Electronic Theory of Solids
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Lecture - 17
Tight binding: lattice with a basis

Hello we have been discussing the consequences of Bloch's theorem and we showed that Bloch's theorem makes life extremely simple for us in making the wave function obey certain symmetries. And, it is just that the lattice translation symmetry gives us the nature or wave function that you should choose for a solution.

Now, we on the basis of that we did this the, we did a proof of the theorem and we showed that you need to show a need to calculate the energy only in the region of the of a reciprocal lattice which is called the first Brillouin zone. And, then rest of it can be obtainable is obtainable from that one that spectrum in that region, but just translation of a reciprocal lattice vector.

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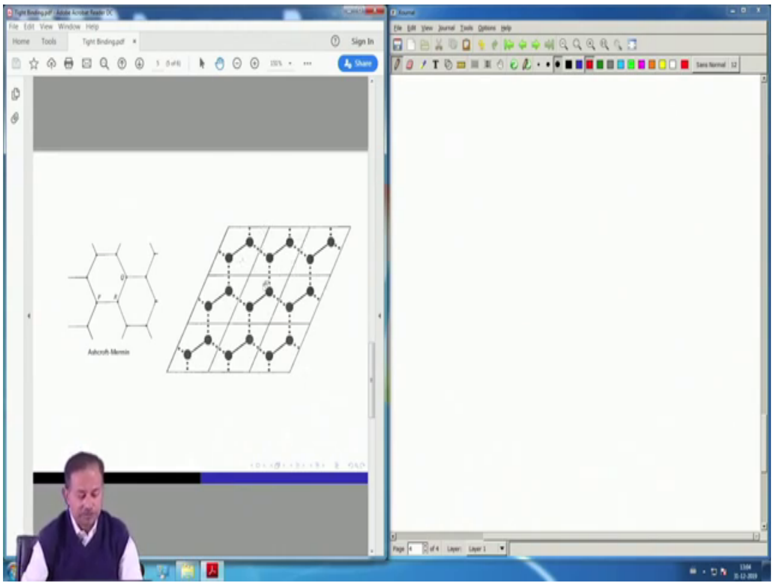

Now, there is this other interesting thing that I mentioned that the this is called the hexagonal lattice which is not a Bravais lattice. But, as I said the previous day that the this lattice of course, you can see that this point P and R are not equivalent you can just check it that P has a point here on the left hand side, upper left hand side whereas, R has no point at the center of this hexagon.

Had it had a point been there at this center then of course, P and R would be equivalent and the lattice would be a triangular lattice or a hexagonal lattice or as I showed in my previous lecture. So; that means, that this is not a Bravais lattice, but we can still work with it. The way to do it is to find out a unit cell such that this new unit cell with two atom basis becomes a Bravais lattice.

So, the choice of unit cell is also not unique in that in the sense that I here for example, I have this region this parallelepiped is the, this is the unit cell.

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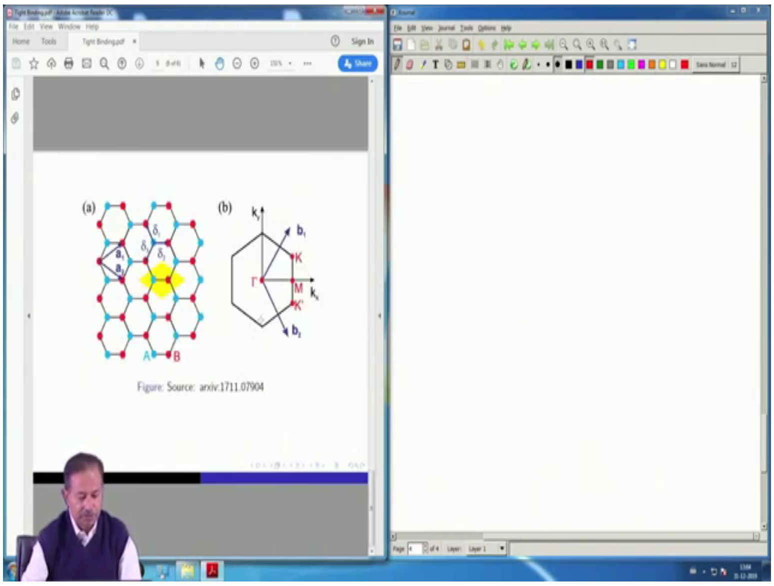

Figure: Source: arxiv:1711.07904

So, for example I can choose the unit cell in this way also the yellow region here. So, these red and blue are the two inequivalent sites, although both of in graphene for example, both of them are carbon these sites are inequivalent. As I said in the previous graph P and Q P and R are inequivalent whereas, P and Q are equivalent view from P and view from Q are identical whereas, V view from P and R are different.

