Electronic Theory of Solids
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Lecture – 12
Bonding and Band Formation (LCAO) (Contd.)

Hello and welcome again. We have been discussing the two proton two electron problem, basically two hydrogen atoms being brought together from a large distance. And, we claimed that represents a two atom solid with one electron in each atom. So, that is a of course, a caricature of a real solid and we will soon take a step towards a n equal to any number of atoms and then we will see what happens. Let me just recap the salient features that we came across while doing this.

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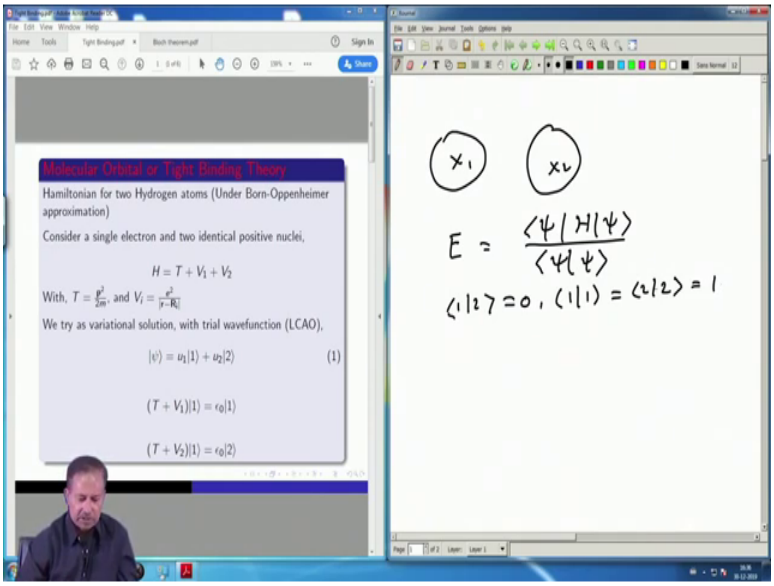

Molecular Orbital or Tight Binding Theory

Hamiltonian for two Hydrogen atoms (Under Born-Oppenheimer approximation)

Consider a single electron and two identical positive nuclei,

$$H = T + V_1 + V_2$$

With, $T = \frac{p^2}{2m}$, and $V_i = \frac{e^2}{|r - R_i|}$

We try as variational solution, with trial wavefunction (LCAO),

$$|\psi\rangle = u_1|1\rangle + u_2|2\rangle \qquad (1)$$

$$(T + V_1)|1\rangle = \epsilon_0|1\rangle$$

$$(T + V_2)|1\rangle = \epsilon_0|2\rangle$$

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$\langle 1|2\rangle = 0, \ \langle 1|1\rangle = \langle 2|2\rangle = 1$$

What we did was that we first took a Born-Oppenheimer approximation which means that the two atoms their nuclei are more or less fixed at in position. And, the nuclei the motion of the nuclei is not considered. So, this approximation is called the Born-Oppenheimer approximation. And, under this approximation one basically neglects all the dynamics concerning the nuclei that is again the same thing that we will do for n equal to n arbitrary number of atoms.

The argument there is even stronger, if the atom has a z number of a nuclei. Then a z number of protons and neutrons in the nucleus then of course, its even a better for us because the mass of the nucleus is very large and the dynamics is very very slow compared to the electronic dynamics. So, that is the assumption first assumption that one takes. So, one looks only at the electron interacting with the nuclei. Remember that in this approximation electron-electron interaction is neglected. So, it is still a single particle description; we do not have a interaction term between the two interactions two electrons.

So, what we did was that we consider the single electron for example, which two interacting with a positive-positive nuclei, its we could as well to take two non-interacting electrons interacting with two nuclei which is the same because we are in a single particle description.

So, we will basically find out the final set of orbitals and put as many electrons as they are into each of these orbitals starting from the lowest. So, this is the Hamiltonian that we wrote T is the kinetic energy of the electron V 1 and V 2 are the electrons interaction with one nuclei with 1 and 2 locations 1 and 2. So, this is the picture we drew.

So, these you may call 1, this maybe called 2 and these two then the electron which is outside the electron that we are talking about is interacting with these two nuclei. So, that was the Hamiltonian we wrote. Then of course, we argued that one more important thing is that the there is something called a trial wave function, a variational principle in which trail wave function is chosen.

