Chemistry Atomic Structure and Chemical Bonding
Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 44
Hydrogen Molecule: Calculations and Molecular Orbital Method

Last lecture we were looking at the Hydrogen Molecule; the Quantum Chemistry of Hydrogen Molecule and we began the discussion with the two methods or the two approaches, which are commonly employed for studying the Hydrogen Molecule namely the Valence Bond Method and the Molecular Orbital Method. And after introducing the molecular orbital method a bit I switched over to the original proposition of hydrogen molecule; the solutions for the Schrodinger equation which was proposed by Hitler and London. And we just started writing down the equation for the energy when we run out of time.

So, let me recall the last equation that we wrote down in today's lecture

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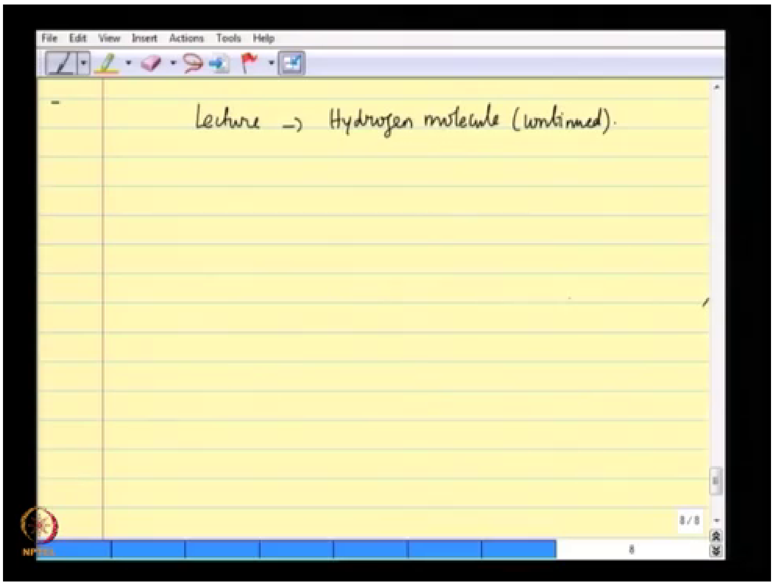

lecture → Hydrogen molecule (continued).

This is on Hydrogen molecule continued.

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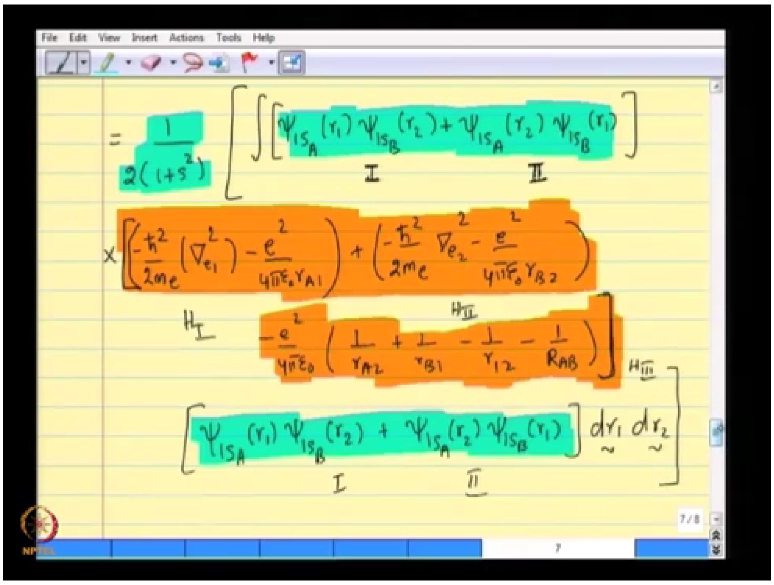

$$= \frac{1}{2(1+S^2)}\Bigg[\int\!\!\int\Big[\underbrace{\psi_{1S_A}(r_1)\,\psi_{1S_B}(r_2)}_{I}+\underbrace{\psi_{1S_A}(r_2)\,\psi_{1S_B}(r_1)}_{II}\Big]$$

$$\times\Bigg[\underbrace{\left(-\frac{\hbar^2}{2m_e}\left(\nabla^2_{e_1}\right)-\frac{e^2}{4\pi\varepsilon_0 r_{A1}}\right)}_{H_I}+\underbrace{\left(-\frac{\hbar^2}{2m_e}\nabla^2_{e_2}-\frac{e^2}{4\pi\varepsilon_0 r_{B2}}\right)}_{H_{II}}$$

$$\underbrace{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A2}}+\frac{1}{r_{B1}}-\frac{1}{r_{12}}-\frac{1}{R_{AB}}\right)}_{H_{III}}\Bigg]$$

$$\Big[\underbrace{\psi_{1S_A}(r_1)\,\psi_{1S_B}(r_2)}_{I}+\underbrace{\psi_{1S_A}(r_2)\,\psi_{1S_B}(r_1)}_{II}\Big]\,d\underset{\sim}{r_1}\,d\underset{\sim}{r_2}\Bigg]$$

Let me go back and recollect the expression for the energy using the valence bond wave function. The valance bond wave function is for the two nuclei called A and B denoted A and B let me just use that. And the electrons denoted 1 and 2 with the electron coordinates r 1 and r 2. The valance bond wave function was what you see here 1 by 2 square root of 2 into 1 plus S square times this wave function; psi 1 S A r 1 psi 1 S B r 2 plus the electrons being indistinguishable their coordinates switched with psi 1 S A r 2 psi 1 S B r 1.

And the energy expression for this wave function was given by the integral psi star psi here the psi is again and with the Hamiltonian in between. The Hamiltonian is that which I wrote as we would calculate because the way it is reorganized gives as some simple things immediately. This is the Hamiltonian and then we have the psi star psi that is psi star h psi and the normalization constant is already there in the form of 1 by 2 into 1 plus s square. So, this is the integral that we wanted to calculate and at this point I stopped.

So, now let us start looking at this integral term by term. The way I have grouped it you can see that there are two wave functions here; products of two wave functions, but two terms here; which I call as may be term I and term II. And the Hamiltonian I have blocked to this in the form of three groups. The group for the Hamiltonian for electron in the atom 1, the Hamiltonian for the electron in the atom 2 plus the potential energy terms are involving the electron 1 being attracted by the nucleus 2 electron 2 with the nucleus 1 and the electron electron repulsion the nuclear nuclear repulsion; all these things being grouped into a separate block.

So, what you have is 1, 2 there are 3 Hamiltonian blocks and 1, 2 you can call this also I and II. So, you have the integrals of various kinds today if we have to write it and let us also call this as may be H I H II and H III; 3 blocks. So, a total of how many terms we have.

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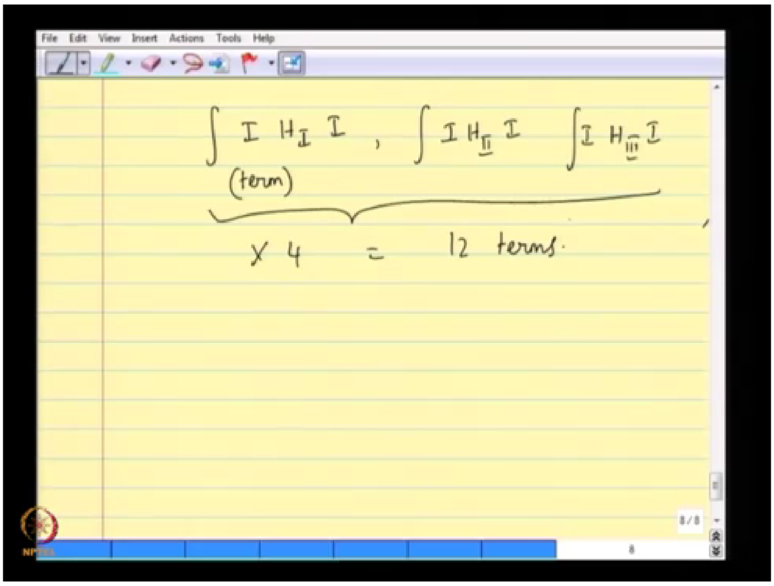

$$\underbrace{\int \underset{(\text{term})}{\mathrm{I}}\; H_{\mathrm{I}}\; \mathrm{I}\;,\quad \int \mathrm{I}\; H_{\mathrm{II}}\; \mathrm{I}\quad \int \mathrm{I}\; H_{\mathrm{III}}\; \mathrm{I}}\quad \times 4 \;=\; 12 \text{ terms.}$$

We have the integral term I H I term I; we have term I H II term I and the last in that will be term I H II term I. So, this involves the first term on both sides. And likewise you have 1 on the left 2 on the right 2 on the left 1 on the right and 2 on the left and 2 on the right, so into 4 a total of 12 terms are there ok. But we do not need to evaluate all the 12 terms because we see that by symmetry some of these terms are equal to the others. So, let us look at the first one.

