Solid State Physics
Lecture 18
Covalent crystals: Linear Combination of Atomic Orbitals

Hello. We have already discussed about ionic bonds in solid, now we are going to discuss about the Covalent bonds. (Refer Slide Time: 00:36)

So, what are the covalent bonds? Where do we find covalent bonds? The covalent bond is formed by sharing electrons between two atoms and this is found in many molecules and many solids. For example, in case of hydrogen molecule we have H_2. So, two hydrogen atoms come close to each other, each hydrogen atom has 1 proton and 1 electron and those electrons are shared between both atoms to form this H_2 molecule. Now, why is this electron shared and why that helps forming a molecule that means, lowering the energy of the entire system? That is something we need to understand. Similar example is nitrogen molecule, oxygen molecule or for example, solid form of carbon say graphite or diamond whatever, diamond is a good example. So, here the bond between two carbon atoms is so strong that it is comparable to that of sodium chloride. That means, the bond of a covalent compound is quite strong; it is not at all weak. There is no electrostatic interaction just by sharing electrons; they form this kind of a strong bond in few cases, not always. But the bond is in general quite strong. Always the bond is quite strong; where, diamond is one of the highest strength examples. That is what we can say. Now, we want to understand how this electron is shared these electrons are shared and how that lowers the energy of the entire system. So, we want to understand covalent bonding in terms of mathematics. So, then, we need to form a model. For simplicity, instead of a solid, let us consider a homonuclear diatomic molecule. Whatever physics we understand for this is valid for the solid as well; but for solid this analysis would be a bit cumbersome. So, in order to avoid that, we analyze the homonuclear diatomic molecule and we will have that insight that can be used in solid as well. So, let us consider for the simplicity, the simplest homonuclear diatomic molecule that is H_2 molecule. And, can we solve the corresponding Schrodinger equation to find the quantum states? If we write down the Schrodinger equation, then there would be along with other terms repulsion between two electrons, the Coulomb repulsion between two electrons and that is going to make our life miserable actually. So, we cannot really calculate that rather we can do a linear combination of atomic orbitals and try to develop a useful insight into the problem. So, let us say ψ represents the molecular state. $|\psi\rangle$ is the electronic state one electron state base actually in the molecule. If we consider this, then we would need a basis to expand $|\psi\rangle$ and if we consider formation of H_2 molecule by bringing two hydrogen atoms close together. Then if we write $|1\rangle$, this state as the electronic state of the first hydrogen atom. And similarly, $|2\rangle$, this would be the electronic state of the second hydrogen atom and in this basis; we would like to expand $|\psi\rangle$. We can do a reasonable job with this representation. Now, these states $|1\rangle$ and $|2\rangle$, these correspond to isolated hydrogen atoms not the molecule and $|\psi\rangle$ corresponds to 1 electron state, but in the molecule. Since we are interested in the ground state of the molecule, we will assume that $|1\rangle$ and $|2\rangle$ these states are the ground states of the corresponding atom that is 1S states in case of hydrogen atom. And if the energy of these electrons in the hydrogen atom be represented as ϵ, so this is the energy, atomic energy of those electrons. If we have small h_1 and small h_2; small h. So, small h_1 and small h_2 are the Hamiltonian's of atom 1 and atom 2 we are putting small h because capital H is reserved for hydrogen, representing hydrogen. So, small h represents the Hamiltonian in this case. So, from our definition, we can write that $h_1|1\rangle = \epsilon_1$. Similarly, $h_2|2\rangle = \epsilon_2$. Now, we make two assumptions; in the first assumption, we assume that the two basis states $|1\rangle$ and $|2\rangle$, they form an adequate basis set in which the ground state of the molecule $|\psi\rangle$ can be expanded. So, you do not we are assuming that we do not need any other state to make the linear combination make the expansion for $|\psi\rangle$. That means, this set of $|1\rangle$ and $|2\rangle$, this gives us an adequate basis state basis set. This is our first assumption and the second assumption is that we assume $|1\rangle$ and $|2\rangle$ to be orthonormal. That means, if we have a state $\langle i|$ and $|j\rangle$, then the inner product between $\langle i|j\rangle$ them is δ_{ij}. This is the ortho-normality condition. So, for one and two we assume orthonormality condition.

