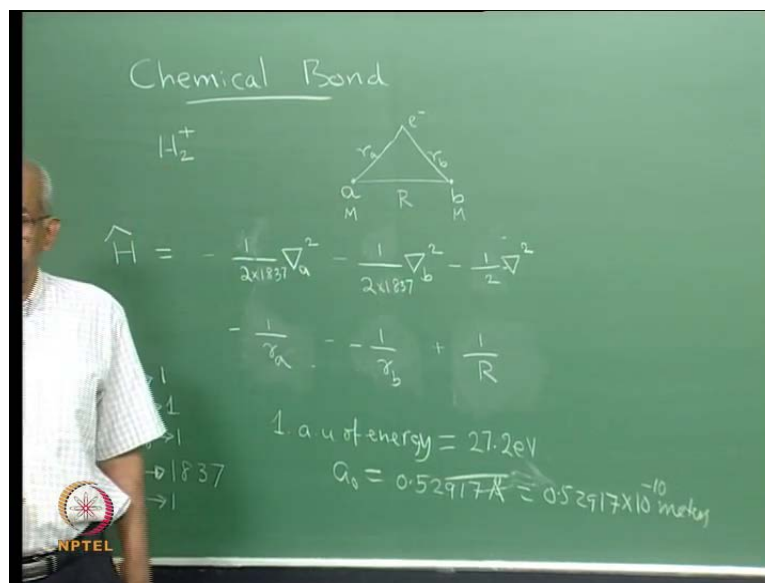


**Introduction Quantum Chemistry**  
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**Lecture - 42**  
**Hydrogen Molecular Ion (Contd.)**

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Today we are going to discuss the most interesting topic, as far as chemistry is concerned this is the formation of a chemical bond. Chemistry is particularly interested in knowing why a chemical bond is formed and of course, it would be very nice, if chemistry can calculate the bond energy and so on, bond length and so on theoretically. And the nice thing is that, these days it is very easy to do this kind of calculations.

So, the topic of today's discussion is the chemical bond. Now of course, even we say that it is two molecules is the simplest molecule, that one can imagine, but even that is a little complex because of the fact that, there are two electrons. Hydrogen molecule has two electrons and two electrons always make things difficult. So, we will imagine an even simpler system which is actually hydrogen molecular ion, you imagine that one electron is removed and this is species which is used to refer to us H<sub>2</sub><sup>+</sup> can be made in lab and studied. In fact, people have been able to determine the bond lengths, the dissociation energy of the molecule and so on. So, if I think of H<sub>2</sub><sup>+</sup> what will be the Hamiltonian of operator. This is our usual style we always write start with the Hamiltonian.

So, this system has three particles. So, one, two, these are the nuclei, which I am going to call a and b and of course, you have one electron so, this is one electron. And the distance between the two nuclei, I am going to call it capital R. Distance of electron from the nucleus a, I am going to call it r a and this distance naturally will be called r b. And if you are asked to write the Hamiltonian for the system how would it look like, well strictly saying I shall write the details Hamiltonian and then see argue that some simplification can be made. You have three particles in the system, so all of them will be moving. So, naturally you would have minus h cross square divide by 2 capital m. Capital m being the mass of nucleus a and capital m will be the mass of nucleus b also, because in the case of H<sub>2</sub> plus these are 2 protons.

So,  $\frac{h^2}{2m_a}$ , why do I put this subscript a there the answer is, reason is simple, because I am concentrating with the kinetic energy of nucleus a. And then I have  $\frac{h^2}{2m_b}$  square were this term represents kinetic energy of nucleus b both are moving I mean in general of course. And then I have kinetic energy of the electron which is  $\frac{h^2}{2m}$  square. So, these terms represent the kinetic energies and then addition to that you have the potential energy.

So, what is the potential energy of the system, they are three charged particles. So, if you think of interaction of the electron with the nucleus a, the interaction energy will be  $\frac{-e^2}{4\pi\epsilon_0 r_a}$ , electron interacting with nucleus a. Then  $\frac{-e^2}{4\pi\epsilon_0 r_b}$  interaction of electron with nucleus b and then there will be the portion between the two nuclei, which is represent as  $\frac{e^2}{4\pi\epsilon_0 R}$ . This case with a positive sign because the interaction is repulsive while these two are interaction can therefore, you have this negatives signs. Now I had spoken about atomic unit in previous lectures. So, we will make use of atomic units because there nice and convenient.

So, in atomic units, what happens is that you will have h cross becoming unity. If you work do with the atomic units the value of h cross will be unity, m is the mass of the electron right. This small m is the mass of the electron. So, what will happen to m? It will be unity and atomic units are such that  $4\pi\epsilon_0$  also becomes 1 right. So, mass of the electron is taken as unit of mass what will happen to capital m, well see a proton is 1800 and roughly 40 times heavier than the electrons. If you measure the mass

of the particles sorry, mass of the proton in terms of the mass of the electron. It will be about 1800 well it says 138 anyway let me just write it has, how much 37 so, 1837.

So, what will happen to the Hamiltonian? If I did these things,  $\hbar$  cross will become unity. So, therefore, this term is 1 and so, I will put a 1 there this capital m will become 1837 and this will become 1 and again that capital m will become 1837, then again this  $\hbar$  cross square by 2 m it becomes 1 by 2, this also simplifies for  $\phi$  epsilon 0 becomes 1 and I should also tell you that in addition to this see you measure charge in them. So, the charge of the electron. So, therefore, e also becomes one. So, therefore this terms simply becomes minus 1 by r a and this term becomes minus 1 by r b and that becomes plus 1 by capital R and you will see that, this is very nice because you do not have to worry about any constant, I mean there are all unity.