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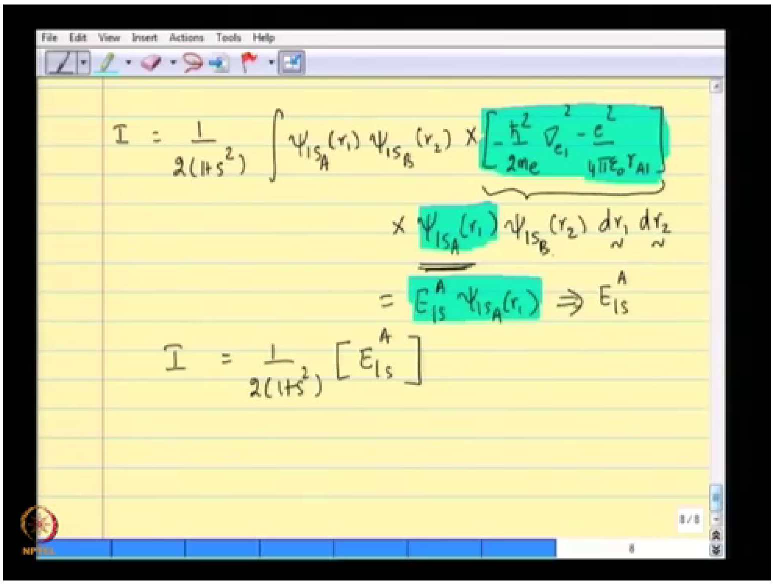

$$I = \frac{1}{2(1+s^2)} \int \psi_{1s_A}(r_1)\, \psi_{1s_B}(r_2) \times \underbrace{\left[-\frac{\hbar^2}{2m_e} \nabla_{e_1}^2 - \frac{e^2}{4\pi\varepsilon_0 r_{A1}} \right] \times \underline{\underline{\psi_{1s_A}(r_1)}}}\, \psi_{1s_B}(r_2)\, d\underset{\sim}{r_1}\, d\underset{\sim}{r_2}$$

$$= E_{1s}^{A}\, \psi_{1s_A}(r_1) \Rightarrow E_{1s}^{A}$$

$$I = \frac{1}{2(1+s^2)} \left[E_{1s}^{A} \right]$$

What I call as term I is this integral 1 by 2 into 1 plus s square integral psi 1 S A r 1 psi 1 S B r 2 multiplied by or with the Hamiltonian operator minus h square by h bar square by 2 m e del e 1 square minus e square by 4 pi epsilon naught or A 1 acting on the wave functions psi 1 S A r 1 psi 1 S B r 2 d r 1 d r 2. Both are three dimensional integrals over the electron coordinates r 1 and r 2 which is nothing, but the first term in this block here the first part of the Hamiltonian H I and first term here ok.

It is very easy because you see this is the Hamiltonian for the electron in atom 1 hydrogen atom 1 acting on the wave function for the electron in the hydrogen atom 1 psi 1 S A r 1 corresponds to the electron associated with the atom A. And therefore, this is nothing, but the h psi is equal to e psi for the hydrogen atom and since we involve the 1 s orbital of atom A we have E 1 S A. So, this will give you E 1 S atom A psi 1 S A r 1 ok, which is this term Hamiltonian acting on the wave function gives you this E 1 S A ok.

And the rest you know that it is going to be normalization, because what is left over is the moment. The Hamiltonian operation is taken as a constant with the eigenvalue, what is left over is the wave functions psi 1 S A r 1 psi 1 S A r 1 d r 1. And then the wave function, which is not changed which is psi 1 S B r psi 1 S B r 2 dr 2 and therefore, that is 1. So, the answer here is simply E 1 S A gives the integral gives. So, term 1 is 1 by 2 into 1 plus S square times E 1 S A sorry it is not A we have just a superscript A as we write here, what about the next one the next term that I would like to do.

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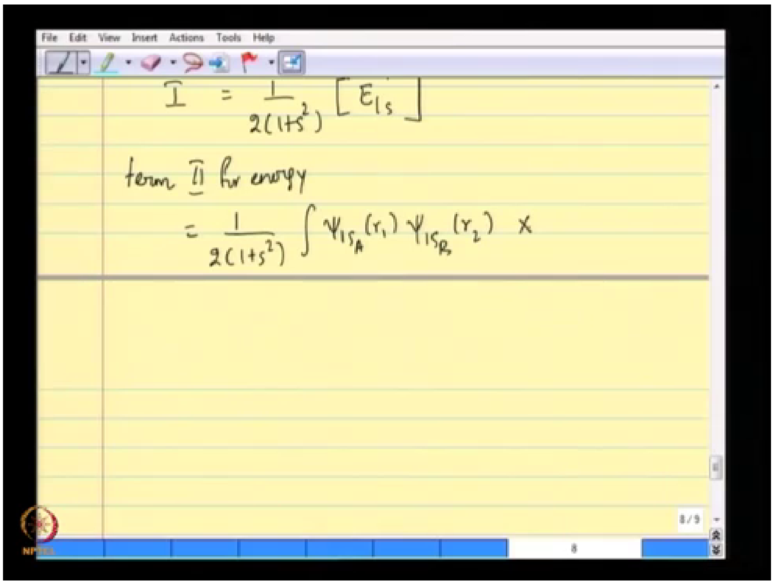

$$I = \frac{1}{2(1+S^2)} \left[E_{1s} \right]$$

term $\underline{II}$ for energy

$$= \frac{1}{2(1+S^2)} \int \psi_{1S_A}(r_1)\, \psi_{1S_B}(r_2) \times$$

Look at S term let us call it term 2 for energy involves the same wave function 1 by 2 into 1 plus S square integral psi 1 S A r 1 psi 1 S B r 2 with the Hamiltonian acting on the left.

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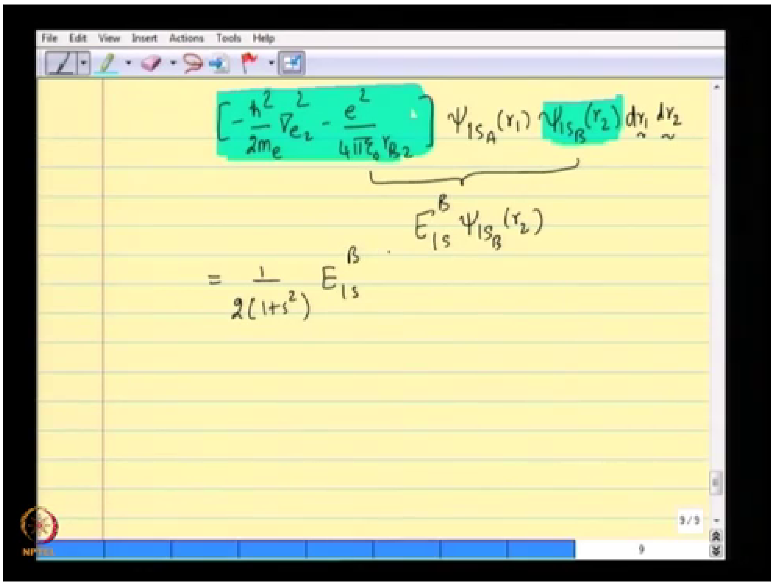

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2_{e_2} - \frac{e^2}{4\pi\varepsilon_0 r_{B2}} \right] \psi_{1S_A}(r_1)\, \psi_{1S_B}(r_2)\, d\tilde{r}_1\, d\tilde{r}_2$$

$$E^B_{1s}\, \psi_{1S_B}(r_2)$$

$$= \frac{1}{2(1+S^2)} E^B_{1s}$$

The Hamiltonian being minus h bar square by 2 m e del e 2 square the second electron minus e square by 4 pi epsilon naught r B 2; as we have written acting on the wave function psi 1 S A r 1 psi 1 S B r 2 d r 1 d r 2 ok.

Again this is exactly the same as the previous term except for this being on the electron 2 ok, that is this is the Hamiltonian for the electron associated with atom 2 and acting on the wave function associated with the electron in atom 2 psi 1 SB and the answer for this is going to give you E 1 S. And B or A does not matter because B or A essentially tells you not which atom I mean both hydrogen atoms are equal. So, E 1 SB and e 1 SA are the same, but acting or multiplied by psi 1 SB r 2.

And the rest you also know that it is going to be normalization, because once the Hamiltonians action on the wave function is given by the energy the wave function is normalized. So, this will also give you exactly the same result that, we had which is 1 by 2 into 1 plus S square E 1 S B ok.

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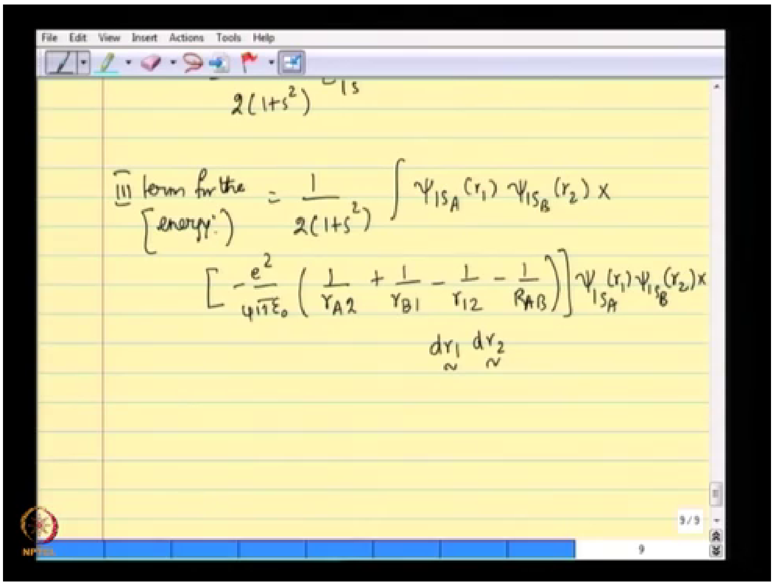

$2(1+S^2)$

III term for the [energy] $= \dfrac{1}{2(1+S^2)} \int \psi_{1S_A}(r_1)\, \psi_{1S_B}(r_2) \times$

$$\left[-\frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r_{A2}} + \frac{1}{r_{B1}} - \frac{1}{r_{12}} - \frac{1}{R_{AB}} \right) \right] \psi_{1S_A}(r_1)\, \psi_{1S_B}(r_2) \times$$

$$d\tilde{r}_1\, d\tilde{r}_2$$

Now the third term in the first block that we wrote the III term for the energy is whatever is remaining namely 1 by 2 into 1 plus S square integral psi 1 S A r 1 psi 1 S B r 2 with the Hamiltonian the remaining term which is minus e square by 4 pi epsilon naught times 1 by r A 2 plus 1 by r B 1 minus 1 by r 12 minus 1 by r A B ok. All of this multiply it by the wave functions psi 1 S A r 1 psi 1 S B r 2 r 2 times d r 1 d r 2 ok.