So, this is why it is there are these two types of sites that has been the highlighted here by blue and red ok. Of course, then you choose a unit cell in such a way that both one blue and one red type of sites are incorporated in the unit cell. And, then you can repeat this unit cell to form a lattice and that is you can check for yourself this really gives a Bravais lattice.

Then choose a for example, the central point of every yellow region and then just add them and you will find it is a Bravais lattice. Now so, in this case there are this a 1 and a 2 are the two lattice vectors primitive lattice vector and delta 1, delta 2 and delta 3 are the nearest neighbor vector vectors from any site to its nearest neighbors..

One can then construct the reciprocal lattice and this is the first Brillouin zone is a hexagon again then this the central point as I say its gamma is basically k equal to 0 0 0 in two dimension. This point is along the x axis and this M point is gamma M is along x direction no change in k y whereas, gamma. So, gamma K for example, if you go in this direction of course, then you have to change both K x and K y.

Now, M K for example, is a vertical movement along this direction y K y direction ok. So, these are the K and K prime an inequivalent points in the Brillouin zone and so, one draws the energy spectrum within this Brillouin zone along certain symmetry reaction as I said. So, gamma M gamma K gamma K prime these are the directions in which one plots the energy spectrum and from that you can actually figure out the nature of the energy bands of this kind of a system, we will come to that at a later stage.

Because, this is called a lattice with a basis these kind of things can as I said these with a basis you can converted into a Bravais lattice. Then again the Bloch theorem will work and one should be able to derive the band structure for these kind of systems ok. Now that is what I will try to introduce you now as to how to do.

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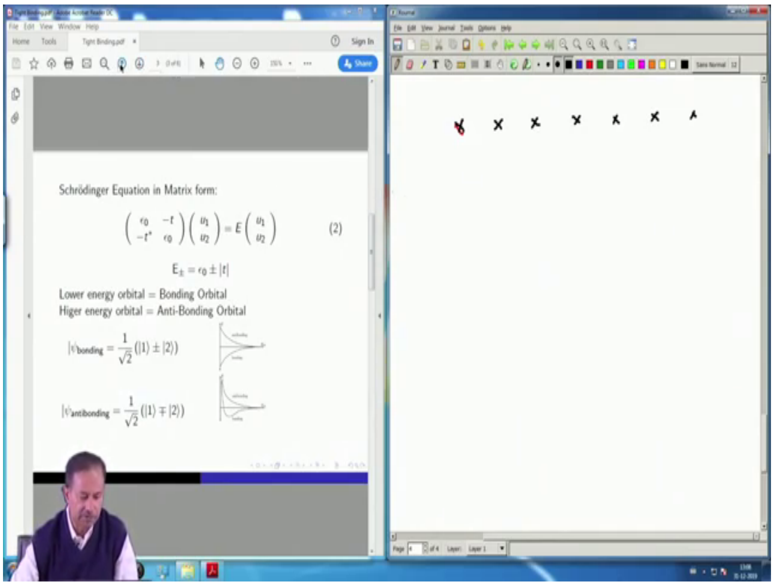

Schrödinger Equation in Matrix form:

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

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

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

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

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

So, remember your calculation for a hydrogen molecule and then I extended that calculation to include the for n number of atoms in still I still remained in one dimension, but that can be extended to any dimension if there is a periodic arrangement.

All you have to do is to change this vector which is a one dimensional vector here into a d dimensional vector if your lattice is in d dimension with appropriate Bravais lattice and corresponding primitive vectors ok. So this we I said was for this kind of situation our trail wave function remember we choose it our method was variational.

