Chemistry Atomic Structure and Chemical Bonding
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Lecture – 43
Hydrogen Molecule: The Valence Bond Method

We shall continue in this lecture the hydrogen molecule a 2 electron 2 nuclei 4 particle system and it is also the first system elementary which brings in the electron repulsion to the 4 of chemical bonding. This is in large electron multi electron system, it is often referred to as the electron correlation term due to many pairs of electron repulsions and it is an extremely important term particularly columbic energy term for chemical bonding aspects.

We shall look at the hydrogen molecule ion hydrogen molecule in a simple manner following 2 elementary treatments and later on indicate what are the developments. When one considers the molecular motion in a more complete fashion including the spectroscopic kind of terms that is the nuclear motion kinetic energy terms and so on. But for today's lecture and also probably the lecture that follows we shall operate on the Born Oppenheimer approximation and assume that the nuclei or stationary.

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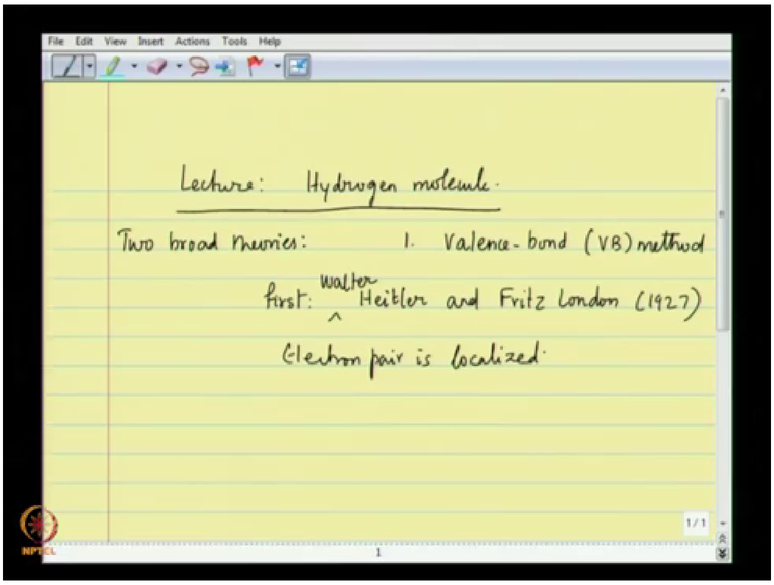

Lecture: Hydrogen molecule.

Two broad theories: 1. Valence-bond (VB) method

first: Walter Heitler and Fritz London (1927)

Electron pair is localized.

So, this lecture hydrogen molecule we shall look at it with the help of 2 broad pictures 2 broad theories, the valence bond theory or valence bond method often called VB method.

First proposed by Heitler Walter, Heitler I think I have to check my history Walter Heitler and fritz London 1927, the year when Born Oppenheimer also published, the approximation for molecular systems and for solving the Schrodinger equation.

Their idea is to use the picture that chemists had until then namely that the electrons are shared between nuclei. You might recall from elementary chemistry that GN Lewis, Gilbert Newton Lewis the most famous American chemist in the early twentieth century who came up with the octet rule and also many other theoretical methods for the study of balance in chemistry 3 quantum mechanical and who was also well known as a Thermo Dynamicists and who wrote probably the best known thermodynamics book.

In chemical thermodynamics the book by Lewis and Randall which is very famous and which has been devised by his colleagues Kenneth Pitzer and brewer it is GN Lewis who had this idea of sharing of electrons between the atoms and you might remember the dot pictures.

The valence bond method is somewhat closely associated with this idea that the electron pair is localized and in bonding the electron pair finds most of it is time between the bond distances. The other method which we talked about in the hydrogen molecule ion the molecular orbital method MO processes.

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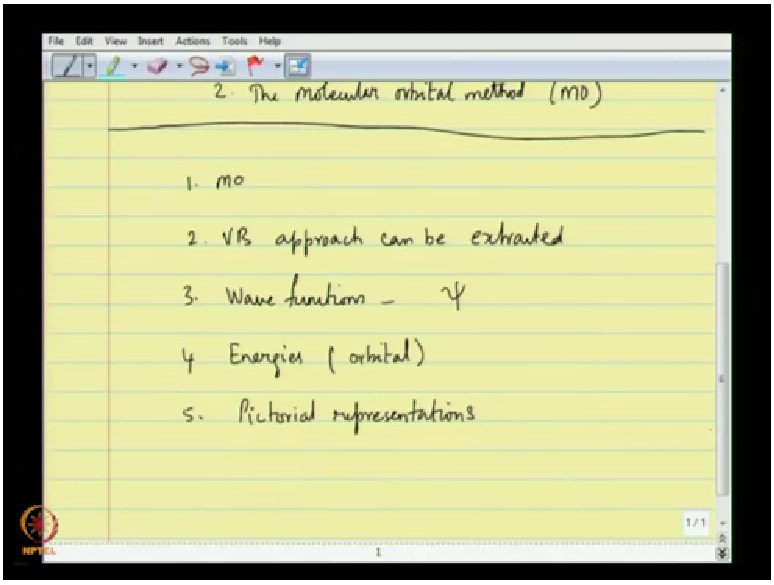

2. The molecular orbital method (MO)

1. MO
2. VB approach can be extracted
3. Wave functions – ψ
4. Energies (orbital)
5. Pictorial representations

Molecular orbital assumes that the electron is more like the electron density being shared all around the molecule using or in a molecular orbital which is a linear combination of the atomic orbital’s the constituent atomic orbital’s. The we will not discuss the differences between the 2 approaches here, first let us study what these approaches or and then later on as we progress further into quantum chemistry and more details.

We can worry about which method is better for which system or if there is any one single method and so on. Most of the time today of course people worry about using the linear combination of atomic orbital’s, but not even the atomic orbital’s that were first proposed for the hydrogen atom. Something else has I have been telling you earlier they used a Gaussian orbital’s and then there are other methods for calculating.

But these theories the VB and the MO theories give you in essence the philosophical thinking that went on at the time when computers are not available and at the time I mean unfortunately I may say so and I am not going to invite friendly criticisms by from my colleagues, that chemistry being turned into your more like a computational machine in the last 15-20 years or maybe about 30 40 years. There is so much more computation to chemistry than chemistry itself in the last several years of maybe even several decades, that some of these theories look very primitive and very naïve. But they are not the fundamental aspects that went into these theories is what revisiting and what looking at again and again.

So, we shall look at the molecular orbital method to start with and then come back to the VB theory later ok. So, my lecture today will contain a bit of description of the MO theory and out of that how the VB approach can be extracted and a bit of calculations on the wave functions the psi and finally as we move for I mean move further. We calculate energies the orbital energies or hydrogen molecular energies and then we shall at the properties that is pictorial representations of these systems.