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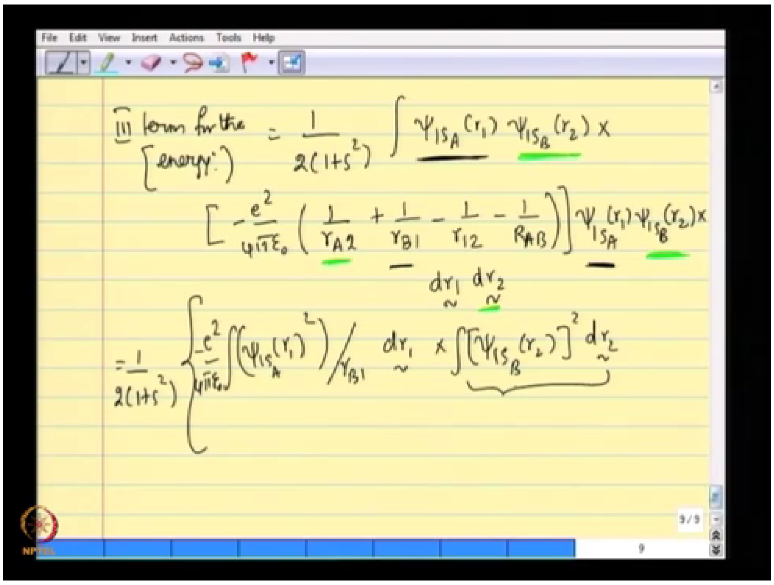

(iii) term for the [energy] $= \frac{1}{2(1+S^2)} \int \underline{\psi_{1s_A}(r_1)}\, \underline{\psi_{1s_B}(r_2)} \times$

$$\left[-\frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{\underline{r_{A2}}} + \frac{1}{\underline{r_{B1}}} - \frac{1}{r_{12}} - \frac{1}{R_{AB}} \right) \right] \underline{\psi_{1s_A}(r_1)}\, \underline{\psi_{1s_B}(r_2)} \times d\underset{\sim}{r_1}\, d\underset{\sim}{r_2}$$

$$= \frac{1}{2(1+S^2)} \left\{ -\frac{e^2}{4\pi\varepsilon_0} \int \left(\psi_{1s_A}(r_1)^2\right) \Big/ r_{B1} \, d\underset{\sim}{r_1} \times \underbrace{\int \left[\psi_{1s_B}(r_2)\right]^2 d\underset{\sim}{r_2}} \right.$$

Now, you can clearly see that the terms can be easily blocked out as 1 by 2 into 1 plus S square let us put a bigger bracket you can take the terms to be psi 1SA r 1 psi 1 S A r 1 and minus e square by 4 pi epsilon naught 1 by r B 1. This is the same thing as the coulomb integral that we calculated for the hydrogen molecule ion all of this correspond to the electron 1, but associated also with the atom 2 the nucleus 2 or B. And therefore, this is the columbic energy for the electron at the atom B due to the electron density of the electron being associated with the atom 1 at the position r 1.

So, this is the charge density it is a divided by the distance, so it is a coulomb integral. By the same token let me remove that do that thing or let us have it that me lets this is already marked r b 1. So, you are going to see r 1 now let us mark the same thing with the next item if you look at psi 1 S B r 2 e square minus e square by 4 pi epsilon naught r A 2 psi 1 S B r 2 d r 2 if you do that that is exactly the same j integral except that everything is now shifted to the electron two. So, these two terms contribute identically.

And then the remaining two terms the remaining product of course, you can see that psi 1 S A r 1 in this case psi 1 S A r 1 d r 1 will be 1. And therefore, you have this whole thing is the electron 1 some density divided by a distance associated with electron 1 coordinate electron 2 density psi star psi divided by the distance associated with the electron 2 nucleus 2 or nucleus 1 that is does not matter it is a charge density by distance. And then you also have psi 1 S A r 1 psi 1 S A r 1 that is electron 1 density square density electron

2 density psi 1 S B r 2 psi 1 S B r 2, 2 electron densities divided by 1 by r 12 which is obviously the columbic repulsion between the 2 charge densities electron 1 and electron 2 separated by a distance r 12 and summed over of course, that integral tells you that you are summing over all such things. Therefore, this whole thing is coulomb and the last term RAB we do not need to worry about it because it does not have electron coordinates. Therefore, it will merely give you the answer minus a square by 4 pi epsilon naught 1 by RAB does not change anything. Therefore, it is an addition to the total energy.

So, this whole integral which when it is blocked out into 3 forms appears like psi 1 S A r 1 squared divided by with the minus e square by 4 pi epsilon naught r B 1 d r 1 and multiplied by of course psi 1 SB r 2 square d r 2 ok; this is of course 1. So, this is the first term in the j integral.

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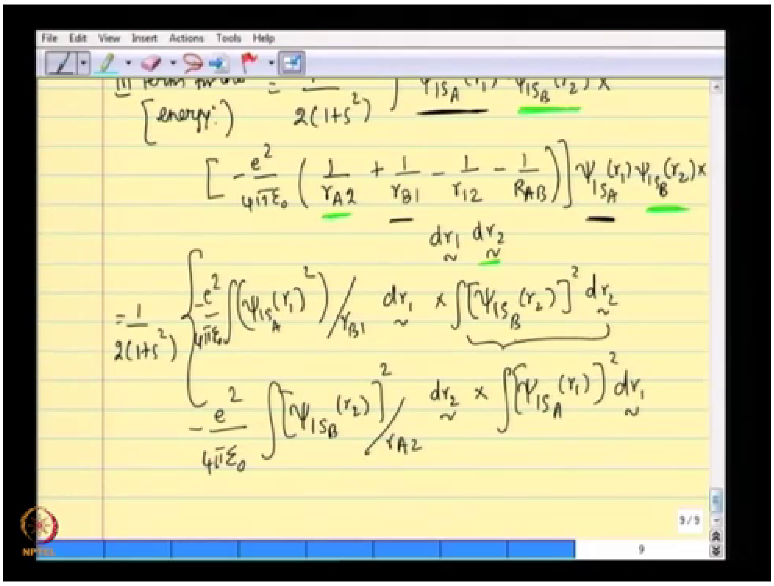

[energy]

$$= \frac{1}{2(1+S^2)}\int \psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2)\times$$

$$\left[-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A2}}+\frac{1}{r_{B1}}-\frac{1}{r_{12}}-\frac{1}{R_{AB}}\right)\right]\psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2)\times \, d\underset{\sim}{r_1}\, d\underset{\sim}{r_2}$$

$$=\frac{1}{2(1+S^2)}\begin{cases} -\dfrac{e^2}{4\pi\varepsilon_0}\displaystyle\int \left(\psi_{1s_A}(r_1)^2\right)\Big/ r_{B1}\, d\underset{\sim}{r_1} \times \underbrace{\int\left[\psi_{1s_B}(r_2)\right]^2 d\underset{\sim}{r_2}} \\ -\dfrac{e^2}{4\pi\varepsilon_0}\displaystyle\int \left[\psi_{1s_B}(r_2)\right]^2\Big/ r_{A2}\, d\underset{\sim}{r_2} \times \int\left[\psi_{1s_A}(r_1)\right]^2 d\underset{\sim}{r_1} \end{cases}$$

And the next term will be exactly the same, but for the electron 2 4 pi epsilon naught. So, what you have is psi 1 S B r 2 square divided by r A 2 d r 1 d r 2 multiplied by the integral psi 1 S A r 1 square d r 1 ok.

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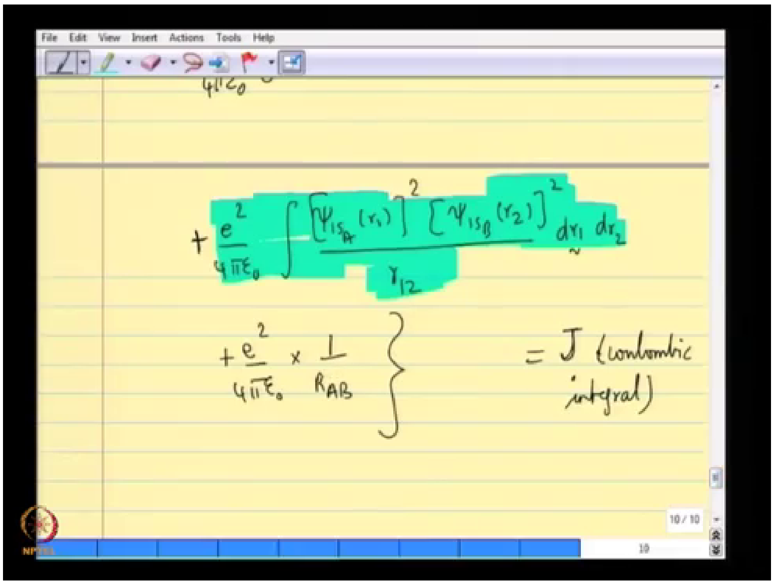

$4\pi\epsilon_0$

$$+\frac{e^2}{4\pi\epsilon_0}\int\frac{\left[\psi_{1s_A}(r_1)\right]^2\left[\psi_{1s_B}(r_2)\right]^2}{r_{12}}\,d\underset{\sim}{r_1}\,d\underset{\sim}{r_2}$$

$$\left.+\frac{e^2}{4\pi\epsilon_0}\times\frac{1}{R_{AB}}\right\} = J \text{ (coulombic integral)}$$

And the last of course, the 2 terms is minus e square by 4 pi epsilon naught integral psi 1 S A 1 S A r 1 squared psi 1 SB r 2 squared divided by r 1 2 plus of course; sorry plus d r 1 d r 2 all inside this big bracket the curly bracket.

