Introductory Quantum Chemistry
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Lecture - 45
MO and VB Theory

We have seen the molecular orbit approach to hydrogen molecule and now, we will look at the Valence bond approach. We show that, the molecular orbit approach this in describe the dissociation limit correctly. And in Valence bond theory the dissociation limit is actually describe correctly, because it starts from the dissociation limit. So, let us imagine that, I start with the molecule such that the distance between the two atoms is very large.

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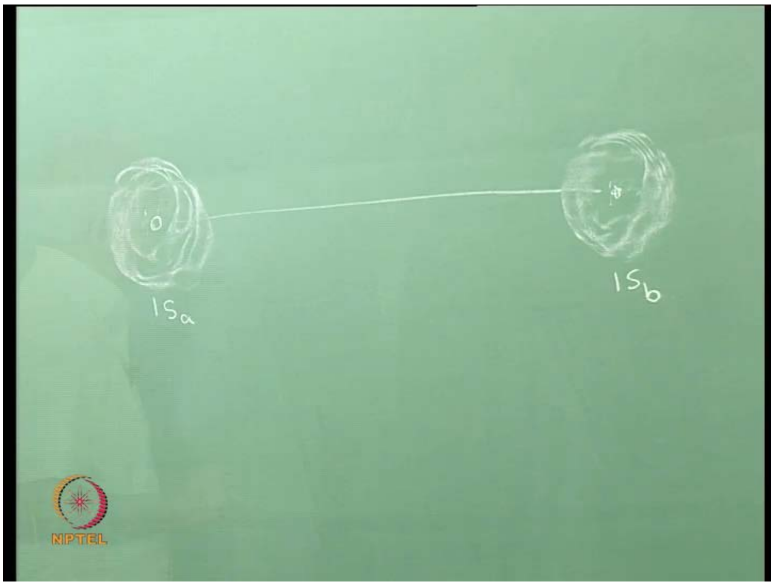

So, let me say here is my molecule; the distance between the two atoms is very large. And if the distance is very large, what would I expect? I would expect there are two separate hydrogen atoms. So, if this is nucleolus a and if that is nucleolus b, what you will have is one electron sitting in this atomic orbital 1 s a and you will have other electron sitting in this other atomic orbital which will label 1 s b. And the two systems are far apart, let us say if the two systems are far apart they are not really interacting with one another, they are independent one another. And if they are independent of one another the total wave function for the system will be the product of the wave function for the individual systems.

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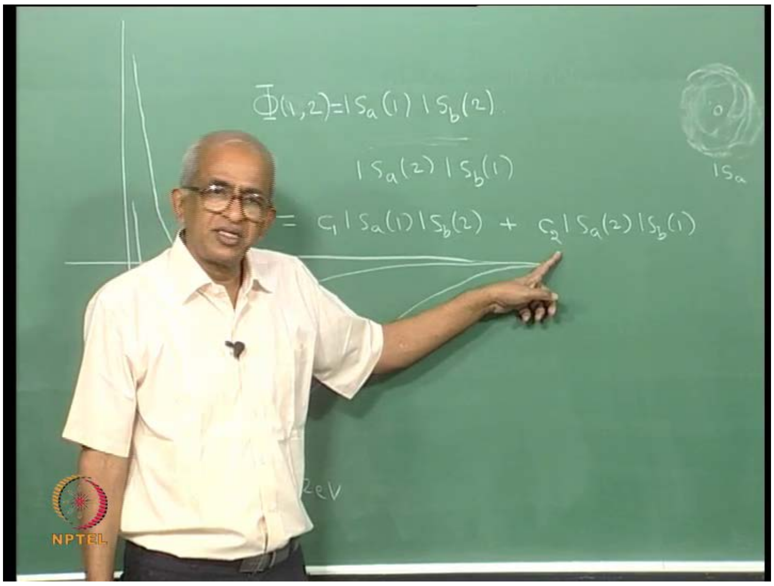

So, therefore, you would have the total wave function given by 1 s a, let me say electron one is in 1 s a and electron two is in 1 s b. So, therefore, the two are not interacting wave function, total wave function will be the product. And you can imagine that, I will use this has the trial function. Well may be I will use the symbol 1 and 2 that will make the notations easier to write. So, now, I can say well, let me take this function actually it is a very approximate wave function, but what I will do is, I will use this as may trial function, which actually means that even at finite distance even they, when they are very close to each other.

I will say the wave function is simply at product of this form. Electron one is associated with nucleus a, electron two is associated with nucleus b and they are sitting in the separate atomic orbitals. There are interactions I know that, but I can try and find out how good this is as an approximate function so, people have done this. And if you did the calculation what happens is you will get, a potential energy curve what do I mean by the potential of the curve. A curve in which the electronic energy is plotted as a function of inter nuclear distance, we have been doing that though I did not use the word earlier. So, I will get a potential energy curve for the system which would looks something like this. In this case, if you did use this as an approximate function and did the calculation you will get a potential energy curve of this form.

