Chemistry Atomic Structure and Chemical Bonding

Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras

Lecture - 41

Hydrogen Molecule Ion: The Molecular Orbital Method

For the next few lectures, we shall look at the Hydrogen Molecule Ion. Possibly the simplest chemical species that we can think of with only one electron and two nuclei both of which have a charge of plus 1.

The study of hydrogen molecule ion using the linear combination of atomic orbital's of the individual hydrogen atoms as constituents, will give us some basic indicators on how to proceed for the larger for the study of the larger molecular systems including many electrons. And the next important species for example, the hydrogen molecule itself which has two electrons and the two electrons of course, it brings in your paradigm shift in quantum chemistry that is it brings in the electron correlation effects. In hydrogen molecule ion the correlation effects are absent.

What we have is one electron shared between shared by the two nuclei. And we have to start with a classical picture of assigning them the coordinates and an approximate geometry.

And then solve the Schrodinger equation for the geometry. And vary the solution as a function of the nuclear geometry. This is well within the born Oppenheimer approximation ok.

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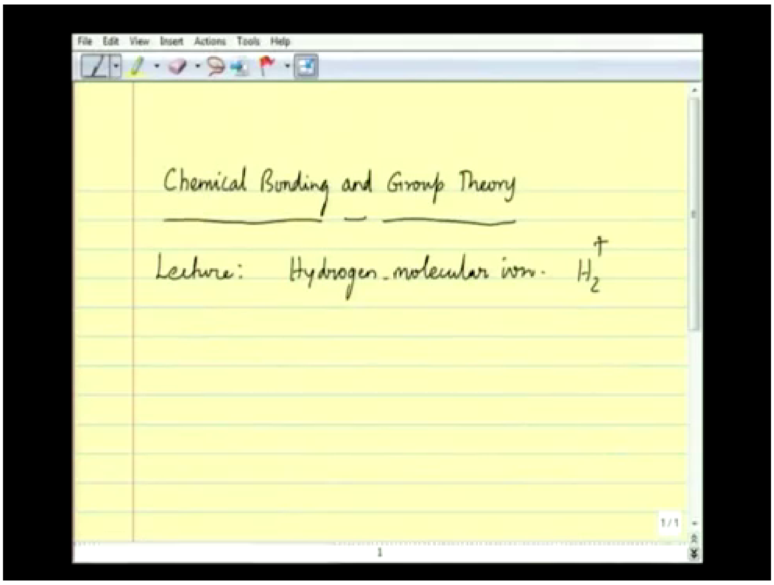

Chemical Bonding and Group Theory

Lecture: Hydrogen molecular ion. H_2^+

So, let us start looking at the problem and also the method of solutions.

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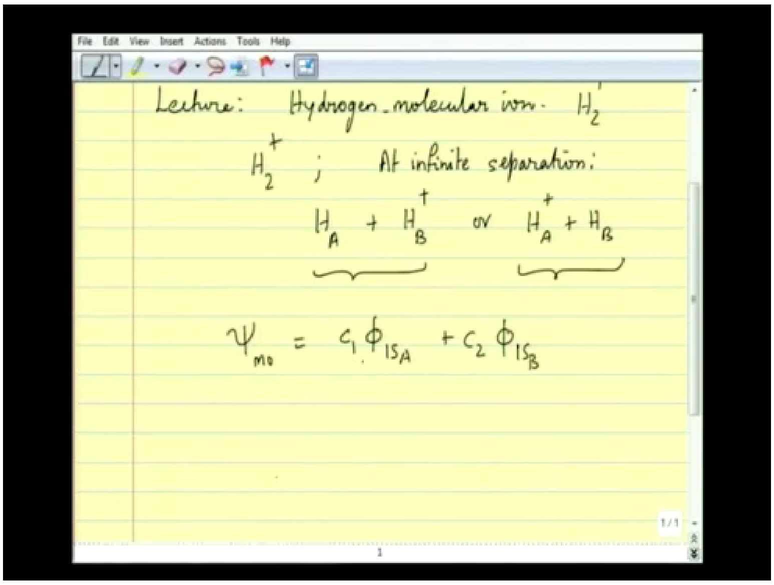

Lecture: Hydrogen molecular ion. H_2^+

H_2^+ ; At infinite separation:

$$\underbrace{H_A + H_B^+} \quad \text{or} \quad \underbrace{H_A^+ + H_B}$$

$$\Psi_{MO} = c_1 \phi_{1S_A} + c_2 \phi_{1S_B}$$

When we talk about the hydrogen molecule ion as H2 plus, at infinite separation of the two nuclei; we have a species H A plus H B plus a proton or H A plus H B the other hydrogen atom and this proton. .

So, the wave function that we can construct for solving this problem.

And using the Schrodinger equation try and obtain solutions for the energies must keep this in mind that when the distance of separation between the two nuclei is very large that the wave function becomes sort of the 1 S electron wave function for the ground state of the electron.

And the 1 s electron is such that is it is with either one of the hydrogen atoms. Therefore, it is possible for us to consider a molecular wave function as a linear combination of the 1 S electron in atom A and the 1 S electron in atom B at infinite separation, but as they come together we have to worry about the linear combination coefficients and see how these two things contribute the in proportion.

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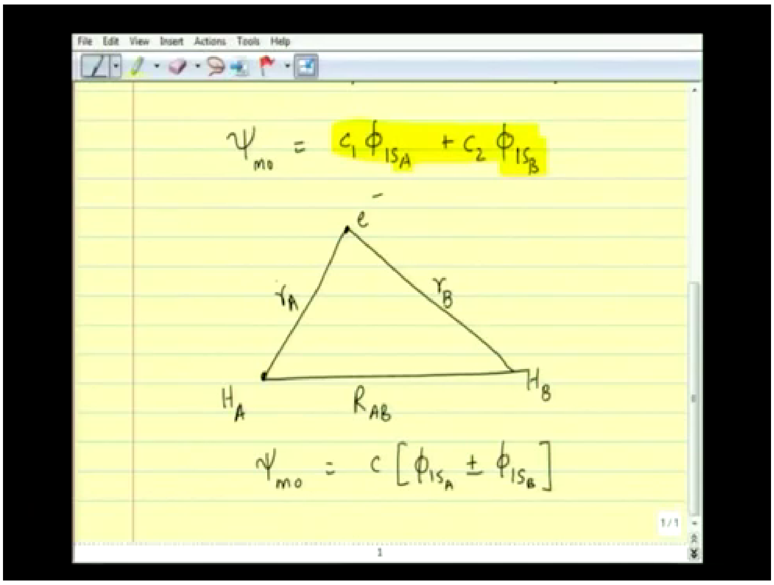

$$\psi_{mo} = c_1 \phi_{1s_A} + c_2 \phi_{1s_B}$$

$$\psi_{mo} = c\left[\phi_{1s_A} \pm \phi_{1s_B}\right]$$

Also if we just draw the picture of the hydrogen molecule ion in a classical sense, I do it isometrically for obvious reasons that we do not know what the electron position or the electron cloud, how it is distributed and so on. So, let us keep the through nuclei and electron and the nuclei at a separation of R AB with the electron with respect to this, this distance being r A and this distance being r B.

So, this gives us a picture of what are the types of what I mean what is the columbic interaction and the kinetic energies and so, we can write the Hamiltonian that is been using the born Oppenheimer approximation. We do not have to worry about the nuclear motion and now you can also see that the molecular orbital that we write down here. Phi 1 S A and phi 1 S B. Distinguishes A and B as two different nuclei, but in principle both nuclei being identical we do not have any reason whatsoever to choose C 2 to be different from C 1. So, one obvious choice would be to write a molecular wave function psi mo as C times phi 1 S A plus or minus phi 1 S B since the probabilities are related to the square of the coefficient C 1 square and C 2 square that is the probability of finding the electron in the 1 1 s orbital of the hydrogen atom A is of course, C 1 square and the probability of finding the electron in the 1S orbital of atom B the hydrogen atom B is C 2 square. And with these two atoms being identical electro negativity I mean there is no reason why C 1 square should be different from C 2 square

Therefore are the most we would expect for real coefficients to C 1 to B plus or minus C 2. So, this is a possible choice please remember this is a proposal.

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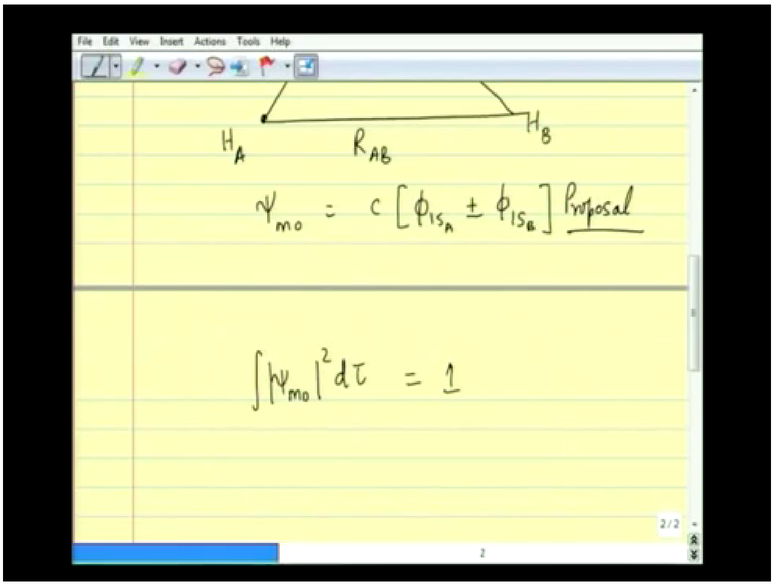

$$\psi_{mo} = c\left[\phi_{1s_A} \pm \phi_{1s_B}\right] \quad \underline{\text{Proposal}}$$

$$\int |\psi_{mo}|^2 d\tau = \underline{1}$$

With this proposal we can impose the condition that we calculate the energy or we solve the Schrodinger equation, but here there is nothing to solve the Schrodinger equation because we have already chosen the wave function. Therefore, given that this is the wave function with the constant C which is a normalization constant essentially, because all that you would do is to make sure that the psi m o square absolute square d tau is one in order for the c is to be the probabilities to be to have the probability interpretation there is nothing to solve here. We only have to calculate the energies.

