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

Lecture - 15
N atoms Solid

Hello. So, what we have done so far is that our in our efforts to find out the bands in a solid in a with a we have worked out the proof of Bloch's theorem, we encountered Bloch's theorem which is a very powerful theorem which tells us that the translation of an wave function is just adding a phase to the wave function which is e to the power i k dot r for a periodic potential. And a periodic potential is what we are studying because in a real solid the potential is periodic and the period is the same as the Bravais lattice of the real solid.

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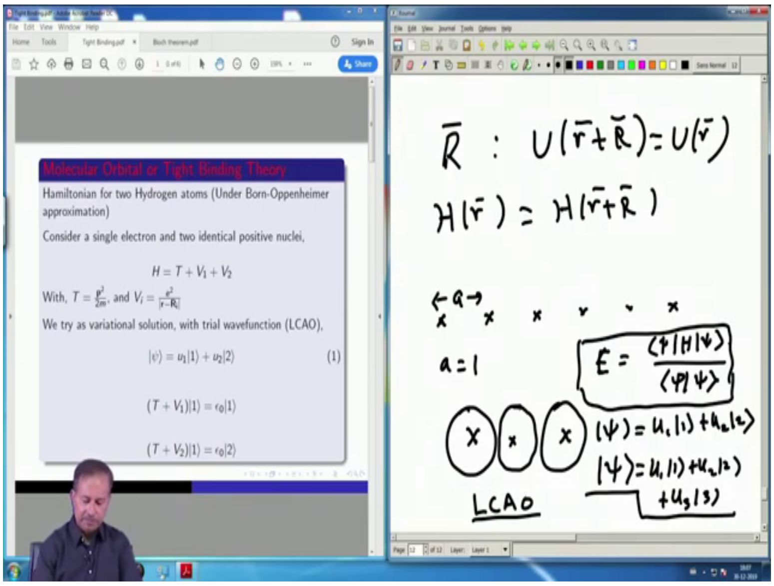

Molecular Orbital or Tight Binding Theory

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),

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

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

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

$\bar{R}$: $U(\bar{r}+\bar{R}) = U(\bar{r})$

$H(\bar{r}) = H(\bar{r}+\bar{R})$

$a = 1$

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

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

$|\psi\rangle = u_1|1\rangle + u_2|2\rangle + u_3|3\rangle$

LCAO

So, if R is the Bravais lattice, then if R belongs to Bravais lattice then the period of the potential is also R. So, once that is true then H of r is of course, H of r plus R. So, the Hamiltonian is also periodic with the same period as the lattice and lattice being defined by the Bravais lattice vectors, ok.

So, now, we go back to what we did for two atom cases. These two atom solid is as I said is a carry catcher of the n atom solid. So, now, let us graduate towards a large number of solid.

So, let me just stick to one-dimension for the time being, life is much simpler in one-dimension; we will we can generalize this to any dimension as we go along. So, this is the periodicity of the lattice and let me just assume that the atomic distances are a and let take a equal to 1. Let me take a equal to 1.

I can put back that dimensions and units any time I want which I will show you how to do; a, the distance between two lattice points which is the same as any other lattice points between the nearest neighbor, these are called nearest neighbors. So, this one for example, has its nearest neighborhood this one and this one. See, similarly the next one this one has its nearest neighbor this one and this one. So, that is how nearest neighbors are defined.

It is just seeing the nearest neighbor the English term nearest neighbor, your nearest neighbor. In your house also at your home you have nearest neighbors on both sides or on four sides. So, these are the same as same definition works here, ok.

So, this is the lattice where we will try to first find out the solution of a particle moving in the potential of these atoms which are located at this points given by cross, with the potential of course is periodic as I showed in the previous picture, in the picture when we did Bloch's theorem. So, we remember the important thing that we have to remember here is that whatever solution we get has to obey Bloch's theorem and that we can check or conversely whatever solution we try we must remember to keep it consistent with Bloch's theorem, ok. So, that is the reason Bloch theorem is so powerful because I know what kind of solutions are admissible, ok.

So, remember that example we did for two atoms just for two atoms with an orbital around it, two hydrogen atoms for example. We obtained an equation which is H, so we calculated the we took a trial route, right. It is called a variational way to calculate the best possible solution, the lowest energy solution. So, E was psi H psi divided by psi, psi and psi was chosen to be u 1 1 plus u 2 2, ok.

