

8.231 Physics of Solids I — Fall 2017

Lecture Note 5

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1 Tight-binding Chain Revisited

Let us compute the energy spectrum for the tight-binding chain more carefully.

1.1 Setup the Hamiltonian

Suppose we have a chain of L atoms with atom spacing a , and there is only one orbital per site. The orbital on n -th atom is denoted as $|n\rangle$. We take periodic boundary condition so that $|n+L\rangle = |n\rangle$. We also assume the atomic orbitals are orthogonal to each other $\langle n|m\rangle = \delta_{nm}$ ¹. The Hamiltonian of an electron in this system is $H = K + \sum_j V_j$, where K is the kinetic energy and V_j is the Coulomb interaction from the nucleus at site j .

Under atomic orbital basis, the Hamiltonian H is a matrix $H_{nm} \equiv \langle n|H|m\rangle$. By definition, $(K + V_n)|n\rangle = \mathcal{E}_{\text{atomic}}|n\rangle$, where $\mathcal{E}_{\text{atomic}}$ is the energy of the atomic orbital. For the remaining terms, we take the assumption that the overlapping of different atomic orbitals decays so rapidly that only the nearest neighbour overlapping is non-vanishing²:

$$\sum_{j \neq m} \langle n|V_j|m\rangle = \begin{cases} V_0, & n = m, \\ -t, & |n - m| = 1, \\ 0, & \text{otherwise,} \end{cases} \quad (1)$$

where t is the called the “hopping strength”. In this way, the Hamiltonian can be written as

$$H_{nm} = \mathcal{E}\delta_{nm} - t(\delta_{n+1,m} + \delta_{n,m+1}). \quad (2)$$

Here $\mathcal{E} = \mathcal{E}_{\text{atomic}} + V_0$. In the matrix form, it looks like this:

$$\begin{pmatrix} \mathcal{E} & -t & 0 & \dots & 0 & 0 & -t \\ -t & \mathcal{E} & -t & \dots & 0 & 0 & 0 \\ 0 & -t & \mathcal{E} & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \mathcal{E} & -t & 0 \\ 0 & 0 & 0 & \dots & -t & \mathcal{E} & -t \\ -t & 0 & 0 & \dots & 0 & -t & \mathcal{E} \end{pmatrix} \quad (3)$$

¹You will need to discard this assumption and find no qualitative change in the results below in the pset.

²You will need to investigate the effect of long range hoppings in the pset.

1.2 Solve the Hamiltonian

For the eigenstate $|\psi\rangle = \sum_{n=0}^{L-1} c_n |n\rangle$, the eigenvalue equation $H|\psi\rangle = E|\psi\rangle$ becomes

$$\sum_{n=0}^{L-1} c_n (\mathcal{E}|n\rangle - t|n-1\rangle - t|n+1\rangle) = E \sum_{n=0}^{L-1} c_n |n\rangle, \quad (4)$$

which can be recast into

$$\sum_{n=0}^{L-1} (\mathcal{E}c_n - tc_{n+1} - tc_{n-1}) |n\rangle = \sum_{n=0}^{L-1} Ec_n |n\rangle. \quad (5)$$

Acting $\langle m|$ on these equations, only term with index $n = m$ will survive in the summation due to orthogonality:

$$\mathcal{E}c_m - tc_{m+1} - tc_{m-1} = Ec_m. \quad (6)$$

This is the eigenvalue equation we need to solve for c_n , $i = 0, \dots, L-1$. There are L such equations and L unknowns.

It seems daunting to solve such many coupled linear equations in Eq. (6) at the same time. However, actually it is not very hard. For the eigenstate $|\psi\rangle = \sum_{n=0}^{L-1} c_n |n\rangle$, we propose the following ansatz:

$$c_n = \frac{1}{\sqrt{L}} e^{-ikna}, \quad (7)$$

where k is the parameter to be determined shortly after. In other words, the eigenvector looks like:

$$|\psi(k)\rangle = \frac{1}{\sqrt{L}} \begin{pmatrix} 1 \\ e^{-ika} \\ e^{-2ika} \\ \vdots \\ e^{-(L-1)ika} \end{pmatrix} \quad (8)$$

In this way, the eigenvalue equation Eq. (6) simply becomes:

$$E = \mathcal{E} - 2t \cos(ka). \quad (9)$$

The electrons in this one-dimensional tight-binding chain can only have energy within $E \in [\mathcal{E} - 2t, \mathcal{E} + 2t]$. This is called an electron “band”, with bandwidth $4t$. Notice that in Eq. (1) t is determined by the overlapping integral, which is further determined by the lattice spacing. In the limit $a \rightarrow \infty$, the atomic orbitals are independent and have the same energy. Therefore $t \rightarrow 0$ and the bandwidth is just 0. When the atoms come closer, t increases and the bandwidth will be larger.

