

Tight binding model

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Chapter 1

Introduction

This text will introduce the basic concept of the tight binding theory. This note is based on several documents. If you need original information, see ref. [1, 2]. In addition, we often use diagonalization of the matrix to solve the equations. Computational calculation may help solve it. All the code for reproducing the result in this document is prepared in Jupyter Notebook form and written in Python. Refer to it if you are interested in.

Chapter 2

Quantum mechanics toward tight binding model

2.1 One potential problem

The atoms are periodically ordered in crystals, and the electrons move around under the periodic potential. As the first step toward constructing the crystalline model, let us think about the state of an electron in a potential. To simplify, we will consider the one-dimensional (1D) case in this chapter.

In basic quantum mechanics, we often consider the rectangular potential because we can easily get the analytic solution. However, the rectangular potential is not realistic. Therefore, here we will try considering much smooth potential and solve the Schrödinger equation by numerical calculation. Figure 2.1(a) shows the potential shape, which is drawn according to the following formula:

$$V(x) = V_0 \exp(-x^2) \quad (2.1)$$

, where $V_0 = 5$ in Fig. 2.1(a). We will solve the Schrödinger equation for this potential. The Schrödinger equation in one dimensional case is written as follows:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi(x) = \epsilon \psi(x). \quad (2.2)$$

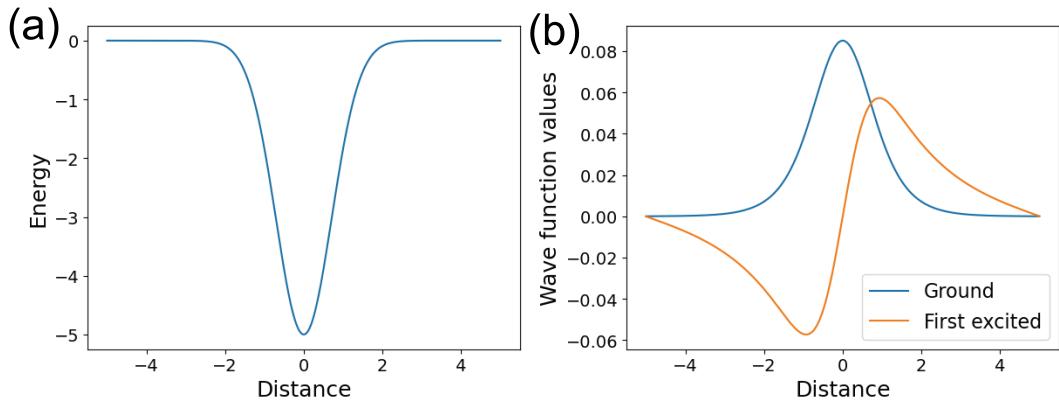


Fig. 2.1: (a) The potential shape in eq.2.1. (b) Calculated wavefunctions for ground and first excited state.

We will ignore the coefficient as follows:^{*1}

$$\left(-\frac{d^2}{dx^2} + V(x) \right) \psi(x) = \epsilon \psi(x). \quad (2.3)$$

For the numerical calculation, we will discrete the x axis like $\dots, x_n - dx, x_n, x_n + dx, \dots$. The second derivative in Schrödinger equation can be rewritten as follows: ^{*2}

$$\frac{d^2}{dx^2} \psi(x) = \frac{\psi(x + dx) - 2\psi(x) + \psi(x - dx)}{dx^2} \quad (2.4)$$

Therefore, the Schrödinger equation at $x = x_n$ is expressed as follows:

$$-\frac{\psi(x_n + dx) - 2\psi(x_n) + \psi(x_n - dx)}{dx^2} + V(x_n) \psi(x_n) = \epsilon \psi(x_n) \quad (2.5)$$

$$\therefore -\frac{1}{dx^2} \psi(x_{n-1}) + \left(\frac{1}{dx^2} + V(x_n) \right) \psi(x_n) - \frac{1}{dx^2} \psi(x_{n+1}) = \epsilon \psi(x_n) \quad (2.6)$$

We can get the Schrödinger equation for all the x_n . The equations can be summarized in the matrix form as follows:

$$\begin{pmatrix} \frac{1}{dx^2} + V(x_0) & -\frac{1}{dx^2} & 0 & 0 & \dots \\ -\frac{1}{dx^2} & \frac{1}{dx^2} + V(x_1) & -\frac{1}{dx^2} & 0 & \dots \\ 0 & -\frac{1}{dx^2} & \frac{1}{dx^2} + V(x_2) & -\frac{1}{dx^2} & \dots \\ 0 & 0 & -\frac{1}{dx^2} & \frac{1}{dx^2} + V(x_3) & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \begin{pmatrix} \psi(x_0) \\ \psi(x_1) \\ \psi(x_2) \\ \psi(x_3) \\ \vdots \end{pmatrix} = \epsilon \begin{pmatrix} \psi(x_0) \\ \psi(x_1) \\ \psi(x_2) \\ \psi(x_3) \\ \vdots \end{pmatrix} \quad (2.7)$$

Because eq.2.7 is a eigen equation

Because eq.2.7 is an eigenequation, the solution (eigenenergy and eigenfunction) is obtained by diagonalization. We can diagonalize the large size matrix using a computer program. Figure 2.1(b) shows the calculated wave function for the ground and first excited state, calculated in the range of $-5 \leq x \leq 5$ discrete for 1000 points ($dx = 0.01$). Using the numerical method, we can solve the Schrödinger equation for any shape of $V(x)$.

2.2 Multiple potential problem

The potential shape becomes closer to the real crystal by aligning several potentials. Let us assume the system with two potentials, as shown in Fig. 2.2(a). The Schrödinger equation for this potential is solved using the same method as the one potential case. Figure 2.2(b) shows the ground and first excited state. The wave function shows that the ground (first excited) state is composed of a bonding (anti-bonding) connection of the ground state of each potential.

By increasing the number of potentials, we may imitate the crystalline lattice. Therefore, in principle, the electronic structure of the crystal can be calculated by this method. However, if we increase the number of potentials without changing the periodicity and accuracy, the size of the matrix becomes larger and harder to calculate. For example, in the above examples, we discrete the x axis into 1000 points for two potentials, indicating that the matrix size is 1000×1000 . If we use four potentials with the same accuracy and periodicity, the matrix size will be 2000×2000 . The increase in the matrix size is much more severe in higher dimensional cases. Therefore, this method is not suitable for calculating the system with a large number of atoms.

^{*1} You can assume that we divide both sides by $\frac{\hbar^2}{2m}$. Hereafter, the potential and energy include this factor.

^{*2} See appendix for this transformation.

2.3 Tight binding model

Seeing the wave function in Fig.2.2(b), the wave function near each potential seems almost identical to the one potential case. It indicates that the wave function of the multiple potential systems can be expressed by the linear combination of the wave functions of one potential case. For example, in the above two potential cases, the wave function may be expressed as follows:

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x) \quad (2.8)$$

Here, ψ_1 and ψ_2 are the wave function for the single potential case, satisfying the following Schrödinger equation :

$$\left(-\frac{d^2}{dx^2} + V_1(x) \right) \psi_1(x) = \epsilon_0 \psi_1(x), \quad (2.9)$$

$$\left(-\frac{d^2}{dx^2} + V_2(x) \right) \psi_2(x) = \epsilon_0 \psi_2(x). \quad (2.10)$$

Each potential is expressed as

$$V_1(x) = V_0 \exp(-(x - x_0)^2), \quad (2.11)$$

$$V_2(x) = V_0 \exp(-(x + x_0)^2). \quad (2.12)$$

The Schrödinger equation for the two potential system is expressed as follows:

$$\left(-\frac{d^2}{dx^2} + V_1(x) + V_2(x) \right) \psi(x) = E\psi(x) \quad (2.13)$$

By substituting eq.2.8 to eq.2.13 and using eqs.2.9 and 2.10, we get the following formula:

$$\left(-\frac{d^2}{dx^2} + V_1(x) + V_2(x) \right) (c_1\psi_1(x) + c_2\psi_2(x)) = E(c_1\psi_1(x) + c_2\psi_2(x)) \quad (2.14)$$

$$\therefore \epsilon_0 c_1 \psi_1(x) + V_2(x)c_1\psi_1(x) + \epsilon_0 c_2 \psi_2(x) + V_1(x)c_2\psi_2(x) = E(c_1\psi_1(x) + c_2\psi_2(x)). \quad (2.15)$$

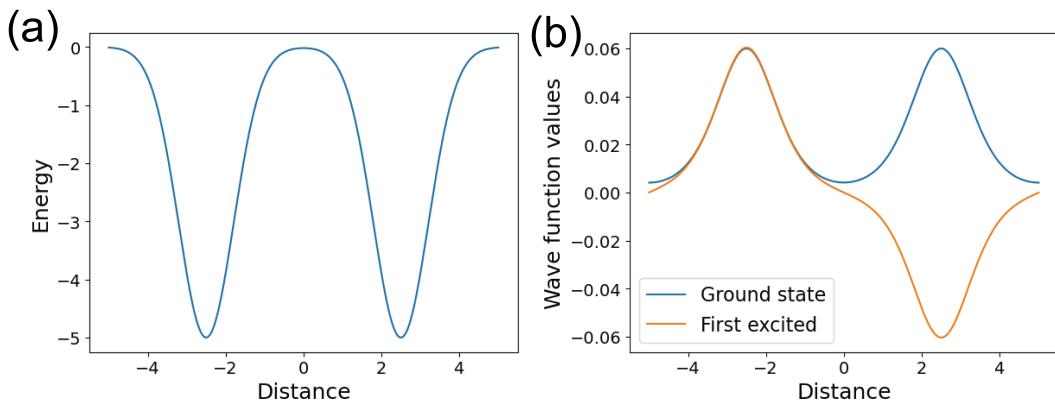


Fig. 2.2: (a) The shape of the potential with two minima. (b) Calculated wavefunctions for ground and first excited state.

