Quantum Chemistry of Atoms and Molecules

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Lecture-55
Valance Bond Theory and Homonuclear Diatomics: Part1

Finally we start talking about molecules and in whatever time is left in this course we will only talk about molecules. We start with a very simple approach valence bond theory which I think most of us would know at least qualitatively and then we end with a very simple approach for pi electron pi electronic system that is Huckel treatment. So, whatever we discuss now is actually much, much simpler than what we have developed so far while discussing atoms.

And it seems that way because while discussing atoms we have built all the tools that we need to discuss molecules that is why it is going to sound much simpler.

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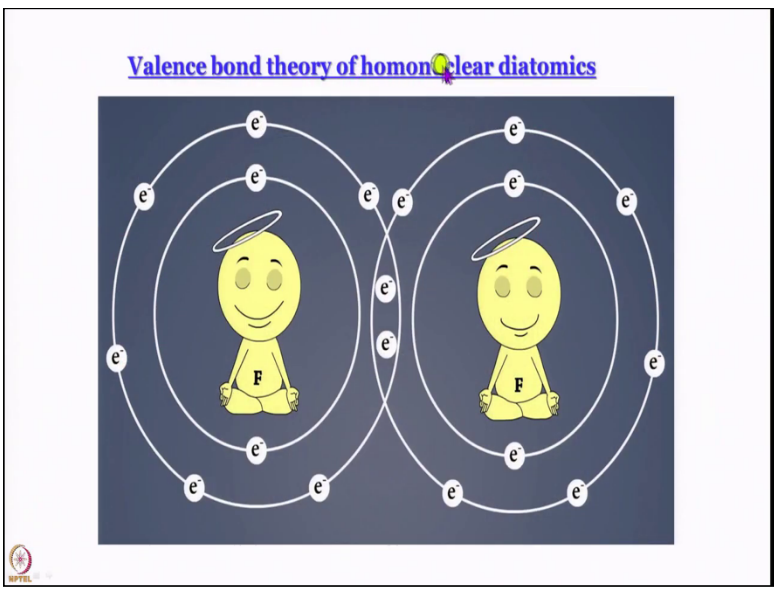

So, here goes we start with valence bond theory of homonuclear dynamics and we get to know how is it that these atoms come close together and are very happy to be with each other even though we have this big fat positively charged nuclei which repel each other strongly. What is the reason for stabilization when these nuclei come together enveloped by the electrons and how are bonds formed? How are molecules formed? As a result and that is what leads to everything in this universe.

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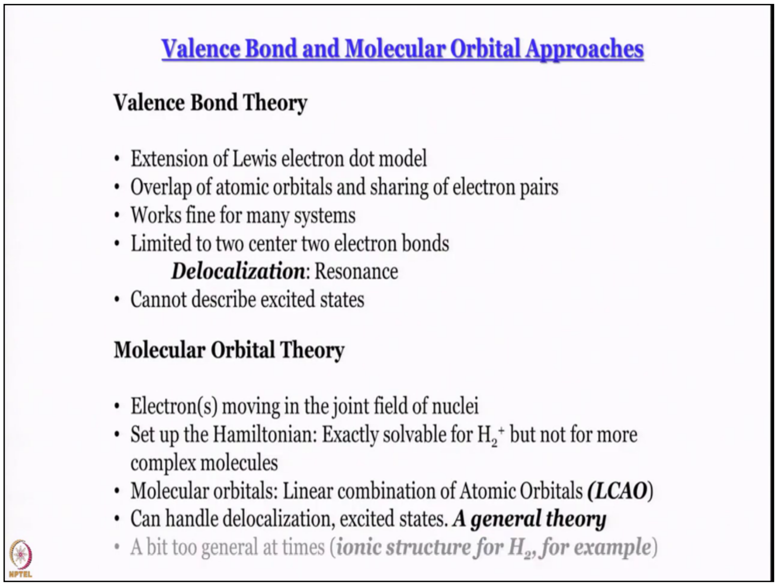

So there are 2 approaches to talk about this 1 is valence bond theory and the other is molecular orbital theory. We start with valence bond theory this essentially is an extension of Lewis electron dot model that everybody has studied in high school right. Remember we used to put dots for electrons and then we used to share and we used to say that there has to be this stable octet and so on and so forth.

