Electronic Theory of Solids
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Lecture – 11
Bonding and Band Formation (LCAO)

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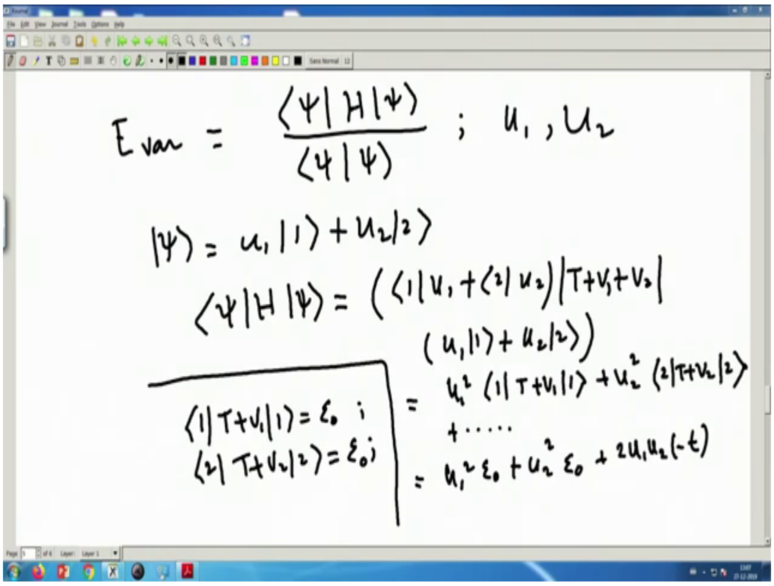

$$E_{var} = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \; ; \; u_1, u_2$$

$$|\psi\rangle = u_1|1\rangle + u_2|2\rangle$$

$$\langle\psi|H|\psi\rangle = \left(\langle 1|u_1 + \langle 2|u_2\right)|T+V_1+V_2|\left(u_1|1\rangle + u_2|2\rangle\right)$$

$$= u_1^2\langle 1|T+V_1|1\rangle + u_2^2\langle 2|T+V_2|2\rangle + \cdots\cdots$$

$$= u_1^2\varepsilon_0 + u_2^2\varepsilon_0 + 2u_1u_2(-t)$$

$$\langle 1|T+V_1|1\rangle = \varepsilon_0 \; ; \quad \langle 2|T+V_2|2\rangle = \varepsilon_0 ;$$

Hello and welcome. So, let us just carry on doing what we have been doing. We wrote down the variational procedure which is here, it will be psi H psi divided by psi, psi and it is a function of u 1 and u 2.

So, I will get two equations and I will have to solve these two coupled questions, so that means, I will write down a matrix which is 2 by 2 and diagonalize that matrix. There is so let us just write down psi again; psi is u 1, 1 plus u 2 sorry u 1, 1 plus u 2 into 2, ok.

Now, let us see what this psi H psi gives me. It is 1 u 1 plus 2 u 2 operating on T plus V 1 plus V 2 and with u 1 1 plus u 2 2, ok. So, as I said in the previous page remember that these energies are so 1 T plus V 1 1 is epsilon naught and 2 T plus V 2 2 is also epsilon naught and that is what I am now going to use.

Remember I have to now expand this. So, the expansion it looks like this. So, there is this u 1 square into 1 T plus V 1 1 for example, that is one term then u 2 square 2 T plus V 2 2 is another term and so on and so forth, right. There are other terms you can write them down.