By integrating both sides after multiplying $\psi_1^*(x)$ from the leftside, we get

$$\begin{aligned} \epsilon_0 c_1 + c_1 \int |\psi_1(x)|^2 V_2(x) dx + c_2 \int \psi_1^*(x) \psi_2(x) V_1(x) dx + \epsilon_0 c_2 \int \psi_1^*(x) \psi_2(x) dx \\ = E(c_1 + c_2 \int \psi_1^*(x) \psi_2(x) dx). \end{aligned} \quad (2.16)$$

Besides, by integrating both sides after multiplying $\psi_2^*(x)$ from the left side, we get

$$\begin{aligned} \epsilon_0 c_1 \int \psi_2^*(x) \psi_1(x) dx + c_1 \int \psi_2^*(x) \psi_1(x) V_2(x) dx + \epsilon_0 c_2 + c_2 \int V_1(x) |\psi_2(x)|^2 dx \\ = E(c_1 \int \psi_2^*(x) \psi_1(x) dx + c_2) \end{aligned} \quad (2.17)$$

We assume that each wave function is well localized near the potential. Thus,

$$\int \psi_2^*(x) \psi_1(x) dx = \int \psi_1^*(x) \psi_2(x) dx \sim 0 \quad (2.18)$$

$$\int |\psi_1(x)|^2 V_2(x) dx = \int |\psi_2(x)|^2 V_1(x) dx \sim 0 \quad (2.19)$$

Thus, eqs.2.16 and 2.17 become

$$\epsilon_0 c_1 + c_2 \int \psi_1^*(x) \psi_2(x) V_1(x) dx = E c_1 \quad (2.20)$$

$$c_1 \int \psi_2^*(x) \psi_1(x) V_2(x) dx + \epsilon_0 c_2 = E c_2 \quad (2.21)$$

These two equations can be summarized using the matrix form as follows:

$$\begin{pmatrix} \epsilon_0 & \int \psi_1^*(x) \psi_2(x) V_1(x) dx \\ \int \psi_2^*(x) \psi_1(x) V_2(x) dx & \epsilon_0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}. \quad (2.22)$$

Equation 2.22 is also the eigen equation. The value of components in the matrix can be calculated from the one potential case, as we have already introduced. The eigenvalues (energy) and coefficients (c_1 and c_2) are obtained by diagonalizing the matrix.

Let us see the calculation process using the two potential cases. The calculation range is $-5 \leq x \leq 5$. Firstly, prepare the single potentials (V_1 and V_2) according to eqs.2.11 and 2.12. We used $x_0 = 2.5$ and $V_0 = 5$. Then, calculate the wave function for each potential. We can solve the Schrödinger equation numerically, as we have learned in section 2.1. The calculated ground states are shown in Fig. 2.3. These wave functions are the $\psi_1(x)$ and $\psi_2(x)$.*³ ϵ_0 is the energy of these states. Now, we have the potential and wave function values and energy. Therefore, the specific values of matrix components in eq.2.22 can be calculated. The eigenenergy and coefficients are obtained by diagonalizing the matrix. The wave function is calculated using eq. 2.8. Figure 2.4 shows the ground and first excited state, similar to the wave function in Fig. 2.2. It indicates that the linear combination model works well.

The model, constructing the whole wave function from the single potential state, is called the “tight-binding model.” In this model, the size of the matrix is only $N \times N$, where N is the number of potentials, indicating that we can apply this model to a large number of atoms.

In the tight-binding model, we assumed that the linear combination of the single potential state expresses the wave function. If the single potential wave function largely overlaps with the

*³ Here, we only consider the ground state for simplisity.

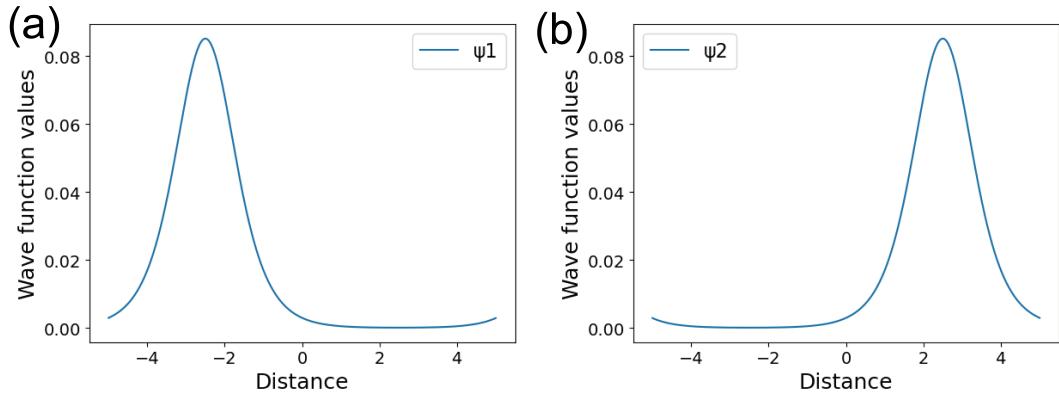


Fig. 2.3: The wave functions for a single potential (a) $V_1(x)$ and (b) $V_2(x)$.

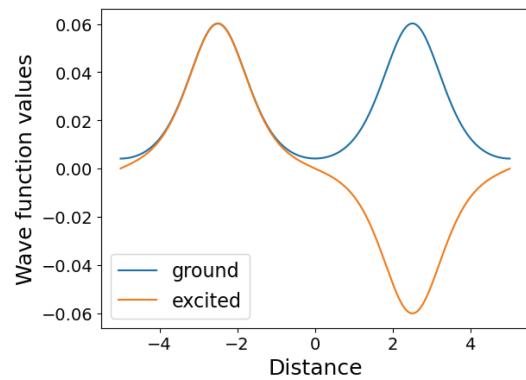


Fig. 2.4: Calculated wavefunction for the two potentials based on tight binding model.

neighbor potential, the wave function would be strongly modified, and the total wave function is no longer expressed by the combination of the single potential state. Therefore, the condition for applying the tight-binding model is that the single potential wave function is well localized around each potential, or in other words, the state is tightly bonded in the potential.

Chapter 3

Simple tight binding models

3.1 Tight binding model for 1D array

Let us consider a 1D array of N atoms in a tight binding model. The matrix can be calculated in the same way as we did in eq.2.22. We assume that the Schrödinger equation for i th atom is expressed as follows:

$$\left(-\frac{d^2}{dx^2} + V_i(x) \right) \psi_i(x) = \epsilon_i \psi_i(x). \quad (3.1)$$

And we will express the Schrödinger equation for the whole system as follows:

$$\left(-\frac{d^2}{dx^2} + \sum_{j=1}^N V_j(x) + \delta V(x) \right) \psi(x) = E \psi(x). \quad (3.2)$$

δV is the modification of the potential, which should be considered if the whole potential differs from the simple sum. Then, we assume that the total wave function (ψ) can be expressed by the linear combination of the wavefunctions at each site as follows:

$$\psi(x) = \sum_{i=1}^N c_i \psi_i(x) \quad (3.3)$$

Substitution of eq.3.3 to eq.3.2 yields

$$\left(-\frac{d^2}{dx^2} + \sum_{j=1}^N V_j(x) + \delta V(x) \right) \sum_{i=1}^N c_i \psi_i(x) = E \sum_{i=1}^N c_i \psi_i(x). \quad (3.4)$$

Using eq.3.1, eq.3.4 can be transformed as follows:

$$\sum_{i=1}^N c_i \epsilon_i \psi_i(x) + \sum_{j=1}^N \sum_{i \neq j} V_j(x) c_i \psi_i(x) + \delta V(x) \sum_{i=1}^N c_i \psi_i(x) = E \sum_{i=1}^N c_i \psi_i(x) \quad (3.5)$$

Integration after multiplying ψ_n yields

$$c_n \epsilon_n + \sum_{j=1}^N \sum_{i \neq j} c_i \int \psi_n(x) V_j(x) \psi_i(x) dx + \sum_{i=1}^N c_i \int \psi_n(x) \delta V(x) \psi_i(x) dx = E c_n. \quad (3.6)$$

Here we assumed that $\int \psi_n \psi_i dx = 0$ if $i \neq n$. The equation can be reorganized as follows:

$$\begin{aligned} & \left(\epsilon_n + \sum_{j \neq n} \int \psi_n(x) V_j(x) \psi_n(x) dx + \int \psi_n(x) \delta V(x) \psi_n(x) dx \right) c_n \\ & + \sum_{i \neq n} \left(\sum_{j \neq i} \int \psi_n(x) V_j(x) \psi_i(x) dx + \int \psi_n(x) \delta V(x) \psi_i(x) dx \right) c_i = E c_n. \end{aligned} \quad (3.7)$$

