Solid State Physics
Lecture 19
Electronic Tunneling in Covalent Bonds

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Now, let us find out whether β is a positive number or a negative number. So, the way we have defined β, it is h_{12} which is nothing but $\langle 1|h|2\rangle$. What is h? The Hamiltonian; the electronic Hamiltonian is given as $-\frac{\hbar^2}{2m}\nabla^2$, this is the kinetic energy plus potential energy due to two atoms; $V_1(\overrightarrow{r}) + V_2(\overrightarrow{r})$. Now, $V_1(\overrightarrow{r})$, what is this? This is the electrostatic potential of the nucleus in atom 1 and V_2 is the electrostatic potential for the nucleus in atom 2. So, if we try to find out $h_{12} = \langle 1| -\frac{\hbar^2}{2m}\nabla^2 + V_1(\overrightarrow{r}) + V_2(\overrightarrow{r})|2\rangle$; we will write this part first, V_2 would be separated. (Refer Slide Time: 02:40)

So, let us write it that way. If we separate V_2, that will give us $h_{12} = \langle 1| - \frac{\hbar^2}{2m}\nabla^2 + V_1(\overrightarrow{r})|2\rangle + \langle 1|V_2(\overrightarrow{r})|2\rangle$. Now, if we have this, then this part here this is the Hamiltonian part here is just the Atomic Hamiltonian for the first atom. And if that is the case, then it acting on the left side state $\langle 1|$ gives us $\langle 1|\epsilon$. So, this operation would give us $\langle 1|\epsilon|2\rangle$ and then. So, the inner product; ϵ is just a constant, it can be taken outside. So, it is an inner product of $\langle 1|2\rangle = 0$. So, the only non-zero term that we have is this one, this quantity $\langle 1|V_2(\overrightarrow{r})|2\rangle \neq 0$; that means, $h_{12} = \langle 1|V_2|2\rangle$. So, the potential V_2 is attractive because it is between electron; one electron and the nucleus from the other atom. This potential is attractive, therefore, it is negative and if it is negative, then β must be negative quantity; β cannot be positive. (Refer Slide Time: 04:37)

So, if we have β negative, then the molecular state $|\psi_b\rangle$, the bonding state, this bonding state has energy $E_0 + \beta$. So, this is less than E_0 and the corresponding symmetrical combination, so this one corresponds to the symmetrical combination $|1\rangle + |2\rangle$ normal before normalization constant times $|1\rangle + |2\rangle$ that kind of a state. So, if we try to plot the wave function and the charge density, we will get this kind of a plot. Here, we first plot the wave function. This is how the wave function would look and if we now plot the charge density that will look somewhat like this. So, you can see that there is some charge accumulated at in between 2 atoms. So, this is the nucleus of one atom, this is the nucleus of another atom and in the y axis, we have plotted $|\psi_b\rangle$ and ρ_b; in the x-axis, it is r. This is how it looks and this is called the bonding state. Let us look at the antibonding state now. The molecular states $|\psi_a\rangle$ that has energy $E_0 - \beta$; β is a negative quantity. So, this energy is greater than E_0 and it corresponds to anti-symmetric combination of the basis elements. If we try to similarly plot the wave function and the charge density, we will find the wave function is will look somewhat like this. Because, the one is there is a positive sign in front of one and negative sign in front of the other and the charge density cannot be negative because its mod square kind of a thing. Sorry, it is $|\psi_a\rangle$ and it is ρ_a which is $|\psi_a(r)|^2$. So, here in between, you do not have any charge density and this is the antibonding state. So, the bonding state leads to charge being accumulated in the region between the atoms and the antibonding has a cusp, there is no charge at the midpoint. Now, after analyzing this, we shall go through the analysis of hydrogen molecule all over again; but starting from a time dependent Schrodinger equation this time. Why do we do that? Once we do that the reasons would be very clear, this is very important and this let us understand the electron sharing in case of a covalent bond; exactly how the electron is shared, we have seen that in case of bonding, there is some charge density in between. But the electron sharing picture as a function of time is not clear to us and we cannot have something as a function of time, when we consider the time independent Schrodinger equation. If we consider the time dependent one, we will understand the physics as a function of time. So, let us go for that ok. (Refer Slide Time: 09:21)

So, let us first write down the time dependent Schrodinger equation. It can be written as $i\hbar\frac{\partial}{\partial t}|\psi\rangle = h|\psi\rangle$. And as we have represented expanded $|\psi\rangle$ earlier in the basis of $|1\rangle$ and $|2\rangle$, we can write $|\psi\rangle = C_1|1\rangle + C_2|2\rangle$ and if we put this expression of $|\psi\rangle$, we would get two coupled differential equations. What are those equations? We will get if by putting $|\psi\rangle$ into the differential into the time dependent Schrodinger equation, $i\hbar\frac{\partial}{\partial t}C_1(t) = h_{11}C_1 + h_{12}C_2$and $i\hbar\frac{\partial}{\partial t}C_2(t) = h_{21}C_1 + h_{22}C_2$. These equations have to be solved with some initial condition for C_1 and C_2. Now, you can note that C_1 and C_2, these are not constants; these are function of time. So, as before we write that $h_{11} = h_{22} = E_0$ and $h_{12} = h_{21} = \beta$ and we know this time that β must be negative. So, we have two first order differential equations. These two that we need to solve. We can start with a trial solution and we will need some initial condition, actually two initial conditions; one for C_1, one for C_2 in order to be able to solve these two coupled differential equations. So, first order differential equations with constant coefficient, it can be solved with exponential functions. So, let us try with exponential functions $C_1 = A_1e^{-i\omega t}$ and $C_2 = A_2e^{-i\omega t}$. Now, if we insert these expressions for C_1 and C_2 into these two coupled differential equations, then we would get ω corresponding to the bonding and antibonding case. So, for bonding ω would be $\omega_b = \frac{E_0+\beta}{\hbar}$ and ω_a antibonding $\omega_a = \frac{E_0-\beta}{\hbar}$. This is what we will find. (Refer Slide Time: 13:50)

