Concepts of Chemistry for Engineering
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Lecture 13
Molecular Orbital Theory 1: Introduction

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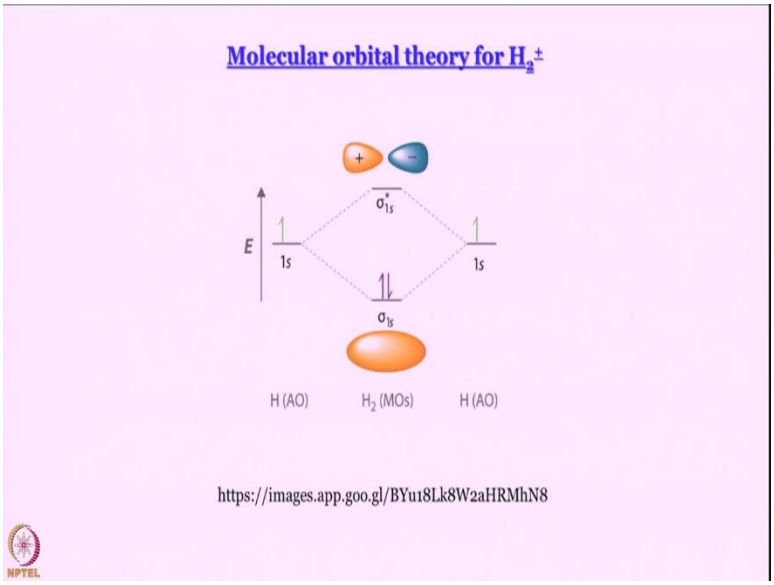

Now, we are going to talk about molecular orbital theory for a very simple system, dihydrogen molecular cation. H_2^+, why H_2^+, because it has 1 electron.

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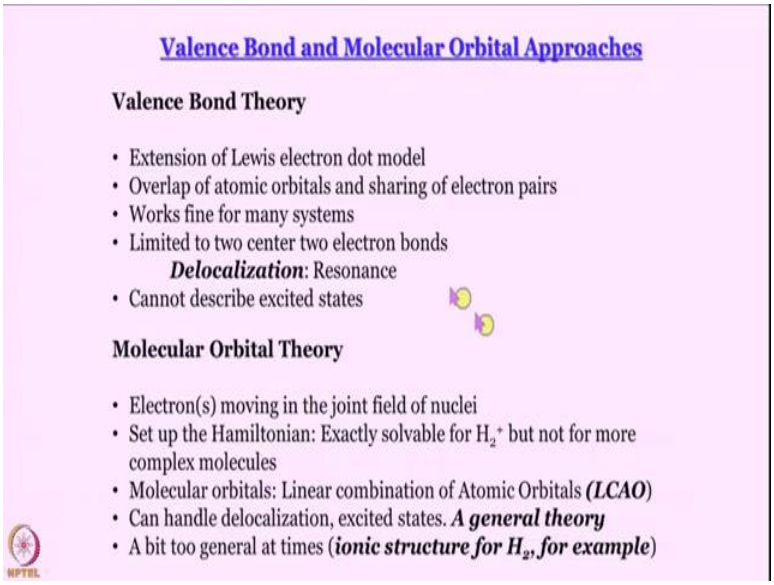

Now, there are two approaches to bonding. In valence bond theory, what we do is we essentially extend Lewis electron dot model. And we retain this concept of overlap of atomic orbitals and

sharing of electron pairs, it is just that we write it in the language of quantum mechanics. And it really works fine for many systems. What it cannot handle is delocalization. And it gives us very limited access to excited states.

And it can talk about singlet and triplet state of dihydrogen, for example, but there are many states that are not accessible. As we will see, molecular orbital theory can give us access to many more things.

So in MOT what we do is, we consider the electrons to move in the joint field of nuclei. I will show you the Hamiltonian shortly, we try to find solutions for H_2^+ and when you try to find solutions for this, for this Hamiltonian for H_2^+, we use some approximation method, we use what is called linear combination of atomic orbitals.

