Quantum Chemistry of Atoms and Molecules
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Lecture-56
Valance Bond Theory and Homonuclear Diatomics: Part2

We are talking about valence bond theory treatment of valence bond well valence bond theoretical treatment of the dihydrogen molecule problem.

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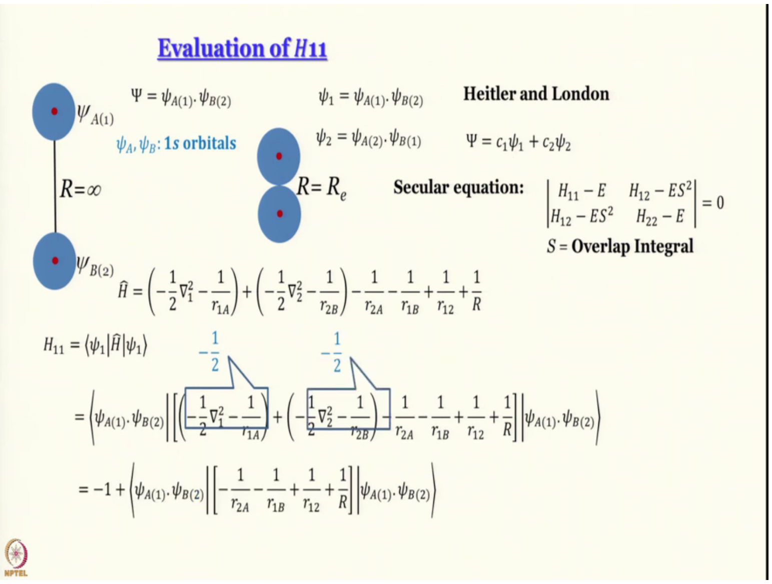

Evaluation of H_{11}

$\Psi = \psi_{A(1)} \cdot \psi_{B(2)}$

ψ_A, ψ_B: 1s orbitals

$\psi_1 = \psi_{A(1)} \cdot \psi_{B(2)}$

$\psi_2 = \psi_{A(2)} \cdot \psi_{B(1)}$

Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

Secular equation: $\begin{vmatrix} H_{11}-E & H_{12}-ES^2 \\ H_{12}-ES^2 & H_{22}-E \end{vmatrix} = 0$

S = **Overlap Integral**

$$\hat{H} = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1A}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{2B}}\right) - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

$$H_{11} = \langle \psi_1 | \hat{H} | \psi_1 \rangle$$

$$= \left\langle \psi_{A(1)} \cdot \psi_{B(2)} \left| \left[\overbrace{\boxed{\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{1A}}\right)}}^{-\frac{1}{2}} + \overbrace{\boxed{\left(-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{2B}}\right)}}^{-\frac{1}{2}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \right] \right| \psi_{A(1)} \cdot \psi_{B(2)} \right\rangle$$

$$= -1 + \left\langle \psi_{A(1)} \cdot \psi_{B(2)} \left| \left[-\frac{1}{r_{2A}} - \frac{1}{r_{1B}} + \frac{1}{r_{12}} + \frac{1}{R} \right] \right| \psi_{A(1)} \cdot \psi_{B(2)} \right\rangle$$

We have written Heitler and London wave function as a product well as a sum of 2 terms 1 is this is your Heitler and London wave function and psi 1 the first one is psi A 1 dot psi B 2 which means electron number 1 is in the 1s orbital of atom A electron number 2 is in the 1s orbital of atom B psi 2 the second term is psi A 2 psi B 1 so we have just interchange the electrons so electron number 2 is in 1s orbital of atom A electron number 1 is in the 1s orbital of atom B.

And when we write this we are remembering that electron number 1 originally belong to atom A electron number 2 originally belong to atom B but then as you know electrons are indistinguishable nuclear indistinguishable. So, once the molecule is formed there is no memory you do not know which is from which but you have to write the complete wave function to denote the situation properly.

Then we said that we wrote Schrodinger equation using Heitler and London wave function and in the usual manner we set up this secular equation. We have also simplified the secular equation a little bit and we have arrived at the concept of overlap integral where this is an integral which depends on the extent of overlap of the 2 wave functions involved in bonding. Next we said that we have to now evaluate the other integrals H 11 H 12 H 22 H 12 that is what we are going to do now.

We start with H 11 so to get find out what H 11 is I hope you remember what my H 11 is H 11 is simply integral psi 1 H psi 1, H psi 1 is this wave function that contributes to the first term we do not know the coefficients yet we will come to that later maybe in this class or maybe in the next. So this is what it is but in order to proceed with H 11 first thing we need to know is the Hamiltonian and remember we had written the Hamiltonian earlier here all we have done is we have written it in atomic units.

And we have also done something else we have clubbed these 1 electron wave functions you see in the first bracket what you have is minus half del 1 square minus 1 by r 1A, 1A means electron number 1 and nucleus a separation between them. So, this is the Hamiltonian 1 electron Hamiltonian for electron number 1 in atom A similarly the second 1 is the 1 electron Hamiltonian or electron number 2 in atom B this term here is minus 1 by r 2A what is that electron number 2 and atom A this is electron number 1 and atom B.

I might as well have written it there but it would have been a little messed up that is why we written it out here because we want to separate the 1 electron Hamiltonians. Then this term is for electron-electron repulsion this term is for nucleus-nucleus repulsion and do not forget R is a constant for every calculation that we do. We can do the calculations for given fixed values of R we do not vary it during our during a particular calculation for electronic energy levels or electronic wave functions.