And the last term which is plus e square by 4 pi epsilon naught into 1 by R AB because whatever is left over is integrated to 1 due to normalization. So, this is the whole thing is called the J or coulombic integral. The calculation of these 2 terms the coulombic integrals involving electron 1 at a distance from the second nucleus and electron 2 at a distance from the second of the first nucleus these two are exactly the same as the h 2 plus molecular ion coulomb integral calculation. Therefore, there is nothing new.

But what is new here is this additional term the electron electron repulsion which is something now we have to carefully evaluate you see that it is centered on two different nuclei A and B and also its a two electron repulsion integral. So, it is a two center 2 electron repulsion integral this requires a bit of time and I will not do that, we will simply call it by the coulombic integral in an assignment I will probably show you how to calculate this its somewhat tedious to evaluate ok.

And the other thing is of course the nuclear nuclear repulsion energy which simply adds to the total energy and as the nuclei or further apart this energy becomes smaller and so on.

So, you see that the calculation of the first term, if we go back the first term namely I H II I H II H II I and I H III I where I S this wave function 1 SA r 1 1 SB r 2 gives you in summary.

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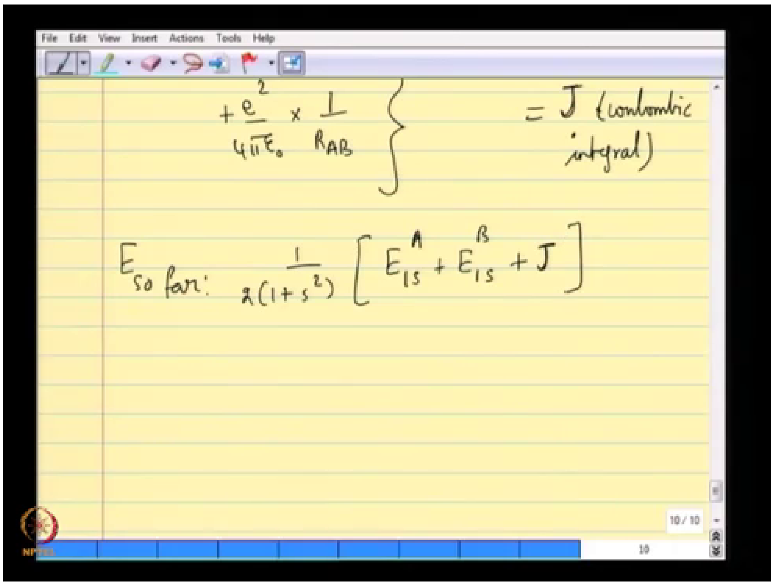

$$+\frac{e^2}{4\pi\varepsilon_0} \times \frac{1}{R_{AB}} \Big\} = J \text{ (coulombic integral)}$$

$$E_{\text{so far}}: \frac{1}{2(1+s^2)}\left[E_{1s}^A + E_{1s}^B + J\right]$$

E so far it gives you 1 by 2 into 1 plus s square E 1 S A plus E 1 S B both are identical plus J ok.

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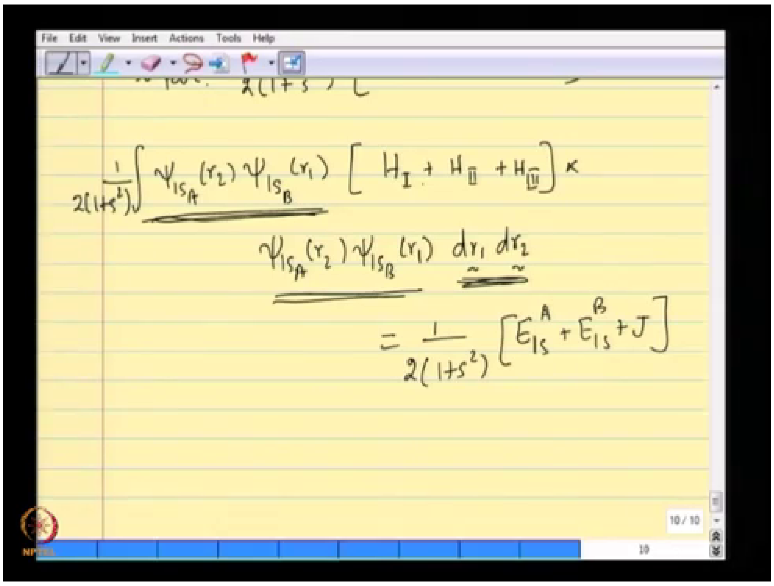

$$\frac{1}{2(1+s^2)}\int \underline{\psi_{1s_A}(r_2)\psi_{1s_B}(r_1)}\left[H_I + H_{II} + H_{III}\right] \times$$

$$\underline{\psi_{1s_A}(r_2)\psi_{1s_B}(r_1)}\, dr_1\, dr_2$$

$$= \frac{1}{2(1+s^2)}\left[E_{1s}^A + E_{1s}^B + J\right]$$

There are nine more terms, that we need to evaluate namely psi 1 SA r 2 let us take the second group of terms psi 1 SB r 1 and of course, it is multiplied by 1 by 2 into 1 plus S square here with the Hamiltonian as H I plus H II plus H III acting on psi 1 SA r 2 psi 1 SB r 1 d r 1 d r 2 ok. This is the second group of the three terms that you have to evaluate and it should be obvious to you if not after my pointing it out, that this term cannot have any value different from what we just discussed; because you have the wave functions with the coordinates r 1 and r 2 interchanged, but its integrated over all the coordinates of r 1 all the d r 1 and all the d r 2. And the Hamiltonian is of course, symmetric to the interchange of these two coordinates, because it is about the two indistinguishable electrons kinetic energy, potential energy and the nuclear potential energy. Therefore, the Hamiltonian is symmetric with respect to the interchange of 1 and 2.

The wave functions are only interchanging the coordinates and d r 1 and d r 2 are sort of dummy variables, when you do the integration therefore, this is exactly the same as what we had calculated. Namely 1 by 2 into 1 plus S square it is also E 1 SA plus E 1 SB plus J no difference, what you call as r 2 and I call as r 1 does not matter, but consistently if you call something as r 2, and the other is r 1 you must consistently do the algebra and you see the choice is a gives you that these two terms to be identical. Therefore, six terms by looking at the symmetry of this calculation we can immediately say that these six terms give you the simple result what about the other six terms.

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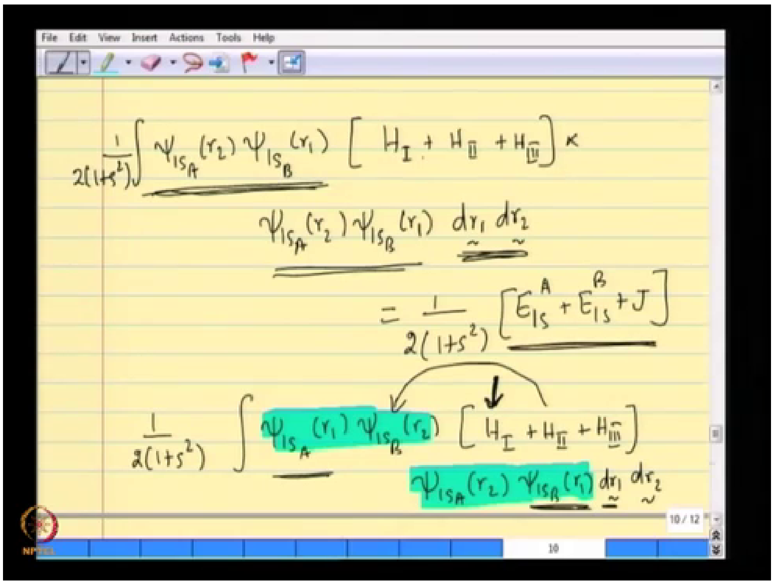

$$\frac{1}{2(1+s^2)}\int \underline{\psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1)}\left[H_I + H_{II} + H_{III}\right] \times$$

$$\underline{\psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1)}\ \underline{d\tilde{r}_1\, d\tilde{r}_2}$$

$$= \frac{1}{2(1+s^2)}\underline{\left[E_{1s}^{A} + E_{1s}^{B} + J\right]}$$

$$\frac{1}{2(1+s^2)}\int \psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2)\left[H_I + H_{II} + H_{III}\right]$$

$$\psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1)\, d\tilde{r}_1\, d\tilde{r}_2$$

Now, let us look at the first set namely 1 by 2 into 1 plus S square integral psi 1 SA r 1 psi 1 SB r 2 with the three Hamiltonian terms H I plus H II plus H III. Now acting on the other wave function namely 1 SA r 2 psi 1 SB r 1 d r 1 d r 2 ok.

