Quick training for the second quantization

ISSP, The University of Tokyo Takeo Kato

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1 Abstract

In understanding the content of solid-state physics, using the second quantization method will make the description easier[1]. This note is intended for readers who are familiar with the bracket notation of quantum mechanics [3]. I will summarize the minimum knowledge for the quick learning of second quantization. The rigor and consistency of the theory is somewhat sacrificed, but it should be enough to take a cursory look at the method.

2 Overview of the second quantization

First, let's take an overview of the second quantization procedure. In solid state physics, we are interested in the electronic states in solids. Here, we mainly deal with electrons (Fermi particles) only. In ordinary quantum mechanics (called the first quantization method), we have considered the wave function of an electron, $\psi(\boldsymbol{r})$. However, the second quantization method does not deal with the wave function directly, but with the linear operator $\Psi(bmr)$, which is called the field operator. Note that the field operator $\Psi(\boldsymbol{r})$ looks like the wave function $\Psi(\boldsymbol{r})$, but its contents are quite different. In fact, $\Psi(\boldsymbol{r})$ is an operator (annihilation operator) that performs the operation of "elliminate out one electron at position $\boldsymbol{r}$" and its Hermit conjugate, $\Psi^\dagger(\boldsymbol{r})$, is an operator (creation operator) that performs the operation of "adding one electron at position $\boldsymbol{r}$". Note that the conventional wave function does not have the meaning of "probability amplitude at position $\boldsymbol{r}$" at all.

In the traditional textbook[1, 2], we first learn the notation of the multiparticle system in the first quantization form, and then rewrite it with a second quantization form. In this note, let's follow the opposite path. First, we introduce an anti-commutation relation that characterizes the field operators of the Fermi particle:

$$\{\Psi(\boldsymbol{r}), \Psi^\dagger(\boldsymbol{r}')\} = \delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{1}$$

$$\{\Psi(\boldsymbol{r}), \Psi(\boldsymbol{r}')\} = \{\Psi^\dagger(\boldsymbol{r}), \Psi^\dagger(\boldsymbol{r}')\} = 0. \tag{2}$$

Here, $\{A, B\} = AB + BA$ (A, B: linear operators). Only a few requests in addition to this anti-commutation relation[2] can lead to all the properties that a Fermi particle should obey. Based on this strategy, this chapter describes the relationship with the first quantization and how to

[1] Most textbooks on solid-state physics do not use the second quantization. However, the technique of second quantization is very useful for description of quantum chemistry and tight-binding models, and is an important tool even in modern solid state physics. It is an important method that even experimentalists should learn.

[2] For real numbers a, b, the product of real numbers can be exchanged because $ab = ba$, i.e., $ab - ba = 0$ holds. However, since the field operators $\Psi(\boldsymbol{r})$ and $\Psi^\dagger(\boldsymbol{r})$ are operators (matrices), the order of the products is not necessarily exchangeable. In fact, the second equation of the anti-commutation relation implies that exchanging the order of the products, such as $\Psi(\boldsymbol{r})\Psi(\boldsymbol{r}') = -\Psi(\boldsymbol{r}')\Psi(\boldsymbol{r})$, $\Psi^\dagger(\boldsymbol{r})\Psi^\dagger(\boldsymbol{r}') = -\Psi^\dagger(\boldsymbol{r}')\Psi^\dagger(\boldsymbol{r})$, produces a negative.

describe multi-particle systems, and finally, how to describe the Hamiltonian of multi-particle systems.

3 Summary of description of the first quantization

Let me briefly summarize the bracket notation used in the first quantization method[3]. For the system Hamiltonian $\hat{h}$, it is assumed that we know all the eigenvalues ϵ_α and eigenvectors $|\alpha\rangle$ ($\hat{h}$ is a linear operator acting on the ket space):

$$\hat{h}|\alpha\rangle = \epsilon_\alpha|\alpha\rangle \quad (\alpha = 1, 2, 3, \cdots). \tag{3}$$

This set of eigenvectors forms a complete orthonormal basis, and

$$\langle\alpha|\beta\rangle = \delta_{\alpha\beta}, \qquad \sum_\alpha |\alpha\rangle\langle\alpha| = \hat{1}, \tag{4}$$

holds for $\alpha, \beta = 1, 2, 3, \cdots$. Here, $\hat{1}$ is the identity operator. Here we define the eigenstate of the position operator $\hat{\boldsymbol{r}}$(= the fixed-position state) as $|\boldsymbol{r}\rangle$:

$$\hat{\boldsymbol{r}}|\boldsymbol{r}\rangle = \boldsymbol{r}|\boldsymbol{r}\rangle. \tag{5}$$

$|\boldsymbol{r}\rangle$ is also a complete orthonormal basis:

$$\langle\boldsymbol{r}|\boldsymbol{r}'\rangle = \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad \int d^3\boldsymbol{r}\, |\boldsymbol{r}\rangle\langle\boldsymbol{r}| = \hat{1}. \tag{6}$$

Using the second equation of (6), the Hamiltonian's eigenstate $|\alpha\rangle$ is written as

$$|\alpha\rangle = \left(\int d^3\boldsymbol{r}\, |\boldsymbol{r}\rangle\langle\boldsymbol{r}|\right)|\alpha\rangle = \int d^3\boldsymbol{r}\, \psi_\alpha(\boldsymbol{r})|\boldsymbol{r}\rangle. \tag{7}$$

Here,

$$\psi_\alpha(\boldsymbol{r}) = \langle\boldsymbol{r}|\alpha\rangle \tag{8}$$

is just the wavefunction of the eigenstate α.