Valence bar theory translates this very simplistic model of Lewis, Jane Lewis in language of quantum mechanics that is all so it is very simple to understand. And it is it relies completely on overlap of atomic orbitals and sharing of electron pairs. As I said it is just a translation of Lewis theory into quantum mechanical language, so atomic orbitals are retained with the modification we are talking about many electron systems.

Well today we will talk only about H 2 but then later on we want to talk about when electron systems so there you have to take care of things like shielding and all. In fact as we will see even for H 2 you have to take care of shielding so atomic orbitals will be modified accordingly. So, actually it works fine for many systems and the beauty of it is its simplicity the problem of it is also its simplicity because it is limited to 2 center 2 electron bonds.

As long as you limit yourself to ground state of 2 center 2 electron bonds it works beautifully problem is the moment you go beyond 2 centers or you have 1 electron or 3 electrons or more electrons then it does not work. So, when you are more than 1 more than 2 centers you need to account for delocalization which is actually not provided for in valence bond theory so you have to invoke this after thought that is called resonance.

Now resonance is something that is absolutely favorite with students of chemistry we know very well we love pushing arrows and we love talking about how a particular resonance structure is stable than the more stable than the others but resonance really is not something that is built into VBT it has been it is an add-on to extend the scope of the theory to delocalize systems. And even if you invoke resonance there is something you cannot do and that is you cannot access excited states.

As we might have mentioned in the passing earlier there is a lot of chemistry in excited states as well all the photo chemistry that you see well the very fact that you see the process of vision all that is something on the other to do with excited states. And valence bond theory is definitely limited to ground state only nothing else. So, that is a very, very severe problem with valence bond theory so the way out is to use molecular orbital theory in which you consider the electrons to move in the joint field of nuclei and you set up the Hamiltonian well we will set up the Hamiltonian for valence bond theory as well today.

So but then in molecular orbital theory you set up the Hamiltonian you can solve Schrodinger equation with the Hamiltonian exactly for H 2 plus and will not even do it. But the moment you add 1 more electron you encounter the usual complications that we got with many electron atoms and we get more because now you not only have more than 1 electrons but you have more than 1 nuclei as well. So, what we do is we generate molecular orbitals and I am sure you have come across this already.

We generate molecular orbitals as linear combination of atomic orbitals LCAO. So, if you remember what we had talked about earlier we are actually synthesizing the wave function by using this orthonormal basis set of atomic orbitals. So, you can use variation theorem there remember. The good thing about molecular orital theory is that it is a general theory it can handle delocalization just like that you do not have to do anything special. It gives you excited states just like that you do not have to do anything special.

It is general theory that is its advantage and that is its disadvantage also perhaps I might seem like I am talking in riddles because I said the same thing for VBT what is advantage is also the disadvantage I am saying the same thing for MOT what is advantage is also the disadvantage but it is true that is how it works your advantage sometimes unchecked advantage can become a disadvantage as we will see that sometimes is a bit too general.

It ionic structure of H 2 for example is grossly over interpreted if you use molecular vital theory but that will be the story for another day.

