Introduction to Solid State Physics
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Lecture - 64
Bloch wavefunction as a linear combination of atomic orbitals
Tight Binding model -I

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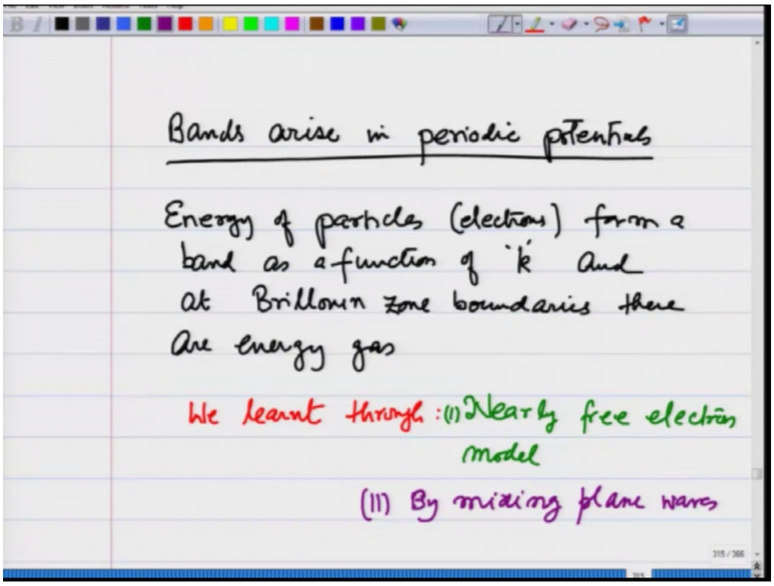

Bands arise in periodic potentials

Energy of particles (electrons) form a band as a function of 'k' and at Brillouin zone boundaries there are energy gas

We learnt through: (I) Nearly free electron model

(II) By mixing plane waves

So, let us see what we have done so far. So, far we have been focusing on how energy bands arise in periodic potentials. I mean; what it means is when particles move in periodic potentials how they go in an energy band. So, that what it means is energy of particles; in particular we are talking about semiconductors metals. So, these particles are electrons form a band as a function of k quantum number which specifies the state it gives you the wave function.

And at Brillouin zone boundaries, there are energy gaps in these bands. So, there is will be one band, second band, third band and so on and all this we learnt through I nearly free electron model and II . So, let me call the previous one I and II by mixing plain waves many of them and you have mixed three of them in one of the assignment problems and where we did not even have the potential to be (Refer Time: 02:25) . So, nearly free electron model works for weak potentials and we showed how energy gap arises an otherwise continuous energy curve and when we mix plane waves when a strong field, we also saw how bands arise.

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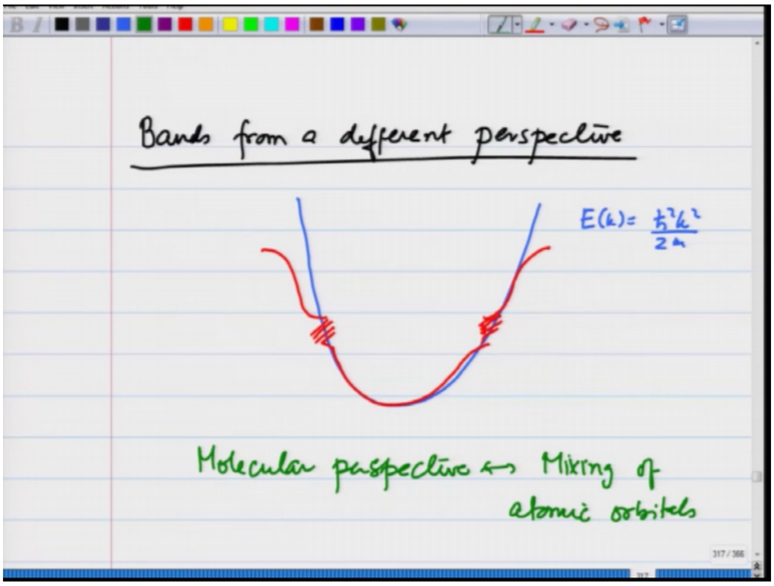

Bands from a different perspective

$E(k) = \frac{\hbar^2 k^2}{2m}$

Molecular perspective ↔ Mixing of atomic orbitals

In this lecture I am going to take a different perspective. Bands from a different perspective, this is important because you should be able to see how bands arise from many many different points of views. So, earlier view was that we had a you know electrons moving freely and then we turned on the perturbation; weak perturbation and that gave rise to band in a otherwise continuous energy structure E k which was h cross square k square over 2 m. In this, we got a continuous energy structure and then there was a gap and so on. So, this was the gap and then we made the potential strong and then we mix more and more and more plane waves and the band structure rows.