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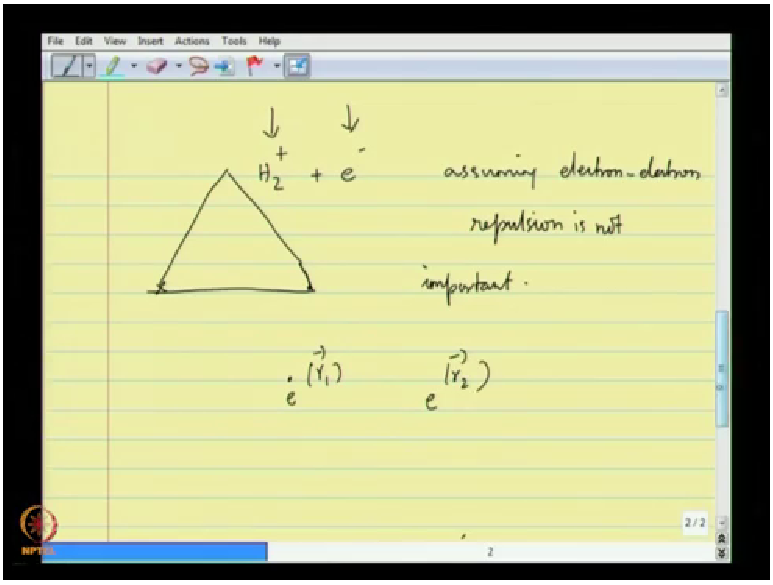

$H_2^+ + e^-$

assuming electron-electron repulsion is not important.

$e(\vec{r}_1)$ $e(\vec{r}_2)$

.

So, let us start with the MO approach by first considering the hydrogen molecule as the hydrogen molecule ion H2 plus an electron, assuming that the electron repulsion is minimal is not. So, important as to change our fundamental description of the orbital of the electron being the 1s orbital, the 1s orbital of the hydrogen atom is an Eigen function for the hydrogen atom electron orbital the Hamiltonian electronic Hamiltonian. It is an exact Eigen function.

In the absence of any external magnetic fields and; therefore it serves as a starting point for many descriptions. The moment you have 2 electrons in a system like for example helium atom or hydrogen molecule where you have also 2 nuclei.

The description of the electronic levels or electronic structure in a molecules 1 s 2 s 2 p 3 s 3 p etcetera, that description is an approximate one is probably good as a 0 order approximation. If I make of perturbation theory as an example they are not exact Eigen solutions. Therefore as a starting point if we are using the hydrogen molecular ion 1 s orbital and we assume that there is one more electron associated with this hydrogen molecule ion. So, that the hydrogen molecule is visualized.

Then what you would expect is the wave function for the 1 s electron for the electron in the hydrogen molecule ion and the wave function for the electron as it approaches the H2 plus to be independent of each other and if you put the electron 1 coordinate as r A r 1 with me r 1 and the electron to coordinate as r 2.

What one can expect is in the same sense as the particle in a 2 d box from a particle in a one dimensional box when the dimension increases or when the number of particles increase and when the particles do not interact, the overall wave function is the product of the wave functions of the non-interacting particle and the overall energy is the sum of the non-interacting particles.

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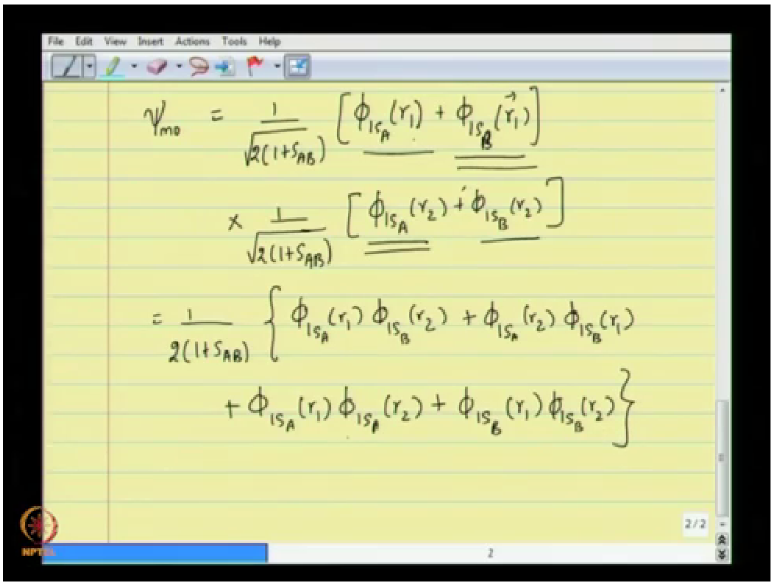

$$\psi_{mo} = \frac{1}{\sqrt{2(1+S_{AB})}} \left[\underline{\phi_{1s_A}(r_1)} + \underline{\underline{\phi_{1s_B}(\vec{r}_1)}} \right]$$

$$\times \frac{1}{\sqrt{2(1+S_{AB})}} \left[\underline{\underline{\phi_{1s_A}(r_2)}} + \underline{\phi_{1s_B}(r_2)} \right]$$

$$= \frac{1}{2(1+S_{AB})} \left\{ \phi_{1s_A}(r_1)\,\phi_{1s_B}(r_2) + \phi_{1s_A}(r_2)\,\phi_{1s_B}(r_1) + \phi_{1s_A}(r_1)\,\phi_{1s_A}(r_2) + \phi_{1s_B}(r_1)\,\phi_{1s_B}(r_2) \right\}$$

So, in that sense if we have to write psi molecular orbital for hydrogen molecule, we may start with this 1 by root 2 into 1 plus S AB times phi 1 SA for 1 SB, same electron in the 1 SB orbital times the wave function for the second electron in which everything is the same except r 1 is r 2. So, that what you have is 1 by root 2 times 1 plus S AB times phi 1 SA r 2 plus phi 1 SB r 2.

So, that the overall wave function consists of 4 terms namely 1 by 2 into 1 plus S AB times, let me write it in a slightly different order not in the order in which you normally do the multiplication. But let me write it as 1 SA r 1 phi 1 SB r 2 one of the terms that come out by multiplying this and this one and likewise we will do the multiplication of these 2 phi 1 SA r 2 phi 1 SB r 1 and then we write the remaining terms namely phi 1 SA r 1 phi 1 SA r 2 plus phi 1 SB r 1 phi 1 SB r 2.

The reason for organizing it this way should be clear in a few minutes when we discuss valence bond theory, but let us look at these terms individually. So, we have a linear combination of the 2 electron wave functions the basis functions, the 2 electron wave functions such that electron 1 is associated with atom A and electron 2 is associated with atom B as you have seen in the highlighted portion here.

Now, let me change the highlight and look at the same term here highlighted with a different color, you see that it is like electron 2 associated with the 1 s atom 1 s orbital of atom A and electron 1 associated with the ones orbital of atom B. If you take the square of the coefficients the linear combination coefficients they represent the probability that the electrons are such that electron 1 is in the 1 s orbital of A electron 2 is simultaneously in the ones orbital of B and vice versa.

That is what these individual terms mean and that is a sort of a localized picture, you are assuming that the electron 1 s not perturbed by the fact that electron 2 is associated with the other atom, what you call as A or B is your label my label atom 1 and 2 electrons are indistinguishable the nuclei are indistinguishable. Therefore, these 2 at the 2 highlighted orbital contributions have to be exactly the same level of contribution.

Now, look at the next 2 terms that I have written at the bottom ok, let us highlight it with a different color. The square of the coefficient associated with this orbital essentially tells you that electron 1 is in the 1 s orbital of atom A and electron 2 is also n the 1 s orbital of atom A. It looks like the hydrogen atom B I mean has lost it is electron and that both the electrons are now associated with the atom A it is like H minus H plus if I may say.