And, the trial wave function is optimized with respect to the parameters in the variational parameters in the wave function. So, that we get the lowest energy solution that lowest energy solution is called the variational lower bond of the energy and that sometimes agrees with the ground state and sometimes does not, but it is still a very good method to get a low energy eigen state of a quantum problem.

Now, the approximation that one does is at the level of wave function, now one chooses a trial wave function which say the electron in the at orbital at 1 and the orbital at 2. So, these are the two wave functions we have and then as I said remember that 1 and 2 do not necessarily have to be the orbitals of are atom 1 and on atom 2, but that is one convenient choice one can always do.

And, one also remembers that these are not necessarily orthogonal, but to a first approximation we choose them to be orthogonal. So, these 1 and 2 are my two orbitals sitting at site 1 and at the location of proton 1 and proton 2, nucleus 1 nucleus 2. And, then the I can solve this solve for this Hamiltonian by calculating the expectation value of E which is the variational energy which is defined as psi H psi divided by psi. This choice that a with co efficients 1 and u 2 which I chose to be real is a linear combination of the two out atomic orbitals.

And, this is in chemistry parlance called the linear combination of atomic orbitals. The name is quite obvious that we are choosing linear combinations of the two atomic orbitals. There could be other choices there are other ways to write things, but this is a trail wave function which is very common.

As I call said its called the LCAO Linear Combination of Atomic Orbitals. So, let us simply the matrix elements are very simple T plus V 1 is basically the first hydrogen atom and its wave function more or less. And so, T plus V 1 operating on 1 will give you this single particle hydrogen like energies.

And, this is the 1 if I choose 1 to be 1 s orbital then epsilon naught will be basically minus 13.6 electron volt. So, nevertheless as I said I do not have to choose, but let us just assume that we know the wave function 1 which is an eigen function of T plus V 1 which is the Hamiltonian for the first hydrogen atom.

Similarly, for the second hydrogen atom number 2 the T plus V 2 is its Hamiltonian. And, this will be 2 sorry this is 2, the second wave function is a eigen function of that Hamiltonian with the same energy because, there is nothing to distinguish between the two atoms.

So, this is how we started and then we assume that 1 2 equal to 0 and 1 1 equal to 2 2 these are orthonormalized. So, this is how we started and then we defined different matrix elements. So, let me show you these matrix elements.

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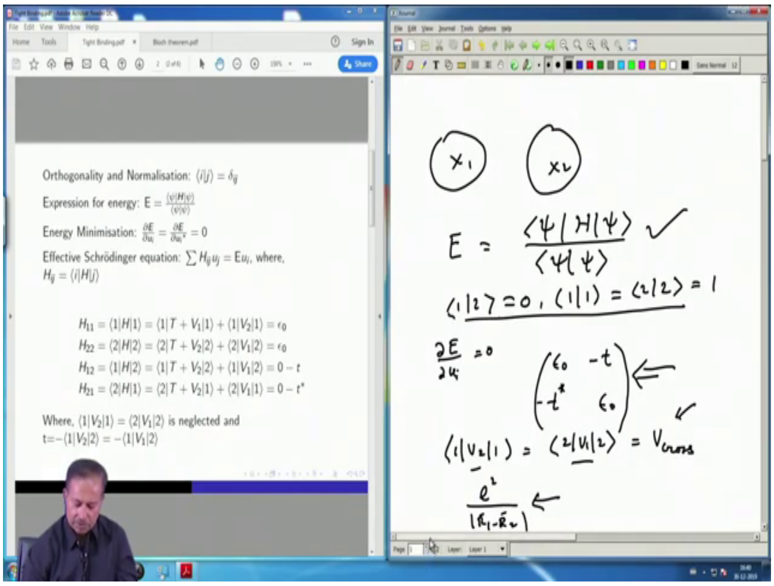

Orthogonality and Normalisation: $\langle i|j\rangle = \delta_{ij}$

Expression for energy: $E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$

Energy Minimisation: $\frac{\partial E}{\partial u_i} = \frac{\partial E}{\partial u_i^*} = 0$