Good thing about MOT is that, it is a general theory, it can easily handle delocalization, it does not necessarily have to be restricted to two centers. But problem is, it is a bit too general. As we will see, when we talk about H_2. As simple as H_2, it over does things and it overemphasizes the ionic structure.

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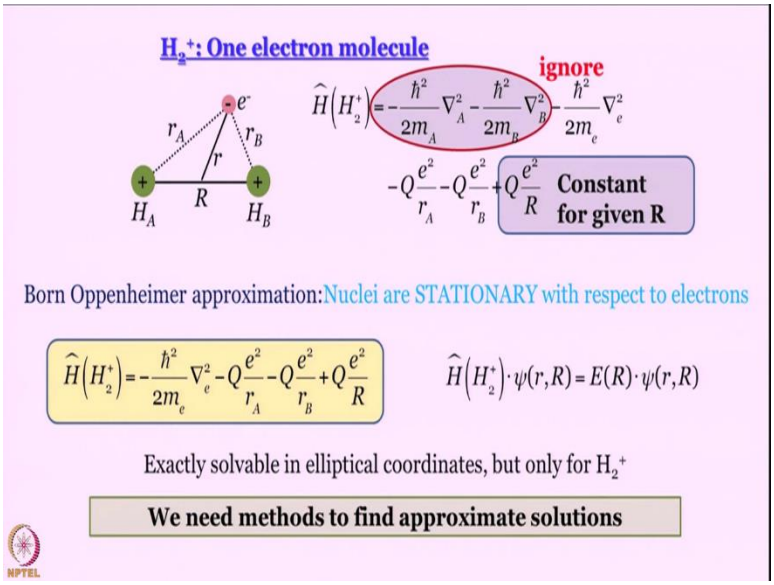

To start with let us write the Hamiltonian for H_2^+, the 1 electron molecule of ours. So, this is sort of an extension of hydrogen atom, like hydrogen atom this also has 1 electron only, the only additional thing here is that it has a second nucleus.

So, we can write the Hamiltonian without much hassle. First, we write the kinetic energy term of the first nucleus H_A, then we write the kinetic energy term of the second nucleus H_B, then we write the kinetic energy term of the lone electron that is there. We have this electron is attracted by both the nuclei, so there will be two attractive potential energy terms, and finally there is inter nuclear repulsion.

Now, before proceeding further, inter nuclear repulsion can be a potential problem. Fortunately, that is taken care of, by this very elegant approximation proposed by Born and Oppenheimer. Now when you say Born and Oppenheimer, if you are not someone who is studying science, you would think of something else.

You would think of Manhattan Project, where atom bomb was made, Oppenheimer was actually the overall in charge of this Manhattan Project. But Born and Oppenheimer did many good things individually and together, they propose this approximation, which says that this big fat nuclei cannot move as fast as this quick fast electron.

So, nuclei are stationary with respect to electrons. Of course, I have put it in a very water down almost scandalous manner, but this is what it essentially means it is okay if we understand that for now. You can consider the nuclei to be stationary with respect to the electrons. So, the moment we do that, we get to ignore the kinetic energy terms in the Hamiltonian, that is a great relief. Moreover, we can consider this last term to be constant. So, essentially, we can work with these 3 terms, kinetic energy of electron and potential energy for attraction of the electrons to with the two nuclei.

And I can take the last part as a constant, so for different values of R, I can set up this Hamiltonian and I can try to find solution. And actually, using elliptical polar coordinates, it is possible to find solution, those solutions are there in some specialized books, not in the books that we study for this course. And we are not interested in getting in it also. You know why, because what is the point? You do it, this is your Hamiltonian fine, you solve it. And you use spherical polar coordinates to solve it exactly.

But what happens if you add 1 more electron it is no longer solvable. Because then you are going to have electron, electron repulsion, which will mess things up completely. So why get into all that

trouble, and people have got into all that trouble. As I said, they are actually available in some higher level textbooks, also on internet, but we are not going to get into that.