So this is your H 11 I do not know why I have to write it when it was written it here anyway. So, this is your H 11 in the expanded form I have written the form of psi 1 I have written the wave function and this is what we have got now let us take them one by one let us worry about what happens when the first 1 electron wave function operates on the sorry when the first 1 electron Hamiltonian operates on the wave function here psi A 1 psi B 2 psi 1, psi 1 is what we are talking about.

So I have made a little bit of a mistake here because I have forgotten the written psi in the left hand side, so I will just write here also you have psi 1 please do not forget and this whole thing sorry this is getting a little messed up. So, what is this Hamiltonian operating on psi B 2 psi A 1 psi B 2 this Hamiltonian if you remember is I can write it like H 11, 1 electron Hamiltonian for electron number 1 in atom A so I will write it as H 1 A that operates on psi A 1 psi B 2.

So since this H 1 A Hamiltonian is in terms of electron number 1 this psi B 2 is going to be a constant and it comes out so I can write it as psi B 2 small h 1 A operating on psi A 1 and that is what I have written here one more thing this gives me the energy of 1s orbital multiplied by psi A 1 that is how I have arrived there perhaps there is no need for me to do every step but just in case. So this is what I get in atomic units that energy of 1s orbital would be minus half so I write minus half psi A 1 psi B 2.

I get a nice Schrodinger equation eigen value equation. So in this expression for H 11 first of all this H 11 I can write it as a sum of all these terms right. So, the first term turns out to be half isn't it so if I left multiply by psi A 1 psi B 2 integrate over all space then I get the first term in H 11 that becomes minus half right. Because what you have inside the integral is integral psi A 1 psi A 1 over all values of R integral psi B 2 psi B 2 over all values of R they are individually normalized so that gives you 1 minus half.

So this gives me minus half similarly you can do an exactly similar treatment for electron number 2 you get minus half here as well. So, I can take those out and the expression I get is 1 plus integral psi A 1 psi B 2 left multiplying the operator is minus 1 by r 2A minus r 1B plus r 12 electron-electron propulsion plus 1 by R nucleus-nucleus propulsion this operator operating on psi A 1 psi B 2. There is no easy way of evaluating this integral.

So since there is no easy way what we will do is we will just write it will give it a name like what we did for many electron atom remember and like what we did for H 11 for that matter. So, I give this a name this name is j and we will see what j is in a minute.

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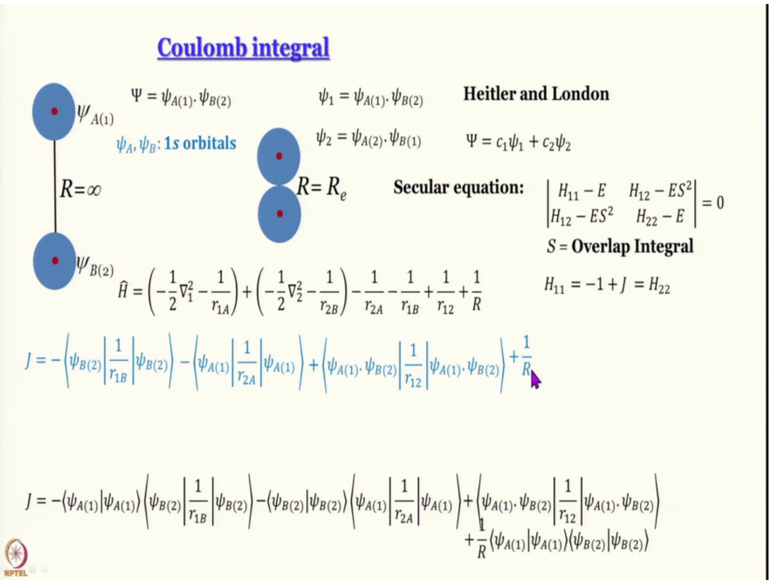

Coulomb integral

$\Psi = \psi_{A(1)}\cdot\psi_{B(2)}$

ψ_A, ψ_B: 1s orbitals

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$H_{11} = -1 + J = H_{22}$

$$J = -\left\langle \psi_{B(2)} \middle| \frac{1}{r_{1B}} \middle| \psi_{B(2)} \right\rangle - \left\langle \psi_{A(1)} \middle| \frac{1}{r_{2A}} \middle| \psi_{A(1)} \right\rangle + \left\langle \psi_{A(1)}\cdot\psi_{B(2)} \middle| \frac{1}{r_{12}} \middle| \psi_{A(1)}\cdot\psi_{B(2)} \right\rangle + \frac{1}{R}$$

$$J = -\langle \psi_{A(1)} | \psi_{A(1)} \rangle \left\langle \psi_{B(2)} \middle| \frac{1}{r_{1B}} \middle| \psi_{B(2)} \right\rangle - \langle \psi_{B(2)} | \psi_{B(2)} \rangle \left\langle \psi_{A(1)} \middle| \frac{1}{r_{2A}} \middle| \psi_{A(1)} \right\rangle + \left\langle \psi_{A(1)}\cdot\psi_{B(2)} \middle| \frac{1}{r_{12}} \middle| \psi_{A(1)}\cdot\psi_{B(2)} \right\rangle + \frac{1}{R}\langle \psi_{A(1)} | \psi_{A(1)} \rangle \langle \psi_{B(2)} | \psi_{B(2)} \rangle$$

So, we have got H 11 to be equal to minus 1 plus j just show you that once again H 11 is minus 1 plus this whole integral is written as j so I got H 11 is equal to -1 +j and this is what j is this j is called coulomb integral we are already familiar with coulomb integrals. So, I think we can guess why it is called coulomb integral but we will work it out why is this called coulomb integral of all things? Well before going there let me just say that H 22 is also equal to -1 + j.