Now the different perspective is going to be molecular perspective and that brings us to mixing of atomic orbitals. So, this is in contrast to what we did in the previous approach and that is why I kept repeating myself over the previous approach. In the previous approach, the electrons were free and then they started interacting through then started interacting with this background periodic potential and that started breaking the energy continuous energy structure.

In this atomic orbital picture, we are going to start from the atomic level; that means, the electrons are going to be bound in the electrons. It is opposite of what happened in free electron or nearly free electron model or when we mix plane waves; plane waves means free electrons. In the molecular perspective or mixing of atomic orbitals, we are going to go the other way and atoms have these electrons bound to them and when we bring them together, the electrons are going to get delocalized. In the previous case electrons were already delocalized. In this case electrons are going to be bound in the atoms and they able to get delocalized.

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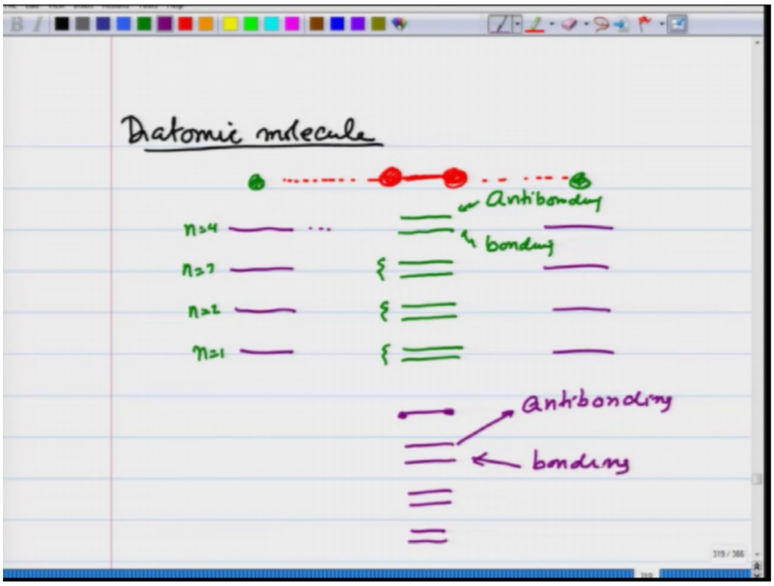

So, let us see what we do. Let us build it up; let us start with a diatomic molecule and see what happens there. If I have two atoms, let us take homogeneous atoms. They have these energy levels; let us make four of them. And when they are brought together, let us bring them close together to form a molecule, but this is the molecule. What happens to these energy levels? They come and form molecular orbitals.

So, I am going to have molecular orbitals corresponding to each level. To start with I had two levels for each n; n equals 1, let us say n equals 2, n equals 3, n equals 4 and I still have two levels for each except that they have gotten split. Why do they split? They split because now the potential has changed and if you recall your chemistry the upper level is called the anti bonding level, the lower level is called bonding level right. So, let me write it here anti bonding and this one is bonding for each one of these. So, let me form this molecule now right and then the levels are like this split right; anti bonding and lower one is bonding.

