vicinity of the nucleus – influence of A is largest; and the influence of B – I do not expect it to be much. Therefore, as an approximation, suppose I say I am interested in the wave function in this region; then I do not really have to worry about this r_B ; only if you are interested in this region near the nucleus. So, if you do not worry about r_B , what will happen? The Hamiltonian is... I forgot about this negative sign, but it is there; you should know that. Then what will happen is that, the Hamiltonian will be kinetic energy minus electron interacting with nucleus A.

And, if you have a single electron interacting with the single nucleus; we are neglecting the influence of the other nucleus; then what is the ground state of the system? I know ground state is; it is nothing but the 1S orbital. It is like a hydrogen atom problem because I am forgetting this r_B ; I am omitting rather – this r_B ; correct? If I omit this r

B, then what will happen? Only $1/r_A$ is important. And all that it is saying is that, the electron is moving with the kinetic energy; but at the same time, it is also interacting with the nucleus A. And therefore, if I solve the Schrodinger equation with that simplified Hamiltonian, what is the answer that I am going to get? The answer is that I am going to get is actually 1S atomic orbital. I will denote it as ψ_{1S} . What will be the coordinate that is going to occur there? It is interacting with the nucleus A. So, naturally, the coordinate that is going to occur is nothing but the distance of the electron from nucleus A.

Therefore, it is going to be this one. If you want to write it in a little bit more detail, what will happen is that, it is actually $1/\sqrt{\pi} e^{-r_A}$. This is the 1S wave function for the hydrogen atom written in polar coordinates of course; and also putting the nuclear charge z equal to 1. This is of course in atomic units; correct? Earlier if we look into the mornings notes, then you will find that, there was a nuclear charge, because you had helium atom. But, we are not thinking of helium atom; we are thinking of the hydrogen molecular ion; and this is the wave function.

So, I know that, if the electron is in the vicinity of this, the wave function should resemble this function. And I can revise the argument; suppose the electron is near this nucleus, what should happen? It should resemble an atomic orbital; 1S atomic orbital, which is centered on that nucleus. And therefore, this is actually near the nucleus A – this one. While near nucleus B, what will happen? I would have the wave function approximately equal to $1/\sqrt{\pi} e^{-r_B}$.

So, what should I say is I want the wave function – actual wave function, which I will denote as ψ to behave like this; it has to be approximately this near the nucleus A; and it has to be approximately equal to that near the nucleus B; correct? Therefore, this gives me an idea how to choose the trial function. So, what I will do is I will say I will have a trial function, which I am going to call ϕ ; and that is going to be written as $\psi_{1S A}$. Some constant is C_1 into $\psi_{1S A}$; maybe I should call it C_A plus $\psi_{1S B}$ into C_B . This is the trial wave function.

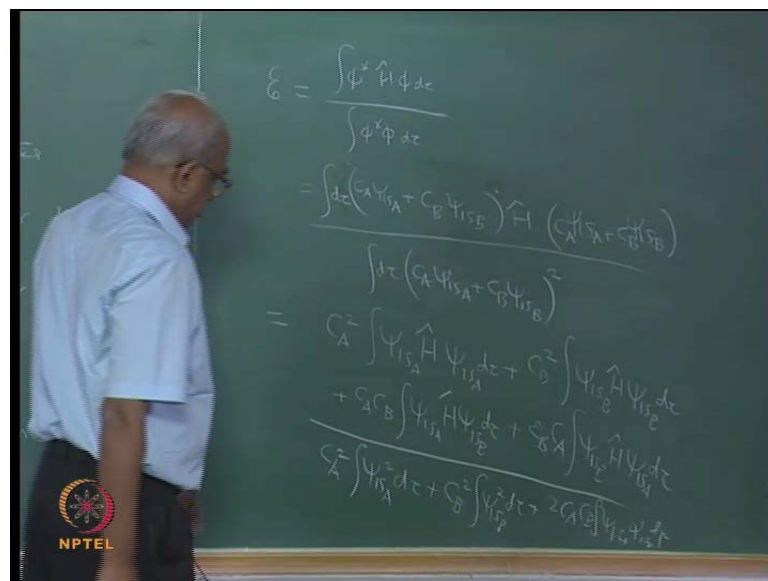
Why do I have the trial wave function? If you are near the nucleus A; where is the nucleus? Here is the nucleus. If you are near that nucleus, then distance of the electron from the other nucleus is large, and if that is large, what about 1S B? 1S B – remember it