Let us say nice thing about this Hamiltonian and this is actually expressed in atomic constant simultaneously atomic units. So, if you find the energy. The energy again is going to the answer, that going to be get will be atomic units. and one atomic units of energy remember in the case of the hydrogen atom is the answer, if you solve the Schrodinger equation. And if you found the energy of the system you will in atomic unit you will get an answer of minus half that is the answer in atomic units. And in the energy of hydrogen atom as you would know is minus 13.6 electron volts.

So, minus half is the 13.6 of atomic unit if the energy is 27.2 electron volts. And this is convenient because, once I get the energy I just need to multiply by 27.2; I shall get the answer in electrons volts. And also in atomic units the  $a_0$  the radius of the first bar orbit is unity in atomic units, but in normal our units, what will normal units it is going to 0.52917 Angstrom, which is actually 0.52917 into 10 to the power of minus 10 meters right remember that.

If I calculate the inter nuclear distance, then I shall get the answer in atomic units, but that can be converted into the Angstrom so, using this. So, with this information let us go ahead and look this Hamiltonian, but this Hamiltonian as it is written it inverse three particles, it inverse as three particles. So, you have differentiation with the respect coordinates of the first, second and the third particle. So, nine variables are there very difficult, I mean, this is almost impossible to solve. I should not say almost it is impossible to solve, but then if you look at this, I did this on purpose if you look at this

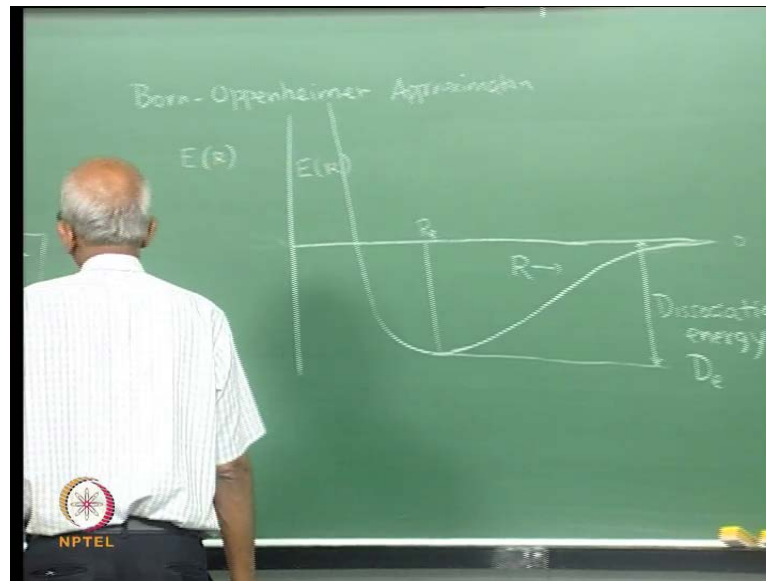
term or that term there is 1 by 2 into 1837 whereas, here there is only 1 by 2 why do you have 1837 simply, because your nucleus is much much more heavier than the electron. This also means that your nucleus would be a silage; I mean you know that heavy objects move only slowly. So, therefore, the movement of the nuclei is going to be rather slow in comparison with the movement of the electron.

So, by the time, the nuclei have moved a little bit, the electrons would have gone around it several times. It essentially means that the nuclei are able to adjust to the instantaneous positions of the nuclei. So, in general electrons are able to adjust to the instantaneous positions of the nuclei. So, if the nuclei have moved a little bit by the time the electron has already adjusted it to the new positions of the nuclei right.

So, therefore even if I did a calculation in which the nuclei are assumed to be fixed at a particular distance. Suppose I do a calculation where the nuclei are assumed to be fixed at a particular distance and then I do another calculation changing the nuclei distance; that means, I am actually changing the nuclei distance very very slowly as essentially. Right.

Even such a calculation is very useful, because even if I obtain the electronic wave function using such an approximate calculation. That is the decent approximation for the electronic wave function, because motion of the electron is actually much much faster than that of the nucleus. So, this is what I am going to do? What I am going to do is, I am going to say, at first I will forget nuclear motion and assume that they are kept fixed at a particular distance. So, I will say that, let me say they are kept fixed at a distance of capital R. Imagine they are not moving, if they are not moving I do not have to worry about these terms; that means, I am not going to worry about nuclear kinetic energy.

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So, because I am assuming that they are kept fixed. This kind of approximate calculation is actually referred to as the Born Oppenheimer approximations. I am not going to describe the mathematics of this, but I have given you the physical idea behind it. Born Oppenheimer approximation, what is the approximation? You see nuclear motion is very slow and therefore, electrons are able to adjust to the instantaneous positions of the nuclei even they are, even when the nuclei are moving.

So, essentially what it says. So, therefore, I what I have do is, I assume that the two nuclear kept fixed at a particular distance and I do an electronics structure calculation. Then I will go on changing in the nuclei distance, I tripped the calculation at different in the nuclear distances and you may ask well what is the use of that well. After having done the calculation I what I will obtain? At any particular distance, I am going to get the electronic energy. I am going to get  $E$  which will be depend upon that  $R$  right. I am assuming that the nuclear kept fixed a particular distance I find the Eigen values of this Hamiltonian. This is my Hamiltonian now that means; I am finding the energy level of the system.