The Schrödinger equation of free electrons is given as

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{9}$$

For simplicity, consider a cube with one side L and impose a periodic boundary condition:

$$\psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L) = \psi(x, y, z). \tag{10}$$

The wavefunction of the eigenstate for the Hamiltonian of free electrons is given as[4]

$$\psi(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{11}$$

[3]For detailed information on quantum mechanics using the bracket description, see Reference [3].

[4]From the normalization condition $\int d^3\boldsymbol{x}\, |\psi(\boldsymbol{x})|^2 = 1$, the normalization factor is $1/\sqrt{V}$.

($V = L^3$ is a volume of the cube.) The eigenenergy is given as $E = \epsilon_{\boldsymbol{k}} = (\hbar \boldsymbol{k})^2/2m$. The wavenumber $\boldsymbol{k} = (k_x, k_y, k_z)$ takes the following discrete values due to the boundary condition (10):

$$(k_x, k_y, k_z) = \Big(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L}\Big), \quad (n_x, n_y, n_z : \text{ integer}). \tag{12}$$

The wavenumber $\boldsymbol{k}$ is the quantity that labels the energy eigenstate, and the electronic state of the wavenumber $\boldsymbol{k}$ can be described by a ket vector $|\boldsymbol{k}\rangle$. If we regard this label in the same light as the energy eigenstate α, we obtain

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \langle \boldsymbol{r}|\boldsymbol{k}\rangle = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \tag{13}$$

which is similar as Eq. (8). $|\boldsymbol{k}\rangle$ forms a complete orthonormal basis:

$$\langle \boldsymbol{k}|\boldsymbol{k}'\rangle = \delta_{\boldsymbol{k},\boldsymbol{k}'}, \qquad \sum_{\boldsymbol{k}} |\boldsymbol{k}\rangle\langle\boldsymbol{k}| = \hat{1}, \tag{14}$$

where the sum for $\boldsymbol{k}$ means the sum for the pair of integers (n_x, n_y, n_z) represented by the expression (12):

$$\sum_{\boldsymbol{k}} (\cdots) = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} (\cdots) \tag{15}$$

In the limit of $L \to \infty$, the sum for $\boldsymbol{k}$ can be replaced with an integral:[5]

$$\sum_{\boldsymbol{k}} (\cdots) = \frac{V}{(2\pi)^3} \int d^3\boldsymbol{k}\, (\cdots). \tag{16}$$

The ket vector $|\boldsymbol{k}\rangle$ is a wavenumber-fixed state, and is a momentum-fixed state at the same time. If the momentum operator is denoted with $\hat{\boldsymbol{p}}$, then $|\boldsymbol{k}\rangle$ is an eigenstate of the operator $\hat{\boldsymbol{p}}$:[6]

$$\hat{\boldsymbol{p}}|\boldsymbol{k}\rangle = \hbar\boldsymbol{k}|\boldsymbol{k}\rangle. \tag{17}$$

If the bra vector $\langle \boldsymbol{r}|$ is multiplied from the left, we obtain

$$\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\boldsymbol{k}\rangle = \hbar\boldsymbol{k}\langle \boldsymbol{r}|\boldsymbol{k}\rangle = \hbar\boldsymbol{k}\frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = -i\hbar\nabla\Big(\frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\Big) = -i\hbar\nabla(\langle \boldsymbol{r}|\boldsymbol{k}\rangle). \tag{18}$$

For a general ket vector $|\varphi\rangle$, we obtain a similar formula using Eq. (14):

$$\begin{aligned} \langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\varphi\rangle &= \sum_{\boldsymbol{k}} \langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\varphi\rangle = \sum_{\boldsymbol{k}} (-i\hbar\nabla)(\langle \boldsymbol{r}|\boldsymbol{k}\rangle)\langle\boldsymbol{k}|\varphi\rangle \\ &= -i\hbar\nabla\Big(\langle \boldsymbol{r}| \sum_{\boldsymbol{k}} (|\boldsymbol{k}\rangle\langle\boldsymbol{k}|)\varphi\rangle\Big) = -i\hbar\nabla(\langle \boldsymbol{r}|\varphi\rangle). \end{aligned} \tag{19}$$

[5] $\sum_{\boldsymbol{k}}(\cdots) = (\Delta k_x \Delta k_x \Delta k_z)^{-1} \sum_{\boldsymbol{k}}(\cdots)\Delta k_x \Delta k_x \Delta k_z \to \frac{L^3}{(2\pi)^3}\int d^3\boldsymbol{k}\,(\cdots)$ $(L \to \infty)$. Here, $\Delta k_x = \Delta k_x = \Delta k_z = 2\pi/L$.

[6] Combining the fact that the magnitude of the wave number is given by $|\boldsymbol{k}| = 2\pi/\lambda$ (λ is the wavelength of an electron wave) with de Broy's principle $|\boldsymbol{p}| = h/\lambda$, we conclude that $|\boldsymbol{p}| = \hbar|\boldsymbol{k}|$. Finally, we obtain $\boldsymbol{p} = \hbar\boldsymbol{k}$ because $\boldsymbol{k}/\!/\boldsymbol{p}$.