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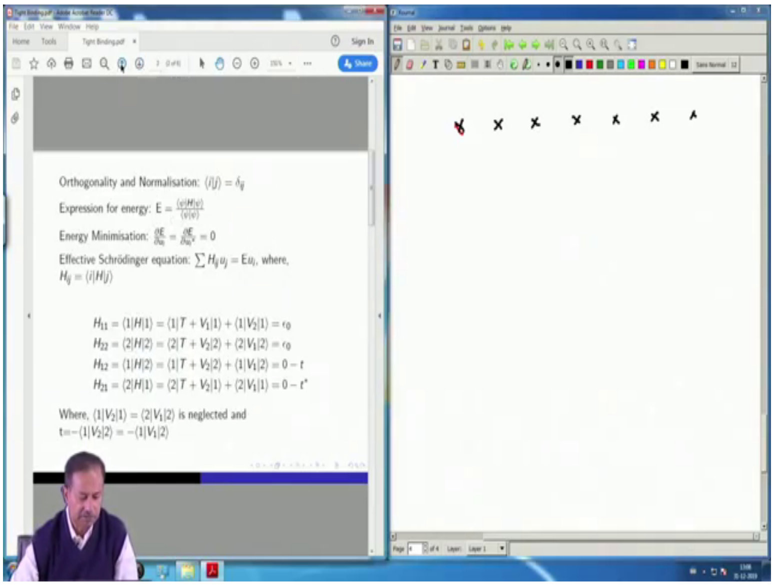

Orthogonality and Normalisation: $\langle i|j\rangle = \delta_{ij}$

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 $t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$

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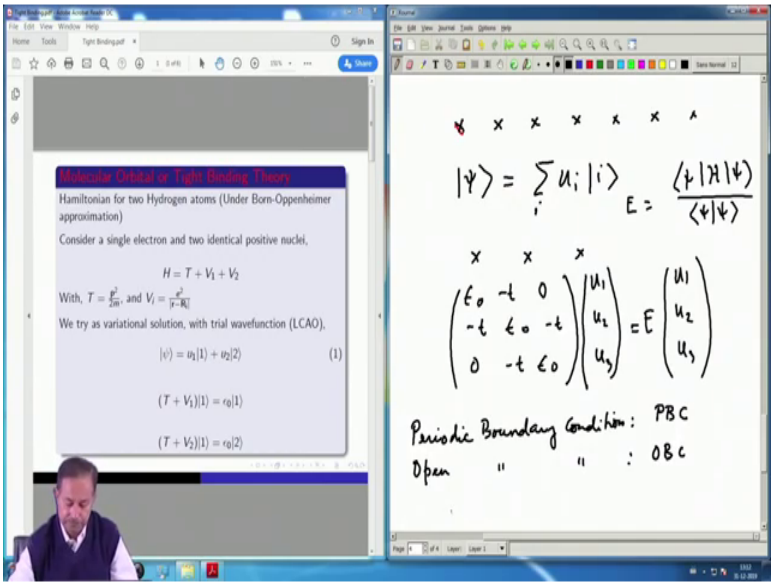

Molecular Orbital or Tight Binding Theory

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),

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

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

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

$$|\psi\rangle = \sum_i u_i |i\rangle \qquad E = \frac{\langle\psi|\mathcal{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

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

Periodic Boundary Condition : PBC
Open " " : OBC

So, the trial wave function we chose was here was u 1 plus u 2 into. So, here we will choose a trial wave function which is sum of our i u i i right and then what we showed is that for example, for a three side problem the matrix becomes epsilon naught epsilon naught epsilon naught and minus t minus t minus t minus t 0 and 0. So, this is the matrix for u 1, u 2 u for a three site problem and this is equal to E times u 1 u 2 u 3 ok.

So, this is basically the equation that you will get if you extremized with respect to u i's this energy variational energy which is E equal to psi H psi divided by psi psi. So, this is the procedure that you have done exactly what we did for two site problem, we can do it for three atom problem, we can go ahead and do it for four atom problem.