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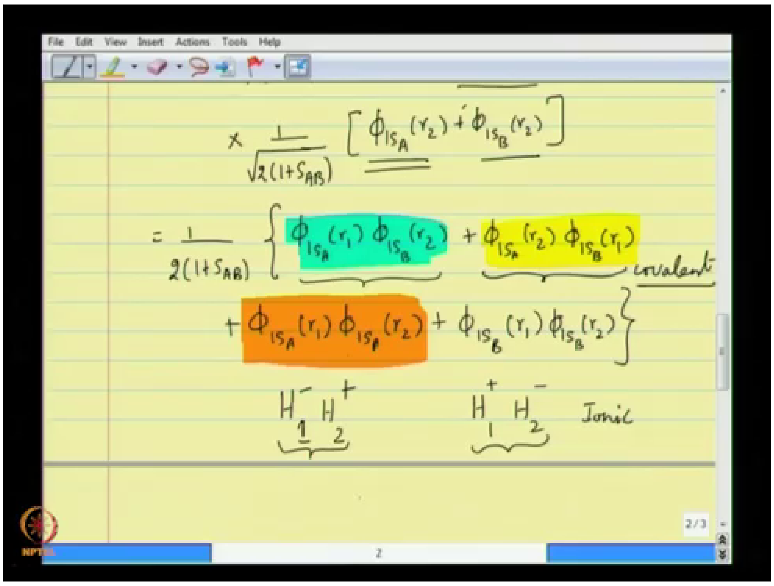

$$\times \frac{1}{\sqrt{2(1+S_{AB})}} \left[\underline{\underline{\phi_{1s_A}}}(r_2) + \underline{\phi_{1s_B}(r_2)} \right]$$

$$= \frac{1}{2(1+S_{AB})} \Big\{ \underbrace{\phi_{1s_A}(r_1)\,\phi_{1s_B}(r_2)} + \underbrace{\phi_{1s_A}(r_2)\,\phi_{1s_B}(r_1)}_{\underline{\text{covalent}}}$$

$$+ \phi_{1s_A}(r_1)\,\phi_{1s_A}(r_2) + \phi_{1s_B}(r_1)\,\phi_{1s_B}(r_2) \Big\}$$

$$\underbrace{\overset{-}{\underset{1}{H}}\ \overset{+}{\underset{2}{H}}} \qquad \underbrace{\overset{+}{\underset{1}{H}}\ \overset{-}{\underset{2}{H}}} \quad \text{Ionic}$$

So, the system is H1 minus, so let me write this H1 minus and H 2 plus. The moment I say this you will immediately notice that the term I have left out without any description, corresponds exactly to the same as the previous 1 with the minus and plus getting interchange H1 plus and H2 minus. What is important is that all these 4 contributions in terms of probabilities of finding the electrons, in the respective orbital's of the respective atoms. If you look at that because the squares of the coefficients here what is the square of these coefficients, it is 1 by 4 into 1 plus S AB whole square that is the same number you add it 4 times ok, with the appropriate normalization constant.

So, you have that all these 4 are equally weighted, that is the possibility that the electrons are equally shared by both these atoms and the possibility that the electrons or likely to be found in one atom absolutely certainly versus the other. Both possibilities are weighted by the same level or to the same degree and that seems like a little bit farfetched and therefore if we argue this on the basis of what we have written down and calculate the energy for the hydrogen molecule. We must expect energy quite different from what the experimentally obtained minimum or what is called the exact minimum.

So, the ionic contributions as you would call them this is the ionic contribution or weighted by the same amount as the covalent contribution as you see here covalent and the, that is not a very comfortable picture. If we were to assume a molecular orbital theory based on 2 non interacting electrons and then we take the product of the electrons are together and then find out. Now, this is coming from one end of the approach.

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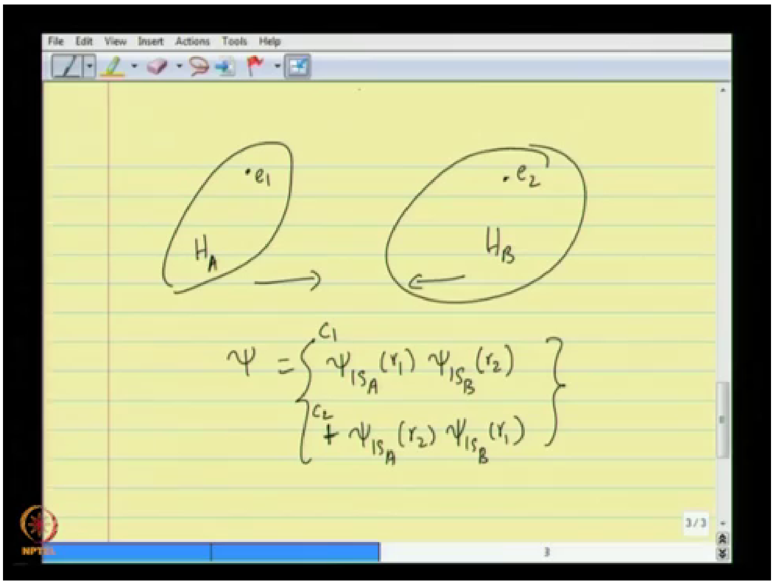

$$\psi = \left\{ \begin{array}{l} \overset{c_1}{} \psi_{1s_A}(r_1)\, \psi_{1s_B}(r_2) \\ \overset{c_2}{+} \psi_{1s_A}(r_2)\, \psi_{1s_B}(r_1) \end{array} \right\}$$

Now valence bond theory which was proposed by Hitler and London also starts with the idea that hydrogen A with it is electron 1 and hydrogen B with it is electron 2. As they approach the distance of what is called the closest approach and the distance of minimum energy at some point. Obviously, they form a bond and therefore the energy is the minimum and the valence bond approach assumes that the wave function for this system should be expressed as the wave function for the 1s electron in atom A r 1 times wave function for the 1 s electron in atom B r 2.

But because the electrons are indistinguishable the valence bond approach, will have to logically correct this by including 1 SA r 2 psi 1 SB r 1 which electron is which when they are close and when the molecule is formed we cannot distinguish the electron and therefore these are the 2 contributions a linear combination that we can think of and the valence bond theory starts with this as a the what is called the a variationaly correct approach ok.

In principle you can write this as C 1 and C 2. If you wish to but again as we have in the case of hydrogen molecule ion, there is no reason to suspect C 1 and C 2 to be different from each other except possibly for a minus sign ok. So, this is the starting point, so where do we begin should we begin at this point that is the psi VB or should we study the psi MO well before I give you the answer. In fact, we are going to look at the answer to the, with the problem using both the methods.