We are going to use a simpler approach, utilizing certain things that we have generated already, hydrogen atom wave functions orbitals. We are going to use linear sums of these orbitals to find approximate solutions. Our interest here is to find electron distribution and energy.

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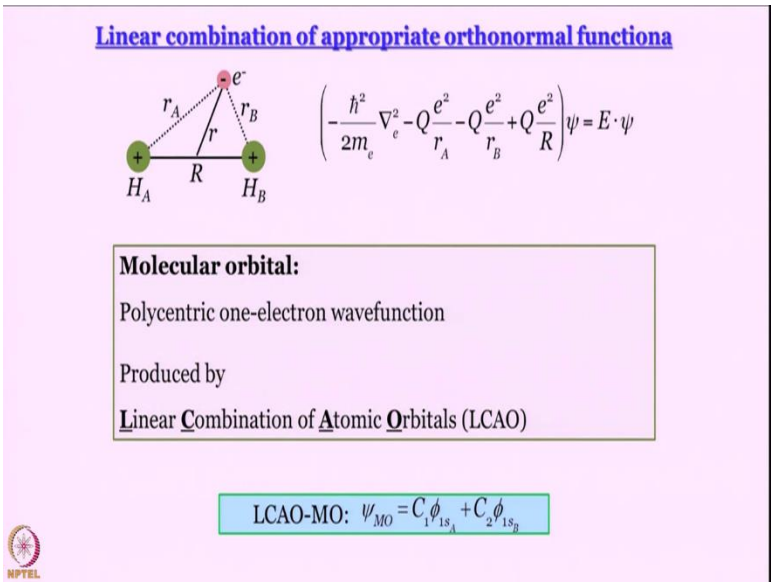

To do that, one common way of doing it, somehow I never correct typos that are there for a long time. So it is not functiona, it is functions. So, if you want to generate some function, a common approach is to take a linear combination of appropriate orthonormal functions, it is not even required to take orthonormal functions. But, it is better if you take them, that makes life a little simpler. And what is the meaning of appropriate, we will elaborate in a minute.

So here, to generate this polycentric one electron wave function, I want to essentially take a Linear Combination of Atomic Orbital. See, atomic orbitals are, they form an orthonormal set, isn't it! and this sort of makes sense. Because, well, actually, they were generated by considering the motion of electron in the field of at least 1 nucleus, all we have here is that we have 2 nuclei together.

So, in some parts or maybe in large parts, the molecular orbital should resemble some atomic orbital or the other or a linear combination, it sort of makes sense, okay. And, but then whenever I say this students are usually not happy, and they say that you are giving some hand waving

argument and all, and I agree with that. So, let me just take this a little further, this is the combination that we are going to use, linear combination of two 1 s1 wave functions, one for atom A, one for atom B.

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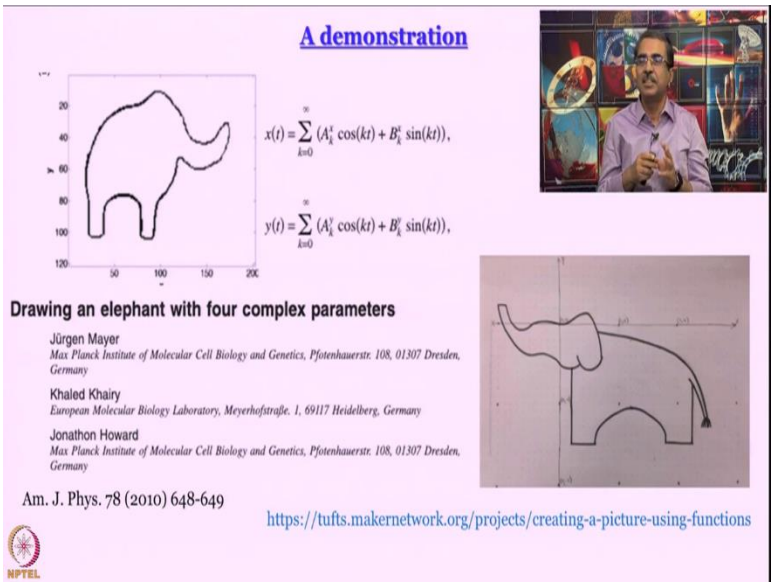