Whereas the actual potential energy curve, we have seen it has the decreases it has dissociation energy of 4.72 electron volts. While if we use this as the appropriate function you will get a something like 0.4 or even less at the bending energy or the dissociation energy is extremely a small. And it says that, the system is only slightly stable in contradiction with the experiment, where the system is find to be quite stable.

Therefore, it is obvious that, this is not a good approximate wave function, but then you look at it physically, I mean never you the physically this function is not a great function because, you are saying that the electron one is always associated with the nucleus a electron two is always associated with nucleus b, but even when the nuclear very close. you are saying electron one is restricted to be confined to 1 s a and electron two is restricted to be confined to 1 s b, but when the distance are very close you cannot say which electron is where.

So, therefore, when the distances are small, defiantly the electron two may be associated with nucleus a and one may be associated with nucleus b and therefore, there is another possible function. The other possible function being 1 s a 2 notice, what is happening I am inter changing the two electrons at to the close distances definitely the two electrons can change places.

So, I would have 1 s a 2, 1 s b 1 as another possible function correct. Now, if you want you can use this alone as your trial function and you will find that again you need to exactly the same result. And therefore, that alone itself is not a reasoned approximation, but if that is the way it is, what will you do? You will say I will take the first function, I will have a function of the form, which is contains the first function and I will also have the second function right.

I take both the functions and multiply the first one by some coefficient c 1 the second by some coefficient c 2 and add the two up right. Notice what is happening, here I am saying electron one is associated with nucleus; electron one is associated nucleus a, electron two is associate with nucleus b, but then at close this is a I allow the electrons to exchange places.

And I get this function and that should also be important. And now, if you have such a trial function what will we do? You have to determine c 1 and c 2 in a variation fashion, but it is not really necessary to do the calculation, because physically we can guess what is going to happen, because you see these two are actually kind of equivalent. And therefore, they should make the same amount of contribution to the final wave function right.

Because, I mean all that you are doing is inter changing the two electrons right. So, therefore, this and that should have the same amount of important in your final wave function and that this immediately tells you that, you have two possibility is just cross it the case of molecular orbitals that were discuss earlier in the case of H 2 plus. You will have a possibility of c 1 being equal to c 2 and the other possibility will be the negative sign, c 1 being equal to minus c 2 right. So, therefore, we have now two functions. What are these two functions? Let me write down.

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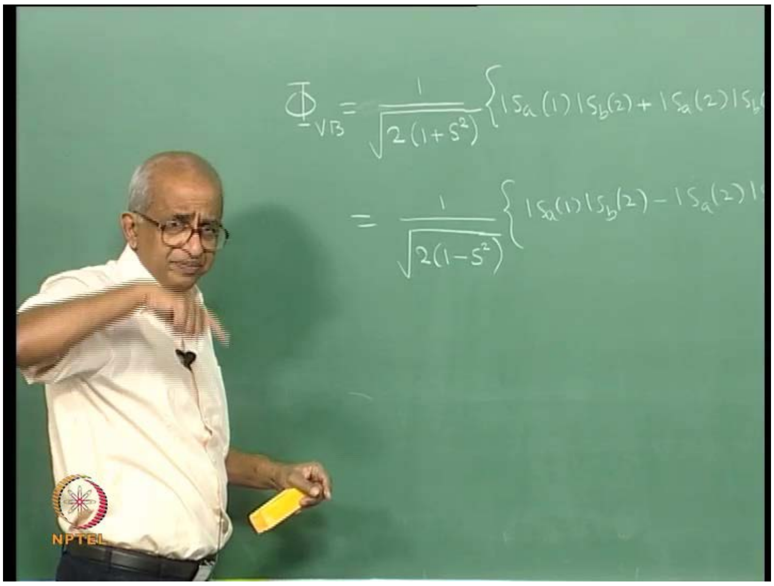

My first function will be phi, which I will denote as 1 s a, which I will write as 1 s a 1,1 s b 2 with the positive sign, I will add the another one 1 s a 2, 1 s b 1 this is just similar to what happen in the case of H 2 plus. H 2 plus, I have two atomic orbital, they added together with a positive sign, over they added together with a negative, one of them having a negative sign. In a similar fashion, I take the first function, but these are not molecular orbital remember that, because these are actually wave functions for two electrons not one electron, this is the wave function for two electron, this is the wave function for the two electrons and I am adding these two functions.