is an atomic orbital having its center on that nucleus. So, its value near the nucleus A is going to be rather small, because the distance of the electron from this nucleus is large. Therefore, if I used such an approximation, what will happen is that, near A, what will happen? This term will not be important; and you will have only that term. And on the other hand, if you are near nucleus; if you are near the other nucleus, what will happen? The reverse thing will happen.

Therefore, you have very recently believed that, this is a fairly decent approximation for the wave function. And if you say that, then the natural question is how will you determine the values of C_A and C_B ? So, the procedure is extremely simple. We will calculate this object, which we have been referring to as ϵ ; correct? And if you look at this function, there are two parameters: C_A and C_B . And what should I do? I have to adjust the values of these two parameters in such a fashion that, the ϵ has the least value. So, that is the procedure. So, let us try to do this.

Now, before I forget, you see this is an atomic orbital having its center on nucleus A. This is an atomic orbital having its center on nucleus B. And so, you are actually combining two atomic orbitals. You are adding one atomic orbital with another. You are taking the linear combinations of two atomic orbitals. And therefore, this is known as... This approximation is known as linear combination of atomic orbitals – LCAO. So, now, I will evaluate the ϵ .

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What is the script E? It is going to be equal to integral. This is phi. So, I am going to have $\psi^* H \psi$ divided by $\int \psi^* \psi$; that is all. So, if you worry about that, this is going to be $\int C_A \psi_{1S_A} + C_B \psi_{1S_B}$ with a star. But, actually the star will not have any effect, because the 1S atomic orbital is actually a real. So, what I am going to do is I am going to forget this star; and then I will have H . And then what is it that it is going to do? It is going to operate upon $C_A \psi_{1S_A} + C_B \psi_{1S_B}$. And there is an integral over the entire volume.

So, you have to multiply this by $d\tau$ and integrate over the entire space. And in the denominator, you have exactly the same kind of expression, but for the fact that, this H is missing. So, what will happen is that, you will $C_A \psi_{1S_A} + C_B \psi_{1S_B}$ the whole square. That is what you are going to have, because H is not there. Therefore, this is... I have made a mistake? No. This is ok. Is there any problem? I do not think so. So, the star has been removed. And now what will happen; I can actually expand this. When you expand this, you will see that, there are four terms in the numerator and the three terms...