Now, H I is associated with electron 1 please remember it is minus h bar square by 2 m e del e 1 square minus e square by 4 pi epsilon naught r A 1 is del 1 that is the electron 1 electron 1 Hamiltonian acting on the electron one wave function on the left Hamiltonian is a Hermitian operator. Therefore, it acts on the function on the left side or on the right side giving you at the most complex conjugate values, but being a Hermitian operator it gives you real eigenvalues. And therefore, H I acting on psi 1 SA on the left hand side is going to give you psi 1 SA times E 1 SA that is will give you E 1 SA again except what is left over is after the say H I acts on.

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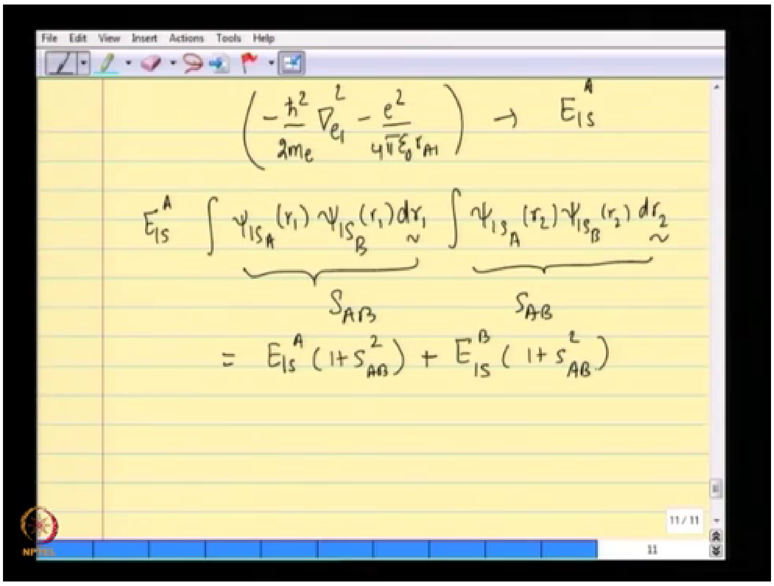

$$\left(-\frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{e^2}{4\pi\varepsilon_0 r_{A1}}\right) \rightarrow E_{1s}^A$$

$$E_{1s}^A \underbrace{\int \psi_{1s_A}(r_1)\psi_{1s_B}(r_1)d\tilde{r}_1}_{S_{AB}} \underbrace{\int \psi_{1s_A}(r_2)\psi_{1s_B}(r_2)\,d\tilde{r}_2}_{S_{AB}}$$

$$= E_{1s}^A(1+S_{AB}^2) + E_{1s}^B(1+S_{AB}^2)$$

What is left over is E 1 SA times psi 1 SA r 1 psi 1 SB r 1 d r 1. If you look at this integral psi 1 SA r 1 sorry psi 1 SA r 1 psi one SB r 1 d r 1. This Hamiltonian has given already the E 1 SA and the remaining is of course, the integral psi 1 S A r 2 psi 1 S sorry psi 1 SB r 2 yes psi 1 SA r 2 psi 1 SB r 2 d r 2 ok.

Now, this is the overlap integral for the two wave functions associated with the 2 nuclei with the electron 1. Therefore, this is s AB and this is the overlap integral for the electron 2 associated with the 2 nuclei AB and this is also SAB. Therefore, the answer that you would get for the first term is E 1 SA times 1 plus s square AB that is only the H I the first term I do not need to tell you now H II will give you exactly the same answer because it is all with reference to the electron to Hamiltonian and the electron to Hamiltonian acting on the wave function for the psi 1 SB is going to give you again E 1 SB. So, the answer here will be plus E 1 SB times 1 plus S square AB.

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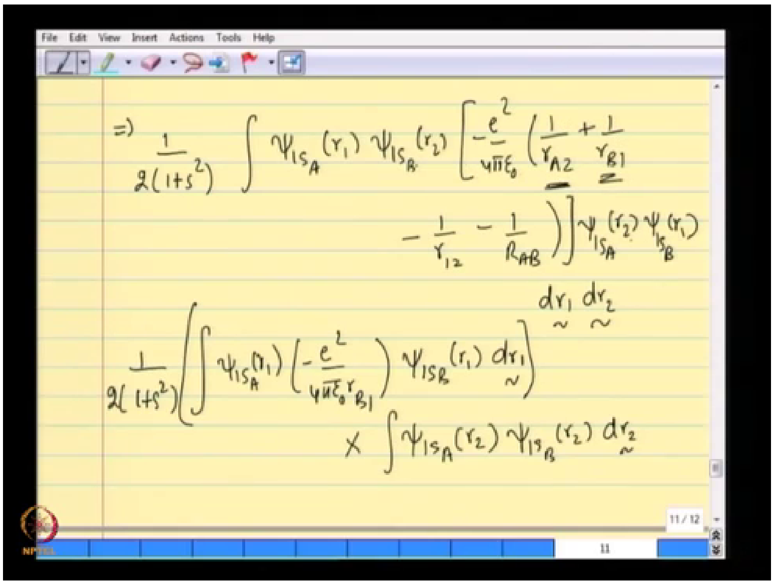

$$\Rightarrow \frac{1}{2(1+S^2)} \int \psi_{1S_A}(r_1)\,\psi_{1S_B}(r_2)\left[-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A2}}+\frac{1}{r_{B1}} - \frac{1}{r_{12}} - \frac{1}{R_{AB}}\right)\right]\psi_{1S_A}(r_2)\,\psi_{1S_B}(r_1)\,d\tilde{r}_1\,d\tilde{r}_2$$

$$\frac{1}{2(1+S^2)}\left(\int \psi_{1S_A}(r_1)\left(-\frac{e^2}{4\pi\varepsilon_0 r_{B1}}\right)\psi_{1S_B}(r_1)\,d\tilde{r}_1\right) \times \int \psi_{1S_A}(r_2)\,\psi_{1S_B}(r_2)\,d\tilde{r}_2$$

And the last term that we are left with namely term 3 that is right that out is 1 by 2 into 1 plus S square integral psi 1 S A I think I had r 1 S r 1 psi 1 S B r 2 with minus e square by 4 pi epsilon naught 1 by r what did we do A 2 plus 1 by r B 1 minus 1 by r 1 2 minus 1 by R AB all of this acting on psi 1 S A r 2 psi 1 S B r 1 d r 1 d r 2 if you look at this and separate this into coordinates of the electrons, what you get is exact exactly similar things to what you had as the k integral in the H II plus ion that is the exchange integral lets write that out it is psi 1 S A r 1.

And the coordinate r 1 is of course, minus e square by 4 pi epsilon naught r B 1 psi 1 S B r 1 d r 1 this is one type and the remaining term which is psi 1 S A r 2 psi 1 S A r 1 psi 1 S B r 2 d r 2 ok, this is the first of the four terms that you have for the B 1. And likewise you can write for the A 2 involving psi 1 SB r 2 and psi 1 S Br psi 1 SA r 2. Therefore, this whole thing is now called the exchange integral K of course, multiplied by 1 by 2 into 1 plus S AB square ok.

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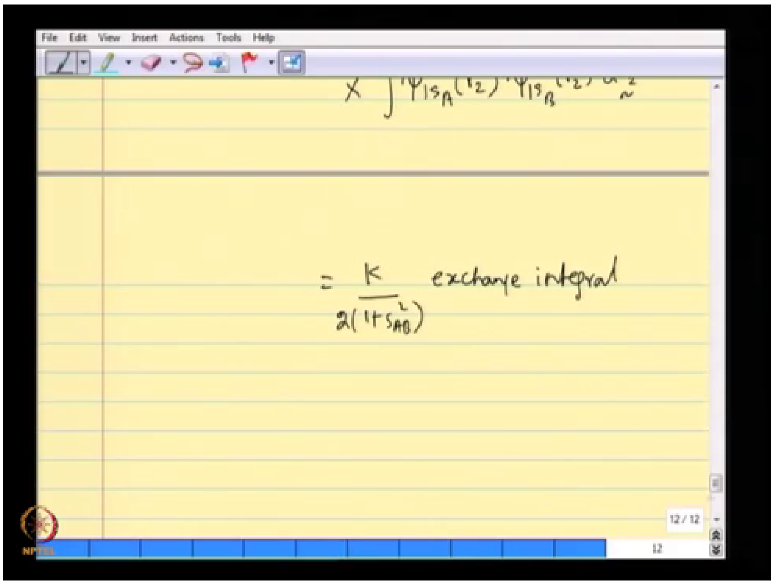

$\times \int \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_2)\, d\underset{\sim}{r}_2$

$= \dfrac{K}{2(1+S_{AB}^2)}$ exchange integral

So, term two or the group of terms, which involve the wave functions the two different wave functions; psi 1 S A r 1 psi 1 S B r 2 and the wave functions psi 1 S A r 2 and psi 1 S B r 1 with the Hamiltonian in between give you the energy E 1 S A the energy E 2 S B both multiplied by 1 plus S square. And of course, the rest of it being simply called as the exchange integral K. So, the answer for the second group of terms is the energy.