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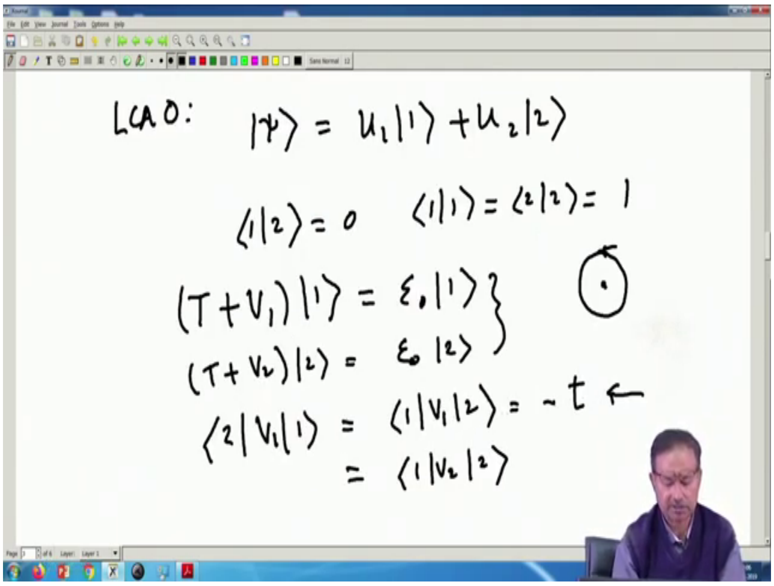

LCAO: $|\psi\rangle = u_1|1\rangle + u_2|2\rangle$

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

$$\left.\begin{aligned}(T+V_1)|1\rangle &= \varepsilon_0|1\rangle \\ (T+V_2)|2\rangle &= \varepsilon_0|2\rangle\end{aligned}\right\} \quad \odot$$

$$\begin{aligned}\langle 2|V_1|1\rangle &= \langle 1|V_1|2\rangle = -t \leftarrow \\ &= \langle 1|V_2|2\rangle\end{aligned}$$

Remember, we had a chosen this definition. So, 1 V 1 2 is minus T this minus sign is just the convention. It is generally these integrals turn out to be negative for most of the cases in the for nearest neighbors and so this minus T is between 2 between V 1 and so it is a cross term on left side you have 2 on right side you have 1 or vice versa. And I have taken T to be again a real quantity, ok.

So, if you go ahead and do it the let me just write down the expression that we will get. This will be u 1 square into epsilon naught plus u 2 square into epsilon naught plus 2 u 1 u 2 into minus T. This is what you will get.

Remember, there is a term which I have neglected here. You will come across this term which is the which is often called the cross term, which is this term that let me just write that term down. This kind of a term. So, I have neglected term of this type.

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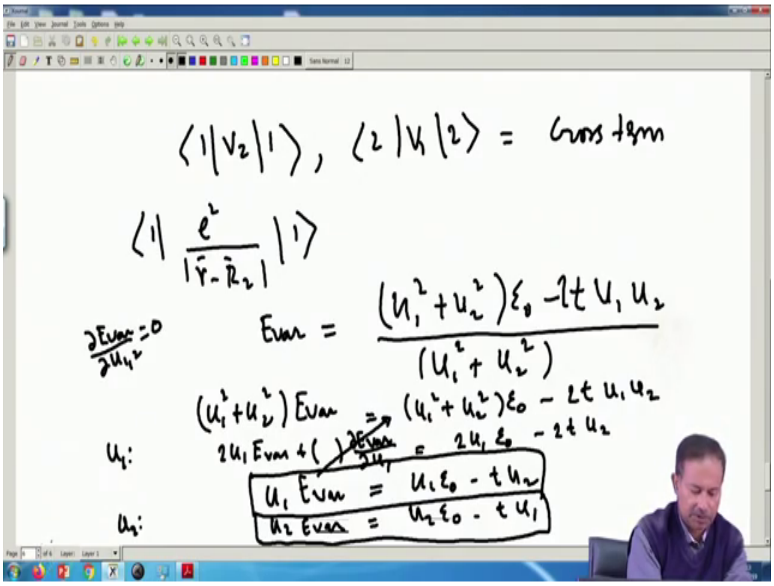

$\langle 1|V_2|1\rangle, \langle 2|V_1|2\rangle$ = Cross term

$\langle 1| \frac{e^2}{|\vec{r}-\vec{R}_2|} |1\rangle$

$\frac{\partial E_{var}}{\partial u_1}=0$

$E_{var} = \frac{(u_1^2+u_2^2)\varepsilon_0 - 2t\,u_1 u_2}{(u_1^2+u_2^2)}$

$(u_1^2+u_2^2)E_{var} = (u_1^2+u_2^2)\varepsilon_0 - 2t\,u_1 u_2$

u_1: $2u_1 E_{var} + (\ )\frac{\partial E_{var}}{\partial u_1} = 2u_1\varepsilon_0 - 2t\,u_2$