There what will happen is that you will have you have more zeros on this the there will be 0s, one more 0 on the second row, there will be two more, one more 0 on the third row so, that is how it will go upon. There is one interesting thing I mentioned in the previous lecture that there are two ways you can do this the, these problems one is a two different boundary conditions.

See one is called the Periodic Boundary Condition boundary condition often called PBC and this was used, remember in the in determining the Born-Oppenheimer boundary condition which is which was used to determine the values of allowed values of k when we found out the density of states.

There is another which is called the Open Boundary Condition which is OBC; and these two give slightly different results for a finite system and then those we will come back to at some point, but at the moment let us consider a very large system and therefore, we do not have to bother about the boundary condition right at the moment, but I will mostly use the periodic boundary condition. So, what does periodic boundary condition entail ok.

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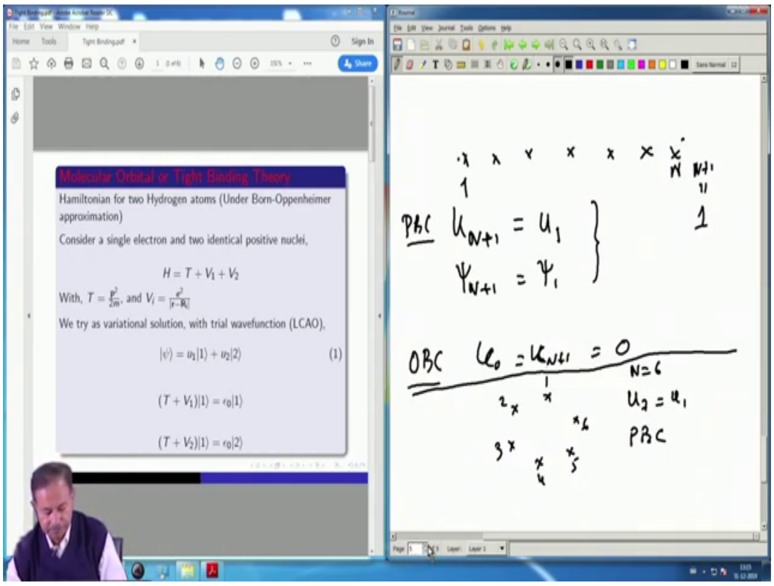

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$$(T + V_1)|1\rangle = \epsilon_0|1\rangle$$

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PBC $U_{N+1} = U_1$

$\Psi_{N+1} = \Psi_1$

OBC $U_0 = U_{N+1} = 0$

N = 6

$U_7 = U_1$

PBC

It basically means that you are using; for example, in one dimension its very simple in one dimension I just wrote this I drew this lattice, then periodic boundary condition means that the last lattice point has its nearest neighbor the first one as well. So, one has to be just fold this lattice.

So, this is N N plus 1 is the same as 1 so; that means, U of N plus 1 is equal to U of 1 in this in this way of doing things; that means, a psi at N plus 1 will be equal to psi at 1. So, let us just well I will use that one mostly. So, whereas, if you have this is PBC in open boundary condition of course, this is not true which means that in.

So, let me just show you what these gives. So, OBC remember that a beyond N there is nothing and before number 1 site number 1 there is nothing. So, C 0 equal to C N plus 1 sorry U 0 equal to U N plus 1 would give me 0 ok. Basically there is nothing beyond N and before 1.

So these are the boundary conditions and this is the one I will be using most of the cases one uses that boundary condition, but for as I said for finite system of course, one has to consider the OBC. See for example, in one dimension this PBC basically means that you will you have this kind of a geometry. So, these are six points 1, 2, 3, 4, 5, 6 then um. So, N capital N equal to 6, then the N the U 7 is same as U 1.

So, that is the periodic boundary condition. So, this in; so, this is the periodic boundary condition in PBC you basically has to convert the one dimension one dimension linear chain to a ring. So, that that just gives the periodic boundary condition.