So, I add the two up naturally what will happen? I will have to have a normalizing factor here. It is possible written in the normalizing factor, I will not write it down. I will not calculate it, but it is easy to see, show that it is given by 1 by square root of 2 into 1 plus S square. In the case of the molecular orbital theory there as only an S that is because you are adding atomic orbital, but here you are adding two electron wave functions and that is, why it is S square. And this is one possibility, what is the other possibility? The other possibility is to have 1 s a 1, 1 s b 2 minus 1 s a 2, 1 s b 1 and naturally the normalization factor will be different over that will happen is, you will have 1 by square root of 2 into 1 minus S square, S is actually our overlap integral that we had earlier.

So, there are these two functions, the first one, I am going to call it Valence bond approximation for the, actually this will turn out to be approximation for the ground state and this will be a valence bond approximation not for the ground state, but for excited state. As similar to what happen in the case of molecular orbital theory, this will represent the ground state; this will represent the possible excited state of the system ok. So, the now, we can do a calculation using this function. You use this as the trial function for each distance; you will calculate the value of script E and then make a plot of that script E against the distance. So, actually what happens is you will get a curve, which looks like this.

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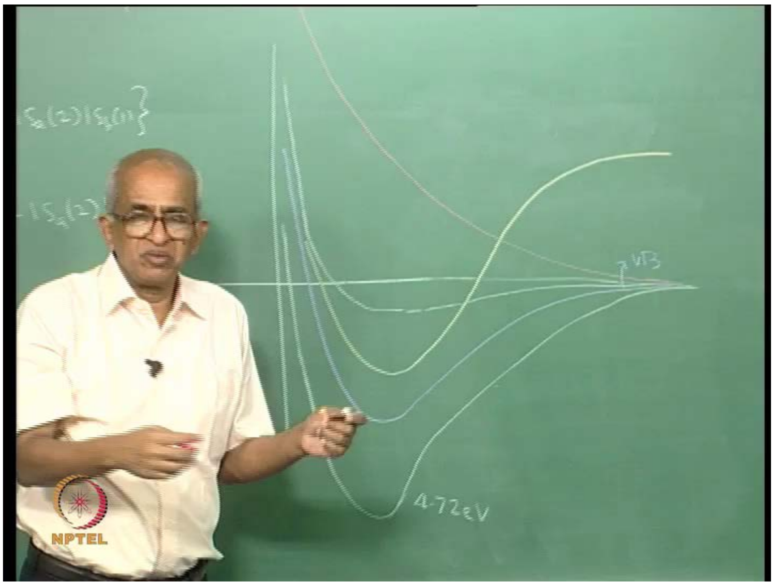

In comparison with this the simple molecular orbital theory curves this is valence bond theory. This approximate function is known as the valence bond wave function for hydrogen molecule and in comparison with that the molecule orbital results are something like that. So, these things are there in the picture that I showed you earlier we will have a look at it once more. So, this is the experimental, this one is the experimental curve.

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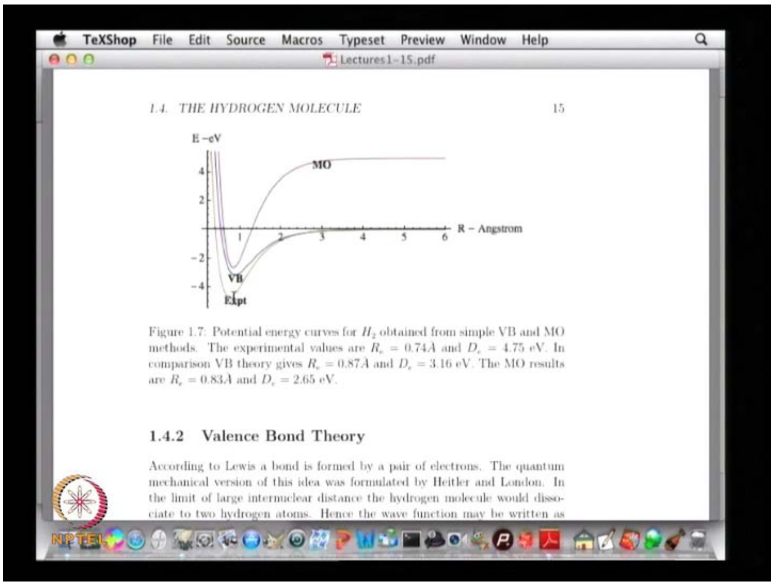

1.4. THE HYDROGEN MOLECULE 15

Figure 1.7: Potential energy curves for H_2 obtained from simple VB and MO methods. The experimental values are $R_e = 0.74Å$ and $D_e = 4.75$ eV. In comparison VB theory gives $R_e = 0.87Å$ and $D_e = 3.16$ eV. The MO results are $R_e = 0.83Å$ and $D_e = 2.65$ eV.

