Chemistry Atomic Structure and Chemical Bonding

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Lecture – 42
Hydrogen Molecule Ion: Calculations and Results

Now, in this lecture I shall do the same thing, using a variational approach and also indicate how to calculate, the quantities that we did not elaborate in the last lecture. So, let me recall what we did in the last lecture.

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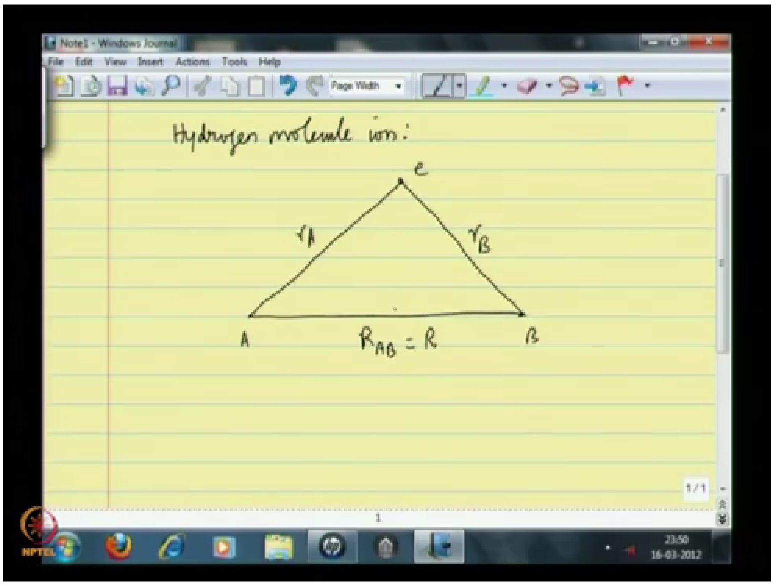

We had the system with the 2 nuclei and an electron A and B and electron with the distances r A between the electron and the nucleus A and the distance r B between the electron and the nucleus B and R AB, which in this lecture we will mark as R, as the distance between the 2 nuclei.

And then, if we mark the center of the electron well, perhaps we do not need it we are not going to use coordinate system, we leave it like this.

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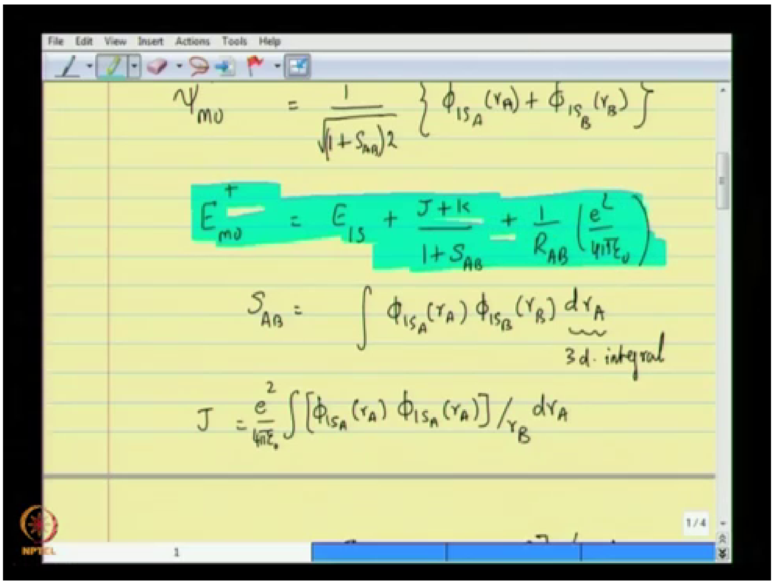

$$\Psi_{mo} = \frac{1}{\sqrt{(1+S_{AB})2}} \left\{ \phi_{1S_A}(r_A) + \phi_{1S_B}(r_B) \right\}$$

$$E^{+}_{mo} = E_{1S} + \frac{J+K}{1+S_{AB}} + \frac{1}{R_{AB}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)$$

$$S_{AB} = \int \phi_{1S_A}(r_A)\,\phi_{1S_B}(r_B)\,\underbrace{dr_A}_{3d\cdot\text{ integral}}$$

$$J = \frac{e^2}{4\pi\varepsilon_0}\int \left[\phi_{1S_A}(r_A)\,\phi_{1S_A}(r_A)\right]/_{r_B}\,dr_A$$

The bonding molecular orbitals psi, mo plus, was shown to be 1 by square root of 1 plus S AB, I think that was a root 2 if I remember, the combination phi 1SA of R 1 rA plus phi 1 SB of rB. That is the electron associated with the nucleus A, as a center and therefore, the electron coordinate the distance coordinator is rA, which is given by the 1 SA orbital phi 1 SA rA. And the other wave function is the electron with the nucleus B as the center.

And the correspondingly the wave function is the S orbital phi 1 SB rB. And if I remember, we wrote down the energy of the mo plus as, the 1 S orbital hydrogen atom energy plus a combination of 2 integrals J and the K called the coulomb integral and the exchange integral divided by the overlap integral 1 plus S, where S is the overlap integral S AB. But we did not elaborate on what is J what is K and what is S etcetera.

So, in this lecture we will do the same thing, but prior to that, let me introduce what is known as the variational approach to the same problem and we will also indicate the calculation of these integrals. The three integrals what you have; S AB, which is given by the integral phi 1 SA rA, phi 1 SB rB with one of the centers, so, that nucleus as a center so, it is d rA. It is essentially a 3 dimensional integral, it is a three dimensional integral.

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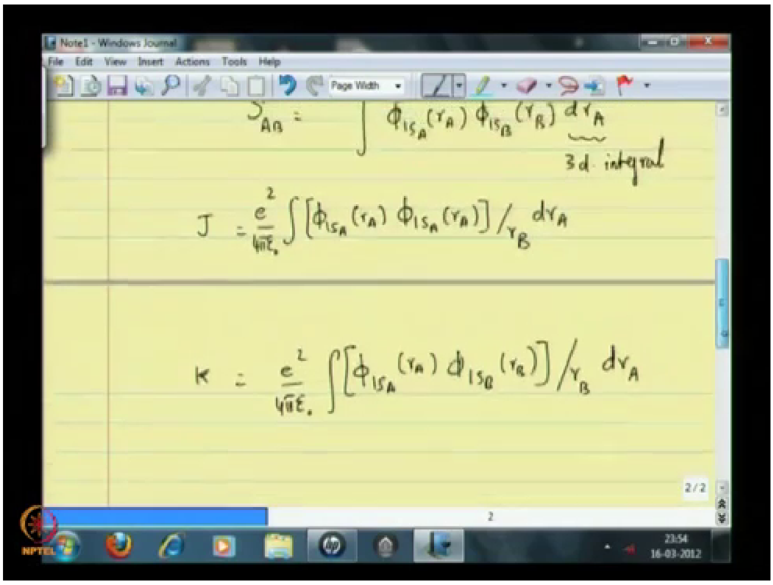

$$S_{AB} = \int \phi_{1s_A}(r_A)\,\phi_{1s_B}(r_B)\,\underbrace{dr_A}_{\text{3d integral}}$$

$$J = \frac{e^2}{4\pi\epsilon_0}\int \left[\phi_{1s_A}(r_A)\,\phi_{1s_A}(r_A)\right]/_{r_B}\,dr_A$$

$$K = \frac{e^2}{4\pi\epsilon_0}\int \left[\phi_{1s_A}(r_A)\,\phi_{1s_B}(r_B)\right]/_{r_B}\,dr_A$$

.

The coulomb integral J, if I recall we wrote this as phi 1 SA rA phi 1 SA rA divided by rB with the factors e square by 4 pi epsilon naught ok. There could be a minus sign, but it does not matter, the J is given by this combination the phi square divided by rB, which is a sort of a columbic energy for the electron from the center rB ok, from the center B. And the exchange integral K was written as, e square by 4 pi epsilon naught phi 1 SA, sorry there should be a d rA here just put that in. Now, the exchange integral is phi 1 SA rA phi 1 SB rB as opposed to A divided by rB or rA dr, one of the coordinates dr A. These are the 3 integrals, that we mentioned and these are what you have here.

So, in today's lecture we will also see how to calculate them, using an elementary method.

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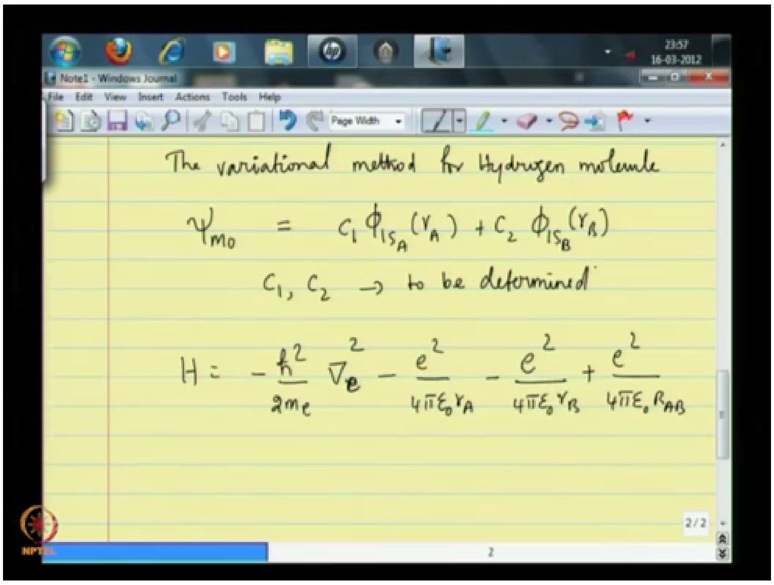

The variational method for Hydrogen molecule

$$\psi_{MO} = c_1 \phi_{1S_A}(r_A) + c_2 \phi_{1S_B}(r_B)$$

$c_1, c_2 \rightarrow$ to be determined

$$H = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$$

And also using a slightly more elegant way of doing with which is the use of confocal and it take a coordinates. I will not say much about it because, there is a separate lecture in which, I will talk about coordinate systems, the spherical polar coordinate system, the polar coordinate system and probably the elliptic coordinate systems. So, you must refer to that lecture for calculating some of the quantities that I mentioned here.

But we will do that at the end. So, let us go back to the variational method or hydrogen molecule ion. And at the end of that, we will get the same answer that we got in the last lecture; obviously, if we get a different answer that there is a problem. So, the surprise is not there, but the process tells you how to handle similar variational calculations. So, it is more an exercise for you to do these calculations on your own and also in that process I will evaluate both J and K.