Now, what I want to show you is this, let us take a little break from there and talk about a general phenomenon. What do you see, what do you see here, perhaps you see an elephant that is drawn by maybe a 3 year or 4 year old kid. But the shape of elephant is discernible, you see an elephant. Now, this elephant was actually not drawn by any 3 or 4 year old kid. This is a figure taken from a legitimate research paper published as recently as 2010 in American Journal of physics.

How was this generate, so it is a plot. You can see, we have x axis and y axis, I have tried, I tried my best to hide x and y. I did hide x but y was not hidden all that efficiently. So, what these guys did was that they expressed x and y in terms of some parameter t, which they called time. And, so they decided some value of time t for that they worked out x and y. So, for that they got this function, for more detail, feel free to read this paper, it is available freely on internet.

So, what I am trying to show is that by using who would think that you can generate an elephant using some functions, actually you can, and the elephant does not have to be as rudimentary as this one, you can draw a better elephant also. And again, if you go to this website, I did not really check it out myself. But I think you get to plot different things, try your hand at using different functions.

This is a more convincing elephant, this elephant is drawn by maybe a 5 year or 6 year old kid. Again, use generating functions. So, if you can generate an elephant using some mathematical function, I should be able to generate the electron distribution also. To be honest, I do not even need to use orbitals, I can use Gaussian functions and exponential functions and stuff like that. And that is what is done in higher level theories.

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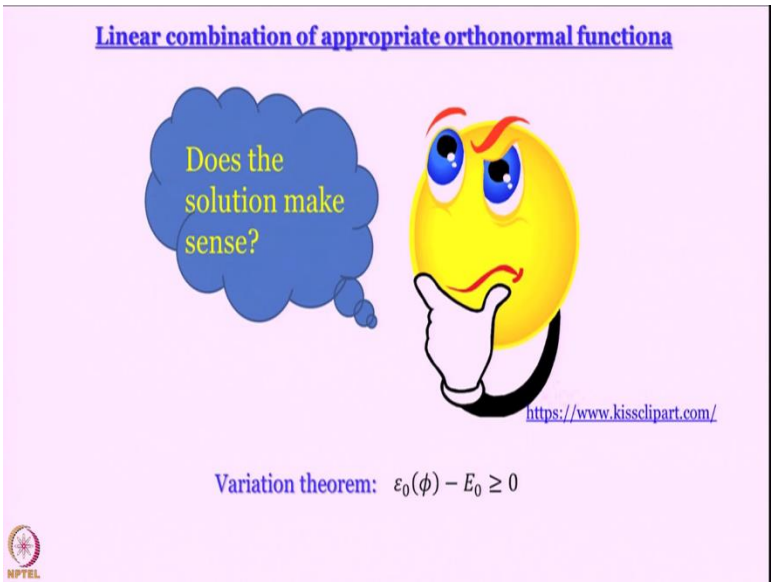

But at least to start, we are going to use wave functions. So, this is what you should be looking like at this point. Should we think does all this makes sense, alright, ok, I generate this function and maybe I can find a solution for energy using that Hamiltonian operator. But is that solution right, does it make sense at all? And here we have a saving grace in the form of variation method, variation theorem, which says that if you calculate energy using some guess function, guess function means the function that you have cooked up.

You call that $\varepsilon_0(\phi)$, actually this is called functional. $\varepsilon_0(\phi)$ minus the actual energy E_0 is always going to be greater than equal to 0. Or in other words, you get an, always get an upper bound to the actual energy if you use some function that you have cooked up. So, whatever function I get I will never do better than the best. The energy I calculate will only approach the actual energy from higher energy side, it will never cross it and become low.

So, it is okay if I use a large number of functions, the energy calculation will never be wrong. The electron distribution can go wrong if you use two orbit functions, that is why it makes sense to use

atomic orbitals at least to start with. This is a very rudimentary introduction to this topic. You might be wondering why it is called variation theorem, that is because we actually, this gives rise to, this is also called the upper limit theorem.