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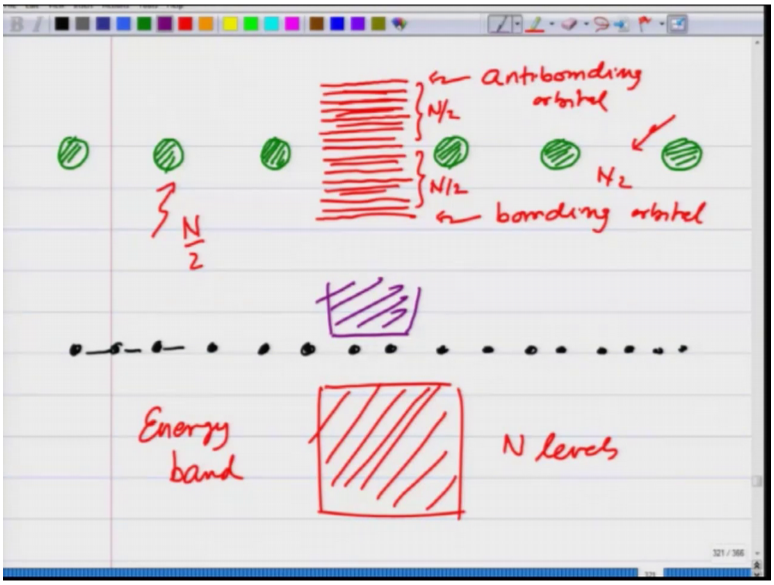

So, when I make this here is my atom here is my atom and I have level I will focus on one particular n equals 1 and n equals 2 level and I have gotten here the anti bonding orbital and here I have got bonding orbital. These are called bonding and anti bonding because when the molecule is formed the bonding orbital energy has gotten lower and the antibonding has gotten higher.

Now, let us bring in two more atoms. Their levels will also split; however, they will not split as much as the ones which are closer. So, they will probably go here. Let us bring in two more atoms their levels are also split; however, they will go little low on splitting and so on. So, as I bring more and more and more atoms together, I am going to have these levels all over. And if these let us say number of atoms on the left is N by 2 on the right is N by 2, I will have N by 2 levels going up N by 2 levels going down. So, the picture I have now is that I have these atoms forming a crystal and their levels now mix and form a continuous distribution of energy. If there are N atoms, these are N levels which I am going to call an energy band.

Remember this picture now is, on the other extreme of the free electron picture. In free electron picture already all the electrons made a band meanings they had continuous energy and then when we introduced a weak potential. There appeared gaps in that energy and each distribution before a gap formed a band. In the atomic picture these atoms had electrons localized on them and when we brought them close together because of the change in the potential the electrons has started getting delocalized and their levels spread and they formed a band. Obviously, then the next excited state will form another band, next exercise a will form another band; so, this is another way of looking at the band picture the atomic levels mix and form bands.

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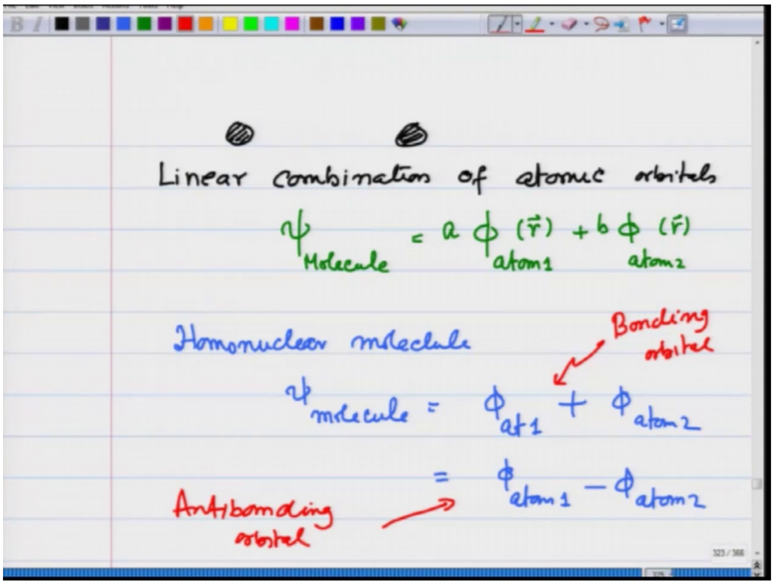

Linear combination of atomic orbitals

$$\psi_{Molecule} = a\,\phi_{atom1}(\vec{r}) + b\,\phi_{atom2}(\vec{r})$$

Homonuclear molecule

Bonding orbital

$$\psi_{molecule} = \phi_{at1} + \phi_{atom2}$$

$$= \phi_{atom1} - \phi_{atom2}$$

Antibonding orbital

Now, what have we done here is if you look at the molecular picture, there is two atoms right. In this case, the very first approximation that one makes is what is called as linear combination of atomic orbitals. In that the molecular orbital, psi molecule is written as the orbital of atom 1 r plus orbital of atom 2 r. Let me write coefficients a and b in front of them and you find a and b such that the total energy is minimized and a know; obviously, a and b also related by normalization relationship.