Because this equation holds for arbitrary $|\varphi\rangle$, we conclude

$$\langle \boldsymbol{r}|\hat{\boldsymbol{p}} = -i\hbar\nabla\langle \boldsymbol{r}|. \tag{20}$$

In the presence of a potential $v(\boldsymbol{r})$, the Hamiltonian of an electron $\hat{h}$ is given as

$$\hat{h} = \frac{\hat{\boldsymbol{p}}^2}{2m} + v(\hat{\boldsymbol{r}}). \tag{21}$$

Combining (20) and

$$\langle \boldsymbol{r}|v(\hat{\boldsymbol{r}}) = \langle \boldsymbol{r}|v(\boldsymbol{r}) = v(\boldsymbol{r})\langle \boldsymbol{r}|, \tag{22}$$

we obtain

$$\langle \boldsymbol{r}|\hat{h} = \langle \boldsymbol{r}|\left(\frac{\hat{\boldsymbol{p}}^2}{2m} + v(\hat{\boldsymbol{r}})\right) = \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)\langle \boldsymbol{r}|. \tag{23}$$

Multiplying $\langle \boldsymbol{r}|$ to the eigenvalue equation (3) for the Hamiltonian $\hat{h}$ from the left, and using Eq. (23), the Schrödinger equation can be derived:

$$\begin{aligned}
&\langle \boldsymbol{r}|\left(\frac{\hat{\boldsymbol{p}}^2}{2m} + v(\hat{\boldsymbol{r}})\right)|\alpha\rangle = \epsilon_\alpha\langle \boldsymbol{r}|\alpha\rangle, \\
\leftrightarrow \quad &\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)\langle \boldsymbol{r}|\alpha\rangle = \epsilon_\alpha\langle \boldsymbol{r}|\alpha\rangle, \\
\leftrightarrow \quad &\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)\psi_\alpha(\boldsymbol{r}) = \epsilon_\alpha\psi_\alpha(\boldsymbol{r}).
\end{aligned} \tag{24}$$

4 One-particle state

Hereafter, we will introduce the second quantization method a little at a time. First of all, consider the case where there is only one electron in space. This is exactly the case for most of the problems we deal with in the first quantization method, and it is easy to see the correspondence with the operators of the second quantization field.

As already mentioned, the field operator $\Psi^\dagger(\boldsymbol{r})$ is an operator that adds one electron to the position $\boldsymbol{r}$. The state in which no electrons are present is called the vacuum state, and is denoted with $|\mathrm{vac}\rangle$. When $\Psi^\dagger(\boldsymbol{r})$ acts on the vacuum state, it produces a position-fixed state of one electron:

$$\Psi^\dagger(\boldsymbol{r})|\mathrm{vac}\rangle = |\boldsymbol{r}\rangle \tag{25}$$

This gives a correspondence to the position basis in the method of first quantization.

Because no electrons are present in the vacuum state, we request the following formula for the annihilation operator:[7]

$$\Psi(\boldsymbol{r})|\mathrm{vac}\rangle = 0. \tag{26}$$

[7]We note that Eqs. (25) and (26) are just requirements in the field theory, and cannot be derived from other formulas. These requests and anti-commutation relations (1), (2) are used to construct a space of multi-electron states.

It is possible to add electrons in various states as well as in a fixed position. For example, let's construct a creation operator $c_\alpha^\dagger$ that adds an electron in the αth energy eigenstate[8]. Using the equation in the first-quantization description

$$|\alpha\rangle = \int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\alpha\rangle = \int d^3\boldsymbol{r}\,(\langle\boldsymbol{r}|\alpha\rangle)|\boldsymbol{r}\rangle, \tag{27}$$

the operator $c_\alpha^\dagger$ should satisfy

$$c_\alpha^\dagger|\mathrm{vac}\rangle = |\alpha\rangle = \int d^3\boldsymbol{r}\,(\langle\boldsymbol{r}|\alpha\rangle)|\boldsymbol{r}\rangle = \left[\int d^3\boldsymbol{r}\,\langle\boldsymbol{r}|\alpha\rangle\Psi^\dagger(\boldsymbol{r})\right]|\mathrm{vac}\rangle. \tag{28}$$

For consistent definition, it seems that $c_\alpha^\dagger$ should be defined as[9]

$$c_\alpha^\dagger = \int d^3\boldsymbol{r}\,\langle\boldsymbol{r}|\alpha\rangle\Psi^\dagger(\boldsymbol{r}) = \int d^3\boldsymbol{r}\,\psi_\alpha(\boldsymbol{r})\Psi^\dagger(\boldsymbol{r}). \tag{29}$$

This equation is a conversion formula for writing $c_\alpha^\dagger$ in terms of $\Psi^\dagger(\boldsymbol{r})$. We can also write an inverse formula for writing $\Psi^\dagger(\boldsymbol{r})$ by $c_\alpha^\dagger$ from the relation

$$\begin{aligned}
&|\boldsymbol{r}\rangle = \sum_\alpha |\alpha\rangle\langle\alpha|\boldsymbol{r}\rangle = \sum_\alpha (\langle\alpha|\boldsymbol{r}\rangle)|\alpha\rangle, \\
&\to \Psi^\dagger(\boldsymbol{r})|\mathrm{vac}\rangle = |\boldsymbol{r}\rangle = \sum_\alpha (\langle\alpha|\boldsymbol{r}\rangle)|\alpha\rangle = \left[\sum_\alpha \langle\alpha|\boldsymbol{r}\rangle c_\alpha^\dagger\right]|\mathrm{vac}\rangle, \\
&\to \Psi^\dagger(\boldsymbol{r}) = \sum_\alpha \langle\alpha|\boldsymbol{r}\rangle c_\alpha^\dagger = \sum_\alpha \psi_\alpha(\boldsymbol{r})^* c_\alpha^\dagger.
\end{aligned} \tag{30}$$