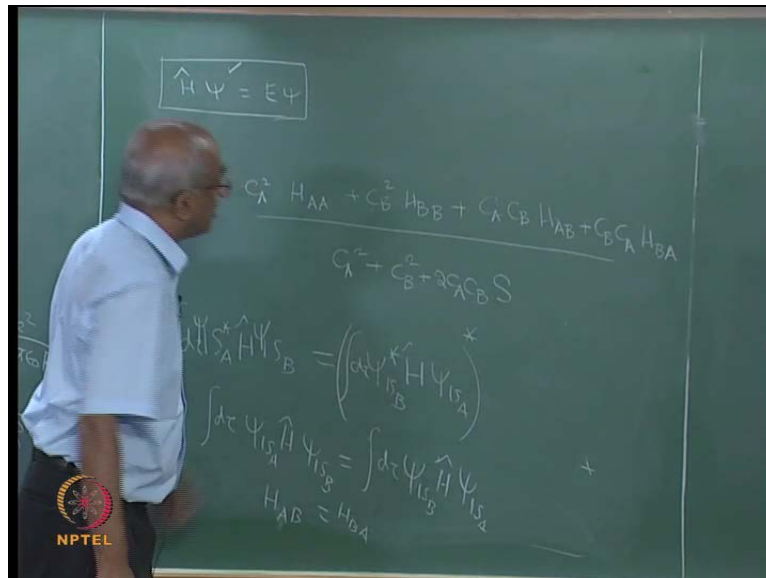
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Thank you. So, if you multiply this, what is going to happen? You will have this into that. So, you will actually get C_A^2 . That will be the first term $\int \psi_{1S_A}^* H \psi_{1S_A} d\tau$ – first term. You will get a similar term from ψ_{1S_B} . So, you will get $C_B^2 \int \psi_{1S_B}^* H \psi_{1S_B} d\tau$. So, that is pretty straightforward; plus you are going to get two cross terms; let me just write them – plus $C_A C_B \int \psi_{1S_A}^* H \psi_{1S_B} d\tau$ plus $C_B C_A \int \psi_{1S_B}^* H \psi_{1S_A} d\tau$ with an $d\tau$ element. So, that is the numerator. And the denominator – it is very simple – $C_A^2 \int \psi_{1S_A}^2 d\tau$ plus $C_B^2 \int \psi_{1S_B}^2 d\tau$ plus – if you just square this, you are going to get two times $C_A C_B \int \psi_{1S_A} \psi_{1S_B} d\tau$. Difficult to write it here; I will write it better later.

Now, if you look at the ψ_{1S_A} ; ψ_{1S_A} is a function that is normalized. So, immediately, I can say that, this integral must be equal to 1. And similarly, this integral must also be equal to 1 because ψ_{1S_B} is normalized. But, if you think of ψ_{1S_A} into ψ_{1S_B} , you might be tempted to say that, that is actually equal to 0; but it is not. The reason is very simple. If they were eigenfunction of the same Hamiltonian, then they will be orthogonal. But, if you think of ψ_{1S_A} , it is the eigenfunction of Hamiltonian in which

there is only interaction with nucleus A; while $1S_B$ is the eigenfunction of Hamiltonian, where there is only interaction with nucleus B. So, the Hamiltonians are different. And therefore, this integral is not 0; it is nonzero. And therefore, what is going to happen is that, I will... Say this is equal to 1; this is also equal to 1; and, this object I do not want to be writing it again and again and again. So, I will use the symbol capital S to denote this; simply because I do not want to be writing those integrals. And I am going to do the same kind of thing with the numerator.

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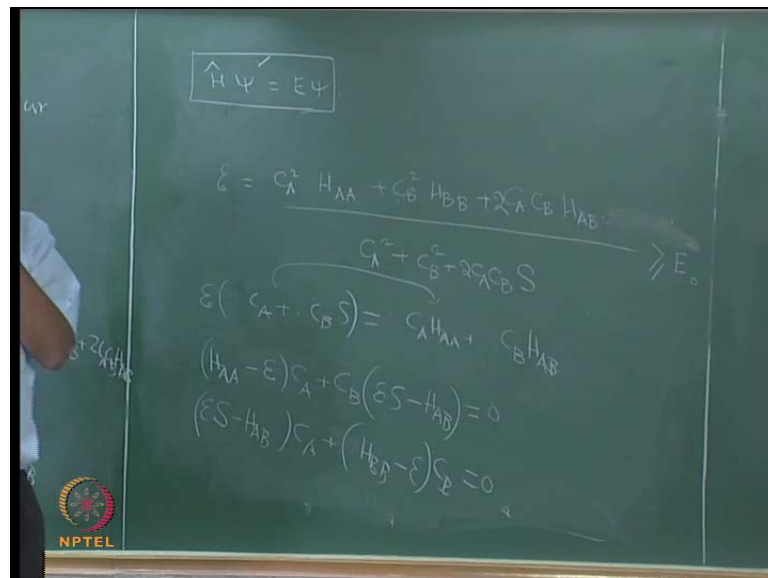
So, what will happen; I will have script E equal to $C_A^2 H_{AA} + C_B^2 H_{BB} + C_A C_B H_{AB} + C_B C_A H_{BA}$. So, what is the notation that I can adopt? I can say it is something that I will denote as H_{AA} , because what happens is that, H is in the middle. So, operating upon $1S_A$; and then you multiply it by $1S_A$; integrate over the entire space. So, if you look at this; it is obvious that, it should be written as H_{AA} . And if that is the way it is, this is going to be H_{BB} . And what about the other two terms? You have $C_A C_B H_{AB}$ plus $C_B C_A H_{BA}$. That is the numerator. And you have to divide this by $C_A^2 + C_B^2 + 2C_A C_B$ into S. Now, I know that, H – the Hamiltonian for the system is a Hermitian operator.