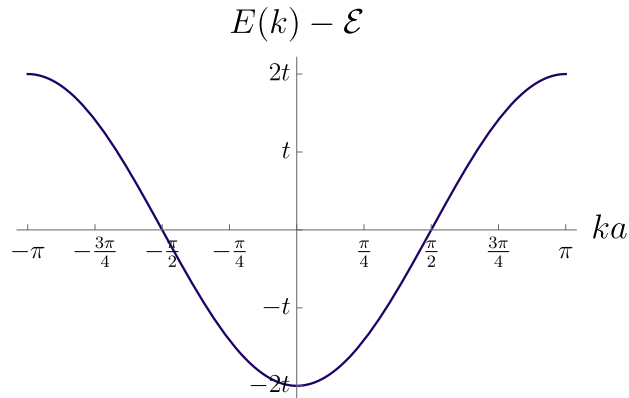


Figure 1: Energy dispersion of a one-dimensional tight-binding chain.

The energy eigenstates are just like plane wave. This is a remarkable result, in the sense that although the potential is in general very complicated, the electron moves freely in the lattice as if it is in the free space. In this way, k can indeed be interpreted as momentum, which is formally dubbed as “crystal momentum”. Later in this course, we will see that the existence of such k is very general, and is a result of the periodicity (discrete translational symmetry) of the lattice.

Before ending this section, let us consider the dispersion near the band bottom. Around $k = 0$, the energy can be expanded as

$$E(k) = \mathcal{E} - 2t \cos(ka) = \mathcal{E} - 2t \left(1 - \frac{(ka)^2}{2} + \dots \right) = (\mathcal{E} - 2t) + ta^2 k^2 + \dots \quad (10)$$

It is quadratic. Comparing with the dispersion of free electrons:

$$E_{\text{free}}(k) = \frac{\hbar^2 k^2}{2m}, \quad (11)$$

we can identify the mass here to be

$$m^* = \frac{\hbar^2}{2ta^2}. \quad (12)$$

This m^* is called the “effective mass” of the electron. It means that the electrons near the band bottom has exactly the same dispersion as that of a free electron. Note that m^* depends on the hopping strength t and has nothing to do with the real electron mass m_e . In fact, effective mass can even be negative! This is the case when k is around $k = \pi/a$, i.e., the band top. We will come back to the physical implication of the effective mass later in this course.

1.3 Filling the Band

We have yet to determine the possible values of k . The periodic boundary condition implies

$$e^{-ikna} = e^{-ik(n+L)a} \Rightarrow e^{-ikLa} = 1 \Rightarrow k = \frac{2\pi m}{La}, \quad m \text{ is an integer.} \quad (13)$$

Let us count how many states there are in this system. Although m in principle can be any integer, states with $k \rightarrow k + 2\pi/a$ are the same state because the wavefunction is exactly the same $e^{-ika} = e^{-i(ka+2\pi)}$. Therefore, we should restrict $ka \in [-\pi, \pi]$ (or $k \in [0, 2\pi]$) in the counting. Since each state occupy a volume of $2\pi/(La)$ in the momentum space, there are

$$\#(k\text{-states}) = \frac{2\pi/a}{2\pi/(La)} = L, \quad (14)$$

in total. This is in accordance with the fact there are L atoms and L atomic orbitals in this system. $k \in [-\pi/a, \pi/a]$ is called the “Brillouin zone”. The energy dispersion in the Brillouin zone is plotted in the Figure 1.

Now let us add electrons into this band and determine the Fermi energy. Due to Pauli’s exclusion principle, each k -state can only admit two electrons (spin degeneracy). Let us consider two cases:

- Monovalent materials. Each atom donates one electron. In this case, the band will be half-filled. The Fermi energy lies in the middle of the band $E_F = \mathcal{E}$.

If we apply a small electric field along the chain, it costs a small amount of energy to shift the Fermi surface, populating a few k -states moving right and depopulating some k -states moving left. In this way, a net current is induced and the system is a metal.

