Electronic Theory of Solids
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Lecture – 20
Energy spectrum (Contd.)

Hello and welcome. So, let us start from where we left. We were working out the band structure for a lattice with a basis, two atom basis and further we set up the LCAO procedure to which is basically tight binding, tight binding procedure to write down the matrix that one needs to diagonalize.

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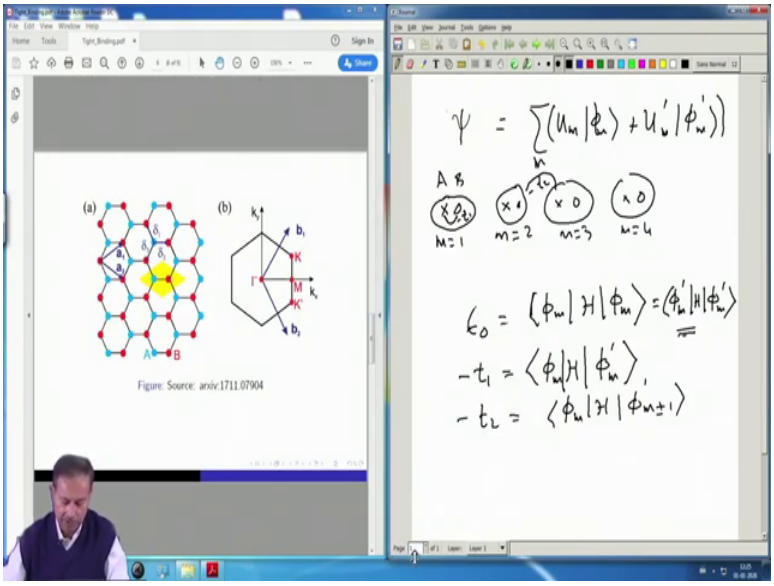

Now, as we discussed , in this case the choice of the LCAO function is contains two parts, one is coming from lattice A and the other one is lattice the lattice point B. So, this was the lattice that I drew and so on. So, there were A and B types of atoms. And so, we wrote down of phi m coming from A type of atoms plus u m prime phi m prime coming from B type of atom. So, this is exactly the same procedure that we followed.

Now, each m denotes, so this is m equal to 1, m equal to 2 and so on. So, these are the unit cells; m equal to 3, m equal to 4 and so on, it goes on. So, in this case for example, for n sites we showed that we will have a matrix of the form which can be represented as a block matrix. So, let me just quickly

go through what we did. So, we wrote down again the epsilon naught, for both the atoms we took the same because our purpose is we are looking at graphene and so in graphene both of them are carbon atoms, for a different system where d 2 atoms are really different one can choose epsilon 1, epsilon 2. So, that is not a problem at all.

So, that was the phi m H phi m which we took to be the same as phi m prime also, but as I said that I could choose this one to be a different value epsilon naught prime or whatever, it really does not matter. The other quantity that we wrote down was minus t 1 equal to phi m H, sorry the I am not using this I am using the bracket notation, so let us stick to that. Could as well write it as an integral phi m H phi m prime is the, so this means that this is the t 1 is between these two, so that we called minus t 1.

And between these we called minus t 2, that hopping is minus t 2 equal to phi m H phi prime m plus minus 1. And, I chose that to be real again that is an approximation that can be dispense to it this is not necessary, but it makes life simple that is all. I do not have deal with mods and all that, but that is not a restriction at all. As I showed as we have already seen in the previous case where, we did one atom per unit cell. So, that is the approximation we did.

We did not take any interaction, any overlap between these wave functions beyond the first neighbour and that is all there is and we chose them to be orthogonal orthonormalized. And they say B is, this B is a basically the similar same and similar approximations that we did for the single atom unit cell case. So, under this we have to now write the matrix in the basis of u m’s.

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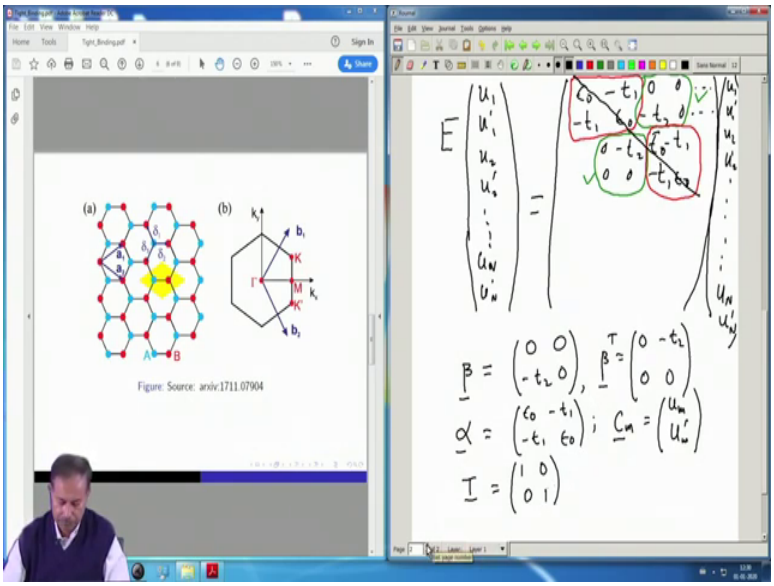