If both sides are Hermite-conjugated, we obtain

$$\Psi(\boldsymbol{r}) = \sum_\alpha \langle\boldsymbol{r}|\alpha\rangle c_\alpha = \sum_\alpha \psi_\alpha(\boldsymbol{r}) c_\alpha. \tag{31}$$

This is the basic relation that describes the basis transformation. Especially for the free electron Hamiltonian, since the eigenstate can be specified by the wavenumber $\boldsymbol{k}$, we obtain

$$\Psi(\boldsymbol{r}) = \sum_{\boldsymbol{k}} \langle\boldsymbol{r}|\boldsymbol{k}\rangle c_{\boldsymbol{k}} = \sum_{\boldsymbol{k}} \psi_{\boldsymbol{k}}(\boldsymbol{r}) c_{\boldsymbol{k}} = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} c_{\boldsymbol{k}} \tag{32}$$

by replacing α with $\boldsymbol{k}$. (In the last equation, we have used Eq. (13).) This equation is a relation that appears to be a Fourier transform of $\Psi(\boldsymbol{r})$ to obtain the Fourier coefficient$c_{\boldsymbol{k}}$, but its essence is a basis transform from $|\boldsymbol{r}\rangle$ to $|\boldsymbol{k}\rangle$.[10]

[8] In this note, we use the character Ψ for the field operator at position $\boldsymbol{r}$ only, and the character c for the other states.

[9] Here, since the formula (28) holds just for the vacuum state, note that even if the formula (28) holds, it does not necessarily mean that the formula (29) holds. Here, the expression (29) has to be accepted as one of the requests, and we move on. In the later discussion, we will confirm that the state of a multi-electron system can be successfully constructed with field operators based on this expression.

[10] The information of the wavefunction is located is the exponential function part of the Fourier transform, as can be seen from $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$.

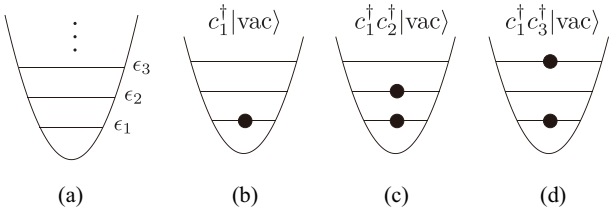

Figure 1: (a) A schematic diagram of the energy levels. (b), (c), (d) Schematic diagrams of the two-electron states.

It is easy to rewrite the expression of the anti-commutation relations, (1) and (eq:expp), with c_alpha, c_alpha^dagger, etc by basis transformation:

$$\begin{aligned}\{c_\alpha, c_\beta^\dagger\} &= \Big\{\int d^3\boldsymbol{r}\psi_\alpha^*(\boldsymbol{r})\Psi(\boldsymbol{r}), \int d^3\boldsymbol{r}'\psi_\beta(\boldsymbol{r}')\Psi(\boldsymbol{r}')\Big\} \\ &= \int d^3\boldsymbol{r}d^3\boldsymbol{r}'\psi_\alpha^*(\boldsymbol{r})\psi_\beta(\boldsymbol{r}')\{\Psi(\boldsymbol{r}), \Psi(\boldsymbol{r}')\} \\ &= \int d^3\boldsymbol{r}\psi_\alpha^*(\boldsymbol{r})\psi_\beta(\boldsymbol{r}) = \int d^3\boldsymbol{r}\langle\alpha|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\beta\rangle \\ &= \langle\alpha|\beta\rangle = \delta_{\alpha\beta}. \end{aligned} \tag{33}$$

In a similar way, we can show

$$\{c_\alpha, c_\beta\} = \{c_\alpha^\dagger, c_\beta^\dagger\} = 0. \tag{34}$$

5 Noninteracting Fermi particle system

Let us consider a system consisting of Fermi particles that do not interact with each other. As an example, consider more than one electron in a system whose energy level is ϵ_α. We assign the number α in order of low energy (Figure 1(a)). Since electrons are indistinguishable from each other, it is ill-advised to number electrons and specify their states, such as, "The number 1 electron is in the energy level α_1, and the number 2 electron is in the energy level α_2, and ...". The natural way to specify the state is to consider "how many electrons there are in each energy level". Suppose that there are $n_\alpha(= 0, 1)$ electrons in the αth energy level, and $\boldsymbol{n} = (n_1, n_2, n_3, \cdots)$ is a label that specifies a state. This way of specifying the state is compatible with the notation of the generation-annihilation operators $c_\alpha^\dagger$ and c_α. For example, the states described by $c_1^\dagger|\mathrm{vac}\rangle$, $c_1^\dagger c_2^\dagger|\mathrm{vac}\rangle$, and $c_1^\dagger c_3^\dagger|\mathrm{vac}\rangle$ are represented by figures 1(b), (c), (d), respectively. Furthermore, by setting $\alpha = \beta$ in the anti-exchange relation (34) as

$$\{c_\alpha^\dagger, c_\alpha^\dagger\} = c_\alpha^\dagger c_\alpha^\dagger + c_\alpha^\dagger c_\alpha^\dagger = 0, \tag{35}$$

we conclude $c_\alpha^\dagger c_\alpha^\dagger = 0$. Therefore, the state in which two electrons are added to the same quantum state α is forbidden. This represents Pauli's law of exclusion for Fermi particles. In general, the electronic state represented by $\boldsymbol{n} = (n_1, n_2, n_3, \cdots)$ is given as[11]

$$|\boldsymbol{n}\rangle = (c_1^\dagger)^{n_1}(c_2^\dagger)^{n_2}(c_3^\dagger)^{n_3}\cdots|\mathrm{vac}\rangle. \tag{36}$$

[11]In some literatures, the state is defined as $|\boldsymbol{n}\rangle = \cdots(c_3^\dagger)^{n_3}(c_2^\dagger)^{n_2}(c_1^\dagger)^{n_1}|\mathrm{vac}\rangle$. In this case, a part of the intermediate calculation is signed differently, but the final result remains the same.