Well if the only difference between H 11 and H 22 is that wherever there is 1 you write 2 wherever there is 2 you write 1 so it wont make any difference in the final form especially when you consider that the integral is actually a constant j constant means is dependent on R as we will see but for a given value of R it does not depend on which function you use H 11 and H 22 will be the same great.

So now let me expand and write j as a sum of 4 terms first 1 will be minus psi A 1 psi B 2 1 by r 2A psi A 1 psi B 2 integrated over all space. The second 1 everything is same instead of r 2A I will write r 1 B in the third term everything is same instead of r 1 B I write r 12 and the last term again just instead of this in the middle I write 1 by R sorry about the overlapping lines this is what we get. So, now what are these what are these so this thing first one again double integral right.

So since I have 1 by r 2A I cannot take psi B 2 out but I can take psi A 1 psi A 1 out of the and write it as an integral psi A 1 psi A 1 yeah this thing is a double integral and the 2 integrations are in terms of coordinates of 1 and 2. The integral in the coordinates of 2 would be integral psi B 2 1 by r 2 B I made a mistake somewhere here I think I have written this first this integral has been written first sorry about that right.

This integral has been written first and then we have taken it out so you can just go ahead and expand this so these 2 integrals have changed places. So everywhere we get a product of an integral of a triple product involving some separation between nuclei or well first one is separation between electron number 1 and nucleus B second one is electron number 1 in nucleus A. Third one is electron-electron separation 4th one is nucleus-nucleus separation.

So in the first one I get when I simplify the double integral I get integral psi A 1 psi A 1 d d r out this will be 1 similarly this integral psi B 2 psi B 2 will be 1 we do not simplify this and here 1 by r will come out and this double integral again becomes product of integral psi A 1 psi A 1 and integral of side B 2 psi B 2 both of which are normalized and so both of the integrals are equal to 1

So, what do I get the first one becomes minus psi B 2 1 by r 1 B psi B 2 second one becomes minus psi A 11 by r 2A psi A 1 integral over all space of course plus we get this complicated integral and finally we get plus 1 by r this 1 by r for whatever reason has gone up it should come down but that is all right. So, that is j.

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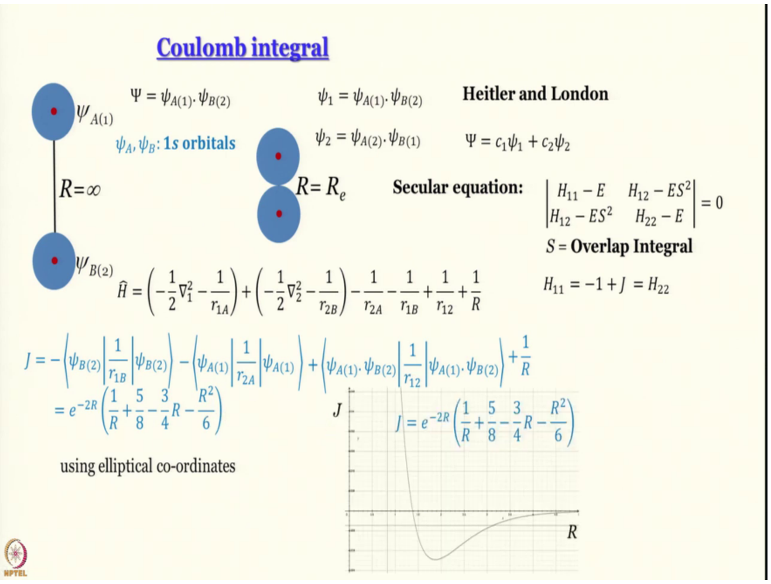

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$$J = -\left\langle \psi_{B(2)} \left| \frac{1}{r_{1B}} \right| \psi_{B(2)} \right\rangle - \left\langle \psi_{A(1)} \left| \frac{1}{r_{2A}} \right| \psi_{A(1)} \right\rangle + \left\langle \psi_{A(1)} \cdot \psi_{B(2)} \left| \frac{1}{r_{12}} \right| \psi_{A(1)} \cdot \psi_{B(2)} \right\rangle + \frac{1}{R}$$

$$= e^{-2R}\left(\frac{1}{R} + \frac{5}{8} - \frac{3}{4}R - \frac{R^2}{6}\right)$$

using elliptical co-ordinates

$J = e^{-2R}\left(\frac{1}{R} + \frac{5}{8} - \frac{3}{4}R - \frac{R^2}{6}\right)$

Now see what is the significance of these terms we have encountered this kind of integrals earlier have not we psi B 2 psi B 2 product of psi B 2 psi B 2 or sine 2 square by r 1 B did we not say that that is the coulombic field for electron number 2 at the position of electron number 1 and is it not just the other way around here so this first 2 terms are essentially for electrostatic attraction between nucleus A and electron 2 nucleus B and electron 1 and the third term is the electrostatic repulsion between 1 and 2 obviously.

And the last term is electrostatic repulsion between the nuclei A-B. So, all these are essentially coulombic interactions electrostatic interactions so this goes as this is called a coulomb integral. Again using elliptical coordinates one can work out the expression for coulomb integral and it turns out to be another exponential decay in R into nuclear separation multiplied by another polynomial in inter nuclear separation when we plot it this is what we get.