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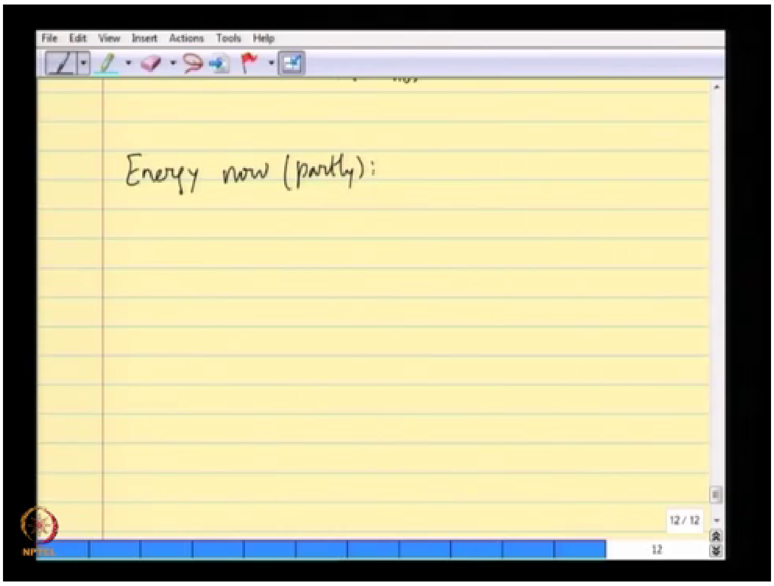

Energy now (partly):

Now, again partly is if you go back to the expression here we had a E 1 SA this is into 2.

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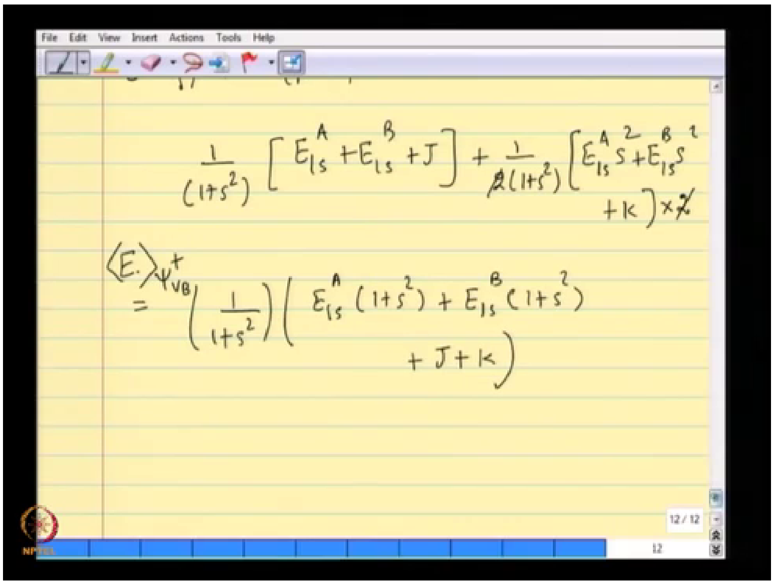

$$\frac{1}{(1+S^2)}\left[E_{1s}^{A}+E_{1s}^{B}+J\right]+\frac{1}{\cancel{2}(1+S^2)}\left[E_{1s}^{A}S^2+E_{1s}^{B}S^2+K\right]\times\cancel{2}$$

$$\langle E.\rangle_{\psi_{VB}^{+}} = \left(\frac{1}{1+S^2}\right)\left(E_{1s}^{A}(1+S^2)+E_{1s}^{B}(1+S^2)+J+K\right)$$

So, we should write 1 by 1 plus S square E 1 S A plus E 1 S B plus J that is for the first two terms and first two or six terms together. And now, what we have is 1 by 2 into 1 plus S square E 1 s A S square sorry plus E 1 S B S square plus K ok.

And the last group of three terms is only going to have these two wave functions interchanged let us go back to the integral. In this integral this wave function and this wave function will be left right interchanged and with the Hamiltonian of course. So, it is not going to give you any different result it is going to give you exactly the same result as we had just now calculated. And therefore, the answer is again into 2 for this part and so, this 2 goes away ok.

So, what is left over is then the total energy now is E psi VB plus is therefore, 1 by 1 plus S square times E 1 SA into 1 plus S square plus E 1 SB into 1 plus S square plus J plus K and of course, you can cancel this out with that. So, what is the total energy what the total energy?

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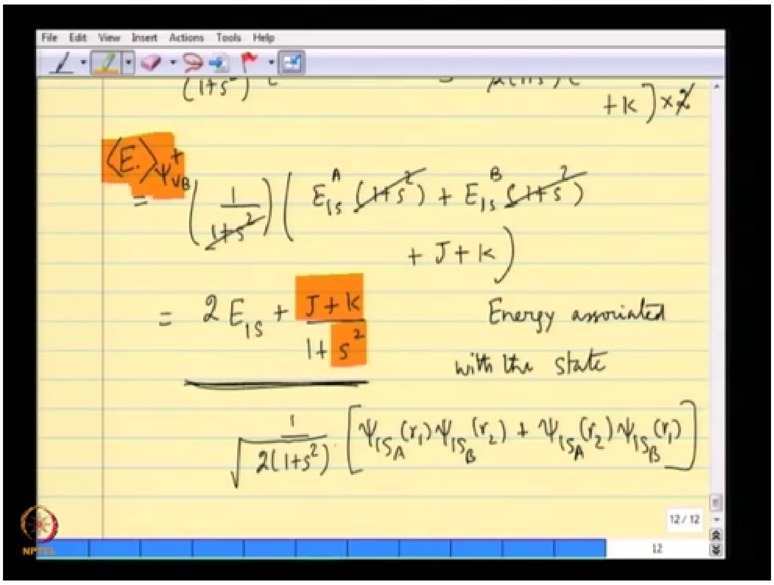

$$+K\Big] \times \cancel{2}$$

$$\langle E \rangle_{\psi_{VB}^{+}} = \left(\frac{1}{\cancel{1+S^2}}\right)\left(E_{1s}^{A}\cancel{(1+S^2)} + E_{1s}^{B}\cancel{(1+S^2)} + J + K\right)$$

$$= 2E_{1s} + \frac{J+K}{1+S^2}$$

Energy associated with the state

$$\frac{1}{\sqrt{2(1+S^2)}}\left[\psi_{1s_A}(r_1)\psi_{1s_B}(r_2) + \psi_{1s_A}(r_2)\psi_{1s_B}(r_1)\right]$$

S it is E 1 twice because A and B refer to basically 1 S electron hydrogen energy. So, twice E 1 S plus J plus K divided by 1 plus S square this is the energy associated with the state 1 by 2 into 1 plus S square square root psi 1 SA r 1 psi 1 SB r 2 plus psi 1 SA r 2 psi 1 SB r 1 ok.

So, we have the coulomb integral and the exchange integral that we have here and we have the overlap integral square and the energy of the valence associated with the valence bond wave function, The average energy associated with the valence bond wave function is in addition the difference between that and the sum of the two hydrogen energies if the hydrogen atoms did not interact with each other do you call that as delta E plus.

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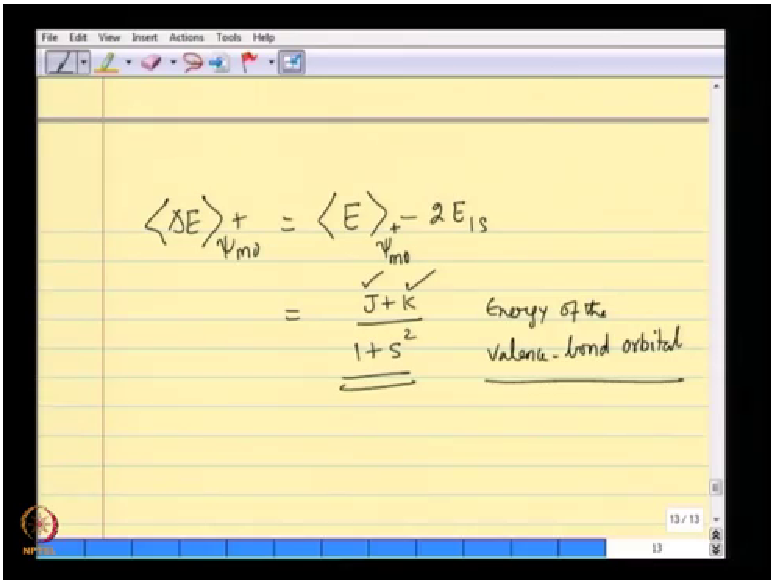

$$\langle \Delta E \rangle_{\psi_{mo}^{+}} = \langle E \rangle_{\psi_{mo}^{+}} - 2E_{1s}$$

$$= \underline{\underline{\frac{\overset{\checkmark}{J} + \overset{\checkmark}{K}}{1+S^2}}}$$

Energy of the valence-bond orbital

That that is e average minus psi mo plus the 2 E 1 s and that is given by J plus K by 1 plus S square ok, both J and K are negative s is positive. And therefore, you see that the delta E plus is now negative which means that as the hydrogen atoms come together as a function as a function of one of the R AB inter nuclear distance you see that there is attraction.

And until the R AB becomes sufficiently small for this whole thing to become positive the energy is decreasing. And therefore, there is an optimal distance of R AB at which the energy is minimum and this is what is called the bonding energy, or energy of the bonding orbital of the valance bond orbital. The calculation of J and the calculation of K in the case of hydrogen molecule involves one additional step namely the electron electron repulsion term electron electron repulsion term. In addition to the terms that we calculated earlier for the hydrogen molecule ion, but they can be done and I am not going to discuss the magnitude of that they are all fairly straightforward integrals.