On the other hand if you do not worry about the C is being equal, but you insist that the C is be different to start with then the Schrodinger equation can be solved with these two coefficients C 1 and C 2 as a 2 by 2 matrix as follows ok.

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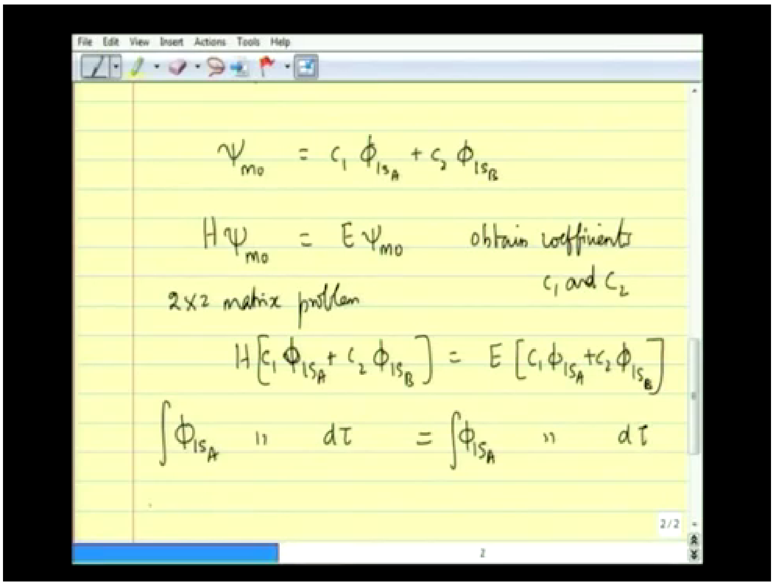

$$\psi_{mo} = c_1 \phi_{1s_A} + c_2 \phi_{1s_B}$$

$H\psi_{mo} = E\psi_{mo}$ obtain coefficients c_1 and c_2

2x2 matrix problem

$$H\left[c_1 \phi_{1s_A} + c_2 \phi_{1s_B}\right] = E\left[c_1 \phi_{1s_A} + c_2 \phi_{1s_B}\right]$$

$$\int \phi_{1s_A} \quad '' \quad d\tau = \int \phi_{1s_A} \quad '' \quad d\tau$$

So, if I have to write psi mo as C 1 phi 1 S A plus C 2 phi 1 S B then I can say that this has to be solved with h psi mo is equal to E psi mo and obtain coefficients C 1 and C 2.

It is no surprise that when you do that you will find the values of C 1 and C 2 to be plus or minus of each other. C 1 is equal to plus or minus C 2. So, it does not matter which way you do you solve this as a 2 by 2 matrix problem for example, because the Hamiltonian has the interactions between the nucleus and the electron and the electron kinetic energy and what you have is H C 1 phi 1 S A plus C 2 phi 1 S B is equal to E C 1 phi 1 S A plus C 2 phi 1 S B.

And therefore, to obtain the coefficients we would try to integrate this with phi 1 S A on the left hand side all of this d tau.

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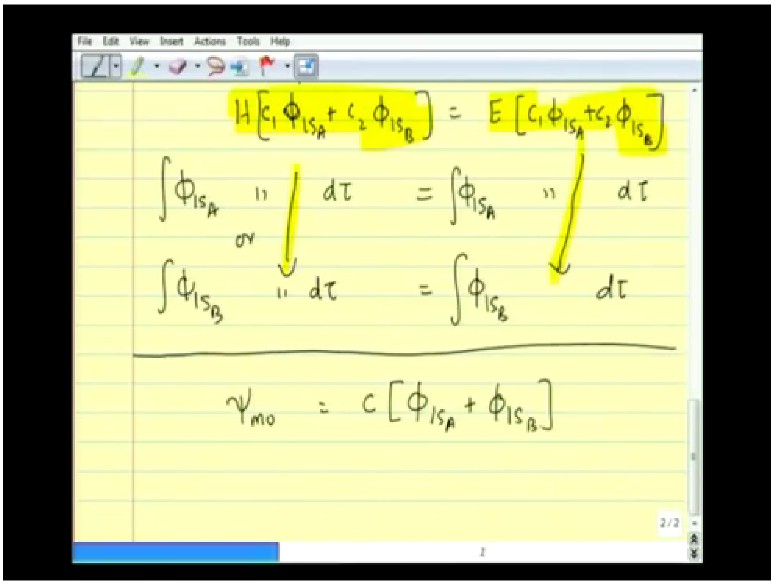

$$H\left[c_1 \phi_{1s_A} + c_2 \phi_{1s_B}\right] = E\left[c_1 \phi_{1s_A} + c_2 \phi_{1s_B}\right]$$

$$\int \phi_{1s_A} \;\; '' \;\; d\tau = \int \phi_{1s_A} \;\; '' \;\; d\tau$$

or

$$\int \phi_{1s_B} \;\; '' \;\; d\tau = \int \phi_{1s_B} \;\; d\tau$$

$$\psi_{mo} = C\left[\phi_{1s_A} + \phi_{1s_B}\right]$$

And we will write the same thing integral of phi 1 S A with all of this d tau or you can do the integration with phi 1 S B the same thing that is h this particular quantity h is to be put in here all of that d tau and that should be equal to the same thing phi 1 S B here. And the all of this d tau since I made the mistake I will make the same mistake here in coloring, but all of this times d tau.

So, you have two equations involving C 1 and C 2. And one can solve this as a matrix problem, but what you would see is not to C 1 and C 2 will turn out to be equal.

So, it does not matter which way we proceed. So, let us stay with the physically reasonable choice namely that psi m o is C times phi 1 S A plus phi 1 S B.

Obviously we are assuming that the1s electron orbital energy is. So, low compared to the 2 s 2 p 3 s 3 p etcetera that in the ground state the molecular orbital has contributions only from the 1 s orbital. It does not have any other orbital contributing to this linear combination ok.

Now, how do we obtain the C, which is the normalization constant we have to impose the condition.

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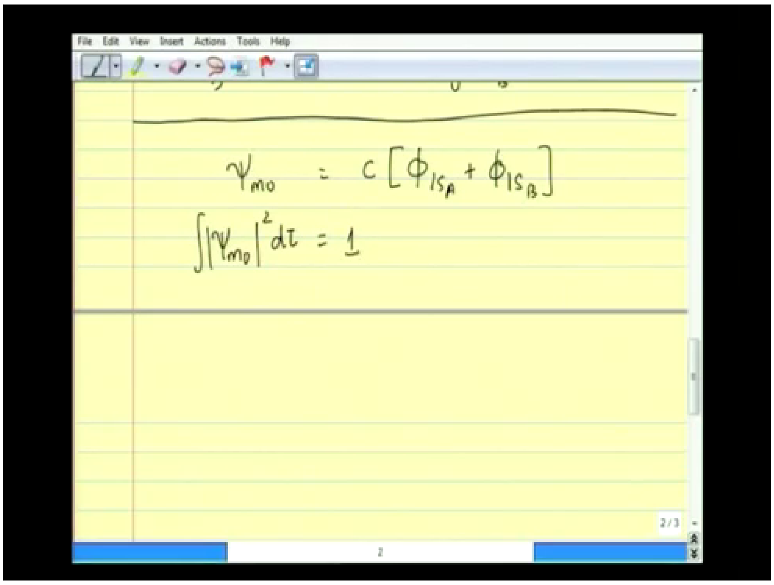

$$\psi_{mo} = c\left[\phi_{1s_A} + \phi_{1s_B}\right]$$

$$\int |\psi_{mo}|^2 d\tau = 1$$

Namely psi mo square d tau is equal to 1 which implies that.

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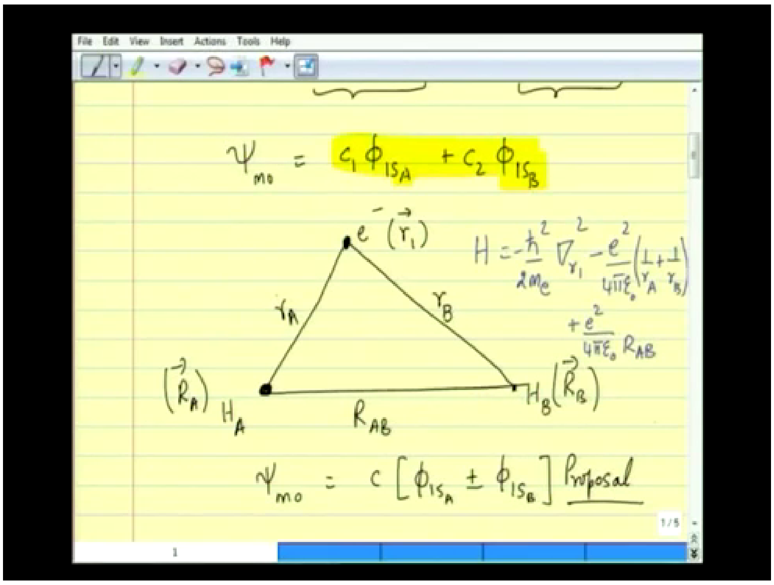

$$\psi_{mo} = c_1\phi_{1s_A} + c_2\phi_{1s_B}$$

$$H = -\frac{\hbar^2}{2m_e}\nabla^2_{r_1} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \frac{e^2}{4\pi\epsilon_0 R_{AB}}$$

$$\psi_{mo} = c\left[\phi_{1s_A} \pm \phi_{1s_B}\right] \text{ Proposal}$$

We do this namely C square phi 1 S A plus phi 1 S B multiplied by phi 1 S A plus phi 1 S B d tau is equal to 1.