Here, we define an operator $\hat{n}_\alpha = c_\alpha^\dagger c_\alpha$. If this operator acts on $|\boldsymbol{n}\rangle$, we obtain

$$\hat{n}_\alpha |\boldsymbol{n}\rangle = n_\alpha |\boldsymbol{n}\rangle, \tag{37}$$

This indicates that $|\boldsymbol{n}\rangle$ is an eigenstate of $\hat{n}_\alpha$, and its eigenvalue is the particle number n_α in the energy level α. To prove this equation, we use the commutation relation

$$[\hat{n}_\alpha, c_\beta^\dagger] = [c_\alpha^\dagger c_\alpha, c_\beta^\dagger] = c_\alpha^\dagger \{c_\alpha, c_\beta^\dagger\} - \{c_\alpha^\dagger, c_\beta^\dagger\} c_\alpha = c_\alpha^\dagger \delta_{\alpha\beta}. \tag{38}$$

Here, $[A, B] = AB - BA$, and we have used the identity $[AB, C] = A\{B, C\} - \{A, C\}B$ and the anti-commutation relations, (33) and (34). Noting that for $\beta \neq \alpha$, $\hat{n}_\alpha$ and $c_\beta^\dagger$ can be exchanged to each other, we can show the following equation for $n_\alpha = 1$:

$$\begin{aligned}
\hat{n}_\alpha |\boldsymbol{n}\rangle &= \hat{n}_\alpha (c_1^\dagger)^{n_1} \cdots c_\alpha^\dagger \cdots |\mathrm{vac}\rangle = (c_1^\dagger)^{n_1} \cdots \hat{n}_\alpha c_\alpha^\dagger \cdots |\mathrm{vac}\rangle \\
&= (c_1^\dagger)^{n_1} \cdots (c_\alpha^\dagger + c_\alpha^\dagger \hat{n}_\alpha) \cdots |\mathrm{vac}\rangle \\
&= |\boldsymbol{n}\rangle + (c_1^\dagger)^{n_1} \cdots (c_\alpha^\dagger) \cdots \hat{n}_\alpha |\mathrm{vac}\rangle
\end{aligned} \tag{39}$$

Using $\hat{n}_\alpha |\mathrm{vac}\rangle = c_\alpha^\dagger c_\alpha |\mathrm{vac}\rangle = 0$, we conclude

$$\hat{n}_\alpha |\boldsymbol{n}\rangle = |\boldsymbol{n}\rangle. \tag{40}$$

On the other hand, noting that $\hat{n}_\alpha$ and $c_\beta^\dagger$ ($\beta \neq \alpha$) can be exchanged to each other, we obtain the following equation for $n_\alpha = 0$:

$$\hat{n}_\alpha |\boldsymbol{n}\rangle = \hat{n}_\alpha (c_1^\dagger)^{n_1} \cdots |\mathrm{vac}\rangle = (c_1^\dagger)^{n_1} \cdots \hat{n}_\alpha |\mathrm{vac}\rangle = 0 \tag{41}$$

Now we have proved the formula (37).

The Hamiltonian H_0 for the noninteracting Fermi-particle system is written as

$$\hat{H}_0 = \sum_\alpha \epsilon_\alpha \hat{n}_\alpha = \sum_\alpha \epsilon_\alpha c_\alpha^\dagger c_\alpha. \tag{42}$$

Actualy, the state $|\boldsymbol{n}\rangle$ is an eigenstate of the Hamiltonian $\hat{H}_0$m and its eigenvalue is obtained from Eq. (37) as

$$\hat{H}_0 |\boldsymbol{n}\rangle = \sum_\alpha \epsilon_\alpha n_\alpha |\boldsymbol{n}\rangle. \tag{43}$$

Thus, we can see that this Hamiltonian indeed gives a correct total energy.

Let us consider the ground state of electrons denoted with $|\mathrm{GS}\rangle$. In the absence of electron-electron interaction, the ground state is given as

$$|\mathrm{GS}\rangle = \prod_{\alpha=1}^{N} c_\alpha^\dagger |\mathrm{vac}\rangle \tag{44}$$

Especially, the Hamiltonian of the electron gas system and its ground state are given as

$$\hat{H}_0 = \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}}^\dagger c_{\boldsymbol{k}}, \qquad (\epsilon_{\boldsymbol{k}} = (\hbar \boldsymbol{k})^2 / 2m), \tag{45}$$

$$|\mathrm{GS}\rangle = \prod_{\epsilon_{\boldsymbol{k}} \leq \epsilon_F} c_{\boldsymbol{k}}^\dagger |\mathrm{vac}\rangle, \tag{46}$$

respectively. Here, $\epsilon_{\rm F}$ is the Fermi energy.