And in specifically, I am interested to the ground stage, and then what I will do is? I will imagine that the nuclei are brought from a large distance to a short distance situation then what will happen the electronic energy of the system will change. And if the electronic energy decreases and reaches a minimum, then I know that there is the formation of a

bond. Imagine I keep the distance nuclei at large distance, this system will have some energy and then if I bring the two nuclei together with one electron of course, if the energy of the system decrease then a bond is form and if energy does not decrease and obviously, no bound is formed. So, what I would like to have is this E of R which is the energy of the ground stage of the molecule. If I can calculate and that make a plot of it against R, R I shall take to be along the horizontal axis E of R will be along the vertical axis right.

If I made a plot of it, what would I expect at the large separation, what will happen to H<sub>2</sub> plus. If I had H<sub>2</sub> plus and if I pull the two species apart, two nuclei apart what is going to happen? The electron will go with one of the nuclei and so, far away you are going to have hydrogen atom and a proton right. If the inter nuclei is very large you are going to have a proton and hydrogen atom and the energy of that system, I will take to be equal to 0 which is convenient. You can take it to have any value if you like, but for convince the energy of the system when they two species I mean when the hydrogen and the proton far apart the energy of the system is taken as 0.

And when I bring two together the another of the system will change and if it decreases like this. Then I said that, there is the attraction between the two species there is attraction and when you push the nuclei together what do you aspects while the energy will decrease let us to say. and then I at sufficiently closed distance that nuclei will repeal each other definitely and therefore, what will happen to this curve it will turn around and increase.

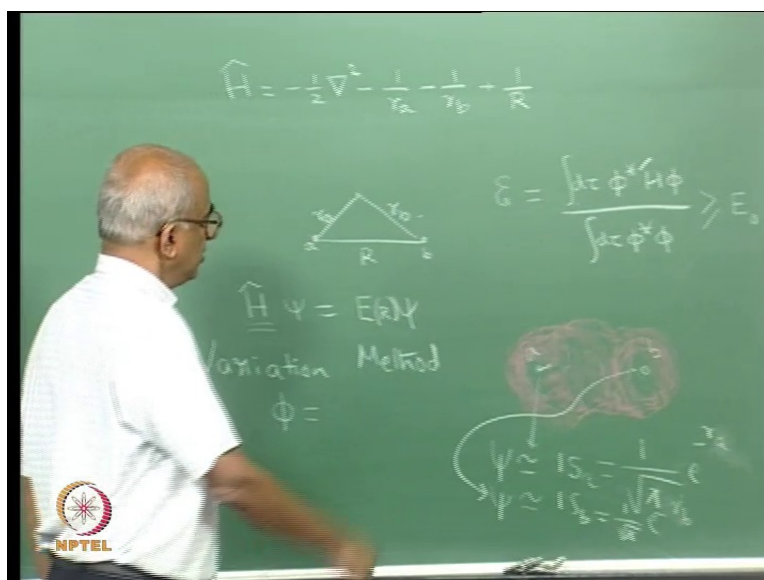
So, this is what I would roughly speaking expect this is my expectation and if this happens then I can say that that is my equilibrium in a nuclei distance which I am denote as R with a subscript e. So, this is a quantity that you can measure experiment. And not only that, suppose you had the molecule with this inter nuclear distance then, the molecule will have an energy which is that much.

And if you supplied from outside that much energy, we supplied that much energy from outside, then you can cause the inter nuclear distance to become very large. Let me repeat, imagine I start with the molecule at the equilibrium inter nuclear distance then it will have that much energy. And now, suppose you supply energy from the outside and how much do you supply? You supply that much energy, then you can cause the inter

nuclear distance to become infinity large; that means, you can cause dissociation of the molecule and then therefore, if you calculate this height then you can get dissociation energy which I will denote by the symbol  $D$  with a subscript  $e$ .

So, if you can calculate this curve, what is this curve? This is a plot of the electronic energy of the system as a function of inter nuclear distance. They can calculate that, then can get the equilibrium inter nuclear distance, I can also get the dissociation energy of the molecule and therefore, we want to do this right. So, how will I do that is the question.

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Let me write the Hamiltonian once again. The Hamiltonian is actually  $H$  equal to minus 1 by 2 del square, minus 1 by  $R$  a, minus 1 by  $R$  b, plus 1 by  $R$ . And let me draw this figure ones more, I have one nucleus a here, I have nucleus b here and there is one electron. And  $H$  of course, is an operator. And what is that I would like to do? I would like to do solve the equation  $H$  operating upon  $\psi$  is equal  $E \psi$ .

And this  $E$  will depend upon;  $E$  will actually depend upon the separation between the two nuclei, which is what I have already told you. So, therefore, this  $E$  is actually a function of  $R$  and then want to know what precious actually, I want to know what this function is? Because it is very useful, I knew it I would able to find equal to equilibrium inter nuclei distance. I would also be able to when the dissociation energy of the molecule. So, therefore, this is very useful. Now this equation is much much, this

Hamiltonian I should say is much much simpler than the original actual Hamiltonian. The actual Hamiltonian involved a kinetic energy of the nuclei also, but I do not know have that, in this Hamiltonian.