Now, what is meant by the variational process, we write the molecular orbital mo as, a linear combination of the 2 atomic orbitals C 1 phi 1 SA rA and coefficient C 2 phi 1 SB rB. At this point, we leave C 1 and C 2 as undetermined or to be determined and having the Hamiltonian, as the electron kinetic energy minus h bar square by 2 me del r square, the electron Hamiltonian or del e square I will write it, minus e square by 4 pi epsilon naught rA, which is the columbic energy associated for the electron width the nucleus A, the attraction between the nucleus A and electron and likewise minus e square by 4 pi epsilon naught rB for the nucleus B.

And then, the nuclear repulsion e square by 4 pi epsilon naught RAB, this is of course, the same Hamiltonian. Now the variational process tells you that, when you have 2 basis functions which are taken as a linear combination, the Hamiltonian matrix that you have to solve; must be solved in such a way that, you find the C 1 and C 2 to satisfy the minimum in energy. And here of course, you will have a 2 by 2 matrix that you need to solve and in this process, you will get a value for C 1 and C 2, in fact, 2 values you will get exactly the same thing namely 1 by a square root of 2 into 1 plus SAB plus or minus for the C 1 and C 2.

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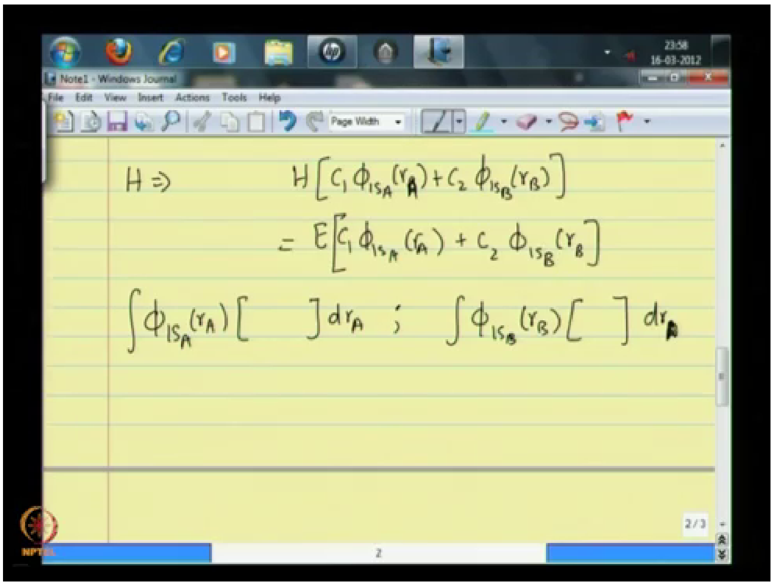

$$H \Rightarrow \qquad H\left[C_1 \phi_{1s_A}(r_A) + C_2 \phi_{1s_B}(r_B)\right]$$

$$= E\left[C_1 \phi_{1s_A}(r_A) + C_2 \phi_{1s_B}(r_B\right]$$

$$\int \phi_{1s_A}(r_A)\left[\quad\right] dr_A \; ; \quad \int \phi_{1s_B}(r_B)\left[\quad\right] dr_A$$

But let us see that. So, the Hamiltonian matrix that we need to write if, we have this equation H on C 1 phi 1 SA rA plus C 2 phi 1 SB rB is equal to E C 1 phi 1 SA r A i am sorry, this is rA rA plus C 2 phi 1 SB rB. So, this is a Schrodinger equation and for the variational matrix we integrate both sides with either phi 1 SA rA of that d rA or that is 1 equation and the other equation you get is, integrate this with phi 1 SB rB, with d rA or rB, 1 of the coordinates ok.

Let us write dr A here ok. So, this gives you the matrix 2 by 2 matrix.

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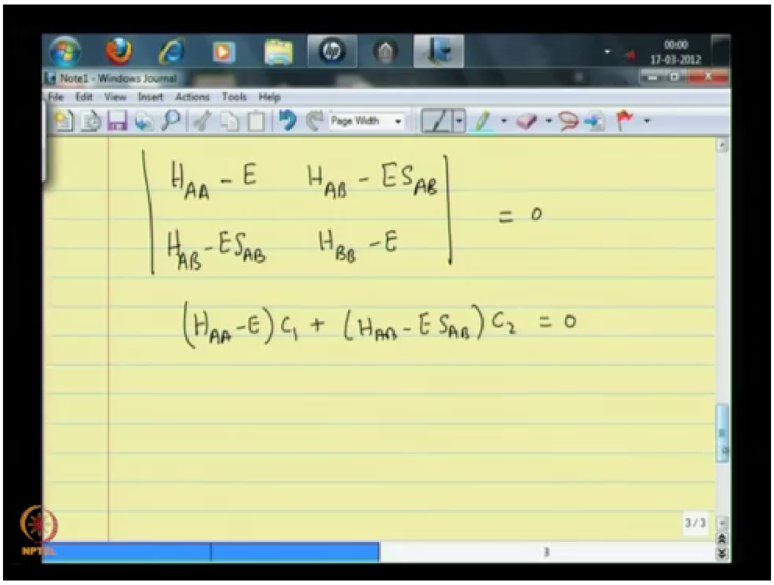

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0$$

$$(H_{AA} - E)c_1 + (H_{AB} - E\,S_{AB})c_2 = 0$$

H A A minus E, H AB minus ES AB, please remember that these wave functions are not orthogonal to each other because, they are centered on two different nuclei. Therefore, this is the variational process, involving non orthogonal basis functions. So, you remember the matrix form that I had in one of the earlier lectures.

So, it is the same thing h AB minus ES AB H BB minus E. This is the determinant that needs to be set to 0 and once you solve for E using this determinant, you substitute the E in the algebraic equation for the C 1 and C 2 namely, H AA minus E times C 1 plus H AB minus E S AB C 2 is equal to 0, to get the C 1 and C 2 either this or the other equation because, anyway they are linearly dependent on and therefore, you need to solve only one of them ok.

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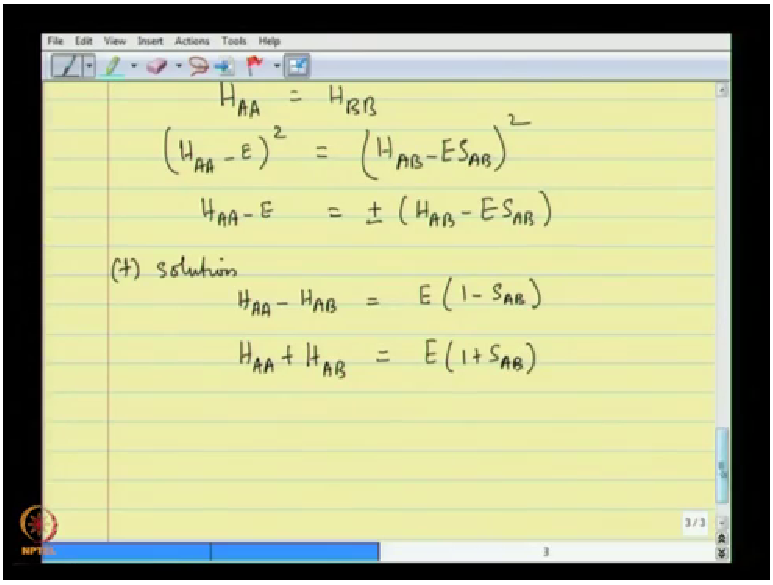

$$H_{AA} = H_{BB}$$

$$(H_{AA} - E)^2 = (H_{AB} - ES_{AB})^2$$

$$H_{AA} - E = \pm (H_{AB} - ES_{AB})$$

(+) solution

$$H_{AA} - H_{AB} = E(1 - S_{AB})$$

$$H_{AA} + H_{AB} = E(1 + S_{AB})$$

.

So, let us look at the determinant also the fact that, H AA and H A H BB are one and the same. Let us go to a full screen yeah, H BB are one and the same because, they are both involving the Hamiltonian with one of the basis functions A or B and in this case, the label A and B is of course, arbitrary we have chosen the label. So, by symmetry that the these two terms are identical. Therefore, the determinantal equation is H AA minus E whole square is equal to H AB minus E S AB whole square ok.

So, we have two solutions namely, H AA minus E is equal to plus or minus H AB minus E S AB. So, if we take the solution plus, solution what we have is H AA minus H AB is equal to E into 1 minus S AB ok, H AA ok. So, the other solution will be H AA plus H AB, when you take the minus part you will get E into 1 plus S AB. Therefore, the solution for the energy e is now H AA plus H AB or plus or minus divided by 1 plus or minus S AB.

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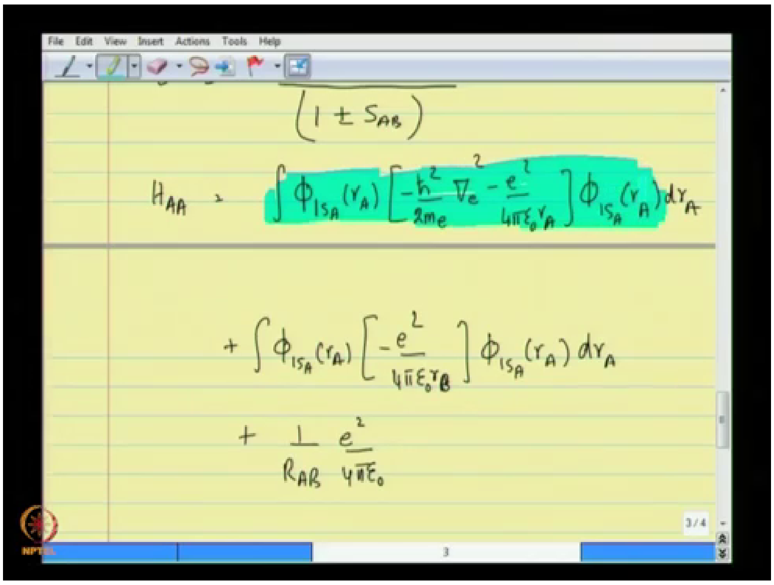

$$(1 \pm S_{AB})$$

$$H_{AA} = \int \phi_{1s_A}(r_A)\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right]\phi_{1s_A}(r_A)\,dr_A$$

$$+ \int \phi_{1s_A}(r_A)\left[-\frac{e^2}{4\pi\varepsilon_0 r_B}\right]\phi_{1s_A}(r_A)\,dr_A$$

$$+ \frac{1}{R_{AB}}\frac{e^2}{4\pi\varepsilon_0}$$

Now, let us calculate the integral, as per the definitions, that we have used so far ok. What is H AA, it is going to be given by the integral phi 1 SA rA the Hamiltonian, which is minus H bar square by 2 me del e square minus e square by 4 pi epsilon naught rA. We will put this together and calculate this as a separate quantity drA and the remaining terms namely plus phi 1 SA rA minus e square by 4 pi epsilon naught rA, rB i am sorry, rB phi 1 SA rA d rA and the last one which is involving only the nuclear separation RAB, so it is e square by 4 pi epsilon naught and the wave function phi 1 SA is normalized.