$\boxed{u_1 E_{var} = u_1\varepsilon_0 - t\,u_2}$

u_2: $\boxed{u_2 E_{var} = u_2\varepsilon_0 - t\,u_1}$

So, the term I neglected is 1 V 2 1 and 2 V 1 2. So, what; so, this is so called cross term. So, this term actually these two terms look what it does. It is e square by r minus say R 2 and you have 1 on this side and 1 on this side.

Now, it is the proton number 2 indirectly having a coulomb interaction with electron number 1 here, ok. So, that kind of terms is being neglected and vice versa; electron number 1 having an interaction with this the nucleus number 1 having an interaction with the electron number 2 here. So, these cross interactions I have so I have neglected at the moment in this if you calculated the matrix element in the previous page you would also find those cross terms in this adding to this epsilon naught.

Now, I will justify later on why I am neglecting it and they are anywhere much smaller than the epsilon naught as you can see because epsilon naught is the energy of that electron in this atomic orbital to start with, which is much smaller than the cross term between nucleus 1 and electron 2, and electron 1 and nucleus 2, ok; so, that I will neglect. So, these kinds of terms are not included here, ok.

So, let us now see what we had. We had these; this is the numerator of this and the denominator is simple. The denominator is will give me just the so, you have u 1 square plus u 2 square into epsilon naught minus t u 1 u 2, twice t, divided by u 1 square plus u 2 square that will be your E variation, ok. So, that is the thing that we have to minimize that is the energy we have to minimize with respect to u 1 and u 2.

So, one can directly do it by taking the derivative of variational E var with respect to u 1 and u 2, but a simpler way to do this thing is just take the denominator to the left hand side; u 1 square plus u 2 square, E var equal to u 1 square plus u 2 square into epsilon naught minus twice t u 1 u 2.

Now, let us use, let us take a derivative of this equation on the left and a right with respect to u 1 and u 2. So, what do you get is 2 u 1 E var, so I am taking a derivative with respect to u 1 plus this quantity in the bracket times del E var del u 1 equal to twice u 1 epsilon naught minus twice t u 2, ok.

Now, as I said in the beginning that my variational scheme involves setting E var del u either 1 or 2, or 2 equal to 0, ok, so that means, this term vanishes . So, I have the equation I have is u 1 into E var equal to u 1 epsilon naught minus t u 2. So, this is the equation I have for E variation for u 2. Similarly, I will have a I did not almost identical equation which is u 2 E var, when I take a derivative with respect to u 2 and set this quantity to be 0 this del E var del u 2 equal to 0, so that will give me u 2 E var equal to u 2 epsilon naught minus t u 1.

As I said this is a coupled these are two coupled equations which are equations between u 1 and u 2 which determines the variational. So, which will set which will give for me the; if I diagonalize I write it as a matrix and then I diagonalize it and I will get the eventual eigenvalues and the eigen functions.

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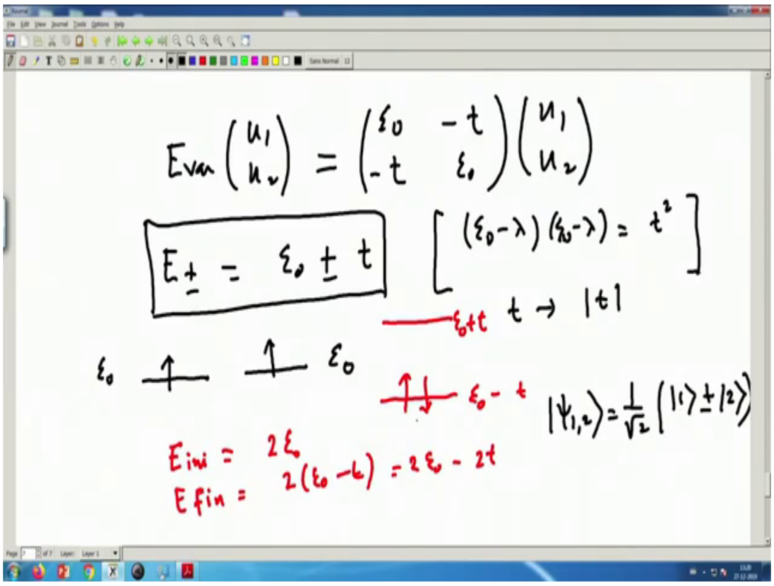