Now, please remember that phi 1 S A associates the electron with this atom. The electron has a coordinate say or 1 3 coordinates r 1 x r 1 y or 1 z if you 1 electron. So, we write it as r 1 and the nucleus has the coordinates R A and H B has the coordinates R B.

Then you see that phi 1 S A is of r 1 with respect to this and phi 1 S B is going to be the distance from this nucleus. This r 1 is essentially this is r 1 r a therefore, this R A is going to be the difference between these two vectors the same position is going to be the difference between these two vectors when you say phi 1 S B.

Therefore the two orbital's are centered on two different nuclei. So, there is no reason why the integral that takes the joint functions phi 1 S A and phi 1 S B inside the integral. There is no reason why it should go to 0 or it should vanish.

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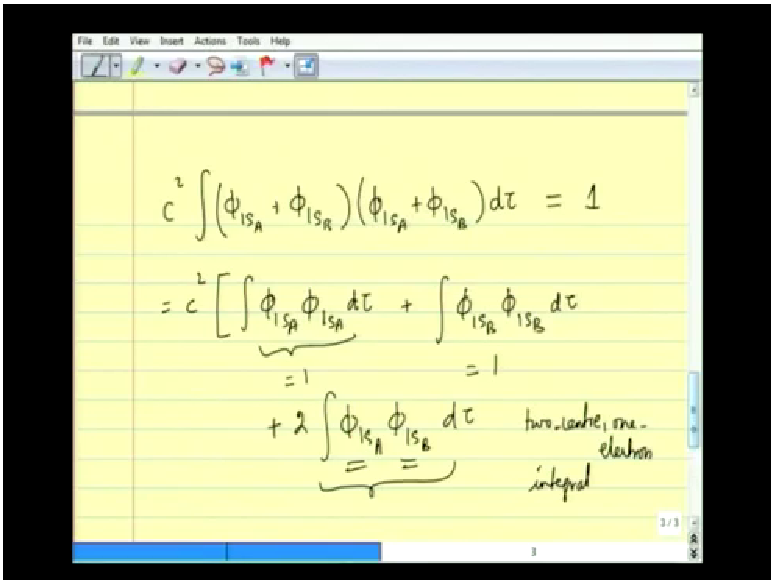

$$c^2 \int (\phi_{1s_A} + \phi_{1s_B})(\phi_{1s_A} + \phi_{1s_B})\, d\tau = 1$$

$$= c^2 \Big[\underbrace{\int \phi_{1s_A} \phi_{1s_A}\, d\tau}_{=1} + \underbrace{\int \phi_{1s_B} \phi_{1s_B}\, d\tau}_{=1}$$

$$+ 2 \underbrace{\int \phi_{1s_A} \phi_{1s_B}\, d\tau}$$

two-centre, one-electron integral

So, in doing this we come up with this additional quantity namely C square the first integral is phi 1 S A, phi 1 S A d tau which is obviously, the normalization of the 1 S into wave function associated with the atom a and therefore, this is equal to 1 plus the integral phi 1 S B phi 1 S B d tau. Which is also the normalization integral for the 1 S B the 1 S orbital of the B, B atom B the electron in the atom B plus twice the integral phi 1 S A phi 1 S B d tau. Where both 1 S A and 1 S B are centered on two different atoms and therefore, this is not generally zero this is a 1 electron to center integral two center 1 electron integral and this is known as the overlap integral. S A B.

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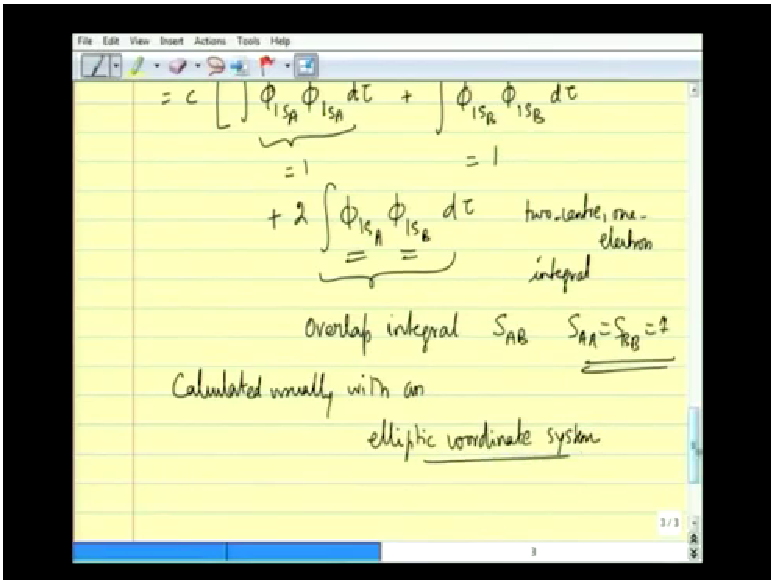

$$= c \left[\underbrace{\int \phi_{1s_A} \phi_{1s_A} d\tau}_{=1} + \underbrace{\int \phi_{1s_B} \phi_{1s_B} d\tau}_{=1} \right.$$

$$+ 2 \underbrace{\int \phi_{1s_A} \phi_{1s_B} d\tau}$$

two-centre, one-electron integral

Overlap integral S_{AB} $\underline{\underline{S_{AA} = S_{BB} = 1}}$

Calculated usually with an elliptic $\underline{\text{coordinate system}}$

Now obviously, S AA is equal to S BB is equal to 1. If you wish to associate this with the previous lecture on variational method in choosing basis functions, which are not necessarily orthogonal and therefore, the Hamiltonian matrix containing the overlap integrals of this various basis functions here is the first case that one has to calculate the overlap integral ok.

The process of calculating the overlap integral is a separate process, we will we will not worry about it in this lecture. In one of the examples I will use the right coordinate system and probably go through a textbook example of how to calculate the overlap integral using what are known as the elliptic coordinates ok calculated usually with an elliptic coordinate system.

But instead of doing that here, let us proceed with the analysis and come up with some answers for the hydrogen molecular ion energy and the hydrogen molecular ion orbital's Let us try and understand the qualitative features first and then we go to the quantitative evaluation of these orbital wave function integrals and so, on

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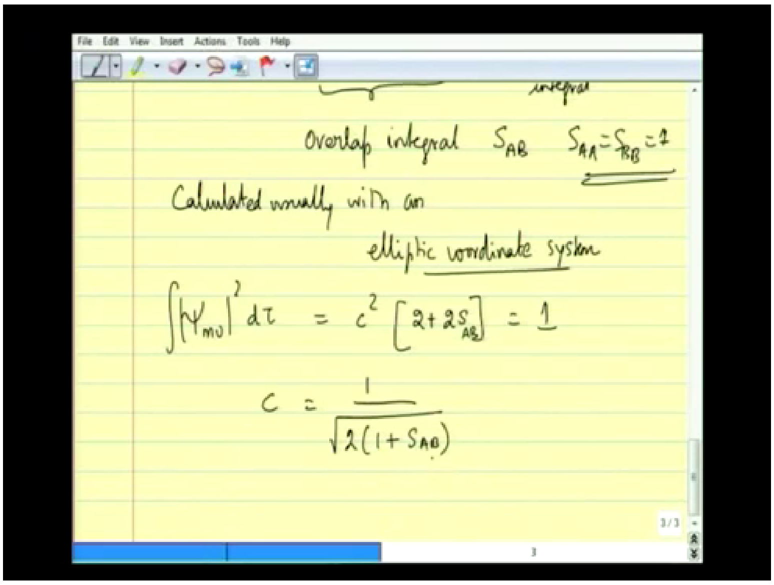

integral

Overlap integral S_{AB} $\underline{\underline{S_{AA}=S_{BB}=1}}$

Calculated usually with an

elliptic coordinate system

$$\int |\psi_{mo}|^2 d\tau = c^2 \left[2+2S_{AB}\right] = 1$$

$$C = \frac{1}{\sqrt{2(1+S_{AB})}}$$

So, we need to therefore, calculate the psi mo integral square d tau we need to put that a C squared times. You recall that there are two unit integrals and twice the overlap integral. So, it is 2 plus 2 S and that should be equal to 1 S is S S B. Therefore, C is equal to 1 by square root of 2 into 1 plus S A B ok. This is because we chose the combination psi mo to be C 1 phi 1 S A plus phi 1 S B which was the plus.

