

# Second Quantization

Naoya Kawakami

March 9, 2023  
version 1.0

# Contents

Chapter 1	Motivation for writing this text	1
Chapter 2	Introduction to second quantization	2
2.1	Description of multiple electrons in basic quantum mechanics . . . . .	2
2.2	Creation and annihilation operator . . . . .	3
2.3	Wave function and second quantization . . . . .	5
2.4	Expresion of operatorss in second quantization . . . . .	5
2.5	Application of second quantization . . . . .	6
Chapter 3	Second quantization and tight binding model	8
3.1	Tight binding model . . . . .	8
3.2	Orthogolanizaon of the one-electron Hamiltonian . . . . .	8
3.3	Multiple electron system . . . . .	9
3.4	Manybody interaction . . . . .	10
3.5	Wave number expression of the Coulomb interaction . . . . .	11
Chapter 4	Application of tight binding model	12
4.1	Hubbard model . . . . .	12
4.2	Superexchange interaction . . . . .	13
4.3	Coulomb interaction in neighbor sites . . . . .	14
Chapter 5	Appendix	16
5.1	Bra-ket expression . . . . .	16
5.2	Number expression and number operator . . . . .	17
5.3	A theorem for orthogonal system . . . . .	18
5.4	Tight binding Hamiltonian . . . . .	19
5.5	Fourier transform of a ket state . . . . .	19
5.6	Matrix element calculation of Hubbard Hamiltonian . . . . .	20
5.7	Python code to get the eigenvectors . . . . .	21
5.8	Spin operator . . . . .	21
5.9	Exchange operator . . . . .	23
Bibliography		24

## Chapter 1

# Motivation for writing this text

Recently, it has been revealed that in some materials, the interactions between the electrons dominate their characteristics. This kind of system is called a strongly correlated electron system. For describing the system with strong electron-electron interaction, multiple electrons should be considered simultaneously. However, describing the multiple interactions is annoying in basic quantum mechanics. Therefore, another method to describe quantum mechanics has been developed: "second quantization."

This text will show how conventional quantum mechanics is revised by the second quantization by introducing two operators, generation and annihilation operators. The formulas will be expressed by these operators instead of position and momentum. Finally, the "Hubbard Model," the most basic mode for describing strongly correlated systems, will be introduced.

## Chapter 2

# Introduction to second quantization

### 2.1 Description of multiple electrons in basic quantum mechanics

The second quantization aims to treat the multiple electrons simultaneously in quantum mechanics. Before introducing the method of second quantization, we will see how it can be described in basic quantum mechanics.

Firstly, let us remind the very base of a function with two variables,  $f(x, y)$ . In this function, the value of  $x$  ( $y$ ) is always expressed as the first (second) variable. For example, if  $x = a_1$  and  $y = a_2$ , the value of the function is expressed by  $f(a_1, a_2)$ . If  $x = a_2$  and  $y = a_1$ , it is  $f(a_2, a_1)$ .

The Schrödinger equation for one and two electrons is described as follows:

$$[T(r) + V(r)] \psi(r) = E\psi(r), \quad (2.1)$$

$$[T_1(r_1) + T_2(r_2) + V(r_1, r_2)] \psi(r_1, r_2) = E\psi(r_1, r_2). \quad (2.2)$$

$\psi(r_1, r_2)$  means that the positions of first and second electrons are expressed by  $r_1$  and  $r_2$ . An important notice is that we label each electron as "first" and "second". Here, we assume that each electron satisfies the Schrödinger equation for an atom (eq.2.1), with the eigenfunction (eigenenergy) of the first and second electron is  $\phi_1(r)$  ( $E_1$ ), and  $\phi_2(r)$  ( $E_2$ ). If we ignore the interaction between the two electrons ( $V(r_1, r_2) = V_1(r_1) + V_2(r_2)$ ), the solution of eq.2.2 is expressed as follows:

$$\psi(r_1, r_2) = \phi_1(r_1)\phi_2(r_2), \quad (2.3)$$

$$E = E_1 + E_2. \quad (2.4)$$

Although eq.2.3 is the solution of eq.2.2, this solution lacks a property of the electron: the electrons are not distinguishable. In other words, the physical property of the system should be identical even if we replace the position of the two electrons. Therefore, for the exchange of the positions, the following relation should be satisfied:

$$\psi(r_1, r_2) = \xi \psi(r_2, r_1). \quad (2.5)$$

$\xi$  is a complex number.  $\psi(r_2, r_1)$  means the first (second) electron is located at  $r_2$  ( $r_1$ ). If we replace the position twice,

$$\begin{aligned} \psi(r_1, r_2) &= \xi^2 \psi(r_1, r_2) \\ \therefore \xi &= \pm 1. \end{aligned} \quad (2.6)$$

The wave function should satisfy the above relations with the  $\xi = 1$  or  $-1$ . The particles with  $\xi = 1$  are called bosons, while those with  $\xi = -1$  are called fermions. Because the electron is a fermion, the replacement of the position of electrons 1 and 2 should satisfy the following relation:

$$\psi(r_1, r_2) = -\psi(r_2, r_1). \quad (2.7)$$

Replacement of the electron position in eq.2.3 yields

$$\psi(r_2, r_1) = \phi_1(r_2)\phi_2(r_1). \quad (2.8)$$

, which does not satisfy the relation in eq.2.7. It indicates that solving the Schrödinger equation is not enough to get the wave function for the system with multiple electrons. We should find another solution to express the characteristics of the electron fully. We can construct the solution by the linear combination of eq.2.3 and eq.2.8 as follows:

$$\psi(r_1, r_2) = \phi_1(r_1)\phi_2(r_2) - \phi_1(r_2)\phi_2(r_1). \quad (2.9)$$

As both terms are the solution of Schrödinger equation, eq.2.9 is also the solution of Schrödinger equation. In addition, eq.2.9 satisfies the relation in eq.2.7.

As shown above, getting the wave function of the system with more than two electrons needs two steps:

- (1) Solving the Schrödinger equation.
- (2) Constructing the solution satisfying the exchange relationship.

This process is complicated, especially for systems with many electrons. Therefore, we should consider another method that directly gets the wave function without step (2).

## 2.2 Creation and annihilation operator

We will introduce creation and annihilation operators to treat multiple electrons easily. Firstly, we define the creation ( $\hat{c}_i^\dagger$ ) operator<sup>\*1</sup> as follows:<sup>\*2</sup>

$$\hat{c}_i^\dagger(\alpha) |a, b, c \dots\rangle = |\alpha, a, b, c \dots\rangle, \quad (2.10)$$

in which  $\hat{c}_i^\dagger(\alpha)$  add an electron with the  $\alpha$  state to the system. If  $\alpha = d$ , we can reorder the states in the ket by replacing the electrons using the relation eq.2.7:

$$|\alpha = d, a, b, c \dots\rangle = (-1)^3 |a, b, c, \alpha = d, \dots\rangle \quad (2.11)$$

We introduce a number expression.<sup>\*3</sup> In the number expression, we numberize each state. Then, the number of electrons in each state is expressed by the numberized order in ket. In the number expression, the creation operator to add an electron at  $i$ -th state works as follows:

$$\hat{c}_i^\dagger |n_0, n_1, \dots, n_i, \dots\rangle = a_i |n_0, n_1, \dots, n_i + 1, \dots\rangle \quad (2.12)$$

$$a_i = (-1)^\lambda, \lambda = \sum_{n=0}^{i-1} n_i \quad (2.13)$$

$n_i$  indicates the number of electrons of the  $i$ -th state.

We will express the relation in eq.2.12 in a simplified form as follows:

$$\hat{c}_i^\dagger |n_i\rangle \propto |n_i + 1\rangle. \quad (2.14)$$

In addition, because two fermions cannot occupy the same state, we assume

$$\hat{c}_i^\dagger |1\rangle = 0. \quad (2.15)$$

Then, we will see the function of the  $\hat{c}_i$ , which acts as the annihilation operator. Let us apply the number operator on  $\hat{c}_i^\dagger |n_i\rangle$ .<sup>\*4</sup>

$$\begin{aligned} \hat{n}_i \hat{c}_i^\dagger |n_i\rangle &= \hat{n}_i |n_i + 1\rangle \\ &= (n_i + 1) |n_i + 1\rangle \\ &= (n_i + 1) \hat{c}_i^\dagger |n_i\rangle \\ &= \hat{c}_i^\dagger (n_i + 1) |n_i\rangle \\ &= \hat{c}_i^\dagger (\hat{n}_i + 1) |n_i\rangle \\ \therefore [\hat{c}_i^\dagger, \hat{n}_i] &= \hat{c}_i \hat{n}_i^\dagger - \hat{n}_i \hat{c}_i^\dagger = -\hat{c}_i^\dagger. \end{aligned} \quad (2.16)$$

<sup>\*1</sup> In this text, the operators are expressed by using ^ to distinguish them from the values.