We can get eq.3.7 for all the n . Although the eigenvalue can be obtained by constructing the matrix and diagonalization from eq.3.7, the form of the formula is still complicated. We will further simplify it with some assumptions. Firstly, we will assume that $\delta V = 0$, indicating that the whole potential is a simple sum of each site. Then, we consider only the interaction with the neighboring sites. Following these assumptions, eq. 3.7 can be transformed as follows:

$$\epsilon_n c_n + \int \psi_n(x) V_n(x) \psi_{n-1}(x) dx c_{n-1} + \int \psi_n(x) V_n(x) \psi_{n+1}(x) dx c_{n+1} = E c_n \quad (3.8)$$

We will express $\int \psi_n(x) V_n(x) \psi_m(x) dx = -t_{n,m}$, which is also known as the harmonic integration. Then,

$$\epsilon_n c_n - t_{n,n-1} c_{n-1} - t_{n,n+1} c_{n+1} = E c_n \quad (3.9)$$

We got a simple expression. The formula for all the n can be summarized in matrix form. The matrix part is expressed as

$$\begin{pmatrix} \epsilon_1 & -t_{1,2} & 0 & 0 & \dots \\ -t_{2,1} & \epsilon_2 & -t_{2,3} & 0 & \dots \\ 0 & -t_{3,2} & \epsilon_3 & -t_{3,4} & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix} \quad (3.10)$$

Furthermore, if each potential has the same shape, we can express $\epsilon_i = -\mu$ and $t_{i,j} = t$. Then, the matrix is

$$\begin{pmatrix} -\mu & -t & 0 & 0 & \dots \\ -t & -\mu & -t & 0 & \dots \\ 0 & -t & -\mu & -t & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix} \quad (3.11)$$

For example, we calculated the eigenenergies for $\mu = 0$, $t = 1$, and $N = 1000$. Figure 3.1(a) shows the histogram of the calculated eigenenergies (that is, the density of state). In this model, the density of the state is high at around the lowest and highest energy states. The density of the state near the Fermi energy is important in determining the electronic property of the crystal.

3.2 Tight binding model in k space

The Schrödinger equation at the n th atom is expressed by

$$-t c_{n-1} - \mu c_n - t c_{n+1} = E c_n. \quad (3.12)$$

The analytical solution of this equation can be obtained by performing a Fourier transform on c_n as follows:^{*1}

$$c_n = \sum_k e^{-ikx_n} c_k \quad (3.13)$$

, where c_k is the intensity of the wave with the wave number of k . Inserting eq.3.13 to eq. 3.12 yields

$$\sum_k (-te^{ikx_{n-1}}c_k - \mu e^{ikx_i}c_k - te^{ikx_{n+1}}c_k) = E \sum_k e^{ikx_n} c_k. \quad (3.14)$$

Assuming that the atomic spacing is a , $x_{n\pm 1} = x_n \pm a$. Then,

$$\sum_k c_k (-te^{ikx_n}e^{ika} - \mu e^{ikx_n} - te^{ikx_n}e^{-ika}) = E \sum_k c_k e^{ikx_n} \quad (3.15)$$

$$\therefore \sum_k e^{ikx_n} c_k (-2t \cos(ka) - \mu) = E \sum_k c_k e^{ikx_n} \quad (3.16)$$

$$\therefore E = -2t \cos(ka) - \mu \quad (3.17)$$

By the Fourier transform the coefficients at the different sites can be summarized into one, yielding the analytical solution of the Schrödinger equation .

3.3 Tight binding model in 2D space

Let us consider the 2D square lattice with the size of (N_x, N_y) . The number of atoms is $N = N_x \times N_y$; thus, the matrix size is $N \times N$. We numerize all the atoms from the top left to the bottom right, as shown in Fig. 3.2(a). The atoms at (n_x, n_y) is numerized as $n_y \times N_x + n_x$, as indicated by the red numbers. We only consider the interaction with the neighbor atoms, indicating that the atom at (n_x, n_y) interacts with four neighbors labeled by $(n_y - 1) \times N_x + n_x$, $(n_y + 1) \times N_x + n_x$, $n_y \times N_x + n_x - 1$ and $n_y \times N_x + n_x + 1$. In this condition, the tight binding matrix is expressed as shown in Fig. 3.2(b). By diagonalizing this matrix, the eigenenergies and eigenvectors are

^{*1} For energy E , we get an array of $\{c_n\}$, which is the intensity of the wave functions at each lattice site. The combination of sinusoidal waves can express this array, that is the Fourier transform.

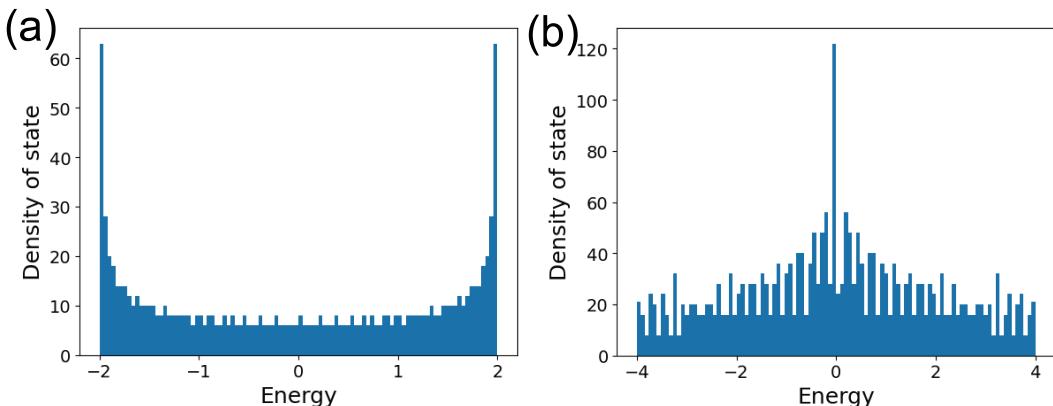


Fig. 3.1: Density of state calculated by tight binding theory for (a) 1D array and (b) 2D square lattices.

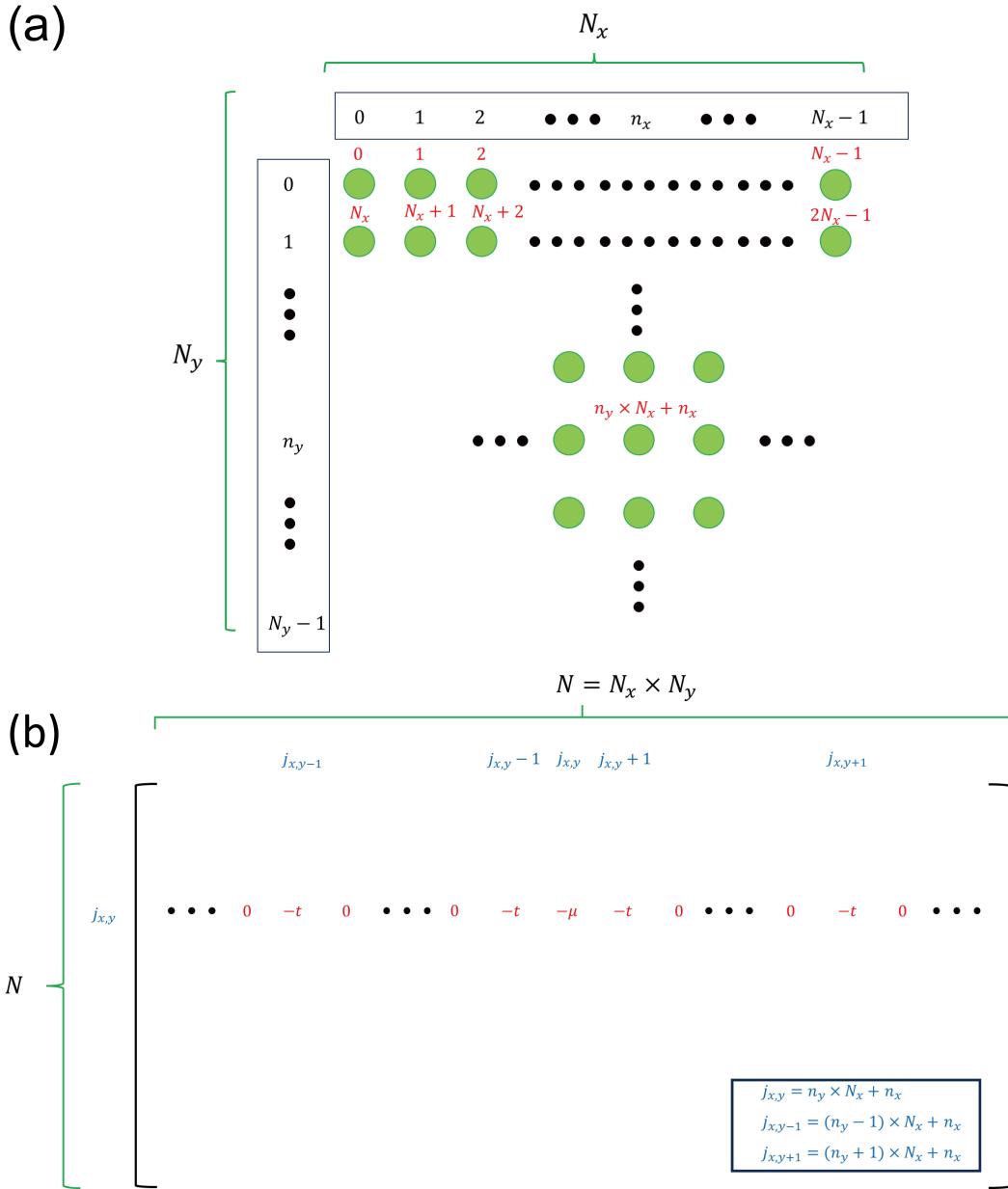


Fig. 3.2: (a) Numerization of atoms in 2D square lattice. (b) Matrix for 2D lattice for the square lattice numbered as (a).

obtained. Figure 3.1(b) shows the calculated density of states for $N_x = N_y = 50, t = 1$ and $\mu = 0$. In the case of a 2D square lattice, the density of state is high near the Fermi level.