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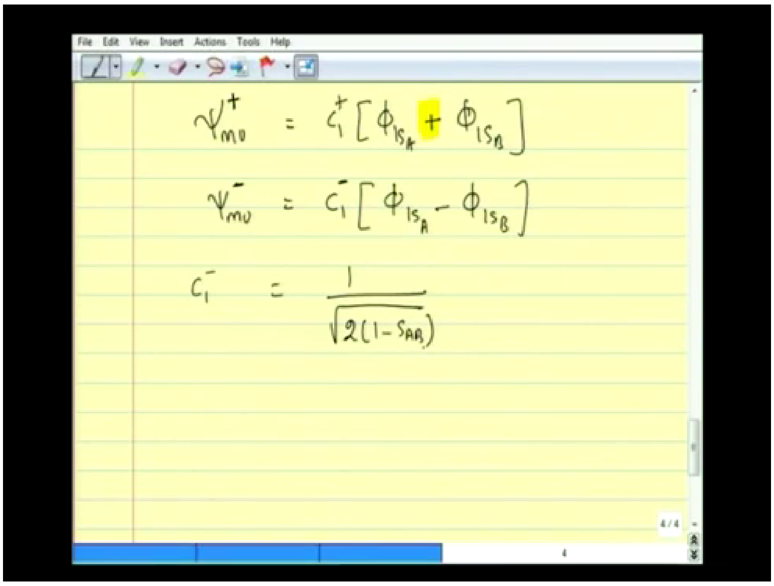

$$\psi_{mo}^{+} = c_1^{+}\left[\phi_{1s_A} + \phi_{1s_B}\right]$$

$$\psi_{mo}^{-} = c_1^{-}\left[\phi_{1s_A} - \phi_{1s_B}\right]$$

$$c_1^{-} = \frac{1}{\sqrt{2(1-S_{AB})}}$$

If we have to take the other linear combination psi mo let us call this as the plus combination and we will call this as the minus combination then you have C 1 if you have phi 1 S A minus phi 1 S B then the C 1 you call this as plus and this is minus then you see that C 1 minus will be by exactly the same argument will be rho 2 into 1 minus S A B the overlap integral.

Therefore, we have the wave functions let us choose the plus 1 for the rest of the calculation and we can do the same thing for the minus later.

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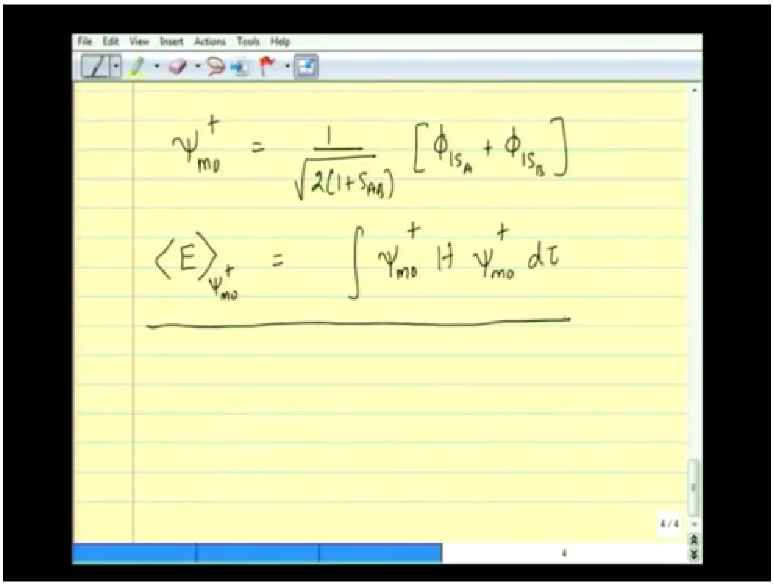

$$\psi^{+}_{mo} = \frac{1}{\sqrt{2(1+S_{AB})}} \left[\phi_{1s_A} + \phi_{1s_B}\right]$$

$$\langle E \rangle_{\psi^{+}_{mo}} = \int \psi^{+}_{mo} \, H \, \psi^{+}_{mo} \, d\tau$$

So, we will choose that square root of 1 by root 2 into 1 plus S A B phi 1 S A plus phi 1 S B. And we shall calculate the energy for this molecular orbital psi mo plus as the integral psi mo plus the Hamiltonian psi mo plus d tau.

So, this is the average value that we have to calculate because we have already chosen the wave function to be psi mo plus. All that we can do is to calculate the energy and any other property that we need to worry about and the process is again fairly straightforward some interesting things happen. So, let us look at the process.

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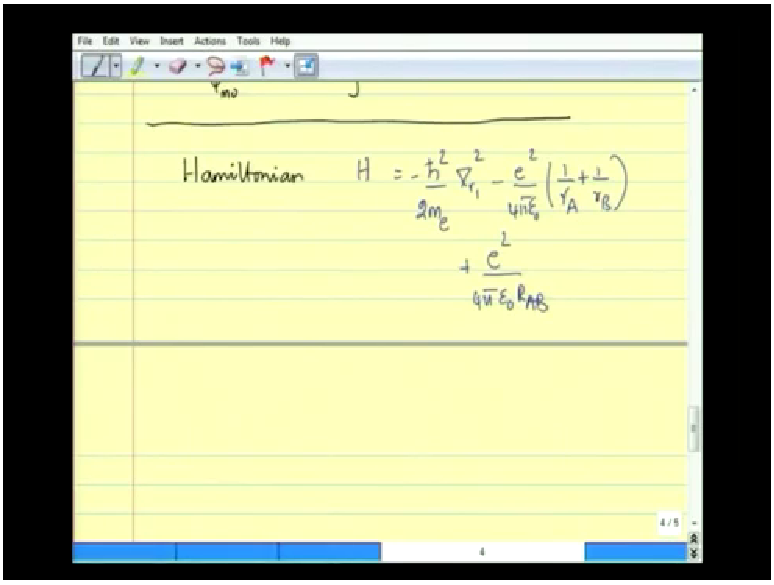

ψ_{MO}

Hamiltonian $H = -\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A}+\frac{1}{r_B}\right) + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$

So, now what is the Hamiltonian? Let us go back to the picture. I will write the Hamiltonian here and then copied back to the bottom that is a choose a slightly different color it is ok. Let us do that. So, the Hamiltonian here if you look at it in the born Oppenheimer limit or the approximation that we have the nuclei do not move we will use the clamped nucleus approximation.

The kinetic energy is due to the electron only and therefore, what you have is the H is given by minus h bar square by 2 m e the del or 1 square which is the 3 derivatives dou square by dou r 1 x square and r 1 y square and. So, on this is the kinetic energy term p square by 2 mu e. And then we have the potential energy which is a sum of three terms namely the electron nucleus a columbic potential energy attraction electron nucleus b columbic potential energy again attraction and the nucleus A the nucleus B repulsion potential energy.

So, we have three terms namely minus e square by 4 pi epsilon naught. The attraction is 1 by r A plus 1 by r B. And we have the nuclear nuclear repulsion energy which is plus e square by 4 pi epsilon naught R A B.

So, we will just copy this back here and start looking at the solution. The Hamiltonian H is minus h bar square by 2 m e del r 1 square minus e square by 4 pi epsilon naught 1 by r A plus 1 by r B plus e square by 4 pi epsilon naught R A B. So, let me switch back to color ok. So, that is a Hamiltonian.

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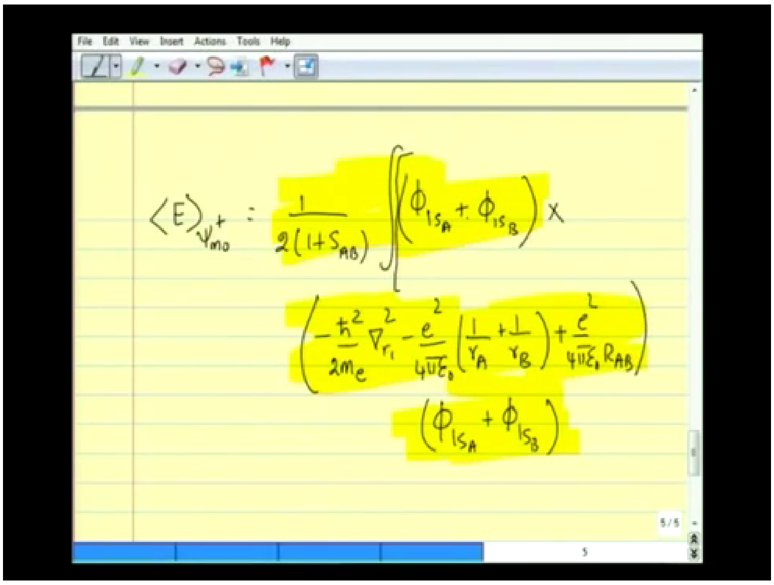

$$\langle E \rangle_{\psi_{mo}^{+}} = \frac{1}{2(1+S_{AB})} \int \left(\phi_{1s_A} + \phi_{1s_B}\right) \times \left(-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}\right) \left(\phi_{1s_A} + \phi_{1s_B}\right)$$

Therefore the average energy E or the expectation value E for the states psi mo plus is going to be.

Because there is a psi star psi the normalization constants appear as 2 into 1 plus S A B outside. And then you have the integral phi 1 S A plus phi 1 S B times within this integral we have the Hamiltonian minus h bar square by 2 m e del r 1 square minus e square by 4 pi epsilon naught into 1 by r A plus 1 by r B plus e square by 4 pi epsilon naught R A B all of which acting on the same wave function phi sorry the same wave function phi 1 S A plus phi 1 S B.

So, this is one long integral the wave function the Hamiltonian acting on the wave function. Now if we look at the A and B. We see some symmetry here because the label A and B are arbitrary the labels are arbitrary and therefore, this Hamiltonian can be simplified further.

So, what I would do is before we proceed to simplify this equation. Let me pass for a break and then in a few seconds we will come back, but this is the quantity that we need to calculate. And the when you have psi mo minus you will do exactly the same calculation except 1 minus S AB phi 1 S A minus phi 1 S B phi 1 S A minus phi 1 S B is the other energy average energy or the expectation energy for the other molecular state. So, we need to look on both of them let us do that after we pause for a short break we will come back in a few seconds.

So, let us now look at the integral more carefully term by term. The first term that I would like to look at is see you have look at this there is two terms here and then 1 2 3 4 4 here and a 2. So, there are 16 terms if you expanded them algebraically, but a lot of them are equal or very similar.

So, we will see them that similarity now. Let us take the first 1 phi 1 S A and the Hamiltonian minus h bar square by 2 me del r 1 square minus a square by 4 pi epsilon naught 1 by r A and phi 1 S A. let us take the first term.