And now, we need to find the solutions for C_1 and C_2. The solutions for C_1 and C_2 can be written as $C_1(t) = a\ \exp\left(-i\frac{E_0+\beta}{\hbar}t\right) +\ b\ \exp\left(-i\frac{E_0-\beta}{\hbar}t\right)$; a is a new constant does not matter. Similarly, $C_2(t) = a\ \exp\left(-i\frac{E_0+\beta}{\hbar}t\right) -\ b\ \exp\left(-i\frac{E_0-\beta}{\hbar}t\right)$; where, a and b are arbitrary constants so far subject to some initial condition, we can determine the values of a and b. Suppose, we have an initial condition, where at initial time t = 0, the molecule was in state $|1\rangle$. If this is the situation, then the initial condition can be written as psi 1 at time equals 0 is given as 1 and sorry, $C_1(0) = 1$ and $C_2(0) = 0$. This is the initial condition that we are assuming just for the sake of understanding. Then, $a = b = \frac{1}{2}$ you can find out and $C_1(t) = \exp\left(-i\frac{E_0}{\hbar}t\right)\cos\left(\frac{\beta}{\hbar}t\right)$. $C_1(t) = \exp\left(-i\frac{E_0}{\hbar}t\right)\sin\left(\frac{\beta}{\hbar}t\right)$. This would be the expression for C_2. The two amplitudes, you can see it oscillate harmonically as a function of time. It is clear from this expression. (Refer Slide Time: 17:17)

Now, the probability of the molecule in state $|2\rangle$, if we try to calculate that, this would be given as $|C_2(t)|^2$ exponential term will go away, if we take complex conjugate and multiply. So, sin term will remain. It is $\sin^2(\frac{\beta t}{\hbar})$. This is what we will this is this will be the probability of the molecule in state $|2\rangle$. So, we are considering 1 electron of the molecule and its state is its state becomes exactly 2 with this probability. Once we have found this that means this probability $|C_2(t)|^2 = 0\ at\ t = 0$; this $|C_2(t)|^2 = 1\ at\ t = \frac{h}{4|\beta|}$ and $|C_2(t)|^2 = 0\ at\ t = \frac{h}{2|\beta|}$ and so on. It is a harmonic function. You can see it is a sin square like a function. So, it will go on oscillating like this between 0 and 1. So, now here is a homework for you; plot $|C_1(t)|^2$ and $|C_2(t)|^2$ with time. That will give you the probability of the electron in the molecule being in state $|1\rangle$ and state $|2\rangle$ as a function of time. So, by plotting this also from whatever we have already seen the behavior of this function that the electron oscillates between atom 1 and atom 2, keeps on hopping. Hence, the term the off diagonal terms are called hopping terms. Now, how can it keep on hopping between two atoms? Because there is a potential barrier in between; the ionization energy of hydrogen atom, how much is it? This equals 13.6 electron Volt; huge energy, the electron cannot so easily cross this kind of a barrier. So, how can it hop between two atoms? The electron actually tunnels through this barrier; it does not overcome the barrier. So, the electron does not go over the barrier. In quantum mechanics even though, it cannot go over the barrier; it is possible to tunnel through the barrier and that is what is happening in this kind of a case. So, we understand something very interesting about the covalent bond, not only the electron hops between two atoms which certainly it does, which we already knew the electron sharing means that. It has to tunnel through the barrier; it cannot go over the barrier that is something very interesting that we have realized at this stage. And the probability of tunneling with time is probability of tunneling per unit time that is given as $\frac{2\beta}{h}$. So, in case of covalent bond, we can see that the electron tunnels through the barrier and this is very different from electron transport. In case of electron transport, the electron would not be confined between these two atoms. It would go far away. Actually, in case of solid, if we consider a solid instead of a diatomic molecule that we have done here, the electron would hop between two atoms and it can actually go far away, but it. So, it can hop from 1 to 2, 2 to 3, 3 to 4 and so on with some finite probability of course, that is the probabilistic dynamics. But still that movement the probability of that hopping is given by this per unit time. So, it is so low that it is not transport. In case of transport, it the electrons behave like free electron; that means, it hardly sees any barrier like this and subject to an external electric field, it can easily move from one place to another. That kind of a movement is moving over the barrier. So, transport is moving over the barrier and tunneling is and covalent bond is tunneling through the barrier, not moving over the barrier. That is how we understand the difference between transport and covalent bond and covalent bond, this is how the covalent bond takes place; mathematically, this is how we can analyze it and it creates a quite strong bond.