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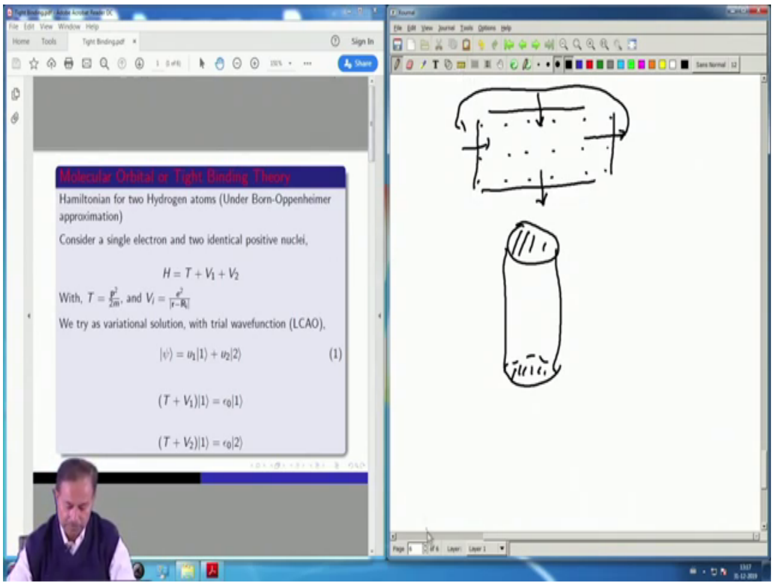

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$$|\psi\rangle = \alpha_1|1\rangle + \alpha_2|2\rangle \quad (1)$$

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

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

In two dimension of course, the scheme the this can also be done for example, for a for a square lattice or a lattice which is like this, let me just do it for these kind of a lattice. Now you have to align this with this boundary these two boundaries have to be aligned and these two boundaries have to be aligned folded. So, if you fold it once from say if you fold this then you will make a ring make a tube ok.

Now, if you fold it again; that means, this the top surface has to join the bottom surface, then it becomes a torus. So, that is the standard practice of doing it in three again two dimension in three dimension of course, the structure is you cannot think about the structure physically, but this is a general procedure by which one goes about doing writing down the periodic boundary condition. So, in two up to two dimension if these possible to show it geometrically; beyond that you have to imagine that each surfaces have been tied together ok.

So, that means, an electron going out of this basically enters this site and electron and going out from this bottom surface is basically entering through the top surface. So, that is that is basically what it means indicative boundary condition.

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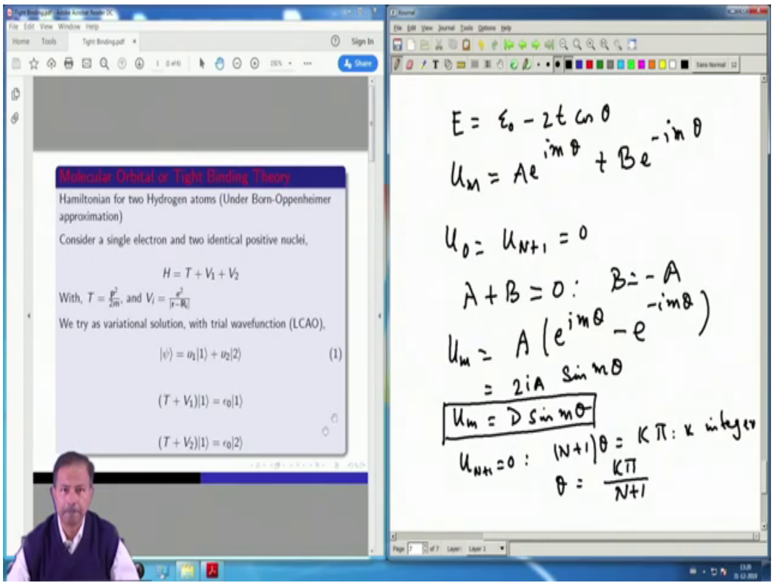

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$$E = \epsilon_0 - 2t \cos\theta$$

$$u_m = Ae^{im\theta} + Be^{-im\theta}$$

$$u_0 = u_{N+1} = 0$$

$$A + B = 0 : \quad B = -A$$

$$u_m = A\left(e^{im\theta} - e^{-im\theta}\right)$$

$$= 2iA \sin m\theta$$

$$\boxed{u_m = D \sin m\theta}$$

$$u_{N+1} = 0 : \quad (N+1)\theta = K\pi : K \text{ integer}$$

$$\theta = \frac{K\pi}{N+1}$$

So, let me just digress a little bit about the solution remember the solution that we got was E equal to epsilon 0 minus twice t cosine theta. Now this theta we said that we will determine theta from the boundary condition. And so, let us look at the just for a simple case let us look at the open boundary condition.