So, this is a standard form that you are already familiar with and you can see that, this is nothing other than the first term that you have here namely this one this integral is nothing other than, the E 1 S A times rA the Hamiltonian acting on the wave function 1 S. Therefore, it gives you the 1 S hydrogen energy and then of course, what is remaining is the normalization integral, so this whole thing is E 1 S as you have you seen earlier. And this of course, you have seen already, this is the definition of our the coulomb integral J and the 1 by RAB is of course, the inter nuclear separation. Of course, when I wrote down this energy earlier, I did not include the 1 by RAB, which is a mistake are technically you should write that e square by 4 pi epsilon naught 1 by RAB.

So, please correct for this, namely the mo E mo plus, that we derived is what we have here and now we are trying to derive the same value through the variational process ok.

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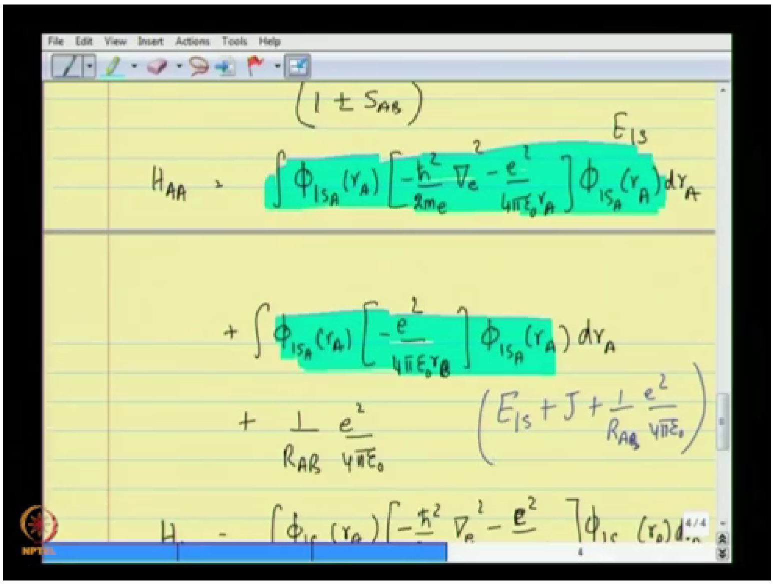

$(1 \pm S_{AB})$

E_{1s}

$$H_{AA} = \int \phi_{1s_A}(r_A)\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right]\phi_{1s_A}(r_A)\,dr_A$$

$$+ \int \phi_{1s_A}(r_A)\left[-\frac{e^2}{4\pi\varepsilon_0 r_B}\right]\phi_{1s_A}(r_A)\,dr_A$$

$$+ \frac{1}{R_{AB}}\frac{e^2}{4\pi\varepsilon_0} \qquad \left(E_{1s} + J + \frac{1}{R_{AB}}\frac{e^2}{4\pi\varepsilon_0}\right)$$

$$H = \int \phi_{1s}(r_A)\left[-\frac{\hbar^2}{}\nabla_e^2 - \frac{e^2}{}\right]\phi_{1s}(r_B)\,d$$

Now, that is for H AA whatever we have written. What about H AB, H AB is going to be the integral phi 1 SA rA with again, the Hamiltonian minus H bar square by 2 me del e square minus 1 e square by 4 pi epsilon naught rA minus e square all of this acting on 1 SB rB d rA.

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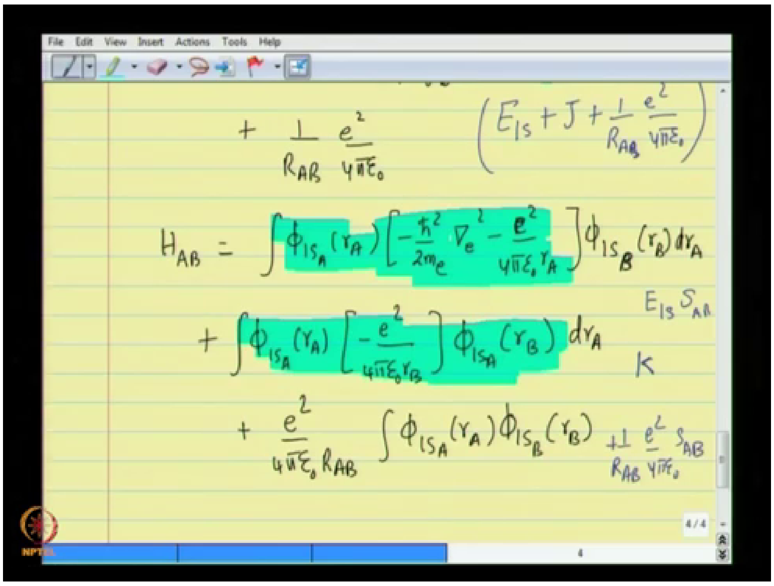

$$+ \frac{1}{R_{AB}}\frac{e^2}{4\pi\varepsilon_0} \qquad \left(E_{1s} + J + \frac{1}{R_{AB}}\frac{e^2}{4\pi\varepsilon_0}\right)$$

$$H_{AB} = \int \phi_{1s_A}(r_A)\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A}\right]\phi_{1s_B}(r_B)\,dr_A \qquad E_{1s}S_{AB}$$

$$+ \int \phi_{1s_A}(r_A)\left[-\frac{e^2}{4\pi\varepsilon_0 r_B}\right]\phi_{1s_A}(r_B)\,dr_A \qquad K$$

$$+ \frac{e^2}{4\pi\varepsilon_0 R_{AB}} \int \phi_{1s_A}(r_A)\phi_{1s_B}(r_B) \qquad + \frac{1}{R_{AB}}\frac{e^2}{4\pi\varepsilon_0}S_{AB}$$

And the remaining terms namely plus phi 1 SA rA times minus e square by 4 pi epsilon naught rB phi 1 SA rB and the last term d rA and the last term is of course, e square by 4 pi epsilon naught rab, with the overlap integral phi 1 SA rA phi 1 SB rB ok.

So, these are the expressions that we have for H AA and HB. If we collect the expression, for H AA let us write this in a different color, just to indicate so, let us write that ok. So, there is E 1S and then there is this term which is the columbic term J and you have the 1 by R AB term times this, which is e square whatever by 4 pi epsilon naught ok. So, we have that contributed from H AA and for H AB, we have the same with the first term that you see here namely, the phi 1 SA rA sorry this one phi 1 SA rA minus H bar square this is of course, the Hamiltonian acting on the wave function here.

And so, this gives you E 1 S, but the remaining part gives you the overlap integral. So, this is given by the E 1 S times S AB and the this of course, as you see here the phi 1 SA rA e square by rB phi 1 SA rB is of course, the coulomb integral and it is a coulomb integral with an S term. So, if we mark that it is e sorry it is J with m, sorry this is the this is the exchange integral, I am sorry this is not the coulomb integral, this is the exchange integral, so, it is K because it is phi 1 SA rA rB divided by rB. So, this is the exchange integral so, you have. ah

And then of course, the last term is 1 by RAB times e square by 4 pi epsilon naught times SAB ok.

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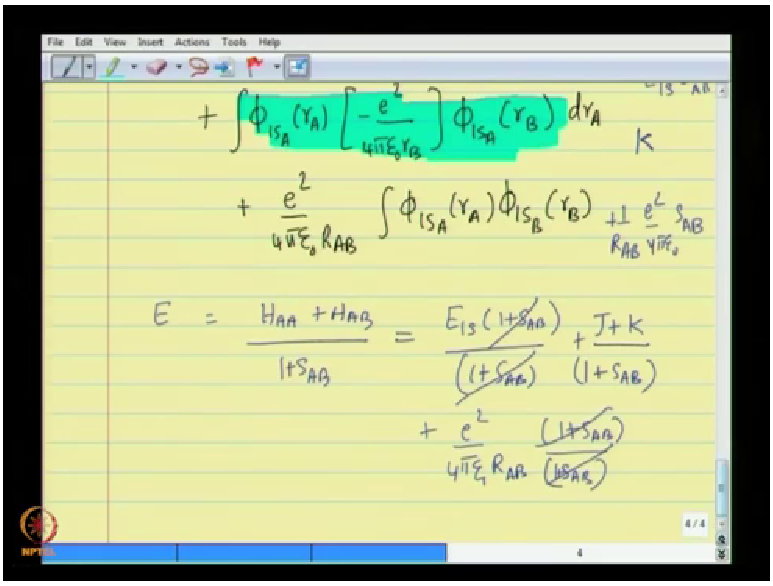

$$+ \int \phi_{1S_A}(r_A) \left[-\frac{e^2}{4\pi\varepsilon_0 r_B} \right] \phi_{1S_A}(r_B)\, dr_A \qquad K$$

$$+ \frac{e^2}{4\pi\varepsilon_0 R_{AB}} \int \phi_{1S_A}(r_A) \phi_{1S_B}(r_B) \quad + \frac{1}{R_{AB}} \frac{e^2}{4\pi\varepsilon_0} S_{AB}$$

$$E = \frac{H_{AA} + H_{AB}}{1 + S_{AB}} = \frac{E_{1S}\cancel{(1+S_{AB})}}{\cancel{(1+S_{AB})}} + \frac{J+K}{(1+S_{AB})} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}} \frac{\cancel{(1+S_{AB})}}{\cancel{(1+S_{AB})}}$$

So, the sum of all of this, if you remember now the solution that we had written down, for E as H AA plus H AB divided by 1 plus SAB then, you get exactly the same answer namely E 1S into 1 plus SAB divided by 1 plus SAB and you get J plus K divided by 1 plus SAB and you have e square by 4 pi epsilon naught r AB with 1 plus SAB divided by 1 plus SAB ok.