Now, suppose I have instead of two atoms I add another atom to it, has to be as big. So, let us just draw it as big as the other ones, ok. So, that is then what do we do? We just do the same thing. We just extend this by u 1 into 1 plus u 2 2 plus u 3 3. So, that is our scheme of LCAO; Linear Combination of Atomic Orbitals, that tells me that the trial wave function of this form can be tried and one can look for the variational energy and solve for the optimized problem, minimization of the energy, ok. So, that is the route we will take again.

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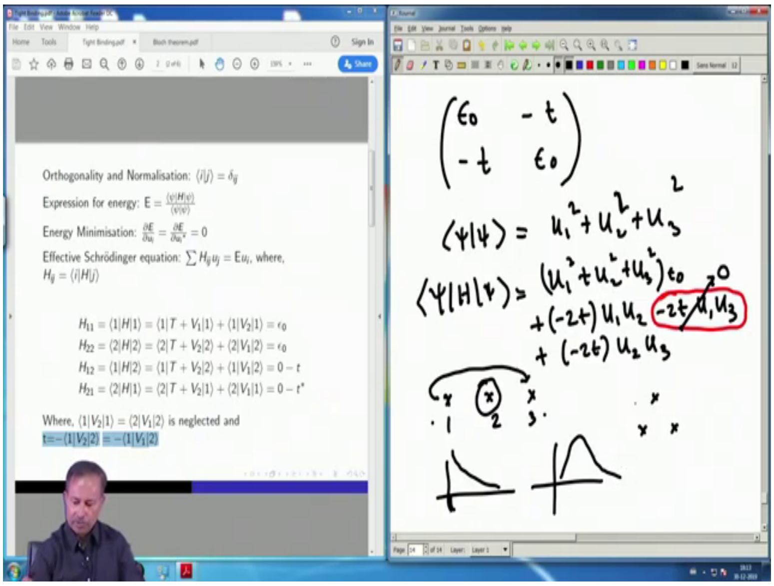

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$$\begin{pmatrix} \epsilon_0 & -t \\ -t & \epsilon_0 \end{pmatrix}$$

$$\langle\psi|\psi\rangle = u_1^2 + u_2^2 + u_3^2$$

$$\langle\psi|H|\psi\rangle = (u_1^2 + u_2^2 + u_3^2)\epsilon_0 + (-2t)u_1u_2 + \boxed{-2t\cancel{u_1}u_3} \to 0 + (-2t)u_2u_3$$

Let me remind you what we got in the previous case. We got a Hamiltonian which was in matrix form E 0 minus t minus t E 0, ok. You know t is taken to be real otherwise I would write minus t star here in the two one element. So, this element, so this is H 1 2, this one is H 1 2 and this one is H 2 1 this is H 1 2 and H 2 1, ok.

Now, if I had one more atom what would have happened? Well, let us see what could happen. So, now, we have the psi has 3 elements. So, the remember that psi psi which appeared in the denominator will now have u 1 square plus u 2 square plus u 3 square and in you know numerator we will again have the I have similar terms. So, this was then psi H psi will have u 1 square plus u 2 square plus u 3 square into epsilon naught plus the minus twice t times u 1 u 2 minus 2 t times u 1 u 3. Now, this term I will come back to plus minus 2 t times u 2 u 3, ok.

Now, if you look at this term, then remember I had a lattice with 1, 2, 3. Now, this the term in the red under the red circle implies that there is a overlap between this and this, right. Now, that overlap of course, in the way I have drawn the lattice is missing because there is a the factor t is only between nearest neighbors, right, it is the remember what t was, is let me show you what t was. Look at what t was, t was 1 V 2 2 or 1 V 1 2.

So, matrix element, between the orbital at 1 and orbital at 2 of the nuclear interaction of the 2 and of the 1. So, it is the cross term between by cross I mean it is the matrix element of V 1 or V 2 between the states 1 and 2. Now, 1 and 2 and nearest neighbor. Suppose I made 1 and 3 on both sides then 1 and 3 are not nearest neighbors, so it is a further neighbor and that cannot be the same as t that has to because the wave function falls off. See the wave functions are they fall off in real space, they are like this and so, or sometimes they are like this and so on.