Now, if it is a homo nuclear molecule in that case, I can write a and b to be equal and sorry molecule becomes phi atom 1 plus phi atom 2 and another possibility arises where I could have phi atom 1 minus phi atom 2. And if you recall from your chemistry this plus sign forms the bonding orbital and the minus sign 1 forms the anti bonding orbital.

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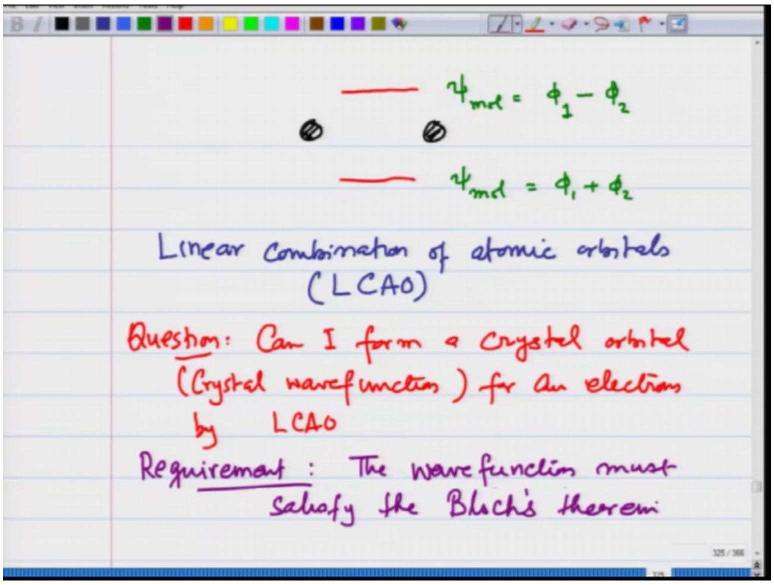

$\psi_{mol} = \phi_1 - \phi_2$

$\psi_{mol} = \phi_1 + \phi_2$

Linear Combination of atomic orbitals (LCAO)

Question: Can I form a crystal orbital (Crystal wavefunction) for an electron by LCAO

Requirement: The wavefunction must satisfy the Bloch's theorem

So, what we have is now, that we have this diatomic molecule. I have energy level up here, energy level down here and this forms the molecular orbital equals phi 1 minus phi 2 and the lower one forms a molecular orbital phi 1 plus phi 2 and the levels get split in the energy. Can I do similar thing in a crystal? So, this is this method we call the linear combination of atomic orbitals or in short LCAO.

So, the question I am asking is should I ignore the [FL] question I am asking now is can I do LCAO for a crystal also where many of these atoms are sitting, can I form a linear combination of atomic orbitals? So, question is can I form a crystal orbital that is the crystal wavefunction for an electron right by LCAO. And keep in mind one requirement would be the wave function must satisfy the Blach's theorem and the answer to this question is, yes.

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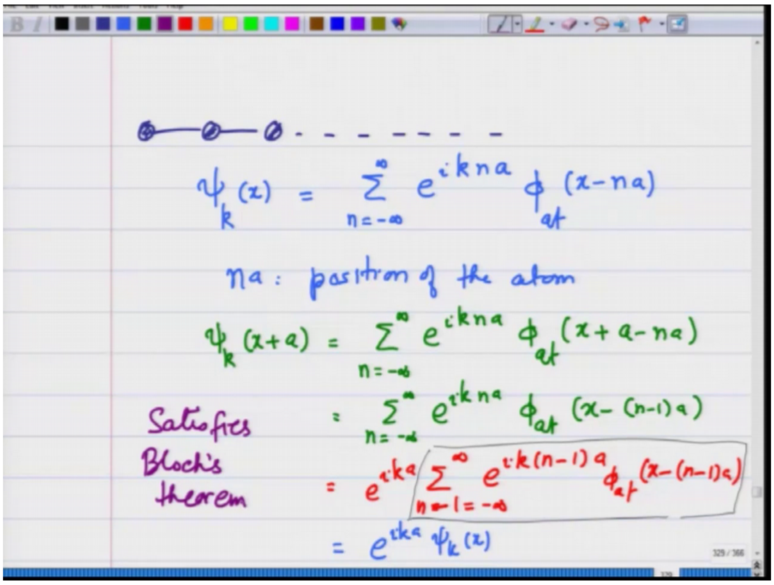

