Solid State Physics
Lecture 32
One Dimensional Chain of Atoms

Hello, we are going to discuss the Electronic Structure; that means, what kind of electronic states materials have, why they have that kind of state and what does it mean? How we can calculate the electronic states and the energy corresponding to that all these things, we are going to discuss now. So, in order to discuss the electronic structure, we have to start from something very simple. And, in order to start from something very simple, we have already discussed the case of hydrogen molecule and now we will consider a 1 dimensional linear chain of many hydrogen atoms. That is the next extension to the hydrogen molecule consideration that we have discussed in the context of covalent bonds. So, let us consider a one dimensional chain of N hydrogen atoms. (Refer Slide Time: 01:27)

We can draw the chain like this. So, this is one hydrogen atom, this is second, third, fourth. Similarly, this is (N - 2), (N - 1), N^{th} hydrogen atom. If we have total N number of hydrogen atoms in the system; 1 2 3 4, (N - 2), (N - 1), N and here I draw the bonds between them. So, this kind of a chain is something that we are going to consider now. Now, each hydrogen atom is associated with an electronic s state. So, we assume that these states the atomic s states. They form a complete basis to represent the molecular single particle state of this system of hydrogen atoms N number of hydrogen atoms arranged on a straight line. So, if we consider the state of this entire system represented as $|\psi\rangle$. Then, we can expand $|\psi\rangle$ in terms of the linear in terms of a linear combination of the basis elements as $|\psi\rangle = \Sigma_{j=1}^{N} C_j|j\rangle$. So, j is the this quantity this ket vector $|j\rangle$ is the s state of j^{th} atom. Now, our task is to find the coefficients C_j, if we can find these coefficients, then we will be able to find out the state and the energy eigenvalue corresponding to the state $|\psi\rangle$. So, we need to write the Schrodinger equation, which is in it is time independent form just an eigenvalue equation $H|\psi\rangle = E|\psi\rangle$. And, this in terms of the linear combination of $|\psi\rangle$ can be represented as $\Sigma_{j=1}^{N} C_j H|j\rangle$ Hamiltonian acting on the state $|j\rangle$. So, this Hamiltonian is the Hamiltonian of this system chain of hydrogen atoms and this ket vector $|j\rangle$, this corresponds to the atomic orbital. So, not necessarily $|j\rangle$ is an eigen state of the Hamiltonian. This quantity according to this eigenvalue equation becomes $\Sigma_{j=1}^{N} C_j H|j\rangle = E\Sigma_{j=1}^{N} C_j|j\rangle$. This is the eigenvalue equation that we can write. Now, in the next step we are going to multiply a bra vector from the left, let us call it $\langle p|$. And, if we multiply this; that means, we are projecting these states on the state from the p^{th} site. And, this equation can this eigenvalue equation can be represented by doing this as $\Sigma_{j=1}^{N} C_j \langle p|H|j\rangle = E \Sigma_{j=1}^{N} C_j \langle p|j\rangle$ inner product of $\langle p|$ and $|j\rangle$. So, this is the secular equation for the chain of N atoms. Now, this requires a few approximations and denoting the terms in some in certain way to be able to progress further. So, in order to be able to solve this, we assign the Hamiltonian terms, Hamiltonian matrix elements. That means, these kind of terms and the overlap terms that is these inner products in certain way. (Refer Slide Time: 08:26)

How do we do that? The simplest assumption would be orthonormality; that means we assume $\langle p|$ and $|j\rangle$, their inner product to be $\langle p|j\rangle = \delta_{pj}$; that means, when p = j, this inner product $\langle p|j\rangle = 1$ when $p \neq j$ then this inner product $\langle p|j\rangle = 0$, which is just the orthonormal condition, orthonormality condition. We have also assumed this orthonormality condition for the hydrogen molecule case, we can work out the problem without assuming this, but then the mathematics would be cumbersome for very little gain. That is the reason we are considering this to be orthonormal. So, this is about the overlap elements. How about the matrix elements of the Hamiltonian? For the matrix elements of the Hamiltonian we consider the following. If we have the Hamiltonian matrix, the Hamiltonian operator sandwiched between 2 same states, then we call for all values of j, $\langle j|H|j\rangle = \alpha$ this kind of matrix element as alpha which is the onsite term. Not that for every system this is this must happen, but for linear chain of hydrogen atom it is going to happen and this is something we consider for simplicity. And, for all values of j α is the same constant that is what we assume. Then, how about the matrix