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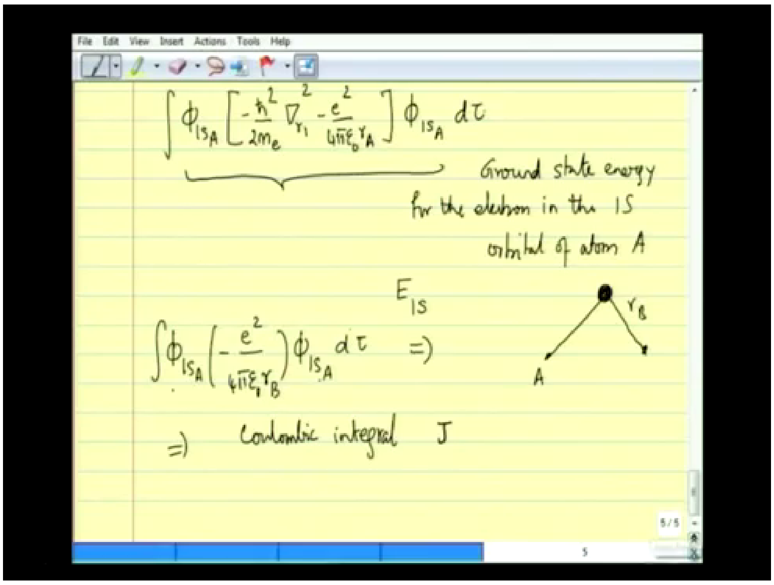

$$\underbrace{\int \phi_{1S_A}\left[-\frac{\hbar^2}{2m_e}\nabla^2_{r_1}-\frac{e^2}{4\pi\varepsilon_0 r_A}\right]\phi_{1S_A}\,d\tau}$$

Ground state energy for the electron in the 1S orbital of atom A

E_{1S}

$$\int \phi_{1S_A}\left(-\frac{e^2}{4\pi\varepsilon_0 r_B}\right)\phi_{1S_A}\,d\tau \Rightarrow$$

$\Rightarrow$ Coulombic integral J

So, we leave the constants out, but the first one that we are looking at is phi 1 S A minus h bar square by 2 m e del r 1 square minus e square by 4 pi epsilon naught r A phi minus a d tau. Quite obviously, this is the electron in the hydrogen atom A the kinetic energy of the electron and the potential energy of the electron with respect to the nucleus a therefore, this is exactly the ground state energy for the electron in the 1 s orbital of atom A. So, if I have to follow the notation that I use in my notes I would call this well it is E 1 S ok.

So, that is the first term. The next term that I would like to look at is phi 1 S A see we since we started with phi 1 S A and we have looked at part of it let us complete the rest of it namely phi 1 S A minus e square by 4 pi epsilon naught r B phi 1 S A d tau. This if you look at carefully the electron you are looking at the r B is this and this is the a nucleus the charge density of the electron in that region phi 1 S A phi 1 S A divided by a distance and therefore, you can look at this as the columbic interaction energy or a columbic integral for the electron with respect to this nucleus ok.

So, what you have is a this integral is called the Columbic integral. In that a classical limit you can see this as a charged density divided by the distance of the electron from each others center. Therefore, you have this as a columbic integral and the notation is that it is called J, we will write that as J and then we will sum it up.

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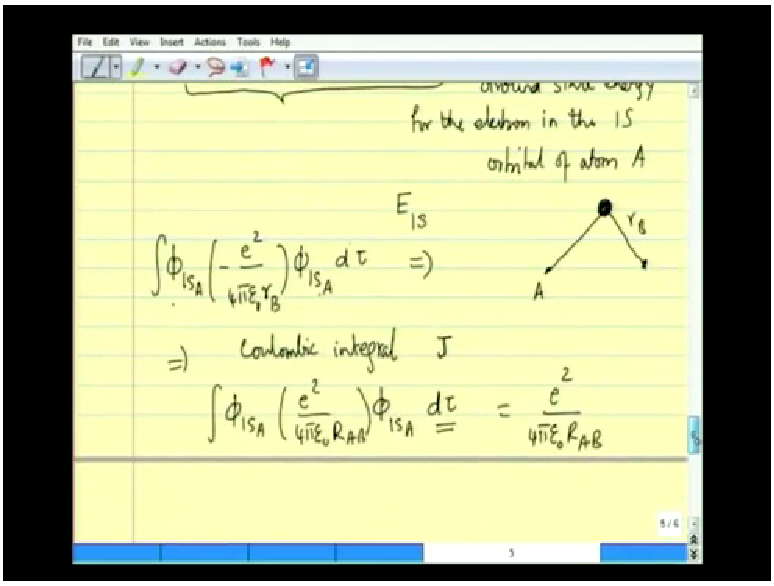

ground state energy
for the electron in the 1S
orbital of atom A

E_{1S}

$\int \phi_{1S_A}\left(-\frac{e^2}{4\pi\varepsilon_0 r_B}\right)\phi_{1S_A}\, d\tau \Rightarrow$

$\Rightarrow$ Coulombic integral J

$\int \phi_{1S_A}\left(\frac{e^2}{4\pi\varepsilon_0 R_{AA}}\right)\phi_{1S_A}\, d\tau = \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$

Now that is with respect to phi 1 S A and the last term that we have is the term namely phi 1 S A e square by 4 pi epsilon naught R A B phi 1 S A d tau. And this is a straightforward nuclear repulsion term because the integral d tau is an integral over the electron coordinates the positions of the electron coordinates and the, the R A B the small depend on the electron coordinates it is the inter nuclear separation.

So, this is given that the phi 1 S A phi 1 S A integral itself is normalized this is nothing other than the nuclear electron repulsion energy 4 pi epsilon naught R A B. Maybe I should make sure that with the minus sign I will call it as J it is fine.

So, this is basically 1 by R A B times the charge the integral that the d tau does not contain any variable from the nuclear positions. Therefore, this is a simple additional term. Now that is as far as the phi 1 S A on this whole thing is concerned I have only taken the phi 1 S A.

Now, we have to do the same exercise with phi 1 S A everything and phi 1 S B. So, let us write this the remaining.

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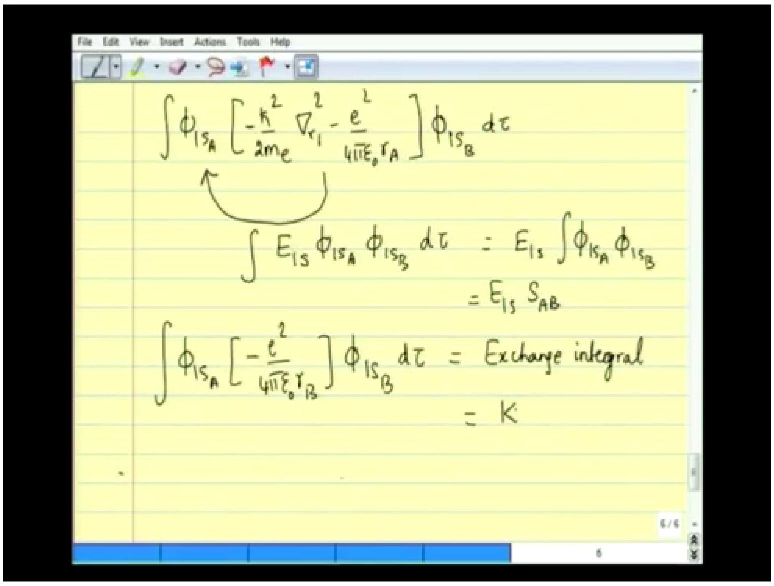

$$\int \phi_{1s_A}\left[-\frac{\hbar^2}{2m_e}\nabla^2_{r_1}-\frac{e^2}{4\pi\epsilon_0 r_A}\right]\phi_{1s_B}\,d\tau$$

$$\int E_{1s}\,\phi_{1s_A}\,\phi_{1s_B}\,d\tau = E_{1s}\int \phi_{1s_A}\,\phi_{1s_B}$$

$$= E_{1s}\,S_{AB}$$

$$\int \phi_{1s_A}\left[-\frac{e^2}{4\pi\epsilon_0 r_B}\right]\phi_{1s_B}\,d\tau = \text{Exchange integral}$$

$$= K$$

The next set with the phi 1 S A would be phi 1 S A minus h bar square by 2 m e del r 1 square minus e square by 4 pi epsilon naught r A we will just keep that term, but then put in phi 1 S B d tau. This is also straightforward you remember that when you put the Hamiltonian operator between the two wave functions. The Hamiltonian operator can act on the function on the right hand side to give you whatever the in this case of course, the energy.

But it can also act on the left side because the Hamiltonian (Refer Time: 30:03) operator. And if you think of the Hamiltonian acting on the function on the left hand side you have nothing other than h acting on phi 1 S A. This is the h of the electron in the 1 s orbital of atom 1 and therefore, this will still give you E 1 S times phi 1 S A.

Therefore this integral will become the integral a 1 S phi 1 S A phi 1 S B d tau. Which if you remember E 1 s is a constant the 1 s electron energy it is nothing, but E 1 s times the integral phi 1 S A phi 1 S B and therefore, this is E 1 s times the S AB ok as simple as that.

Next the integral that we are still left with, with the first term phi 1 S A or the following namely minus E square by 4 pi epsilon naught r B phi 1 S B d tau. Now there is no classical interpretation for a quantity like this which involves the electron centered at one nucleus that is the centered at one atom phi 1 S A. And the wave function with the coordinate with the center at another nucleus and the 1 over r. There is no this is this does not have any classical interpretation and it is called exchange integral.