Remember the polynomial we got for S earlier in case of 1s orbital all the values were positive right it became zero at R equal to infinity. Here however since there is a minus sign here and a minus sign here for smaller values of R you see there is it goes down first of all it starts with negative with 0 then goes negative reaches a minimum and then goes up. So if you have seen the potential energy curve for a diatomic molecule then roughly the shape is something like this right. So we are slowly getting there so this is coulomb integral.

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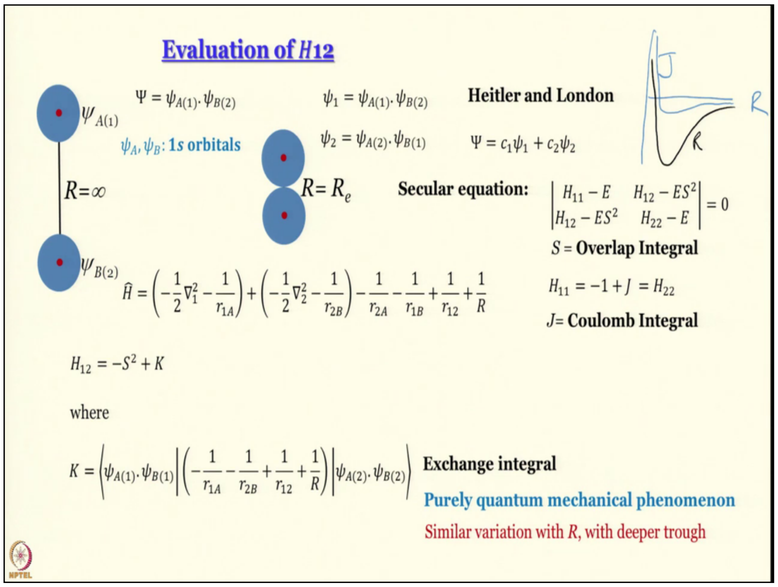

Evaluation of H_{12}

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$H_{11} = -1 + J = H_{22}$

J= **Coulomb Integral**

$H_{12} = -S^2 + K$

where

$$K = \left\langle \psi_{A(1)} \cdot \psi_{B(1)} \middle| \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}\right) \middle| \psi_{A(2)} \cdot \psi_{B(2)} \right\rangle$$

Exchange integral

Purely quantum mechanical phenomenon

Similar variation with R, with deeper trough

So, j is coulomb integral and we write H 11 and H 22 in terms of this coulomb integral. What is H 12? Similarly you can work it out I will not do it but I encourage you to do it yourself it is not difficult at all once you have worked out H 11 and H 12. H 12 turns out to be minus Ss square plus k now what is k now remember exchange integral that we encountered earlier k is actually this integral here and here you see the main difference between this and H 11 that integral we started from is this is psi A 1 psi B 2 and this wave function is psi A 2 psi B 2 right.

What does that mean for the first time until now we were saying that when electron number 1 is in A electron number 2 is in B and the other way round. Here we account for delocalization of the electron over the entire nucleus the electron of A can exchange its position and be near B also right and reside there that is what this tells us, so this integral is called exchange integral and it is very important to understand and I think I mentioned it in the passing earlier.

It is very important to understand this is a purely quantum mechanical phenomenon there are text books in which hand waving arguments are given to justify this exchange integral in terms of classical mechanics is a wrong approach we should never do it. It is important to understand that is a purely quantum mechanical phenomenon but it contributes immensely to the energies of stabilization of molecules that arise out of bonding.

Now the variation of with R working this out is more complicated so not even write the expression but it is similar to that of j coulomb integral it is just that the trough is much, much deeper so if I draw it very qualitatively this is R if this is j if this is a variation of j with r then the variation of k the exchange integral with r is something like this much deeper trough. The picture is given in the textbook but today my scanner broke down so I could not scan it sorry about that but please do read the textbook do not just rely on what we say in class.

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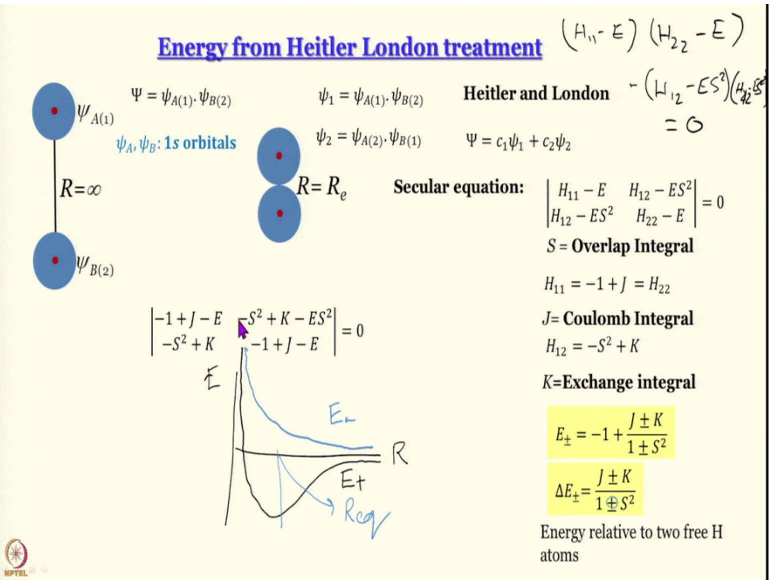