So, what will happen if I had a Hermitian operator? I can do the following. I take the Hermitian operator; allow it to operate upon $1S_B$ multiplied by the complex conjugate of $1S_A$ and integrate over the entire space. A property of a Hermitian operator implies

that, this must be equal to... I keep on forgetting to write the psi; but psi's has to be there – psi 1S B, psi 1S A. So, what will happen is that, I can say this is equal to H; instead of H operating upon 1S B, it can operate upon 1S A – psi 1S A. And I will multiply it by psi 1S B star; and the volume element d tau – integrate over the entire space and take its complex conjugate. This is what follows from the fact that, H is a Hermitian operator; something that we have been using. But, then we know that, everything in here; they are all real; 1S A is real; 1S B is real; H is real; you can look at the Hamiltonian; there is no square root of minus 1 anywhere.

Therefore, you see these star operations have no effect. So, what is it that I will get? I will get integral d tau psi 1S A H psi 1S B is equal to integral d tau h – not h – psi 1S B H psi 1S A. This is the answer that I will get. And if that is the answer, immediately, you can say that, in our notation, this actually means that H AB; left-hand side is H AB. What about the right-hand side? H BA. Therefore, interestingly, what happens is that, these two terms are the same, because H AB and H BA is equal to one another. And therefore, what I can do is I can remove one of them and put it a 2 here.

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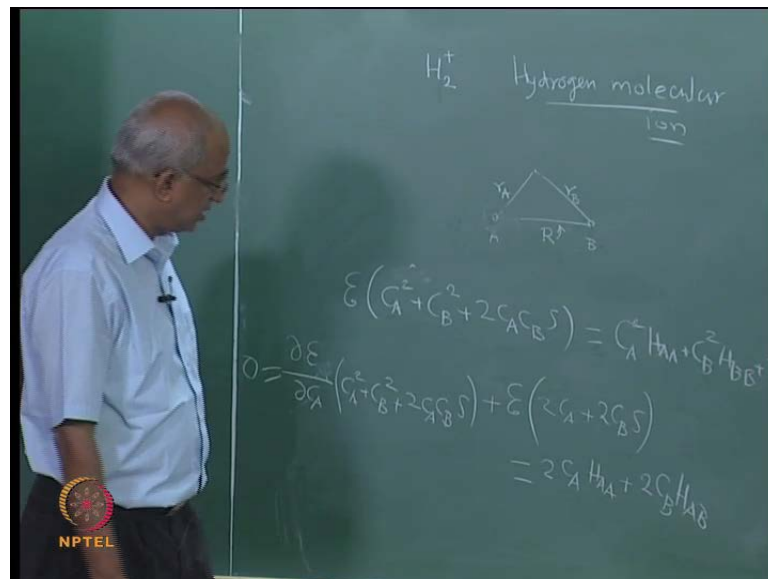


So, if you look at the expression for the script E, what is that you find? We now have an explicit expression for script E in terms of the parameters C A and C B; we have an explicit expression; H AA and H BB, H AB and S – these are integrals, which we can evaluate; it is not a difficult thing. The only thing is that, you have to be clever enough to

evaluate the integral. And you will find that, these are some numbers. Therefore, let us say you have evaluated these numbers and then you have put it in here; and then you will get the value of script E. But, I know that, this has to be greater than or equal to the actual ground state energy. It does not matter what the values of C A and C B are. For all values of C A and C B, this must be true; that is what the variation theorem says; correct? So, what is the procedure now?