$$\psi_k(x) = \sum_{n=-\infty}^{\infty} e^{ikna} \phi_{at}(x-na)$$

na : position of the atom

$$\psi_k(x+a) = \sum_{n=-\infty}^{\infty} e^{ikna} \phi_{at}(x+a-na)$$

Satisfies Bloch's theorem

$$= \sum_{n=-\infty}^{\infty} e^{ikna} \phi_{at}(x-(n-1)a)$$

$$= e^{ika} \boxed{\sum_{n-1=-\infty}^{\infty} e^{ik(n-1)a} \phi_{at}(x-(n-1)a)}$$

$$= e^{ika} \psi_k(x)$$

So, if I take this collection of atoms the wave function psi k x that I form is equal to summation n equals minus infinity to infinity e raise to i k n a, the atomic orbital; I am writing as phi a t x minus na where na is the position of the atom. Let us take psi k x plus a to check whether it satisfies the Blach's theorem or not.

So, it will be n equals minus infinity to infinity e raised to i k na phi atomic x plus a minus na which I can write as summation n equals minus infinity to infinity e raised to i k na phi atomic x minus n minus 1 a; which I can further write as e raised to i k a summation n minus 1 equals minus infinity to plus infinity e raise to i kn minus 1 a phi atomic x minus n minus 1 a. This summation, since the summation extends from minus infinity to plus infinity is again psi k x and therefore, I get e is equal to e raise to i k a psi k x. So, I can easily write that this satisfies Bloch's theorem.

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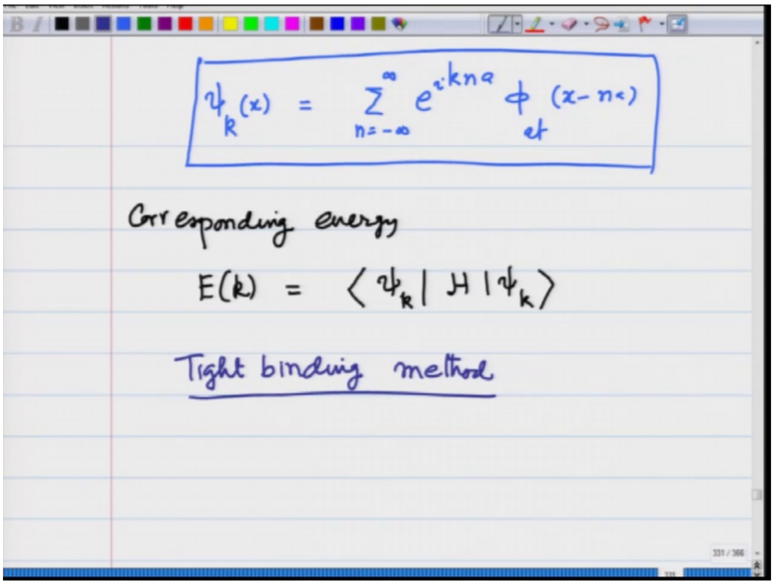

$$\boxed{\psi_k(x) = \sum_{n=-\infty}^{\infty} e^{ikna} \phi_{at}(x-na)}$$

Corresponding energy

$$E(k) = \langle \psi_k | H | \psi_k \rangle$$

Tight binding method

So, I formed the wavefunction for a particle moving in a crystal; right now I am writing only a one dimensional form as summation n equals minus infinity to infinity e raise to i k na phi atomic x minus na, by using linear combination of atomic orbitals. This is an approximate wave function I am not solve the Schrodinger equation and if I want to calculate the corresponding energy E k, it will be given as the expectation value of the Hamiltonian of the crystal with respect to the psi k Hamiltonian psi k.

When we calculate this expectation value with this LCAO wave function, we make certain approximations and this method is known as the tight binding method. As the name suggests, we are starting from the extreme where the electrons were tightly bound to each atom and become delocalized as a result of the Hamiltonian changing when the atoms are brought close together and it is the opposite end of the spectrum of where we chose the electrons to be free to start with and then they started forming Bloch waves when the weak periodic potential was introduced.