element being sandwiched between sorry the Hamiltonian operator being sandwiched between two different states? If, we have $\langle p|H|j\rangle = \beta$ this kind of a situation, then we call it β on which is a hopping term rather hopping element, this is the onsite element. So, the hopping element if p and j are nearest neighbors so, we are going to restrict the hopping between two nearest neighbors. And, if they are not nearest neighbors p and j are not nearest neighbors, then this kind of hopping term is $\langle p|H|j\rangle = 0$, this is something we assume for simplicity ok. Now, we can determine α and β by evaluating the integrals or by fitting with experimental data, but for this particular problem there is no experimental data for a chain of N hydrogen atoms. So, let us consider the theoretical aspects of it. As we have learned that linear combination of atomic orbital's the method that we are practicing here, it is not very accurate. But, we obtain a lot of physical insight into the problem by exercising this kind of a method that is the reason we are going to do this. So, we are not very much interested in the accuracy of α and the values of the α and β parameters here. But, we are interested in the fact that these parameters may be in principle determined and what kind of understanding we can develop from this kind of an approach ok. Now, if we consider different values of p, we can find different forms of this secular equation this equation here. (Refer Slide Time: 13:04)

And, if we write that down, it will look like I go to a next page for different values of p we can so, that equation becomes for p = 1 it is, $\alpha C_1 + \beta C_2 = EC_1$, for p = 2 we have $\beta C_1 + \alpha C_2 + \beta C_3 = EC_2$. Subsequently for p = 3, we can write $\beta C_2 + \alpha C_3 + \beta C_4 = EC_3$. Similarly, we can go up to j^{th} term there we can write $\beta C_{j-1} + \alpha C_j + \beta C_{j+1} = EC_j$ this is for p = j. We can move forward just like that for p = (N - 1) we can write $\beta C_{N-1} + \alpha C_N = EC_N$, this is for p = (N - 1) and for p = N we will have for the end atom $\beta C_{N-1} + \alpha C_N = EC_j$ this is for p equals N. So, these are the equations that we have the series of secular equations for this system of linear chain of hydrogen atoms, N number of hydrogen atoms ok. So, these are N number of coupled differential equations. And, we need to solve them to obtain the values of the coefficients C_j those values. Now, if we put if we substitute the quantity $\frac{E-\alpha}{\beta} = x$, then the j^{th} equation, this equation here can be written as $C_{j-1} - xC_j + C_{j+1} = 0$. this is what we obtain. And, if we use a trial solution for C_j in this case, if we try C_j having the form $e^{ij\theta}$, where $i = \sqrt{-1}$ and θ is to be determined. If, we try this kind of a solution to this differential equation here, the set of coupled differential equations, sorry it is not differential equation, it is just coupled linear equations; there is no differential form in here. So, if we put this kind of a trial solution to this coupled linear equation here, these coupled linear equation, which is taking this kind of a form. (Refer Slide Time: 19:05)

Then, we can write the following $e^{i(j-1)\theta} - xe^{ij\theta} + e^{i(j+1)\theta} = 0$. Then, x turns out to be by simplifying this $x = e^{i\theta} + e^{-i\theta}$, which makes it $2\cos\theta$. So, here our θ could be real or imaginary or complex we did not determine that yet and depending on that. What the kind of form of $\cos\theta$ will also depend, whether it would be a genuine cosine function or hyperbolic function that will be determined by that. So, if we here replace θ with $-\theta$ the result does not change it remains the same that we can see readily. Therefore, the general solution for C_j would be $C_j = Ae^{ij\theta} + Be^{-ij\theta}$, where A and B these are arbitrary constants. How do we determine A and B? If, we go to the end positions, that is the left side end of the chain this first equation here and right side end of the chain that is the last equation here. These equations will actually help us determine A and B. So, if we consider p = 1, that is the first atom of the chain, we can write $C_2 = xC_1$. And, if we have that then from this equation we can write from this equation here, we can sorry from the general solution. General solution is this from this one, we can write $Ae^{2i\theta} + Be^{-2i\theta} = 2\cos\theta(Ae^{i\theta} + Be^{-i\theta})$. This equation is satisfied if we set A = - B; that means, wherever we have B we will put - A. And, if we do that then C_j this quantity becomes $C_j = A(e^{ij\theta} - e^{-ij\theta})$, this is what we obtain. A is still an arbitrary constant and we did not determine it is value so far. Now, let us do the following. Let us write down $C_j = D\sin\theta$. If, we do that what would be the value of D as you can see would be $D = 2iA$, which is another arbitrary constant D. And, if we consider the other end atom the extreme right atom this equation here. (Refer Slide Time: 24:27)