The procedure is actually find those values of C A and C B such that script E has the least value. And how will you do that? You will differentiate script E with respect to C A; you will also differentiate with respect to C B; put the derivatives equal to 0 and solve for C A and C B. This will be the procedure. So, that means I have to evaluate the derivative of script E with respect to C A and C B. Now, the way it is written, it is tedious. And therefore, what I am going to do is this – I am going to write that equation as script E into C A square plus C B square plus 2 C A C B S.

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I am just multiplying throughout by this factor, it is equal to C A square H AA plus C B square H BB plus 2 C A C B H AB. That is what the right-hand side is. And what I will do is I will differentiate this equation partially with respect to C A and then I will also differentiate it partially with respect to C B. And when I do that, what will happen? I will do E by dou C A; I will also have dou E by dou C B. And what should I do? I will have to put those derivatives equal to 0. So, let us carry out this differentiation. First, I

differentiate with respect to C_A throughout. So, you will have a term, which will be of this form. That will be the first term. And you will have one more term, which actually is the script E into derivative of this expression with respect to C_A – partial derivative of this expression with respect to C_A .

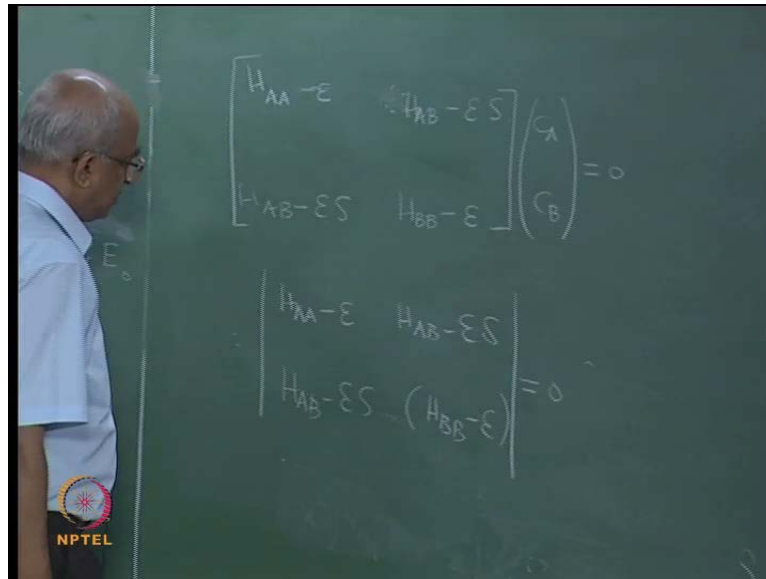
So, what is the partial derivative value? When you think about it; partial differentiation with respect to C_A means you are keeping C_B constant. So, this is going to give me $2 C_A$ plus this is going to be 0 plus $2 C_B S$ must be equal to derivative of the right-hand side. And that is fairly simple and straightforward – $2 C_A H_{AA}$ – will be the first term coming from differentiating this. You differentiate that; answer will be 0, because C_B is kept constant. And from the last term, you are going to get 2 times $C_B H_{AB}$. So, that is the equation. And if you want, you can actually solve this expression for dou . I seem to have to put a substitute here, which is totally unnecessary. So, $dou E$ by $dou C_A$ – if you want, you can rearrange this and get an expression. But, why should I do that? After all my aim is after finding the $dou E$ by $dou C_A$, I am going to put it equal to 0. So, why should I solve it? I will just put $dou C_A$ equal to 0 in this expression. I can do that without any difficulty.