Energy from Heitler London treatment

$(H_{11}-E)(H_{22}-E)$

$-(H_{12}-ES^2)(H_{12}-ES^2$

$=0$

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ψ_A, ψ_B: 1s orbitals

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J= **Coulomb Integral**

$H_{12} = -S^2 + K$

K=**Exchange integral**

$$\begin{vmatrix} -1+J-E & -S^2+K-ES^2 \\ -S^2+K & -1+J-E \end{vmatrix} = 0$$

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

$$\Delta E_{\pm} = \frac{J \pm K}{1 \pm S^2}$$

Energy relative to two free H atoms

So this is now we arrive at this concept of exchange integral and what we see is that the energy that we get from Heitler and London treatment is expressed in terms of your overlap integral coulomb integral and exchange integral how do we get it? You expand this determinant I am not going to do it but please to try and see what kind of expressions you get. When you expand you are going to get a this will give me something in E square this minus something in E square right I just write the expression in the easiest form at least.

So I get something like H 11 minus E multiplied by H 22 minus E gives me no I do not say gives me minus that is a little that would be a little easier minus H 12 minus ES square multiplied by H 12 minus A square is equal to 0, so this is a quadratic equation expand it and use that usual formula for roots of quadratic equation we are going to get 2 roots right. I will show you the final result directly the final result is something like this now before that I should sorry I forgot this step.

Well this secular equation of course has to be written in terms of these overlap integrals before or you can just take this and substitute here and the result that you get is the 2 roots of this quadratic equation turn out to be -1 + j + k divided by 1 +- S square this is 1 expression that you should perhaps know so the confusion that usually arises is where is the plus minus here or here remember where the plus minus is now what is -1? -1 if you remember is the energy of these free hydrogen atoms right.

So if I just subtract that from E plus minus then I get delta E plus minus that is the energy relative to the 2 free hydrogen atoms and once again since my scanner broke down I am going to draw the same kind of diagram here exactly same some difference will be there sorry about the poor quality of drawing. So, I am plotting this e energy as a function of R for E plus the variation is something like this sorry bad drawing even for me it is unacceptable 0 when it is very far away coming close goes down goes down then turns around goes up and something like this.

This is little better E plus what about E minus? I think you know up to this whatever we said you I am sure you knew all these things but this is something that might be new for you E minus is simply this draw from the other side minus is just like this what does that mean that means that when you take plus then you get a minimum in energy that is this value of R this is your equilibrium bond length.

However when you take this minus combination then you get you just get repulsion you do not get any stabilization at all one more thing I am I wrote e that may not be a very accurate let me write actually this is delta E please do not forget. So this is the kind of plot we get in one case when I use this plus combination there is stabilization and in the second kind of energy the we get a an increasing repulsion as internuclear separation keeps on decreasing. So what does E minus stand for what does E plus stand for we will come to that.

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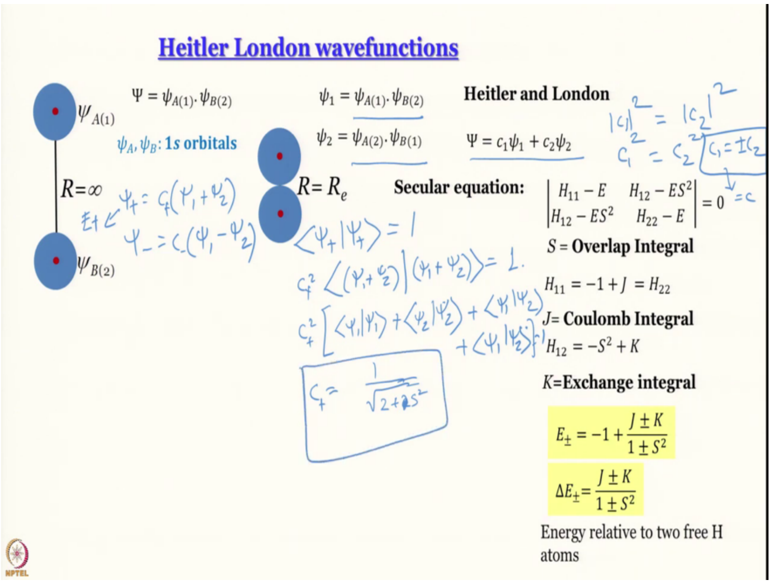

Heitler London wavefunctions

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$\Psi = c_1\psi_1 + c_2\psi_2$

$|c_1|^2 = |c_2|^2$

$c_1^2 = c_2^2 \quad \boxed{c_1 = \pm c_2} = c$

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$\Delta E_{\pm} = \frac{J \pm K}{1 \pm S^2}$

Energy relative to two free H atoms

$E_+ \swarrow \psi_+ = c_+(\psi_1 + \psi_2)$

$\psi_- = c_-(\psi_1 - \psi_2)$

$\langle \psi_+ | \psi_+ \rangle = 1$

$c_+^2 \langle (\psi_1 + \psi_2) | (\psi_1 + \psi_2) \rangle = 1.$

$c_+^2 [\langle \psi_1 | \psi_1 \rangle + \langle \psi_2 | \psi_2 \rangle + \langle \psi_1 | \psi_2 \rangle + \langle \psi_1 | \psi_2 \rangle] = 1$

$\boxed{c_+ = \frac{1}{\sqrt{2 + 2S^2}}}$

So this is what we get now before we address that question what does this what is the meaning of that uniform increase what is the meaning of going through minimum let us come back and discuss the wave function just a little there is a little more complicated way of doing it if you read Macquarie's book they have done it by or they have not really done it they have given you pointers on how to do it from the expression for energy.