$$E_{var}\begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} \varepsilon_0 & -t \\ -t & \varepsilon_0 \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

$$\boxed{E_{\pm} = \varepsilon_0 \pm t} \qquad \left[(\varepsilon_0-\lambda)(\varepsilon_0-\lambda) = t^2 \right]$$

$\varepsilon_0 + t$ $\quad t \to |t|$

ε_0 $\uparrow$ $\quad$ $\uparrow$ ε_0

$\uparrow\downarrow$ $\varepsilon_0 - t$ $\quad |\psi_{1,2}\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle \pm |2\rangle\right)$

$E_{ini} = 2\varepsilon_0$

$E_{fin} = 2(\varepsilon_0 - t) = 2\varepsilon_0 - 2t$

So, this can be written as E var into u 1 u 2, this vector equal to epsilon naught minus t minus t epsilon naught into u 1 and u 2. You can check that this is exactly the equation that I had written down. Let us go back and see, see this is the equation I have, u 1 times E var is u 1 times E naught minus t times u 2 that is exactly it produced by this matrix equation. So, of course, the energies that I will get the eigenvalues of this matrix is basically the E plus minus equal to E 0 plus minus t.

Now, if t was taken to be taken as a, see what I have done is that epsilon naught minus lambda into epsilon naught minus lambda this is equal to minus t square, so this is equal to t square, so that is the equation I have solved for lambda. So, that gives me this E plus lambda, so this solution, so lambda I have written as E plus minus and this is the, are the solutions.

If t was a complex number I would replace t by goes to mod t that is all, that is to be done if t were complex. But just for the time being let us just take t to be a real part and that is all I that, so that gives me the value of t is it is the difference of t that makes the new eigenvalues.

So, what did I have? So, I had originally epsilon naught two epsilon naught wave functions. Now, I have a wave function we have two solutions these are the two degenerate levels originally. Now, I have a level which is at epsilon naught minus mod t, the value of t. If t is taken has been taken to be positive because there is a minus sign that I have already put in.

So, I can just to write this as epsilon naught minus t and epsilon naught plus t. So, these are the two eigenvalues of this wave function, of this problem now because of this t matrix element that connects the two electrons in the two atoms that is going to be the new eigenvalues of this problem.

So, what do I do now? As I said that now I will just put the electrons which were here, originally here I had two electrons, I have to now put them here. And how do I put them? The way to put them is put them up and down and this is a singlet again, the singlet wave function is the one that stabilizes the energy. So, how much is the, how much was the original energy? The original E initial was simply twice epsilon naught and E final is 2 into epsilon naught minus t, so that 2 epsilon naught minus 2 t. And that is again the 2 t amount of energy, t is taken positive here remember, so this is minus 2 t amount of energy is what one gets gains by doing this.

This is interesting actually. This one could have guessed by even basic quantum mechanical principles because if you have two protons then they if they come close by the electrons now have a much bigger radius to move around and we know in quantum mechanics that Heisenberg principle likes to delocalize things. The more you localize a quantum object, the more you pay in terms of its momentum and that means energy.

So, delocalization is always favored and it gives to lowering of energy and that is exactly what this has done. More than that it has also given us the new orbitals which are the what? The new orbitals are just the eigen functions corresponding to these two; so psi of psi 1 comma 2 is basically 1 by root 2 1 plus minus 2. And if we know that you can actually do a direct calculation and check that for this guy this Hamiltonian that I have written down the plus sign gives you lower energy, it corresponds to the eigenvalue epsilon 0 minus t, epsilon naught minus t.