It is purely a quantum mechanical term, integral due to the fact that we took the linear superposition of wave functions and put the Hamiltonian and calculated it. The linear superposition is a quantum mechanical idea and this integral is a quantum mechanical quantity this is called exchange integral. And the usual notation for that is K.

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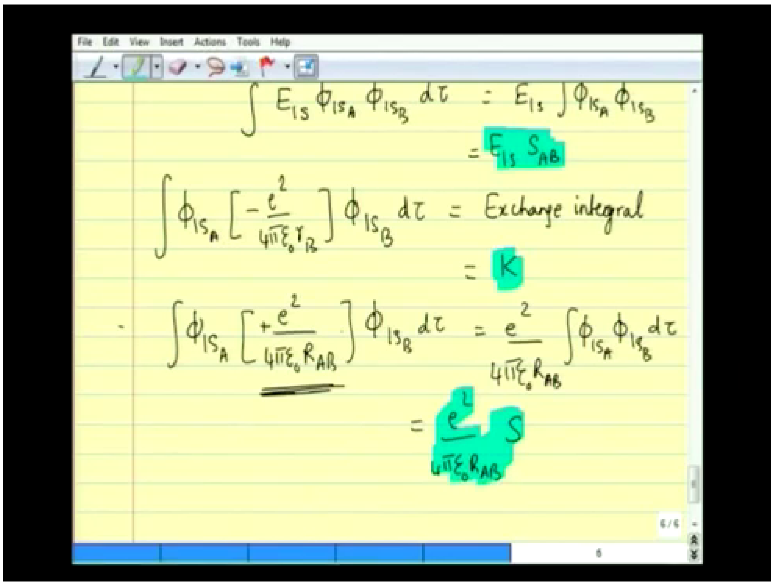

$$\int E_{1s}\phi_{1s_A}\phi_{1s_B}\,d\tau = E_{1s}\int \phi_{1s_A}\phi_{1s_B}$$

$$= E_{1s}S_{AB}$$

$$\int \phi_{1s_A}\left[-\frac{e^2}{4\pi\varepsilon_0 r_B}\right]\phi_{1s_B}\,d\tau = \text{Exchange integral}$$

$$= K$$

$$\int \phi_{1s_A}\left[+\frac{e^2}{\underline{\underline{4\pi\varepsilon_0 R_{AB}}}}\right]\phi_{1s_B}\,d\tau = \frac{e^2}{4\pi\varepsilon_0 R_{AB}}\int \phi_{1s_A}\phi_{1s_B}\,d\tau$$

$$= \frac{e^2}{4\pi\varepsilon_0 R_{AB}}S$$

And the last term with phi 1 S A on the left hand side is of course, the minus e square sorry plus e square by 4 pi epsilon naught R A B phi 1 S B d tau. Again you remember that R A B does not contain any coordinates of the electron in it and therefore, this integral is essentially this constant coming out R A B and the integral phi 1 S A phi 1 S B d tau which is e square by 4 pi epsilon naught R A B times S.

So, what we have done in this exercise let us collect all the eight quantities that we have with phi 1 S A here. Ok phi 1 S A. Let me do a little more messy thing here let us put the phi 1 S A here and I have taken the everything all of this. And I have taken phi 1 S A and phi 1 S B those are the eight quantities that we have calculated.

So, far and the answer was there is some namely E 1 S plus J plus K. Let us write that E 1 s plus J plus R A B this term. Then we had E 1 S, S A B and we had K and we had e square by 4 pi epsilon naught R AB Ss. So, these are the five results that we got.

Now, what is left over is the same integration process that needs to be carried out with the quantity phi 1 S B here everything here and everything here phi 1 S A plus phi 1 S B. So, exactly eight more terms need to be calculated. Now what is the difference between A and B that is your choice and my choice I mean if I had to switch the A and B around, how are we going to get any different result from what we already got.

Therefore, by looking at the symmetry of the whole thing right away I can say I am going to get twice the result the moment I put in the phi 1 S B, and calculate this result I am going to get exactly the same answer as I got for phi 1 S A and therefore, the answer is exactly twice and that 2 and this 2 will sort of cancel each other. So, what do we have therefore, as the energy.

This is true because the nuclei are identical.

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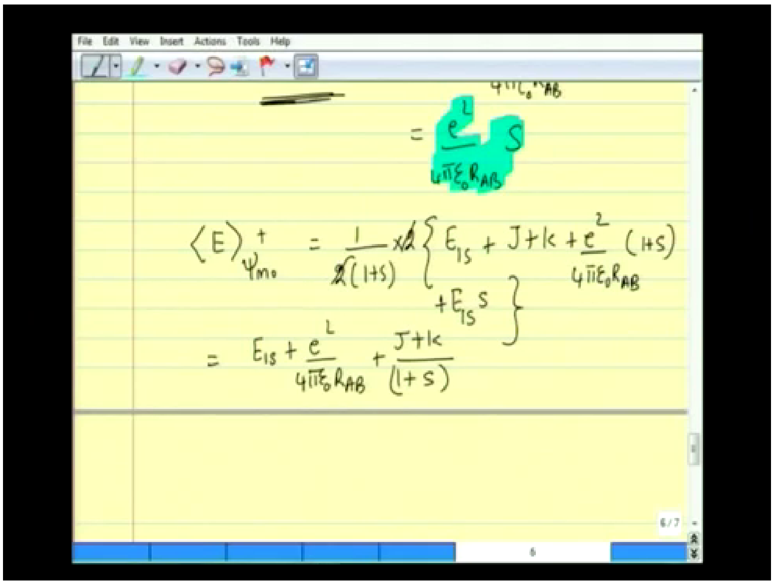

$$= \frac{e^2}{4\pi\varepsilon_0 R_{AB}} S$$

$$\langle E \rangle^{+}_{\psi_{mo}} = \frac{1}{\cancel{2}(1+S)} \times \cancel{2} \left\{ E_{1s} + J + k + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}(1+S) + E_{1s} S \right\}$$

$$= E_{1s} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}} + \frac{J+k}{(1+S)}$$

So, the final answer therefore, for the average value E psi mo plus is going to be 1 by 2 times 1 plus S into 2 times E 1 S plus J plus K plus e square by 4 pi epsilon naught R A B into 1 plus S plus E 1 S times S.

So, this will simplify to goes away and the 1 plus S can be cancelled with the E 1 S term and plus e square by 4 pi epsilon naught R A B that also has the 1 plus s canceling and what is left over is J plus K divided by 1 plus S (Refer Time: 36:36). So, that is all we have.

The integrals J and K are both negative, E 1 S is also negative please remember that is minus 13.6 electron volts for the hydrogen atom the ground state 1 s electron energy s is a positive quantity the overlap integral because both phi 1 S A and phi 1 S B the 1 s wave functions are positive everywhere therefore, the product of this and the integral of that cannot be negative.

So, you have a small positive quantity, you have negative quantities you have E 1 S which is a negative quantity and the only thing that contributes positively here is the E square by 4 pi epsilon naught R A B and therefore, you see as R A B changes you are going to have varying values for the psi mo plus.

But this is actually a the inter nuclear separation this electron energy is calculated for 1 inter nuclear separation. If we have to calculate the electron energy for a different inter nuclear separation we will get different energies.

So, the whole thing is a negative energy and it is less than E 1 s and therefore, the psi mo plus leads to an E mo plus less than E 1 s.

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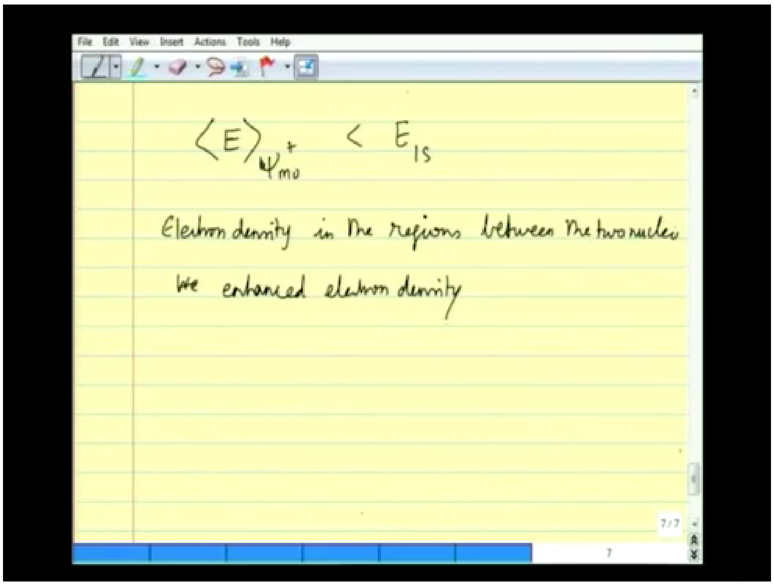

$$\langle E \rangle_{\psi_{mo}^{+}} < E_{1s}$$

Electron density in the regions between the two nuclei

We enhanced electron density

Also if you look at the electron density, in the regions between the two nuclei we will see an enhanced electron density, due to the overlap.