But I prefer to do it in a simpler way it involves less mathematical manipulation and more common sense so that is why I like it. See have a look at this equation C 1 psi 1 + C 2 psi 2 what could the values of C 1 and C 2 be? First of all coming back to the question what is the ratio of the magnitudes of C 1 and C 2? What is the meaning of this say C 1 square? What is the meaning of this mod square of C 2? If you remember they give you the contribution of psi 1 and psi 2 respectively to the total Heitler and London wave function psi.

Is there any reason why this mod square of C 1 and mod square of C 2 should be any different from each other there is none. So actually this should be equal to each other and we work with real complexes here so I can write C 1 square equal to C 2 square. So C 1 equal to plus minus C 2. So I can write C 1 equal to plus minus C 2 equal to C also. So then I get 2 kinds of wave functions I will write those wave functions here psi plus is equal to C psi 1 plus + psi 2 psi minus is equal to C psi 1 - psi 2.

And the good thing about working out that problem in Macquarie's book is that you can see that this psi plus corresponds to energy E plus where you got that minimum that is the only thing that we are not doing here today. Now the next thing is to find C and the way to find C is very simple integral psi plus psi plus overall space equal to 1 normalization condition. So, I can write C square integral psi 1 plus psi 2 multiplied by again psi 1 + psi 2 over all space is equal to 1.

So C square multiplied by integral psi 1 psi 1 over all space plus integral psi 2 psi 2 overall space and when I am writing this I am actually cheating a little bit right because there are 2 integrals remember so I am actually not showing you the step in which I get rid of one plus integral psi 1 psi 2 plus integral psi 1 psi 2 that is equal to 1. So you simplify this and to simplify this you have to put in this psi A 1 psi B 2 psi A 2 psi B 1 you can work this out we have actually worked these out already earlier so I am not doing it again.

We are going to get S so C is going to be 1 by root over maybe I should write C plus and C minus C plus will be equal to 1 over 2 plus 2S 2 plus S square. Similarly you can work out the coefficient for C minus also. So this way we have completely defined the wave functions and we have found the normalization constants. sSo I have not really worked out this C plus C minus that is homework for you you can of course check with the textbook.

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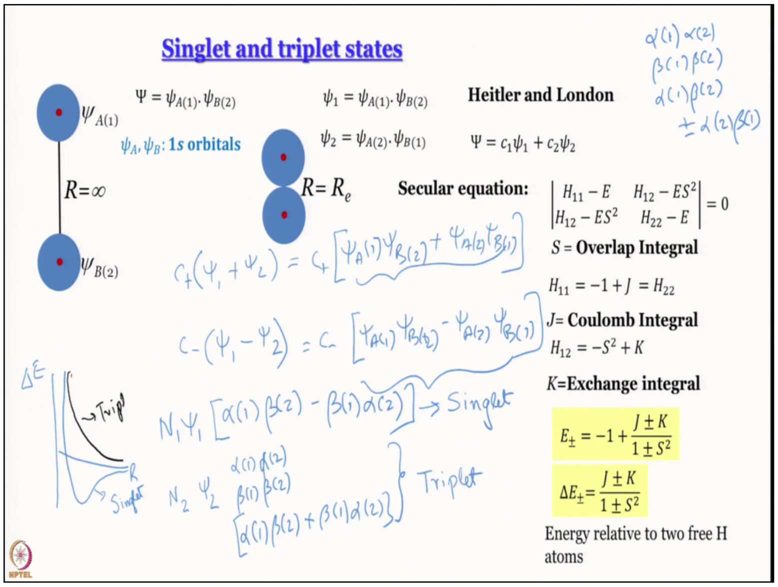

Singlet and triplet states

$\Psi = \psi_{A(1)} \cdot \psi_{B(2)}$

ψ_A, ψ_B: 1s orbitals

$\psi_1 = \psi_{A(1)} \cdot \psi_{B(2)}$

$\psi_2 = \psi_{A(2)} \cdot \psi_{B(1)}$

Heitler and London

$\Psi = c_1\psi_1 + c_2\psi_2$

$\alpha(1)\alpha(2)$
$\beta(1)\beta(2)$
$\alpha(1)\beta(2)$
$\pm\alpha(2)\beta(1)$

Secular equation: $\begin{vmatrix} H_{11}-E & H_{12}-ES^2 \\ H_{12}-ES^2 & H_{22}-E \end{vmatrix} = 0$

S = **Overlap Integral**

$H_{11} = -1 + J = H_{22}$

J= **Coulomb Integral**

$H_{12} = -S^2 + K$

K=**Exchange integral**

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

$\Delta E_\pm = \frac{J \pm K}{1 \pm S^2}$

Energy relative to two free H atoms

$C_+(\psi_1 + \psi_2) = C_+\left[\psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)}\right]$

$C_-(\psi_1 - \psi_2) = C_-\left[\psi_{A(1)}\psi_{B(2)} - \psi_{A(2)}\psi_{B(1)}\right]$

$N_1\psi_1\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \rightarrow$ Singlet

$N_2\ \psi_2$ $\left.\begin{matrix}\alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]\end{matrix}\right\}$ Triplet

Now we go ahead and say something else see we have got 2 things 1 is 2 wave functions right one wave function is something like psi 1 plus psi 2 multiplied by C plus which we have worked out or rather you are supposed to work out and the other one is C minus multiplied by psi 1 minus psi 2. So if I write this out what do I get C 1 multiplied by psi A 1 psi B 2 + psi A 2 psi B 1 and this is this is plus this is minus C minus psi 1 is psi A 2 psi B no what am I doing psi A 1 psi B 2 minus psi A 2 psi B 1.