<sup>\*2</sup> Hereafter, we will express the state of electrons using the bra-ket expression. If you are not familiar with this expression, see Appendix 5.1.

<sup>\*3</sup> See Appendix 5.2 for the detail.

<sup>\*4</sup> Number operator  $\hat{n}_i$  produces the number of the electron in the  $i$ -th state, defined by  $\hat{n}_i |n_0, n_1, n_2, \dots\rangle = n_i |n_0, n_1, n_2, \dots\rangle$ .

The Hermite conjecture of eq.2.16 is<sup>\*5</sup>

$$\begin{aligned} [\hat{c}_i^\dagger, \hat{n}_i]^\dagger &= \hat{n}_i^\dagger \hat{c}_i - \hat{c}_i \hat{n}_i^\dagger = -\hat{c}_i \\ \therefore \hat{n}_i \hat{c}_i &= \hat{c}_i (\hat{n}_i - 1) \end{aligned} \quad (2.17)$$

By applying eq.2.17 to  $|n_i\rangle$ , we get the following relation:

$$\begin{aligned} \hat{n}_i \hat{c}_i |n_i\rangle &= \hat{c}_i (\hat{n}_i - 1) |n_i\rangle \\ &= (n_i - 1) \hat{c}_i |n_i\rangle \\ \therefore \hat{c}_i |n_i\rangle &\propto |n_i - 1\rangle. \end{aligned} \quad (2.18)$$

It indicates that the operator  $\hat{c}_i$  reduces the number of electrons at  $i$ -th state. Because the number of electron should not be less than 0, we define

$$\hat{c}_i |0\rangle = 0. \quad (2.19)$$

In addition, we define the anihilation operators including the coefficient as follows:

$$\hat{c}_i |n_i\rangle = b_i |n_i - 1\rangle. \quad (2.20)$$

Then,

$$\langle n_i | \hat{c}_i \hat{c}_i^\dagger | n_i \rangle = \langle n_i | \hat{c}_i a_i | n_i + 1 \rangle = \langle n_i | b_i a_i | n_i \rangle = b_i a_i, \quad (2.21)$$

$$\langle n_i | \hat{c}_i \hat{c}_i^\dagger | n_i \rangle = [\hat{c}_i^\dagger | n_i \rangle]^\dagger \hat{c}_i^\dagger | n_i \rangle = |\hat{c}_i^\dagger | n_i \rangle|^2 = |b_i|^2 \quad (2.22)$$

$$\therefore b_i = a_i. \quad (2.23)$$

We will derive several relationships between  $\hat{c}_i$  and  $\hat{c}_i^\dagger$ . Firstly, according to the above definitions, we can derive the following relationships:

$$\hat{c}_i^\dagger \hat{c}_i |0\rangle = 0 \quad (2.24)$$

$$\hat{c}_i \hat{c}_i^\dagger |0\rangle = \hat{c}_i |1\rangle = |0\rangle \quad (2.25)$$

$$\hat{c}_i^\dagger \hat{c}_i |1\rangle = \hat{c}_i^\dagger |0\rangle = |1\rangle \quad (2.26)$$

$$\hat{c}_i \hat{c}_i^\dagger |1\rangle = 0 \quad (2.27)$$

These relations can be summarized as the following exchange relation:

$$[\hat{c}_i^\dagger, \hat{c}_i] = \hat{c}_i^\dagger \hat{c}_i + \hat{c}_i \hat{c}_i^\dagger = 1. \quad (2.28)$$

Considering the orthogonarity of the different state, both the  $\hat{c}_i^\dagger \hat{c}_j$  and  $\hat{c}_j \hat{c}_i^\dagger$  becomes zero if  $i \neq j$ . This property can be combined with eq.2.28 as follows:

$$[\hat{c}_i^\dagger, \hat{c}_j] = \hat{c}_i^\dagger \hat{c}_j + \hat{c}_j \hat{c}_i^\dagger = \delta_{i,j} \quad (2.29)$$

In addition, because the fermion is asymmetric to the replacement, the exchange relation of the operators are

$$\hat{c}_i^\dagger \hat{c}_j^\dagger = -\hat{c}_j^\dagger \hat{c}_i^\dagger \quad (2.30)$$

$$\therefore [\hat{c}_i^\dagger, \hat{c}_j^\dagger] = \hat{c}_i^\dagger \hat{c}_j^\dagger + \hat{c}_j^\dagger \hat{c}_i^\dagger = 0, \quad (2.31)$$

$$[\hat{c}_i, \hat{c}_j] = \hat{c}_i \hat{c}_j + \hat{c}_j \hat{c}_i = 0. \quad (2.32)$$

The number operator can be defined as  $\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i$ , proofed as follows:

$$\hat{c}_i^\dagger \hat{c}_i |0\rangle = 0 \quad (2.33)$$

$$\hat{c}_i^\dagger \hat{c}_i |1\rangle = 1 \times |1\rangle \quad (2.34)$$

In this section, we introduced the creation and annihilation operators. In addition, several theorems are derived. The important features of creation and annihilation operators are summarized as follows.

---

<sup>\*5</sup> Note that  $\hat{n} = \hat{n}^\dagger$ .

$$\hat{c}_i |n_i\rangle = a_i |n_i - 1\rangle \quad (2.35)$$

$$\hat{c}_i^\dagger |n_i\rangle = a_i |n_i + 1\rangle \quad (2.36)$$

$$[\hat{c}_i^\dagger, \hat{c}_j] = \delta_{i,j} \quad (2.37)$$

$$[\hat{c}_i^\dagger, \hat{c}_j^\dagger] = [\hat{c}_i, \hat{c}_j] = 0 \quad (2.38)$$

$$\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i \quad (2.39)$$

## 2.3 Wave function and second quantization

We introduce two creation and annihilation operators:

$$\hat{\psi}^\dagger(r) |0\rangle = |r\rangle, \quad (2.40)$$

$$\hat{\psi}(r) |r\rangle = |0\rangle. \quad (2.41)$$

These operators generate (or annihilate) an electron at the position  $r$ .<sup>\*6</sup>  $|r\rangle$  represents a state with an electron at  $r$ . Two electron state with the electrons at  $r_1$  and  $r_2$  is expressed by

$$|r_1, r_2\rangle = \hat{\psi}^\dagger(r_1) \hat{\psi}^\dagger(r_2) |0\rangle. \quad (2.42)$$

Let us consider the relationship between the state  $|\psi\rangle$  and the wave function  $\psi(r)$ . Using eq.5.14,<sup>\*7</sup> the relationships are expressed as follows:

$$|\psi\rangle = \int \int \psi(r'_1, r'_2) |r'_1, r'_2\rangle dr'_1 dr'_2. \quad (2.43)$$

The state with the electrons are located at  $r_1$  and  $r_2$  is obtained by the inner product with the  $\langle r_1, r_2|$ :

$$\begin{aligned} \Psi(r_1, r_2) &= \langle r_1, r_2 | \psi \rangle \\ &= \int \int \psi(r'_1, r'_2) \langle r_1, r_2 | r'_1, r'_2 \rangle dr'_1 dr'_2 \\ &= \int \int \psi(r'_1, r'_2) \langle 0 | \hat{\psi}(r_1) \hat{\psi}(r_2) \hat{\psi}^\dagger(r'_1) \hat{\psi}^\dagger(r'_2) | 0 \rangle dr'_1 dr'_2. \end{aligned} \quad (2.44)$$

We can transform the equation by replacing the order of the operators by using eq.2.37. Note that the terms like  $\hat{\psi}(r) |0\rangle$  is zero. Finally, we get

$$\begin{aligned} \Psi(r_1, r_2) &= \int \int [\delta(r'_1 - r_1) \delta(r'_2 - r_2) - \delta(r_2 - r'_1) \delta(r_1 - r'_2)] \psi(r'_1, r'_2) dr'_1 dr'_2 \\ &= \psi(r_1, r_2) - \psi(r_2, r_1). \end{aligned} \quad (2.45)$$

We got  $\Psi(r_1, r_2)$  according to the calculation rule of the creation and annihilation operators. Note that we directly got the wave function that satisfies eq.2.7 without the construction process.