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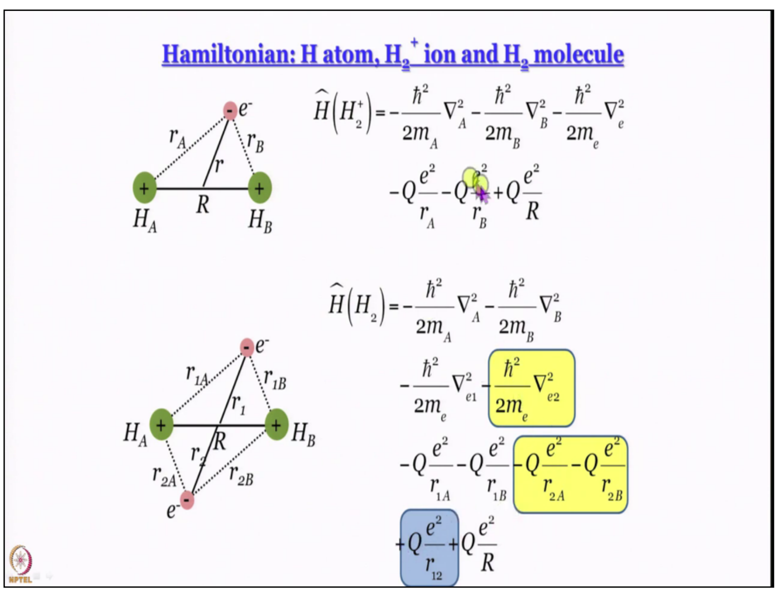

Now you see let us write the Hamiltonian and to write the Hamiltonian will start with a hydrogen atom then even though your molecular even though valence bond theory it has no scope for discussing H 2 plus iron we will write the Hamiltonian for H 2 plus ion just because it has fewer terms and then will go on to H 2 molecule. So, this is something that is very familiar to us right ignore the picture for the moment just look at the expression for Hamiltonian.

Hamiltonian for hydrogen atom something is wrong yeah hydrogen atom Hamiltonian now you can now in the picture is correct sorry about goofing up there. So, hydrogen atom you remember nucleus and electron so the height the Hamiltonian would be minus H cross square by 2 m e del e square minus H cross square by 2 m e del e square where A stands for the nucleus or the atom as a whole e stands for the electron in it and minus Q e square by r a gives you the potential energy for attraction of the electron experienced the attraction experienced by the electron because of the nucleus.

So this potential energy the first term here is kinetic energy of the atom as a whole largely kinetic energy of the nucleus. This is the kinetic energy of the electron and very soon we are going to write all this in atomic units. So, now what we will do is we will go in steps we will add 1 more nucleus 1 more proton actually and we will discuss the case of H 2 plus ion. Now when we do that all these 3 terms will remain of course some more terms will come in. Which more terms will come first of all we will have a kinetic energy term for this nucleus B.

We will have electrostatic attraction between this electron and the nucleus B so what we will have to write is we have to write something like minus Q square by r B for the potential energy term and for the additional kinetic energy term of the nucleus we have to write something like minus H cross square by 2 m B del s del v square of course do not forget m A and m Bb are one and the same they are just protons.

An additional term will come and that is due to nucleus-nucleus proton-proton repulsion that will be plus Q e square divided by R where R is the inter nuclear separation right. So, this is the kinetic energy term for the second nucleus attraction potential energy for attraction between the electron and the second nucleus and this is the term for nucleus-nucleus repulsion. Now what happens if you want to go to H 2 molecule because remember valence bond theory has no scope for H 2 plus we have to talk about H 2.

So we add 1 more electron right and the moment we add 1 more electron we add many terms how many more terms do we add whatever is there will remain and moreover since there is a second electron we have to use a little different nomenclature. So, what we should do is that instead of del e square we have to write del 1 square where 1 is the well index of the first electron and there will be another term minus H cross square by 2 m e del 2 square that is for the second electron.

Then the second electron will also feel attraction with H A and with H B so now the distances will also have to be rewritten, so this separation between the first electron and nucleus A will write it as r 1 A separation between first electron and nucleus v will be r 1 B between second electron and nucleus a will be r 2 A and that between the second electron and nucleus v will be r 2 B and accordingly we will get how many more terms well will get something like minus Q e square divided by r 2 A minus Q e square divided by r 2 B this is due to attraction of this electron by these 2 nuclei.