- Divalent materials. Each atom donates two electrons. In this case, the band will be fully-filled. The Fermi energy lies at the top the band $E_F = \mathcal{E} + 2t$.

If we apply a small electric field along the chain, there is no way to shift the Fermi surface to build up some currents because all the states are already occupied—there are always equal number of left movers and right movers. We thus conclude that a filled band carries no current. The system is an insulator.

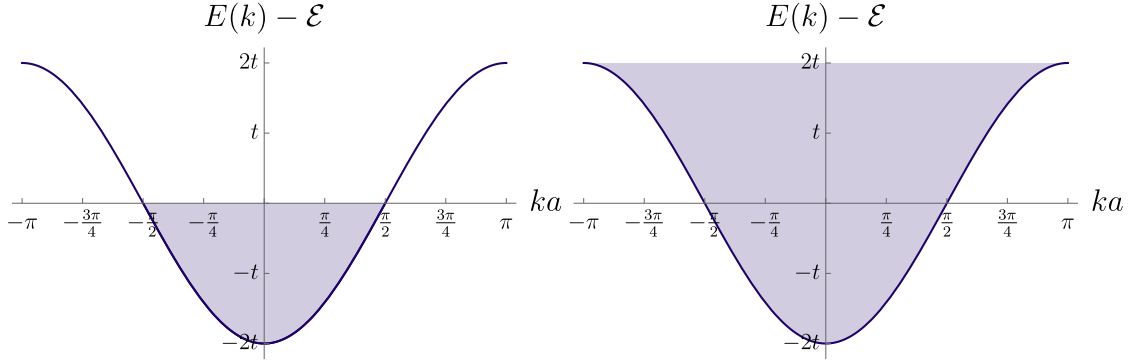


Figure 2: Filling of the one-dimensional tight-binding chain. Left: monovalent material, half-filling. Right: divalent material, full-filling.

1.4 Multiple Bands

Suppose there are two orbitals per atom denoted as A and B . These two orbitals are perfectly decoupled³. In this case, we have two bands with energy

$$E_A = \mathcal{E}_A - 2t_A \cos(ka), \quad (15)$$

$$E_B = \mathcal{E}_B - 2t_B \cos(ka). \quad (16)$$

If we still consider divalent materials, we may experience a metal-insulator transition (MIT) by decreasing the atomic distance, and hence increasing the bandwidth. The transition happens when one band bottom and one band top touch. Suppose $\mathcal{E}_A > \mathcal{E}_B$. The transition happens when $\mathcal{E}_A - 2t_A = \mathcal{E}_B + 2t_B$.

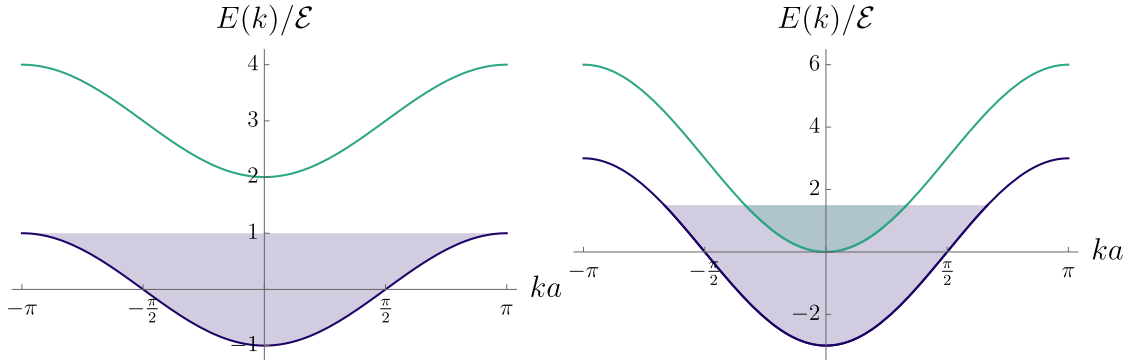


Figure 3: Metal-insulator transition when atomic distance is increased. Here $\mathcal{E}_A \equiv \mathcal{E}$ and $\mathcal{E}_B = 0$. Left: $t_A = t_B = \mathcal{E}/2$, which is an insulator. Right: $t_A = t_B = 3\mathcal{E}/2$, which is a (semi)metal.

For an insulator, the highest filled band is called the “valence band”, and the lowest unfilled band is called the “conduction band”. In between we have the “band gap”. When both conduction band and valence band

³You will need to investigate the effect of this coupling in the pset.

are occupied, the system becomes conductive. This is called a semimetal⁴.