And therefore, this is the much simpler equation and in fact, it is actually possible to solve it exactly. The Schrodinger equation for H<sub>2</sub> plus with this approximation it can be solved exactly, but we are not going to look at the exact solution simply, because you see it is possible to do that only for H<sub>2</sub> plus. If you had H<sub>2</sub> molecule then you cannot do it or if you have some other more complex molecule we cannot find the exact solution.

And therefore, finding the exact solution for H<sub>2</sub> plus alone, what is the fun. We want the method which can be applied in general for any molecule that one has and so, what we do is we use an approximation procedure. In fact, we will use the variation technique. So, how does one proceed, well the answer is here. I have to think of is suitable trial wave function  $\phi$  right.

For some physical reason, I expect some trial function to be decent trial function and therefore; I have let me say this  $\phi$ . And once I had  $\phi$  what I will do? Well I will evaluate something which I have been referring to a script E which is define to be, 
$$\frac{\int d\tau \phi^* H \phi}{\int d\tau \phi^* \phi}$$
 So, this is my variational estimate for the energy of the system.

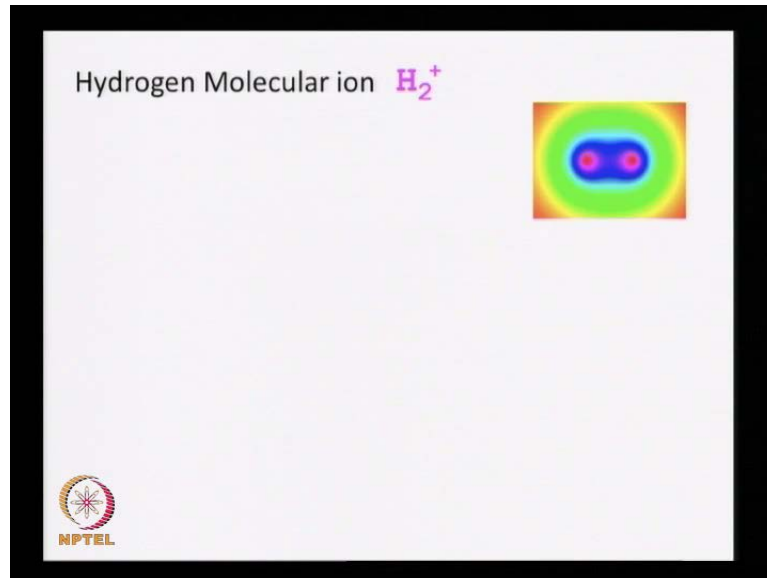
So, I will calculate this and what is the use of this? This quantity is such that it always is greater than or equal to the ground state energy of the system right. This is the some content of the variation theorem and therefore, I can actually use the variation techniques to have an estimate of the ground state energy of the system. So, question is what is the variational function that I will use? And that is where physical induce actually helps.

So, let us think about the physical situations. Now what would I aspect to happen? Well what I aspect that, if I have the two nuclei right. The single electron it will be spread you see the wave functional spreads throughout the system and therefore what would I expect the way function may be something like this, it will be spreads throughout something like that, this is what I would expect. In fact, I am interested in the ground state of the system; that means, if you think of the wave function for the electron. Well it should be spread throughout, not only it is should be spread throughout it, I do not expect, it have any nodes, I know that because this is always the case.



When you are in the ground state the wave function has no node. So, therefore, you would expect that, the wave function may be spread something like this. Why should be it spread, because you see the two nuclei are equivalent. There is no preferred nuclei with which the electron will go, so the electron will spend time near both the nuclei.

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I think I have a picture of that in my power point presentation. So, this is a pictorial representation of the same thing, but more accurate than what I have drawn there. Because, I see the different colours are used to show different regions where the density is different. But now if this is the way, the wave function is what the approximate function that I can use, well the answer is this one. See, suppose you are thinking of the wave function very close to this nucleus, suppose I have a point here and imagine you are very close to this nucleus.

If you are very close to the nucleus well then I would expect that the influence from this nucleus is much much more than the influence from the other nucleus. So, other nucleus is far away. So, in a region that is very close to this nucleus I can actually take this Hamiltonian and this is nucleus a and that is nucleus b. So, if you are very close to nucleus a, this  $1/R_a$  is much much larger than  $1/R_b$ . And therefore, at least as an approximation I can neglect this, if I am confining myself to this region where the electron is very close to the nucleus.

So, if you can neglect  $R_b$ , if you neglect this term what does it mean? It means that the electron is predominantly feeling only the nucleus  $a$ . And if you completely neglected the nucleus  $b$  you have one electron moving in presence of one nucleus and if you solve the Schrodinger equation, what is the answer that you will get? You will get the answer that; the electron is sitting in a  $1s$  atomic orbital having its center on that nucleus right.