Nucleus-nucleus repulsion is accounted for and the other term that you have to bring in is well of course kinetic energy of the second electron minus H cross square by 2 m e del 2 square and finally the additional term is electron-electron repulsion electron-electron separation is r 1 2. So, that will be plus Q e square by r 1 2. So, I have shown you the additional terms that come in with respect to H 2 plus Hamiltonian in highlights great.

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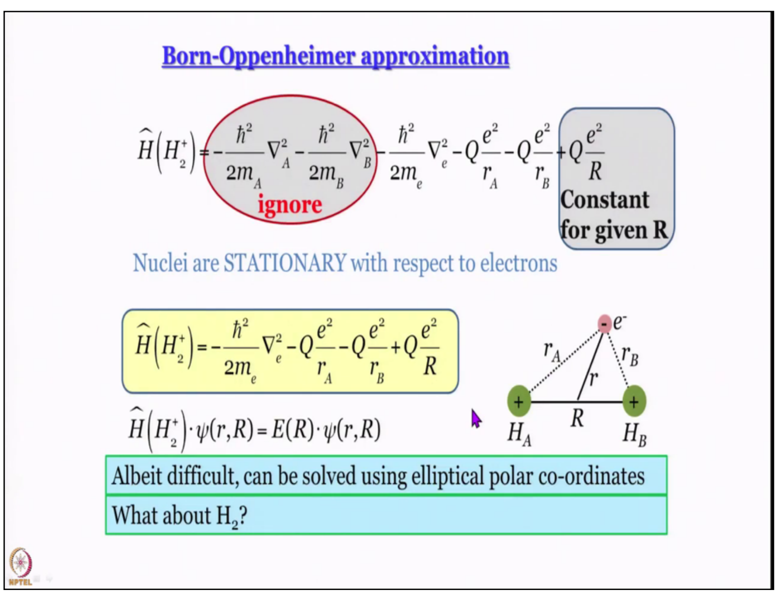

Now of course this is a very complicated situation and we need some kind of an approximation before we can go ahead and fortunately we have in our hands something called Born-

Oppenheimer approximation which essentially says that the total energy is a sum of all these energies so wave functions are all products of Hamiltonians and everything is separable. So, the statement of Born-Oppenheimer approximation or the consequence of Born-Oppenheimer approximation that will use here is this.

When we talk about the electron there is no need to worry about the nucleus. Nucleus is much more bulky it takes much longer it its movement is in a different time scale altogether. So, when we do electronic calculations we might as well take the nuclei to be stationary this is extremely important. So, it is like the something that is very light that moves fast something that is extremely heavy moves slower.

When we talk about the motion of the light particle we do not have to worry about the motion of the heavy particle that is all. So, when we use this consequence of Born-Oppenheimer approximation how does this expression for the Hamiltonian simplify and to keep things very simple I am working with the Hamiltonian for H 2 plus for H 2 we will just add those additional terms. So, first of all this del A square will you agree with me that this becomes 0.

Will you agree with me that del v square term becomes 0 because we are considering the nuclei to be stationary so there is no question of their kinetic energy. So, these 2 we can ignore under Born-Oppenheimer approximation what else if these are stationary then this inter nuclear separation will remain constant for our calculation so R can be taken to be a constant and we can perform the electronic calculation for a particular value of R.

See what the energy is then go back and do it for another particular value of R see what the energy is and we can plot energy as a function of R and see whether there is a minimum. If there is a minimum then that is the happiest situation and that separation R is your equilibrium bond length. So, it becomes very, very simple all you have to work with now for H 2 plus is this minus H cross square by 2 m e del square minus Q square by r A minus Q square by r B.

So, life is simpler than what it is and in fact you can using elliptical polar coordinates you can actually solve it and get wave functions but will not do it because again they will become useless the moment you go to H 2 so what we do is we actually use linear combination of atomic orbitals as we will discuss later. But today let us think how we handle this H 2 problem hydrogen molecule the hydrogen molecule problem by this valence bond theory.