It, it is utilize the variation method where you play around with the contributions of these different functions and you see what is the best value of energy you can get and you have the assurance that it will never be less than the actual value of energy. Okay.

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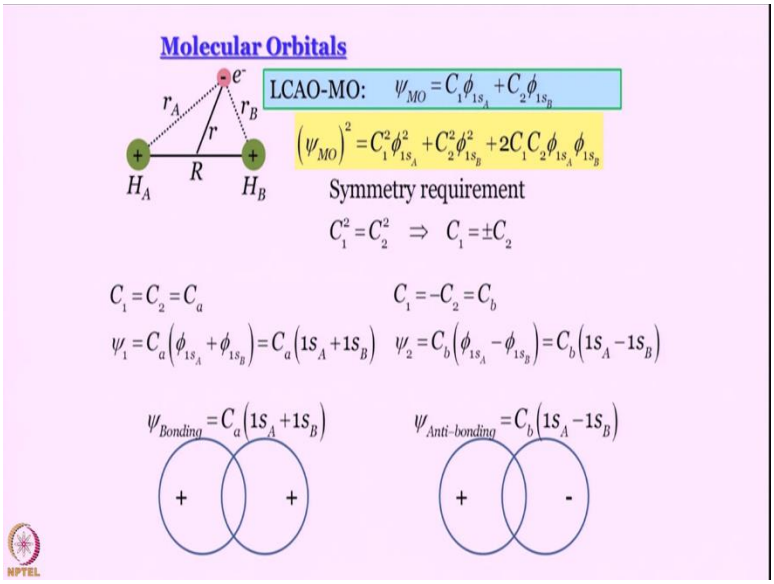

So, this is where we are, we have molecular orbitals. We have given you some kind of an argument to say that this is not absolute nonsense. We generate the molecular orbitals by linear combinations of these '**s**' orbitals. What do I do next? Let us see what your square of this molecular orbital is, why am I calling it molecular orbital, because it is a molecular wave function and this molecule has only 1 electron. Okay.

So, I get $C_1^2\phi_{1s_A}^2 + C_2^2\phi_{1s_B}^2 + 2C_1C_2\phi_{1s_A}\phi_{1s_B}$. And since it's dying to say, ϕ so many times I am going to say just $1s_A$, $1s_B$ later on or I might even say, s_A, s_B or even I might say A and B they are all one on the same please bear with me. Now see, there is no logical reason to think that C_1 and C_2 should have different magnitudes. In this expression for energy, for probability density, there is no reason why A should contribute more or less than B.

So, $C_1^2 = C_2^2$ which implies that $C_1 = \pm C_2$. So, when $C_1 = C_2 = C_a$, when $C_1 - C_2 = C_b$. Actually, this is an ill-conceived nomenclature, it would have been better to call the first one C_b, it would

have been better to call the second one C_a, you will see why I am saying this. So, this is the first wave function, I take the plus combination. So, $\psi_1 = C_a(1s_A + 1s_B)$. The other one is $\psi_2 = C_b(1s_A - 1s_B)$.

How do I proceed now, usually, I want to normalize, I want to see what is the expectation value of energy and so on and so forth. But before that, let me tell you this, that this is called a bonding orbital $1s_A + 1s_B$. And this ($1s_A$ - $1s_B$) is called an anti-bonding orbital. Again, I will take a raincheck on why this is called bonding, why it is called anti bonding later on, you can sort of guess.

But do you see why I said that this coefficient naming was ill conceived, $\psi_{bonding} = C_a(1s_A + 1s_B)$ $\psi_{anti-bonding} = C_b(1s_A - 1s_B)$. If I would only interchange A and B, then it would have been better, bonding b, antibonding a, would have been easier to remember but when then earlier yet is yes, we just leave with this. So we have obtained two kinds of molecular orbitals bonding and anti-bonding. Great.