Effective Schrödinger equation: $\sum H_{ij} u_j = E u_i$, where, $H_{ij} = \langle i|H|j\rangle$

$$H_{11} = \langle 1|H|1\rangle = \langle 1|T + V_1|1\rangle + \langle 1|V_2|1\rangle = \epsilon_0$$
$$H_{22} = \langle 2|H|2\rangle = \langle 2|T + V_2|2\rangle + \langle 2|V_1|2\rangle = \epsilon_0$$
$$H_{12} = \langle 1|H|2\rangle = \langle 1|T + V_2|2\rangle + \langle 1|V_1|2\rangle = 0 - t$$
$$H_{21} = \langle 2|H|1\rangle = \langle 2|T + V_2|1\rangle + \langle 2|V_1|1\rangle = 0 - t^*$$

Where, $\langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$ is neglected and $t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$

x_1 x_2

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \checkmark$$

$$\langle 1|2\rangle = 0,\ \langle 1|1\rangle = \langle 2|2\rangle = 1$$

$$\frac{\partial E}{\partial u_i} = 0 \qquad \begin{pmatrix} \epsilon_0 & -t \\ -t^* & \epsilon_0 \end{pmatrix} \Leftarrow$$

$$\langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle = V_{cross}$$

$$\frac{e^2}{|\vec{R}_1 - \vec{R}_2|} \leftarrow$$

These are matrix elements. So, these i j equal to delta i j gives me this is the same approximation as this one. So, energy variational energy is given already this one. So, minimization involves the parameters as we wrote. So, u i equal to 0 since we have two u's we will get two equations and these two equations we already obtained in the previous class.

So, let me just quickly show that to go ahead and remember that this is the energy T plus V 1 between 1s bra 1 and ket 1 the expectation value of T plus V 1 is basically epsilon naught; T V 2 does not contribute to this 1. So, that is perfectly alright, I could as well so, this is basically 1 H 1 which is a the 1 1 element of the Hamiltonian matrix. Similarly, 2 2 element of the Hamiltonian matrix is also epsilon naught. So, the Hamiltonian is epsilon naught epsilon naught in the basis of u 1 and u 2.

Then H 1 2 is the Hamiltonian matrix element between 1 and 2 and this does not give any contribution from the first term. Because, it is this part is the diagonal part of the Hamiltonian, it will not have a cross term and this is the; this is the term 1 V 1 2 or 2 V 1 1, these are basically the these are called the hopping terms.

These is this is the term that mix the allows the electron to move from a orbital 1 to orbital 2, atom 1 to atom 2 when they are brought close together and vice versa of course from 2 to 1 as well. And, they are necessary they are not necessarily different and it is a convention to choose t and t star, 1 is just the Hermitian conjugate of the other.

This these could also be taken to be real. So, there is a I in the previous class I took them to be real both as t otherwise I have to work with just mod t. Now, there is term this term which is 1 V 2 1 equal to 2 V 1 2 is basically V cross term was set to 0.

Because, as such it is a the effect of a nucleus 1 on orbital 2 and nucleus 1 V 1 on orbital 2 and effect of a nucleus 2 1 orbital 1, these are anyway small. And, the other important thing one notices is that this actually is canceled by this nucleus-nucleus interaction R 1 minus R 2 which is repulsive, remember these terms are attractive because these are the 1 V 2 1, this V cross is an attractive term whereas, this is a repulsive term.

So, this will this basically cancels that term. So, I just do not have to bother about these are diagonal elements remember, these are contribute to very very little to the Hamiltonian to the energetics ok. So, this is the matrix that we are going to consider.