The analytical solution for 2D lattice can also be obtained by the Fourier transform. The Schrödinger equation at each atom is expressed as

$$-tc_{x,y-1} - tc_{x,y+1} - tc_{x-1,y} - tc_{x+1,y} - \mu c_{x,y} = Ec_{x,y} \quad (3.18)$$

Using the following Fourier transform

$$c_{x,y} = \sum_{k_x,k_y} e^{-ik_x x} e^{-ik_y y} c_{k_x,k_y}, \quad (3.19)$$

eq. 3.18 is expressed as follows:

$$\begin{aligned} & -t \sum_{k_x,k_y} e^{-ik_x x} e^{-ik_y (y-a)} c_{k_x,k_y} - t \sum_{k_x,k_y} e^{-ik_x x} e^{-ik_y (y+a)} c_{k_x,k_y} - t \sum_{k_x,k_y} e^{-ik_x (x-a)} e^{-ik_y y} c_{k_x,k_y} \\ & - t \sum_{k_x,k_y} e^{-ik_x (x+a)} e^{-ik_y y} c_{k_x,k_y} - \mu \sum_{k_x,k_y} e^{-ik_x x} e^{-ik_y y} c_{k_x,k_y} = E \sum_{k_x,k_y} e^{-ik_x x} e^{-ik_y y} c_{k_x,k_y} \end{aligned} \quad (3.20)$$

$$\therefore -te^{ik_y a} - te^{-ik_y a} - te^{ik_x a} - te^{-ik_x a} = E \quad (3.21)$$

$$\therefore E = -2t(\cos(k_x a) + \cos(k_y a)) - \mu \quad (3.22)$$

Here a is the lattice constant, and eq.3.22 is the analytic solution for the 2D lattice.

Chapter 4

Tight binding models in Graphene relatives

4.1 Graphene

Figure 4.1 shows the atomic arrangement of graphene, in which carbon atoms form a honeycomb lattice. Two carbon atoms with different configurations are included in a unit cell. We will consider the band structure of graphene using the tight-binding model.

Let us construct the matrix for the graphene model with $N \times M$ unit cells. Firstly, we will label each unit cell as (n, m) , as shown in Fig. 4.2. The two atoms in the cell, colored red and blue, are labeled as 0 and 1. In this labeling, we can number the red and blue atoms in the cell (n, m) as $2(m \times N + n)$ and $2(m \times N + n + 1)$, respectively. The red atom interact with three neighbors labeled by $(n - 1, m, 1)$, $(n, m - 1, 1)$, and $(n, m, 1)$, while the blue atoms interact with $(n + 1, m, 0)$, $(n, m + 1, 0)$ and $(n, m, 0)$. We can construct the matrix for this honeycomb model

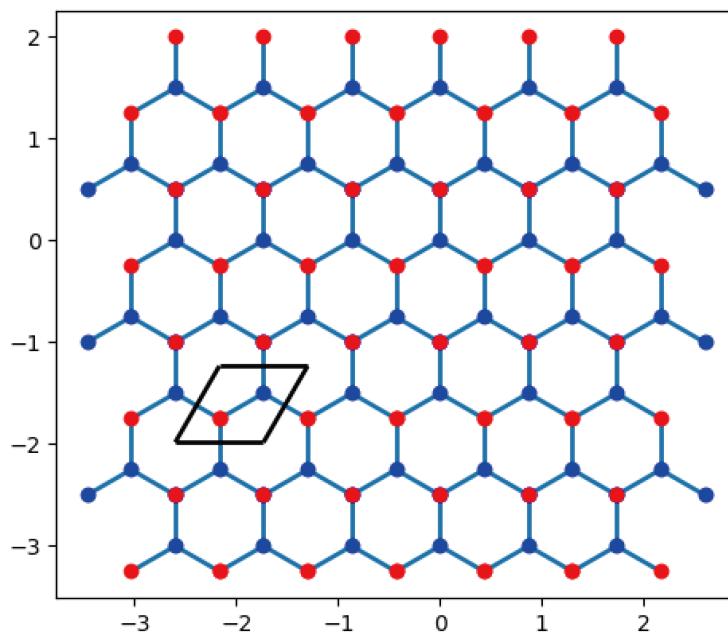
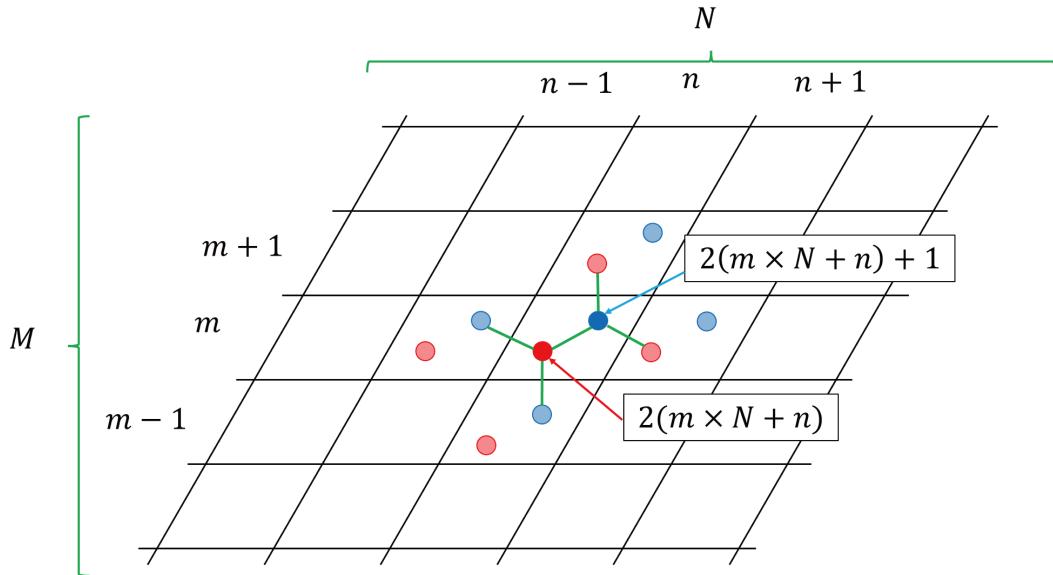


Fig. 4.1: Schematic illustration of graphene. The black rhombus indicates the unit cell. Red and blue spheres show two kinds of atoms with different configurations.

**Fig. 4.2:** Numerical labeling of grphene lattice.

using a matrix with the size of $2N \times M$. The eigenstate can be obtained by the diagonalization. Figure 4.3(a) shows the calculated density of state of the graphene model for $N = M = 50$, $\mu = 0$, and $t = 1$. In this model, we obtain two kinds of Schrödinger equation corresponding to the two atoms in the cell. The Schrödinger equation for red and blue atoms is expressed as follows:

$$-tc_{n-1,m,1} - tc_{n,m-1,1} - tc_{n,m,1} - \mu c_{n,m,0} = Ec_{n,m,0} \quad (4.1)$$

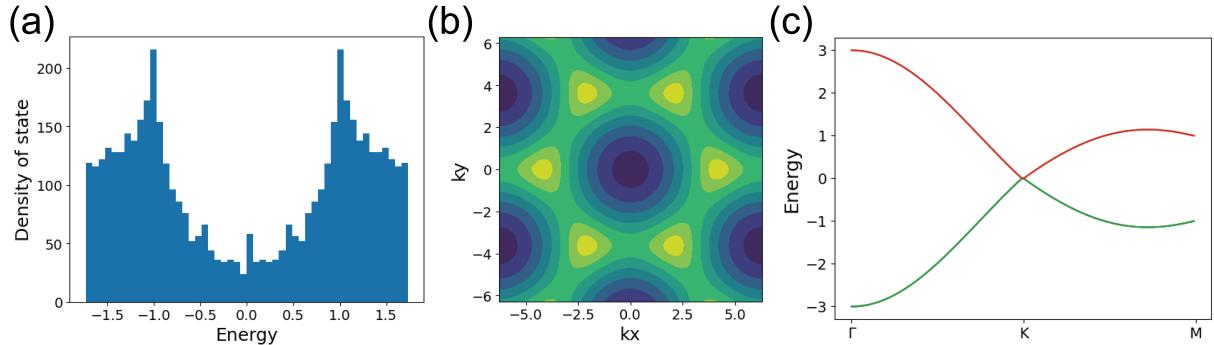
$$-tc_{n+1,m,0} - tc_{n,m+1,0} - tc_{n,m,0} - \mu c_{n,m,1} = Ec_{n,m,1} \quad (4.2)$$

We will perform the Fourier transform for red and blue atoms:

$$c_{n,m,0} = \sum_{k_x, k_y} e^{-ik_x x_n} e^{-ik_y y_m} c_{\mathbf{k},0} \quad (4.3)$$

$$c_{n,m,1} = \sum_{k_x, k_y} e^{-ik_x x_n} e^{-ik_y y_m} c_{\mathbf{k},1} \quad (4.4)$$