Finally, we will rewrite the Hamiltonian of the free electron system with a position-fixed basis. By replacing α with $\boldsymbol{k}$ in Eq. (29), we obtain

$$c_{\boldsymbol{k}} = \int d^3\boldsymbol{r}\, \psi_{\boldsymbol{k}}(\boldsymbol{r})^* \Psi(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \int d^3\boldsymbol{r}\, \Psi(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}, \tag{47}$$

$$c_{\boldsymbol{k}}^\dagger = \int d^3\boldsymbol{r}\, \psi_{\boldsymbol{k}}(\boldsymbol{r}) \Psi^\dagger(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \int d^3\boldsymbol{r}\, \Psi^\dagger(\boldsymbol{r}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{48}$$

By using these equations, the Hamiltonian (42) for the electron gas can be modified as

$$\begin{aligned}
\hat{H}_0 &= \sum_{\boldsymbol{k}} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}}^\dagger c_{\boldsymbol{k}} \\
&= \sum_{\boldsymbol{k}} \frac{(\hbar\boldsymbol{k})^2}{2m} \times \frac{1}{\sqrt{V}} \int d^3\boldsymbol{r}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \Psi^\dagger(\boldsymbol{r}) \times \frac{1}{\sqrt{V}} \int d^3\boldsymbol{r}'\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'} \Psi(\boldsymbol{r}') \\
&= \frac{1}{V} \int d^3\boldsymbol{r} d^3\boldsymbol{r}'\, \Psi^\dagger(\boldsymbol{r}) \left[\sum_{\boldsymbol{k}} \left(\frac{(\hbar\boldsymbol{k})^2}{2m} \right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}'} \right] \Psi(\boldsymbol{r}') \\
&= \frac{1}{V} \int d^3\boldsymbol{r} d^3\boldsymbol{r}'\, \Psi^\dagger(\boldsymbol{r}) \left[\left(-\frac{\hbar^2}{2m} \nabla_{\boldsymbol{r}'}^2 \right) \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \right] \Psi(\boldsymbol{r}') \\
&= \frac{1}{V} \int d^3\boldsymbol{r} d^3\boldsymbol{r}'\, \Psi^\dagger(\boldsymbol{r}) \left[\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \right] \left(-\frac{\hbar^2}{2m} \nabla_{\boldsymbol{r}'}^2 \right) \Psi(\boldsymbol{r}').
\end{aligned} \tag{49}$$

($\nabla_{\boldsymbol{r}}$ is a nabla symbol acting on position $\boldsymbol{r}$.) In the final line, we have used the formula for a function $f(\boldsymbol{r}')$, which approaches 0 fast enough in the limit of $|\boldsymbol{r}'| \to \infty$, and the field operator $\Psi(\boldsymbol{r}')$:[12]

$$\int d\boldsymbol{r}'\, \nabla_{\boldsymbol{r}'}^2 (f(\boldsymbol{r}')) \Psi(\boldsymbol{r}') = \int d\boldsymbol{r}'\, f(\boldsymbol{r}') \nabla_{\boldsymbol{r}'}^2 \Psi(\boldsymbol{r}'). \tag{50}$$

Here, we note that in the limit of $L \to \infty$,

$$\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} = \frac{V}{(2\pi)^3} \int d^3\boldsymbol{k}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} = V\delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{51}$$

holds. Using this, we can perform the integral on $\boldsymbol{r}'$, and obtain

$$\hat{H}_0 = \int d^3\boldsymbol{r}\, \Psi^\dagger(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \Psi(\boldsymbol{r}). \tag{52}$$

($\nabla_{\boldsymbol{r}}$ has been replaced with ∇.) Note that the differential operator $-\hbar^2\nabla^2/2m$ that appears in the Schrödinger equation for free electrons appears in the part of the equation that is sandwiched between $\Psi^2 dagger(\boldsymbol{r})$ and $\Psi(\boldsymbol{r})$.

[12] It is an extension of the standard formula used in electromagnetism, etc., to the operator. For sufficiently large surfaces S including $\boldsymbol{r}$ and $\boldsymbol{r}'$, we prove it by using Gauss's theorem twice. The surface integral on S is negligible when S is large enough, since $f(\boldsymbol{r})$ approaches 0 quickly.

6 How to describe one-body interaction

Let us consider the case where the potential of $v(\boldsymbol{x})$ is added to the electronic system. As indicated from the Hamiltonian for free electrons in the previous section, the Hamiltonian of electrons under the one-body potential $v(\boldsymbol{x})$ can be inferred as

$$\hat{H}_0 = \int d^3\boldsymbol{r}\, \Psi^\dagger(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)\Psi(\boldsymbol{r}). \tag{53}$$

Let's check that this is the correct Hamiltonian. We assume that the eigenvalues and the eigenstates for the Hamiltonian are given in the first-quantization description as

$$\hat{h}|\alpha\rangle = \epsilon_\alpha|\alpha\rangle, \quad (\alpha = 1, 2, 3, \cdots). \tag{54}$$

Then, using the formula of basis transformation

$$\Psi(\boldsymbol{r}) = \sum_\alpha \langle \boldsymbol{r}|\alpha\rangle c_\alpha, \quad \Psi^\dagger(\boldsymbol{r}) = \sum_\alpha \langle\alpha|\boldsymbol{r}\rangle c_\alpha^\dagger, \tag{55}$$

we can modify Eq. (52) as

$$\begin{aligned}\hat{H}_0 &= \int d^3\boldsymbol{r} \sum_\alpha \langle\alpha|\boldsymbol{r}\rangle c_\alpha^\dagger \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right) \sum_\beta \langle\boldsymbol{r}|\beta\rangle c_\beta \\ &= \sum_\alpha \sum_\beta \left[\int d^3\boldsymbol{r}\, \langle\alpha|\boldsymbol{r}\rangle \left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)\langle\boldsymbol{r}|\beta\rangle\right] c_\alpha^\dagger c_\beta.\end{aligned} \tag{56}$$