And so what we did is again a variational approach, if you just go through the variational approach what you will land up with is this u 1 u 2 prime u 2 u 2 prime and u n, u prime n for n sites will be equal to a matrix of the form that I wrote down the other day which is epsilon naught along the diagonal then minus t 1 here, then minus t 1 of course, is here epsilon naught and this will be minus t 2. These are 0s and so on, it will go on.

So, I can write. So, this is minus t 2; that means, this one also by hermeticity this will be minus t 2 0 epsilon naught and then t 1 and it goes on and on. So, then what I showed was that then what you can do is that you can identify two blocks of 2 by 2 matrices this one and this one. And its transpose here, the transpose will appear here. So, this will become t 2, 0, 0, 0.

The diagonal you will always have this red block or 2 by 2 block and in the off diagonal you will have the, so this will be epsilon naught minus t 1 and you will continue doing. So, this will be the matrix. So, they you can divide the matrix into these 2 by 2 blocks. So, then if you realize then what we have achieved is that it is again a tridiagonal matrix if we can write these blocks themselves as one entity, one unit.

So, this is the diagonal block and these green ones are the two off diagonal blocks just after the diagonal and nothing else survives as exactly as previous case. So, and then of course, you have this u 1

u prime 1 u 2 u prime 2 and so on, u n, u prime n. So, that is about the, that is the equation I mean that is all you need to know. So, then we define something which we called beta which is 0 0 minus t 2 0 then beta transpose. So, I put an underline to emphasize that these are 2 by 2 matrices, so this will be 0 minus t 2 0 0.

Then we had the diagonal 2 by 2 matrix which is epsilon naught minus t 1 minus t 1 epsilon naught and the vectors which I now write as C m equal to u m, u m prime and exactly as before we will now look at the mth row and so we will write down the equation for the mth row. But let me just write down the matrix first using these conventions; these 2 by 2 conventions. I also use the identity matrix which is 1 0 0 1 in two-dimension, ok.

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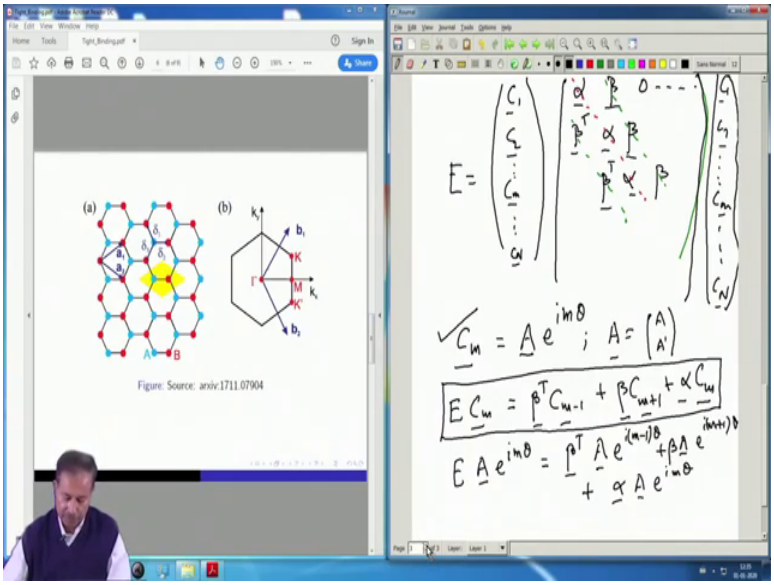

So, how does the matrix look like now? It is E equal to C 1, C 2, some C m C n each of them is a 1 by 2 entry. So, vector into these matrices alpha bar alpha, underline beta underline beta transpose underline alpha underline then 0s all the way. So, then here you will have a beta, then you will have a alpha here, beta transposed here, again beta here and it goes on exactly. So, this is my diagonal line and these are the two off diagonals, then again this C 1, C 2, C m, C n. So, this is the procedure.

So, now again we have a tri diagonal matrix, but the each entry is itself a 2 by 2 matrix, but that is not a big complication. We have to just work with this in this 2 by 2 space. But the matrix is similar to the

previous case where we used just one atom for unit cell. So, let us again do the same thing. We just assume a form which is A e to the power i m theta, here A is a matrix again and A is say a I can choose these matrix as A, A prime. A is basically a constant.