Let us substitute them on the Schrödinger equation for the red atom. Note here that the two unit vectors are not orthogonal in this case. Therefore, the change in the label m accompanies

**Fig. 4.3:** (a) Density of state of graphene. (b) Contour image of the band structure. (c) Band structure along $\Gamma - K - M$.

the positional shift not only y but also in x direction as follows:

$$c_{n-1,m,0} = \sum_{k_x, k_y} e^{-ik_x(x_n-a)} e^{-ik_y y_m} c_{\mathbf{k},0} \quad (4.5)$$

$$c_{n,m-1,0} = \sum_{k_x, k_y} e^{-ik_x(x_n-a/2)} e^{-ik_y(y_m-\sqrt{3}a/2)} c_{\mathbf{k},0} \quad (4.6)$$

Using these relations, the Schrödinger equation for the red atom in eq. 4.3 can be transformed as follows:

$$\begin{aligned} & -t \sum_{k_x, k_y} e^{-ik_x(x-a)} e^{-ik_y y} c_{\mathbf{k},1} - t \sum_{k_x, k_y} e^{-ik_x(x-a/2)} e^{-ik_y(y-\sqrt{3}a/2)} c_{\mathbf{k},1} \\ & - t \sum_{k_x, k_y} e^{-ik_x x} e^{-ik_y y} c_{\mathbf{k},1} - \mu \sum_{k_x, k_y} e^{-ik_x x} e^{-ik_y y} c_{\mathbf{k},0} = E \sum_{k_x, k_y} e^{-ik_x x} e^{-ik_y y} c_{\mathbf{k},0} \end{aligned} \quad (4.7)$$

$$\therefore -te^{ik_x a} c_{\mathbf{k},1} - te^{ik_x a/2} e^{ik_y \sqrt{3}a/2} c_{\mathbf{k},1} - tc_{\mathbf{k},1} - \mu c_{\mathbf{k},0} = Ec_{\mathbf{k},0}. \quad (4.8)$$

For the blue atoms, we obtain

$$-te^{-ik_x a} c_{\mathbf{k},0} - te^{ik_x a/2} e^{-ik_y \sqrt{3}a/2} c_{\mathbf{k},0} - tc_{\mathbf{k},0} - \mu c_{\mathbf{k},1} = Ec_{\mathbf{k},1}. \quad (4.9)$$

Equations 4.8 and 4.9 can be analytically solved to be

$$E = \pm t \sqrt{3 + 2 \cos k_x + 4 \cos\left(k_y \frac{\sqrt{3}}{2}\right) \cos\left(\frac{k_x}{2}\right)}. \quad (4.10)$$

We assumed $a = 1$ and $\mu = 0$ for simplification. The band structure of graphene can be drawn using eq. 4.10. The other way to get the solution is to use the diagonalization. The two equations (eq. 4.8 and 4.9) can be summarized in the matrix form as follows:

$$\begin{pmatrix} -\mu & -t(e^{-ik_x} + e^{-ik_x/2} e^{-ik_y \sqrt{3}/2} + 1) \\ -t(e^{ik_x} + e^{ik_x/2} e^{ik_y \sqrt{3}/2} + 1) & -\mu \end{pmatrix} \begin{pmatrix} c_{\mathbf{k},0} \\ c_{\mathbf{k},1} \end{pmatrix} = E \begin{pmatrix} c_{\mathbf{k},0} \\ c_{\mathbf{k},1} \end{pmatrix} \quad (4.11)$$

Diagonalizing the matrix for desired \mathbf{k} yields the band structure. Figure 4.3(b) shows the contour of band structure along $\Gamma - K - M$, and 4.3(c) shows the band structure along $\Gamma - K - M$. The upper and lower bands touch at the K point, called the Dirac point.

4.2 Zigzag nanoribbon

Let us think about the band structure of nanoribbons. Figure 4.4(a) shows the zigzag nanoribbon. In the nanoribbon, the atoms are periodic in the x direction while not in the y direction. Thus, we perform Fourier transform only on x direction:

$$c_{n,m,0} = \sum_{k_x} e^{-ik_x x_n} c_{k_x, m, 0}, \quad (4.12)$$

$$c_{n,m,1} = \sum_{k_x} e^{-ik_x x_n} c_{k_x, m, 1}. \quad (4.13)$$

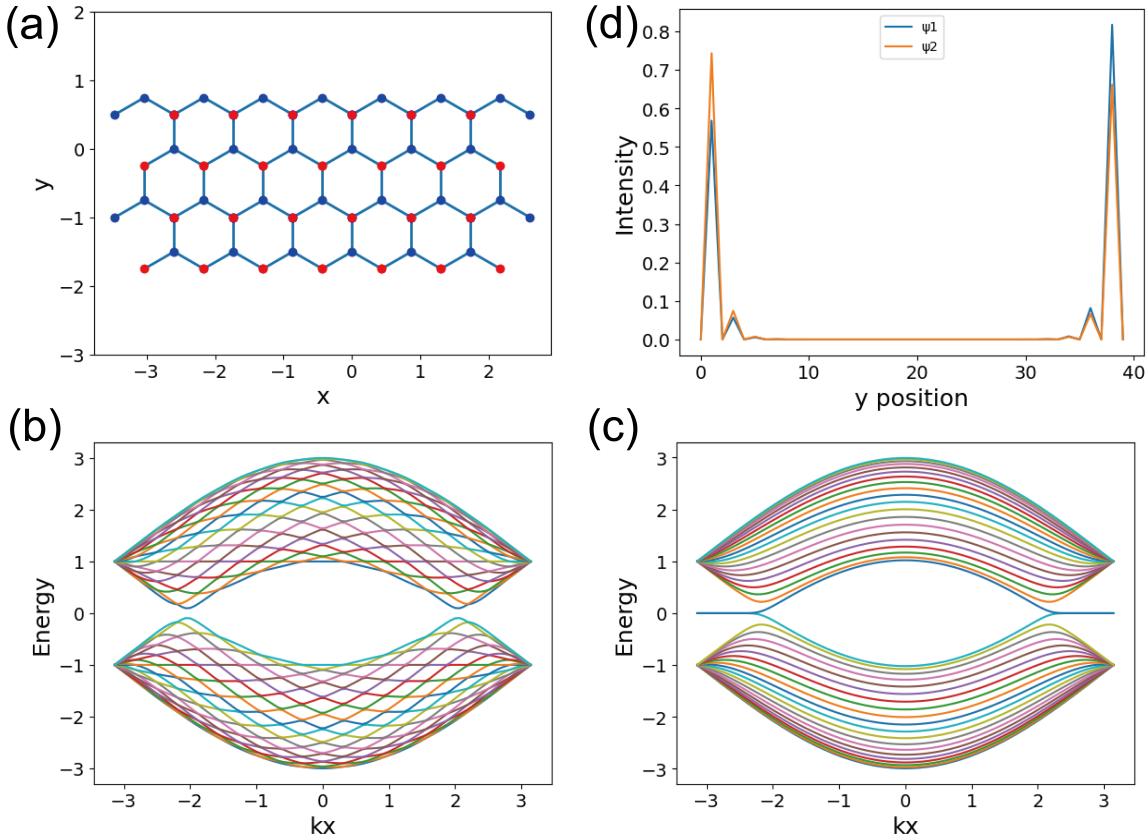


Fig. 4.4: (a) Atomic structure of zigzag nanoribbon. (b) Band structure with periodic boundary conditions (that is, normal graphene). (c) Band structure of zigzag nanoribbon with $N_y = 20$. (d) The distribution of the wavefunction along y for $E = 0, k_x \sim 3.14$.

The Schrödinger equation for the atoms is the same for eq. 4.1 and 4.2 except for the edge atoms. After the Fourier transform, the label for the x axis can be removed as follows:

$$-te^{-ik_x}c_{k_x,m,1} - tc_{k_x,m-1,1} - tc_{k_x,m,1} - \mu c_{k_x,m,0} = Ec_{k_x,m,0}, \quad (4.14)$$

$$-te^{ik_x}c_{k_x,m,0} - tc_{k_x,m+1,0} - tc_{k_x,m,0} - \mu c_{n,m,1} = Ec_{k_x,m,1}. \quad (4.15)$$

At the edge atoms (red atoms at $m = 0$ and blue atoms at $m = M - 1$), there is no hopping for the atoms at the lower (higher) index. Therefore, the Schrödinger equation for the edge atoms are expressed as follows:

$$-te^{-ik_x}c_{k_x,m,1} - tc_{k_x,m,1} - \mu c_{k_x,m,0} = Ec_{k_x,m,0} \quad (4.16)$$

$$-te^{ik_x}c_{k_x,m,0} - tc_{k_x,m,0} - \mu c_{n,m,1} = Ec_{k_x,m,1} \quad (4.17)$$

By constructing a matrix based on eq. 4.14 to eq. 4.17 and diagonalization, we obtain the band structure for the zigzag nanoribbon. First, let us see the band structure considering the periodic boundary condition along the x and y directions, that is, normal graphene. The band structure is shown in Fig. 4.4(b). Then, let us see how it changes by removing the boundary condition in the y direction to form a nanoribbon. It is done by using eq. 4.16 and 4.17 for the edge atoms. The band structure is shown in Fig. 4.4(c). A significant difference appears near the Fermi level, where two flat bands appear. Figure 4.4(d) shows the distribution of the wave functions for $E = 0$ and $k_x \sim 3.14$.^{*1} The wave function is localized at the edge atoms. Therefore, this band is called the edge state.