1.4.2 Valence Bond Theory

According to Lewis a bond is formed by a pair of electrons. The quantum mechanical version of this idea was formulated by Heitler and London. In the limit of large internuclear distance the hydrogen molecule would dissociate to two hydrogen atoms. Hence the wave function may be written as

That is the valence bond result and this curve is the molecular orbital result. You can see that valence bond theory actually is better in two respects, better in that it describe the dissociation limit correctly. It is not surprising; because that is how we started with the wave function, this is how we constructed the wave function. So, that part is not surprising, but you also find that the energy predicted by the valence bond theory actually is better than the molecular orbital theory.

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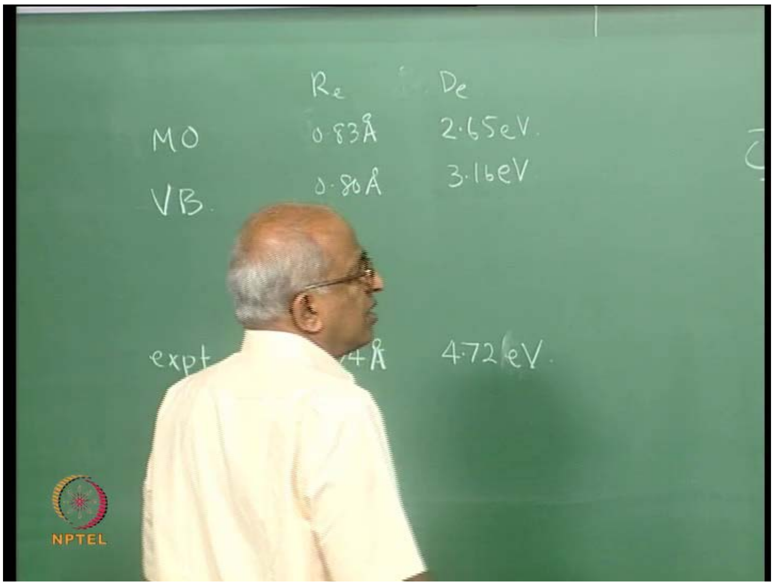

Let me tell you the value of dissociation energy, as well as the bond lengths. I will list the values of R e and the dissociation energy. Simple M O theory which we have discussed earlier, it gives you R e to be 0.83 angstrom and dissociation energy to be 2.65 electron volts. Valence bond theory gives you 0.80 and 3.16. Comparison with this experimental values 0.74 and 4.72, but the even though valence bond theory is better.

You see it is, that is true correct, thank you, it is electron volts. So, even though the valence bond theoretical answer is better, it is still far away from the experimental value it does predict to that a bond is formed and it predict the bond length to be it I mean, not a bad value 0.80 were as the experimental value is 0.74. So, therefore, you can see that there is still room for improvement correct. So, people have done. So, many kinds of calculations, many many calculations have been done, all this calculations where done long ago.

For example, what you can do is, I mean, I can tell you one typical way in which the modification will proceed. These atomic orbital write 1 s a, 1 s b is they are taken to be atomic orbitals, each one of them is taken to be atomic orbitals, which feel the nuclear charge of unity right. They are taken to be same atomic orbital as in the case of hydrogen atom and then the case of the hydrogen atom each electron, not each electron, electron feels only one nuclear charge, but here you have two nucleus and therefore, may be what would happen the effective nuclear charge felt by this atomic orbitals need not be unity, but it may be a new number, different from unity.

So, you can introduce an effective nuclear charge, but once you introduce an effective nuclear charge, you will have to do a calculation for different effective nuclear charge and find out which effective nuclear charge is the best. And this will leave to improvement in the energy of the system and people have done this kind of calculation. I will tell you details of one such calculation, not in details, but I will give essentially I will give answer for that.

But before I do that, we have to understand why is that the molecular orbital method. Gives a totally wrong dissociation limit, we will try to understand that. So, we will look at the molecular orbital wave function, oh before I go into that description I should also tell you what happens? If you did a variation calculation, using this as the trial function. In that case, you will find that there is no bond formation, but this system is acutely repulsive. Repulsive meaning there is no formation of a molecule, there is no bond formed. If you say that is the wave function for this system.