So, in this case for example, our remember our solution; the solution was U of m at the mth site was A e to the power i m theta, I can also add the minus e to the power i m theta ok. So, this is the general solution for the for use of m and it obeys the. So, we will show the condition the boundary condition that leads to the chosen values of theta ok. So, let us just put this boundary condition that uu U of 0 equal to U of N plus 1 equal to 0.

So, C 0; that means, U 0. So, U 0 is A plus B that has to be equal to 0. So, B equal to minus A, So, the u sub m is A e to the power i m theta minus e to the power minus i m theta. So, twice i times A sin of m theta which I can write as just D sin m theta.

So this is my solution. Now I also know that U of N plus 1 equal to 0 which immediately tells me that N plus 1 into theta has to be equal to K pi where the K is an integer K is integer ok; that means, theta equal to K pi by N plus 1.

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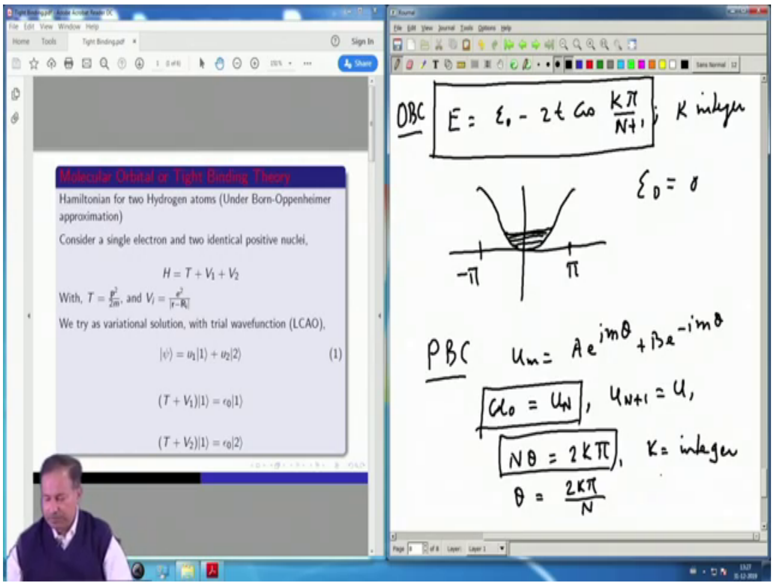

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$$(T + V_1)|1\rangle = \epsilon_0|1\rangle$$

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

OBC $\boxed{E = \epsilon_0 - 2t\cos\frac{K\pi}{N+1}}$; K integer

$\epsilon_0 = 0$

PBC $u_m = Ae^{im\theta} + Be^{-im\theta}$

$\boxed{u_0 = u_N}$, $u_{N+1} = u_1$

$\boxed{N\theta = 2K\pi}$, K = integer

$\theta = \frac{2K\pi}{N}$

So, the solution therefore, is E equal to epsilon naught minus 2 t cosine K pi by N plus 1 ok; 2 minus 2 t cos K pi by N plus 1 and K being integer. So this immediately identify as the values of the energies within the now we can choose the Brillouin zone first Brillouin zone the k values the integer values are to be chosen in such way that you in one dimension for example, the Brillouin zone is from minus pi by a to. So, remember I took a equal to 1. So, if I have to put a now if I want to put it, put a in it I will just multiply K into change K to K in to a. So, a was taken to be 1.

So, in that unit I can actually drop this a here and my Brillouin zone is from minus pi to plus pi and all I will have to do is to choose values of k within this range. So, the spectrum is a. So, suppose epsilon naught is 0, then the spectrum is minus 2 t cos of this. So, which is a cosine kind of spectrum ok. So, it is a cosine spectrum generally looks like this and it is restricted between minus pi and plus pi.