^{*1} Plotting the series of $\{c_{k_x,m}\}$ for $E = 0$ and $k_x \sim 3.14$.

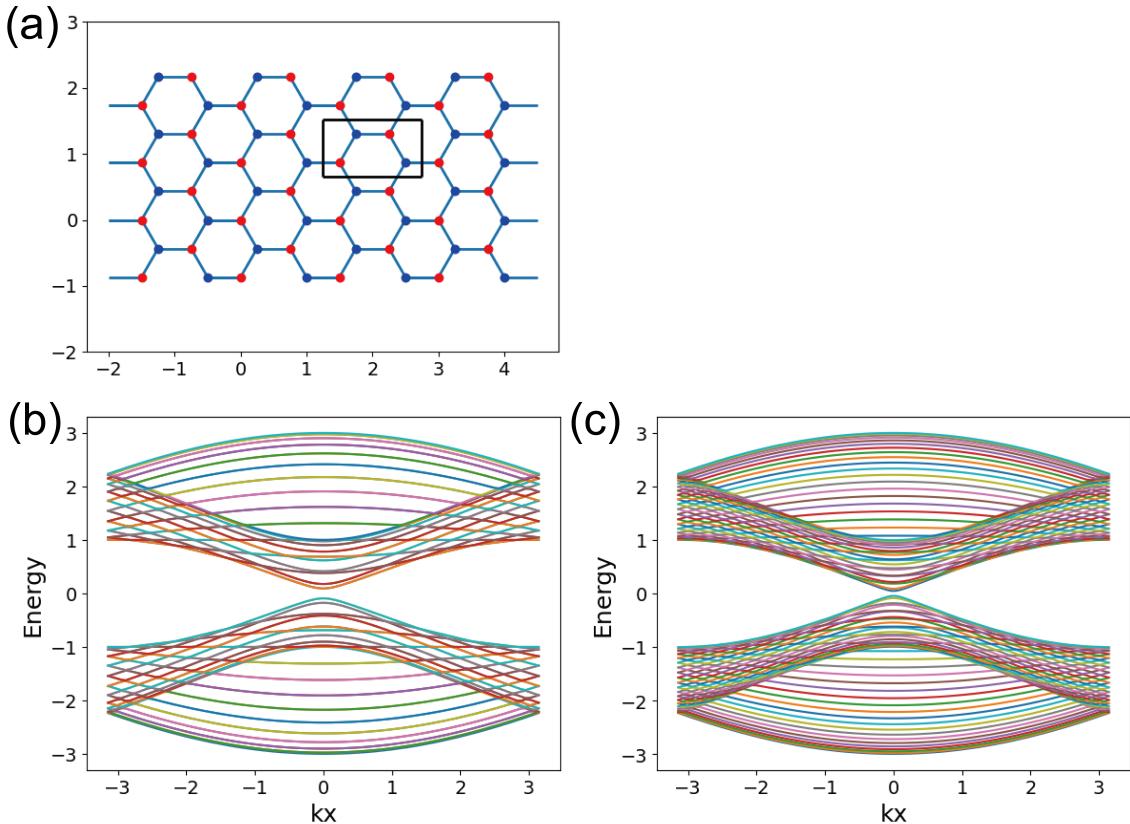


Fig. 4.5: (a) Atomic structure of armchair nanoribbon. (b) Band structure with periodic boundary conditions (that is, normal graphene). (c) Band structure of armchair nanoribbon with $N_y = 20$.

4.3 Armchair nanoribbon

Let us consider the nanoribbon with another edge type, armchair nanoribbon. Figure 4.5(a) shows the atomic structure of the armchair nanoribbon. The honeycomb lattice is rotated 90 degrees from Fig.4.4 to form another type of edge along the x axis. We will consider the band structure of this armchair ribbon. Using the rhombohedral unit cell shown in Fig.4.5(a) is convenient for armchair ribbons. We will label the four atoms in the cell (n, m) as $i = 0 - 3$ from the left. Each atom interacts with the three atoms labeled as follows:

- $(n, m, 0)$: $(n - 1, m, 3)$, $(n, m, 1)$, and $(n, m - 1, 1)$.
- $(n, m, 1)$: $(n, m, 0)$, $(n, m + 1, 0)$, and $(n, m, 2)$.
- $(n, m, 2)$: $(n, m, 1)$, $(n, m + 1, 3)$, and $(n, m, 3)$.
- $(n, m, 3)$: $(n, m, 2)$, $(n, m - 1, 2)$, and $(n + 1, m, 0)$.

Each atom can be uniquely numbered by $(m \times N + n) \times 4 + i$, which is used for constructing the matrix. The matrix size is $N \times M \times 4$, as the cell has four atoms.

The Schrödinger equation for these atoms are thus expressed as follows:

$$-tc_{n-1,m,3} - tc_{n,m,1} - tc_{n,m-1,1} - \mu c_{n,m,0} = Ec_{n,m,0} \quad (4.18)$$

$$-tc_{n,m,0} - tc_{n,m+1,0} - tc_{n,m,2} - \mu c_{n,m,1} = Ec_{n,m,1} \quad (4.19)$$

$$-tc_{n,m,1} - tc_{n,m+1,3} - tc_{n,m,3} - \mu c_{n,m,2} = Ec_{n,m,2} \quad (4.20)$$

$$-tc_{n,m,2} - tc_{n,m-1,2} - tc_{n+1,m,0} - \mu c_{n,m,3} = Ec_{n,m,3} \quad (4.21)$$

We perform the Fourier transform in the x direction:

$$c_{n,m,i} = \sum c_{k_x,m,i} e^{-ik_x x_n} \quad (4.22)$$

The four equations become

$$-te^{ik_x} c_{k_x,m,3} - tc_{k_x,m,1} - tc_{k_x,m-1,1} - \mu c_{k_x,m,0} = Ec_{k_x,m,0} \quad (4.23)$$

$$-tc_{k_x,m,0} - tc_{k_x,m+1,0} - tc_{k_x,m,2} - \mu c_{k_x,m,1} = Ec_{k_x,m,1} \quad (4.24)$$

$$-tc_{k_x,m,1} - tc_{k_x,m+1,3} - tc_{k_x,m,3} - \mu c_{k_x,m,2} = Ec_{k_x,m,2} \quad (4.25)$$

$$-tc_{k_x,m,2} - tc_{k_x,m-1,2} - te^{-ik_x} c_{k_x,m,0} - \mu c_{k_x,m,3} = Ec_{k_x,m,3} \quad (4.26)$$

At the upper edge, the Schrödinger equation for atom 1 and 2 is expressed as follows:

$$-tc_{k_x,m,0} - tc_{k_x,m,2} - \mu c_{k_x,m,1} = Ec_{k_x,m,1} \quad (4.27)$$

$$-tc_{k_x,m,1} - tc_{k_x,m,3} - \mu c_{k_x,m,2} = Ec_{k_x,m,2} \quad (4.28)$$

At the lower edge, the Schrödinger equation for atom 0 and 3 is expressed as follows:

$$-te^{ik_x} c_{k_x,m,3} - tc_{k_x,m,1} - \mu c_{k_x,m,0} = Ec_{k_x,m,0} \quad (4.29)$$

$$-tc_{k_x,m,2} - te^{-ik_x} c_{k_x,m,0} - \mu c_{k_x,m,3} = Ec_{k_x,m,3} \quad (4.30)$$

By solving the matrix by diagonalization, we can see the effect of the armchair edge. Figure 4.5 shows the calculated band structure (b) with and (c) without periodic boundary conditions. In contrast to the zigzag edge case, there is no flat band in the band structure, indicating no edge state in the armchair ribbons.

Chapter 5

Two orbital system

5.1 Fe based superconductor

In this chapter, we will try to understand the band structure of Fe-based oxypnictides, reported in [3].^{*1} These materials show a high-temperature superconductivity, and it is thought that the band near the Fermi level is composed of the Fe-d orbitals. They constructed a model in which a two-dimensional square lattice with two orbitals (d_{xz} and d_{yz}) per site, as shown in Fig. 5.1(b). Each orbital interacts with the orbitals at the surrounding eight sites. Let us try constructing the tight binding model for this model.