So, that goes away that goes away. So, you get exactly the same expression for E plus

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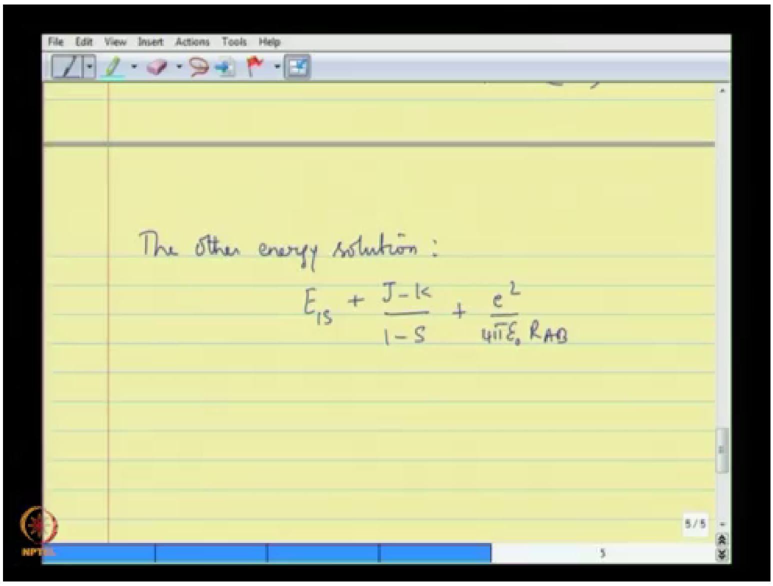

The other energy solution:

$$E_{1S} + \frac{J-K}{1-S} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$$

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And the likewise the other energy solution using the variational method is going to be E 1S plus J minus K divided by 1 minus S plus e square by 4 pi epsilon naught RAB ok. Therefore, the variational method does not give you any different result the way we have presented it; it gives you the same result. Therefore, we are comfortable either we use the variational method or we choose the coefficient using some physical reasoning, that the electron will not see these two nuclei as a different because they are both identical.

And therefore, choosing the C is to be a constant and the C square to be the probabilities being the same the electron being the same in the associated with the 1S orbital of the hydrogen atom a or 1 S orbital of the hydrogen atom B we used that argument.

So, either the physical argument or the variational method, in this case gives you the same answer and it is not a surprise.

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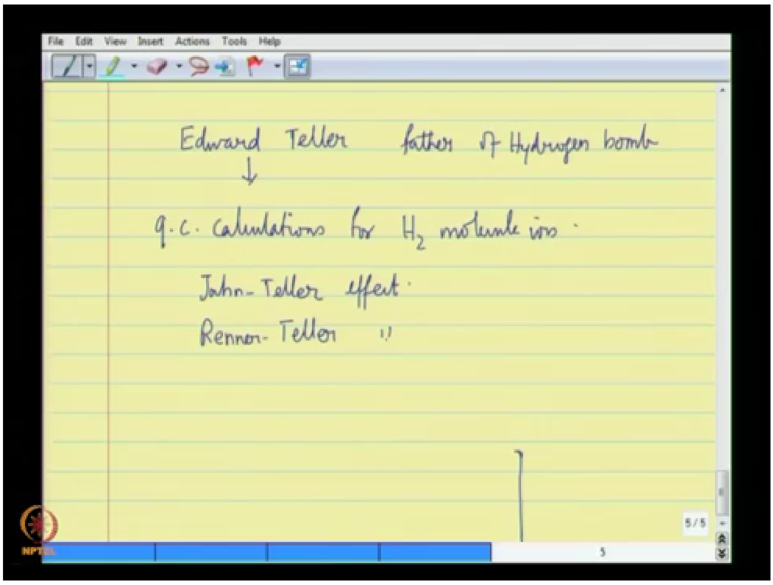

Edward Teller father of Hydrogen bomb

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q.c. calculations for H_2 molecule ion.

Jahn-Teller effect.

Renner-Teller "

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Just on a historical note I want to mention that the hydrogen molecule ion was first discussed in detail by Edward Teller, who is often considered to be the father of the hydrogen bomb project though, he was not officially associated with it when the bomb was discovered, he was preliminary was involved in the as I see it the historical discussions, I found them in the web, I will just read very exactly what it is it says. Edward Teller of course, did his phd thesis with Werner Heisenberg and in the 1930's and he dealt with the first accurate quantum chemical calculations for hydrogen molecule ion quantum chemical calculations, for hydrogen molecule ion.

So, he is also the very famous teller of the young teller effect that, many of you as chemist when you see this in the electronics spectroscopy and in crystal field theory distortion of a equilibrium structures and so on. It is extremely well known and he is also associated with the Renner Teller effect, it is the same Teller ok. So, his contributions to chemistry have been quite substantial and he was the first one to look at the hydrogen molecule ion, almost soon after the Schrodinger equation was discovered and the born oppenheimer approximation was proposed. Just about that time, the paper by Hitler and London had also appeared on the calculation of the hydrogen molecule, which will be my next lecture.

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So, you could see that as soon as the Schrodinger equation was discovered, there was a lot of this activity on applying this equation to the study of molecules using approximation procedures, which would make sense from the point of view of quantum mechanics, but which also should make sense from the point of view of chemistry given that, valency and chemical bonding is more the territory of the chemical physicists and chemists. At that time chemical physics was not yet recognized as a discipline, I think that happened in 1935 or 34 when Harold Urey founded the journal of chemical physics.

So, there is a bit of history that goes along with the calculations of these quantum chemical approaches for bonding. And in this case of course, it is important for me to mention that it was Edward Teller who as a phd thesis development looked on the hydrogen molecule ion in detail. Of course, there are many many more calculations since then and many many approaches, but historically it is also important to recognize this contribution.

Now, the rest of the lecture, well let me have a pause at this point of time because, the rest of the lecture I would like to actually tell you how to calculate the J integral the K integral and the S integral and in this lecture, I would tell you what the method that I use for the S integral following some simple procedures. There are other approaches; we will see them as we go along. Let us just stop for a few seconds and then come back to the calculation on the S integral.

Let us do this algebraic calculation of the overlap integral as an example ok.

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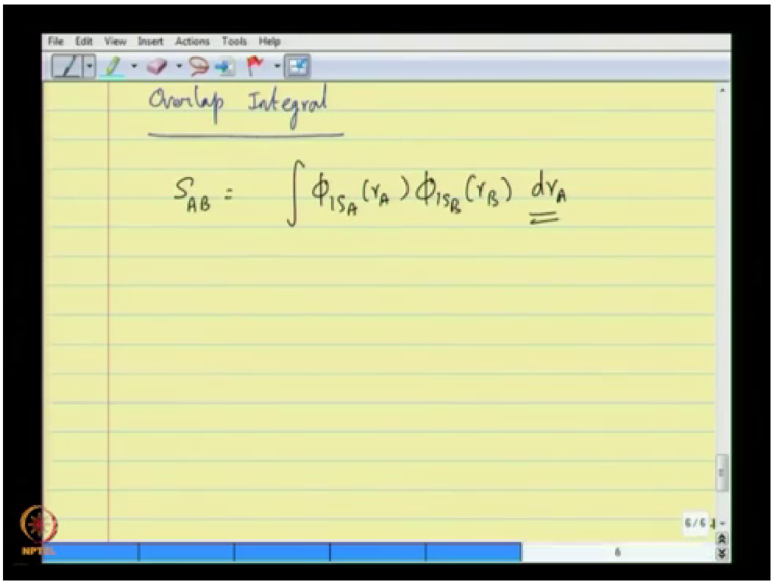

Overlap Integral

$$S_{AB} = \int \phi_{1S_A}(r_A)\,\phi_{1S_B}(r_B)\,d\underline{\underline{r_A}}$$

So, the integral that we have S AB is phi 1 SA rA phi 1 S B rB and the 3 dimensional integral d rA, which of course, if we write this in a coordinate system with polar coordinates, let me draw the polar coordinates.

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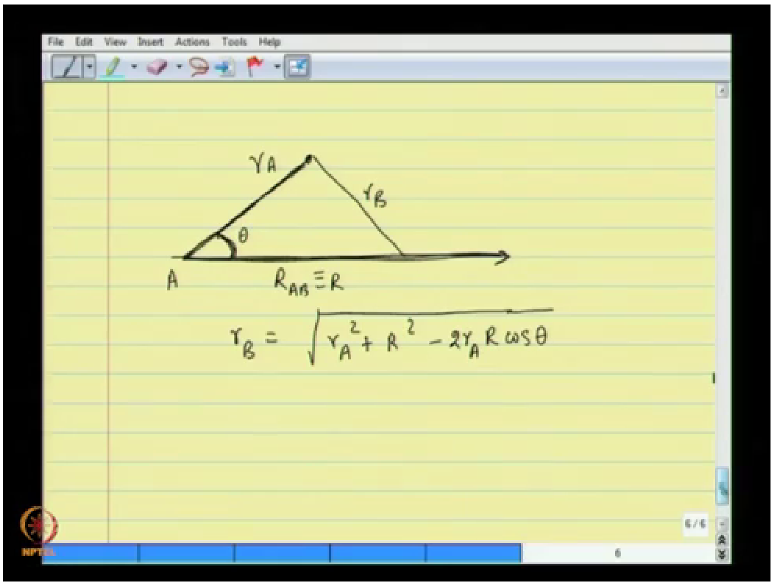

$$r_B = \sqrt{r_A^2 + R^2 - 2r_A R\cos\theta}$$

As this is the R, the inter nuclear separation and we are talking about rA this part the nucleus A and this is rB sorry this is the coordinate R the value RAB is this which we will write for this lecture as R and this is rB. And you can see that if we choose this as the polar z axis then, rA as a vector as the distance from this and the angle theta that rA makes ok, this is the polar angle theta associated with this coordinate system and therefore, in this coordinate system, we can write rB using the triangular formula for the three distances on the angle between the other two sides, rB as square root of rA square plus RA B square minus 2 rA R, let us drop the AB anyway this is just a notation to rA R times cos theta and that is the distance rB.

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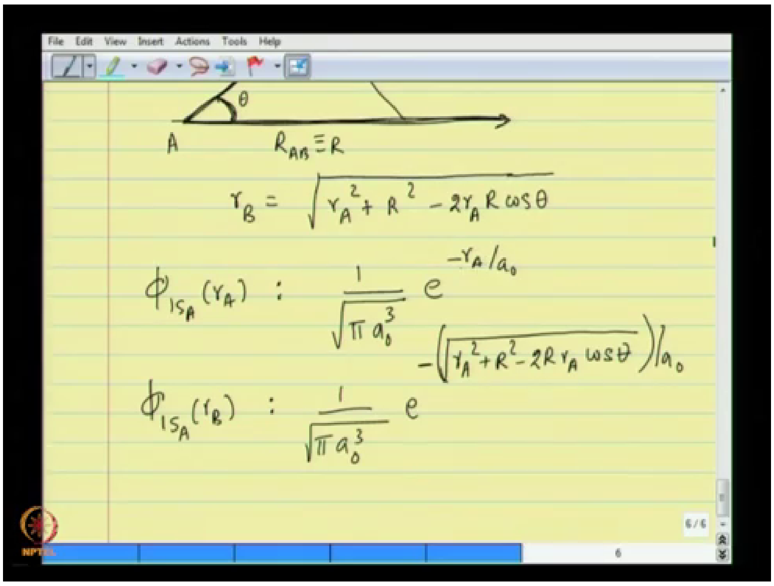

$R_{AB} \equiv R$

$$r_B = \sqrt{r_A^2 + R^2 - 2 r_A R \cos\theta}$$

$$\phi_{1s_A}(r_A) : \frac{1}{\sqrt{\pi a_0^3}} e^{-r_A/a_0}$$

$$\phi_{1s_A}(r_B) : \frac{1}{\sqrt{\pi a_0^3}} e^{-\left(\sqrt{r_A^2 + R^2 - 2 R r_A \cos\theta}\right)/a_0}$$

And phi 1 SA rA the normalized wave function that you have to use is, the square root of pi a naught cube, the Bohr radius and the function is exponential minus rA by a naught. The corresponding 1S A function for the rB coordinate is rB is again 1 by square root of pi a naught cube and it is e to the minus rB by a naught, which is given by this square root factor namely rA squared plus R square, minus 2 R rA cos theta the whole divided by a naught ok.

