Electronic Theory of Solids
Prof. Arghya Taraphder
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 10
Variational Method: Molecular Orbitals, Bonding and anti-bonding Orbitals

Hello and welcome. So, we have been studying the effect of 2 hydrogen atoms being brought close together and the eventual formation of a molecular state, molecular orbital where the 2 electrons lose their individual identities and go to form a single orbital; where they reside. Now, this was the motivation for this is of course, that we want to know the; so called want to understand the so called band formation.

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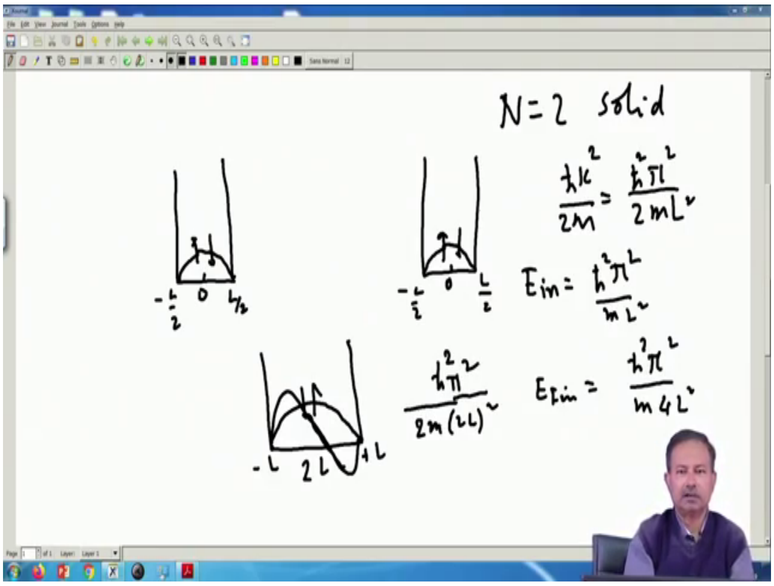

And to that effect two as we said in the other day the 2 hydrogen atoms fairly far apart with electrons in there say one is orbital; if they come closer, then we want to know what happens to this so called N equal to 2 solid, right. So, this can be thought of as a solid with only 2 atoms; of course, to generalize it to a large number of atoms is non-trivial, but that is what we are after.

And the reason here I am doing this N equal to 2 example is simply because it brings out the essential physical picture that dictates the bond formation. So, this kind of an approach that we discussed the other day is called the covalent bond formation of covalent bonds. And the combination of atomic orbitals and that lead to the formation of a molecular orbital is often referred to as linear combination of atomic orbitals or LCAO in chemistry literature; this actually translates to the so called tight binding approximation that we use for a large number of atoms and that we will eventually study.

So, let us recap again as to what is the physics under this picture and let me just remove these orbitals. And, consider this as I did the other day as a simple example of say two particles in a box picture and I argued that the energy of individual orbitals; individual particles in a box which is h cross square k square by twice m which is k's pi by h. So, h cross square pi square by twice m a square right for each of these atoms these wave functions are like this.

So, I am considering a 2 hydrogen atoms as two separate particles in a box; what the electrons are confined to. Of course, the real part real hydrogen atom is not a infinite potential, but let us mimic it for the time being and then I argued that once; so this is L by 2; 2 minus L by 2 and so on is 0.

Now, this when these two are brought together close together and then at some point they start talking these wave functions; of course, if you have infinite potential of, there is no way these electrons can talk to each other. But suppose the potential is now considered finite and these electrons are allowed to talk to each other and then of course, one and in extreme situation we will find; we will form a well of length 2 L.

So, which is minus L 2 plus L and so in that d wave function will be like this and the energy is h cross square pi square by 2 m L square; so 2 m into 2 L square. Now, as I argued the other day that if you add two of these; so that will be h cross square. So, final energy the initial energy was E initial was twice this amount h plus square pi square by m L square. Here the final energy is h plus square pi square by m into 4 L square.