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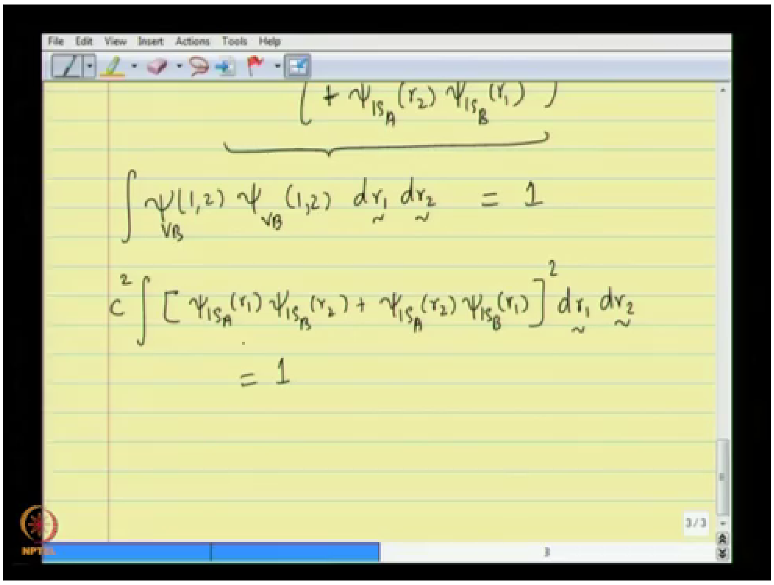

$$\underbrace{\left(+ \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1) \right)}$$

$$\int \psi_{VB}(1,2)\,\psi_{VB}(1,2)\,d\underset{\sim}{r_1}\,d\underset{\sim}{r_2} = 1$$

$$C^2 \int \left[\psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2) + \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1) \right]^2 d\underset{\sim}{r_1}\,d\underset{\sim}{r_2}$$
$$= 1$$

Let me just also point out that the moment you write the psi valence bond like this, the wave function normalization if you are looking at psi 1 2, v being this is essentially psi 1 2 VB 1 2 ok; psi star psi 1 2 since these are all real orbital's and the coefficients we assume are real we can write psi 1 2 dr 1 dr 2 integration.

Over both the electron coordinates the normalization of this wave function leading to one must give us this condition namely. Let us write this as C squared times psi 1 SA r 1 plus psi 1 SB r 2 oh I am sorry not A plus psi 1 SB 2 plus psi 1 SA r 2 psi 1 SB r 1 whole square dr 1 dr 2 integration of all the 3. Directional coordinates of the electron one and the electron 2 that is the total space for both the electrons and that should be one which tells us immediately that we can write this as 4 integrals.

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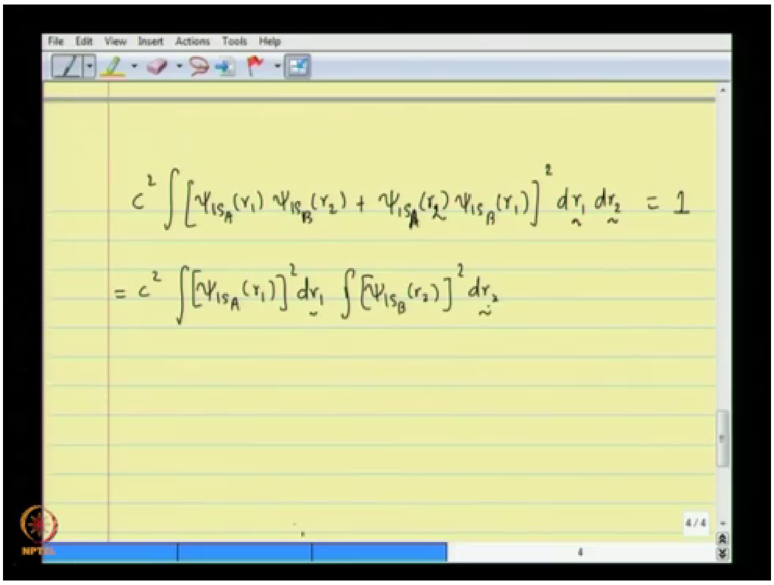

$$c^2 \int \left[\psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2) + \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1)\right]^2 d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2 = 1$$

$$= c^2 \int \left[\psi_{1s_A}(r_1)\right]^2 d\underset{\sim}{r}_1 \int \left[\psi_{1s_B}(r_2)\right]^2 d\underset{\sim}{r}_2$$

So, expand this we will get 4 terms C square the integral psi 1 SA r 1 square dr 1 times psi 1 SB r 2 squared dr 2 that is the first term and the other 3 terms are integrals psi 1 SA r 2 squared.

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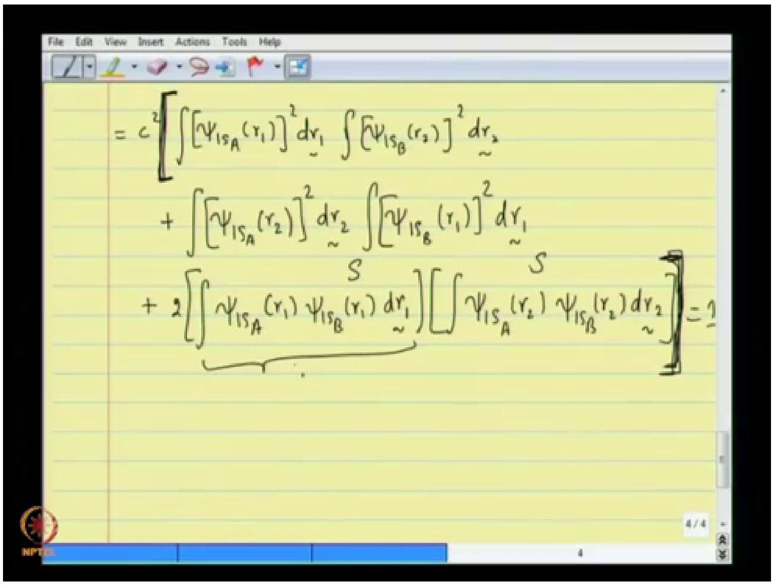

$$= c^2 \Bigg[\int \left[\psi_{1s_A}(r_1)\right]^2 d\underset{\sim}{r}_1 \int \left[\psi_{1s_B}(r_2)\right]^2 d\underset{\sim}{r}_2$$
$$+ \int \left[\psi_{1s_A}(r_2)\right]^2 d\underset{\sim}{r}_2 \int \left[\psi_{1s_B}(r_1)\right]^2 d\underset{\sim}{r}_1$$
$$+ 2 \underbrace{\overset{S}{\left[\int \psi_{1s_A}(r_1)\,\psi_{1s_B}(r_1)\, d\underset{\sim}{r}_1\right]}}_{} \overset{S}{\left[\int \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_2)\, d\underset{\sim}{r}_2\right]} \Bigg] = 1$$

But let me do the, with r 2 and psi 1 SB r 1 squared and integrate that over the dr 1. So, these are all the integrals of the atomic orbital’s normalized and then you have the term which is what I have done is a square plus B square this is A square and this is B square and then we have, so if we call this A and B this is 2 AB is what we have. So, therefore twice the integral psi 1 SA r 1 psi 1 SB r 1 d r 1 and this is 1.

So, what should I have I should have a bigger square bracket here covering this c square ok, so let us do that that is what this is. So, what we have is the first integral is nothing other than the atomic orbital normalization for electron in atom 1 an electron in atom 2. So, that product is one is to one times one and likewise the second integral we just call r 1 and r 2 as coordinate.

So, if in it is integrated over the entire coordinate r 2, therefore psi 1 SA r 2 whole square dr 2 SA is the same as psi 1 SA r 1 square dr 1 these all the 3 dimensional space is covered, therefore this is also one and this you have recognized immediately as the overlap integral that we talked about in the last 2 lectures 1 SA r 1 1 SB r 1 that is electron 1 in 1 SA and 1 SB before the 2 orbital overlap integral and what you see here is S squared this is an S this is an S.