So, therefore, the integral that we have to calculate involves, the product of these two functions and integrated over the rA in three dimensional integral namely, it is rA square Br sin theta d theta d phi. And since, the functions do not depend on phi, we can immediately write the integral as follows.

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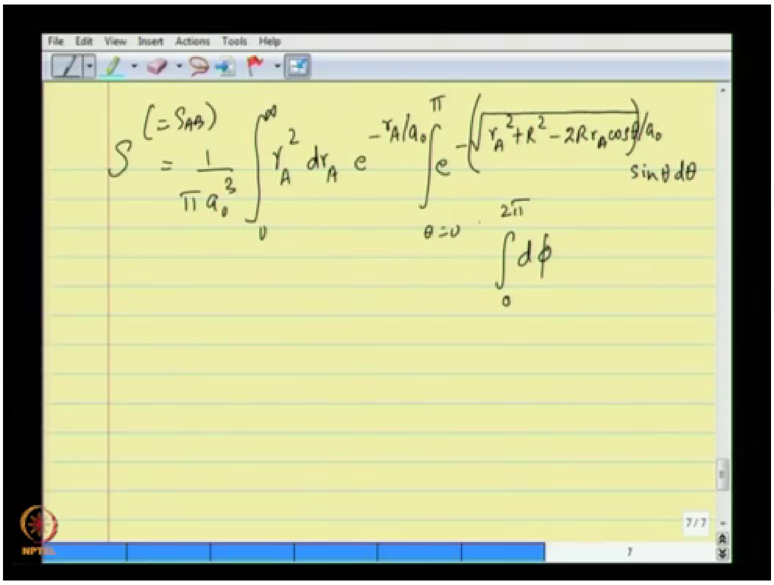

$$S \; (= S_{AB}) = \frac{1}{\pi a_0^3} \int_0^{\infty} r_A^2 \, dr_A \, e^{-r_A/a_0} \int_{\theta=0}^{\pi} e^{-\left(\sqrt{r_A^2+R^2-2Rr_A\cos\theta}\right)/a_0} \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

So, let us write S, which is essentially equal to SAB in our notation ok. S is given by 1 by pi a naught cube, we are taking the square the two functions together and the integral is 0 to infinity r A squared dr A that is, a three dimensional integral for the radial coordinate and you have the function e to the minus rA by a naught and you have the function let us write, the theta integral theta is equal to 0 to pi and we have e to the minus square root of r A square plus R square minus 2 Rr A cos theta sin theta sorry, divided by a naught the whole thing is divided by a naught, sin theta d theta.

And then we have the integral d phi between 0 and 2 pi which of course, it is easy to see that it actually cancels this phi. So, we do not need to worry about the phi integral with of course, there is a two ok.

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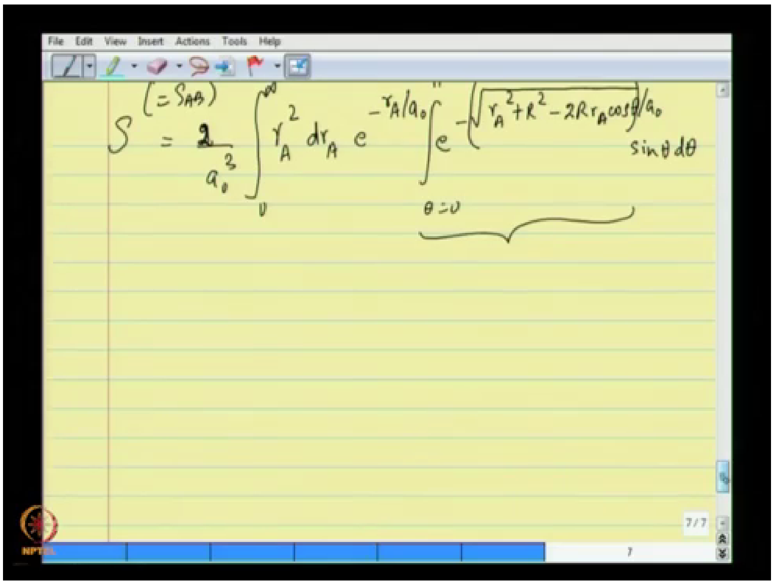

$$S \; (= S_{AB}) = \frac{2}{a_0^3} \int_0^{\infty} r_A^2 \, dr_A \, e^{-r_A/a_0} \underbrace{\int_{\theta=0}^{''} e^{-\left(\sqrt{r_A^2+R^2-2Rr_A\cos\theta}\right)/a_0} \sin\theta \, d\theta}$$

That comes from the 2 pi ok. So, what we have is this is the integral that, we have to evaluate using theta and this is the one which is algebraically somewhat tedious and therefore, let me explain this way this procedure ok.

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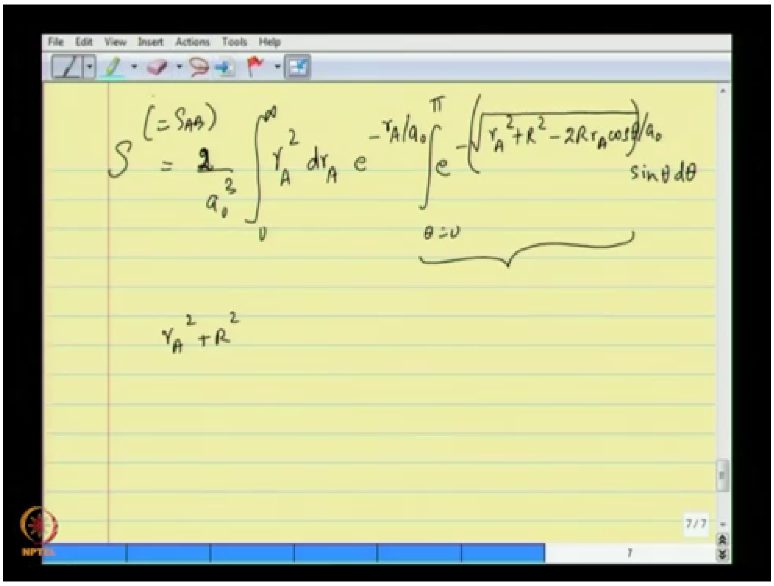

$$S \; (= S_{AB}) = \frac{2}{a_0^3} \int_0^{\infty} r_A^2 \, dr_A \, e^{-r_A/a_0} \underbrace{\int_{\theta=0}^{\pi} e^{-\left(\sqrt{r_A^2+R^2-2Rr_A\cos\theta}\right)/a_0} \sin\theta \, d\theta}$$

$$r_A^2 + R^2$$

So, let me write rA square plus R square ok, first of all let us do a simple coordinate transformation, so that, we will get rid of the a naughts ok.

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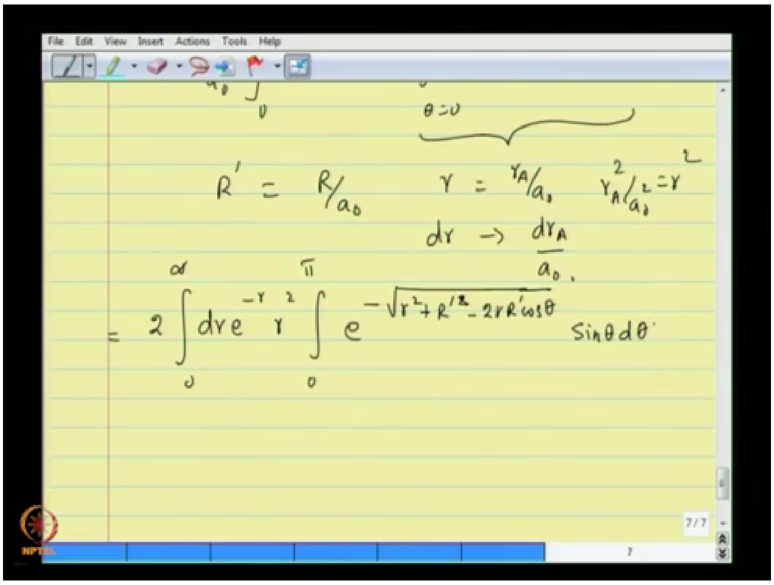

$$\theta = 0$$

$$R' = R/a_0 \qquad r = r_A/a_0 \qquad r_A^2/a_0^2 = r^2$$

$$dr \rightarrow \frac{dr_A}{a_0}.$$

$$= 2\int_0^\infty dr\, e^{-r} r^2 \int_0^\pi e^{-\sqrt{r^2 + R'^2 - 2rR'\cos\theta}} \sin\theta\, d\theta$$

So, let me use the R prime your dimensionless R namely R by a naught and a small r as rA by a naught, then you can see that the d r is going to be dr A by a naught and the rA square by a naught square is going to be r square and see that therefore, this integral immediately changes to 2, 0 to infinity dre to the minus r and there is an r square and 0 to pi e to the minus square root of r square plus R prime square minus 2 r R prime cos theta, the a naught has disappeared and the what you have is sin theta d theta.

So, that we have dimensionally we have taken care of the a naught ok, we will always substitute that back later.