With this assumption, our work becomes simpler and that is the reason, we make this assumption. Even without making this assumption, we can in principle solve the problem; but then, working it out would be more cumbersome ok. (Refer Slide Time: 09:24)

Now, making these two assumptions; from assumption 1, we can write $|\psi\rangle = C_1|1\rangle + C_2|2\rangle$ where C_1 and C_2 are coefficients to the basis states in general these are complex numbers. And from assumption 2, we can write C_1 because of orthonormality, it can be represented as $\langle 1|\psi\rangle$. Similarly, $C_2 = \langle 2|\psi\rangle$. From 1 and the orthonormality condition, you can easily understand that this would be the case. Now, we need to find $C_1,\ C_2$ and the energy eigenvalues of the molecule. So, the energy eigenvalues of the molecule, we write as E. That let us start with the time-independent Schrodinger equation. If the molecular Hamiltonian is small h, then $h|\psi\rangle = E|\psi\rangle$ this is the time independent Schrodinger equation for the molecule. And with the help of this expansion here, we can write that $h(C_1|1\rangle + C_2|2\rangle) = E(C_1|1\rangle + C_2|2\rangle)$, this is what we obtain. Now, if we want to solve this Schrodinger equation, we project this equation onto states $|1\rangle$ and $|2\rangle$. What do we mean by doing that? Consider this equation and take from the left side of bra state $\langle 1|$ and project this equation on to that and in the next step of bra state $\langle 2|$ and project this equation on to that. So, we do this $\langle 1|h(C_1|1\rangle + C_2|2\rangle) = \langle 1|E(C_1|1\rangle + C_2|2\rangle)$ and for $\langle 2|$, this is $\langle 2|h(C_1|1\rangle + C_2|2\rangle) = \langle 2|E(C_1|1\rangle + C_2|2\rangle)$. This is what we have. Now, if we have something like $|h|j\rangle$, we will denote this kind of a matrix element as h_{ij}. This is our convention to follow. (Refer Slide Time: 14:18)

With this, we can write the equations that we have found earlier as E_0C_1. Where did we get E_0 from? We will see that later. Let me write this first $E_0C_1 + h_{12}C_2 = EC_1$ and $h_{21}C_1 + E_0C_2 = EC_2$. So, we have used the orthonormality of the basis set to eliminate the other terms. So, this is all we have and we have considered $\langle 1|h|1\rangle$. This is $h_{11} = \langle 2|h|2\rangle = E_0$. So, here h is the molecular Hamiltonian, not the atomic Hamiltonian. So, this $E_0 \neq \epsilon$ and so, our h_{11} and h_{22}, these quantities are called the onsite matrix element. This operation is on one site, one hydrogen atom that is the reason, it is called onsite matrix element and h_{12}, h_{21}, these are hopping matrix elements. Why these are called hopping matrix elements? We will understand that later. So, this these equations that we have that may be represented in a matrix form and to determine the nontrivial solution for C_1 and C_2. We will need the secular determinant to be 0; that means, we will require $\begin{vmatrix} (E_0 - E) & h_{12} \\ h_{21} & (E_0 - E) \end{vmatrix} = 0$. And that means, we get a quadratic equation from this $E^2 - 2E_0E + {E_0}^2 - h_{12}h_{21} = 0$ and since the Hamiltonian is a Hermitian operator, we must have $h_{12} = h_{21}^*$. This is something we must have. Now, if we assume that we have considered only real orbitals, real atomic orbitals in this situation that is like 1S orbitals, then h_{12} becomes real and h_{21} also becomes real. So, $h_{21}^* = h_{21}$ itself which is equal to h_{12} and let us call that another real number β which would be handy for writing. So, the solution to this quadratic equation here would be one solution, we are calling $E_b = E_0 + \beta$ and the other solution $E_a = E_0 - \beta$. This is the solution for the eigenvalues. (Refer Slide Time: 18:24)

How about the eigenstates? The normalized state vector corresponding to E_b would be given as $|\psi_b\rangle$; b stands for bonding and a stands for antibonding. We will realize their meaning later on. So, $|\psi_b\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ and the one corresponding to E_a that is $|\psi_a\rangle$, $|\psi_a\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$.