So, they always fall off at a distance. And typically their distance is less than even the nearest neighbor, so that the interaction between an orbital at a particular site and its nearest neighbor is much stronger than what it is between this one and its next nearest neighbor. So, 1 and 3 almost barely talk to each other. So, I can basically for the time being I can just throw out this term, right 2 is 0.

So, u 1 u 2, u 2 u 3 these terms are there, right. So, let us just then write the Hamiltonian. I mean if you now minimize this equation with respect to u 1, u 2 and u 3 you will similarly get exactly the same kind of Hamiltonian. So, you will have a t term between the nearest neighbors and minus t and the diagonal term will always be epsilon naught. And only 2, the site 2 this one has two nearest neighbors. The once the site 1 and the atom 1 and atom 3 have no nearest neighbor other than one on the right here for 1 and one on the left here for 3.

If you put a periodic boundary condition of course, then you make it into a triangle and everyone is a nearest neighbor of the other one. So, that is a case we will not discuss right at this moment, we will come back to it later.

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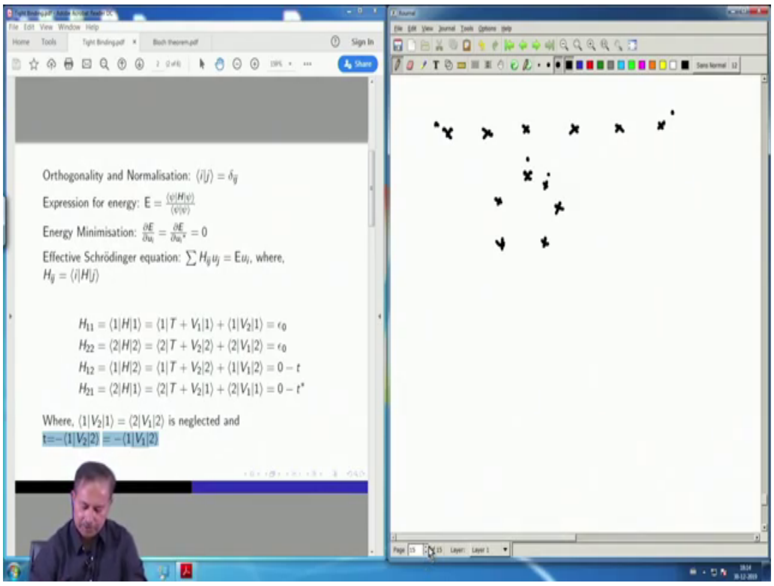

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In a large lattice for example, this is suppose you have you want to put a periodic boundary condition in a one-dimensional solid then the equivalent description is similarly here are 6 points for example, so what I will do is that I will put them in a circle, 1, 2, 3, 4, 5, 6. So, this is the way, the periodic boundary condition means that you actually close the loop and that means, this one now, 1 has a nearest neighbor which is 6 which is 1 and 6. So, we will we are not discussing that now. Right at the moment let me just write down the matrix elements that the matrix of the Hamiltonian that I will get for 3 sites and where the periodic boundary condition is not used.

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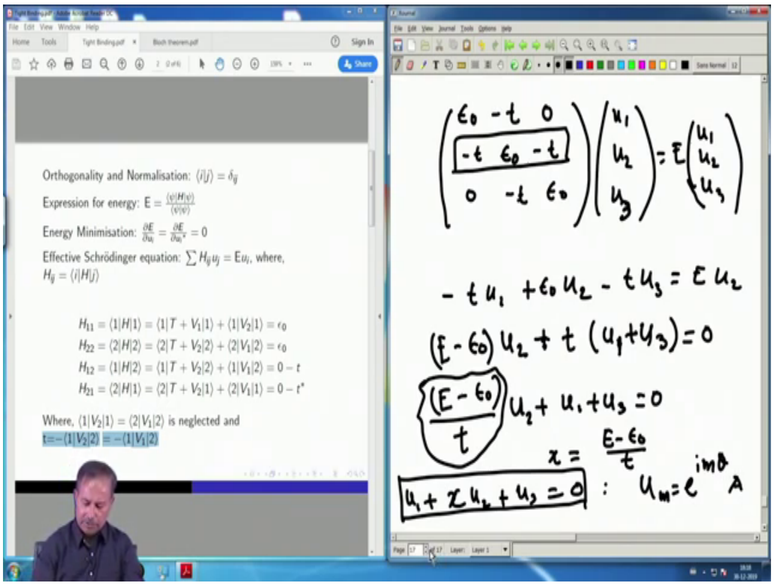