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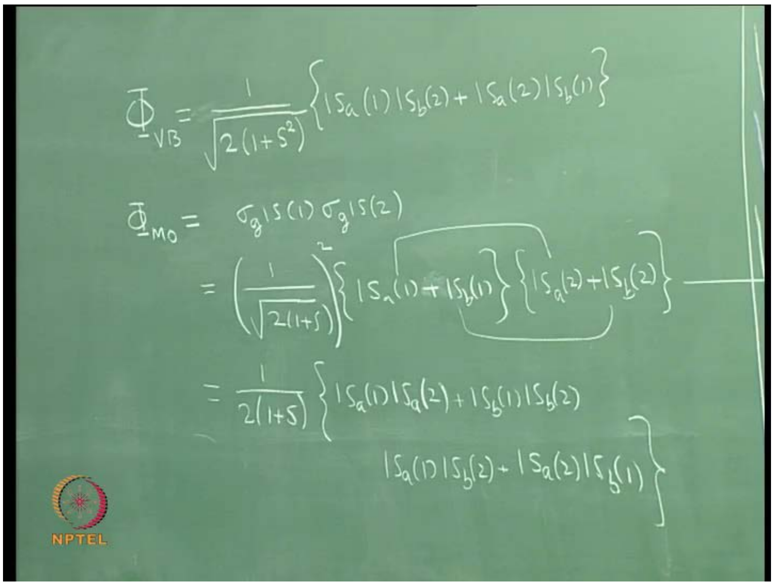

$$\Phi_{VB} = \frac{1}{\sqrt{2(1+S^2)}}\left\{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)\right\}$$

$$\Phi_{MO} = \sigma_g 1s(1)\,\sigma_g 1s(2)$$

$$= \left(\frac{1}{\sqrt{2(1+S)}}\right)^2 \left\{1s_a(1) + 1s_b(1)\right\}\left\{1s_a(2) + 1s_b(2)\right\}$$

$$= \frac{1}{2(1+S)}\left\{1s_a(1)1s_a(2) + 1s_b(1)1s_b(2)\right.$$
$$\left. 1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)\right\}$$

And so, it is some excited state of the system. Let us forget this, we are not interested. This is the case where is a bond formed. Now, we look at phi M O once again, what is phi M O? It is actually sigma g 1 s with the first electron and sigma g 1 s with the second electron right. And what is sigma g 1 s? Let me just remind you, it is just given by 1 by square root of 2 into 1 plus S into 1 s a 1, 1 s sorry, plus 1 s b 1 that is sigma g 1 s. And sigma g 2 s has the similar appearance; it will also contain this factor 1 by square root of 2 into 1 plus S. So effectively there are two such factors, I would have the square of that and then I would have 1 s a 2 plus 1 s b 2 correct. Now, this is just a normalization factor that is worry about what is in the wave function. So, it is actually going to be if I squared this, I will get 1 by 2 into 1 plus S multiplied by, see there are two terms here, there are two terms there, so if you multiplied out and added them together, you will get four terms.

I am going to write those four terms, the way I am going to write those four terms is like this. I am going to multiply this with that, that is acutely 1 s a 1, 1 s a 2 right. And then I will multiply this with that so, this plus 1 s b 1, 1 s b 2. And then, I will have what are repeated cross term, this multiplying that, that is acutely 1 s a 1, 1 s b 2 plus 1 s a 2, 1 s b 1. So, this is exactly what my molecular orbital wave function is for the hydrogen molecule, is it ok, you have made a mistake; I do not think I have made the mistake right. So, then if you look at this function, you will notice something very, very interesting. See if you looked at this part of the function and compared it with the valence bond wave function. We will find that, this and that are the same.

So, contained inside your molecular orbital wave function is acutely the valence bond wave function. And what does the violence bond wave function say? The violence bond wave function says that ok. There is one electron associated with nucleus a right and that is the way it is the other electron is associated with nucleus b. And if you look at this one, what will happen? The electrons simply have inter change their positions. So, therefore, what is acutely happening is that ok, there is one electron with nucleus a, one electron with nucleus b right. And further I think this is the best point for me, to introduce the spin part of the wave function.

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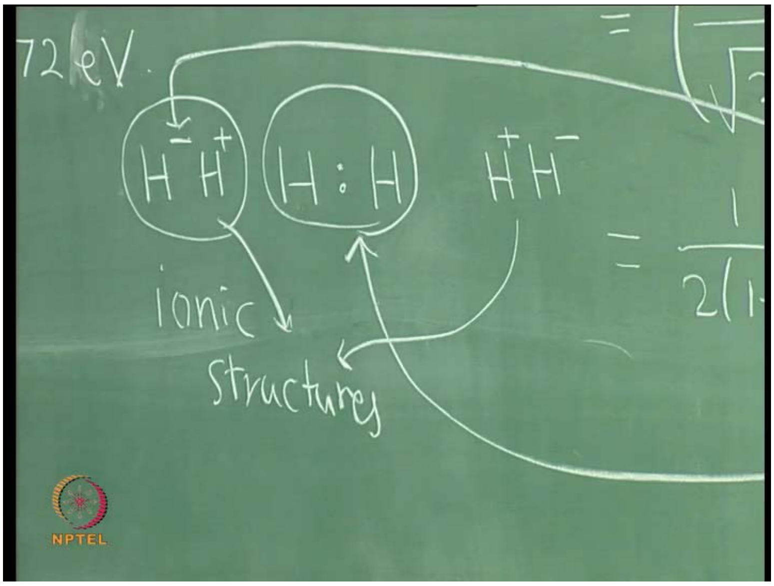

Let me just introduce a spin part for this function, how would this spin part look like. Well here, I have written only the spatial part of my wave function. And if you looked at the spatial part if suppose you interchange the electrons 1 and 2, suppose you interchange the electrons 1 and 2 what will happen? This function if you interchange the electron 1 and 2 you will find that, this function does not change sign. And therefore, strictly speaking you see the wave function as it starts does not satisfy the Pauli Exclusion Principle, but then you can make it satisfy the Pauli Exclusion Principle by adjusting the spin part.