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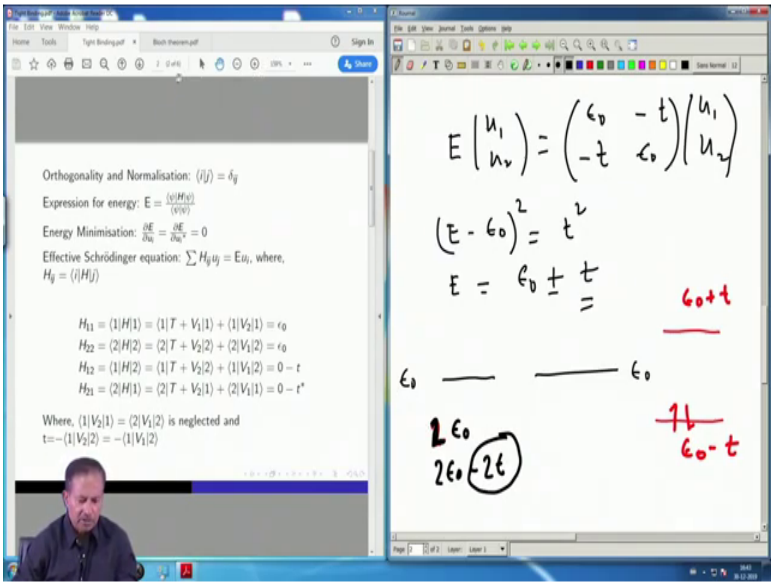

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Where, $\langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$ is neglected and $t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$

$$E\begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} \epsilon_0 & -t \\ -t & \epsilon_0 \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

$$(E - \epsilon_0)^2 = t^2$$

$$E = \epsilon_0 \pm t$$

$\epsilon_0 + t$

ϵ_0 ϵ_0

$\epsilon_0 - t$

$2\epsilon_0$

$2\epsilon_0 \boxed{-2t}$

So, our equation of motion equation is basically then E times u 1 u 2 equal to epsilon naught minus t, this minus is just a convention. Let me take to be real take this to be real epsilon naught, this minus is explicitly taken here because in most of the cases this matrix element t turns out to be negative.

But, this is also quite clear that this should be negative because if this is the you just see that this is the energy lowering that happens. And, if it is a its basically matrix element between the two the these this matrix element 1 V 1 2 and 2 V 1 1.

So, 2 V 2 so, 1 V 2 2 and 1 V 1 2 all these matrix elements or vice versa for V 2, these are basically the hopping as I said. It takes the electron from site 1 to site 2 or proton 1 atom 1 to atom 2 or atom 2 to atom 1. So, that is the way it gains energy the system gains energy delocalizes electrons gain energy. So, the t here is positive, the negative sign is already taken care of. So, this is my equation of motion should be the basically the Schrodinger equation written it on here.

So, we just we diagonalize this E minus epsilon naught square equal to t square right. So, this matrix is basically E minus I can put this I can bring the left hand side on the right and this will become E minus epsilon naught square. So, E equal to epsilon naught plus minus t. So, as I said the this is the gain in energy. So, we started with two epsilon naught's which were degenerate and we landed up with the two eigenvalues which are here and here. So, these are my epsilon naught plus t and epsilon naught minus t.

So, that is the; so, I now what do I do? I have to put two electrons in the system. So, these two electrons will now go here and my gain in energy will be minus basically original energy was twice epsilon, let me choose the color original energy was 2 epsilon naught and the final energy is 2 epsilon naught minus 2 t. So, this 2 t is the amount of energy that are gain by forming a so called molecular orbital right, its a combined orbital of the 2 atoms.

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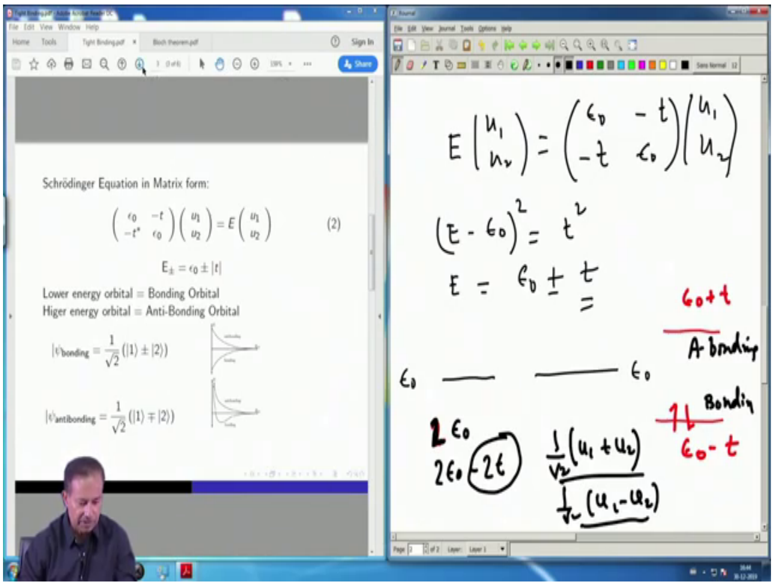