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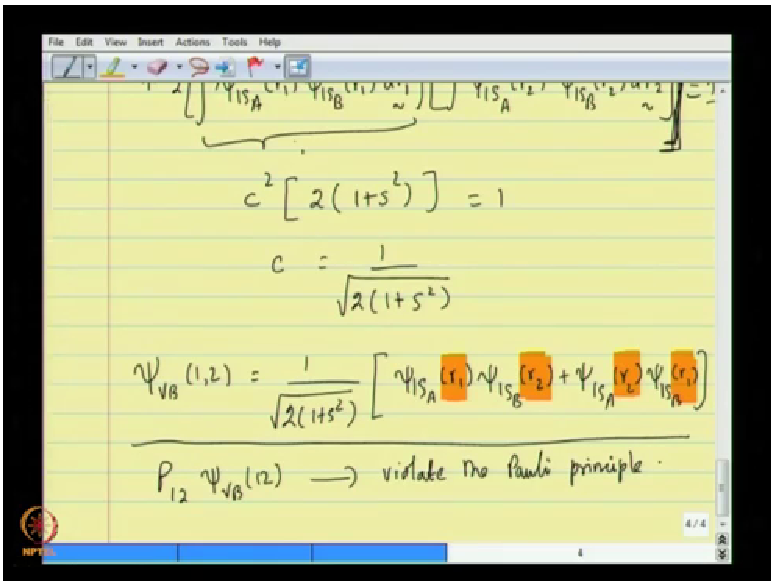

$$c^2\left[2(1+S^2)\right] = 1$$

$$c = \frac{1}{\sqrt{2(1+S^2)}}$$

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

$P_{12}\,\psi_{VB}(12) \longrightarrow$ violate the Pauli principle.

Therefore the normalization constant for this problem is C squared 2 into 1 plus S squared that should be 1 and therefore C is 1 by square root of 2 into 1 plus S square. So, what we have therefore is the wave functions psi VB of 1 2 yes, 1 by square root of 2 into 1 plus S square times psi 1 SA 1 r 1 psi 1 SB r 2 plus psi 1 SA r 2 psi 1 SB r 1.

So, if you go back and look at the molecular orbital picture that we discussed, you see if retaining only these 2 colored terms the blue and the green and the yellow term. You see that that is going to be a small problem with respect to the normalization constant if we keep only these, but neglect to these that is exactly what we did here.

So, if we start with the valence bond orbital we have this as the overall electron orbital for the 2 electrons, but there is still one more problem this is not satisfying the anticipatory principle of the 2 electrons. Now we have 2 electrons therefore it is important for the wave function to be overall negative, if the coordinates of both the wave functions both the electrons are interchanged.

So, if I do a permutation of the electrons 1 and 2 on psi VB 1 2, obviously I violate the Pauli’s Anti Symmetry principle, therefore this picture is not a complete picture. The 2 electrons when they are together in an orbital system you have to worry about the exchange of both the space and the spin coordinates and we have not included the spin in this part.

If we have to include the spin part should be anti symmetric because the space part is symmetric, remember if you interchange r 1 and r 2. If you interchange r 1 and r 2 you are going to get exactly the same wave function therefore the wave function is symmetric. The electron being a fermions that is not what we want, we want and the electron to be the electron wave function to be anti symmetric to the interchange of the 2 electron coordinates.

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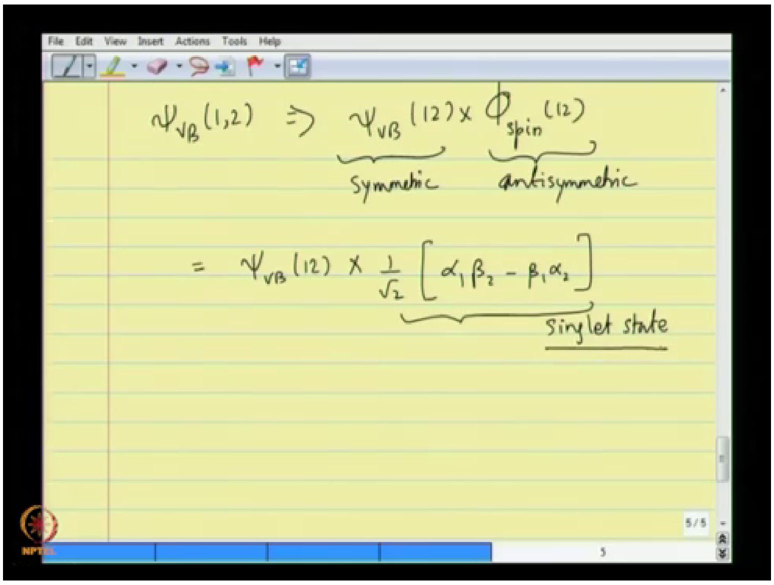

$$\psi_{VB}(1,2) \Rightarrow \underbrace{\psi_{VB}(12)}_{\text{Symmetric}} \times \underbrace{\phi_{spin}(12)}_{\text{antisymmetric}}$$

$$= \psi_{VB}(12) \times \underbrace{\frac{1}{\sqrt{2}}\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]}_{\underline{\text{Singlet state}}}$$

Therefore it is important to have the spin of this psi VB 1 2 to contain to be replaced by psi VB 1 2 times a spin function phi spin 1 2 and because this is symmetric as we have chosen, it is important for us to have this S anti symmetric. Therefore, the wave function that we choose must be psi VB 1 2 multiplied by 1 by square root 2, you remember the anti-symmetric spin wave function is alpha 1 beta 2 minus beta 1 alpha 2 this is a singlet state ok.

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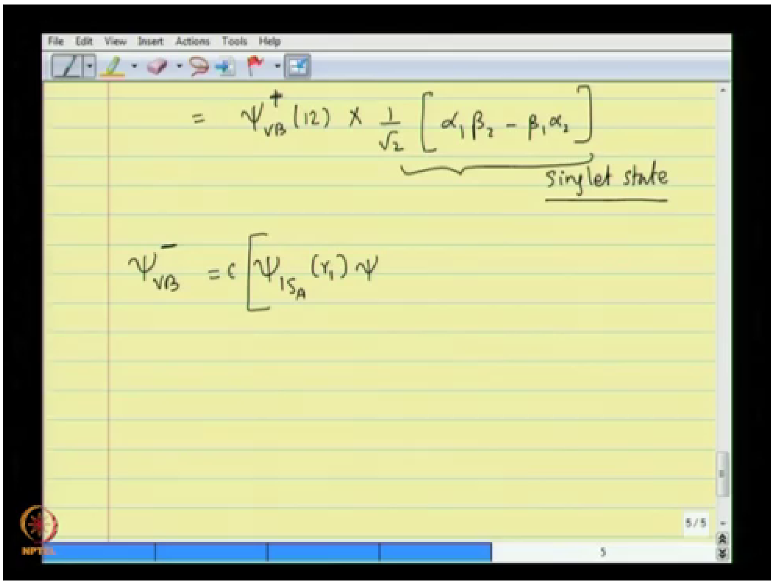

$$= \psi^{+}_{VB}(12) \times \underbrace{\frac{1}{\sqrt{2}}\left[\alpha_1\beta_2 - \beta_1\alpha_2\right]}_{\underline{\text{Singlet state}}}$$

$$\psi^{-}_{VB} = c\left[\psi_{1s_A}(r_1)\psi\right.$$

On the other hand, if we take the linear combination of psi VB, let us call this plus and if you take the linear combination minus which we call as psi 1 SA, which we write psi 1 SA r 1. We write this as we do not need the constants I know what this constant. It is easy to verify that it is 1 minus S square into square root 2, you will get the combinations psi 1 SA r 1 psi 1 SB r 2 minus psi 1 SA r 2 psi 1 SB r 1.