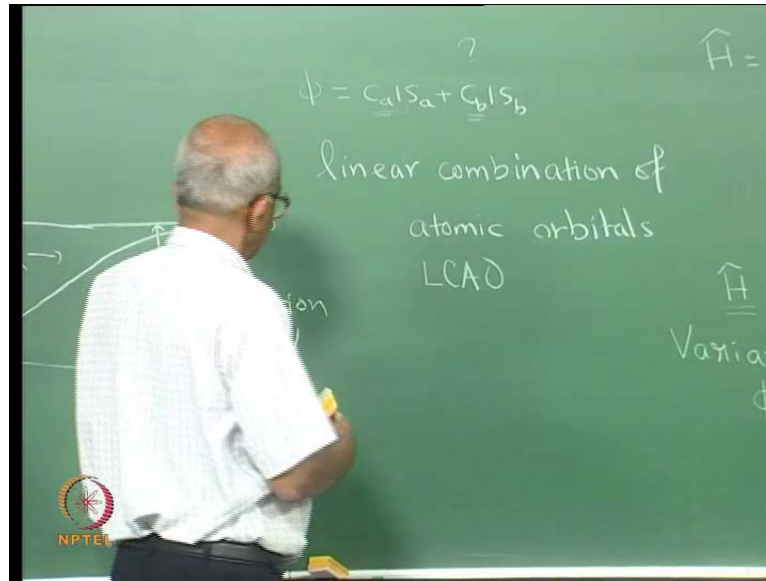
So, therefore, I realized that in the region that is closed to this nucleus. The wave function for the electrons  $\psi$  should approximately be resembling a  $1s$  atomic orbital having its center on nucleolus  $a$ . So, therefore, I would say that  $\psi$  has to resemble  $1s_a$ . what is  $1s_a$  is the question, well  $1s_a$  is actually  $\frac{1}{\sqrt{\pi}} e^{-r_a}$  to the power of minus  $r_a$ , this is the expression for  $1s$  atomic orbit, that we have look at long ago, but because we are working with atomic units what will happen in the atomic units  $a_0$  is 1.

So, I can remove this  $a_0^3$  and this is 1 so, therefore, I could have to the power minus  $r_a$ , this is the convenience of working with atomic units. And further if why do have this subscript  $a$ , this says that, you says this is atomic orbital having its center nucleus  $a$ . And as for the electron is concerned now, they I have to think a distance of the electron from that nucleus, that is the meaning of saying that the orbital is  $1s_a$ . So, therefore, in here  $e^{-r_a}$ , you all have  $e^{-r_a}$  to the power minus  $r_a$ , but that  $r_a$  is the distance of the electron from the nucleus  $a$  and therefore, you will have to put  $r_a$ .

So, therefore, you will say that in the region that is very close to nucleus  $a$ ,  $\psi$  may be approximates as  $1s_a$ , which is actually chotta notation. I do not want write this whole thing, that is why, I right  $1s_a$ , but when I write  $1s_a$ , it means that I have  $\frac{1}{\sqrt{\pi}} e^{-r_a}$ , where  $r_a$  is the distance of the electron from the nucleus. Similarly if you are the thinking of the region very close to nucleus  $b$ .

Suppose you think a point somewhere here, what should be the expression for  $\psi$ ?  $\psi$  should at  $b$  same kind of arguments,  $\psi$  should resembled what in that region? In this region  $\psi$  should be approximately  $1s_b$  where,  $1s_b$  is an atomic orbital having its centre on nucleus  $b$  and its functional form will be  $\frac{1}{\sqrt{\pi}} e^{-r_b}$  to the power of minus  $r_b$ . So, therefore, you can physically argue that near nucleus  $a$ , the function should resembled  $1s_a$  while near nucleus  $b$ , the function should resembled  $1s_b$  and therefore, what would be suitable approximation for the entire wave function.

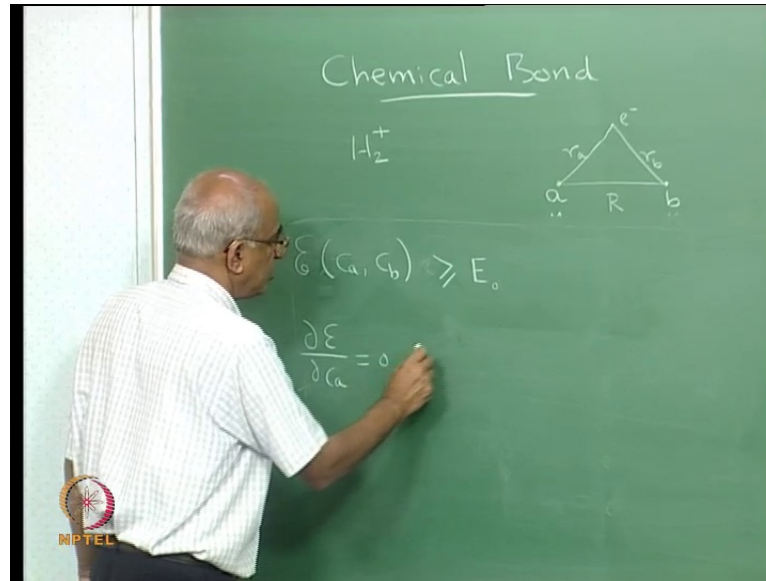
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It is clear that, I can say well trial function of the form  $\psi$  equal to some  $c_a$  into  $1s_a$  plus  $c_b$  into  $1s_b$  may be it suitable approximation. Why do I say that, well in the region that is close to nucleus a,  $r_a$  is a small and therefore,  $1s_a$  will have a large value.  $r_b$  is large and therefore,  $1s_b$  will have small value. And therefore, in the region that is close to nucleus a, I cannot neglect the second term, while if you are thinking regions closed to nucleus b, then you can neglect the first term. So, in the region that is closed to one nucleus a, the function will resembled  $1s_a$  and the region that is closed to nucleus b, the function will resembled  $1s_b$  and therefore, I expect that this is a decent reasonable approximation for the wave function.