We label the d_{xz} and d_{yz} orbitals as 0 and 1. Because there are two orbitals in a unit cell, we get two Schrödinger equation for a cell (n, m) . The Schrödinger equation for the orbital 0 is expressed as

$$\begin{aligned} -\mu c_{n,m,0} + t_3 c_{n-1,m-1,0} - t_4 c_{n-1,m-1,1} + t_2 c_{n,m-1,0} + t_3 c_{n+1,m-1,0} \\ + t_4 c_{n+1,m-1,1} + t_1 c_{n+1,m,0} + t_3 c_{n+1,m+1,0} - t_4 c_{n+1,m+1,1} \\ + t_2 c_{n,m+1,0} + t_3 c_{n-1,m+1,0} + t_4 c_{n-1,m+1,1} + t_1 c_{n-1,m,0} = E c_{n,m,0} \quad (5.1) \end{aligned}$$

^{*1} S. Raghu et al. S. Rachu et al. Phys. Rev. B 77, 220503(R) (2008)

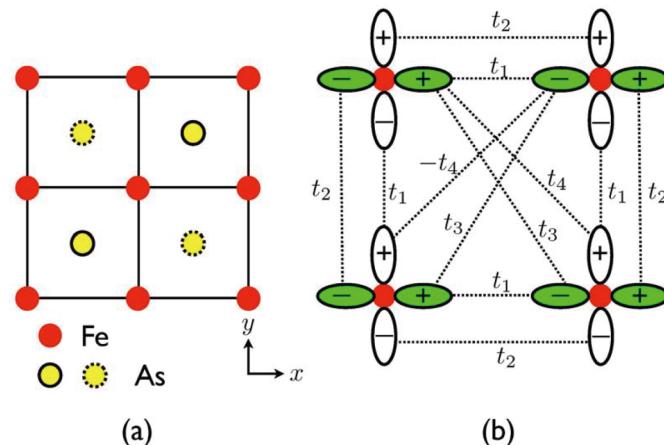


Fig. 5.1: (a) Atomic structure of Fe compounds in a Fe layer. (b) Tight binding model for (a). This picture is copied from [3]

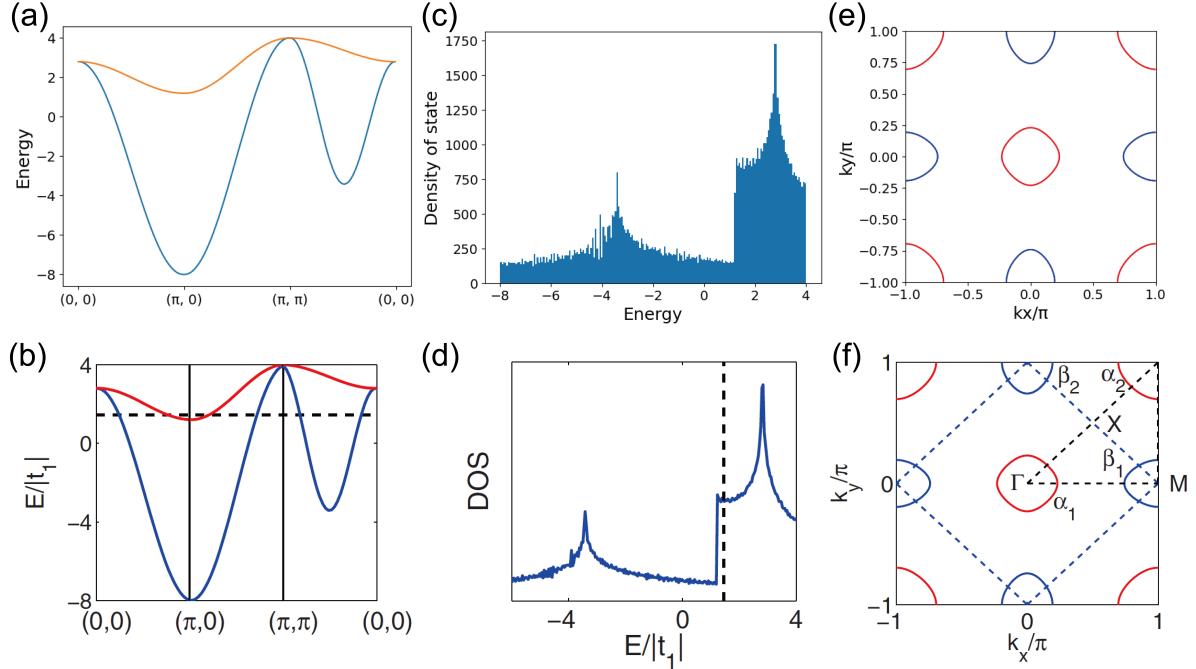


Fig. 5.2: Calculated (a) band structure, (c) density of state, and (e) Fermi surface. Corresponding figures from ref. [3] are shown in (b), (d), and (f) for comparison.

, while that for orbital 1 is

$$\begin{aligned} & -\mu c_{n,m,1} - t_4 c_{n-1,m-1,0} + t_3 c_{n-1,m-1,1} + t_1 c_{n,m-1,1} + t_4 c_{n+1,m-1,0} \\ & + t_3 c_{n+1,m-1,1} + t_2 c_{n+1,m,1} - t_4 c_{n+1,m+1,0} + t_3 c_{n+1,m+1,1} \\ & + t_1 c_{n,m+1,1} + t_4 c_{n-1,m+1,0} + t_3 c_{n-1,m+1,1} + t_2 c_{n-1,m,1} = E c_{n,m,1} \end{aligned} \quad (5.2)$$

We perform the following Fourier transform:

$$c_{n,m,i} = \sum c_{\mathbf{k},i} e^{-i\mathbf{k}\cdot\mathbf{r}} = \sum c_{\mathbf{k},i} e^{-ik_x x} e^{-ik_y y}. \quad (5.3)$$

The Fourier transform yields the following formula:

$$\epsilon_x c_{\mathbf{k},0} + \epsilon_{xy} c_{\mathbf{k},1} = E c_{\mathbf{k},0}, \quad (5.4)$$

$$\epsilon_{xy} c_{\mathbf{k},0} + \epsilon_y c_{\mathbf{k},1} = E c_{\mathbf{k},1} \quad (5.5)$$

, where

$$\epsilon_x = -2t_1 \cos k_x - 2t_2 \cos k_y - 4t_3 \cos k_x \cos k_y, \quad (5.6)$$

$$\epsilon_y = -2t_2 \cos k_x - 2t_1 \cos k_y - 4t_3 \cos k_x \cos k_y, \quad (5.7)$$

$$\epsilon_{xy} = -4t_4 \sin k_x \sin k_y. \quad (5.8)$$

Therefore, by diagonalizing the following matrix,

$$\begin{pmatrix} \epsilon_x & \epsilon_{xy} \\ \epsilon_{xy} & \epsilon_y \end{pmatrix} \quad (5.9)$$

, we can obtain the band structure corresponding to this model. Following the paper, we set $t_1 = -1.0$, $t_2 = 1.3$, $t_3 = t_4 = -0.85$, and $\mu = 1.45$. The calculated band structure and density of states are shown in Fig. 5.2(a) and (c). We also show the corresponding figures shown in ref. [3] to see that our calculation well reproduces the paper. We also plot the Fermi surface of this band, as shown in Fig. 5.2(e), which also well matches the paper.

Chapter 6

Topology in band structure

6.1 Topology in 1D chain

Consider the 1D chain where two atoms are in a unit cell. Two atoms in the same cell interact with $t + dt$ each other, while the interaction with the atoms in the neighbor cell is $t - dt$, as shown in Fig. 6.1. We get two Schrödinger equation for the two atoms in m th cells as follows:

$$-c_{m-1,1}(t - dt) - c_{m,1}(t + dt) = Ec_{m,0}, \quad (6.1)$$

$$-c_{m,0}(t + dt) - c_{m+1,0}(t - dt) = Ec_{m,1}. \quad (6.2)$$

We will apply the following Fourier transform:

$$c_{m,0} = \sum_k e^{-ikm} c_{k,0}, \quad (6.3)$$

$$c_{m,1} = \sum_k e^{-ikm} c_{k,1}. \quad (6.4)$$

Equations 6.1 and 6.2 is transformed as follows:

$$-c_{k,1}e^{ik}(t - dt) - c_{k,1}(t + dt) = Ec_{k,0} \quad (6.5)$$

$$-c_{k,0}(t + dt) - c_{k,0}e^{-ik}(t - dt) = Ec_{k,1} \quad (6.6)$$

$$\therefore \begin{pmatrix} 0 & -e^{ik}(t - dt) - (t + dt) \\ -(t + dt) & 0 \end{pmatrix} \begin{pmatrix} c_{k,0} \\ c_{k,1} \end{pmatrix} = E \begin{pmatrix} c_{k,0} \\ c_{k,1} \end{pmatrix} \quad (6.7)$$

By diagonalizing the matrix in eq. 6.7, we can get the eigenenergy and corresponding eigenstates of this system. Figures 6.2(a) and (b) show the band structure for the case of $dt = 0.2$ and $dt = -0.2$, respectively ($t = 1$). The band structures are identical to each other.

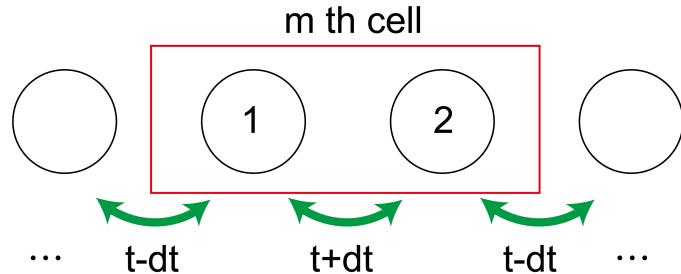


Fig. 6.1: Schematic illustration of the 1D chain with twice periodicity.