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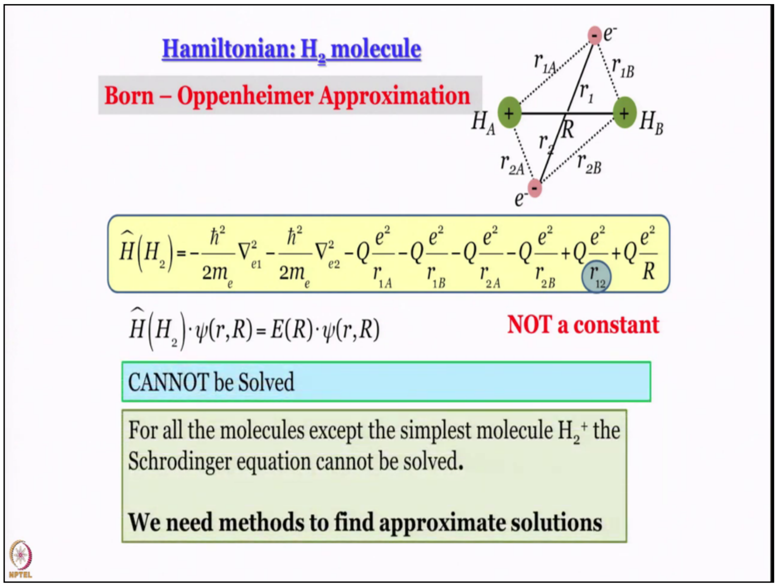

So we start with the Hamiltonian for H 2 molecule more terms as we have said earlier I am going a little fast here because see it is not all that difficult and we have discussed this many times. So, if there is a problem please go back and just do iterations I think you will be fine. So, this is our Hamiltonian and we have said what this different kinetic energy and potential energy terms are everything is accounted for kinetic energy of the electrons we ignore the kinetic energy of the nuclei by Born-Oppenheimer approximation.

We consider the electron-electron repulsion we consider electron nucleus attractions four of them and we consider nucleus-nucleus repulsion keeping in mind that we can keep R to be a constant. So, this is the Hamiltonian and if you write Schrodinger equation using this Hamiltonian this is what we get if we write in shortcut. Our purpose is to get an idea of wave function our purpose is to make an estimate of the energy.

And energy of course as we said a little while earlier the energy is going to be a function of R inter nuclear separation remember that. So, the complicating factor here is that this r 1 2 inter nuclear separation is not a constant you might remember from our discussion of main electron atom that whenever you have more than 1 electron in the system they move deviously they like to avoid each other.

But it is not as if their separation is always the same it is not. So we cannot really solve this directly so we need some simple some approximate solutions and we know by now how to use approximation methods. So, we will start with the trial solution and see whether it makes sense.

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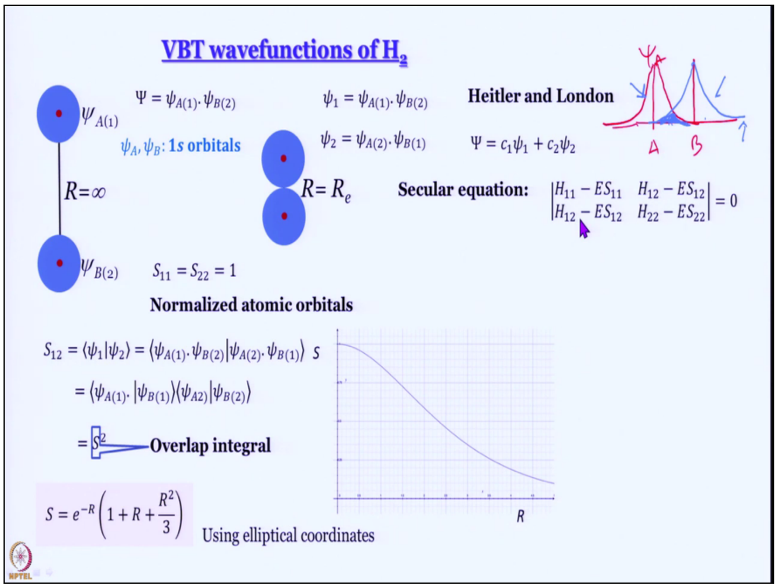