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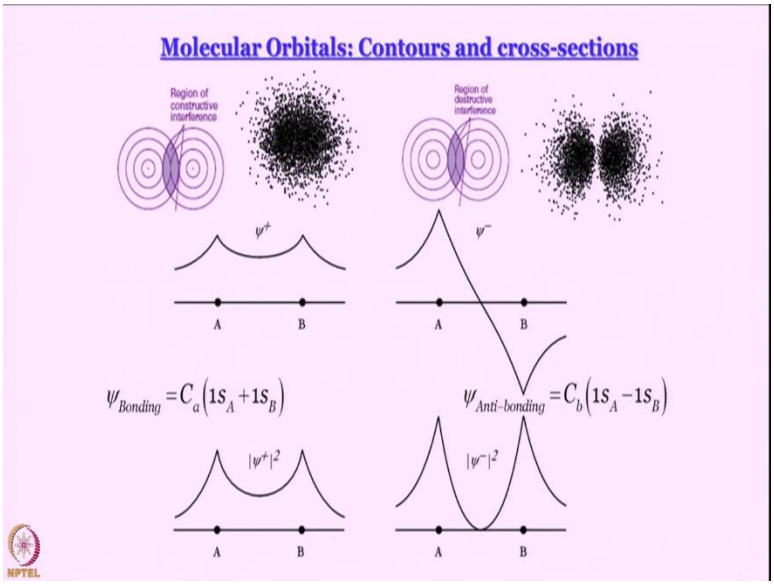

This is where we are so far. If I plot them, this is what you get when they are at equilibrium bond distance, there is some overlap of the orbitals. So, in this region, you see, they actually add. In regions where a has some value of ψ , but b does not have too much, then it is practically a, here it is practically b, so when you add them up for ψ^+ or ψ_1, you get this kind of a profile, these are the contour diagrams, this is a profile like a circus tent.

And here you see this kind of a profile where you get a node. So, in bonding orbital the wave function has no node, in anti-bonding orbital, you do have a node. If you take ψ^2, then you see you get this more well defined circus tent here as the profile. Here, you have 2 separate circus tents, there is no circus tents two separate tents. Two people who want their own individual tents, that kind of a function is there.

So now, the rudimentary discussion that is there in most textbooks is that here, you end up increasing electron density between the 2 nuclei. So, they act as cement effectively. Here you end up decreasing electron density, if we just plotted the wave functions, they would have had some more electron density between the 2 nuclei, that is why this is anti-bonding, energy associated with anti-bonding should be more, energy associated with bonding should be less. This is okay but it is not the last word. So, for now, we can live with it, but there is more to it than what meets the eye.

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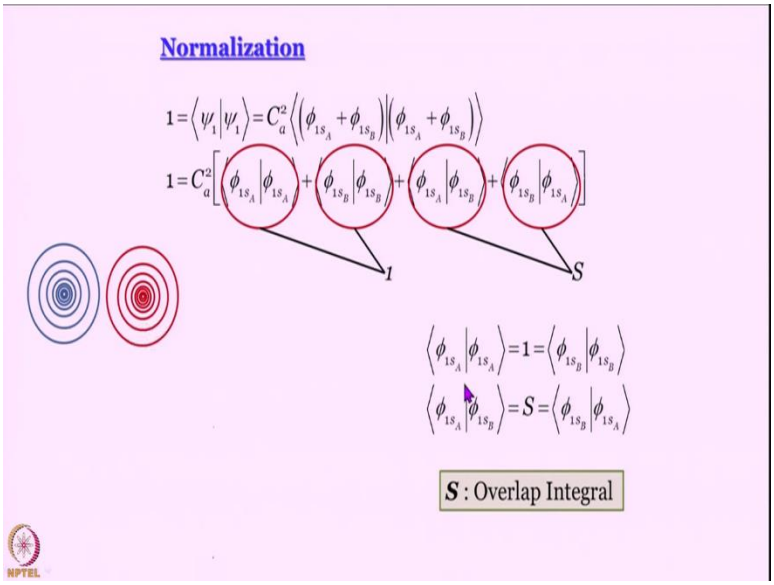