Then, we can write down that $C_{N-1} = xC_N$. And, once we have that then in terms of D the equation becomes $D \sin(N-1)\theta = xD \sin N\theta$. Which is $2D \cos\theta \sin N\theta$, how did we obtain $\cos\theta$?. Because $x = 2\cos\theta$ by putting this in place of x we obtained this quantity. And, if we have this then we can write that $\sin(N-1)\theta = 2\cos\theta \sin N\theta$, which is $\sin N\theta \cos\theta - \cos N\theta \sin\theta$. So, in this form we have the constant D cancelled out we did not determine D, but we got rid of it as long as the calculation of eigenvalue is concerned ok, we can now rewrite this. So, D still remains arbitrary yet to be determined, we can write that $\tan N\theta + \tan\theta = 0$. So, this $\sin(N-1)\theta$ has been represented this way. And, now if we divide this quantity, by cosine N theta, we will get this kind of a form and we will see that it goes to 0, it becomes 0 ok. With this kind of a situation in other words we can write $\frac{\sin N\theta \cos\theta + \cos N\theta \sin\theta}{\cos\theta \cos N\theta} = 0$, which tells us that $\sin(N+1)\theta$ that is the numerator not the denominator, the numerator must be 0. And, if that is true then we can solve for θ as $\theta = \frac{m\pi}{N+1}$, where m is an integer. We can see that θ is real, this is not imaginary this is not complex, this is real. And, we will have N distinct solutions possible for distinct values of m, while m can take the value of any integer, but by taking more than N number of values, it will repeat some of the solutions, that is obvious it is a $\sin$ function. So, some of the solutions would be repeated, it would not create new solutions. (Refer Slide Time: 29:37)

And, now if we find out the allowed values of E allowed energies, for this linear chain of hydrogen atoms with finite number of that is N number of hydrogen atoms. So, the allowed energy values would be $E = \alpha + 2\beta \cos(\frac{m\pi}{N+1})$, where m can be taken in the range 1, 2 up to N for distinct solutions. You can see that the energy eigenvalues here are discrete, because m is an integer N is a finite integer. So, the energy eigenvalues cannot be continuous for finite number of hydrogen atoms in the system. But, if $N \to \infty$ you can see that the energy eigenvalues will reach the continum limit ok. Now, let us find the m^{th} state of the system, m^{th} eigenstate of the system, which we denote as $|\psi^{(m)}\rangle$. And, if we take the expansion coefficients C_j with this index m, where j can also have values from 1 2 up to the number of atoms, then $C_j^{(m)}$ can be written as $D^{(m)}$, D is not yet determined $C_j^{(m)} = D^{(m)} \sin(\frac{mj\pi}{N+1})$. So, in order to determine the state vector, we need to determine the coefficients of the basis elements and in order to determine that we want to find out this arbitrary constant D at this stage. So, how do we determine that, we can now use the normalization condition, $\langle\psi^{(m)}|\psi^{(m)}\rangle = 1$ for orthonormality. And, for that we need to have $D^{(m)} = \sqrt{\frac{2}{N+1}}$. Then, we have something interesting to find out the eigenvalues. If, we have N = 1, we will just have 1 eigenvalue here which is the atomic eigenvalue. If, we have N = 2 we will have a bonding state and an antibonding state, these are the levels energy levels as we have seen in the case of hydrogen molecule. If, we have N = 3, we will have 3 states here, bonding antibonding and nonbonding and so on. If, we have $N \to \infty$, then we will have a continuous spectrum of energy eigenvalues, that you can see right away. Now, let us consider something interesting. We cannot really calculate for infinite number of atoms, but we can put periodic boundary condition in place, which means $zero^{th}$ atom and N + 1 atom these are the same.