Remember another thing that for very low values of k for values of k which is much much lower than capital N capital, N is huge, you actually restore cosine function is like a cosine theta can be expanded as 1 minus theta squared by 2, and its again a k square spectrum. So, at low case for very close to the gamma point where the at the bottom of the energy band, you will have the spectrum which looks still like a free particle.

So, if you have a very low density of electrons when you are only filling up to this part, then your field only up to say this then the spectrum is very much like a free electron spectrum. The changes happen at a bit larger k which means that a for very low k values or very low density of electrons, you can treat this spectrum as a free particle spectrum.

Remember the energy zero of energy can be chosen as per your wish, as per your convenience. So, one can actually subtract any constant part from the energy, it just moves the entire energy band up and down. So, choosing epsilon is equal to 0 is not a not anything wrong one can always subtract out a constant total energy from the from the energy constant value from the total energy, because the entire spectrum just moves up and down by addition of a constant.

So, it really does not matter if you if your intention is to calculate the derivative and higher derivatives of the energy and plotting the energy. So, you can shift the 0 as per your wish and then absorb this epsilon naught in that shift and make it 0. So, this is the this is what open boundary condition for example, it gives, I will come back to the periodic boundary condition, I actually can leave it as a problem for you to do.

For PBC so, all you have to do is you have to choose take the solution as U m equal to e to the power i m theta again and or plus B e to the power minus i m theta and. So, what you have to do is you have to choose u 0 equal to U N and U N plus 1 equal to U 1. So, these are the conditions you apply, you only basically. You use this C this condition will give you the energy spectrum and the spectrum will be such that N times theta equal to twice K times pi; where K is integer again.

So, then theta equal to 2 K pi by N; you can easily see this right U 0 is m equal to 0 put m equal to 0, then put m equal to n and just that will give you n theta equal to 2 K pi. They have to be equal and so, that that leads to this boundary condition to this condition that n theta equal to 2 K pi.

So, this is a; so, this is what; so, this is OBC and this is PBC ok. For very large lattice of course, this distinction is very small, but for finite lattice is there is a distinction you can you can actually check for yourself by plotting in a computer just go ahead and plot these two energy spectrum for take say N equal to 6 or 8 or 10 and then plot this energy levels..

Do two things take first N equal to even and also N equal to odd and in both cases plot for with OBC and PBC and see how the energy spectrum looks like ok. So, that will be a very beautiful exercise for you to do and see that the difference on a finite in a finite size system.

Of course, if you go to the infinite size system these differences do not matter much and spacing between two energy levels is so, small that they are you will have 10 to the power 23 energy levels within a distance of as I said the previous day the bandwidth for example, in this case is from.

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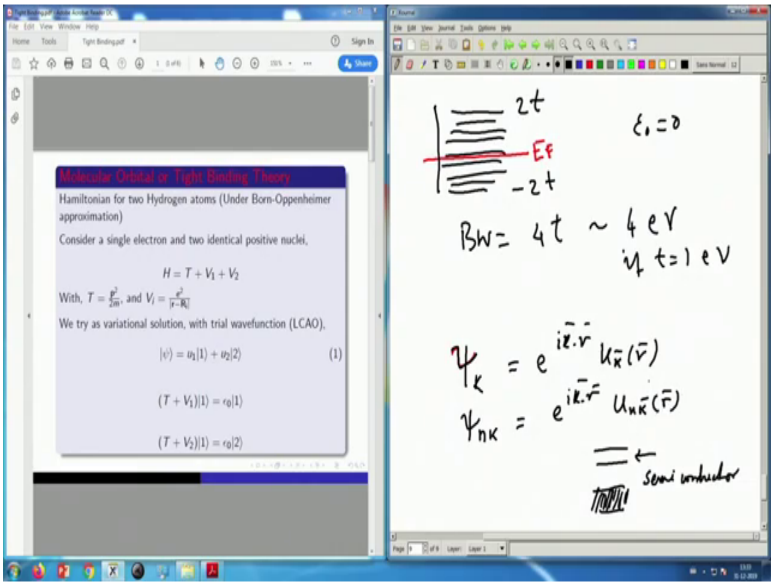