Now I ask you to remember something that we had discussed when we talked about many electron atoms many electron atom wave functions remember the remember spin orbitals remember that the total wave function including this spatial part and the spin part for fermions has to be anti symmetric with respect to exchange. So see the first 1 this is symmetric with respect to exchange is not it. If you change the labels 1 and 2 it does not change but this 1 is anti symmetric.

So what will be the corresponding spin wave functions for psi 1 since it is symmetric it has to be associated with the anti symmetric spin wave function alpha 1 beta 2 minus beta 1 alpha 2 all right I am let me just write N 1 overall normalization constant. Remember if for 2 electron systems we said that you can have several spin wave functions first is electron number 1 can have alpha spin electron number 2 can also have alpha spin.

Similarly both can have beta spins but if you write alpha 1 beta 2 you cannot write it by itself because 1 and 2 are indistinguishable. So you have to write either plus or minus alpha 2 beta 1 as well to account for the fact that you do not know whether it is alpha 1 whether it is electron number 1 or electron number 2 that has alpha spin whether it is electron number 2 or electron number 1 that has beta spring right.

So both are required now see if you interchange 1 and 2 then the first 3 wave functions do not change the last 1 with the minus sign that changes sign. So that is the only anti-symmetric wave function so this wave function this spin wave function would be associated with psi 1 which is symmetric with respect to exchange and the other one maybe I can write N 2 the psi 2 will be associated with alpha 1 alpha 2 beta 1 beta 2 alpha 1 beta 2 plus beta 1 alpha 2.

We had encountered such things when we talked about the excited states of helium atom remember. So, similarly so 3 wave functions this is the triplet state and this one there is only 1 wave function this is called the singlet state right. So, singlet and triplet this 1 if you remember goes to an energy minimum if I plot delta E this time versus R then this kind of plot that we get is for the singlet state and the other plot that we get I think I used exactly opposite in color but that does not matter the dissociative plot that we get this is for your triplet state.

What does that mean that means that for according to VBT for high dihydrogen H2 molecule the singlet state has an energy minimum however triplet state does not ok. So, ground state is singlet triplet state is dissociative for hydrogen and that makes perfect sense. So you see we can actually make significant advances using valence bond theory at least for hydrogen we have to we have been able to do it very nicely. What are the things that we have not accounted for delocalization and all yes of course we have not.

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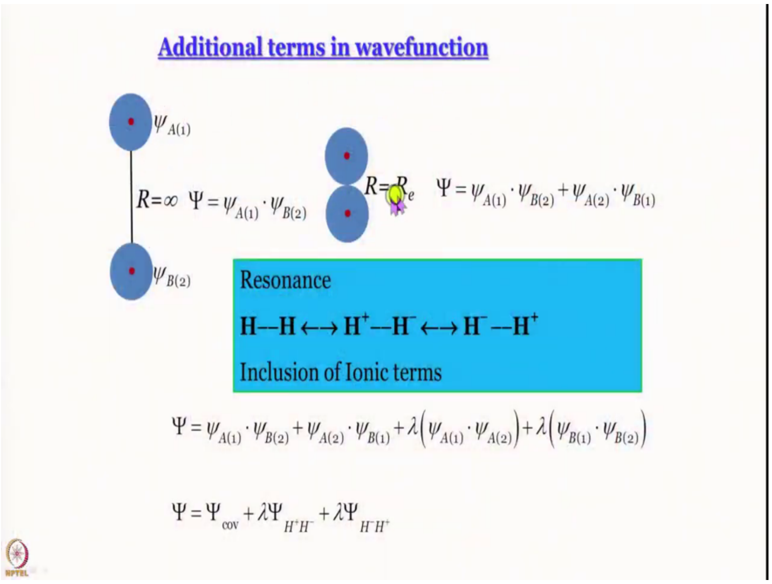

Additional terms in wavefunction

$\psi_{A(1)}$

$R=\infty \quad \Psi = \psi_{A(1)} \cdot \psi_{B(2)}$

$\psi_{B(2)}$

$R=R_e \quad \Psi = \psi_{A(1)} \cdot \psi_{B(2)} + \psi_{A(2)} \cdot \psi_{B(1)}$

Resonance

$\mathbf{H{-}{-}H \longleftrightarrow H^{+}{-}{-}H^{-} \longleftrightarrow H^{-}{-}{-}H^{+}}$

Inclusion of Ionic terms

$$\Psi = \psi_{A(1)} \cdot \psi_{B(2)} + \psi_{A(2)} \cdot \psi_{B(1)} + \lambda\left(\psi_{A(1)} \cdot \psi_{A(2)}\right) + \lambda\left(\psi_{B(1)} \cdot \psi_{B(2)}\right)$$

$$\Psi = \Psi_{\text{cov}} + \lambda\Psi_{H^{+}H^{-}} + \lambda\Psi_{H^{-}H^{+}}$$

Another thing that we have not accounted for so far is possibility of existence of ionic forms. See this kind of resonance can be there and I am saying resonance only because I am working within the ambits of valence bond theory. So these ionic terms can make some contribution of course if you have studied resonance you know that they do not make too much of contribution that is why in the wave function we use the scaling factor.