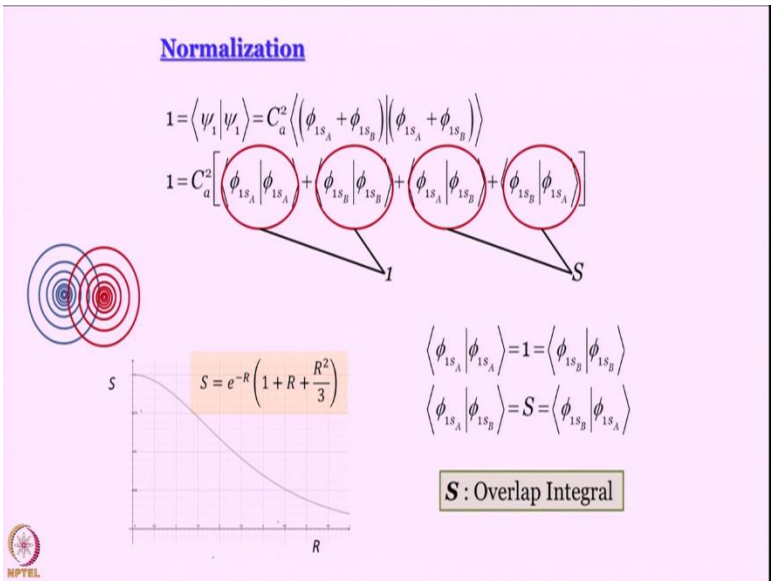

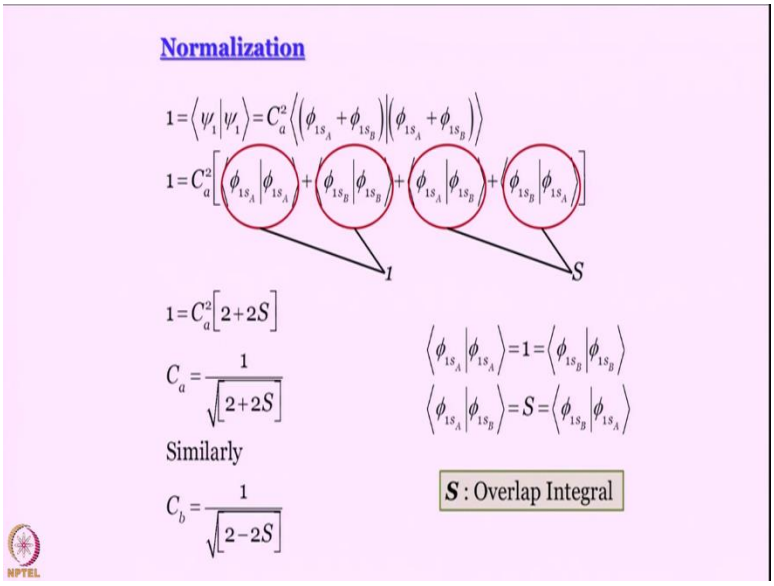

Now, let us try to do our favorite exercise. Let us try to normalize. And here I want you to do the normalization yourself. I am sure at this point; you will be able to do it. So, please stop the video. Maybe after the next one. This is what you want to get. Stop the video, do the normalization yourself. This is what you get, $1 = C_a^2\left[\langle\phi_{1s_A}|\phi_{1s_A}\rangle + \langle\phi_{1s_B}|\phi_{1s_B}\rangle + \langle\phi_{1s_A}|\phi_{1s_B}\rangle + \langle\phi_{1s_B}|\phi_{1s_A}\rangle\right]$.

These ($\langle\phi_{1s_A}|\phi_{1s_A}\rangle$ & $\langle\phi_{1s_B}|\phi_{1s_B}\rangle$) as we know are 1, because the 's' orbitals are individually normalized. What about these 2 ($\langle\phi_{1s_A}|\phi_{1s_B}\rangle$, $\langle\phi_{1s_B}|\phi_{1s_A}\rangle$), these are not 0. These are quantities that come up when we do valence bond theory treatment as well. The only difference is that for

valence bond theory, we cannot work with H_2^+, we have to work with H_2 because it requires two center, two electron.