So, how was the spin part look like? It would be 1 by square root of 2 into alpha 1 beta 2 minus beta 1 alpha 2, remember we have seen this kind of spin function earlier. And this function has the nice feature that, if you interchange the two electrons, the wave function will change signs. So, therefore, with along with the spin part if it took this function what is the result? The result is that it is anti symmetric. Similarly for this function also you can use exactly the same spin part for the molecular orbit function also you can use the exactly the same spin part without any difficulty because when you interchange the 2 electrons you see this function does not change sign.

And if I use the exactly the same spin part everything is fine the wave function satisfies the anti symmetric principle. Now, if you look at this function, it says that one electron is associated with nucleolus a, the other is associated with nucleolus b. And further it says that one of them if it is pointing up, the other is pointing down. Now this is actually very nice for the chemist, because you see if you remember what Lewis said what the chemist were thinking of the formation of a bound in hydrogen molecule. They would say that you have one electron from hydrogen one and the hydrogen a and you have the other electron from the other hydrogen and these 2 electrons are paired. And the bond means the pair of electrons, which are acutely paired in such a fashion that there spins are anti parallel.

That is the Lewis way of thinking about the bond electrons form a paired and so, you have the bond. And you will see that the valence bond description acutely is very much resembling that because you are saying the two electrons are paired, there spins are anti parallel and when one electron is on associated with nucleus a other electron is associated with nucleus b and these two electrons are getting pared. And you will also realize that, the same thing as contained inside the M O function, the same thing is contained, but M O function has other possible contribution also from, a case like 1 s a 1, 1 s a 2.

So, how will I represent that well, we can say this represent a situation where the electrons are shade equally by the two nuclei. This part represent the case where the electrons are shade equally by the nuclei, but if you look at this 1 s a 1, 1 s a 2, this means that both the electrons are associated with nucleus a, while that represent the situation were both the electrons are associated with the nucleolus b. And therefore, if I wanted, I can say that this one represent a chemical structure which I will denote as H minus H plus. While this part represents a chemical structure according to the chemist it would represent the structure which would be written as H plus and H minus right. This is acutely H minus and H plus and this will be H plus and H minus. Yeah there is the plus there right. Everything is been added it up ok.

So, therefore, if I looked at the molecular orbital descriptions, what happens is that contain in the molecular orbital description are the valence bond wave function which is this. It also has contribution from what may be referred to as ionic structure, these are the ionic structures right. And if you looked at the contribution ionic structures inside the molecular orbital wave function you have the ionic structure, but what happen is that ionic structures and this structure, which is acutely referred has the covalent structure this one, because you see it is representing the covalent bond. So, this is covalent structure. So, the covalent structures and ionic structures have the same amount of importance in this description.

So, therefore, if you think of dissociate the molecule, what will happen? This is the system the molecule may dissociate to give you two hydrogen atoms. That is what will happen? If you had only this part of the function, but this part of the function implies that this system may also dissociate into the ionic structures, which are H plus H minus. So, if you dissociate the molecule, the molecular orbital theory will say that, it is possible for you to dissociate in such a fashion that, you will get H plus and H minus.

And that is the reason why the plot of energy this is molecular orbital energy, energy according to molecular orbital calculation, it does not give you the correct dissociation limit. It does not dissociate to hydrogen atoms, but instead it disassociate sometimes. I mean, if when you dissociates, you can get two hydrogen atoms, because it contains this part, but you cannot also get positive ion on one side and the negative ion on other side, that is what the molecular orbital theory says and that definitely cannot be true. And this is the reason for M O theory gives you totally incorrect disassociate limits fine. But then you look at the Valence bond theory, Valence bond theory actually has only the neutral structure.

Now, if I wanted to improve the valence bond theory, what can I do? Well these ionic structures are acutely possible that is the way in which valence bond theory would think. It would say that, this structures must be possible, but they should not have the same amount of importance has the covalent structure. So, therefore, an improved valence bond theory wave function can be written, how will I write the function.