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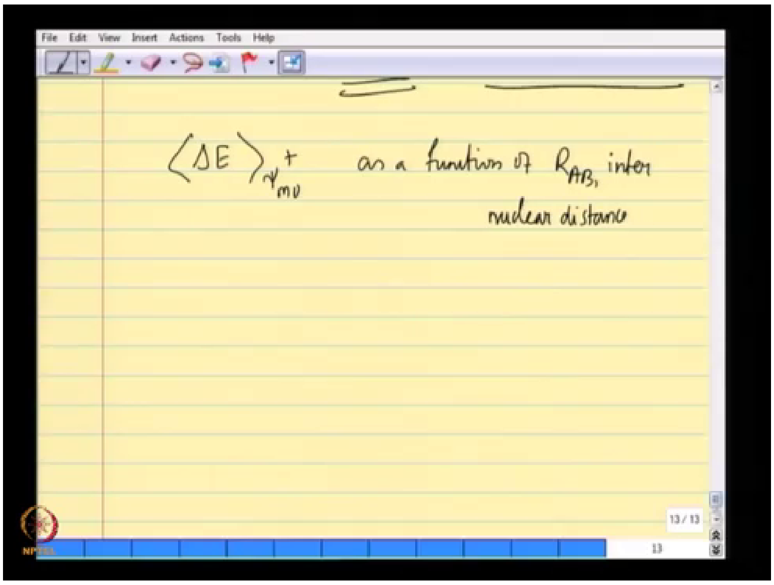

$\langle \Delta E \rangle_{\psi_{mo}^{+}}$ as a function of R_{AB}, inter nuclear distance

And then you do that the final result E or delta E plus delta E for this psi mo plus as a function of R AB inter nuclear distance can be plotted. And I am going to give you the results that others have done calculated earlier.

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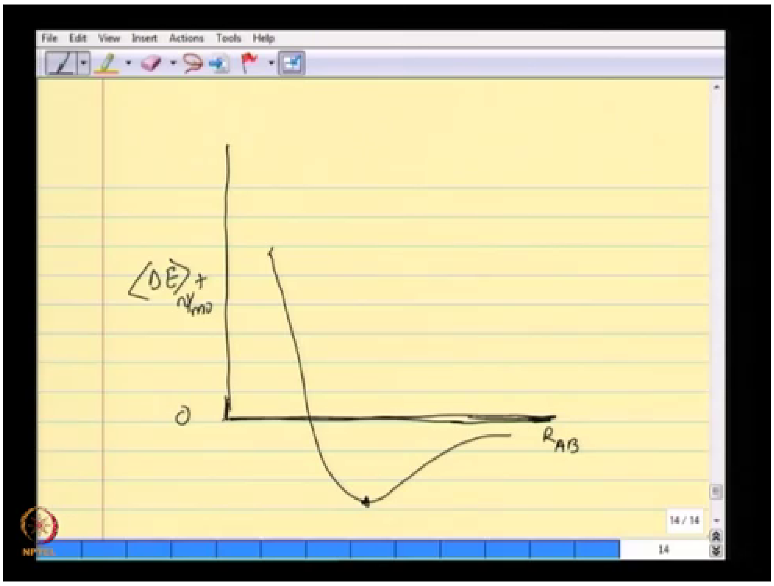

So, if you plot the delta E psi mo plus as a function of the inter nuclear distance R AB, what you see is you calculate the graph looks like that and this is 0 0; that is this is where the absolute energy scale it is the sum of the two hydrogen 1 S energies namely minus 27.2 electron volts you remember that the 1 S electron of the hydrogen atom is stable by minus 13.6 electron volts and when you have two such hydrogen atoms non interacting sitting next to each other the total energy of the system is minus 27.2 electron volts and that is the baseline with respect to which the energy of the valance bond orbital is less. And therefore, this distance where the system minimum.

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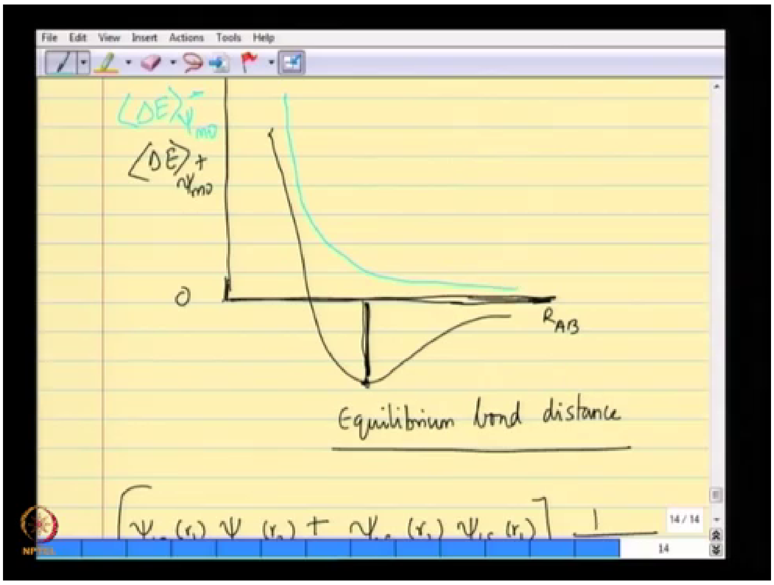

The energy is the delta E is the maximum this distance this is the Equilibrium bond distance ok. We use the valence bond orbital with the plus between the two wave functions namely r 1 and r 2 psi 1 S A r 2 psi 1 S B r 1.

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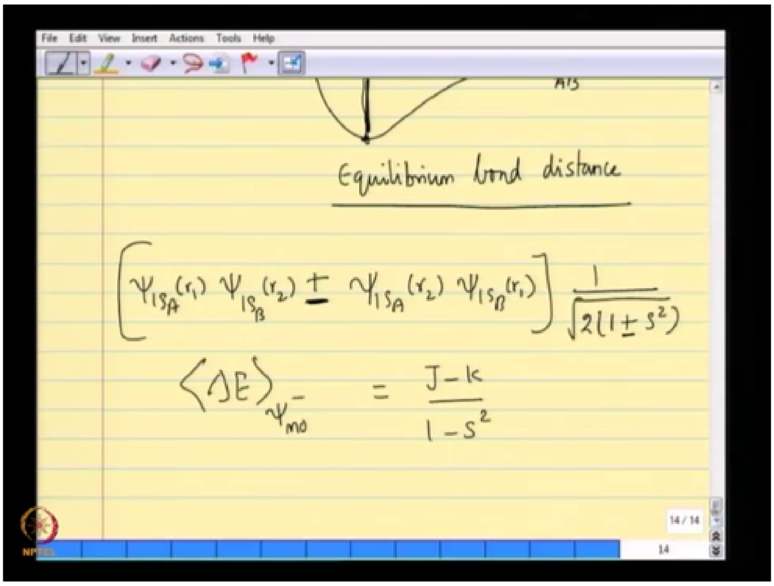

$$\left[\psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2) \pm \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1)\right]\frac{1}{\sqrt{2(1 \pm S^2)}}$$

$$\langle \Delta E \rangle_{\psi^-_{mo}} = \frac{J-K}{1-S^2}$$

Now, if we use a minus combination the normalization constant can be shown without much algebra, that it is 1 plus or minus S square ok, that would be in the wave function. And if you calculate the energies delta E plus it will turn out to be delta E for the minus combination psi mo minus it will be J minus K divided by 1 minus S square.

So, if we plot this value delta E minus that is for the psi mo minus in the same graph lets use a different color ok. So, if I plot delta E minus psi mo minus then the graph shows no minimum which means, that when the energy is calculated for the anti symmetric combination. Please note that this is an anti symmetric combination with the minus sign if you write this.

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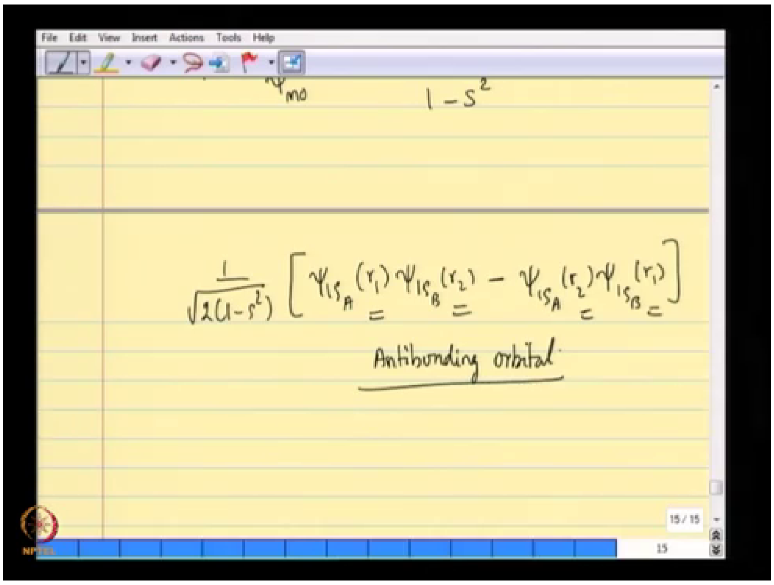

ψ_{mo} $\quad 1 - S^2$

$$\frac{1}{\sqrt{2(1-S^2)}}\left[\psi_{1S_A}(r_1)\psi_{1S_B}(r_2) - \psi_{1S_A}(r_2)\psi_{1S_B}(r_1)\right]$$

Antibonding orbital.

1 by square root of 2 into 1 minus S square psi 1 S A r 1 psi 1 S B r 2 minus psi 1 S A r 2 psi S B r 1. This wave function is anti symmetric with the respect to the interchange of the coordinates of 1 and 2 because when you interchange r 1 and r 2 the wave function becomes a negative of itself. Therefore, this is an anti symmetric combination and this anti symmetric combination gives rise to no stability, you can see that that the energy is always above what is called the minimum in the scale which is the sum of the 2 hydrogen atoms. Therefore, in that state the electrons if they are placed the electronic energy is greater than the sum of the 2 hydrogen atoms. And therefore this is; what is obviously not even nonbonding its anti to the bonding and so this combination is known as the antibonding valence orbital antibonding orbital.