Schrödinger Equation in Matrix form:

$$\begin{pmatrix} \epsilon_0 & -t \\ -t^* & \epsilon_0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} \quad (2)$$

$$E_\pm = \epsilon_0 \pm |t|$$

Lower energy orbital = Bonding Orbital
Higer energy orbital = Anti-Bonding Orbital

$$|\psi\rangle_{\text{bonding}} = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$$

$$|\psi\rangle_{\text{antibonding}} = \frac{1}{\sqrt{2}}(|1\rangle \mp |2\rangle)$$

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$$(E - \epsilon_0)^2 = t^2$$

$$E = \epsilon_0 \pm t$$

ϵ_0 ϵ_0

$\epsilon_0 + t$ A-bonding

Bonding $\epsilon_0 - t$

$2\epsilon_0$

$2\epsilon_0 \boxed{-2t}$

$\frac{1}{\sqrt{2}}(u_1 + u_2)$

$\frac{1}{\sqrt{2}}(u_1 - u_2)$

And so, the electron basically both the electrons try to gain energy from this and remember that this is a the lowest energy state is a singlet. So that means, the orbital part of the wave function is a 1 by root 2 u 1 plus u 2 which is this symmetry wave function. The excited energy this is called the bonding, this is called the anti-bonding.

So, the bonding is this one, the anti-bonding will be just the other combination. So, the symmetric one is the bonding one if a t is positive; that means, I gain energy by doing this ok. So, how do it how does the orbital look like?.

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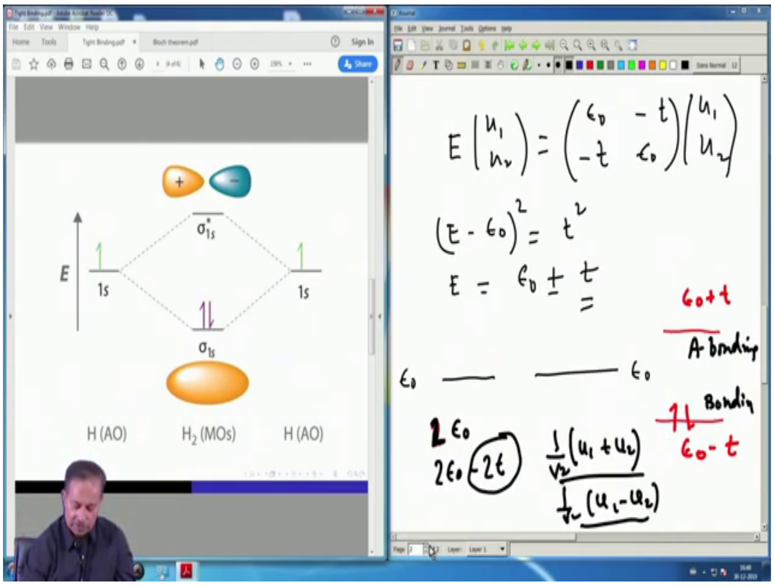

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$$(E-\epsilon_0)^2 = t^2$$

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$\epsilon_0 + t$

ϵ_0 ϵ_0

$2\epsilon_0$

$2\epsilon_0 \boxed{-2t}$

$\frac{1}{\sqrt{2}}(u_1+u_2)$

$\frac{1}{\sqrt{2}}(u_1-u_2)$

$\epsilon_0 - t$

Let me just show you first how does it look like starting if I had started from just 1 s orbitals, this is how it the picture is. I had two electrons to start with here one, here one. And, there are these two orbitals that have formed, they are conventional in chemistry, they are called 1 sigma 1 s and sigma 1 s star.

So, this is the bonding orbital and this is the anti-bonding orbital. Look at the nature of this wave function, the orbital part of the wave function is symmetric here around the center and that symmetry basically reflects the fact that the spin part is singlet. And, the electrons are now equally shared by the two nuclei. And so, what is happening? What has happened basically? What has happened is that because of this t matrix element the electron is no longer stuck at either atom 1 or atom 2.