Now this technique that, I am going to usually referred to as linear combination of atomic orbitals, why the name? The answer is actually simple, these two are atomic orbitals and I am combining them after multiplication with some constant  $c_a$  and  $c_b$  are constants which I would like to determined, but they are constant, you take  $1s_a$  multiplied by  $c_a$ , you take  $1s_b$  multiplied by  $c_b$  and add. Your linearly combining them after multiplying some constant you are just adding them up that is why this is refer to us linear combination of atomic orbitals. And for short repeat would say LCAO in a combination, this technique is refer to us LCAO technique, but then you have the next question, how will you determined the coefficients  $c_a$  and  $c_b$ ? Answer is actually extremely simple. What you will do is you will evaluate script E using this approximate function ok.

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You will evaluate script E using this approximate function. And what will happen this script E when evaluates? It is going to depend upon, see if this is my trial function. The trial function depends upon  $c_a$  and  $c_b$ . So, naturally when you evaluates script E, it is going to depend upon  $c_a$  and  $c_b$ . So, this script E is going to be function of  $c_a$  and  $c_b$ , if you evaluated it. The definition of script E is actually here it is written here. So,  $E$  is the function of  $c_a$  and  $c_b$ .

So, naturally script E will be depend upon  $c_a$  and  $c_b$ . Now our variation derivations says that for any value of  $c_a$  and  $c_b$  is greater than or equal to the actual ground state energy of the system, that is what it says the various theorem. So, therefore, what will I do I will do the following I will adjust  $c_a$  and  $c_b$  and such a fashion that script E has the least value because, even that least value will be actually greater than or perhaps equal to the ground state energy. And therefore, if I found the minimum of the script E, the minimum value for script E even that will be greater than the actual ground state energy.

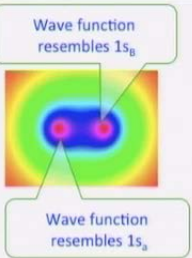
So, therefore, they what I do? I first evaluate it script E and then adjust the coefficient  $c_a$  and  $c_b$  such that script E has the least value that is my procedure. So, that actually made if I know this function or what I will have to do is I will have to take is derivative with the respect to  $c_a$ . Why do I have to take the derivative because, I am looking for the minimum value of this script E. So, how define the minimum, you will put  $dE/dc_a = 0$

c a equal to 0 and you will put dou E by dou c b equal to 0. Let us look at these slides for a second.

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Hydrogen Molecular ion  $H_2^+$

$$\phi = c_a 1s_a + c_b 1s_b$$

$$\mathcal{E} = \frac{c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}}{c_a^2 + c_b^2 + 2c_a c_b S}$$


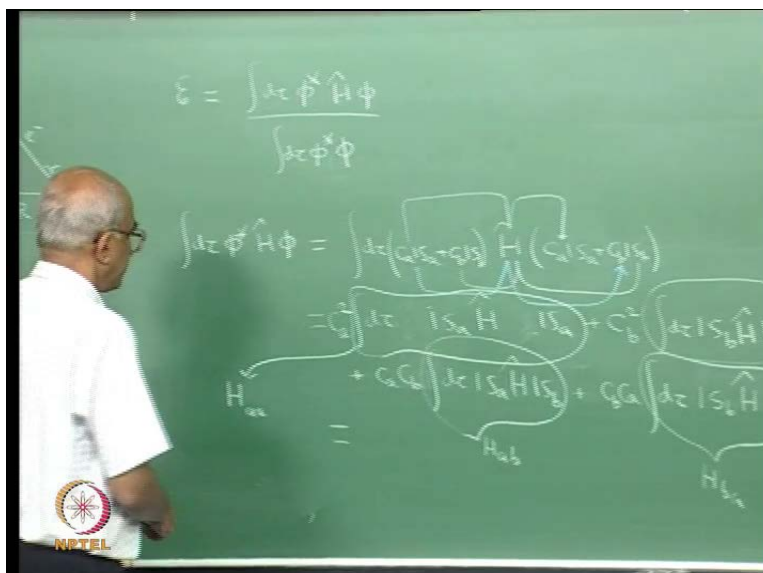
Wave function resembles  $1s_b$

Wave function resembles  $1s_a$



So, here what I am saying is that the wave function actually resembles in this region. The way function resembles  $1s_a$ , while there it resemble  $1s_b$  and so, take your linear combination of  $\phi$  will equal to  $c_a 1s_a$  plus  $c_b 1s_b$ .

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$$\mathcal{E} = \frac{\int d\tau \phi^* \hat{H} \phi}{\int d\tau \phi^* \phi}$$

$$\int d\tau \phi^* \hat{H} \phi = \int d\tau (c_a 1s_a + c_b 1s_b) \hat{H} (c_a 1s_a + c_b 1s_b)$$

$$= c_a^2 \int d\tau 1s_a \hat{H} 1s_a + c_b^2 \int d\tau 1s_b \hat{H} 1s_b$$

$$+ c_a c_b \int d\tau 1s_a \hat{H} 1s_b + c_a c_b \int d\tau 1s_b \hat{H} 1s_a$$

$$= c_a^2 H_{aa} + c_b^2 H_{bb} + 2c_a c_b H_{ab}$$


Now, I have to calculate script E, the expression for script E is already written there, but I will do the calculation and convince you that, this is the expression. So, how do I do the

calculation, the answer is very simple, I have script E which is equal to  $\int d\tau \psi^* H \psi$  divided by  $\int d\tau \psi^* \psi$ . So, this is the expression for script E. Now let me first calculate the numerator, what is the numerator? That is actually this object.