So, what is this integral, this is called overlap integral, they are the same first of all, the sequence does not matter. It is called overlap integral, why is it called overlap integral, this is something that we study, when we study valence bond theory as well, but here let us state it independently, these are the contours of the two 1S orbitals.

What happens to the value of the integral when they are like this, very far apart, practically there is no overlap. So, there is no point in space where $1S_A$ and $1S_B$ simultaneously have some non-zero value. So, their product is 0 when the distance is large and integral is also 0. What happens when they move closer, as overlap increases say in this region, let us say that contours denote significant values of psi, in this region of overlap both, $1s_A$ and $1s_B$ will have significant value, product will have significant value.

So, when you integrate the value of the integral is going to increase. And as they come closer and closer, the value is also going to increase to a saturation something like this. And this as is worked out using elliptical coordinates in McQuarrie and Simon book, this can be written in terms of the inter nuclear distance capital R, this is the functional form, which we do not have to remember.

We should understand the shape of the curve, it is like this, initially 0, at very large R, then it increases to a saturation value. Of course, if this is 0 that means what, they will both be together, saturation value what should it be, you work out yourself, these are normalized orbitals. So, if capital R is equal to 0, this is your exercise, please work out what is the value of the overlap integral when capital R is equal to 0.

And this is what I have shown for two 1s orbitals, you might as well work it out for say, s and p, p and p orbitals in different orientations, so on and so forth. This is your overlap integral which plays a very, very important role in bonding. Now, let us go a little further ahead. This is what it is. I have written the first two terms, each of this is 1, add up to two. Second two terms, each of these is overlap integrals add up to 2S.

So, this is the condition I get from normalization. Ca square is equal to, well, $1 = C_a^2[2 + 2S]$. Now I do not know if you had stopped the video, if you would have reached it here, if you did not

have a prior knowledge of S. But well now you know what it is. So, Ca turns out to be, $C_a = \frac{1}{\sqrt{2+2S}}$. Similarly, you can work out yourself this time. C_b, the coefficients for the antibonding orbital turns out to be $C_b = \frac{1}{\sqrt{2-2S}}$.

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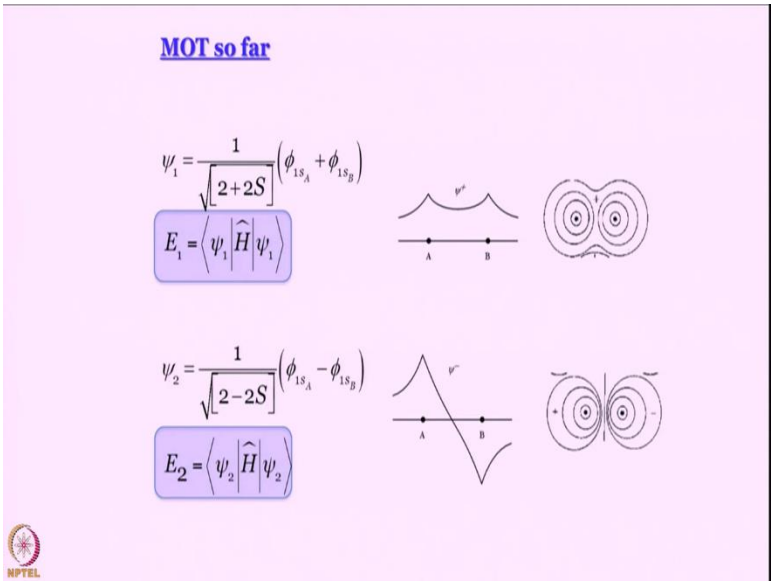

So now we have the wave functions completely defined. With these, what we can try to do is that we can try to find the values of the energies. And remember, the best we can do now is we can try to find expectation values of the energies.