So, the 2 power 2 electrons so, individually I earlier the 2 electrons were here they could be along any direction so now the electrons of course, have to form a singlet because they are in the same orbital and the orbital is a symmetric orbital. So, the spin function has to be anti symmetric; these are things we learned in our quantum mechanics that two particular functions has to be anti symmetric fermionic wave function has to be anti symmetric.

So, when the two fermions form a wave function of this kind it you have to anti symmetries it and then anti symmetrization. Since the orbital part is symmetric the spins, spin part has to be anti symmetric; so it is a singlet. Nevertheless, the point that I meant was that there is a gain in energy in doing this of course; I also mentioned that if you have for example, instead of hydrogen, you had helium so you already had two protons and two electrons then you had to use the other orbital the x.

So, you had 2 electrons here and 2 electrons here; so 4 electrons and then you have to put the other electron other 2 electrons in an excited state which is like this which is. So, and then of course, you can show that you do not really gain any energy because that energy is higher.

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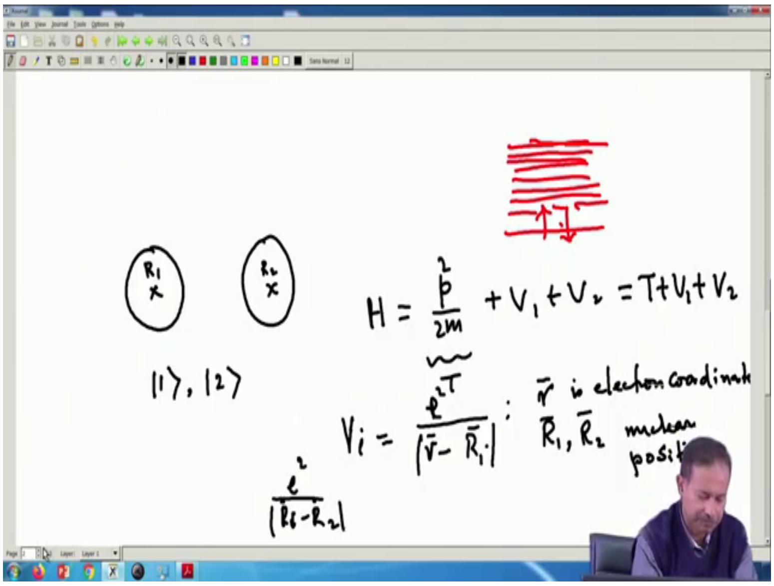

So, what you did is that you; we started with two energy states and then on interaction, we create on they are talking when the start talking to each other we created two energy states of this kind. And, we put the two electrons in hydrogen in this orbital and we gained an energy because the original energies were here and the final energies are; see the original energies are these two this and this and there is the sum of these two would be twice this amount. And, then since this energy is lower this one is lower than we put 2 electrons here and gain the energy.

So, that is the standard practice in form in molecular molecule formation. But, then if you had helium for example, you had to put two more electrons here and that immediately tells us that you do not really gain much energy by doing this. In fact, you do not gain any energy in this approximation by forming this helium molecule and that is one of the ways to see that actually helium molecule never forms ok. So, this digression basically tells us that the formation of molecule can be thought of as a formation of two orbitals; these are called bonding and anti bonding orbitals which are separated in energy.

And as I said the other day when we will have much much more number of atoms coming in; then we will have states in between and there is a large number of states because each atom will contribute one state for example, for a in hydrogen and then will have large number of states. And as you can see this as in as this number increases this is like a continuum of states which is; which we eventually called a band out of this orbital.

So, let us just go a bit more further and we look at this problem two hydrogen atom problem; a bit more mathematically. In the sense, we write a Hamiltonian and we try to justify certain approximations and under those approximations see how this molecular orbital formation takes place. So, again I have these two hydrogen atoms with their electrons in their typically one is orbitals when they are very far apart.