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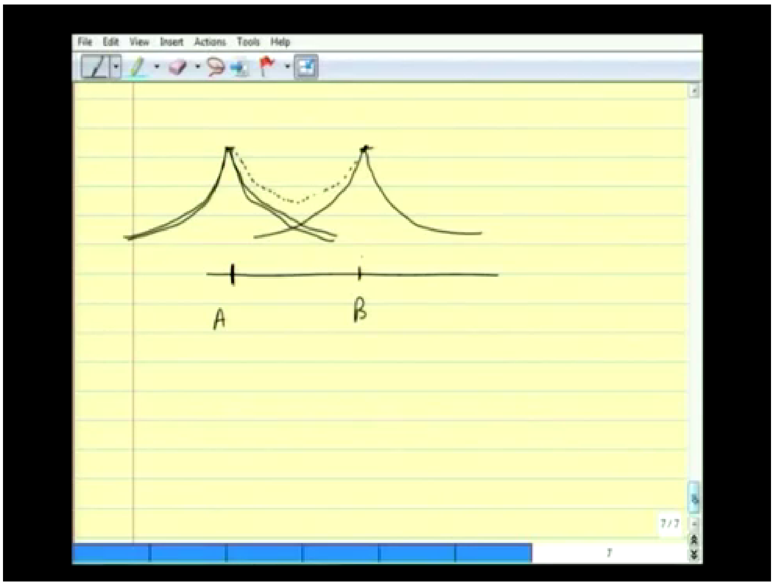

Let us look at that again we have the two nuclei here A and B well maybe not this for let us a put the B a little bit closer and we have the R A B separation. If the electron wave function is a 1 S A wave function obviously, the 1 s wave function for this you remember when this has the 0, is going to go something like this it is an exponential function.

Now, the phi 1 SB is exactly the same also has the same maximum is again since the radius is unsigned quantity the electron wave function on a sphere of r is going to vary like this. For the phi 1 S B the electron wave function is going to be something like this ok.

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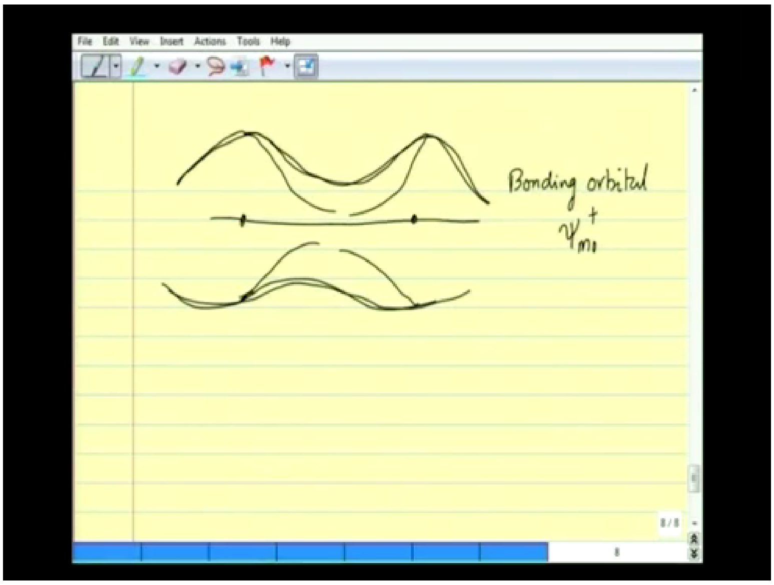

This is positive this is positive all of all quantities are positive. Therefore, now if you see the overall electron wave function C 1 plus C 2 plus that phi 1 S A and phi 1 S B the sum of the two is obviously, like that increased value.

So, if you take the square of that and calculate the electron density you would see that the electron density due to the psi mo plus that is all is going to be an increased quantity than the individual quantities.

So, this increase in the electron density which is cylindrical in this case because the coordinate dependent is only the inter nuclear separation all around that at any given point in a cylinder you see that the electron density is going to be the same. Therefore, this is a cylindrical enhanced electron density and for obvious reasons this is called the bonding orbital. Because now the electron is more likely to be found between the two nuclei for this particular molecular orbital and it is called the bonding orbital or psi mo plus.

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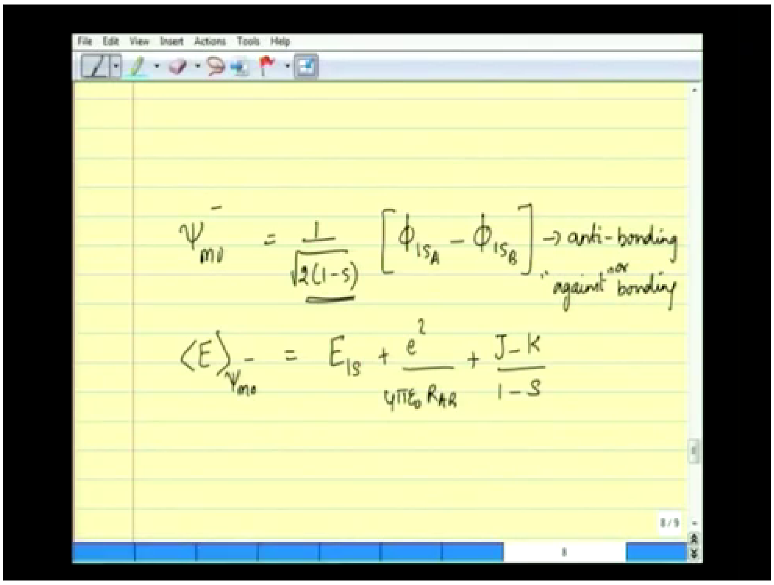

$$\psi_{mo}^{-} = \frac{1}{\underline{\sqrt{2(1-S)}}} \left[\phi_{1S_A} - \phi_{1S_B} \right] \rightarrow \text{anti-bonding}$$

"against" or bonding

$$\langle E \rangle_{\psi_{mo}^{-}} = E_{1S} + \frac{e^2}{4\pi\epsilon_0 R_{AB}} + \frac{J-K}{1-S}$$

On the other hand if we were to do the same calculation with the psi mo minus which is 1 by root 2 into 1 minus S phi 1 S A plus minus phi 1 S B. If you were to do this calculation you recall that the integral that we did evaluate the sixteen in terms of the evaluator by doing the first eight and then multiplying the whole thing by two the integral that we evaluated is going to have 1 minus s and therefore, the corresponding quantities.

So, let me go back and here all that people would have is E 1 S will remain the same this will remain the same, but the integral J plus K by 1 plus S will change over to J minus K by 1 minus S. So, the answer would be if you calculate E for psi m o minus. The answer would turn out to be E 1 S plus e square by 4 pi epsilon naught R A B which is a constant for this then what you will have is plus J minus K by 1 minus S.

When you actually calculate this value using all the wave functions and the integrals J and K you evaluate. You find out that the e psi mo minus is always greater than the E 1 S hydrogen. And therefore, this is a case in which the energy for this particular molecular orbital wave function is higher than the energy of the 1 s orbital. And the electron density that you look at because of the minus sign the electron density in the inter nuclear region between the two nuclei the electron density is depleted from what would be the electron density due to either 1 of these 1 s orbitals alone.

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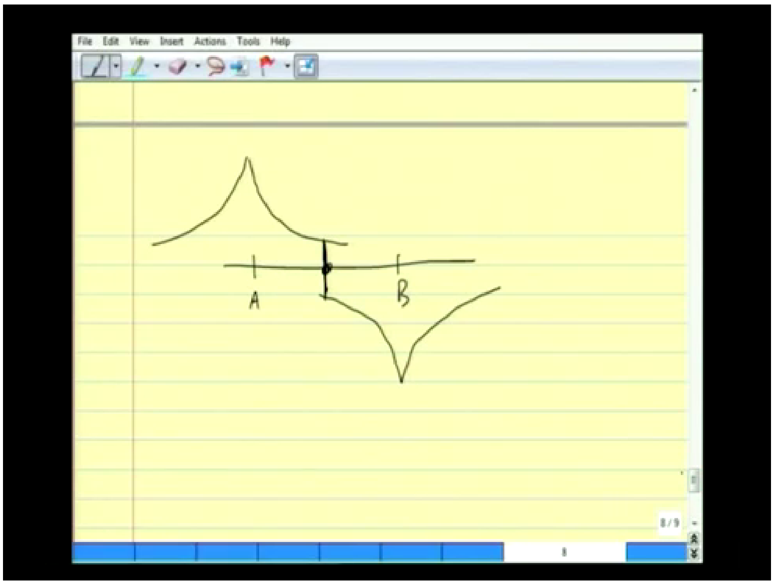

So, if you draw this picture on the wave function A and B exactly the same picture that you draw, if you choose the phi 1 S A same with the positive sign of course, the wave function is going to be like this and if B is the phi 1 S B is with a negative sign obviously, you are going to have the wave function come out like that and the wave function come out like that. And the sum of the two wave functions at exactly the midpoint you see it is going to be 0 this is 0 at this point.

Therefore 0 at this point and also the electron density you will see that the value of the electron density at this point is 0 and the value of the electron density in any intermediate point between A and B is going to be less than the electron density due to the nucleus A alone or due to the nucleus B alone therefore, the electron density is depleted.

So, for obvious reasons we therefore, call this psi mo minus as the anti bonding against bonding call this as anti bonding or against bonding. It is a higher energy.

So, these are some of the basic results that one looks at when you study the hydrogen molecule ion closely. And where are we with respect to the energy that we calculate what is the experimental energy? Please remember variational principle tells you that the exact energy that you obtain for the system is always going to be lower than any energy that you calculate using any combination of a functions except when those wave functions coincide exactly with the Eigen function of the system, which in this case we know it is not therefore, you see that the experimental energies that we can calculate that we obtained from spectroscopy and the energies that we calculate for the psi mo plus and psi mo minus as a function of the inter nuclear distance the energy.

Here is as we vary the nuclear distance we calculate electronic energies for different nuclei nuclear configurations and then we find a minimum for the psi mo plus we do not find any minimum for the psi mo minus and therefore, the picture that we have when we do this.