And then I will get an equation. What is the equation? The equation say is that, script E into $2 C_A$ plus $2 C_B$ is equal to how much? $2 C_A H_{AA}$ plus $2 C_B H_{AB}$, correct? This is the equation. So, if you solve this equation, you are going to get... I mean there is only one equation yet; but if you solve; I mean I will be getting one more equation and then you solve both of them; you are going to get the best possible values of C_A and C_B . But, then when you think about this, 2 is common throughout. So, let me cancel that, and not only that; let us take this term to the other side. So, what you will get is H_{AA} minus script E into C_A . That will be the first term, which depends upon C_A , because I have taken this to the other side plus C_B script E into S minus H_{AB} must be equal to 0; correct? This is the equation that you will get.

So, in a similar fashion, if you like, you can differentiate this expression now with respect to c_B ; put the derivative of script E with respect C_B equal to 0; and you are going to get an exactly similar equation. I hope I can just write down that equation. What would that be? It will say that, C_A into epsilon script E into S minus H_{AB} plus H_{BB} minus script E into C_B must be equal to 0. That is what this equation will tell you. In exactly the same fashion, you are going to get this equation; fine? So, we now have two

equations. And of course, we should be able to solve these two equations to find the best possible values of C_A and C_B . And once we have solved for the best possible values of C_A and C_B , what will I do? I will choose, I will put those values of C_A and C_B into this equation and get the best value for script E; correct? So, that is the procedure that we will adopt. But, now, what I am going to do is a simple trick.

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See if this is an equation, which I am going to write as if it is a matrix equation. $H_{AA} - \epsilon$ minus ϵ ... There is a mistake; the signs got reversed; this should have been plus and that should have been minus. And I suppose the same kind of thing has happened there. So, this should have been minus and that should have been plus. You can check it; the equation actually follows from here. See whether from here you get that equation or the equation that was written previously. You are taking this to the right-hand side. So, naturally, you will see that, script E here will occur with a negative sign and script E there also will occur with the negative sign. So, I can say that, this equation is going to be written as $H_{AB} - \epsilon S$. And what am I going to have here? The same kind of thing – $H_{AB} - \epsilon S$ and $H_{BB} - \epsilon$ multiplying C_A C_B must be equal to 0; correct?

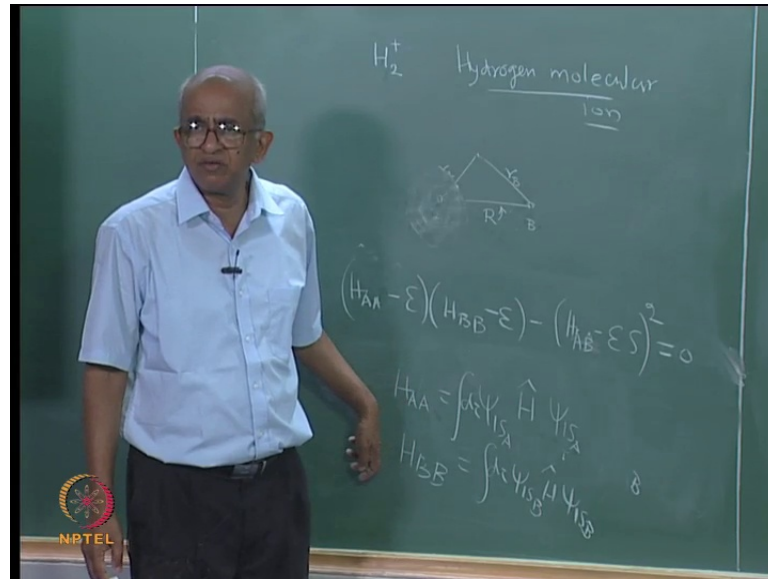
Now, you may say what is it that you gain? This is only the fancy way of writing two linear equations using matrices. But, the moment you see such an equation; this is actually of the following form. You have a square matrix A and that is multiplying... A

is actually this matrix. And it is multiplying a column matrix, which is C . And what it says is that, A into C must be equal to 0. That is what this says. Now, suppose this matrix A was such that, it has an inverse. Suppose A is a matrix, which is such that, it has an inverse; then what will happen? You will multiply this by A inverse from both the sides. And then what will you find? You will find C is equal to 0. But, what is C ? C is nothing but $C A$ and $C B$. Therefore, what is going to happen is if you say C is equal to 0; that actually means $C A$ is 0 as well as $C B$ is equal to 0. And the trial function – what is the trial function? The trial function actually has the form ϕ is equal to $C A \psi_1 + C B \psi_2$. This is the trial function.