## 2.4 Expression of operators in second quantization

An operator for the single electron is expressed as follows by using the creation and annihilation operators:

$$\sum_i h(r_i) \rightarrow \int dr \hat{\psi}^\dagger(r) h(r) \hat{\psi}(r). \quad (2.46)$$

<sup>\*6</sup> Note that  $\hat{\psi}^\dagger(r)$  and  $\hat{\psi}(r)$  is totally different from the wave function  $\psi(r)$ .

<sup>\*7</sup> See Appendix 5.1.

For the two-electron operators,

$$\sum_{i < j} V(r_i - r_j) \rightarrow \frac{1}{2} \int dr_1 dr_2 \hat{\psi}^\dagger(r_1) \hat{\psi}^\dagger(r_2) V(r_i - r_j) \hat{\psi}(r_2) \hat{\psi}(r_1). \quad (2.47)$$

I do not show the proof here as it is complicated.

## 2.5 Application of second quantization

As we defined in the previous section, the operator  $\hat{\psi}^\dagger(r)$  adds an electron at the position  $r$ . However, the real electron has the distribution defined by the wave function  $\phi_n(r)$ . Therefore, we define another creation operator,  $\hat{c}_n^\dagger$ , which adds an electron at the state  $\phi_n(r)$ . The relationship between  $\hat{\psi}^\dagger(r)$  and  $\hat{c}_n^\dagger$  is expressed as follows:

$$\hat{c}_n^\dagger = \int \phi_n(r) \hat{\psi}^\dagger(r) dr, \quad (2.48)$$

representing that  $\hat{c}_n^\dagger$  creates the electron at all the  $r$  with the amplitude of  $\phi_n(r)$ .

When  $\{\phi_1(r), \phi_2(r), \dots\}$  composes the normalized orthogonal system, the following theorem is derived:<sup>\*8</sup>

$$\sum_n \phi_n^*(r) \phi_n(r') = \delta(r - r'). \quad (2.49)$$

Applying  $\phi_n^*(r)$  and summarizing for all the  $n$  on eq.2.48 yields

$$\begin{aligned} \sum_n \hat{c}_n^\dagger \phi_n^*(r) &= \sum_n \int \phi_n(r') \phi_n^*(r) \hat{\psi}^\dagger(r') dr' \\ &= \int \left[ \sum_n \phi_n(r') \phi_n^*(r) \right] \hat{\psi}^\dagger(r') dr' \\ &= \int \delta(r - r') \hat{\psi}^\dagger(r') dr' \end{aligned} \quad (2.50)$$

$$\therefore \hat{\psi}^\dagger(r) = \sum_n \hat{c}_n^\dagger \phi_n^*(r). \quad (2.51)$$

In the same way, we can get

$$\hat{\psi}(r) = \sum_n \hat{c}_n \phi_n(r). \quad (2.52)$$

By using these relationships, we will revise the Hamiltonians.

Let us consider the Schrödinger equation for  $N$  electrons.<sup>\*9</sup> The Schrödinger equation of this system is expressed as follows:

$$\sum_i \left[ \frac{1}{2m} \nabla_i^2 + V(r_i) \right] \Psi(r_1, r_2, \dots) = E \Psi(r_1, r_2, \dots). \quad (2.53)$$

We also assume that the Schrödinger equation for a single electron has been solved. That is,

$$\left[ \frac{1}{2m} \nabla^2 + V(r) \right] \phi_n(r) = \epsilon_n \phi_n(r). \quad (2.54)$$

<sup>\*8</sup> See Appendix 5.2 for the proof.

<sup>\*9</sup> Here, we assume the electrons do not interact with each other.



As we have already shown in eq.2.46, the Hamiltonian can be expressed as follows in the second quantization form:

$$\begin{aligned} H &= \sum_i \left[ \frac{1}{2m} \nabla_i^2 + V(r_i) \right] \\ &\rightarrow \int dr \hat{\psi}^\dagger(r) \left[ \frac{1}{2m} \nabla^2 + V(r) \right] \hat{\psi}(r). \end{aligned} \quad (2.55)$$

Substitution by eq.2.51 and eq.2.52 yields

$$\begin{aligned} H &= \int dr \hat{\psi}^\dagger(r) \left[ \frac{1}{2m} \nabla^2 + V(r) \right] \hat{\psi}(r) \\ &= \int dr \sum_{n,n'} \hat{c}_n^\dagger \phi_n^*(r) \left[ \frac{1}{2m} \nabla^2 + V(r) \right] \phi_{n'} \hat{c}_{n'} \\ &= \sum_{n,n'} \hat{c}_n^\dagger \hat{c}_{n'} \int dr \phi_n^*(r) \left[ \frac{1}{2m} \nabla^2 + V(r) \right] \phi_{n'} \\ &= \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n. \end{aligned} \quad (2.56)$$

We used eq.2.54 in the final conversion.

Therefore, the Schrödinger equation in the second quantization form is expressed by

$$H |\psi\rangle = \left[ \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n \right] |\psi\rangle = E |\psi\rangle. \quad (2.57)$$

The solution is

$$|\psi\rangle = c_{q_1}^\dagger c_{q_2}^\dagger \cdots c_{q_N}^\dagger |0\rangle, \quad (2.58)$$

$$E = \sum_i^N \epsilon_{q_i}. \quad (2.59)$$

$q_i$  represents any combination of  $n$ . For example, the ground state is realized when  $q_i = i$ , which yields

$$E = \sum_i \epsilon_i, \quad (2.60)$$

$$|\psi\rangle = c_1^\dagger c_2^\dagger \cdots c_N^\dagger |0\rangle. \quad (2.61)$$

## Chapter 3

# Second quantization and tight binding model

### 3.1 Tight binding model

The wave function of an electron is localized at a minimum under the strong potential, as shown in Fig. 3.1. A system with strong potential can be described by a tight binding model. In this section, we will briefly see the basic concept of the tight-binding model.

We number each potential minima as 1, 2, 3, ...,  $j$ , ... and the localized state at the  $j$ -th minima is expressed by  $|j\rangle$ . We assume the wave function between the neighbor minima overlaps slightly. These relationships are expressed as follows:

$$\langle j|l\rangle = \begin{cases} 1 & (j = l) \\ 0 & (j \neq l) \end{cases}, \quad (3.1)$$

$$\langle j|H|l\rangle = \begin{cases} E_0 & (j = l) \\ -\gamma & (|j - l| = 1) \\ 0 & (else) \end{cases}. \quad (3.2)$$

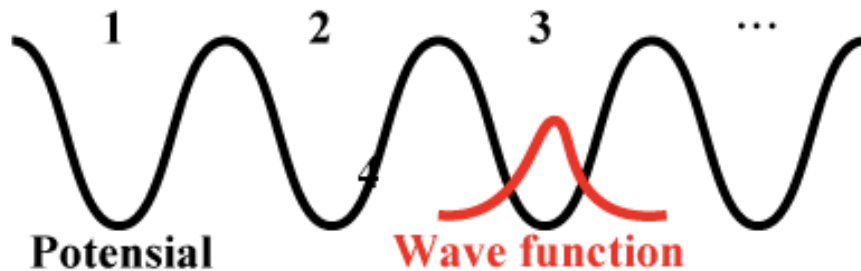
$E_0$  is the eigen energy of the  $|j\rangle$ , and  $-\gamma$  represents the interaction energy with the neighbor cites. The Hamiltonian satisfying the above relation is expressed by<sup>\*1</sup>

$$H^{(1)} = -\gamma \sum_l (|l\rangle \langle l+1| + |l\rangle \langle l-1|) + E_0 \sum_l |l\rangle \langle l| \quad (3.3)$$

The notation of <sup>(1)</sup> indicates that this Hamiltonian is for one electron system.

### 3.2 Orthogonalization of the one-electron Hamiltonian

We will orthogonalize the Hamiltonian eq.3.3 to get the eigenenergy and eigenstate. An effective way is to express each state by the wavenumber by applying Fourier transformation. The Fourier transform of



**Fig. 3.1:** Concept of a tight binding model.

---

<sup>\*1</sup> See Appendix 5.4 for detail.

a state  $|l\rangle$  yields<sup>\*2</sup>

$$\begin{aligned} |l\rangle &= \frac{1}{\sqrt{N}} \sum_k e^{ikl} |k\rangle \\ &= \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} e^{i\frac{2\pi}{N}ml} |m\rangle. \end{aligned} \quad (3.4)$$

Here we assume that the system is periodic with  $N$  atoms. By substituting eq.3.4 to eq.3.3, each term can be summarized by  $|m\rangle$  as follows:

$$H^{(1)} = \sum_{m=0}^{N-1} \left( -2\gamma \cos \frac{2\pi}{N}m + E_0 \right) |m\rangle \langle m|. \quad (3.5)$$

This formula indicates that  $-2\gamma \cos \frac{2\pi}{N}m + E_0$  is the eigen energy of the state  $|m\rangle$ . As the  $m$  is the notation for the possible wave number  $k = \frac{2\pi}{Na}m$ ,<sup>\*3</sup> we can draw the dependence of energy on the wavenumber, that is the band diagram.