So, electrons are now allowed to move. Remember if you had a time dependent Schrodinger equation. So, in the time dependent Schrodinger equations originally these are stationary states epsilon naught and both the epsilon naught, two atomic states where far separated then there is no chance for the electrons to move from one side to the other. And, they would be stuck to their individual orbitals which in this picture for example, on the left in this picture on these two 1 s orbitals.

But, now once the two electrons two protons come close by the electrons start talking to each other then of course, this time dependence Schrodinger equation allows now, for the electrons to reside part of the time in the first electron, first atom part of the time in a second atom; that means, it can hop over between the two atoms two protons.

And, it says state which is a linear combination in this picture it is a linear combination of these two atomic orbitals. So, these off diagonal matrix elements always do this it allows you to have a state in which the electron resonates between the two atoms. If you have a multiple atom we will show soon that it will basically now start resonating with all the atoms which basically means that the electrons are now getting free from its parent nucleus.

Here of course, it still attached to its parent nuclei-nuclei two nuclei have formed a hydrogen molecule and it with the two electrons they had. So, and the anti-bonding orbital as you can see puts the electrons the in the middle there is a 0; that means, that is the R equal to 0 point.

That means, it is putting a node at R equal to 0 two electrons are the orbital part is the anti-symmetric part. So, the two electrons are not going to be close to each other in the orbital part of the wave function. So, there is a node at R equal to 0, remember particle in a box; particle in a box wave function was like this.

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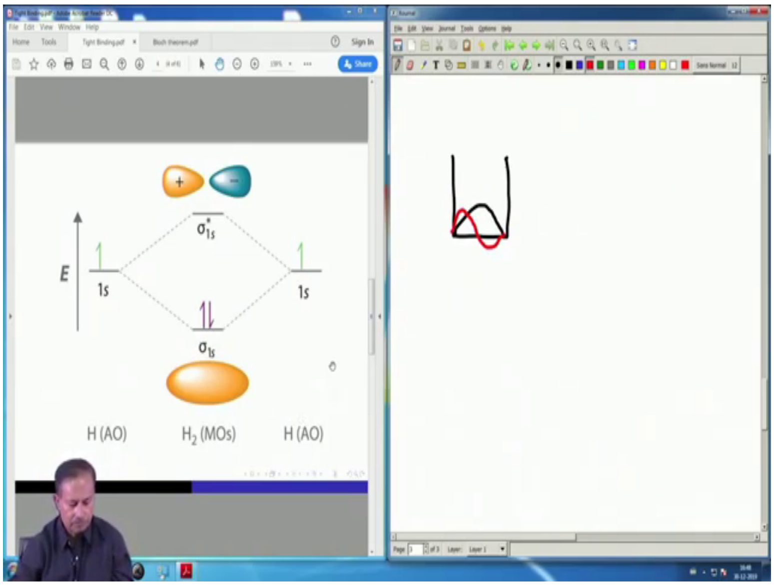

Right, see the final the first ground state is this symmetric whereas, the excited state has a node at the origin. So, this is the same picture, it is not exactly the same, but it is similar picture that we are getting here. We have the excited state has a node at R equal to 0 whereas, the orbital part of the ground state has no nodes. This is a symmetric wave function.

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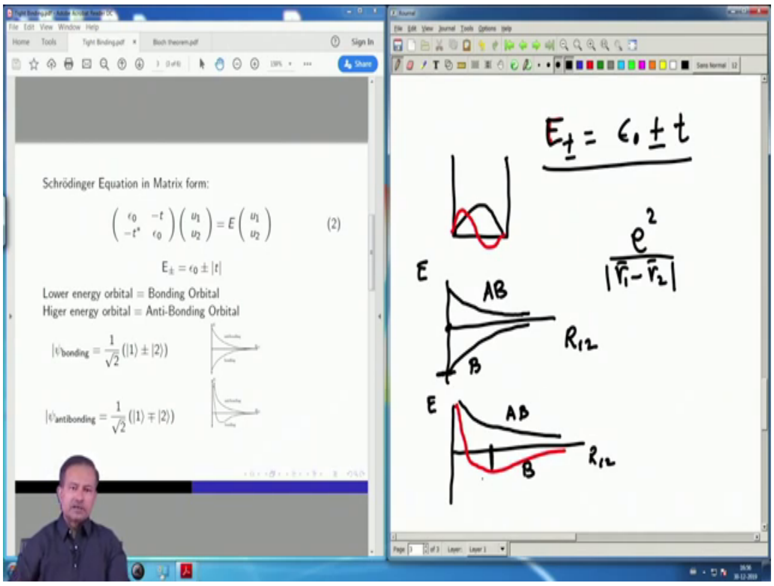