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$$\begin{pmatrix} \epsilon_0 & -t & 0 \\ -t & \epsilon_0 & -t \\ 0 & -t & \epsilon_0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix}$$

$$-t u_1 + \epsilon_0 u_2 - t u_3 = E u_2$$

$$(E - \epsilon_0) u_2 + t (u_1 + u_3) = 0$$

$$\frac{(E - \epsilon_0)}{t} u_2 + u_1 + u_3 = 0$$

$$x = \frac{E - \epsilon_0}{t}$$

$$\boxed{u_1 + x u_2 + u_3 = 0} : \quad u_m = e^{im\theta} A$$

Again, it will be be in the basis of u 1, u 2, u 3 equal to E times u 1, u 2, u 3. So, epsilon naught minus t 0 then epsilon naught here minus t here minus t here. Remember number site number 2 has both the neighbors both nearest neighbors available whereas, site number 1 and 3 has only one nearest neighbor. So, that will be the matrix then. This is the column, this is this one is the column for site number 2, this is the row for the site number 2 and it has both the both on both sides it will get minus t, except the other ones we will not have that, ok.

So, let me just consider this the equation for this second row, ok. So, this is minus t u 1 plus epsilon naught u 2 minus t u 3 equal to E u 2. So, that means, E minus epsilon naught into u 2 equal plus t into u 1 plus u 3 equal to 0, ok.

Now, I divide both sides by throughout by t then this is the equation I get. Remember t is positive, so sign of t is already been accounted for as before plus u 1 plus u 3 equal to 0. Now, let me call this quantity, this quantity as x. Let me define it as x equal to E minus E naught by t. Then my question is x u 2 plus u 1 plus x u 2 plus u 3 equal to 0, this is the equation I have to solve. So, this is the equation corresponding to the second row, ok.

So, first let me just stop here and then recap again what we have done. We have just extended the number of protons number of hydrogen atoms for example, by one more and that means I have 3 atoms now; 3 atoms puts in an interesting feature in the in the sense that the number 2 atom, now has nearest neighbors on both sides. And in the sense and the number 1 and number 3 they remain the same equation as before.

So, the equation for they have only one neighbor in the open boundary condition and so they are they will those rows will be epsilon naught minus t and minus t epsilon naught. So, the only change that will happen is now in the second row which has two neighbor. So, the diagonal element is again epsilon naught, the off diagonal elements on both sides will now become minus t.

Now, can we just extend this to a higher number of sites? Yes, we can. I will just come back to it. So, let me first try to find out a solution for this equation, ok. So, let me choose a solution which is u of m equal to e to the power i m theta times some constant A, ok.

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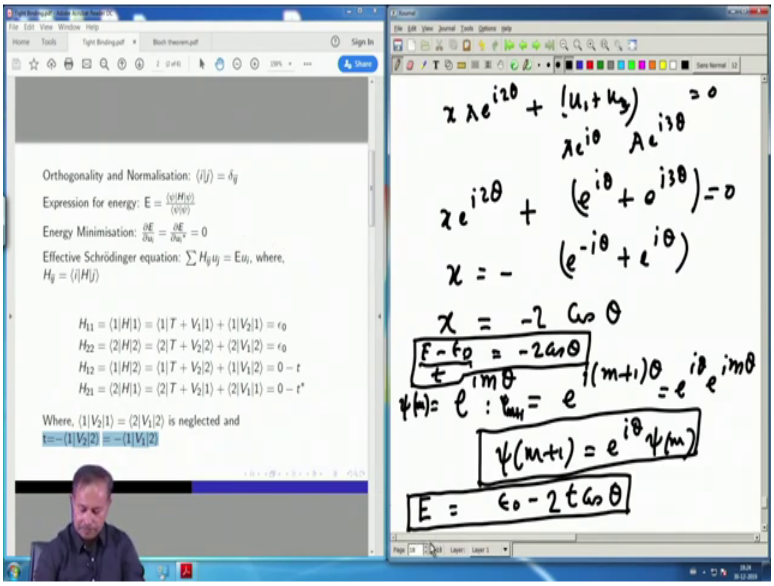