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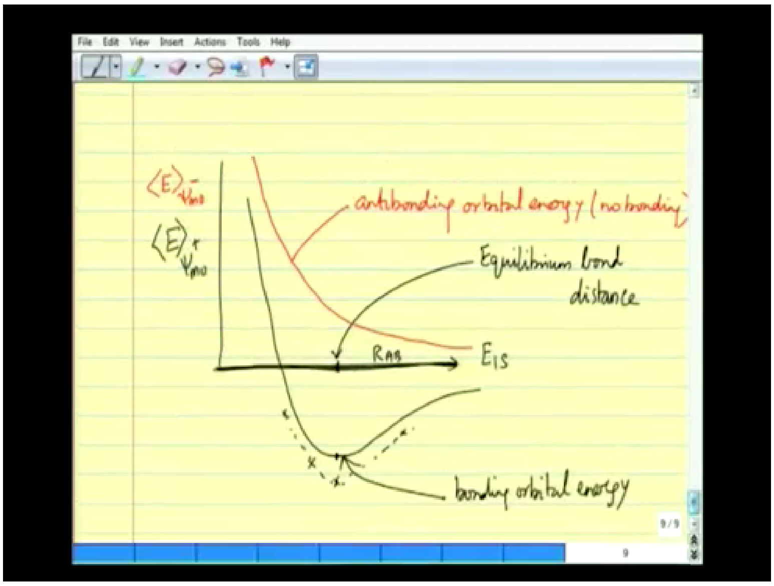

For E plus this E psi m o plus if we do that the picture we have is if this is like the E 1 s then what you have is as a function of R A B the coordinate here is the inter nuclear separation or A B. You see that there is a minimum that is some value of r which we call as the equilibrium bond distance.

If on the other hand if we calculate the e psi mo and for the orbital with the minus sign if we do that e psi mo minus and we plot the energy as a function of R A B what we get out is that never goes to a minimum it is always higher than the E 1 S hydrogen energy. And therefore, this is the anti bonding orbital energy no bonding this is the bonding orbital energy as a function of the inter nuclear positions for A B.

And the experimentally when we find out what the energies are I do not have the experimental graph, but I will put those things in the lecture notes that you will see on the website the experimental graph seems to be some there of course, you do not have a continuous graph for experiments you know you determine the things spectroscopically. So, you have something like that.

So, if you were to connect to this the experimental minimum is lower than the minimum that you calculated using this phi 1 SA and phi 1 S B. Therefore, how do we now try to get the best value that matches close to the experiment ok. We have choices we chose the experimentally the basis function as phi 1 S A and phi 1 S B. Now let us look at a simple logical factor and see whether we can do a variational calculation on that with that I will close this lecture.

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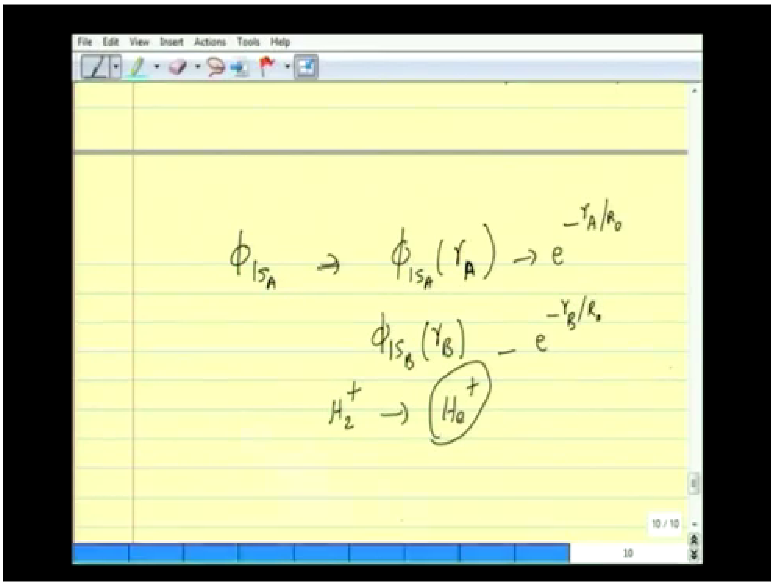

$$\phi_{1s_A} \to \phi_{1s_A}(r_A) \to e^{-r_A/R_0}$$

$$\phi_{1s_B}(r_B) - e^{-r_B/R_0}$$

$$H_2^+ \to \boxed{He^+}$$

When you talk about phi 1 S A you are talking about the wave function phi 1 S A at the position of the nucleus I mean the electron which is r 1 which is r A that is the distance from the nucleus a and you know that this is like e to the minus r A by the Bohr radius what do you call that R 0 And there is a normalization constant phi 1 S B would be obviously, the inter nuclear distance I mean the electron nuclear distances r B it will be like e to the minus r B by r naught the Bohr radius.

This is with the assumption that when the two nuclei are infinitely far apart from each other that these are the corresponding limiting wave functions. But what happens if the nucleus one nucleus falls on the other. So, that the h 2 plus becomes a helium plus. I mean let us forget the fact that the proton repulsion is going to be enormous etcetera, but let us assume that the r AB goes to 0. And therefore, H 2 plus becomes a helium plus this is an exactly solvable problem because you see this is a 1 electron system with the nuclear charges it is equal to 2 and therefore, the wave function is not any one of these it is not a linear combination of any one of these but it is essentially going to be e to the minus 2 r by A naught the Bohr radius ok.

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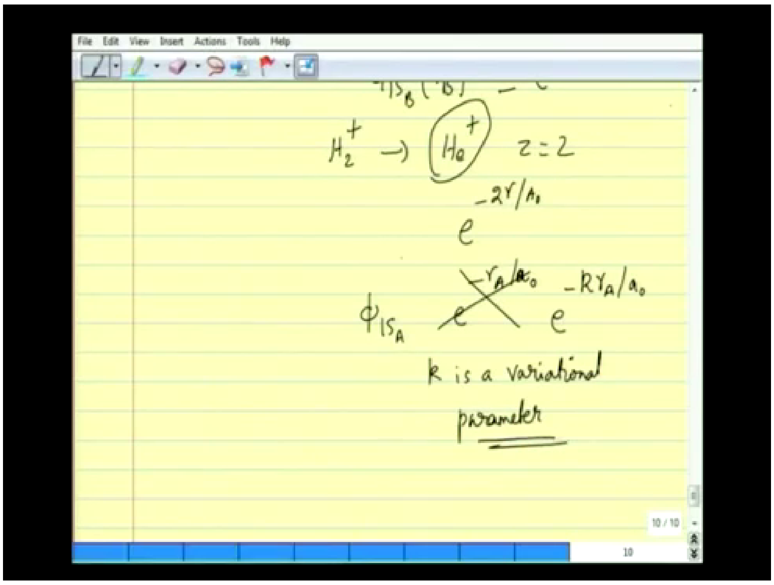

So, therefore, in one limit it is e to the minus r in another limit it is e to the minus 2 r. So, what should we do? Do a variational calculation introduce a parameter called the K which is an effective nuclear charge. So, you would rather write phi 1 S A naught as e to the minus r A by a naught sorry I think I have been using capital a naught, but a naught this is this a standard symbol for the Bohr radius. Instead do not use this instead use your parameter e to the minus k r A by a naught and minimize the energy that you get using that linear combination, minimize that energy with respect to k as a variational parameter k is a variational parameter. This is very nicely done in the textbook by Levine.

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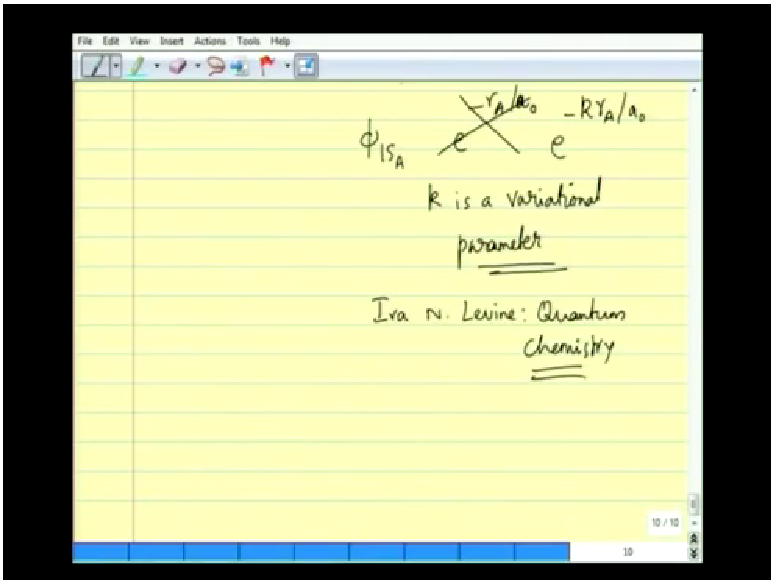

ϕ_{1s_A} $\cancel{e^{-r_A/a_0}}$ e^{-kr_A/a_0}

k is a variational parameter

Ira N. Levine: Quantum Chemistry

Quantum chemistry I have an older version of the book. So, I do not know the exact pages in the current version, but this integral is calculated with this as a variational parameter and simple ideas are explained.

So, there is room for us to do a slight improvement in our calculation by introducing a variational constant. Therefore, you see that the methods that we have already learned are going to be implemented in the way in which we see the orbital energies to match with what we think should be the experimental frequencies that we obtain. Experimentally you do not measure the energy you measure the frequencies, but if you calculate the molecular orbital bonding and if you calculate the anti bonding orbital the difference between the two is obviously, the frequency that we are worried about in raising the electron from the lower orbital to the higher energy orbital. And that difference should be matched with the experimental frequencies and then one back calculates these things.

So, it is possible to do a variational calculus the calculation on this and hydrogen molecular ion is one of the most thoroughly studied and most very well documented subject on the literature of chemical bonding. So, we will continue this with any further additional data that you need in the lecture notes, but in the next lecture I will talk about the hydrogen molecule and not hydrogen molecular ion, that is two electrons we will do it using a different method known as the valence bond method until then.

Thank you very much.