And so these two orbitals I call 1 and 2. So, what we do is that we first write the Hamiltonian; so the Hamiltonian has several terms see the Hamiltonian will have basically this is the energy function. So, Hamiltonian will have the energy of this each of these orbitals. So, for example, if it is hydrogen atom since it is hydrogen atom one is orbital atom, one is orbital energies are the energies for these isolated atoms for the electrons in these isolated atoms.

So, that will have the kind that is the kinetic energy plus the potential energy. So, let us just write this as simply as p; p square by twice m which is the kinetic energy. So, this is the kinetic energy T, then of course, you have a term which is we let me call it V 1 plus V 2. So, where V 1; V i is 1 by V square by r minus R i. So, what are these r, r is the coordinate of the electron; r is electron coordinate.

So, the position of the electron and capital R; R 1 and R 2 are nuclear positions right the positions nuclear positions. So, these are the these are my R 1 and R 2; so; that means, V 1 is like for example, if I think about V 1; V 1 is the interaction of electron of the nucleus 1 with the electron at R 1. And V 2 is the interaction of coulomb interaction of electron at r with the nucleus 2.

Now of course, there is the other term which I have not written here which is the interaction between the two nuclei R i; R 1 minus R 2 which I will come back to the another interest important term is that we are just assuming that the nuclei are fixed and they are; they have no kinetic energy of the nucleus is included here and the; so this I write as T plus V 1 plus V 2.

Now, the fact that the nuclei are fixed and the electrons move about them is actually not a very bad approximation. Because if you look at the nuclei; they are basically protons their masses are nearly 2000 times more than the masses of the electrons and so they are dynamics is far far slower than the dynamics of the electrons. So, by the time an electron moves about a large number of times, the nucleus will not probably move even once.

So, their dynamics are very very separate dynamics; the nuclei are morally, as far as the electron is concerned, electrons are concerned here the nuclei are almost like static nuclei. Their movement is very slow compared to the electronic motions. And this kind of approximation is called a Born-Oppenheimer approximation and it; it actually is a fairly good approximation for the first calculation one does.

The corrections due to these are there they can be included and those are much more detailed calculations that we will not get into here. For us, these nuclei are more or less static and their dynamics is very slow compared to the dynamics of the electrons. We concentrate on the electron dynamics and their interactions with the nuclear; both the nuclei.

There is one more term that is of course, could be significant and that term is the electron electron Coulomb interactions. So, if the these two electrons that are they come close together then of course, that interaction can become very large. So, those are things we are neglecting for the time being and we will proceed with this; this Hamiltonian and see what this kind of an approach gives us ok.

So; so it is certainly better than the approximation that we did just some a while back of putting the two the two atoms as replicating the two atom; mimicking the two atoms as two particles in infinite boxes, this is much more realistic. So, let us go ahead and see what we can do with it. So, our Hamiltonian is basically these three terms the kinetic energy of the electron, the coulomb interaction of the electron with its own nucleus and the nucleus of the other atom ok. So, to first approximation, which is called the linear combination of atomic orbital.

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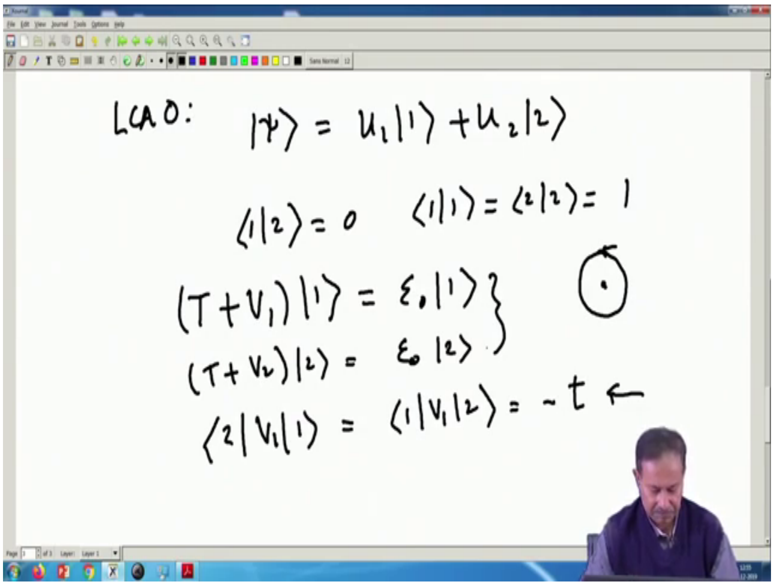