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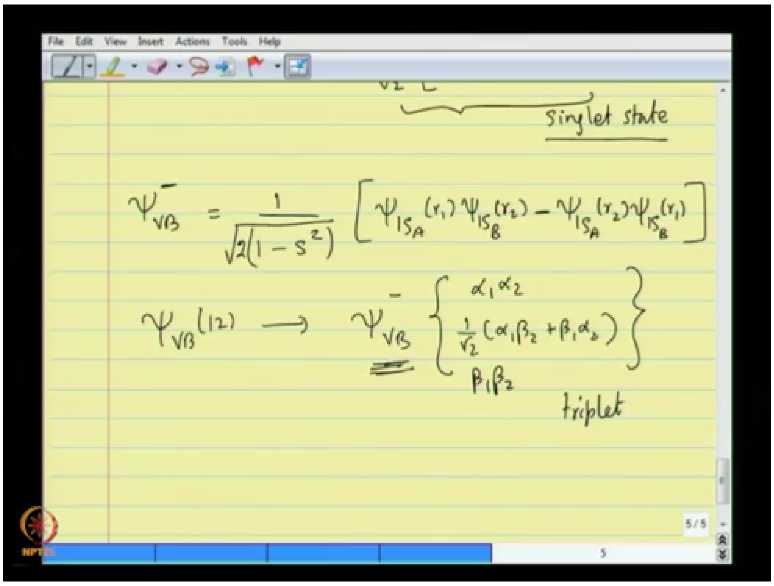

Singlet state

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

$$\Psi_{VB}(12) \longrightarrow \underline{\underline{\Psi_{VB}^{-}}}\left\{\begin{array}{l}\alpha_1\alpha_2\\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2+\beta_1\alpha_2)\\ \beta_1\beta_2\end{array}\right\}$$

triplet

If we do this the spin part the psi MO psi valance bond orbital of 1 2 should now be replaced by psi VB minus times a symmetric part, which is alpha 1 alpha 2 for the 2 spins r 1 by root 2 alpha 1 beta 2 plus beta 1 alpha 2 r beta 1 beta 2.

Any one of the 3 is as good as the other because, what we have is the spin part is symmetric with respect to the interchange and in the absence of interactions of the electron spins with each other or the spin with the electron orbital or with an external magnetic field all these 3 states are degenerate and therefore you see that this is called the triplet state. The anti-symmetric linear combination of the spatial orbital's of the electrons has to be associated with the triplet state of the pair of electrons in their spin quantum numbers.

So, these are things that one has to keep in mind, but for the calculations that we are going to do in the this lecture and the next lecture we are not going to worry about the spin part of it. Therefore, the spin part is not going to change the energy levels by any means, but it has to be kept in mind that it is there and the 2 electrons are either paired as you might normally would like to imagine in an anti-symmetric combination that has been 0.

This been 0 essentially means spin up and spin down in the same orbital and now you have the Polly's principle of all the 4 quantum numbers of the 2 electrons not being the same because, is been quantum number of one of the electron it is a plus half the ever electron is a minus half, so the anti-symmetry principle is satisfied.

Whereas, if you have the 2 electrons in the 2 different orbital's it does not matter whether they are like this or whether they are like this or whether they are like this up and down it is not matter up and down or this way that way. That is what we call as a triplet state and that is of course we will find out that it is a very highly energetic state and therefore it is not a bonding orbital for our purposes.

So, the valence bond theory when we introduce this linear combination which is a truncated linear combination from this, from the molecular orbital theory keeping only the covalent contribution in in the chemical sense. If we do that and make amendments for the yes by writing this as 1 by square root of 2 into 1 plus r squared we have now a wave function and that is a proposed wave function we calculate the energy of the system and that is the valence bond orbital energy. So, let us proceed with that calculation in the remaining time, we will come back to molecular orbital theory later.

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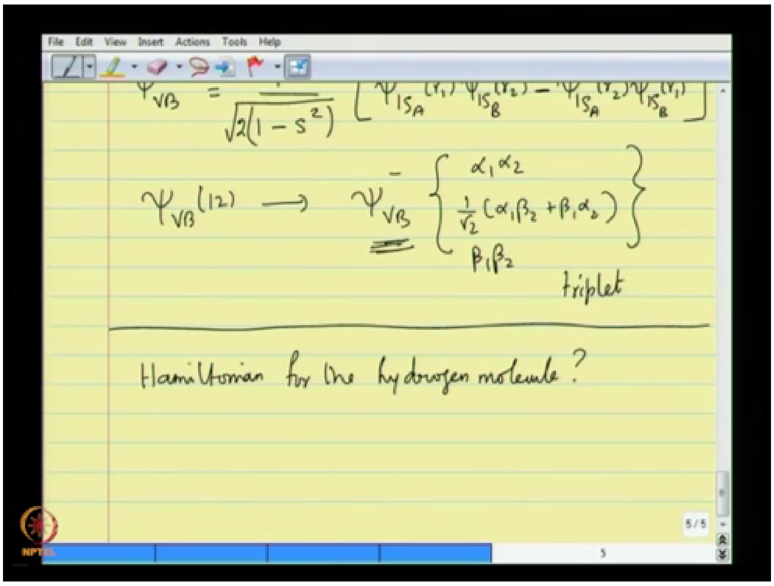

$$\Psi_{VB} = \frac{\quad}{\sqrt{2(1-s^2)}}\left[\psi_{1s_A}(r_1)\psi_{1s_B}(r_2) - \psi_{1s_A}(r_2)\psi_{1s_B}(r_1)\right]$$

$$\Psi_{VB}(12) \longrightarrow \underline{\underline{\bar{\Psi}_{VB}}} \left\{ \begin{matrix} \alpha_1\alpha_2 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ \beta_1\beta_2 \end{matrix} \right\}$$

triplet

Hamiltonian for the hydrogen molecule?

So, what is the Hamiltonian for the hydrogen molecule Hamiltonian for the hydrogen molecule?