So, in this representation then I can write down the mth column, equation for the mth column which is E C m equal to beta transpose C m minus 1 plus beta C m plus 1 plus alpha C m, ok. Alpha is also a matrix. So, this is my equation which is absolutely similar to the one we obtained for the for the LCAO for two atoms or for n atoms, for the n atoms system for in the case of one atom per unit cell, ok. So, we now use this approximation and let us see what we get.

So, this will be E A with your i m theta equal to beta these will remain then A e to the power i m minus 1 theta plus beta A i m plus 1 theta plus alpha A e to the power i m theta. So, I can just take out the e to the power i m theta from both sides and the equation that I get is absolutely similar to the previous one that we obtained.

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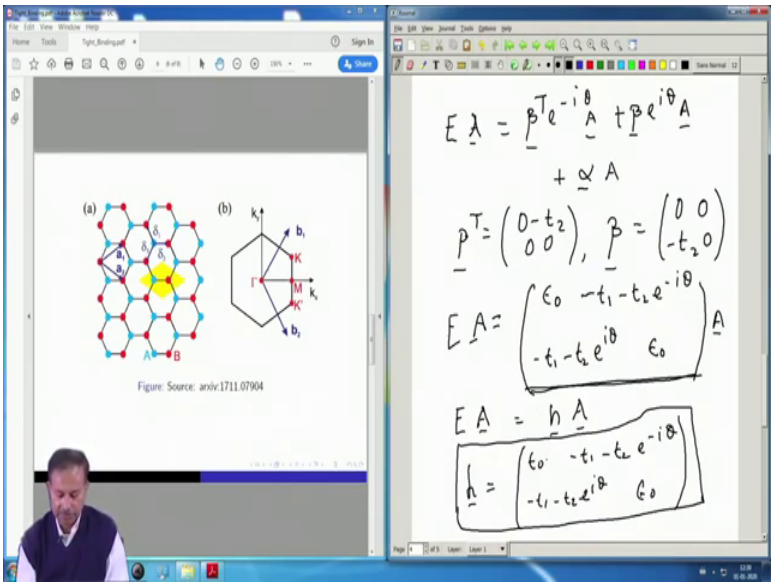

So, the calculation is now basically done what you will get is E times A equal to beta transpose. So, let us write down beta, so beta transpose e to the power minus i theta e to the power minus i theta e times A. So, this A also I can a, A also I can take out I do not need this A, but let us just keep it. I mean A is a

matrix, so you cannot take it out that way. In the one electron case we could easily take it out because we just had scalar equation, but this is a matrix equation.

So, A has to be kept, but we will rearrange the matrices in such a way that we have one matrix times A. So, this is A plus beta e to the power i theta A plus alpha A. Now, remember beta transpose, what was beta? Beta was 0 0 minus 2 0. So, beta transpose let me rewrite 0 minus 2 0 0. Beta was 0 0 minus 2 0. Now, you put the put it in then what you will get is basically E A equal to epsilon naught plus minus t 1 minus t 2 e to the power minus i theta minus t 1 minus t 2 e to the power i theta epsilon naught. So, that is the matrix equation that you get.

So, this is basically a matrix equation of the form equal to h, h is basically a Hamiltonian times A, where h is equal to just this matrix. So, this matrix is called h epsilon 0 minus t 1 minus t 2 e to the power minus i theta minus t 1 minus t 2 e to the power i theta and epsilon naught. So, all I have done here is that I have just multiplied between beta transpose, e to the power minus i theta and the beta by e to the power i theta and alpha and sum these 3 matrices. These 3 matrices combined gives me this matrix h matrix.

So, that h matrix is what I have and I have to just diagonalize this matrix to get my eigen value and eigenvectors. So, I can bring this e on the right hand side then you will get this. So, that is basically the diagonalization procedure. So, that will give me the eigenvalues E, ok.

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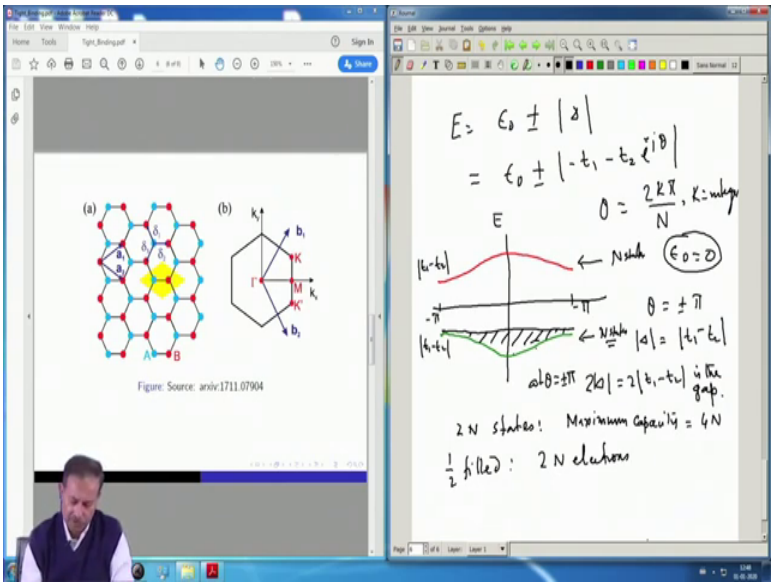