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$$x A e^{i2\theta} + (u_1 + u_3) = 0$$
$$A e^{i\theta} \quad A e^{i3\theta}$$
$$x e^{i2\theta} + (e^{i\theta} + e^{i3\theta}) = 0$$
$$x = -(e^{-i\theta} + e^{i\theta})$$
$$x = -2\cos\theta$$
$$\boxed{\frac{E - \epsilon_0}{t} = -2\cos\theta}$$
$$\psi(m) = e^{im\theta} : \psi_{m+1} = e^{i(m+1)\theta} = e^{i\theta} e^{im\theta}$$
$$\boxed{\psi(m+1) = e^{i\theta}\psi(m)}$$
$$\boxed{E = \epsilon_0 - 2t\cos\theta}$$

So, then what do I get? x times A e to the power i, ok. So, let me just remember; u's of m is e to the power i m theta into A. So, x times A e to the power i 2 theta plus u 1 plus t into sorry, let me go back. So, remember the solution was t u 1 plus u 2 into x into u 2; u 2 I have already put in, so here I will put A e to the power i theta, here I will put this is u 3 A e to the power i 3 theta, and so that is equal to 0. So, this is x. So, A's with all cancel x e to the power i 2 theta plus t e to the power i theta plus e to the power i 3 theta equal to 0, ok.

I just take just divide both sides by e to the power i 2 theta, then I have x equal to minus t e to the power minus theta plus e to the power i theta, which means that this is minus t into 2 cosine of theta. So, that is x if I choose this as a solution.

Now, can I choose this as a solution? Of course, I can because I know that the solution has to be has to satisfy the Bloch's theorem and you can easily check that this solution e to the power i m theta does obey Bloch's theorem, because if I go one more lattice spacing which is plus 1 is basically e to the power i m plus 1 into theta equal to e to the power i theta e to the power i m theta. So, this is my psi for example, psi at site m and then I am I went to psi m plus 1.

So, that is e to the power i m plus 1 e to the power i theta into A; so that means, psi of m plus 1 is e to the power i theta psi of m which is exactly what psi Bloch's theorem tells me, that if I move by one lattice spacing which is a Bravais lattice vector in one-dimension of course, this is the only one direction and I moved one unit I picked up a phase of e to the power i theta. This theta of course, will be will determined and I will show you later on that it is the same that we got earlier A dot A. So, this is basically consistent with the idea of Bloch, the theorem of Bloch.

So, now, x equal to minus 2 t cosine theta. What was x? Let us go back. E minus epsilon naught by t was my x. So, let us see what I can do; E minus epsilon naught by t. So, E minus epsilon naught sorry, there was no t here I already cancelled the t; t I divided by t, so there is no t here. So, E minus epsilon naught by sorry E minus epsilon naught by t is equal to minus 2 cosine theta. So, that is what myself solution for E is. So, E equal to epsilon naught minus twice t cosine theta. So, this gives me the solution for the energy for this 3 site problem.

So, now, let us try to generalize it to an n site, yes. So, in n site case what will happen? Remember that matrix, remember the matrix E minus epsilon naught minus t 0 minus t epsilon naught 0 minus t 0 minus t epsilon naught. So, this matrix had 3 elements in only the second row.

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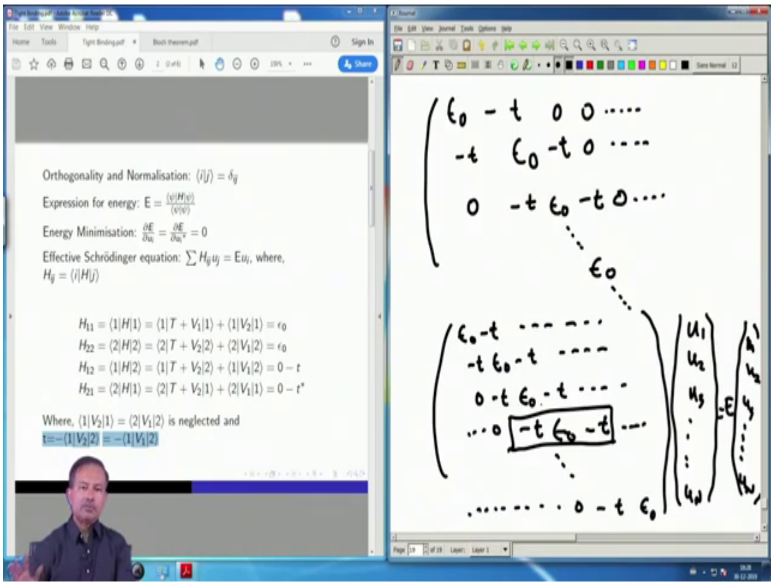