But, now, you are saying; you are finding a solution; where, $C A$ and $C B$ – both are 0. Is that acceptable? Definitely not, because the electron – you know it is there; it is there in the molecule; you cannot have the wave function for the electron identically equal to 0. That is impossible. So, what is the way out? The way out is that, this matrix A , which is actually this square matrix – this one; it should not have an inverse. If it has an inverse, you are in trouble. Therefore, this matrix should not have an inverse. Now, when is it that the matrix does not have an inverse? The answer is very simple. If the determinant of the matrix is 0, then it does not have an inverse. Therefore, what is it that we have found? We have found that, the determinant of this matrix actually has to be equal to 0.

So, let us write that equation. So, now, you find again something nice you see; actually, I wanted to solve for $C A$ and $C B$ and then put it into the equations and so on; get the value of E . But, now, what is it that I find? I have an equation for E . Therefore, this is very nice; I just have to solve this equation for E . That will give me the value of E . So, it is not really necessary to solve for $C A$ and $C B$. But, of course, if you are interested in the wave function, you should do it. But, if you are interested in the energy, this is all that you need to do, and so this determinantal equation... Let me expand this; and then ask what happens.

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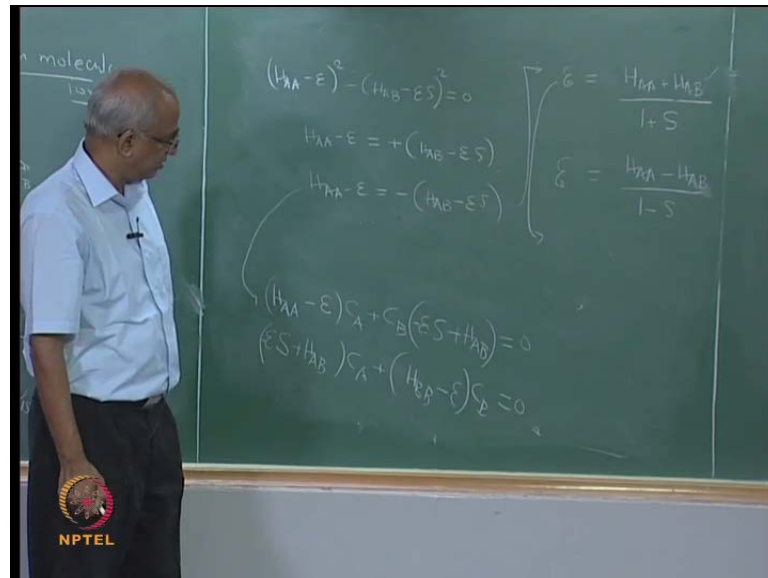


What you will find is that $H_{AA} - E$ into $H_{BB} - E$ minus... You expand the determinant; fairly simple thing to do. $H_{AB} - ES$ the whole square must be equal to 0. That is what happens if we expanded the determinant. Now, here I can actually make a simplification. In the problem that we are considering, A and B – both are protons; both of them are protons. So, if you think of ψ_{1sA} , how is it? It is actually spread around that nucleus. And what is H_{AA} ? It would be equal to... You take the Hamiltonian H ; allow it to operate upon ψ_{1sA} ; multiply it by ψ_{1sA} and then the volume element $d\tau$; integrate over the entire space. So, H_{AA} would have been the expectation value of the energy; expectation value of the Hamiltonian if the wave function for the electron was actually ψ_{1sA} ; that means if you imagine somehow, you are able to confine the electron to what ψ_{1sA} . Then this would be an estimate of the energy of that electron; correct?