So, let us think what kind of wave functions we can think of for H 2 and while doing that we are going to use the atomic orbitals that we are so familiar with to try and construct the wave functions of the molecule the molecular wave function. So, and of course we will do that using common sense by and large. So, let us think. What happens when R equal to infinity now when I say infinity I do not mean infinity-infinity certain angstrom is sufficient to qualify as infinity for these atomic and molecular systems.

Because if you think of the potential energy between these 2 atoms that becomes 0 asymptotically but becomes close to 0 within say 10 angstroms of inter nuclear separation. So, such separation which we can say roughly is infinity for all practical purposes. Electron number 1 moves in the field of nucleus A electron number 2 moves in the field of nucleus B. So, electron number 1 would reside in the 1 s orbital of nucleus A.

Electron number 2 would reside in the 1s orbital of electron B. So, what would the wave function be? Wave function would be the product of psi A 1 and psi B 2 psi A 1 means electron number 1 is in the 1 s orbital of electron a sorry of nuclei of atom A psi B 2 means electron number 2 is in the 1 s orbital of atom B so A and B are the names of atoms 1 and 2 are the indices for electrons. So, this is what it is when they are very far apart electron number 1 is happily blissfully ignorant about the presence of this nucleus B.

And electron number 2 is happily ignorant of the presence of nucleus A. Now what happens when they come close together let us say when the inter nuclear separation is close to equilibrium bond length does not even have to be exactly equal to equilibrium bond length. Close enough so that these electrons experience that nucleus and the other way around. Then it is not sufficient to write the wave function as psi A 1 psi B 2 that is only 1 of the components of the wave function we write it as psi 1.

The other possibility is that electron number 2 might reside on in the 1 s orbital of nucleus of atom B electron number 1 might reside in the 1 s orbital of atom A so that is the second possibility and that would be the second term psi 2 that would contribute to the wave function psi A 2 psi B 1 all right. What is the wave function then the wave function would be capital psi is equal to C 1 psi 1 plus C 2 psi 2 we are going to evaluate C 1 and C 2 may be in the next class but we can actually make a sort of a guess that what C 1 and C 2 could be if you do not worry about normalization of psi.

Can you think what I expect the ratio of C 1 and C 2 to B or rather what do I expect the ratio of the magnitude of C 1 and magnitude of C 2 to be. Please think about it we are going to come to that eventually right. So, this is my wave function to start with. This wave function was proposed by Heitler and London and so this is called Heitler and London wave function. Using this wave function we can write down Schrodinger equation H psi equal to E psi.

And then the problem is to evaluate the coefficients and evaluate the energy. I hope you remember what we do when we have problems like that let me write Schrodinger equation I just write it in terms of H for now H operates on C 1 psi 1 + C 2 psi 2 to give me something I will just call it eE for now C 1 psi 1 + C 2 psi 2 well we have done similar things earlier. So, what we do is we left multiply by this psi 1 and integrate over all space.

So what do I get then integral psi 1 H psi 1 well and C 1 comes out plus C 2 integral psi 1 H psi 2 is equal to C 1 E integral psi 1 psi 2 + C 2 E I am taking E to be a constant on the right hand side because E is the eigen value even though we cannot solve it and find it well it is there so we just take it out integral oh whatever sorry sorry first one is wrong I got distracted a little bit so C 1 E psi 1 integral psi 1 psi 1 overall space remember I am left multiplying by psi 1 and integrating over all space.