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$$\begin{pmatrix} \epsilon_0 & -t & 0 & 0 & \cdots \\ -t & \epsilon_0 & -t & 0 & \cdots \\ 0 & -t & \epsilon_0 & -t & 0 \cdots \\ & & \ddots & & \\ & & & \epsilon_0 & \\ & & & & \ddots \end{pmatrix}$$

$$\begin{pmatrix} \epsilon_0 & -t & \cdots & & \\ -t & \epsilon_0 & -t & \cdots & \\ 0 & -t & \epsilon_0 & -t & \cdots \\ \cdots 0 & \boxed{-t \;\; \epsilon_0 \;\; -t} & & & \cdots \\ & & \ddots & & \\ \cdots & \cdots & 0 & -t & \epsilon_0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ \vdots \\ \vdots \\ u_N \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ \vdots \\ \vdots \\ u_N \end{pmatrix}$$

Now, suppose I go beyond 3 sites and I go to 4 sites or 5 sites or even more, so let us just write down the matrix and then you will realize that what I am writing is absolutely correct, then there will be all 0s because the first site it has no other neighbor. The second one will always the diagonal elements will always be epsilon naught. The second row for example, had minus t here and minus t here then all are 0s.

Now, the third row again I have minus t on its two sides, but all others higher further ones will all be 0. So, this will be 0 and so on. So, anything which is not the first one or the any row which is not does not correspond to the first atom or the last atom will always have these 3 elements in the in that row, there will be not more than 3 elements. There will be a diagonal element which is epsilon naught and on both sides I will get minus t.

So, the matrix has a structure which then is it is very simple. It is epsilon naught along its diagonals and minus t along the off diagonals; just the two off diagonals. So, this will be epsilon naught then minus t minus t and so on. So, this kind of a matrix is called and the last element, the last column, the last row will have epsilon naught at the last and minus t just next to it all others are 0, ok. So, these are all the 0s. This is dots that I am putting in are all 0s; these dashes that I am putting it in are all 0s.

So, this is the matrix times u 1, u 2, u 3 dot dot dot dot u's of N for N sites and this will be equal to E u E times; again u 1, u 2, u 3 dot dot dot u N. So, that is the structure of this matrix equation. And this is the Hamiltonian matrix that I need to diagonalize. So, again the I take any row for example, this row for example, if you take this row this is the third row now, or take the fourth row it is identical equation to the one that I had just I have just solved in the previous one. There is an epsilon naught minus E which comes from the right hand site and there is minus t on the left and the plus t on the right.

So, the solution that I got for 3 sides is a generic solution that solution will work for N number of sites. So, that is the beauty of this whole treatment that all I have done is this in the nearest neighbor hopping approximation which is the LCAO and using LCAO my calculation just reduced to diagonalizing a tri-diagonal, this is called a tri-diagonal matrix because it has this diagonal element and on both sides it has a element. It has one off diagonal element on either side of the diagonal.

So, that kind of a matrix is I mean this is basically reflecting the periodicity of the problem of the Hamiltonian and this the solution to that as I said is consistent with I chose a solution which is consistent with Bloch's theorem and that solution gave me an eigenvalue which is E equal to epsilon naught minus twice t cosine of theta.