And, if you think of H_{BB} , you can make a similar argument; right? It would have been an estimate of the energy of the electron if it was confined to $1sB$ in the molecular ion. If you think of the molecular ion and you say electron somehow has a wave function, which is ψ_{1sA} ; then what would be an estimate of its energy? It will be equal to H_{AA} . Or, you can say instead of having it in ψ_{1sA} , it is sitting in ψ_{1sB} . Then the estimate of its energy would have been H_{BB} . And with this information, what would you say regarding the values of H_{AA} and H_{BB} ? Remember the two nuclear are identical and they have the same charge. So, the $1s$ atomic orbitals also have the same

shape X; the only thing is that, one atomic orbital is on nucleus A; the other is on nucleus B. And therefore, if I confined it to first nucleus – to the vicinity of the first nucleus or to the vicinity of the second nucleus, I would expect that, the energy should be the same. And this physical argument convinces me that, H_{AA} must be equal to H_{BB} .

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So, what will happen to this equation? This equation will become H_{AA} is equal to H_{BB} . Therefore, you will actually get $H_{AA} - E$ the whole square minus $H_{AB} - ES$ – not H_{BB} , but $H_{AB} - ES$ the whole square must be equal to 0. And this is a simple equation; we can easily solve it. What is the solution? You take this to the other side; you will find that, there are two solutions. This is one possible solution. And what is the other possible solution? $H_{AA} - E$ must be equal to negative of $H_{AB} - ES$. This is the other solution.

So, imagine I am confining myself to the negative sign – this one. So, then what will happen? If you have... There are two solutions; when... Is it surprising that, there are two solutions? No, it is not surprising, because this is a quadratic equation in E . A quadratic equation – when you solve it, you naturally should get two equations. And then the question is – are these two solutions basically meaningful? We will see that, they are basically meaningful. What will happen is that, one of them represents the ground state of the system and the other one represents a possible excited state of the system. That is what will happen.

So, let us look at the negative sign. If you looked at the negative sign, what is going to happen? I need an expression for script E; put the negative sign and solve for script E. What is the answer that you are going to get? You are going to get $H_{AA} + H_{AB}$ divided by $1 + S$. Convince yourself that, this is the answer. And what is the other solution? The other solution actually is script E is equal to $H_{AA} - H_{AB}$ divided by $1 - S$. You put the plus sign; then you will find that, this is the solution. So, we have found two possible values for script E.

And, which one will be the best approximation for the energy of the ground state? The one that is lower. And of these two, what actually happens is that, this is the one that is lower; which you may find surprising; but the reason is that, H_{AB} actually is negative. When you evaluate this integral with the expression for the integral is written earlier; when you actually evaluate it, you will find that, H_{AB} is negative; because of it, this is lower and that is having a higher value, because you see if H_{AB} is negative, you have some number from which you are subtracting a number; while here you have some number, which you are actually adding a number, because of the negative sign. Therefore, you see you have these two solutions.

And now, I want to find the wave functions also. So, how will I find the wave function? The answer is actually extremely simple. If you think of this negative sign; but here you have put the negative sign; so, what you will do is this equation is valid for the script E, that is, obtained by solving this equation. Therefore, what you do is if you want to find out the coefficient correspond with the coefficients C_A and C_B corresponding to this solution, what will you do? You can actually take this equation and use it here; correct?

You can take this equation; use it there. If you used it there, what is the result that you are going to get? This equation – if you put it into this equation, what you are going to get is – on the left-hand side, you have $H_{AA} - \text{script E}$ into $C_A + C_B$, but C_B into this; that is actually $H_{AB} - \text{script E}$ into S . So, if you took this negative sign to the other side, you are going to get minus 1 into $H_{AA} - \text{script E}$; and that should be equal to 0. And what does this mean? This means that, C_A is equal to C_B . Therefore, you find that, in this case, C_A is equal to C_B . You can do a similar thing with the other solution – with the negative solution. And what you will find is that, C_A is equal to minus C_B . That is the answer that you will find if you did the same kind of thing with

the other solution. We will analyze these solutions in the next lecture. Thank you for listening.