LCAO: $|\psi\rangle = u_1|1\rangle + u_2|2\rangle$

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

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

$\langle 2|V_1|1\rangle = \langle 1|V_1|2\rangle = -t \leftarrow$

One can since these two orbitals are now talking to start talking to each other these two atoms; then there is a possible that these is quite likely actually that the final orbital is going to be a linear combination of these two orbitals. So, let us write it as u 1; 1 plus u 2; these two kets 1 and 2 are the ones are the state eigenstates of the of; the original atomic wave function and so typically people can people do take them as just the one is orbitals of the two hydrogen atoms.

But it is not necessary that you have to do it because particularly when the two nuclei start coming closer that kind of an approximation does not hold anymore. So but for us let us just assume that these are the two atomic wave functions centered at the two respective nuclei 1 and 2. The other assumption which we will make is that these two wave functions are orthonormal ok. So, the 1 and 2 are orthogonal and we will also assume that u1 and u2 are real.

So, 1 and 2 are orthogonal means that we will take them to be 1 2 equal to 0 and 1; 1 1 1 equal to 2; 2 equal to 1. So, they are orthonormal wave functions these. See again let me reiterate that this approximation is not really a very easy correct approximation, but it does not cause too much of a trouble simply because we can always change this 1 and 2 as suitable wave functions. We do not have to use the atomic wave functions of the original separated atoms like 1 s for example. Obviously, as you can see when the nuclei come closer this kind of approximation is not going to hold too much water ok.

So, what we do now is that we write down the things that we already know. So, T plus V 1 operating on 1 wil l give me epsilon 0, 1. Again, as if we have the atomic picture then of course, this epsilon 0 is just the energy of the 1 s orbital, but as I said it is not necessarily have it does not have to be this atomic orbital. So, let us just assume that this is epsilon naught which is the energy of this; for example, the atom 1 and so this is T plus V 1; that means, these electrons kinetic energy and the its interaction we put a coulomb interaction with its own nucleus; so that is included in this epsilon naught.

Similarly, T plus V 2 into 2 is also epsilon naught 2 ok. So, that is again this is the same thing that I assume that the two electrons are degenerate; their energies were degenerate when they are far separated; which is a very valid approximation because I cannot really there is nothing to distinguish between the two atoms, when they are far apart they are the same.

So, this 1 is basically the in this approximation the 1 is the ground state wave function of the separated atom 1 and 2 r and then we have chosen them to be orthogonal. So, let us now do a calculation where we will; we will see what how to calculate the energy of this and how do how do we calculate u 1 and u 2 for the best possible solution.

So, we want to minimize the energy and of course, the Hamiltonian matrix is the one that we need to find out. And, it is a matrix now because there are two wave functions and we have to we have to diagonalize this problem in the space of these two basic basis 1 and 2 and find out the weights u 1 and u 2. I have chosen u 1 and u 2 to be real here that is; that I could relax easily could choose them to be complex, but just for simplicity of calculation, I am choosing them to be real there is no loss of generality in that.

So, the other thing that I would like to point out is that there are these terms that 2 V 1; 1 or 1 V 2; 2. So, the 1; so 1 V 1 2 and these kind of terms I am assuming to be minus this let me write as a minus T and I am assuming them to be the same ok. So, as you can see this; basically this says that this interaction of the electron between two and one. So, this is basically called the hopping integral or transfer integral which brings the connection between the mixing of these two orbitals via the potential V 1 and similarly, for V 2 between the electrons 2 and 1.