### 3.3 Multiple electron system

We saw in the previous chapter that second quantization is effective in treating multiple electron systems. Therefore, we will introduce the second quantization to the tight binding model.

In this chapter, we define creation and annihilation operators as follows:

$$\hat{c}^\dagger(\alpha) |\psi_1, \psi_2, \dots, \psi_N\rangle = |\alpha, \psi_1, \psi_2, \dots, \psi_N\rangle, \quad (3.6)$$

$$\hat{c}(\beta) |\psi_1, \psi_2, \dots, \psi_N\rangle = \sum_{k=1}^N (-1)^{k-1} \langle \beta | \psi_k \rangle |\psi_1, \dots, \psi_{k-1}, \psi_{k+1}, \dots, \psi_N\rangle, \quad (3.7)$$

in which  $\hat{c}^\dagger(\alpha)$  add an electron with the state  $\alpha$ , while  $\hat{c}(\beta)$  annihilates the electron at the state  $\beta$ .<sup>\*4</sup> The factor  $(-1)^{k-1}$  is necessary to satisfy the exchange relation of fermions.<sup>\*5</sup> In addition, the following expression is used to express the multiple electron system:

$$|\Psi\rangle = |\psi_1, \psi_2, \dots, \psi_N\rangle = |\psi_1\rangle \times |\psi_2\rangle \times \dots \times |\psi_N\rangle \quad (3.8)$$

In this definition, the number operator is expressed as follows:

$$\begin{aligned} &\hat{c}^\dagger(\alpha) \hat{c}(\beta) |\psi_1, \psi_2, \dots, \psi_N\rangle \\ &= \sum_{k=1}^N (-1)^{k-1} \langle \beta | \psi_k \rangle \hat{c}^\dagger(\alpha) |\psi_1, \dots, \psi_{k-1}, \psi_{k+1}, \dots, \psi_N\rangle \\ &= \sum_{k=1}^N (-1)^{k-1} \langle \beta | \psi_k \rangle |\alpha, \psi_1, \dots, \psi_{k-1}, \psi_{k+1}, \dots, \psi_N\rangle \\ &= \sum_{k=1}^N \langle \beta | \psi_k \rangle |\psi_1, \dots, \psi_{k-1}, \alpha, \psi_{k+1}, \dots, \psi_N\rangle \\ \therefore \hat{c}^\dagger(\alpha) \hat{c}(\beta) |\Psi\rangle &= \sum_{k=1}^N \langle \beta | \psi_k \rangle |\psi_1, \dots, \psi_{k-1}, \alpha, \psi_{k+1}, \dots, \psi_N\rangle. \end{aligned} \quad (3.9)$$

<sup>\*2</sup> See Appendix 5.5 for details.

<sup>\*3</sup>  $a$  is the lattice constant.

<sup>\*4</sup> You can check the function of  $\hat{c}(\beta)$  by assuming some state, such as  $\beta = \psi_j$ . You may find that only the state  $(-1)^{j-1} |\psi_1, \dots, \psi_{k-1}, \psi_{k+1}, \dots, \psi_N\rangle$  remains.

<sup>\*5</sup>  $|\psi_1, \psi_2\rangle = -|\psi_2, \psi_1\rangle$ .

In the final part, we used the characteristics of the electron that the state is antisymmetric against the exchange of two electrons.\*<sup>6</sup> We will use this relation to revise the operators.

Here we assume an operator for an electron is expressed as follows:

$$A^{(1)} = |\alpha\rangle \langle\beta|. \quad (3.10)$$

We will express the operator for applying  $A^{(1)}$  for all the electrons in the system as  $A$ . Applying  $A$  on the many-body state  $|\Psi\rangle$  yields

$$\begin{aligned} A|\Psi\rangle &= \left[ A^{(1)}|\psi_1\rangle \right] \times |\psi_2\rangle \times \cdots \times |\psi_N\rangle \\ &\quad + |\psi_1\rangle \times \left[ A^{(1)}|\psi_2\rangle \right] \times \cdots \times |\psi_N\rangle \\ &\quad + \cdots \\ &\quad + |\psi_1\rangle \times |\psi_2\rangle \times \cdots \times \left[ A^{(1)}|\psi_N\rangle \right] \\ &= \langle\beta|\psi_1\rangle |\alpha\rangle |\psi_2\rangle \times \cdots \times |\psi_N\rangle \\ &\quad + \langle\beta|\psi_2\rangle |\psi_1\rangle \times |\alpha\rangle \cdots \times |\psi_N\rangle \\ &\quad + \cdots \\ &\quad + \langle\beta|\psi_N\rangle |\psi_1\rangle \times |\psi_2\rangle \cdots \times |\psi_{N-1}\rangle |\alpha\rangle \\ &= \sum_{k=1}^N \langle\beta|\psi_k\rangle |\psi_1, \psi_2, \cdots, \psi_{k-1}, \alpha, \psi_{k+1}, \cdots, \psi_N\rangle \\ &= \hat{c}(\alpha)\hat{c}(\beta)|\Psi\rangle \end{aligned} \quad (3.11)$$

In the final line, we use the relation eq.3.9. Equation 3.11 reveals that  $\hat{A} = \hat{c}^\dagger(\alpha)\hat{c}(\beta)$  corresponds to the  $A^{(1)} = |\alpha\rangle \langle\beta|$ . This correspondence indicates that tight-binding Hamiltonian for multiple electron systems can be expressed as follows from eq.3.3:

$$H^{(1)} = -\gamma \sum_{l=0}^{N-1} (|l\rangle \langle l+1| + |l\rangle \langle l-1|) + E_0 \sum_{l=0}^{N-1} |l\rangle \langle l| \quad (3.12)$$

$$H = -\gamma \sum_{l=0}^{N-1} \left( \hat{a}_l^\dagger \hat{a}_{l+1} + \hat{a}_l^\dagger \hat{a}_{l-1} \right) + E_0 \sum_{l=0}^{N-1} \hat{a}_l^\dagger \hat{a}_l \quad (3.13)$$

### 3.4 Manybody interaction

[Not complete]

In the previous section, we just considered the hopping between the neighbor site. Here we briefly introduce the manybody interaction in the second quantization format.

The most basic manybody interaction between the two electrons is the Coulomb potential:

$$V(r_1, r_2) = \frac{1}{|r_1 - r_2|} \quad (3.14)$$

Here we assume that the Coulomb constant  $e = 1$  for simplicity. The Hamiltonian for the Coulomb interaction should satisfy the following relation:

$$\hat{V} |r_1, r_2\rangle = V(r_1, r_2) |r_1, r_2\rangle \quad (3.15)$$

We will show that the following expression satisfies the above relation:

$$\hat{V} = \frac{1}{2} \int d^3x d^3y \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(y) V(x, y) \hat{\Psi}(y) \hat{\Psi}(x) \quad (3.16)$$

---

\*<sup>6</sup> For example,  $|\alpha, \psi_1, \cdots, \psi_{k-1}, \psi_{k+1}, \cdots, \psi_N\rangle = -|\psi_1, \alpha, \cdots, \psi_{k-1}, \psi_{k+1}, \cdots, \psi_N\rangle$ . Repetition of this exchange for  $(k-1)$  times produces  $|\psi_1, \cdots, \psi_{k-1}, \alpha, \psi_{k+1}, \cdots, \psi_N\rangle$ . This exchange cancels the factor  $(-1)^{k-1}$ .

Let us try applying this operator to the two electron state  $|r_1, r_2\rangle$ .

$$\hat{V} |r_1, r_2\rangle = \frac{1}{2} \int d^3x d^3y \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(y) V(x, y) \hat{\Psi}(y) \hat{\Psi}(x) \hat{\Psi}^\dagger(r_1) \hat{\Psi}^\dagger(r_2) |0\rangle \quad (3.17)$$

$$= \frac{1}{2} \int d^3x d^3y \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(y) V(x, y) [\delta(x - r_1) \delta(y - r_2) |0\rangle - \delta(x - r_2) \delta(y - r_1) |0\rangle] \quad (3.18)$$

$$= \frac{1}{2} V(r_1, r_2) \hat{\Psi}^\dagger(r_1) \hat{\Psi}^\dagger(r_2) |0\rangle - \frac{1}{2} V(r_2, r_1) \hat{\Psi}^\dagger(r_2) \hat{\Psi}^\dagger(r_1) |0\rangle \quad (3.19)$$

$$= V(r_1, r_2) |r_1, r_2\rangle \quad (3.20)$$

In the final part we used the exchange relation. The function for the many body state  $|r_1, r_2, \dots, r_N\rangle$  can also be shown in the same way.