All R in this case because we are talking about 1 is orbitals C 2 e psi 1 psi 2 now first thing is this is not equal to 0 this is very important to understand. Why is this not equal to 0 because see first of all your these are products of wave functions and secondly we are talking about one 1s orbital of this atom and one 1s orbital of this atom. These 2, 1s orbitals are not mutually orthogonal this is a concept where sometimes we get confused.

2 orbitals or 2 wave functions of the same system if they are not the same of course they have to be orthogonal to each other but of different systems they are not orthogonal. In fact as we will see we are going to get some new quantity out of all this. So, this is what you get and similarly if you left in left multiply by psi 2 what do you get you get something like C 1 integral psi 2 H psi 1 + C 2 integral psi 2 H psi 2 equal to C 1 E integral I just write psi 1 psi 2 because the order does not matter plus C 2 E integral psi 2 psi 2.

We are going to evaluate all these for now what we do is we call this H 11 we call this H 12 we have encountered these earlier remember we call this H 21 and we call this H 22 and with this we can rearrange the equation also we can write something like C 1 we will write here multiplied by H 11 minus E S11 I will call this S 11 we have encountered these have not we. This is S 12 + C 2 multiplied by H 12 minus E S 12 and this way we get another equation also in C 1 and C 2.

So system of linear equations will get the secular determinant and for a non trivial solution that secular determinant has to be equal to 0. So, now let me show you that secular determinant here is the secular equation you remember what we had written a little while ago we got this H 11 - E S 11 as a coefficient of C 1 H 12 - C S 2 as coefficient of C 2 in 1 for the first equation. In the second 1 this was the coefficient of C 1 this was the coefficient of C 2 so of course this is your secular equation.

Now we have to evaluate these integrals one by one to do that first thing will remember is that we are using normalized atomic orbitals and since we are using normalized atomic orbitals S 11 equal to S 22 has to be equal to 1 is that correct let us write what is S 11? S 11 is equal to integral psi 1 multiplied by psi 1 over all values of R so that will turn out to be integral psi A 1 psi B 2 and the same thing. Now I hope with all our previous discussions of atoms it is not very difficult for us to see that this is really a double integral one in coordinates of electron number 1 one in terms of coordinates of electron number 2 and I can write it conveniently as a product of 2 single integrals one in terms of 1 one in terms of 2.

So I get psi A 1 psi A 1 multiplied by psi B 2 psi B 2 very simple and as these 1s orbitals themselves are normalized we get that these are this is equal to 1 this is also equal to 1 not very difficult to understand. In fact I just erase this. So, one thing is out of the way S 11 and S 22 are both conveniently equal to 1 what is S 12? S 12 is integral psi 1 psi 2 over all values of R. So I write down the expressions for psi 1 and psi 2 psi A 1 psi B 2 multiplied by psi A 2 psi B 1 integrated over all values of R.

And remember this also has to be a double integral because there are 2 kinds of coordinates one for 1 one for 2 this again factorizes into an integral in electron number 1 integral in electron number 2 psi A 1 psi B 1 multiplied by psi A 2 psi B 2. Now what is the meaning of psi A 1 psi A 1 is psi 1 essentially means electron number 1 in the 1s orbital of atom A psi A psi B 1 means same electron number 1 but in a different 1s orbital different atom B.

So this integral is not equal to 0 right psi A and psi B are not orthogonal to each other because there are vitals of 2 different atoms A and B this is something that we have discussed earlier. So, what we say is and of course there is no difference between the 2. The indices are different but that is all so we call this S we call this S and we call this S square and it has a name S is called an overlap integral. Why is it called an overlap integral because if I just draw these 1s orbitals for you hopefully I do not have anything here so it is to draw here.