But it is interesting, now to go back and look at what I said regarding these two wave functions in the last lecture; that the overall wave function for the 2 electrons which involves not only the spatial coordinates r 1 and r 2, but involve also the spin coordinates namely the alphas and betas the wave functions of the 2 electrons. You see that the anti symmetric combination in the coordinate space obviously, requires the spin wave functions to be symmetric.

So, there are three spin wave functions namely alpha 1 alpha 2 alpha 1 beta plus beta 1 alpha 2 and beta 1 beta 2 there are 3 of them and in the absence of any external magnetic field or in the absence of the perceived absence of the electron orbital spin angular momentum interactions ok. We assume that it is not there in the absence of those these three states are obviously degenerate the spin states are degenerate. Therefore, the anti symmetry combination has three possible states degenerate states, whereas, the symmetric combination, which we took with the plus sign has only one possible spin state which is anti symmetric and that is called the ground state.

So, the ground state of the hydrogen molecule with the 2 electrons in the same molecular or the bonding orbital the valence bond orbital if you think of that the ground state is such that its a spin 0 state both the spins are paired. And therefore, in the in the magnetic field the spin quantum number will be 0 for that, and the anti symmetric state has the spin quantum number is corresponding to the triplet state the total spin will be 1. And there are 3 possible states for a spin one namely 10 minus 1 and those 10 minus 1 states are the states given by alpha 1 alpha 2 alpha 1 beta 2 plus beta 1 alpha 2 and the last one beta 1 beta 2.

So, you see that this kind of approach, when it is meshed with the spin angular momentum states gives you a reasonable picture, which does not violate any fundamental principle particularly the paulis exclusion principle. And so, let me summarize this with the correlation energy diagram.

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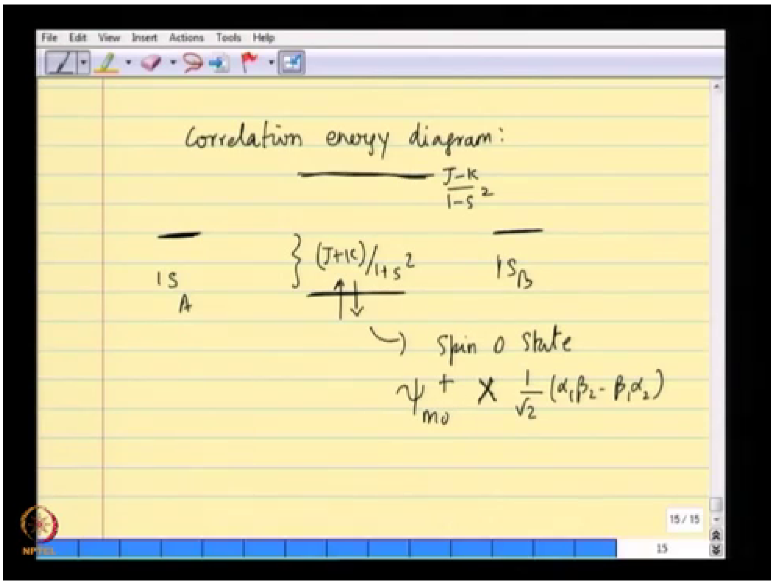

Correlation energy diagram:

That we have namely if you start with the 2, 1 S states for nucleus A and nucleus B the symmetric combination gives rise to an energy which is let me put it in such a way should be able to draw that within this screen.

So, the symmetric combination this difference is in our calculation its J plus K by 1 plus S square and the other state is J minus K by 1 minus S square and so you have the 2 electrons in this state, which is a spin 0 state for the spin. And this is given by 1 by square root of alpha 1 beta 2 minus beta 1 alpha 2 times psi mo plus times if on the other hand.

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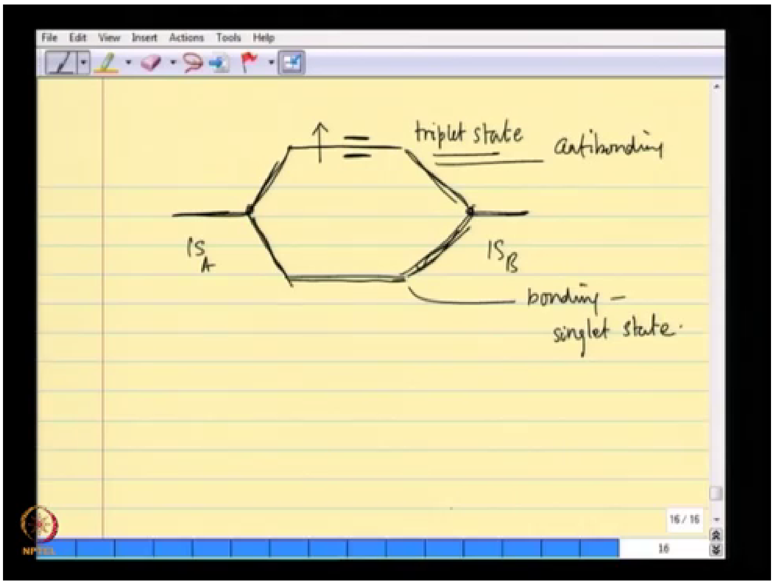

You have the 2 electrons excited, then what you have is the 2 1 S orbitals of the electron A 1 S B and the lower state and the upper state if we do that here and connect that these states originate from these 2, 1 S wave functions and that is the connection and these this state also originates from this 2, 1 S and that is a connection.

So, if you put the two electrons here, then you see that the electron has to have three possible states it is a triplet state. And you have to see that you have to put in the it is a threefold degenerate in terms of in the absence of any spin interactions and the electrons can be with the plus plus or plus minus and minus plus and minus minus. So, this is a triplet state the excited antibonding state and the bonding state is a singlet state ok.

There is a whole set of data available, and I would like to refer you for example, for some preliminary data to the book by MCQuarrie, and I think there is a table in chapter 9; I would not write those things please refer to the textbook.

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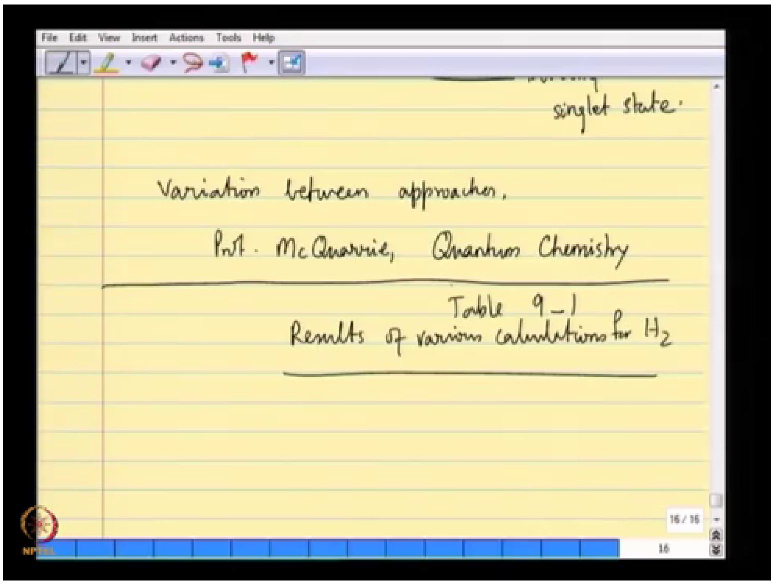

singlet state.

Variation between approaches,

Prof. McQuarrie, Quantum Chemistry

Table 9-1

Results of various calculations for H_2

For variation in different approaches variation between approaches along with the references to the original papers is given by Professor MCQuarrie Quantum Chemistry. I am sure you can find them elsewhere as well, but it is a ready reference for you in case you need to know where things are and I think it is table 9.1; table 9 1 ok and results of various calculation. This table contains many many data various calculations of H 2 o for H 2 o there is a reference to the valence bond method two different ways of doing it. There is also a reference to the molecular orbital method two different ways of doing it. Then you remember that in the molecular orbital approach we identified the valence bond contribution and then we had this h minus h plus and h plus h minus contribution; namely the electron one and electron two both associated with the 1 S orbital of the hydrogen atom A. The term corresponding to that was psi 1 S A r 1 psi 1 S A r 2. And then we had the h plus h minus, which has the electron both the electrons associated with the atom B.

So, if you do that that is called the ionic contribution and so, valence bond plus some ionic contribution with different weightings different combination coefficients what are the results and so on. So, you see that this is a very rich field for the electronic structure theorist to provide, what are called good gases of the molecular orbital wave functions. Finally, with those energies which are very close to what we measure experimentally as frequencies. Therefore, these energies are such that the difference between these energy should give you the match between the experimental frequencies and theoretically calculated values. I believe the valence bond plus ionic contribution and another method which I will discuss later known as the Hartree-Fock method are very close to experimental results.

So, that is that there is a whole list of things about the hydrogen molecule that you would like to refer to and some of these things would be put up in my lecture notes along with the Pdf file. But the basic calculational aspects I have exemplified here with the some blocking of the terms. And I hope that it is helpful to you in understanding how to do such molecular bonding calculations.

So, in the next lecture we move on to other Homonuclear diatomic molecules and we will do more qualitatively the bonding and the antibonding orbital picture, we will draw that. And we will draw what are known as the electronic correlation diagrams or correlation of energy diagrams. We will look at for both the homonuclear and heteronuclear diatomic molecules. And later on we move on to what are known as simply the poly atomic molecular chemical bonding picture.

Until then thank you very much.