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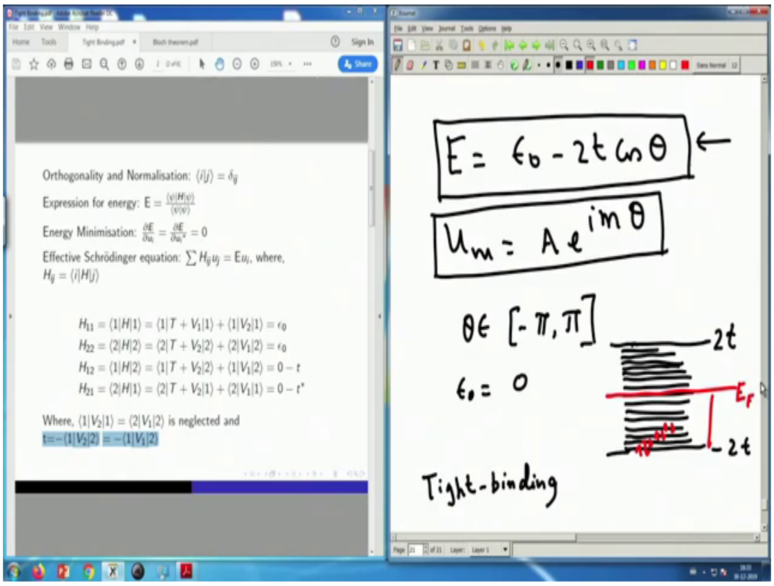

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$$\boxed{E = \epsilon_0 - 2t\cos\theta} \leftarrow$$

$$\boxed{u_m = Ae^{im\theta}}$$

$\theta \in [-\pi, \pi]$

$\epsilon_0 = 0$

Tight-binding

What that theta is we will calculate and the beauty of this is that the solution is u m is A e to the power i m theta. So, these are the simple solutions to this problem and the obey Bloch's theorem and they give me a variational energy which is what I have just written down this is my variational energy. So, look at how it is spread out.

So, depending on the values of theta it will be, suppose theta is suppose theta goes from minus pi to plus pi then in discreet values which is what as I am anticipating that we will I will show you that it is just again k basically, k times k dot r, k r here is just one-dimensional, so r is equal to a, so it is just k a.

And in that case the solution is simply epsilon naught, Suppose I said epsilon naught equal to 0 that is my 0 of energy then the solution goes from plus 2 t to minus 2 t and there are as many orbitals I started with as there will be solutions because I cannot lose my states, number of states remains the same, so I have this n number of states starting from plus 2 t to minus 2 t.

So, these are not equi space, but these are very closely packed as n becomes very large and this is a finite width the minus 2 t to plus t plus 2 t there you have to pack n states in that and so, these basically form the bands. And these are the these are almost semi continuous states, because the gap the distance between states energy difference between states is exceedingly small, if n goes to a very large number. So, that is the story of band formation. In this approximation the life becomes very simple and this is called this, in condensed matter we call this tight binding approximation.

Why tight binding? Because it assumes that the electrons are more or less tightly assigned to their bound to their nuclei, but they can talk to the next nearest, just the next nearest neighbor. This is the next nearest neighbor tight binding approximation. You can actually choose a higher neighbor interactions also that exist depending on the lattice you may have to choose that as well, but in the this primitive form of this calculation we basically took this LCAO approach and extended to n atoms and that is called the tight binding approximation. Because tight binding simply means that the electron is still considered bound to its nucleus, but not entirely its tightly bound, but once it start interacting with this its nearest neighbors once is starts talking to its neighbors, it becomes delocalized and a band forms.

And suppose you have n number of each of these has had only one electron then of course, you know that you have to fill up the lowest n by 2 states because each state will take 2 electrons. So, out of all these n states you will only fill up n by 2 only up to a half of this and that means, you are in a metallic state. So, this part the part below it this part is filled up and the rest is unfilled and this is the your Fermi, this will become your Fermi energy. And right above Fermi energy almost at infinitesimal distance away in terms of energy there is another state available, so that means, there are almost 0 energy excitations available which is a characteristics of a metal. There is no gap for the excitations.

So, this is what this will in this case for example, if you have less than twice n number of electrons in this picture you will get a metallic state. You just keep on filling the number of states. You can put 2 n number of electrons if there are n sites, and anything less than 2 n will give you a metallic state.

So, that is the picture of so called tight binding model. And this is a very powerful model one uses it all the way, even in research people actually use it as a first approximation when other effects become important, then one starts from a tight binding model and starts to put in the other effects. Of course there are situations where tight binding will not work. You have to consider higher neighbors or you may have to completely abundant the band picture, but those are details that beyond the scope of this. But remember that this is a very powerful and nice approximation that one can do and it just reuses the problem to single particle problems of formation of bands.