Remember scaling factor that we used in case of vari variation method that lambda that we brought in as a regulator if you increase lambda then the change is more yeah well even perturbation theory perturbation theory we use lambda we bring in a similar lambda here. And we say that this is a small number by which we multiply and that gives you the small contribution of H plus and H minus and what you could do is you can use that as a variational parameter and find the minimum energy.

So does this help is this required does it help we this module is becoming a little longish but please bear with me we are almost done if complete this discussion.

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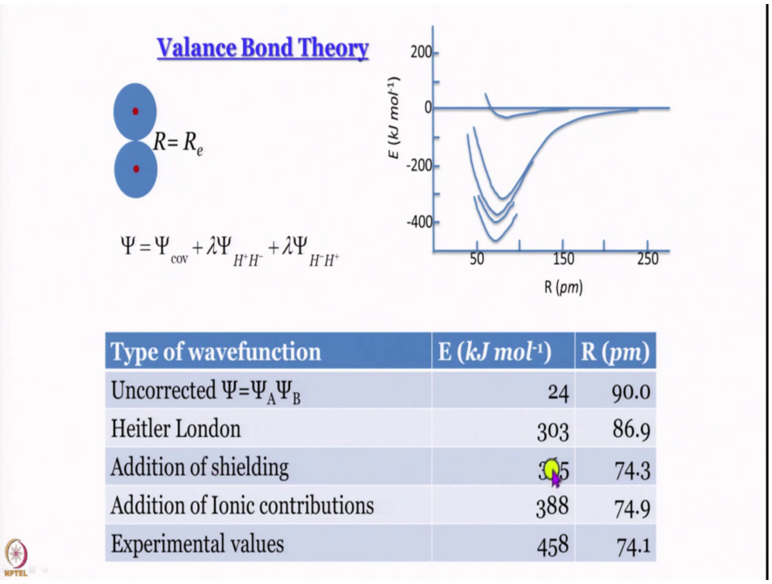

Valance Bond Theory

$R = R_e$

$\Psi = \Psi_{cov} + \lambda\Psi_{H^+H^-} + \lambda\Psi_{H^-H^+}$

Type of wavefunction	E ($kJ\ mol^{-1}$)	R (pm)
Uncorrected $\Psi = \Psi_A\Psi_B$	24	90.0
Heitler London	303	86.9
Addition of shielding	365	74.3
Addition of Ionic contributions	388	74.9
Experimental values	458	74.1

So, let us complete this discussion with a comparison with experiment what you see here and I am not showing the entire curve only near the equilibrium because in experiment you cannot really get the entire thing this is the kind of energy that you get using experiment. And the experiment gives you an energy value of 458 kilo joule per mole stabilization energy there is a minus sign and the equilibrium bond length is 74.1 and I do not remember if I said this Max Planck had said that experimental results are the only truth everything else is poetry and imagination.

So this is the truth whatever theory we do is poetry and imagination to try and match this experimental result. What are we doing here? We are trying to use this kind of a function and we will see what happens when you bring in terms one by one. First let me show you the plot for uncorrected wave function psi A Psi B even that has an energy minimum but very shallow. So this gives you a stabilization of 24 kilo joule per mole only compared to 458 kilo joule per mole and the equilibrium bond length also is much longer 90 picometer compared to 74 picometer not so great.

So but then we know this is a bad wave function right because we started our discussion with our Heitler and London wave function. When we use Heitler and London wave function we get a dramatic improvement dramatic increase in stabilization energy from 24 it goes to 303 and equilibrium bond length becomes say 86.9 so dramatic improvement in stabilization energy compared to uncorrected wave function little bit of improvement in the equilibrium bond length as well but well good but not good enough.

So what we can do is we can bring in something like shielding after all there are 2 electrons here 2 nuclear here some kind of shielding will be there. So when you bring in shielding there is a further improvement from 303 you go to 365 which is a little bit of improvement compared to what we had upon going from uncorrected to Heitler and London wave function but the remarkable improvement that you see is in the equilibrium separation equilibrium bond length from 86.9 it goes to 74.3 which is more or less the actual value.

So shielding is an important role because there is shielding the nuclei can approach each other shielding means the electrons actually shield the nuclear charges from each other so that is why nuclei can come closer to each other than they would have otherwise. And finally when we bring in our ionic terms is there any improvement actually there is actually the internuclear separation gets a little worse.

But what we see is energy goes from stabilization energy goes from 365 to 378 significantly closer to 458 even that is not close enough I agree but much better than what we started from. So this in a nutshell is our valence bond theoretical treatment of dihydrogen and this can be expanded with approximation methods to other whole nuclear diatomic molecules and we can try to handle homonuclear heteronuclear diatomic molecules also that is 1 part will not go into that.

But I hope you can believe me after this discussion that it can be done. Next we want to discuss what happens in polyatomic molecules. What is the major difference between polyatomic molecules and diatomic molecules? Diatomic molecules can only be linear polyatomic molecules can have many different shapes. So in the next class we will have a brief discussion of shapes of molecules and then we will say that see we do not have atomic orbitals that can sustain those shapes.

How do we generate orbitals that can sustain those molecular shapes that are determined by VSEPR by invoking a concept called hybridizations? So in the next 3 or 4 classes we will talk in detail about SP, SP 2, SP 3 hybridization will also talk about hybridization in which it is you get non equivalent hybrid orbitals.