Using the formula of Eq. (23), we can continue the calculation as follows:

$$\begin{aligned}\hat{H}_0 &= \sum_\alpha \sum_\beta \left[\int d^3\boldsymbol{r}\, \langle\alpha|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\hat{h}|\beta\rangle\right] c_\alpha^\dagger c_\beta \\ &= \sum_\alpha \sum_\beta \epsilon_\beta \left[\int d^3\boldsymbol{r}\, \langle\alpha|\boldsymbol{r}\rangle\langle\boldsymbol{r}|\beta\rangle\right] c_\alpha^\dagger c_\beta \\ &= \sum_\alpha \sum_\beta \epsilon_\beta \langle\alpha|\beta\rangle c_\alpha^\dagger c_\beta = \sum_\alpha \sum_\beta \epsilon_\beta \delta_{\alpha\beta} c_\alpha^\dagger c_\beta = \sum_\alpha \epsilon_\alpha c_\alpha^\dagger c_\alpha.\end{aligned} \tag{57}$$

Finally, we have obtained the Hamiltonian for the noninteracting electron system, which is the same as Eq. (42)). [13]

7 Two-electron states

Next, let's describe the electronic state when there are two electrons in space. Using the generation operator $Psi^dagger(\boldsymbol{r})$, we write the state of the electron at positions bmr_1 and $\boldsymbol{r}_2$

[13] In general, the Hamiltonian for noninteracting systems is given as $H = \sum_{\alpha\beta} c_\alpha^\dagger h_{\alpha\beta} c_\beta$ ($h_{\alpha\beta}$: a square matrix). Using the unitary transformation $c_\alpha = \sum_j U_{\alpha j} c_j$, we obtain $H = \sum_{jj'} \sum_{\alpha\beta} c_j^\dagger U_{j\alpha}^\dagger h_{\alpha\beta} U_{\beta j'} c_{j'} (U_{j\alpha}^\dagger = U_{\alpha j}^*)$. Here, the matrix $\Lambda_{jj'} = \sum_{\alpha\beta} U_{j\alpha}^\dagger h_{\alpha\beta} U_{\beta j'}$ can be diagonalized if we choose a proper $U_{\alpha j}$ (diagonalization of a matrix). Then, we obtain a diagonalized expression, $H = \sum_j \Lambda_{jj} c_j^\dagger c_j$. This procedure of the diagonalization corresponds to the energy eigenvalue problem in the method of the first quantization.

as[14]

$$|\boldsymbol{r}_1\boldsymbol{r}_2\rangle = \Psi^\dagger(\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)|\mathrm{vac}\rangle \tag{58}$$

If we apply the annihilation operator $\Psi(\boldsymbol{r})$ to this two-electron state, the result should be a one-electron state. Actually, we can show

$$\begin{aligned}\Psi(\boldsymbol{r})|\boldsymbol{r}_1\boldsymbol{r}_2\rangle &= \Psi(\boldsymbol{r})\Psi^\dagger(\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)|\mathrm{vac}\rangle \\ &= \big(\delta(\boldsymbol{r}-\boldsymbol{r}_1) - \Psi^\dagger(\boldsymbol{r}_1)\Psi(\boldsymbol{r})\big)\Psi^\dagger(\boldsymbol{r}_2)|\mathrm{vac}\rangle \\ &= \delta(\boldsymbol{r}-\boldsymbol{r}_1)|\boldsymbol{r}_2\rangle - \Psi^\dagger(\boldsymbol{r}_1)(\delta(\boldsymbol{r}-\boldsymbol{r}_2) - \Psi^\dagger(\boldsymbol{r}_2)\Psi(\boldsymbol{r})\big)|\mathrm{vac}\rangle \\ &= \delta(\boldsymbol{r}-\boldsymbol{r}_1)|\boldsymbol{r}_2\rangle - \delta(\boldsymbol{r}-\boldsymbol{r}_2)|\boldsymbol{r}_1\rangle. \end{aligned} \tag{59}$$

(In the last line, we have used $\Psi(\boldsymbol{r})|\mathrm{vac}\rangle = 0$.) Only when $\boldsymbol{r} = \boldsymbol{r}_1$ or $\boldsymbol{r} = \boldsymbol{r}_2$, we can see that the electron is removed and the final state is the one-electron state.

Let us evaluate the probability amplitude density when two electrons are observed at positions, $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, for a two-electron state $|\boldsymbol{r}_1'\boldsymbol{r}_2'\rangle$:

$$\langle \boldsymbol{r}_1\boldsymbol{r}_2|\boldsymbol{r}_1'\boldsymbol{r}_2'\rangle = \langle \mathrm{vac}|\Psi(\boldsymbol{r}_2)\Psi(\boldsymbol{r}_1)|\boldsymbol{r}_1'\boldsymbol{r}_2'\rangle. \tag{60}$$