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$$(T + V_1)|1\rangle = \epsilon_0|1\rangle$$

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

$\epsilon_0 = 0$

$BW = 4t \sim 4\,eV$

if $t = 1\,eV$

$$\psi_k = e^{i\bar{k}\cdot\bar{r}}\,u_{\bar{k}}(\bar{r})$$

$$\psi_{nk} = e^{i\bar{k}\cdot\bar{r}}\,u_{n\bar{k}}(\bar{r})$$

So, again epsilon naught equal to 0 I am setting. So, from plus 2 t to minus 2 t; so the bandwidth is 4 times t. Now, typical values of p in a material is about maybe half an electron volt to 0.1 electron volt to maximum 1 electron volt and so on; so, this could be say.

So, even at the high energy level a high value of t say 4 e v for example, if I take if t is equal to 1 equal to 1 V and this bandwidth is to be divided by 10 to the power 23 to find the number of states right. So, you can imagine what the there are 10 to the power 23 states to be accommodated within these two values plus 2 t and minus 2 2 t. So, you can imagine how close these energy levels are.

And, that is again I said that if you have a feeling which is somewhere if you filled up only up to this suppose your e f is here then by this argument that there are so, large energy so, many energy levels and they are so, close to each other you can realize that this is almost a gapless spectrum. Above e f there is there is another energy level we did not an extremely small proximity. So, that means that there is almost no gap.

On the other hand for a discrete system of course, suppose you had a 6 atoms of course, you had you put 6 suppose you put 6 electrons it will be exactly at the middle and there will be a gap for the next level. So, the gap will be basically the discreteness of the number of the system.

So, it is so, a finite size system the system is discrete and finite in that case you will have a band gap means of by necessity, because the energy levels are spaced from each other. In a gap of 4 t in a in a range of 4 t you will have to place only 6 states and you know how to place them because of this theta values that I have just the calculated in the open and periodic boundary condition.

In the open boundary condition you can just check that there are there will be gaps between states. So, a finite size system has a gap simply because of quantum mechanics and for infinite system of course, that gap is exceedingly small and one treats them as gapless. So, if you have your Fermi level somewhere inside the band not at the top, then of course, you will have a metallic system which means there is no gap at the Fermi level.

The one other thing is that in some books you will find that psi is written as psi n the solution psi that I wrote for Bloch in the Bloch theorem psi K equal to e to the power i k dot r U k of r, there is a another index n added. So, some books use n k this basically means that.

So, that will be you is your i k dot r U of n k of r. This n basically signifies that in plane terms if you have say multiple orbitals for example, if you are dealing with an atom which has multiple orbitals occupied then these inter orbital interactions maybe small. Or, if they are a there is a finite interorbital excitation, then you have to diagonalize a matrix which is not only just these number of sites, its dimension will be number of sites into the number of orbitals because each site will contribute say you are a dealing with one s and 2 p the. So, each site will contribute two orbital.

So, this n index then denotes how many orbitals were originally involved per site and appropriately you will have one band and then above that you will have. So, you will have one set of bands then you will have another set of bands and. So, this is suppose this band is completely full, then you will have a gap and then this band is empty. So, this is a case of a semiconductor.

So, n index basically tells you how many bands you will form. For in this example that I we worked out there was only one orbital considered per atom. So, we had only one band. So, see the band can be either full or less than full these here for example, if you had two orbitals considered you will have two bands coming out of them and then of course, you can have the situation that you are first the lower band is completely full and then there is a gap and then you have a upper band which is empty.

So, that is the recipe for having a semiconductor or an insulator. So, this n index basically tells you how many bands you are dealing with how many states you started with originally and per atom or per unit cell and then you will have to keep that index in your solution. But, it is just a additional bookkeeping nothing more than that, there are the matrix dimension is larger and you have to diagonalize that matrix again in the same way and you will get the solutions of.

And, then you will get various bands, you can have 1, 2, 3, 4 and multiple bands in a system which has large number of atoms in its unit cell and large number of orbitals involved in it ok. So, that is how the band structure works.