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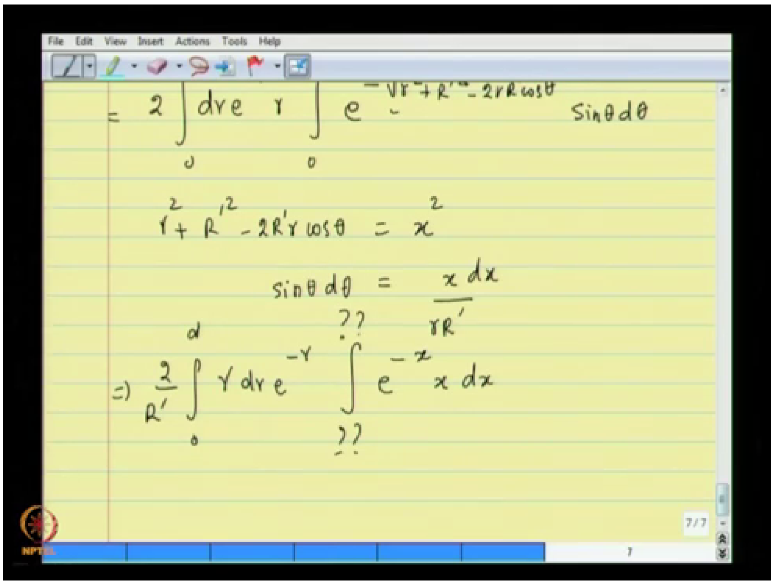

$$= 2\int_0 dr\, e\ r \int_0 e^{-\sqrt{r^2+R'^2-2rR\cos\theta}} \sin\theta\, d\theta$$

$$r^2 + R'^2 - 2R'r\cos\theta = x^2$$

$$\sin\theta\, d\theta = \frac{x\,dx}{rR'}$$

$$\Rightarrow \frac{2}{R'}\int_0^{\infty} r\,dr\, e^{-r} \int_{??}^{??} e^{-x}\, x\, dx$$

Now, use the square root factor namely, define r square plus R prime square minus 2 R prime r cos theta, as a let me see, what I have here. We have ok, what I did was to write that as i guess x ok, so that, when you do the integration if you call it is a x square, so that this is 2 x dx, when you differentiate this you will get of course, with respect to theta you are only worried about the theta coordinate here.

So, this gives you 2 R prime r sin theta d theta is equal to 2 x dx ok. So, canceling the 2 out, we have xdx. Therefore, sin theta d theta is going to be x divided by r R prime dx. So, substitute that and therefore, the integral becomes 2 integral 0 to infinity because, of the R and the r square that is r remaining, dr e to the minus r and the rest of it becomes e to the minus x. And since it is x dx, sin theta d theta becomes x and there is a 1 by R prime here ok.

So, you get 2 by R prime r dr e to the minus r and e to the minus x and what about the limits. Because you see the limits for theta is 0 to pi, but we have defined the theta in terms of x square.

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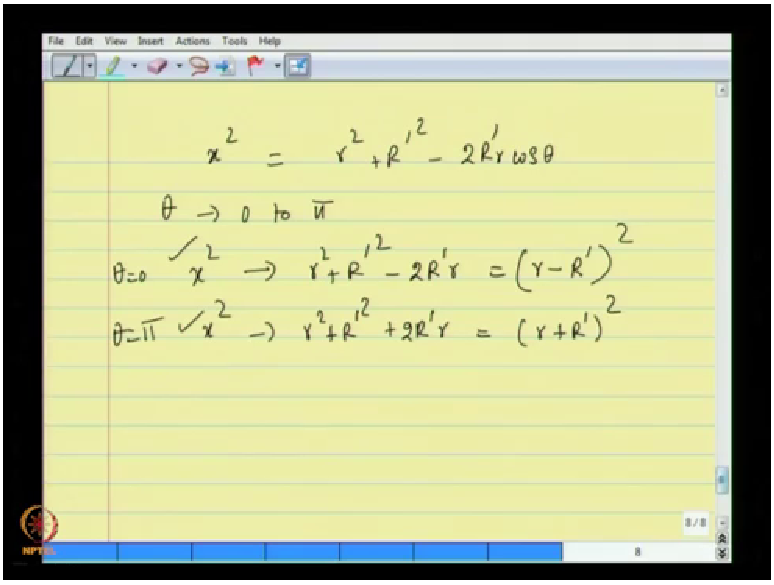

$$x^2 = r^2 + R'^2 - 2R'r\cos\theta$$

$$\theta \to 0 \text{ to } \pi$$

$$\theta=0 \quad \checkmark x^2 \to r^2+R'^2-2R'r = (r-R')^2$$

$$\theta=\pi \quad \checkmark x^2 \to r^2+R'^2+2R'r = (r+R')^2$$

So, if you look at the x square definition as r square plus R prime square minus 2 R R prime R cos theta and if, theta goes from 0 to pi then, x square goes from r square plus R prime square, when theta is 0 of course, it is minus 2 R prime r which is equal to r minus R prime square and the when x is equal to this is for theta is equal to 0. This is for theta is equal to pi of course, cos theta is minus 1 therefore, x square goes to r square plus R prime square plus 2 R prime r and so, it goes to r plus R prime square.

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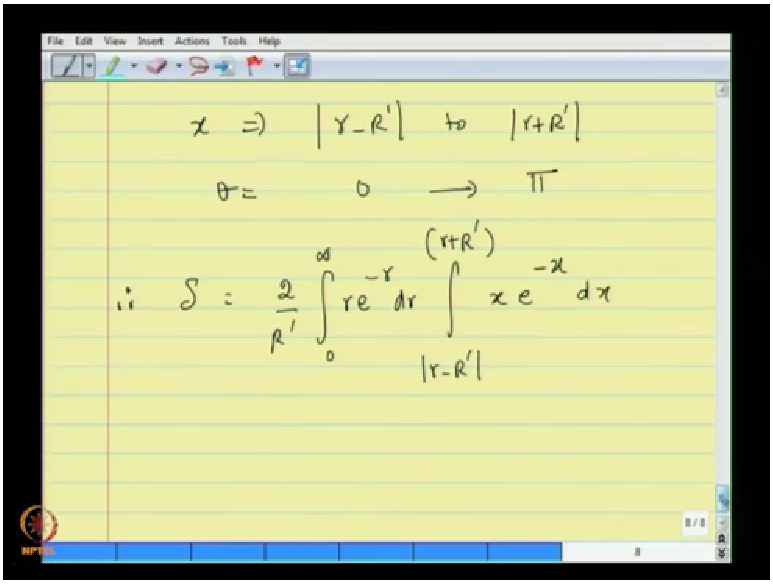

$$x \Rightarrow |r-R'| \text{ to } |r+R'|$$

$$\theta = 0 \longrightarrow \pi$$

$$\therefore S = \frac{2}{R'}\int_0^\infty re^{-r}\,dr\int_{|r-R'|}^{(r+R')} xe^{-x}\,dx$$

.

And since you are talking about x square, the value of x is of course, the modulus of r minus R prime to r plus R prime that is when theta is equal to 0 to pi So, the limits of the integral therefore, what we have here is that, the absolute value of r minus R prime and the sum of the r on R prime here, so that is important ok. Therefore, we write the integral the coulomb integral S is 2 by R prime, 0 to infinity r e to the minus r dr and then, you have the limits given by r minus R prime to the absolute value to r plus R prime. Since, both r and R prime are positive, we do not need to worry about the absolute values, it is just a sum of the two and what you have is x e to the minus x dx is not it, then x e to the minus x dx.

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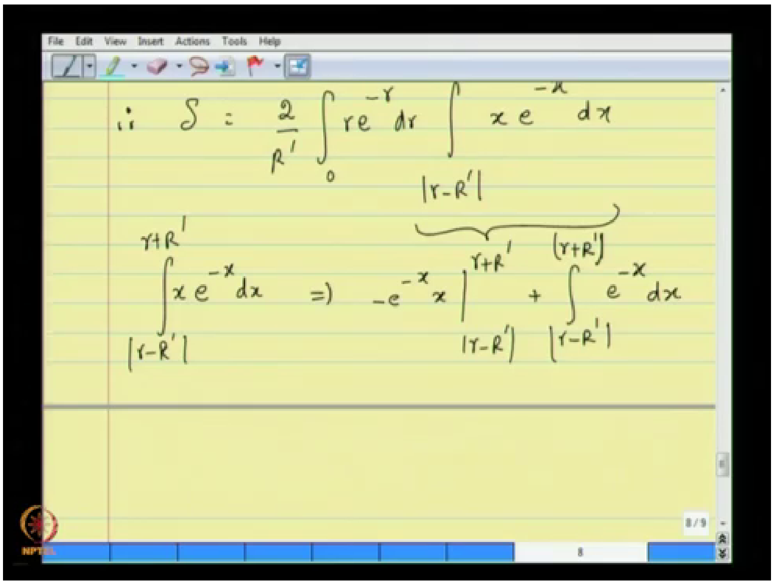

$$\therefore \quad S = \frac{2}{R'} \int_0 r e^{-r} \, dr \int_{|r-R'|} x e^{-x} \, dx$$

$$\int_{|r-R'|}^{r+R'} x e^{-x} \, dx \Rightarrow \underbrace{-e^{-x} x \Big|_{|r-R'|}^{r+R'} + \int_{|r-R'|}^{(r+R')} e^{-x} \, dx}$$

Therefore this integral is the one that needs to be evaluated.

So, this is a very simple coordinate transformation using the polar coordinates in which, the bond axis is the z axis for the system and the angle that r makes to the bond axis is the theta and therefore, we are very easily transforming this. Of course, such integrals are easy to do and let me just again take you through two or three steps; will not do all of them, but you give the method, so that you feel that overlap integral is not all that difficult to calculate for some simple systems.

So, let us look at to this. The integral x e to the minus x dx is of course, very elementary, so, what you have is it is minus e to the minus x, x between the limits namely r minus R prime, r plus r prime. So, what you have is the absolute value r minus R prime between the limits and r plus R prime and what is left over is there is a minus sign. So, you have a plus r minus R prime to r plus R prime is some e to the minus x dx ok.

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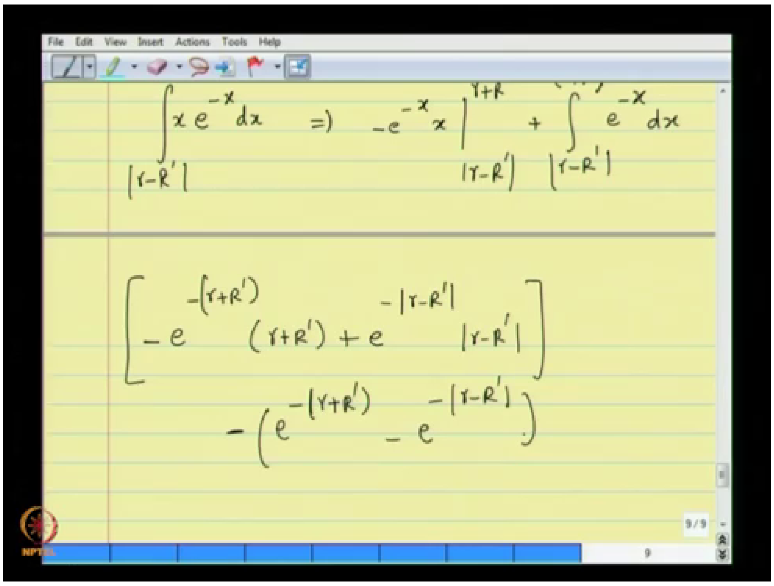

$$\int_{|r-R'|} x e^{-x} dx \Rightarrow -e^{-x} x \Big|_{|r-R'|}^{r+R} + \int_{|r-R'|} e^{-x} dx$$

$$\left[-e^{-(r+R')}(r+R') + e^{-|r-R'|}|r-R'| \right]$$

$$-\left(e^{-(r+R')} - e^{-|r-R'|}\right)$$

So, which if you expand you have the values namely, minus e to the minus r plus R prime times the absolute value sorry times the sum r plus R prime.