Let us say this is where A is; it is 1s orbital is an exponential decay and since we have drawn 3d plots in the past I hope its if I draw on this side also sorry that it has gone below let us see if I can correct this entire thing will go so this is your psi A and let us say your nucleus B is here for that we will use a different color this is the 1s orbital, 1s orbital is an exponential decay remember now think what is the value of this integral.

The value of the integral at this point is of course 0 because it is a product of this wave function and this wave function. Here also it is practically 0 the only region in which this integral has non 0 values is this, the region in which both 1 psi A and psi B have reasonably non 0 values well values are actually if you want to be very, very rigorous they are non 0 everywhere because it becomes they become 0 only asymptotically.

But here what we are saying is practically I mean if it is 0.0001 that we take that to be 0. So, only in this region where both the orbitals have more or less good non 0 values only in that region this integral will have non 0 value so this is a region of overlap that is why the name is overlap integral and it is not very difficult to see from what we discussed just now that overlap integral is going to have dependence on R is going to be 0 at a very large separation.

And for 1s orbital it is going to be maximum at separation of 0, R equal to 0 right so using elliptical coordinates one can work out will not work out it is given as a problem in Macquarie's book you can work out an expression and the expression turns out to be an exponential decay in R, R here is inter nuclear separation multiplied by a polynomial in R and when we plot this, this is the kind of plot that we get and this is what we are expected qualitatively also becomes 0 asymptotically.

But as you come closer and closer and closer it becomes maximum. This is the variation of overlap integral as a function of inter nucleus separation. In the assignments we are going to have several such exercises where we will give you different kinds of orbitals and ask you to work out how overlap integral varies as a function of inter nucleus separation and you will see you will not get this kind of a variation always but that you work out in the assignments.

Now we are back to what we are talking about we have simplified a secular equation a little bit this is how it was remember H 11 - E S 11 H 12 – E S 12 and so on and so forth. We have sort of taken care of the SS, we have said this S 11 equal to S 22 equal to 1 so this term will become H 11 - E this term will become H 22 - E and we have said that S 12 is equal to S square so this will become H 12 - E S square this 1 will become H 12 minus E S 12 sorry E S square again. Now here H 12 and H 21 are the same as we have said earlier remember you can use turnover rule. So, we are writing H 12 and not H 21.

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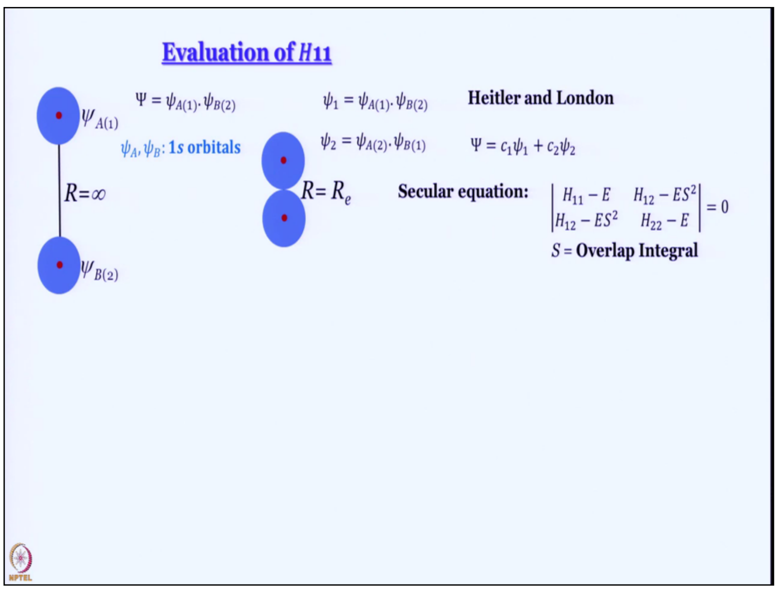

So here it is we have got this concept of overlap integral we have introduced it and we have got this secular equation which is a little simpler than what it was earlier. We have made some advance. Next we want to evaluate the H 11 integral this is where we will start from in the next class.