So, you will have  $d\tau$ ; let me write the H here, H is going to operate upon this linear combination  $c_a |s_a\rangle + c_b |s_b\rangle$ . And after that operation is performed you have to multiply by  $c_a |s_a\rangle + c_b |s_b\rangle$  with the star right. This is your numerator, but if you look at this object, you have this star operation. Star operation can be taken inside you will have the complex conjugate of  $c_a$  you will also have the complex conjugate of  $|s_a\rangle$ . Similarly you have the complex conjugates of all these things. You will make a simplifying assumption.

Which would be that  $c_a$  and  $c_b$  may be through to be a real. So, that the star operation has no effect. And  $|s_a\rangle$  and  $|s_b\rangle$  the expressions are already written here right. To the expressions are written here. You will see that they are already real. So, there is no square root of minus 1 anywhere and therefore, complex conjugation has no effect on  $|s_a\rangle$  or  $|s_b\rangle$ . And if I, for simplicity if I assume that  $c_a$  and  $c_b$  are real, then this star has absolutely no effect on this function. This is not absolutely necessary, but it is very convenient. Now, what about this object, well you have two terms here and you have two terms there and you of course, you have a sandwich in the middle, but if you have two terms here and two terms there when you multiply things I would expect four terms.

So, I will write these four terms separately. So, the first time will be  $\int d\tau$ , I would have  $c_a |s_a\rangle H c_a |s_a\rangle$ , how do I get that, this is one of the four terms. There are four separate terms so, what you do is, you take these and you imagine this H and this H goes and operates upon that, then you are going to get this term right. Now, you see,  $c_a$  is just a parameter, it has, it does not depend upon the possession of the electron.

What is the possession dependent term with  $|s_a\rangle$  will depend upon the possession of their electron. So,  $c_a$  does not depend upon possession of the electron, they just a parameter or I can say it is a constant. So, this H of course which involves differentiates with respect to coordinates of the electron, but this H would not have any effect on  $c_a$ , which is just a constant.

So, I can move this from there, this will become  $a^2$ , but if you are integrating over the entire space that integration is done over the possession of electron, there again  $a^2$  is a constant. So, you can take it out, it is completely unaffected by process of the integration. So, that is only one of the term, plus you have other terms in an exactly simplification, you will have a term which will involve  $c^2$  integral  $d\tau$  right, that will obtain by combining this, that and that. And what it will be? It will be  $\frac{1}{2} \int c^2 d\tau$  correct. And then you will have another term where you will have  $c$  into  $b$ , this is what should I say to refer to cross term. Why it is the cross term, because what happens is that you have this term combining with  $H$  and combining with that.

So, what will be it is going to be equal to integral  $d\tau$   $\frac{1}{2} \int c^2 d\tau$  right. And then you will have a term, which I will write  $c b$  integral  $d\tau$ , well here it is  $\frac{1}{2} \int c^2 d\tau$  is coming from the right and  $\frac{1}{2} \int b^2 d\tau$  coming from the left now what will happen is that, the reverse things. So,  $\frac{1}{2} \int b^2 d\tau$  from the left and  $\frac{1}{2} \int c^2 d\tau$  from the right so, you get that. So, these are four terms that you get. Now these four terms are actually  $\int d\tau$  to right, you have to keep on the writing them again and again and again.

So, what you do is you adapt a chotta notation. What would be an approximation chotta notation, well this whole thing what is it? You have  $\frac{1}{2} \int c^2 d\tau$  operate upon by  $H$  multiplying by  $\frac{1}{2} \int b^2 d\tau$  and then multiply by  $d\tau$  integral over the entire space. It is usual to adapt a chotta notation, where you say that this object is  $H a a$ , very convenient notation. And if you adapted that kind of notation well there is this term, while be the notation for that term  $H b b$ .

So, that is going to called  $H b b$ , then you have this term and naturally you will called this term  $H a b$  will notice that  $a$  on put the left hand sides with respect to  $b$  that is because, you see on the left side  $\frac{1}{2} \int b^2 d\tau$ , on the right hand side  $\frac{1}{2} \int c^2 d\tau$ . And so, naturally this term will be denoted as  $H b a$  right, and therefore this whole expression you can, I can modify or I can rewrite in this notation.

(Refer Slide Time: 42:38)

$$E = \frac{\int d\tau \phi^* \hat{H} \phi}{\int d\tau \phi^* \phi}$$

$$\int d\tau \phi^* \hat{H} \phi = \int d\tau (c_a |s_a\rangle + c_b |s_b\rangle) \hat{H} (c_a |s_a\rangle + c_b |s_b\rangle)$$

$$= c_a^2 H_{aa} + c_b^2 H_{bb} + c_a c_b H_{ab} + c_b c_a H_{ba}$$

So, it will turn out to be  $c_a^2 H_{aa} + c_b^2 H_{bb} + c_a c_b H_{ab} + c_b c_a H_{ba}$  that is all right. And straight away, I can make one more simplification, I am going to claim that  $H_{ab}$  is equal to  $H_{ba}$ , this is claim, which I will proof now, how do I will proof this.