And the other value is of course, between the limits. So, we take the limits it is e to the minus the absolute value r minus R prime and the absolute value r minus R prime. And that is what you have for the first term and the next term is of course, e to the minus x and so, there is a minus sign e to the minus. So, what you will have is a minus you have e to the minus r plus R prime minus e to the minus absolute value r minus R prime ok.

So, this is the whole for this integral and therefore, now if you write the S as 2 by R integral 0 to infinity r e to the minus r dr then, everything else is with the minus sign.

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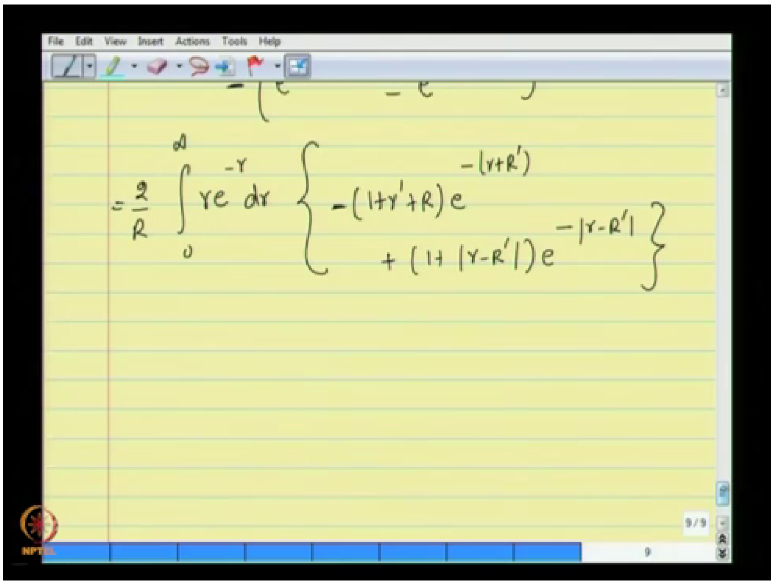

$$= \frac{2}{R}\int_0^\infty r e^{-r} dr \left\{ -(1+r'+R)e^{-(r+R')} + (1+|r-R'|)e^{-|r-R'|} \right\}$$

Here let me write the final answer, the final answer is it is given as 2 by R with this whatever is in here minus 1 plus R prime plus r e to the minus r plus R prime plus 1 plus the absolute value of r minus R prime time’s e to the minus r minus R prime.

So, this is the integration that needs to be calculated, this is the integral that needs to be calculated. Since it involves absolute values it is better to split the R value to cover this namely do this integral 0 to infinity as 0 to R prime and then from R prime to infinity dr dr ok.

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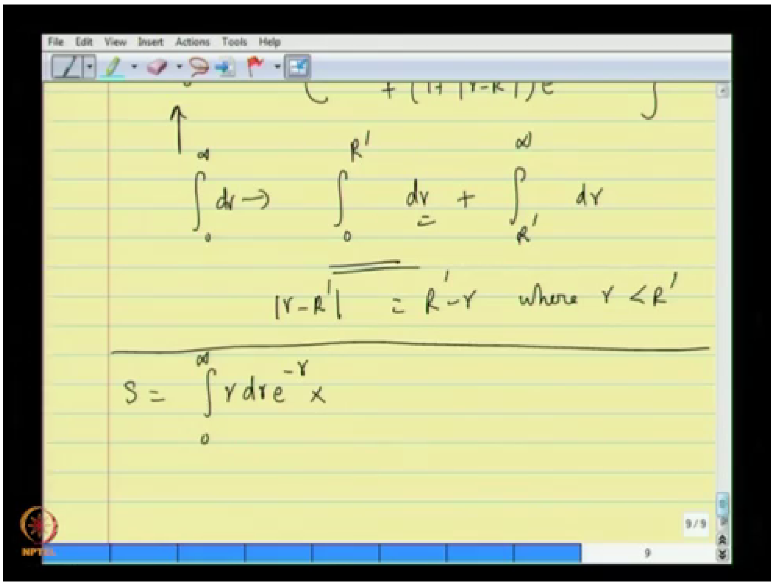

$$\int_0^\infty dr \rightarrow \int_0^{R'} dr + \int_{R'}^\infty dr$$

$$|r-R'| = R'-r \quad \text{where } r < R'$$

$$S = \int_0^\infty r\, dr\, e^{-r} \times$$

So, that we know that in this part 0 to R prime the absolute value r minus R prime since, r is less than R prime, it is always R prime minus r, we just change the sign and put the correct quantities and so that is the only thing that you need to know how to evaluate the absolute integrals namely, you put the limits in such a way that the absolute values come up to simple algebraic values.

So, when R prime is when a when the small r is less than R prime, r minus R prime absolute value becomes obviously, R prime minus r when r is less than R prime and we do not need to worry about the r plus R prime because, it is always the sum. So, this integral the S integral therefore, now splits into two terms S is equal to integral 0 to infinity r dr e to the minus r and then, times we have two terms. The first one is 2 by R, let me keep the minus sign here and the terms are 1 plus r plus R prime this is 0 to infinity is we will write this as 0 to capital R prime, that is the first a term.

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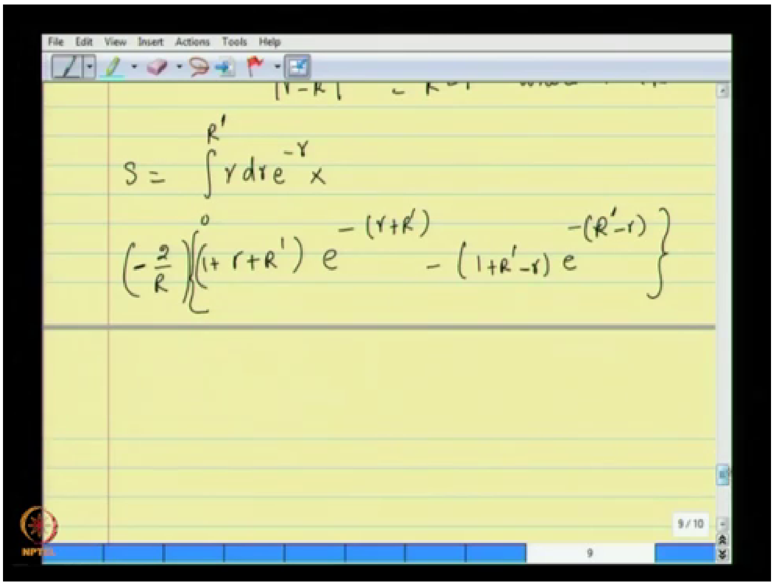

$$S = \int_0^{R'} r\,dr\,e^{-r} \times$$

$$\left(-\frac{2}{R}\right)\left\{(1+r+R')\,e^{-(r+R')} - (1+R'-r)\,e^{-(R'-r)}\right\}$$

So, what you have is 1 plus r plus R prime e to the minus r plus R prime ok. So, let me just sum this term minus 1 plus R prime minus r e to the minus r R prime minus r, this is the first term.

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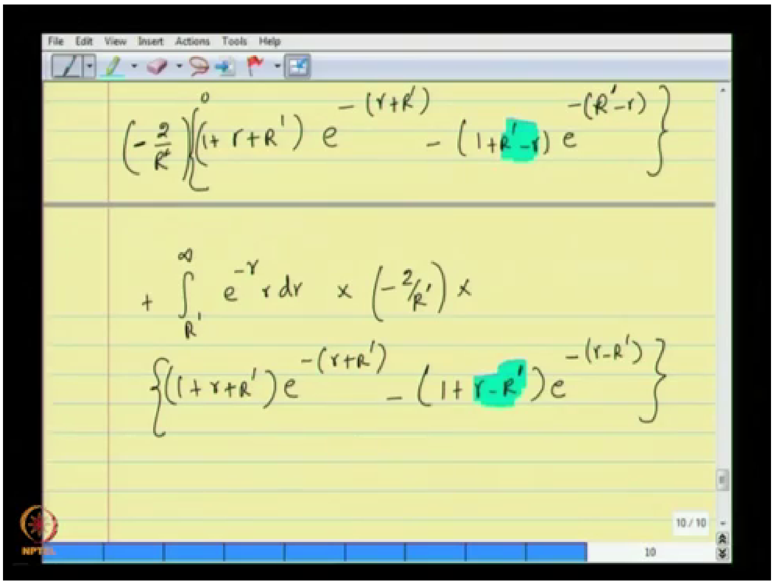

$$\left(-\frac{2}{R'}\right)\left\{(1+r+R')\,e^{-(r+R')} - (1+R'-r)\,e^{-(R'-r)}\right\}$$

$$+\int_{R'}^{\infty} e^{-r}\,r\,dr \times \left(-2/R'\right) \times$$

$$\left\{(1+r+R')\,e^{-(r+R')} - (1+r-R')\,e^{-(r-R')}\right\}$$

And the other integral is plus R prime to infinity again e to the minus r r dr multiplied by minus 2 by R prime R prime and the remaining terms are 1 plus r plus R prime e to the minus r plus R prime and with the minus 1 plus r minus R prime, you see that this changes sign this is because, the absolute value is positive here the absolute value is positive this way for this value.

So, all that you need to do is to take care of the and then write the exponent also as e to the minus r minus R prime because, R prime the the value of r is always greater than R prime. So, you see that that is done, so this closest me. So, this is the only trick that you have to do. So, two things, one is the coordinate transformation, the second is to take care of the absolute values by splitting the two integrals. So, these are small mathematical tricks, as chemistry students and as chemistry graduates we have to learn, how to do these integrals very quickly, of course, ultimately all of this reduces down now, if you look at this expression. All of this reduces to an r squared and an r and a constant multiplied by an exponential of minus r dr.