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Now, of course, this picture that I have just shown you with this Hamiltonian and diagonalizing it to get these two wave functions, two eigen energies E plus minus equal to epsilon naught plus minus t, t positive again remember. So, this energy see here is mod t because the I had taken complex t, t star here. So, therefore, product is mod t square, but if I take just t as real then mod t star mod t is basically t. So, this in picture what does it look like? How does it look like?

So, if you look at this left hand side picture the energy as a function of the distance between the two nuclei R 1 2 in the bonding case it goes like this, in the anti-bonding case it goes like this as a function of R 1 2. So, it is clear that the bonding 1 is the lower energy; this is bonding, this is anti-bonding.

The problem here is a bit more complicated in the sense that although this gives me right energetics, it is not entirely correct as you go down to R 1 2 very small. And why is it not?

Because, you can see that the electrons in this picture will finally, come down to R 1 2 equal to 0 this point.

So, the this is R 1 2 equal to 0, this is the energy it will have. So, this is not correct because the solution is not that to the two nuclei just a merged to form that will become a helium nucleus. So, that is very different from a hydrogen molecule right. So, that is incorrect solution although this prediction, where does it go wrong. So, when it goes wrong in the sense that there are several approximations we have taken one was for example, the orthogonally.

Now, the orthonormality of two wave function the they do not remain orthogonal as R 1 2 becomes small. Because, then there is this lot of overlap between the two wave functions and you cannot neglect the non-orthogonality of the two wave functions.

The 1s character of the wave function for example, atomic character for example, will not remain as such. So, you have to consider non-orthogonal wave functions that is one issue. Then there are these other V cross terms that we neglected, the other major thing that we neglected was this interaction between the two nuclei.

So, if I had a these, this is the interaction between the two nuclei, suppose R 1 and R 2 are the two sorry the electrons. So, if R 1 and R 2 are their coordinates then this is the interaction that that we will have to consider. And so therefore, neglecting that interaction entirely you will have; obviously, give me a wrong answer. So, what is the right answer? The right answer is shown on the bottom picture, the picture is like this that this is the anti-bonding and this is the bonding.

So, there is a finite lengths distance here somewhere where the there is a minimum in the energy and as R 1 2 becomes a closer of course, the energy becomes very large. So, that had to be the case because Coulomb interaction basically diverges if R 1 2 equal to 0. So, so there has to be a minimum somewhere in between and that is exactly what this kind of a picture gives you.

So, this is the anti-bonding and this is the bonding. And, this is where the stable distance at which the atom in the nuclei will settle down. So, this is basically the picture that emerged from the previous calculation and that we have been doing.

And, this is a picture that we will now go beyond it and we will try to find out the case for a large number of atoms, but our approximations will remain the same. These approximations work fairly well in a solid because of two major things. One is that in a solid particularly in a metallic solid, there is a the electrons are highly mobile we know that right.

It has a very large conductivity electrons. We know that the velocities or speeds are large and so, they are not delocalized. And, one of the advantages of de localized electrons is that the any in Coulomb interaction gets screened out very quickly within a short distance.

So, the Coulomb interaction is much weaker than in an atom; particularly electron-electron interaction nucleus one nucleus interacting with the neighboring electron. These kind of interactions are not going to be very relevant for a solid which is particularly a metallic solid where the atoms are located at fixed distances.

And, this they are heavy atoms and they are electrons can freely move about in the atoms because, of this matrix element t that we wrote down. So, there will be t is there are large number I mean in principle you can have now a number of t's which is a one electron interacting with its neighbor, next neighbor, next neighbor and so on.

These are all possible choices that one has depending on the material at hand. So, that makes a life actually simpler in the sense that interactions often in metallic systems particularly do not play a very very major havoc. And, a one gets nice beautiful pictures of bands that emerged from such calculations.