(Refer Slide Time: 43:14)

$$E = \frac{\int d\tau \phi^* \hat{H} \phi}{\int d\tau \phi^* \phi}$$

$$\phi = (c_a |s_a\rangle + c_b |s_b\rangle)$$

$$= c_a^2 H_{aa} + c_b^2 H_{bb} + 2c_a c_b H_{ab}$$

$$= \int d\tau (c_a |s_a\rangle + c_b |s_b\rangle)^2$$

$$= c_a^2 \int d\tau |s_a|^2 + c_b^2 \int d\tau |s_b|^2 + 2c_a c_b \int d\tau |s_a| |s_b|$$

Well I know that,  $H$  the Hamiltonian operator is a Hermitian operator. What is the meaning of saying that, the meaning is that if I had any two acceptable functions, what notation shall I use for acceptable functions may be  $\chi_1$  and  $\chi_2$ . I take  $\chi_2$  allow it



is operate upon it multiply by  $\chi_1^*$  integrate over the entire space. You remember the definition of the Hermitian operator, allow  $\chi_2$  to be operate upon by  $H$  then multiply by  $\chi_1^*$  in  $d\tau$  integral over the entire space. You are going to get an answer; some number as the answer, because you have integrated over the entire space.

So, for a Hermitian operator what will happen is, that instead of doing this, you allow us to operate upon  $\chi_1$  first and then multiplied result by  $\chi_2^*$   $d\tau$  and integrate over the entire space. You will get another number, but for a Hermitian operator the second number will be the complex conjugate of the first number. That is the definition of a Hermitian operator. For any acceptable  $\chi_1$  and  $\chi_2$ , Hermitian operator will satisfy this research. So, if that is the way, it is imagine I take  $\chi_1$  to be  $\psi_a$  and  $\chi_2$  to be  $\psi_b$  suppose, then what would I have between I would have  $H$  and the star I will have to put  $d\tau$  right.

If I identified  $\chi_1$  with  $\psi_a$  and  $\chi_2$  with  $\psi_b$  the left hand side will be that much and what about the right hand side? The right hand side will be  $\int d\tau \psi_b^* H \psi_a$  the whole things star correct. But then of course, I remember that  $\psi_a$  completely real. So, star has no effect on it. So, I can remove this star and here again  $\psi_b$  completely the real. So, the star has no effect and if you look at this term everything in here  $\psi_a^* H \psi_b$  there are all real. So, this star also has no effect. And therefore, what is the result that I obtain, the left hand side is in my notation  $H_{ab}$  and what is the right hand side, right hand side is my notation is  $H_{ba}$ .

So, the fact that  $H$  is a, Hamiltonian operator is a Hermitian operate implies that  $H_{ab}$  must be equal to  $H_{ba}$ . You do not have actually evaluated them separately, it is enough if you evaluate it one of them because then this is equal to the other. So, therefore, here this term and that term if you think about it, they are both the same and therefore, you can say well I will remove one of them, maybe I will remove this one, but then naturally I will have to put it here. So, this is the numerator and it is exactly that numerator that is sitting in this expression for the quantity script that appears on the slides right, you see that, this is just what I have now shown. Now, what about the denominator? In denominator you do not have this  $H$  that is all. What you have is  $\int \psi^* \psi d\tau$  integral over the entire space.

So, that will be equal to  $\int d\tau c_a \psi_a + c_b \psi_b$  right. Strictly speaking I should say stars, but that stars has no effect on this function. So, it is the function itself and you have a exactly the same terms. So, what can I do? I can put a square here, why should I write the other term, it is just a square, integrate over the entire space. And now if you evaluate this by taking the square, what is going to happen is, the first term will be  $c_a^2 \int d\tau \psi_a^2$  that will be the first term. That you evaluate this after taking the square, but in here what will happen? You can take this  $c_s^2$  square an outside the integral sign.

So, therefore, I can write this as  $c_s^2 \int d\tau \psi_s^2 + c_b^2 \int d\tau \psi_b^2 + 2 c_a c_b \int d\tau \psi_a \psi_b$  multiply by  $\int d\tau \psi_a \psi_b$  integral over the entire space. So, these are the three terms that you will get. But then you see, what is  $\int d\tau \psi_a^2$  is the electron density of atomic orbital. If you integral over the entire space that is going to be equal to unity. So, this is actually equal to 1 because, my atomic orbital is normalized and this integral also an exactly similar function, it is normalized. And therefore, this is 1, but this integral is not equal to 1 it is not 0 also and it is actually this is refer to us the overlap integral and denote by the simple  $S$ . So, then what will happen this object actually works out to be let me just remove this and write the results.

The result is actually  $c_a^2 + c_b^2 + 2 c_a c_b S$  this is the denominator. And that is precisely the denominator that the case in this equation and therefore, I have now to proof that this expression for script  $E$  is correct. And now what is next step? Now this is, now we have a function of  $c_a$  and  $c_b$  the script  $E$  has written in the slide is a function of  $c_a$  as well as  $c_b$ . So, what shall I do, I will I have to find the value of  $c_a$  and  $c_b$  such that, this function has the least value and their, what I will do in the next lecture.

Thank you for listening.