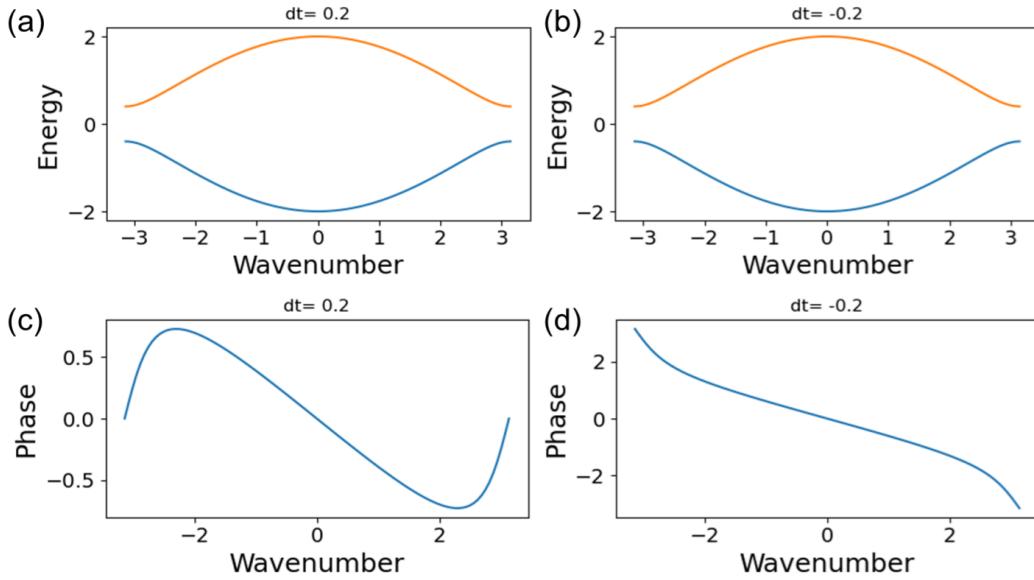


Fig. 6.2: Band structure and relative phase of the wave function for (a)(c) $dt = 0.2$ and (b)(d) $dt = -0.2$, respectively.

Then, let us see the property of the eigenstates. The eigenstates are expressed by a complex number. Thus, each eigenstate has the argument of complex, that is, the phase. Generally, the eigenstate phase does not affect the physical property because the square of it is interpreted as the probability, which cancels the phase information. However, the relative phase between the two states can affect the physical properties through the interference effect. Figure 6.2(c) and (d) show how the relative phase of two eigenstates change for $dt = 0.2$ and $dt = -0.2$, respectively. Although these two bands show the same band structures, the relative phase changes differently: When $dt = 0.2$, the relative phase oscillates and backs to the original value while constantly decreasing and returning to the original value by rounding from πi to πi in the case of $dt = -0.2$. In other words, in the latter case, the phase turns around the circle in an imaginary space. The two systems can be distinguished by the number of turns, called the topological number. The latter case is an example of a system with a nontrivial topological number.

6.2 Topology in graphene

We introduced the band structure of a honeycomb lattice in Chapter 4. Remind that there are two atoms in a cell. How does the phase change in the case of a honeycomb lattice? Let us consider the phase of two eigenstates in the case of a honeycomb lattice.

Figure 6.3(a) shows the 2D plot of the relative phase of two eigenstates. The phase changes between π and $-\pi$ between two K points in the Brillouin zone, indicating that the phase rotates by 2π when the wavenumber changes around a K point. The phase change is called the Berry phase. The non-zero Berry phase around the K points shows that the honeycomb lattice is topologically nontrivial.

In the discussion of physics, some related quantities are often used. Here, we will introduce the Berry connection (\mathbf{a}_n) and Berry curvature (\mathbf{F}_n), which is defined as follows:

$$\mathbf{a}_n(\mathbf{R}) = -i \langle \phi_n(\mathbf{R}) | \nabla_{\mathbf{R}} | \phi_n(\mathbf{R}) \rangle, \quad (6.8)$$

$$\mathbf{F}_n(\mathbf{R}) = \nabla_{\mathbf{R}} \times \mathbf{a}_n(\mathbf{R}). \quad (6.9)$$

The notation n indicates the n th band, and the wave function depends on a parameter \mathbf{R} , that is wavenumber here. Figure 6.3(b) and (c) shows the Berry connection and Berry curvature of

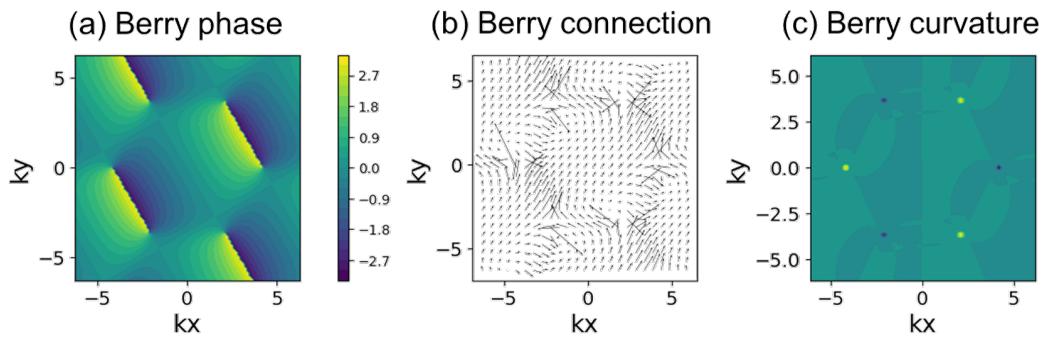


Fig. 6.3: (a) Relative phase of two eigenstates, (b) Berry connection, and (c) Berry curvature of a honeycomb lattice.^{*1}

the honeycomb lattice.^{*1}

^{*1} See the code for the details of the calculation.

Chapter 7

Appendix

7.1 Transformation of derivative equation

Following the basic definition of the derivative, the first derivative can be written as follows:

$$\begin{aligned}\frac{d}{dx}\psi(x) = \psi'(x) &= \left(\frac{\psi(x+dx) - \psi(x)}{dx} + \frac{\psi(x) - \psi(x-dx)}{dx} \right) / 2 \\ &= \frac{\psi(x+dx) - \psi(x-dx)}{2dx}.\end{aligned}\quad (7.1)$$

In the first line, we averaged the forward and backward slopes. We can get the formula for the second derivative in the same way using the $dx/2$ as the discrete unit. If we used $dx/2$, the first derivative is expressed as follows:

$$\begin{aligned}\frac{d}{dx}\psi(x) = \psi'(x) &= \left(\frac{\psi(x+dx/2) - \psi(x)}{dx/2} + \frac{\psi(x) - \psi(x-dx/2)}{dx/2} \right) / 2 \\ &= \frac{\psi(x+dx/2) - \psi(x-dx/2)}{dx}.\end{aligned}\quad (7.2)$$

Using eq. 7.2, the second derivative can be calculated as follows:

$$\begin{aligned}\frac{d^2}{dx^2}\psi(x) &= \frac{d}{dx}\psi'(x)' \\ &= \frac{\psi'(x+\frac{dx}{2}) - \psi'(x-\frac{dx}{2})}{dx} \\ &= \frac{\psi(x+dx) - \psi(x) - \psi(x) + \psi(x-dx)}{dx^2} \\ &= \frac{\psi(x+dx) - 2\psi(x) + \psi(x-dx)}{dx^2}.\end{aligned}\quad (7.3)$$

Finally, the term including $dx/2$ disappears, and the second derivative can also be calculated from the neighbor points. The second derivative of the wave function can be calculated from the value at the discrete points by using eq. 7.3.,

7.2 Diagonalization

Here, we introduce what is happening in diagonalization. We often get a matrix, such as like

$$\mathbf{H} = \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{pmatrix}. \quad (7.4)$$

In quantum mechanics, we often get the extenuation using the matrix as follows:

$$\begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \quad (7.5)$$

$$\therefore \mathbf{H}\mathbf{c} = E\mathbf{c} \quad (7.6)$$

In this form, the energy value and corresponding state are unclear. Thus, we will consider diagonalization. Diagonalization means converting a matrix to another one with only the diagonal components. We should find other matrix \mathbf{P} that convert \mathbf{H} to a diagonal matrix \mathbf{D} as follows:

$$\mathbf{P}^{-1}\mathbf{H}\mathbf{P} = \mathbf{D}, \quad (7.7)$$

$$\mathbf{D} = \begin{pmatrix} d_{11} & 0 & \dots & 0 \\ 0 & d_{22} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & d_{nn} \end{pmatrix} \quad (7.8)$$

Refer to some mathematical textbook to learn how to find \mathbf{P} . Substitution to eq.7.6 yields

$$\mathbf{P}\mathbf{D}\mathbf{P}^{-1}\mathbf{c} = E\mathbf{c} \quad (7.9)$$

$$\therefore \mathbf{D}(\mathbf{P}^{-1}\mathbf{c}) = E(\mathbf{P}^{-1}\mathbf{c}), \quad (7.10)$$

$$\therefore \mathbf{D}\mathbf{c}' = E\mathbf{c}'. \quad (7.11)$$

Now, we have new eigen equations. The equations can be decomposed to be

$$d_{mm}c'_m = E c'_m. \quad (7.12)$$

Because the matrix only has the diagonal component, the left side formula only has the c'_m component. Thus, this formula indicates $E = d_{mm}$, and the corresponding eigenstate is c'_m .

7.3 Sumamry and Memo

Processes to construct tight binding Hamiltonian:

1. List up all the atomic orbitals, with their energy and position.
2. Number the orbitals.
3. Construct a matrix. The matrix elements of (i, j) are:
 - Diagonal element: E_{ii} (energy of i th orbital).
 - Off diagonal element: $E_j\alpha_{ij} + t_{ij}$ (interaction of i th orbital with j th orbital), where $\alpha_{ij} = \int \psi_i \psi_j dx$ and $t_{ij} = \int V_i \psi_i \psi_j dx$. α_{ij} is often ignored by assuming that each orbital is well localized. The phase factor of e^{-ikx} should be multiplied depending on the position of j th orbital.

Bibliography

- [1] https://qiita.com/cometscome_phys/items/2bc0859cec8bb12e8d83
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- [3] S. Rachu et al. Phys. Rev. B 77, 220503(R) (2008).