So, what are these Es? Es are extremely easy to calculate. So, let me just write down E equal to. So, the so this is obtained from epsilon naught plus minus delta, where delta is remember this e to the power I theta and minus i theta where there, so the I wrote a mod here plus minus mod of minus t 1 minus t 2 e to the power i theta, ok. I can write plus i theta minus i, ok. So, this is the equation that I, that is all I need to calculate and. So, this is what does this tell me? It tells me that now I have a spectrum which looks like that.

So, see this is the mod of this you have to calculate, ok. So, the spectrum if you do that it will look like this. Remember theta is again by periodic boundary condition to some k pi by n and that k, I will k will be integer. Again from the Brillouin zone is minus pi by a minus pi a was taken to be 1 so, minus pi to plus pi and you will find that you have two energy bands because of this plus minus you have two solutions, one is this and the other is this. So, these are the E plus and E minus solutions.

As you can easily check for yourself that at theta equal to plus minus pi at this ends two ends of the Brillouin zone is your value of delta is basically t 1 plus t 2, sorry t 1 minus t 2 sorry. So, this is t 1 minus t 2, this is also t 1 minus t 2. So, there is a gap which is 2 delta equal to at that point the gap is, so, let me write at theta equal to plus minus pi 2 delta is equal to t 1 minus t 2 into 2 is the gap. The gap is much higher at this point of course.

Now, the interesting thing about this calculation is that now what you have is that there are you started with two atoms per unit cell. So, there are two n states, we started from each of these bands this one and this one contain contains n number of states. Now, how many electrons do you want to put in? So, in case for example, in the half filled system if you have two n number of atoms then half-filled means you can put in 2 n electrons.

So, maximum number of electrons you can put in maximum capacity is 4 n, right because each of these states we can accommodate two electrons, but at half-filling we are going to only put half of that, so 2 n electrons. Basically, one electron per site per orbital is what makes it two, two makes it 2 n electrons which is half-filled. So, in this case what will happen?

Well, you will you will start putting states in this green band in the lower band which is like an anti-bonding band here which is like a bonding band here that it is like an anti-bonding band and these two this green band gets completely filled up if you are at half-filling because it accommodates n number of states n here, n states here n states here. So, these n states will get filled up if you have half-filled system and that is what we will we one does for grapheme. And so, once this is filled up now you can see that this is, so you do not to confuse this with graphene in the sense that this band does not represent the band of bands of graphene. This is the k the system that we have just hypothetically took with two electron two atoms per unit cell. We will come to graphene soon.

So, then this one, so this band these two bands have a gap that gap is minimum gap is at the zone boundary and for the boundary of the first Brillouin zone and that is still a finite value which is twice t 1 minus t 2. If that is the case then what will happen? You will fill up at half-filling you will fill up this band completely the green band. And, the next available state is at a gap of this value two t 1 minus t 2 mod of t 1 minus t 2. So, since t 1 t 2 are real, I chose them to be real, so it is just 2 t 1 minus t 2.

Now, that gap that value mean is a finite value unless t 1 is equal to t 2, and if that value is finite then of course, then there is a gap; that means, you are you have an insulating system, ok. So, and there is of another thing that has happened. He said there is a large amount of energy gained because this the lower band has come down from the 0 energy level or this is epsilon naught is taken to be 0 here in this picture. So, I have said epsilon naught equal to 0.

So, this set of states n states have come down below 0 and a set of states have gone above 0 and since you are filling up only the lower band, then your you have actually gained a lot of energy. Because remember to start with we you had every electron at epsilon naught energy, now by forming the band you have gained a lot of energy which is every electron is gaining t 1 minus t 2 amount of energy at least if not more because the band has a width and so this huge amount of energy that this system gains in this by forming these bands.

So, that is an interesting thing. And that is why the system the electrons will form a band and they will try to delocalize and move from one atom one site to another, more or less try to be free as free as possible, ok. So, in the next lecture I will show you what does this mean. It means actually that there is an instability of the Fermi [surface], it can lead to an instability of the Fermi surface which is interesting, but before that we will discuss the; I will come back to it, but off before this I will discuss the band structure of graphene and how to get the band structure because this is just one more step to get to graphene's band structure.