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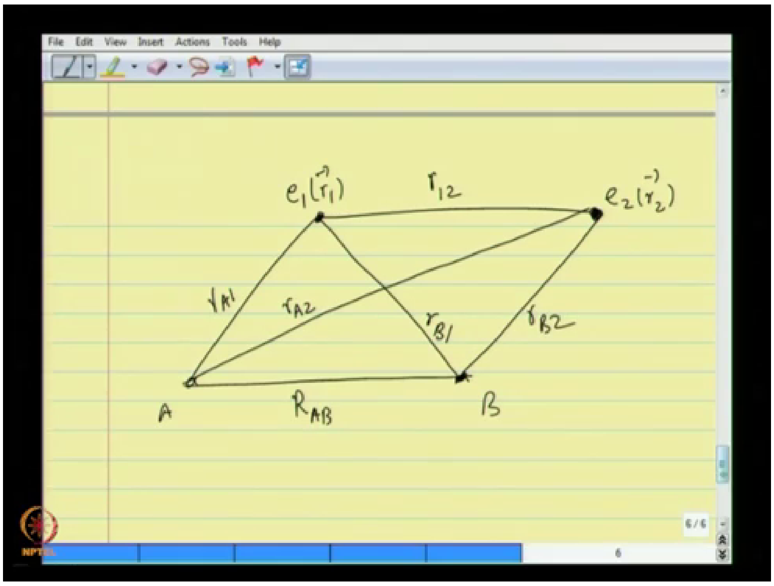

Of course, we need this classical picture of having the 2 electrons at a parallelogram exactly, but it is 2 electrons in 2 arbitrary positions this is a nucleus A B electron 1 electron 2 and if we call this as the coordinates r 1 and r 2. We have this is electron A so we call this r A1 and this is R AB similar to our previous notation, this is r 1 2 the electron classical charge point charge the distances between the 2 point charges and then we have r A2 electron 2 from the nucleus A electron 1 from the nucleus B, we will write this as r B1 and the electron 2 from the nucleus B as r B2 and once we have written this the Hamiltonian is within the Born Oppenheimer approximation of not worrying about the nuclear kinetic energies.

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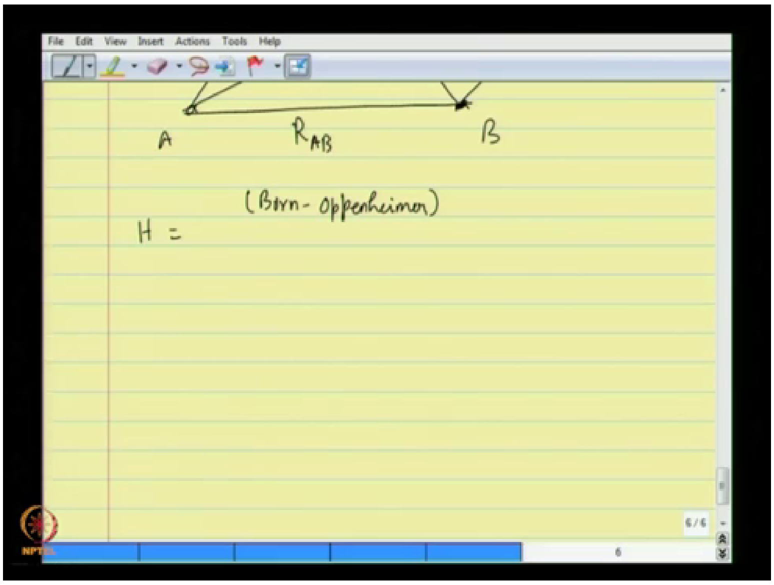

(Born- Oppenheimer)

H =

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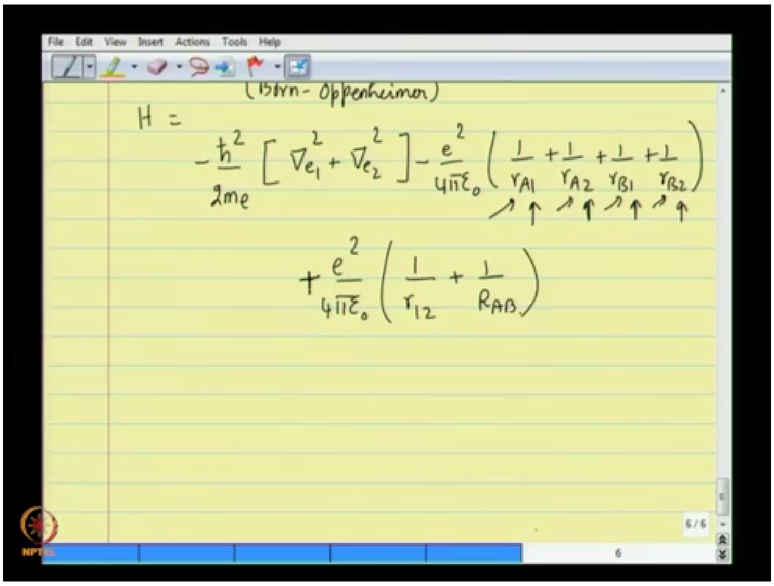

(Born- Oppenheimer)

$$H = -\frac{\hbar^2}{2m_e}\left[\nabla_{e_1}^2 + \nabla_{e_2}^2\right] - \frac{e^2}{4\pi\varepsilon_0}\left(\underset{\nearrow\uparrow}{\frac{1}{r_{A1}}} + \underset{\nearrow\uparrow}{\frac{1}{r_{A2}}} + \underset{\nearrow\uparrow}{\frac{1}{r_{B1}}} + \underset{\nearrow\uparrow}{\frac{1}{r_{B2}}}\right)$$

$$+ \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}} + \frac{1}{R_{AB}}\right)$$

So, we have minus h bar square by 2 me we have del electron 1 square, whatever is the coordinate that we need to potent and electron 2 square for the kinetic energy of the 2 electrons and the potential energy is now going to be a sum of for attraction terms columbic attraction terms, electron 1 with the nucleus A electron 1 with the nucleus B, electron 2 with the nucleus A electron 2 with the nucleus B. We have 4 electron nuclear attraction terms and then we also have 2 electron and nuclear repulsion terms electron 1 bit electron 2 and nucleus 1 and nucleus 1.

Will include the nuclear repulsion term in our calculation because, we want to calculate the hydrogen molecule energy. As a function of the inter nuclear separation between the 2 hydrogen atoms to find out what is the minimum and there is a minimum and what that distance corresponds to and how does it correlate with the experimentally determined in the bond energy and the bond distances.

So, to include those terms we have to write minus e square by 4 pi epsilon naught and the columbic attraction terms are 1 by r A1 by r A2 plus 1 by r B1 plus 1 b r B2. Which are the distances of the electrons 1 and 2 from the nucleus A and B and the last term is of course, minus e square by 4 pi epsilon not, 1 by r 1 2 the inter sorry there should be a plus here. The inter nuclear distant inter electron repulsion electron repulsion and the nuclear nuclear repulsion R AB so this is the Hamiltonian.