2 Diatomic Tight-binding Chain

2.1 Setup the Hamiltonian

Let us consider another scenario of multiple bands. Suppose there are two kinds of atoms A and B arranged in the following way:

$$-A - B - A - B - A - B-$$

The distance between the *same* kind of the atoms is a . Each atom has one orbital. The repeating unit of a lattice is called the “unit cell”. In this case, the unit cell spacing is also a , and there are two atoms and orbitals per unit cell. Effectively, one can treat A and B as two orbitals on an artificial atom, with some particular coupling between these orbitals. Denote the orbital on A and B as $|n, A\rangle$ and $|n, B\rangle$. Assume $\langle n, A|m, A\rangle = \langle n, B|m, B\rangle = \delta_{nm}$ and $\langle n, A|m, B\rangle = 0$. The Hamiltonian matrix element is specified by

$$\langle n, A|H|m, A\rangle = \mathcal{E}_A \delta_{nm} \quad (17)$$

$$\langle n, B|H|m, B\rangle = \mathcal{E}_B \delta_{nm} \quad (18)$$

$$\langle n, B|H|m, A\rangle = \begin{cases} -t, & m - n = 0, 1, \\ 0, & \text{otherwise.} \end{cases} \quad (19)$$

Since the spatial period of the unit cell is a , we should expect a dispersion relation in a Brillouin zone of size $2\pi/a$. Also, there are two atoms per unit length a , we should expect two bands after solving the eigenvalue problem.

2.2 Some Observations

Before doing any calculation, let us consider several limits which we should know the band dispersion.

- $t = 0$. We must have two perfectly flat band in the Brillouin zone, whose energies are \mathcal{E}_A and \mathcal{E}_B .
- $\mathcal{E}_A = \mathcal{E}_B$. This is actually the same as the simple chain we discussed previously but with $a \rightarrow a/2$. We must reproduce the dispersion relation $E = \mathcal{E} - 2t \cos(ka/2)$ in a Brillouin zone of size $4\pi/a$. How could this requirement be satisfied when we have two bands in a Brillouin zone of size $2\pi/a$? This can be achieved by “folding” the band in $[-2\pi/a, -\pi/a]$ and $[\pi/a, 2\pi/a]$ as the second band:

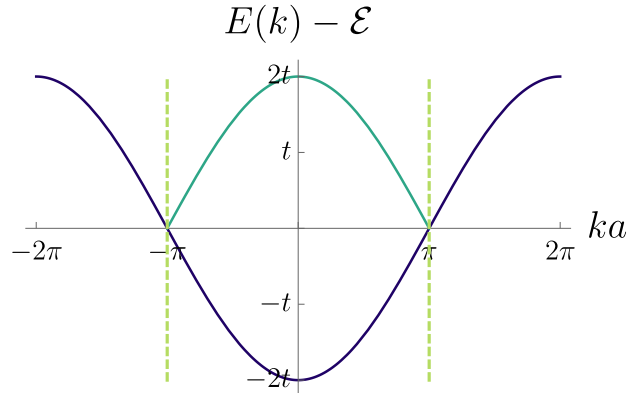


Figure 4: Band folding when the lattice spacing is artificially enlarged $a/2 \rightarrow a$ to give a second band.

⁴You will find the reason for the name “semi” in the pset.

We can interpolate the continuous transition between these two scenarios.

2.3 Solve the Hamiltonian

For the eigenstate $|\psi\rangle = \sum_{n=0}^{L-1} (c_n |n, A\rangle + d_n |n, B\rangle)$, the eigenvalue equation $H|\psi\rangle = E|\psi\rangle$ becomes

$$\begin{aligned} & \sum_{n=0}^{L-1} c_n (\mathcal{E}_A |n, A\rangle - t |n-1, B\rangle - t |n, B\rangle) \\ & + d_n (\mathcal{E}_B |n, B\rangle - t |n+1, A\rangle - t |n, A\rangle) = E \sum_{n=0}^{L-1} (c_n |n, A\rangle + d_n |n, B\rangle). \end{aligned} \quad (20)$$

which can be recast into

$$\sum_{n=0}^{L-1} (\mathcal{E}_A c_n - t d_{n-1} - t d_n) |n, A\rangle + (\mathcal{E}_B d_n - t c_{n+1} - t c_n) |n, B\rangle = \sum_{n=0}^{L-1} (E c_n |n, A\rangle + E d_n |n, B\rangle). \quad (21)$$