### 3.5 Wave number expression of the Coulomb interaction

memo: second quantization note v5.pdf

## Chapter 4

# Application of tight binding model

### 4.1 Hubbard model

One of the most simple models with electron-electron interaction is the Hubbard model. In the Hubbard model, we consider a crystal consisting of atoms with an  $s$  orbital. We assume that the number of electrons is the same as that of atoms, leading to half-filled metal in classical condensed matter physics. We consider two energies in this model:

- Hopping energy between the neighbor atoms.
- Coulomb repulsion between the electrons. The Coulomb repulsion acts only when two electrons occupy the same orbital.

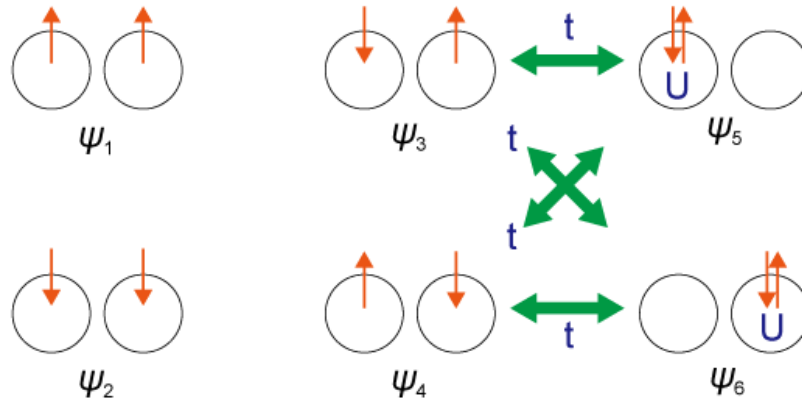
The Hamiltonian of this system is written as follows:

$$H = \sum_{(i,j),\sigma} (t_{ij} \hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma} + t_{ji} \hat{c}_{j,\sigma}^\dagger \hat{c}_{i,\sigma}) + U \sum_j n_{j\uparrow} n_{j\downarrow}. \quad (4.1)$$

This Hamiltonian takes the spin state ( $\sigma$ ) into account. Thus, an orbital can store two electrons with opposite spins.  $t_{ij}$  is the hopping energy between the atom  $i$  and  $j$ . The second term represents the Coulomb repulsion; When an orbital has both up and down spins, an energy  $U$  is added to the system. To simplify, we will consider the system with two atoms (labeled as 1 and 2). In addition, we also write  $t_{ij} = -t$  to make clear that the hopping stabilizes the system. The Hamiltonian of this system is expressed by

$$H = -t \sum_{\sigma} (\hat{c}_{1,\sigma}^\dagger \hat{c}_{2,\sigma} + \hat{c}_{2,\sigma}^\dagger \hat{c}_{1,\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}). \quad (4.2)$$

The possible states are summarized in Fig. 4.1. The arrows indicate the energetic relation between each



**Fig. 4.1:** Possible states in Hubbard model with two atoms.

state. The matrix elements of the Hamiltonian can be expressed as follows:<sup>\*1</sup>

$$H = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & t & t \\ 0 & 0 & 0 & 0 & -t & -t \\ 0 & 0 & t & -t & U & 0 \\ 0 & 0 & t & -t & 0 & U \end{pmatrix} \quad (4.3)$$

The eigenvalues and eigenvectors are calculated as follows:<sup>\*2</sup>

$$E_2 = 0 \quad |\Psi_1\rangle = |\psi_1\rangle \quad (4.4)$$

$$|\Psi_2\rangle = |\psi_2\rangle \quad (4.5)$$

$$|\Psi_3\rangle = |\psi_3\rangle + |\psi_4\rangle \quad (4.6)$$

$$E_4 = U \quad |\Psi_4\rangle = |\psi_5\rangle - |\psi_6\rangle \quad (4.7)$$

$$E_1 = \frac{U}{2} - \frac{\sqrt{U^2 + 16t^2}}{2} \quad |\Psi_5\rangle = \frac{U + \sqrt{U^2 + 16t^2}}{4t} (|\psi_3\rangle - |\psi_4\rangle) - |\psi_5\rangle - |\psi_6\rangle \quad (4.8)$$

$$E_3 = \frac{U}{2} + \frac{\sqrt{U^2 + 16t^2}}{2} \quad |\Psi_6\rangle = \frac{U - \sqrt{U^2 + 16t^2}}{4t} (|\psi_3\rangle - |\psi_4\rangle) - |\psi_5\rangle - |\psi_6\rangle. \quad (4.9)$$

Note that the eigenvectors are not normalized. If  $U \gg 4t$ , the ground state is approximated to be

$$E_1 \sim -\frac{4t^2}{U} \quad |\Psi_5\rangle \sim |\psi_3\rangle - |\psi_4\rangle, \quad (4.10)$$

and the excited state is

$$E_3 \sim U \quad |\Psi_6\rangle \sim |\psi_5\rangle + |\psi_6\rangle. \quad (4.11)$$

The system should pass the states  $|\Psi_6\rangle$  for the electrons to transport. However,  $|\Psi_6\rangle$  is an excited state when the Coulomb interaction is large. It indicates that the electron should be excited like insulators for electron transport. Thus, the system with strong electron-electron interaction behaves like an insulator even though the system is half-filled. This kind of insulator is called a Mott insulator. In addition, the ground state shows antiferromagnetic spin order because of the stabilization by the hopping. In other words, the ferromagnetic state ( $|\psi_1\rangle$  and  $|\psi_2\rangle$ ) shows the higher energy because the electrons cannot hop without spin flip. These facts indicate that, in general, the Mott insulator is an anti-ferromagnet.

## 4.2 Superexchange interaction

In the Hubbard model, the spin texture of the system affects the energy of the system, leading to the antiferromagnetic ground state. We will discuss it in detail in this section. The ground and first excited state of the Hubbard model is summarized as follows:

$$E_1 \sim -\frac{4t^2}{U} \quad |\Psi_5\rangle \sim |\psi_3\rangle - |\psi_4\rangle = |\downarrow; \uparrow\rangle - |\uparrow; \downarrow\rangle \quad (4.12)$$

$$E_2 = 0 \quad |\Psi_1\rangle = |\psi_1\rangle = |\uparrow; \uparrow\rangle \quad (4.13)$$

$$|\Psi_2\rangle = |\psi_2\rangle = |\downarrow; \downarrow\rangle \quad (4.14)$$

$$|\Psi_3\rangle = |\psi_3\rangle + |\psi_4\rangle = |\downarrow; \uparrow\rangle + |\uparrow; \downarrow\rangle \quad (4.15)$$

The spin state of the system can be expressed by two quantum numbers, the total spin ( $S$ ) and the z-spin component ( $s_z$ ). As you may have learned in basic quantum physics, two operators,  $\hat{S}^2$  and  $\hat{S}_z$ ,

<sup>\*1</sup> See Appendix 5.6 for the calculation.

<sup>\*2</sup> I used a python code to get them, as shown in Appendix 5.7.

can take the eigenvalues simultaneously. The relationship between these operators and the eigenvalues are expressed as follows:<sup>\*3</sup>

$$\hat{S}^2 \rightarrow S(S+1)\hbar = \frac{3}{4}\hbar, \quad (4.16)$$

$$\hat{S}_z \rightarrow s_z\hbar. \quad (4.17)$$

The  $S$  and  $s_z$  for eq.4.12 to eq.4.13 are calculated to be

$$|\Psi_5\rangle : S = 0, s_z = 0, \quad (4.18)$$

$$|\Psi_1\rangle : S = 1, s_z = 1, \quad (4.19)$$

$$|\Psi_2\rangle : S = 1, s_z = -1, \quad (4.20)$$

$$|\Psi_3\rangle : S = 1, s_z = 0. \quad (4.21)$$

It indicates that the ground state is the spin-singlet ( $S = 0$ ), while the first excited state is the spin-triplet ( $S = 1$ ).