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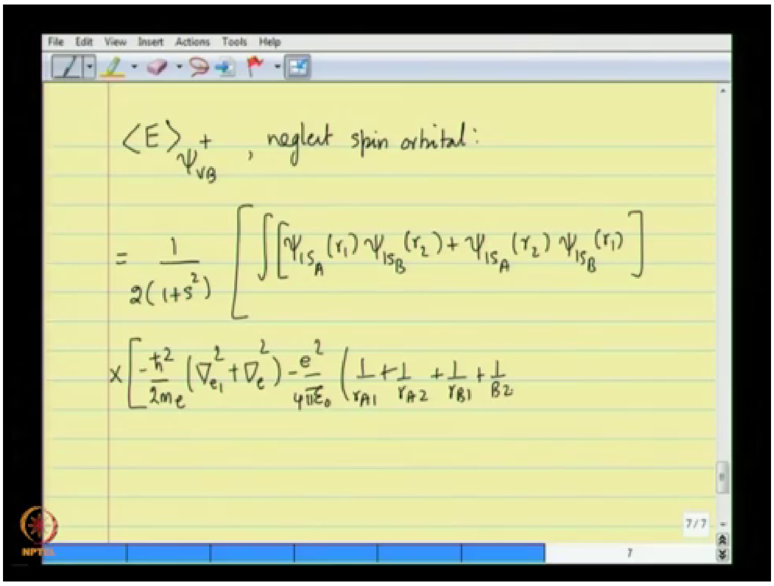

$\langle E \rangle_{\psi_{VB}^{+}}$, neglect spin orbital:

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

$$\times \left[-\frac{\hbar^2}{2m_e}\left(\nabla_{e_1}^2 + \nabla_{e}^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B1}} + \frac{1}{B2}\right.\right.$$

Therefore, the energy that we have to calculate the average value for this psi VB with the plus combination neglect to the spins orbital's at the moment, it does not matter even if you put that in the spin coordinates are independent of the spatial coordinates. So, you will write 1 by square root of 2 alpha 1 beta 2 minus beta 1 alpha 2, the ket times the bra state times the ket state and that of course is normalized already. Therefore, the anti symmetric state normalized to give you one and it disappears from the calculation because the Hamiltonian does not contain any spin orbit interaction.

So, it is pedantic to include or not to include, but it is important to remember that it is there otherwise all the calculations are technically wrong, because the electron wave function does not satisfy the Pauli principle. So, let us write this energy as the integral ok, let us have the molecular the normalization constant 1 by 2 into 1 plus S square.

That is the psi star psi normalization constant and then we have the integral psi 1 SA r 1 psi 1 SB r 2 plus psi 1 SA r 2 psi 1 SB r 1 times the Hamiltonian which is minus h bar square by 2 me del e 1 square plus del e 2 square minus e square by 4 pi epsilon naught times 1 by r A 1 plus 1 by r A2 plus 1 by r B1 plus 1 by r B2.

Now, having written this let me perhaps rewrite this in a slightly different way ok. Let us do it let us do it somewhat differently, to get the picture that we will simplify these energies very quickly.

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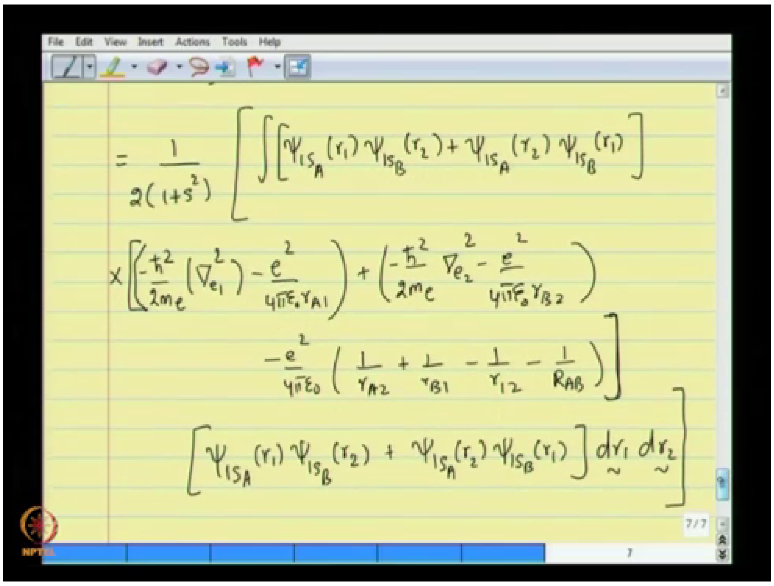

$$= \frac{1}{2(1+s^2)} \Bigg[\int \Big[\psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2) + \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1) \Big]$$

$$\times \Bigg[\left(-\frac{\hbar^2}{2m_e}\left(\nabla_{e_1}^2\right) - \frac{e^2}{4\pi\varepsilon_0 r_{A1}} \right) + \left(-\frac{\hbar^2}{2m_e}\nabla_{e_2}^2 - \frac{e^2}{4\pi\varepsilon_0 r_{B2}} \right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A2}} + \frac{1}{r_{B1}} - \frac{1}{r_{12}} - \frac{1}{R_{AB}} \right) \Bigg]$$

$$\Big[\psi_{1s_A}(r_1)\,\psi_{1s_B}(r_2) + \psi_{1s_A}(r_2)\,\psi_{1s_B}(r_1) \Big] d\underset{\sim}{r_1}\, d\underset{\sim}{r_2} \Bigg]$$

So, let us write the del e 1 square and let us write the term corresponding to e square by 4 pi epsilon naught r A1 as one set of terms, then we have minus h bar square by 2 me del e 2 squared minus e square by 4 pie epsilon naught r B2 and then write the remaining terms. Namely minus e square by 4 pi epsilon naught 1 by r A2 plus 1 r B1 minus 1 by r 1 2 minus 1 by R AB all of this as a Hamiltonian acting on the wave function on the right.

Which is psi 1 SA r 1 psi 1 SB r 2 plus psi 1 SA r 2 1 SB r 1 and integrated over both the electron variables namely dr 1 3 dimensional integral dr 2, this is the r 1 square theta sine theta 1 dr 1 d theta 1 d phi 1 and likewise for the r 2 square it is r 2 square dr 2 sine theta 2 d theta 2 d phi 2 etcetera. That we have to define the theta some phi is carefully and therefore the evaluation of some of the integrals in this in the way in which it is written, you would see that it involves 2 electron coordinates centered on 2 nuclei particularly for the odd one to term the electron repulsion terms.

So, you are going to get more complicated integrals to calculate, but for the hydrogen electron they function with the ones orbital function, some of these electrons can be exactly calculated and I will do that in the assignment later on.

But let me stop at this point before expanding this any further, nearly because from this point onwards the calculation of the energies we need to apply the same symmetry and the labeling problems that we had with the hydrogen molecule ion. In seeing that certain orbital's are exactly the same as certain other orbital's, certain integrals are exactly the same as certain other integrals and therefore you have to do a counting carefully and that we will start afresh in the next lecture. But let me just summarize what I had for today's lecture.

That the hydrogen molecule system that we are studying, we are starting with the premises of the valance bond approach namely that the electrons are localized, which means electron 1 in orbital 1 electron 2 in orbital 2 of the 2 different nuclei and because the electrons are indistinguishable and interchange between these 2 coordinates is as much important as considering only one term and therefore there is a weight of these 2 being put together. We have used a linear combination psi 1 SA r 1 psi 1 SB r 2 that we see here in the screen plus psi 1 SA r 2 psi 1 SB r 1 as a starting point. Then we also talked about the spin of the 2 electrons because, the overall wave function of the 2 electron system must be anti-symmetric to the interchange of the coordinates of both the electron or the interchange of both the electrons and so when the spin and the spatial coordinates are interchanged.

It is important to have a symmetric combination of the linear combination to be associated with an anti-symmetric combination of the spin wave functions and vice versa and then we just wrote down the hydrogen molecule energy expression. But we have not calculated our starting point for the next lecture would be this integral namely the, what you see in the screen. So, we will start from here and we will calculate this until then.

Thank you very much.