So, this is a symmetric wave function, this is the orbital part of the wave function. So, the spin part now has to be anti-symmetric which is what I have written down here, it is a spin part is a singlet. That is the solution actually, that is exactly what happens in hydrogen atom problem.

Although the energies that I am writing down are not all (Refer Time: 17:26), this is just an approximation, there are terms we have neglected, but nevertheless the physics that do get is contained in this very simple minded description of a hydrogen molecule.

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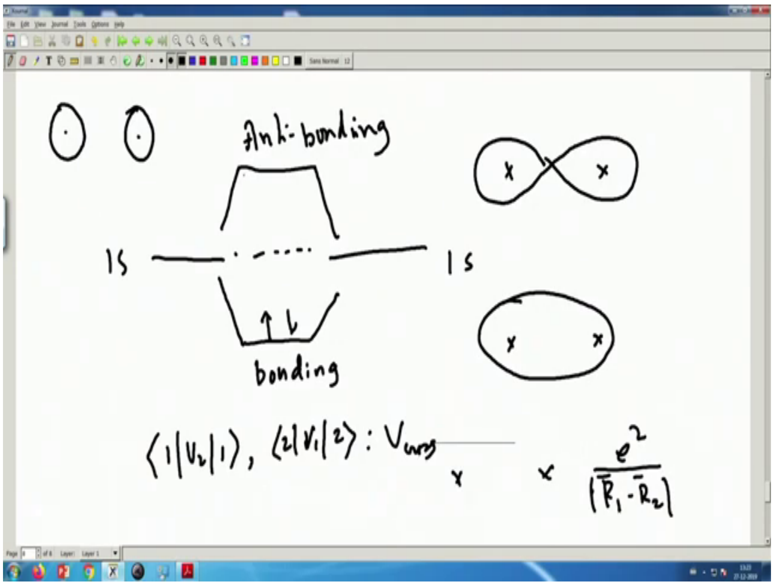

So, what has happened then? Basically what has happened is that you had the two; for example, if I even started with 1S orbitals, these were the orbitals these were the say 1S orbitals, two 1S orbitals . They talk to each other and formed two other orbitals, this is called the sigma. This is called the sigma orbitals, this is the bond called bonding orbitals, the lower energy, and this is the anti-bonding orbital, and I put two electrons in here and I gain reasonable amount of energy.

And the wave functions if you look at the wave functions are like this, the two atoms were here and the anti-bonding wave function is somewhat like this, whereas the bonding one which is a symmetric wave function is symmetric with respect to the two nuclei. So, from the original ones which were the original wave functions were both like 1S for example, and the final wave function is a two linear is two are two linear combinations, one is anti one has a node, the other one is symmetric and the corresponding spin functions are singlet here for example. So, the ground state is a singlet wave function with a symmetric orbital part of the wave function.

So, this is actually the picture of a real hydrogen molecule. Though as I said the energies that we used are not perfect, they are approximations. There is just one more comment I would like to make is that this cross term that I had written down originally, the 1 V 2 1 or 2 V 1 2 these I had neglected. One of the reasons is that this is small much smaller, but the other reason is also that there are these two nuclei, these two nuclei which also had a interaction between the two, R 1 minus R 2 and it turns out that this interaction between the two nuclei more or less cancels the contribution coming from this cross terms; this I called cross.

So, neglecting the cross term was not a bad idea and but of course, neglecting the coulomb interaction between the two electrons changes many things and that is something that is not a part of this scheme of things that we are dealing with and that is a very different advance topic. So, we will not discuss that here.

But for the time being this is this gives the picture that I have given, gives me two states; at epsilon 0 plus t and epsilon 0 minus t and energy gain, energy is gained by forming the molecule for hydrogen. So, that is what the message that you should carry back and we will then consider a larger set of atoms. But before that we will do some analytical exact ideas. We will just discuss those ideas for a periodic lattice because after a lattice is a periodic structure, potentially it is periodic and we will discuss a few things about that kind of a potential.

Thank you