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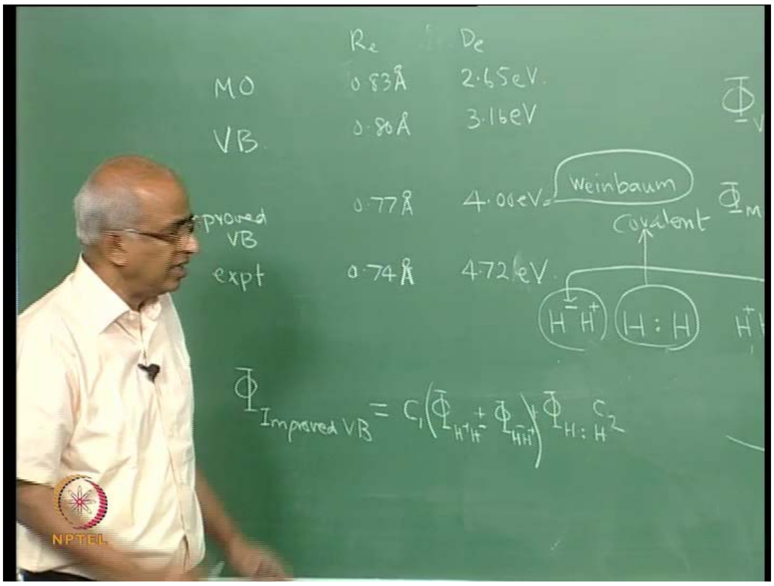

And improved valence bond theory function will have phi improved M O sorry, improved valence bond would be, you will have this neutral structure right. So, let me just say that, it is written as some phi H H, I do not want to be writing all this things in detail. But when I write phi H H, may be I will put two dots between, what that is it represents? It just represents this part of my function. And then I would have phi H plus H minus, what would that be, it would be this one. It would represent 1 s b 1 into 1 s b 2 and then I would have what is the other one phi H minus H plus.

So, these are three possible functions, right and what does the molecular orbital method say, it simply add all of them right, with the same amount of importance and does the calculation and that gives you wrong answers. Now simple valence bond theory what does it do? It does not include these or that, but it just says, the function is just this. So, a better calculation will be, to say that I will take combinations of these things after multiplying them by suitable Constance.

So, what I will do is, I will multiply this by may be constant, which I will referred to as c 1 and these two, I would accept hopefully would have the same amount of importance right. Because you see a structure in which, you have H plus on one side and H minus on the other side over structure in which H minus is one this side and H plus on the other side. They would make the same amount of contribution. So, therefore, these two I would accept would have the same amount of importance.

So, what I will do is? I will simply add them together multiply them with a coefficient which maybe, I should call this c 1 and that c 2. Now, if you did that, what will be your next step? You will take c 1 and c 2 to be variation parameters and find their value in such a fashion that 50 as the least value. And because of the wave, the wave function is constructed it is guaranteed that dissociate correctly and it is also guaranteed that the energy will be better than the valence bond theatrical calculation. And such calculations have been done. There are too many curve in this picture, but any way, let me draw this one also I can find chalk of different color, I will use that.

So, this one will actually lead to an improvement in the energy and the one length so, this is improved valence bond theory. Now I will write with the answer of one such calculation, the bond length is actually 0.77 angstroms and the dissociation energy is 4.00 electron volts and I should also tell you that, this particular calculation was due to represent to Weinbaum. And in addition to taking this as the function, what it did was introduce this idea of effective nuclear charge and varied the nuclear charge in such a fashion that you got the best energy. And you can see that the answer that you got for the energy was fairly decent dissociation was 4 and the bond length was to be found 0.77 angstroms.

Now, you may ask it is possible to improve molecular orbital theory and the answer is that, yes it is possible to improve the molecular orbital theory also. In a similar fashion and in fact, if you try to improve the molecular orbital theory what will happen is that? You will get exactly the same kind of function now, I mean when you look at it in detail you will find that the function is of this form. And such procedures are known as configuration interaction procedures.

Now, even for a system like hydrogen molecule this calculations, which are require to configuration interaction calculation are very difficult they are quite involved and quite difficult to perform. But I should also tell you that, in the case of hydrogen molecule, there was a calculation done long ago by two scientists. Let me remove everything else. I will just say James and Coolidge these were the name of the scientists who did the calculation. And effectively I mean they had large number of variation parameters, but you should also remember that the more variational parameter you have, the more difficult is the calculation.