Here we introduce an exchange operator as follows:<sup>\*4</sup>

$$\hat{P}_{ij} = 2(\hat{S}_i \cdot \hat{S}_j + \frac{1}{4}). \quad (4.22)$$

The exchange operator generates +1 (-1) for the triplet (singlet) state. By using this operator, the effective Hamiltonian for the low-energy states (ground and first excited) can be expressed as follows:

$$\begin{aligned} H_{eff} &= \frac{2t^2}{U}(\hat{P}_{12} - 1) \\ &= \frac{4t^2}{U}(\hat{S}_1 \cdot \hat{S}_2 - \frac{1}{4}) \\ &= -J(\hat{S}_1 \cdot \hat{S}_2 - \frac{1}{4}), J = -\frac{4t^2}{U} < 0. \end{aligned} \quad (4.23)$$

Except for the constant part, the energy depends on the relative orientation of two spins ( $\hat{S}_1 \cdot \hat{S}_2$ ). This interaction is called the Heisenberg exchange interaction. Especially the interaction originating from the hopping of electrons is called superexchange interaction.

### 4.3 Coulomb interaction in neighbor sites

In the Hubbard model, we only consider the Coulomb interaction when the two electrons are located at the same site. In this section, we briefly consider the coulomb interaction in neighboring sites.

As we have seen, the ground state (eq.4.12) is a spin singlet, while the first excited states (eq.4.13-4.15) are triplets. The singlet is antisymmetric against the exchange of electrons, while the triplet is symmetric. Because the electron is a fermion, it should be antisymmetric against the electron exchange. Therefore, the orbital part of the wave function of singlets (triplets) should be symmetric (antisymmetric). Thus, the orbital wave function of singlet and triplet is expressed by

$$\Psi_s^{(+)}(r_a, r_b) = \frac{1}{\sqrt{2}}(\phi_1(r_a)\phi_2(r_b) + \phi_2(r_a)\phi_1(r_b)), \quad (4.24)$$

$$\Psi_t^{(-)}(r_a, r_b) = \frac{1}{\sqrt{2}}(\phi_1(r_a)\phi_2(r_b) - \phi_2(r_a)\phi_1(r_b)). \quad (4.25)$$

The expected value of Coulomb energy of these orbitals is calculated as follows:

$$E_{Coulomb}^{\pm} = \int dr_a dr_b \Psi^{(\pm)}(r_a, r_b) \frac{e^2}{r_{ab}} \Psi^{(\pm)}(r_a, r_b) \quad (4.26)$$

$$= K_{12} \pm J_{12}, \quad (4.27)$$

<sup>\*3</sup> See Appendix 5.8 for the detail.

<sup>\*4</sup> See Appendix 5.9.



where

$$K_{12} = \int dr_a dr_b |\phi_1(r_a)|^2 \frac{e^2}{r_{ab}} |\phi_2(r_b)|^2 \quad (4.28)$$

$$J_{12} = \int dr_a dr_b \phi_1^*(r_a) \phi_2^*(r_b) \frac{e^2}{r_{ab}} \phi_2(r_a) \phi_1(r_b) \quad (4.29)$$

$K_{12}$  describes the classic Coulomb interaction.  $J_{12}$  is called exchange integration, originating from the symmetry of the orbital. It indicates that the spin state correlates with the Coulomb energy through the exchange symmetry of the electrons. The triplet state shows the lower Coulomb energy, indicating that ferromagnetic spin order is favored.

The above energy can be expressed using  $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ . The eigenvalue for  $\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$  for the singlet and triplet are  $\frac{1}{4}$  and  $-\frac{3}{4}$ , respectively. Thus, if we define two operators

$$\hat{P}_s = \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \frac{3}{4} \quad (4.30)$$

$$\hat{P}_t = -\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \frac{1}{4} \quad (4.31)$$

$$(4.32)$$

, then  $\hat{P}_s$  ( $\hat{P}_t$ ) produces 1 for singlets (triplets), while 0 for triplets (singlets). Thus, the Coulomb interaction can be expressed by

$$H = (K_{12} - J_{12})\hat{P}_t + (K_{12} + J_{12})\hat{P}_s \quad (4.33)$$

$$= K_{12} - 2J_{12}(\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \frac{1}{4}). \quad (4.34)$$

This component should be added to the Hubbard Hamiltonian to describe the spin-dependent energy fully.

In many Mott insulators, the antiferromagnetic interaction by the hopping is much stronger than the Coulomb interaction. Thus, the Mott insulator is generally antiferromagnetic. However, if the hopping energy is small, ferromagnetic order can also be realized.

## Chapter 5

# Appendix

### 5.1 Bra-ket expression

A wave function of a state can be expressed by the linear combination of orthonormal basis set,  $\{u_i\}$ . Here we define two wavefunctions as follows:

$$\psi = \sum_i a_i u_i \quad (5.1)$$

$$\phi = \sum_j b_j u_j. \quad (5.2)$$

$a_i$  and  $b_i$  is the expansion coefficient. If the wave functions are normalized,

$$\sum_i |a_i|^2 = 1, \sum_j |b_j|^2 = 1 \quad (5.3)$$

We will consider the integration of the multiple of the wave functions, which often appear in quantum mechanics;

$$\begin{aligned} \int \psi^* \phi d\tau &= \int \sum_i \sum_j a_i^* b_j u_i^* u_j d\tau \\ &= \sum_i \sum_j a_i^* b_j \int u_i^* u_j d\tau \\ &= \sum_i \sum_j a_i^* b_j \delta_{ij} \\ &= \sum_i a_i^* b_i. \end{aligned} \quad (5.4)$$

If we express the wave functions in a matrix form,

$$\psi = (u_1, u_2, \dots) \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} \quad (5.5)$$

$$\phi = (u_1, u_2, \dots) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \end{pmatrix}, \quad (5.6)$$

then eq.5.4 is expressed by

$$\begin{aligned} \int \psi^* \phi d\tau &= \sum_i a_i^* b_i \\ &= (a_1^*, a_2^*, \dots) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \end{pmatrix}. \end{aligned} \quad (5.7)$$

As indicated in eq.5.7, the integration of the two states is expressed by the coefficients of the wave functions. We will express the vector of the coefficients as follows:

$$|\psi\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}, \quad (5.8)$$

$$\langle\psi| = |\psi\rangle^\dagger = (a_1^*, a_2^*, \dots). \quad (5.9)$$

$\langle$  and  $|$  is called bra and ket, respectively. Then the integration is simplified to be

$$\int \psi^* \phi d\tau = \langle\psi|\phi\rangle \quad (5.10)$$

The vector expressed by bra and ket is called the state vector. The inner product of the state vector corresponds to the integration of the wave function.

Let us consider expanding the wave function by position  $r$ . In this expression,  $\psi(r)$  becomes the coefficient. Therefore,

$$\psi(r) \rightarrow \begin{pmatrix} \psi(r_0) \\ \psi(r_1) \\ \psi(r_2) \\ \vdots \end{pmatrix} = |\psi\rangle. \quad (5.11)$$

Then, we consider each position as the unit vector as follows:

$$r_0 \rightarrow \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} = |r_0\rangle, r_1 \rightarrow \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} = |r_1\rangle, r_2 \rightarrow \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{pmatrix} = |r_2\rangle, \dots \quad (5.12)$$

In this expression, the amplitude of the wave function at  $r = r_n$  is obtained by the inner product of vectors:

$$\psi(r_n) = (0, 0, \dots, 1, \dots) \begin{pmatrix} \psi(r_0) \\ \psi(r_1) \\ \vdots \\ \psi(r_n) \\ \vdots \end{pmatrix} = \langle r_n | \psi \rangle. \quad (5.13)$$

The relationship between the original wavefunction ( $\psi(r)$ ) and the ket ( $|\psi\rangle$ ) are expressed by

$$\begin{aligned} |\psi\rangle &= \begin{pmatrix} \psi(r_0) \\ \psi(r_1) \\ \psi(r_2) \\ \vdots \end{pmatrix} = \psi(r_0) \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} + \psi(r_1) \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} + \dots \\ &= \psi(r_0) |r_0\rangle + \psi(r_1) |r_1\rangle + \dots \\ &= \int \psi(r) |r\rangle dr \end{aligned} \quad (5.14)$$

## 5.2 Number expression and number operator

In basic quantum mechanics, we considered the position of each electron like "the electron 1 is located at  $r_1$ ". However, this description is not good considering that the electron cannot be distinguished. Thus,

we introduce another description called number expression. In the number expression, the number of electrons at each state is shown in the ket like

$$|n_0, n_1, n_2, \dots\rangle \quad (5.15)$$

, where  $n_\alpha$  denotes the number of electron at the state  $|\alpha\rangle$ . Because the electrons are not labeled, number expression is suitable for treating indistinguishable particles.