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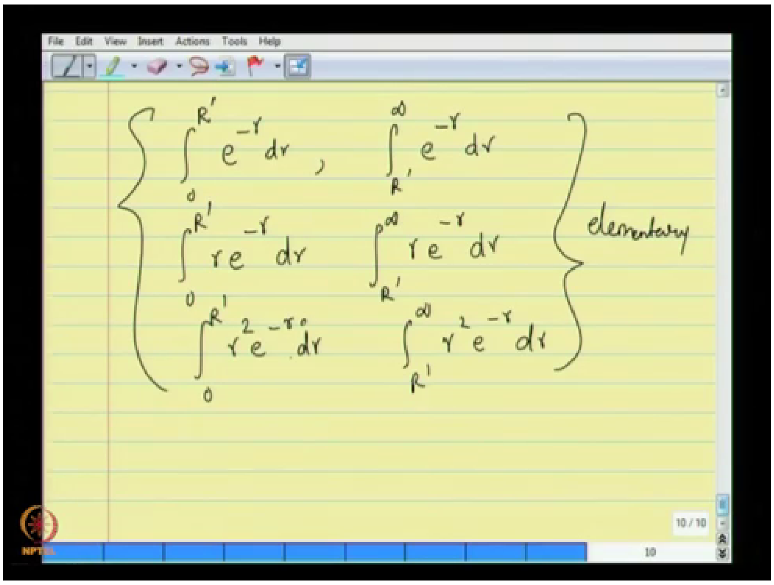

$$\left\{\begin{array}{ll} \int_0^{R'} e^{-r}\,dr , & \int_{R'}^{\infty} e^{-r}\,dr \\ \int_0^{R'} r e^{-r}\,dr & \int_{R'}^{\infty} r e^{-r}\,dr \\ \int_0^{R'} r^2 e^{-r}\,dr & \int_{R'}^{\infty} r^2 e^{-r}\,dr \end{array}\right\} \text{elementary}$$

So, we have only 3 or 4 integrals namely 0 to A constant R prime, e to the minus r dr, R prime to infinity e to the minus r dr, 0 to R prime r e to the minus r dr, R prime to infinity r e to the minus r dr and the last two namely 0 to R prime r square e to the minus rdr and R prime to infinity r square e to the minus r dr.

All of these are very elementary and of course, you must know how to do this. And so, I will leave the rest of this algebra for you to actually do and the calculator takes a few minutes to an hour or so depending on how algebraically you are able to do this without mistakes and so on.

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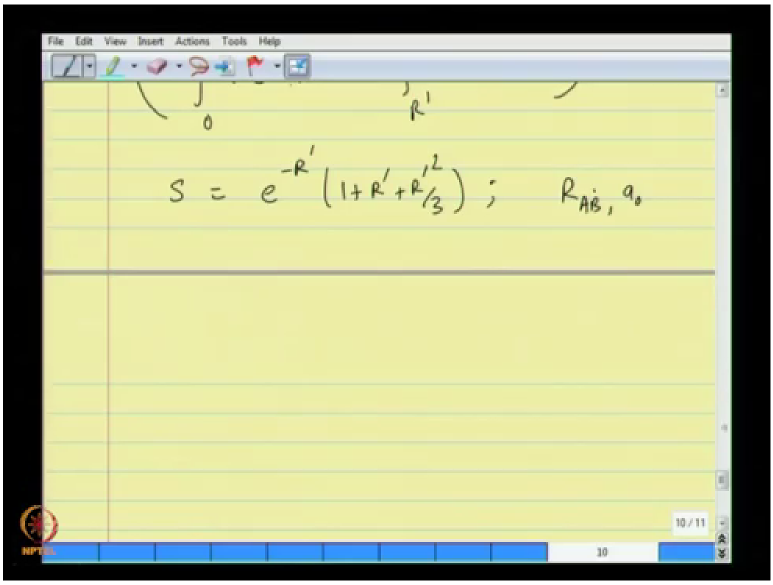

$$S = e^{-R'}\left(1+R'+R'^2/3\right); \quad R_{AB}, a_0$$

.

But it is trivial at this point of time and therefore, let me write the final answer for the S AB or the S as after doing all this integral the answer is e to the minus R prime, 1 plus R prime plus R prime square by 3, which if I convert this into the actual radial distance RAB and a naught the Bohr radius, please remember that we defined R prime as a RAB by a naught.

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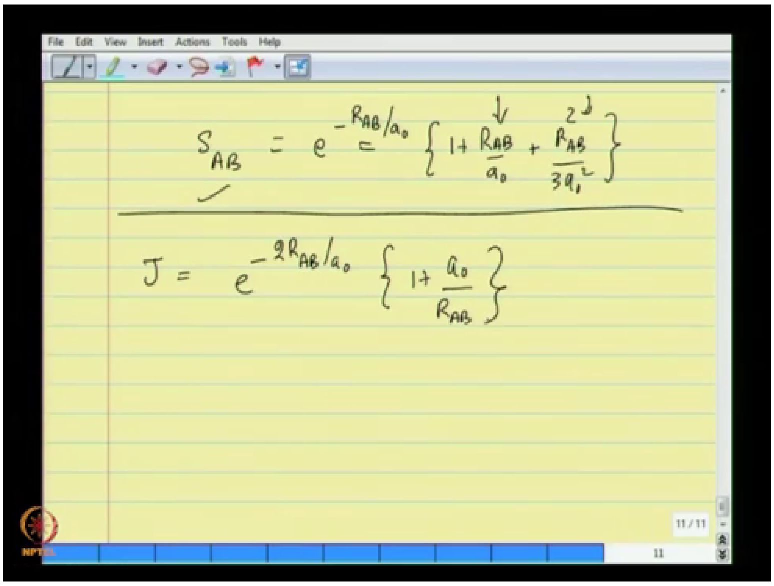

$$S_{AB} = e^{-R_{AB}/a_0}\left\{1+\frac{R_{AB}}{a_0}+\frac{R_{AB}^2}{3a_0^2}\right\}$$

$$J = e^{-2R_{AB}/a_0}\left\{1+\frac{a_0}{R_{AB}}\right\}$$

So, if you do that SAB in the final form is e to the minus RAB by a naught times 1 plus RAB by a naught plus R square RAB square by three a naught square.

So, SAB depends on the inter nuclear distance RAB in this particular form. And likewise if you have to calculate the coulomb integral J the answer is e to the minus 2R AB by a naught into 1 plus a naught by RAB ok.

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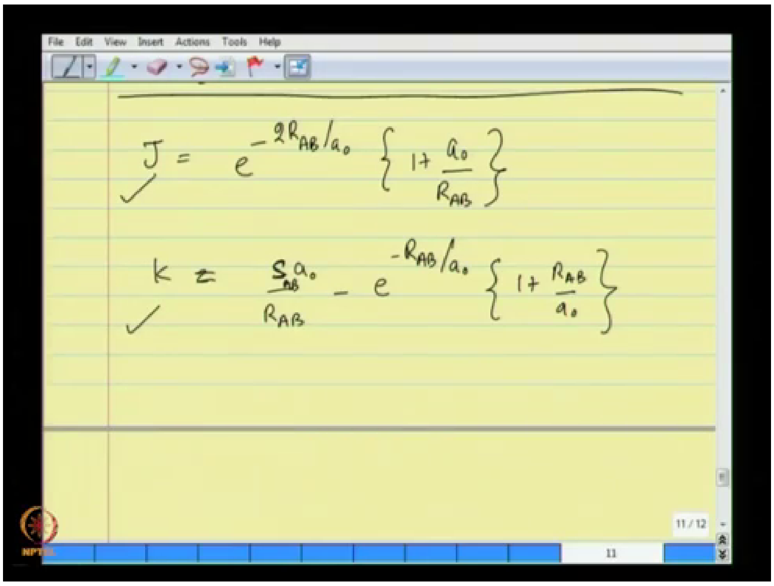

$$J = e^{-2R_{AB}/a_0}\left\{1+\frac{a_0}{R_{AB}}\right\} \checkmark$$

$$K = \frac{S_{AB}\,a_0}{R_{AB}} - e^{-R_{AB}/a_0}\left\{1+\frac{R_{AB}}{a_0}\right\} \checkmark$$

And the last integral K which is also calculated in a similar way, it involves S by RAB times a naught minus e to the minus RAB by a naught times 1 plus RAB by a naught. So, that the integrals are all dependent on the S is already calculated this is the S AB.

So, we know how to do SAB J K etcetera. So, I have demonstrated how to do the S AB using a very simple procedure. It is all published in books; it is something not something new. There are other ways of calculating it, there are more elegant ways of calculating these two center one electron, two center two electron integrals that you will have in the case of hydrogen molecule, using coordinate systems which are not familiar to you namely, the confocal elliptic coordinates system. I do not want to do that in this lecture, but in a separate lecture I will talk a little bit about the different coordinate systems that quantum chemists and quantum physicists use with relevance to chemistry.

So, at that point of time we will revisit this integral using the confocal elliptic coordinates. But this procedure I hope is simply enough for you to have a handle or how to do the multiple integral the multicenter electron integrals and in the hydrogen molecule we will again have more of these. And as we go to higher and higher molecular systems that is atomic number being very large you see that these integrals are going to get very complicated and it is also mainly or may not be the right thing to use the exponential form because, 1S orbital is no longer the eigen function of an atomic system in which, there are 2 electrons, 2 p orbitals, 2 S orbitals, 3 D orbitals they all become approximate eigen functions, when we neglect the electron electron correlation, they can be considered to be reasonably good eigenvalues and eigen functions.

Therefore we no longer have good eigen functions or what is called analytic eigen functions, when we have many electrons. So, this whole procedure will then be turned over into a computational procedure using other types of basis functions, as you recall from variational processes that we chose variational basis functions and then, we minimize the energies using these functions. So, this is only what we could do this because, we could do the exact calculations in this case it is a demonstration of how to do the algebra.

But much of the algebra for many electron systems is done today using the computers. So, we will get to the point when we needed, but let me close this lecture by saying that, the hydrogen molecule ion which by whichever method we look at the variational or physically reasonable method of the linear combination of atomic orbital, gives you the energy of the system for the bonding and the anti bonding orbital as a function of the inter nuclear separation and it is a complicated inter nuclear function because it involves exponential minus r and 1 by RAB.

So, when you plot that you get the graphs that, you got in the last lecture namely the bonding orbital combination gives rise to a minimum the anti bonding orbital does not give rise to a minimum. And the experimental energies that we determine from the spectroscopic and other methods, the experimental energies lower than the lowest minimum that we calculate. But today results are so accurate that, we can pretty much calculate the H2 plus ion energy accurately. So, that is the state of the arc and we will leave this and start looking at the hydrogen molecule in the next lecture until then.

Thank you very much.