Act $\langle m, A|$ and $\langle m, B|$ on these equations. We get two sets of coupled equations

$$\mathcal{E}_A c_m - t d_{m-1} - t d_m = E c_m, \quad (22)$$

$$-t c_{m+1} - t c_m + \mathcal{E}_B d_m = E d_m. \quad (23)$$

We propose the ansatz

$$c_n = \frac{C}{\sqrt{L}} e^{-ikna}, \quad d_n = \frac{D}{\sqrt{L}} e^{-ikna}. \quad (24)$$

Eq. (22) and (23) become

$$\mathcal{E}_A C - t(1 + e^{ika}) D = EC, \quad (25)$$

$$-t(1 + e^{-ika}) C + \mathcal{E}_B D = ED. \quad (26)$$

We obtain an eigenvalue equation for vector (C, D) . In other words, we want to find the eigenvalue of the following matrix:

$$\begin{pmatrix} \mathcal{E}_A & -t(1 + e^{ika}) \\ -t(1 + e^{-ika}) & \mathcal{E}_B \end{pmatrix} \quad (27)$$

$$= \frac{\mathcal{E}_A + \mathcal{E}_B}{2} I - t[1 + \cos(ka)] \sigma_x - t \sin(ka) \sigma_y + \frac{\mathcal{E}_A - \mathcal{E}_B}{2} \sigma_z, \quad (28)$$

whose eigenvalues are⁵

$$E = \frac{\mathcal{E}_A + \mathcal{E}_B}{2} \pm \sqrt{\left(\frac{\mathcal{E}_A - \mathcal{E}_B}{2}\right)^2 + 2t^2 [1 + \cos(ka)]}. \quad (29)$$

The difference between the two bands are minimal when $ka = \pm\pi$, which takes the value $|\mathcal{E}_A - \mathcal{E}_B|$. This is called the band gap between the two bands. This model explains the fact that monovalent ionic materials like LiF are very good insulators.

⁵The eigenvalues for matrix $M = aI + \mathbf{b} \cdot \boldsymbol{\sigma}$ are $E = a \pm \sqrt{\mathbf{b} \cdot \mathbf{b}}$.

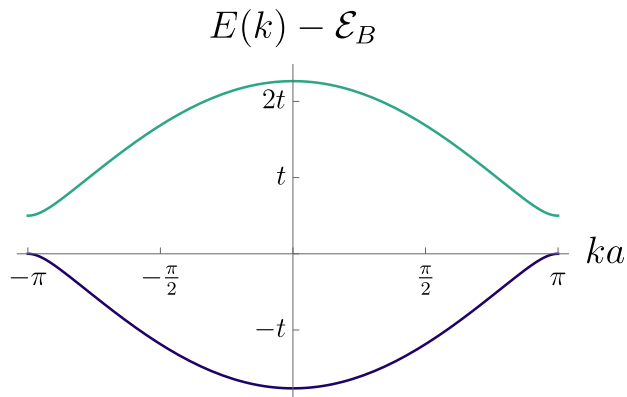


Figure 5: Energy dispersion of a one-dimensional diatomic tight-binding chain. Here $\mathcal{E}_A - \mathcal{E}_B = t/2$.

Generically, one needs to solve a $N \times N$ matrix like Eq. (27) when there are N orbitals in the unit cell.

2.4 Level Repulsion

Without doing any calculation, we can actually predict that the system generally must be gapped when $\mathcal{E}_A \neq \mathcal{E}_B$.

A two-band Hamiltonian in its most general form is

$$H = a(k)I + \mathbf{b}(k) \cdot \boldsymbol{\sigma}, \quad (30)$$

whose eigenvalues are

$$E = a(k) \pm |\mathbf{b}(k)|. \quad (31)$$

The band is gapless only when $|\mathbf{b}(k)| = 0$, which needs all three components of \mathbf{b} to vanish. This generally requires to tune three independent parameters. In one dimension, in the Brillouin zone there is only one parameter k to tune. Therefore $|\mathbf{b}(k)| = 0$ cannot be satisfied and the band is gapped. This is called the level repulsion in a two-level system. The gapless case when $\mathcal{E}_A = \mathcal{E}_B$ is really very special.

As the dimension goes higher, the situation will be different. Particularly, in three dimensions, there are three momenta k_x, k_y, k_z to tune, and one should expect a band degeneracy in the 3D Brillouin zone very general. These points are called “Weyl points”.