In addition, we also introduce an operator to get the number of particles at the  $i$ -th state. The operator is called the number operator, defined as

$$\hat{n}_i |n_0, n_1, n_2, \dots\rangle = n_i |n_0, n_1, n_2, \dots\rangle. \quad (5.16)$$

As the eigenvalue is the real value,  $\hat{n}$  is an Hermitian operator ( $\hat{n} = \hat{n}^\dagger$ ). If all the  $n_i = 0$ , the state is called a vacuum state, which is expressed by,

$$|0, 0, \dots\rangle = |0\rangle. \quad (5.17)$$

### 5.3 A theorem for orthogonal system

By using an orthonormal basis set, a function can be expanded as follows:

$$f(x) = \sum_n c_n \phi_n(x). \quad (5.18)$$

Multiplying  $\phi_m^*(x)$  and integration yields,

$$\begin{aligned} \int \phi_m^*(x) f(x) dx &= \int \sum_n c_n \phi_m^*(x) \phi_n(x) dx \\ &= \sum_n c_n \int \phi_m^*(x) \phi_n(x) dx \\ &= c_m \\ \therefore c_m &= \int \phi_m^*(x) f(x) dx. \end{aligned} \quad (5.19)$$

Substitution of eq.5.19 to eq.5.18 yields

$$\begin{aligned} f(x) &= \sum_n \int \phi_n^*(x') f(x') dx' \phi_n(x) \\ &= \int \left[ \sum_n \phi_n^*(x') \phi_n(x) \right] f(x') dx \\ \therefore \sum_n \phi_n^*(x') \phi_n(x) &= \delta(x - x') \end{aligned} \quad (5.20)$$

## 5.4 Tight binding Hamiltonian

When the set of all the  $|i\rangle$  forms an orthogonal normalized system, the following theorem is derived:

$$\begin{aligned}
 \sum_i |i\rangle \langle i| &= \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} (1, 0, 0, \dots) + \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} (0, 1, 0, \dots) + \dots \\
 &= \begin{pmatrix} 1 & 0 & \dots \\ 0 & 0 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} + \begin{pmatrix} 0 & 0 & \dots \\ 0 & 1 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} + \dots \\
 &= \begin{pmatrix} 1 & 0 & \dots \\ 0 & 1 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} = 1.
 \end{aligned} \tag{5.21}$$

An operator can be expressed as follows using eq.5.21 :

$$H = \sum_{j,l} |j\rangle \langle j| H |l\rangle \langle l| \tag{5.22}$$

If we assume that

$$\langle j| H |l\rangle = \begin{cases} E_0 & (j = l) \\ -\gamma & (|j - l| = 1) \\ 0 & (else) \end{cases} \tag{5.23}$$

, we get

$$H = -\gamma \sum_l (|l\rangle \langle l+1| + |l\rangle \langle l-1|) + E_0 \sum_l |l\rangle \langle l| \tag{5.24}$$

## 5.5 Fourier transform of a ket state

The Fourier transform of a function can be expressed as follows:

$$\begin{aligned}
 u(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{ikx} v(k) dk \\
 &= \frac{1}{\sqrt{2\pi}} \sum_k e^{ikx} v(k).
 \end{aligned} \tag{5.25}$$

Applying the periodic boundary condition,  $u(x) = u(x + Na)$ , yields

$$e^{ikx} = e^{ik(x+Na)} \tag{5.26}$$

$$\therefore k = \frac{2\pi}{Na} m \quad (m = 0, 1, \dots). \tag{5.27}$$

By expressing the state at  $x = al$  as  $|l\rangle$  ( $u(al) = |l\rangle$ ), and  $k = \frac{2\pi}{Na} m$  as  $|m\rangle$  ( $v(k) = |m\rangle$ ), a ket state can be Fourier transformed as follows:

$$\begin{aligned}
 |l\rangle &= \frac{1}{\sqrt{N}} \sum_k e^{ikl} |k\rangle \\
 &= \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} e^{i\frac{2\pi}{N} ml} |m\rangle.
 \end{aligned} \tag{5.28}$$

Equation 5.28 is the discrete Fourier transform of a state  $|l\rangle$ .

## 5.6 Matrix element calculation of Hubbard Hamiltonian

As explained in section 4.1, the Hubbard Hamiltonian is expressed as follows:

$$H = -t \sum_{\sigma} (\hat{c}_{1,\sigma}^{\dagger} \hat{c}_{2,\sigma} + \hat{c}_{2,\sigma}^{\dagger} \hat{c}_{1,\sigma}) + U(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow}). \quad (5.29)$$

We will show how to get the matrix element of this Hamiltonian in eq. 4.3. Firstly, let us remind the function of creation and annihilation operators:

$$\hat{c}_i |n_i\rangle = a_i |n_i - 1\rangle \quad (5.30)$$

$$\hat{c}_i^{\dagger} |n_i\rangle = a_i |n_i + 1\rangle \quad (5.31)$$

$$a_i = (-1)^{\lambda}, \lambda = \sum_{n=0}^{i-1} n_i \quad (5.32)$$

In calculating the matrix element, we should take care of the coefficient. To make it clear, we will express the spin state of the two-electron system in number expression as follows:

$$|n_{1,\uparrow}, n_{1,\downarrow}, n_{2,\uparrow}, n_{2,\downarrow}\rangle \quad (5.33)$$

For examples, the spin states  $|\psi_3\rangle$ ,  $|\psi_4\rangle$ , and  $|\psi_5\rangle$  is expressed by

$$|\psi_3\rangle = |\downarrow\rangle |\uparrow\rangle = |0, 1, 1, 0\rangle, \quad (5.34)$$

$$|\psi_4\rangle = |\uparrow\rangle |\downarrow\rangle = |1, 0, 0, 1\rangle, \quad (5.35)$$

$$|\psi_5\rangle = |\uparrow\downarrow\rangle |0\rangle = |1, 1, 0, 0\rangle. \quad (5.36)$$

In this expression, the first term of the Hamiltonian is expressed as follows:<sup>\*1</sup>

$$\begin{aligned} H &= -t \sum_{\sigma} (\hat{c}_{1,\sigma}^{\dagger} \hat{c}_{2,\sigma} + \hat{c}_{2,\sigma}^{\dagger} \hat{c}_{1,\sigma}) \\ &= -t(\hat{c}_1^{\dagger} \hat{c}_3 + \hat{c}_3^{\dagger} \hat{c}_1 + \hat{c}_2^{\dagger} \hat{c}_4 + \hat{c}_4^{\dagger} \hat{c}_2) \end{aligned} \quad (5.37)$$

Application of  $H$  on  $|\psi_3\rangle$  and  $|\psi_5\rangle$  yields

$$\begin{aligned} H |\psi_3\rangle &= -t(\hat{c}_1^{\dagger} \hat{c}_3 + \hat{c}_3^{\dagger} \hat{c}_1 + \hat{c}_2^{\dagger} \hat{c}_4 + \hat{c}_4^{\dagger} \hat{c}_2) |0, 1, 1, 0\rangle \\ &= -t(-|1100\rangle + 0 + 0 - |0011\rangle) \\ &= t(|1, 1, 0, 0\rangle + |0, 0, 1, 1\rangle) \end{aligned} \quad (5.38)$$

$$\begin{aligned} H |\psi_4\rangle &= -t(\hat{c}_1^{\dagger} \hat{c}_3 + \hat{c}_3^{\dagger} \hat{c}_1 + \hat{c}_2^{\dagger} \hat{c}_4 + \hat{c}_4^{\dagger} \hat{c}_2) |1, 0, 0, 1\rangle \\ &= -t(0 + |0, 0, 1, 1\rangle + |1, 1, 0, 0\rangle + 0) \\ &= -t(|0, 0, 1, 1\rangle + |1, 1, 0, 0\rangle). \end{aligned} \quad (5.39)$$

Therefore, the matrix element with the  $|\psi_5\rangle = |1, 1, 0, 0\rangle$  is calculated to be

$$\langle \psi_5 | H | \psi_3 \rangle = t \quad (5.40)$$

$$\langle \psi_5 | H | \psi_4 \rangle = -t \quad (5.41)$$

The other matrix elements can be calculated in the same way.

---

<sup>\*1</sup> In this section, we ignore the second term because it will be zero in the following examples.

## 5.7 Python code to get the eigenvectors

The following code calculates the eigenenergy and eigenvector of the Hubbard Hamiltonian.