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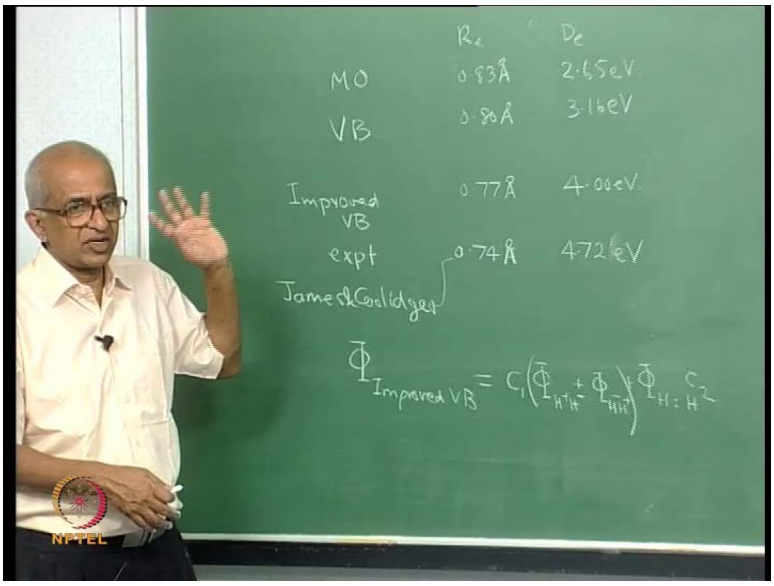

	R_e	D_e
MO	0.83 Å	2.65 eV
VB	0.86 Å	3.16 eV
Improved VB	0.77 Å	4.00 eV
expt James & Coolidge	0.74 Å	4.72 eV

$$\Phi_{\text{Improved VB}} = c_1(\Phi_{H^+H^-} + \Phi_{H^-H^+}) + \Phi_{H:H}\, c_2$$

Because, each variational parameter you have to find it is value in such a fashion that script E has the least value. And these were the days in which computers were not there at all you had only hand, you had only mechanize, I mean mechanical calculators using this mechanical calculators. They did the lot of work to get the best possible value is for all the parameter and then essentially you got the experimental values back right. They did such a calculation that the answers were in agreement, perfect agreement with the experimental results are available and that time, but that involve lot of calculations.

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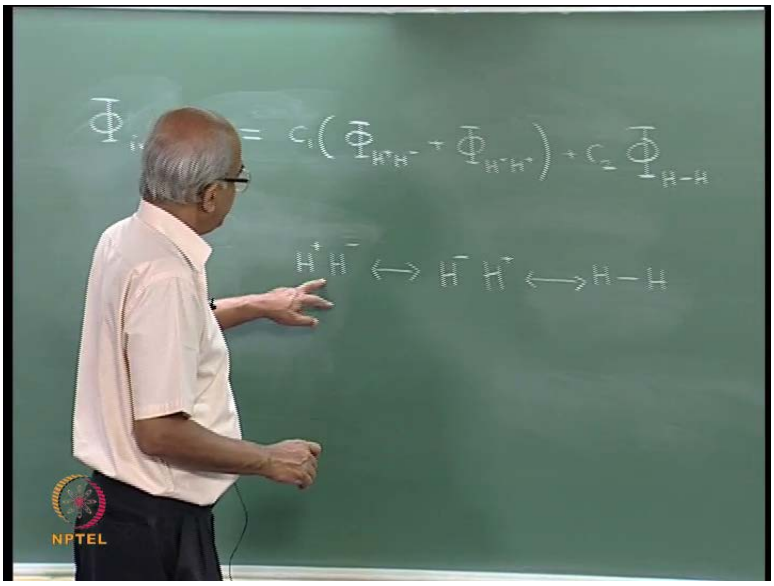

$$\Phi_{i} = c_1(\Phi_{H^+H^-} + \Phi_{H^-H^+}) + c_2\,\Phi_{H-H}$$

$$H^+H^- \longleftrightarrow H^-H^+ \longleftrightarrow H-H$$

We have seen that our improved wave function according to valence bond theory is given by phi improved is equal to some constant c 1 phi which corresponds to H plus and H minus plus phi which corresponds to H minus and H plus, plus another constant c 2 into phi which corresponds to natural sector which we may write as H H just remind you, this means that, both the electrons are associated with the hydrogen atom on the right hand side. While this means that both the electrons are associated with the molecule are both the electrons are the associated with the left hand side electron. While this wave function means that, the two electrons are shared equally. And the acutely wave function is a linear combination of these three functions. And this has been used essentially in chemistry particular by the organic chemist.

And instead of writing such a wave function, what they will do is? They will say that the actual structure is a mixture of all this things. And hence they would say that the acutely structure is that resonance hybrid of this structure which is H plus H minus, the second structure which is H minus H plus and the third structure which is H H. And to tell you that it is a resonance hybrid, what they would do is? They would put double ended arrows in this fashion. So, this as to be very clearly understood if you put this double ended arrows what it means, is that actually structure the wave function for the actually structure is a linear combination of the wave function corresponding to each one of these structures. Having seen this, we will now look at diatomic molecules. Thank you for listening.