So, this is the term which will which give this is the term which causes the mixing otherwise these two are basically the atomic energies ok. So, let me just go ahead and do the calculations now. To do the calculation, let me just introduce you to some a concept which we commonly use is called the variational; variational theory. In variational calculations in quantum mechanics what one does is that one choose a trial wave function right.

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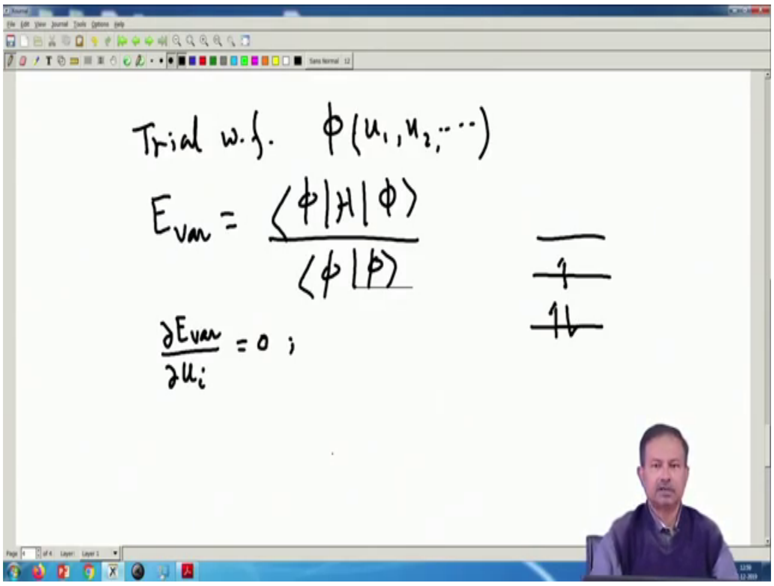

Trial w.f. $\phi(u_1, u_2, \cdots)$

$$E_{var} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$\frac{\partial E_{var}}{\partial u_i} = 0 \;;$$

One choose a trial wave function say call it phi and then phi has some; it depends on some parameters u, u 1, u 2 dot dot dot dot. And, this phi is then the Hamiltonian is then this quantity variational is the expectation value of phi with respect to h and divided by the phi phi; if phi is not normalized then you have to divide by the phi to phi this denominator. Now, this quantity is of course, a function of all these parameters u 1, u 2, u 3 and so on.

So, what one does there is there minimizes the variational energy extremizes the variational energy with respect to this u i and then set it to 0; so that is the extremum condition and then this will give me this as many equations as there are use. So, if you had 10 used for example, you want to you 10; then I will get 10 such equations and then try to solve these equations either in whichever way I can the easiest way to solve such equations is write it as a matrix. Because these are coupled equations u 1, u 2, u 3; all of them get coupled in each equation; so it is better to write them as a set of coupled equations.

As a matrix this set of equation can be written as a matrix; just as one does in linear theories. So, the linear combination you will get u 1, u 2, u 3, u 4 and so on and you have to just write that coupled equation as a matrix equation. And, then diagonalize the matrix and that matrix the diagonal eigenvalues are the new energies of this system. And, then you have to put the electrons in the lowest energy; number of depends on how many electrons you have to put you will put them from the bottom obeying Pauli principle; so that is the basic idea of this whole thing.

Suppose, you had three use then you will get three solutions and you will if you have say 3 electrons, then you will put 2 electrons here and 1 electron here for example. So, that is the way to go about doing this; this kind of a calculation. The variational theory is a very standard theory in quantum mechanics and that is what one uses to calculate this is one way to use to find out the best possible solution in a variational way.

So, you are minimizing with respect to certain set of parameters; I have chosen a particular linear combination. It is not guaranteed to go give you the exact ground state, but it is going to give you a state which is low in energy. And, if you are lucky enough you can hit the right state; right ground state by doing this ok.

So, that is what I will I am going to do now.