**Code 5.1:** Code

```

1 import sympy
2
3 sympy.var("t,U")
4 A = sympy.Matrix(
5     [
6         [0, 0, 0, 0, 0, 0],
7         [0, 0, 0, 0, 0, 0],
8         [0, 0, 0, 0, t, t],
9         [0, 0, 0, 0, -t, -t],
10        [0, 0, t, -t, U, 0],
11        [0, 0, t, -t, 0, U],
12    ]
13 )
14
15 eig = A.eigenvals()
16 vec = A.eigenvects()
17
18 print(eig)
19 print(vec)

```

**Code 5.2:** Output

```

1 {0: 3, U: 1, U/2 - sqrt(U**2 + 16*t**2)/2: 1, U/2 + sqrt(U**2 + 16*t
   **2)/2: 1}
2 [(0, 3,
3  [Matrix([[1], [0], [0], [0], [0], [0]]],
4  Matrix([[0], [1], [0], [0], [0], [0]]],
5  Matrix([[0], [0], [1], [1], [0], [0]]])),
6  (U, 1,
7  [Matrix([[0], [0], [0], [0], [-1], [1]]])),
8  (U/2 - sqrt(U**2 + 16*t**2)/2, 1,
9  [Matrix([[0], [0], [-U/(2*t) + (U/2 - sqrt(U**2 + 16*t**2)/2)/(2*t)], [U
   /(2*t) - (U/2 - sqrt(U**2 + 16*t**2)/2)/(2*t)], [1], [1]]])),
10 (U/2 + sqrt(U**2 + 16*t**2)/2, 1,
11 [Matrix([[0], [0], [-U/(2*t) + (U/2 + sqrt(U**2 + 16*t**2)/2)/(2*t)], [U
   /(2*t) - (U/2 + sqrt(U**2 + 16*t**2)/2)/(2*t)], [1], [1]])))]

```

## 5.8 Spin operator

In general, an electron can take two spin states. We can express these states by

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (5.42)$$

The spin operators are expressed as follows.\*2

$$\hat{S}_x = \frac{\hbar}{2}\sigma_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (5.43)$$

$$\hat{S}_y = \frac{\hbar}{2}\sigma_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (5.44)$$

$$\hat{S}_z = \frac{\hbar}{2}\sigma_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (5.45)$$

$$\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z) \quad (5.46)$$

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (5.47)$$

$\hat{\mathbf{S}}^2$  and  $\hat{S}_z$  can have the eigenvalues simultaneously. The relationship between the operators and the eigenvalues are

$$\hat{\mathbf{S}}^2 : S(S+1)\hbar^2 \quad (5.48)$$

$$\hat{S}_z : m_z\hbar \quad (5.49)$$

Thus, the spin state is often expressed by the total spin angular momentum number ( $S$ ) and z-spin number ( $m_z$ ). For example, for an up spin,

$$\begin{aligned} \hat{\mathbf{S}}^2 |\uparrow\rangle &= \frac{3\hbar^2}{4} |\uparrow\rangle \\ \therefore S(S+1) &= \frac{3}{4} \therefore S = \frac{1}{2} \end{aligned} \quad (5.50)$$

$$\begin{aligned} \hat{S}_z |\uparrow\rangle &= \frac{\hbar}{2} \cdot |\uparrow\rangle \\ \therefore m_z &= \frac{1}{2} \end{aligned} \quad (5.51)$$

$$(5.52)$$

Then, we will apply these operators to the two-spin system. There are four possible states:\*3

$$|\uparrow\rangle_1 |\uparrow\rangle_2 \quad (5.53)$$

$$|\downarrow\rangle_1 |\downarrow\rangle_2 \quad (5.54)$$

$$\frac{1}{\sqrt{2}}(|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2) \quad (5.55)$$

$$\frac{1}{\sqrt{2}}(|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2) \quad (5.56)$$

The operators for calculating a total spin and z-spin is expressed as follows:

$$\hat{\mathbf{S}}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2 = \hat{\mathbf{S}}_1^2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2^2 \quad (5.57)$$

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \hat{S}_{x,1}\hat{S}_{x,2} + \hat{S}_{y,1}\hat{S}_{y,2} + \hat{S}_{z,1}\hat{S}_{z,2} \quad (5.58)$$

$$\hat{S}_z = \hat{S}_{z,1} + \hat{S}_{z,2}. \quad (5.59)$$

Note that the operator with the notation 1 (2) only acts on spin 1 (2). Let us try to apply the operators

\*2  $\sigma_x, \sigma_y, \sigma_z$  are the Pauli matrices.

\*3 All the states should have symmetry to the exchange.



to eq.5.55:

$$\begin{aligned}\hat{S}_z |\Psi_3\rangle &= \frac{1}{\sqrt{2}} ([\hat{S}_{z,1} |\uparrow\rangle_1] |\downarrow\rangle_2 + |\uparrow\rangle_1 [\hat{S}_{z,2} |\downarrow\rangle_2] + [\hat{S}_{z,1} |\downarrow\rangle_1] |\uparrow\rangle_2 + |\downarrow\rangle_1 [\hat{S}_{z,2} |\uparrow\rangle_2]) \\ &= 0 |\Psi_3\rangle \\ \therefore m_z &= 0\end{aligned}\tag{5.60}$$

$$\begin{aligned}\hat{S}^2 |\Psi_3\rangle &= \frac{1}{\sqrt{2}} ([\hat{S}_1^2 |\uparrow\rangle_1] |\downarrow\rangle_2 + [\hat{S}_1^2 |\downarrow\rangle_1] |\uparrow\rangle_2 + |\uparrow\rangle_1 [\hat{S}_2^2 |\downarrow\rangle_2] + |\downarrow\rangle_1 [\hat{S}_2^2 |\uparrow\rangle_2] \\ &\quad + 2\hat{S}_1 \cdot \hat{S}_2 |\uparrow\rangle_1 |\downarrow\rangle_2 + 2\hat{S}_1 \cdot \hat{S}_2 |\downarrow\rangle_1 |\uparrow\rangle_2) \\ &= 2 |\Psi_3\rangle \\ \therefore S &= 1.\end{aligned}\tag{5.61}$$

Therefore, the spin state of eq.5.55 is expressed as follows:

$$|S, m_z\rangle = |1, 0\rangle\tag{5.62}$$

The other spin states can be calculated in the same way.

## 5.9 Exchange operator

Firstly we will apply  $\hat{S}_1 \cdot \hat{S}_2$  to the triplet (eq.5.55) and singlet (eq.5.56):<sup>\*4</sup>

$$\begin{aligned}\hat{S}_1 \cdot \hat{S}_2 (|\uparrow\rangle_1 |\downarrow\rangle_2 \pm |\downarrow\rangle_1 |\uparrow\rangle_2) &= \hat{S}_{x,1} |\uparrow\rangle_1 \hat{S}_{x,2} |\downarrow\rangle_2 \pm \hat{S}_{x,1} |\downarrow\rangle_1 \hat{S}_{x,2} |\uparrow\rangle_2 \\ &\quad + \hat{S}_{y,1} |\uparrow\rangle_1 \hat{S}_{y,2} |\downarrow\rangle_2 \pm \hat{S}_{y,1} |\downarrow\rangle_1 \hat{S}_{y,2} |\uparrow\rangle_2 \\ &\quad + \hat{S}_{z,1} |\uparrow\rangle_1 \hat{S}_{z,2} |\downarrow\rangle_2 \pm \hat{S}_{z,1} |\downarrow\rangle_1 \hat{S}_{z,2} |\uparrow\rangle_2 \\ &= \frac{1}{4} (|\downarrow\rangle_1 |\uparrow\rangle_2 \pm |\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2 \pm |\uparrow\rangle_1 |\downarrow\rangle_2 \\ &\quad - |\uparrow\rangle_1 |\downarrow\rangle_2 \mp |\downarrow\rangle_1 |\uparrow\rangle_2) \\ &= \begin{cases} \frac{1}{4} (|\uparrow\rangle_1 |\downarrow\rangle_2 + |\downarrow\rangle_1 |\uparrow\rangle_2) & (S = 1) \\ -\frac{3}{4} (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2) & (S = 0). \end{cases}\end{aligned}\tag{5.63}$$

Therefore, we can define the exchange operator as follows:

$$P_{ij} = 2(\hat{S}_i \cdot \hat{S}_j + \frac{1}{4}).\tag{5.64}$$

The exchange operator generates 1 for triplet and -1 for singlet, reflecting the exchange symmetry of the spin state.

---

<sup>\*4</sup> The normarization factor is ignored.

# Bibliography

[1]