Using the formula (59), we obtain

$$\begin{aligned}\langle \boldsymbol{r}_1\boldsymbol{r}_2|\boldsymbol{r}_1'\boldsymbol{r}_2'\rangle &= \langle \mathrm{vac}|\Psi(\boldsymbol{r}_2)\Big[\delta(\boldsymbol{r}_1-\boldsymbol{r}_1')|\boldsymbol{r}_2'\rangle - \delta(\boldsymbol{r}_1-\boldsymbol{r}_2')|\boldsymbol{r}_1'\rangle\Big] \\ &= \delta(\boldsymbol{r}_1-\boldsymbol{r}_1')\langle \boldsymbol{r}_2|\boldsymbol{r}_2'\rangle - \delta(\boldsymbol{r}_1-\boldsymbol{r}_2')\langle \boldsymbol{r}_2|\boldsymbol{r}_1'\rangle \\ &= \delta(\boldsymbol{r}_1-\boldsymbol{r}_1')\delta(\boldsymbol{r}_2-\boldsymbol{r}_2') - \delta(\boldsymbol{r}_1-\boldsymbol{r}_2')\delta(\boldsymbol{r}_2-\boldsymbol{r}_1'), \end{aligned} \tag{61}$$

Looking at this, the probability amplitude is not zero when $\boldsymbol{r}_1 = \boldsymbol{r}_1'$, $\boldsymbol{r}_2 = \boldsymbol{r}_2'$, or when $\boldsymbol{r}_1 = \boldsymbol{r}_2'$, $\boldsymbol{r}_2 = \boldsymbol{r}_1'$. It is through the anti-commutation relations of the field operators that the non-individuality of the particles is incorporated.

Similarly, if we put one electron in the energy eigenstate α, and one more electron in in the energy eigenstate β, such a state is written as

$$|\alpha\beta\rangle = c_\alpha^\dagger c_\beta^\dagger|\mathrm{vac}\rangle. \tag{62}$$

For the two-electron state described by $|\alpha\beta\rangle$, the probability amplitude density (the two-electron wave function) is calculated from Eq. (31) as

$$\begin{aligned}\langle \boldsymbol{r}_1\boldsymbol{r}_2|\alpha\beta\rangle &= \langle \boldsymbol{r}_1\boldsymbol{r}_2|c_\alpha^\dagger c_\beta^\dagger|\mathrm{vac}\rangle \\ &= \int d^3\boldsymbol{r}_1' d^3\boldsymbol{r}_2' \psi_\alpha(\boldsymbol{r}_1')\psi_\beta(\boldsymbol{r}_2')\langle \boldsymbol{r}_1\boldsymbol{r}_2|\Psi^\dagger(\boldsymbol{r}_1')\Psi^\dagger(\boldsymbol{r}_2')|\mathrm{vac}\rangle \\ &= \int d^3\boldsymbol{r}_1' d^3\boldsymbol{r}_2' \psi_\alpha(\boldsymbol{r}_1')\psi_\beta(\boldsymbol{r}_2')\langle \boldsymbol{r}_1\boldsymbol{r}_2|\boldsymbol{r}_1'\boldsymbol{r}_2'\rangle \\ &= \psi_\alpha(\boldsymbol{r}_1)\psi_\beta(\boldsymbol{r}_2) - \psi_\alpha(\boldsymbol{r}_2)\psi_\beta(\boldsymbol{r}_1). \end{aligned} \tag{63}$$

In the last line, we have used Eq. (61). This can be rewritten in the form of a determinant as

$$\langle \boldsymbol{r}_1\boldsymbol{r}_2|\alpha\beta\rangle = \begin{vmatrix} \psi_\alpha(\boldsymbol{r}_1) & \psi_\beta(\boldsymbol{r}_1) \\ \psi_\alpha(\boldsymbol{r}_2) & \psi_\beta(\boldsymbol{r}_2) \end{vmatrix}. \tag{64}$$

[14]The bra vector correponding to this state is $\langle \boldsymbol{r}_1\boldsymbol{r}_2| = \langle \mathrm{vac}|\Psi(\boldsymbol{r}_2)\Psi(\boldsymbol{r}_1)$.

We call this the Slater determinant. A characteristic of the Fermi particle is that the probability amplitude density (two-electron wave function) has a negative sign when the position (or eigenstate) of two electrons is exchaned by the expression (63). We note that this property appears naturally from the anti-commutation relation of field operators.

It is not difficult to extend the above argument to the N electronic state. We define the position-fixed N-electron state as

$$|\boldsymbol{r}_1\boldsymbol{r}_2\cdots\boldsymbol{r}_N\rangle = \Psi^\dagger(\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)\cdots\Psi^\dagger(\boldsymbol{r}_N)|\mathrm{vac}\rangle. \tag{65}$$

When $\Psi(\boldsymbol{r})$ acts on this N-electron state, we obtain

$$\Psi(\boldsymbol{r})|\boldsymbol{r}_1\boldsymbol{r}_2\cdots\boldsymbol{r}_N\rangle = \sum_{\alpha=1}^{N}(-1)^{\alpha-1}\delta(\boldsymbol{r}-\boldsymbol{r}_\alpha)|\boldsymbol{r}_1\cdots(\text{no } \boldsymbol{r}_\alpha)\cdots\boldsymbol{r}_N\rangle. \tag{66}$$

(The proof is similar as the case of two electrons.) This formula is an extension of the formula (59) to N electrons, and we can see that the annihilation operator $\Psi(\boldsymbol{r})$ certainly annihilates one electron, leaving the remaining $N-1$ electronic states intact. Furthermore, if we calculate the N-electron wavefunction $\langle\boldsymbol{r}_1\boldsymbol{r}_2\cdots\boldsymbol{r}_N|\alpha_1\alpha_2\cdots\alpha_N\rangle$, we obtain the Slater determinant of a dimenstion N. I will leave this to the reader's exercise.

8 How to describe two-body interaction

Finally, let us describe the Hamiltonian in the case of a potential working between particles, such as the Coulomb interaction between electrons, using the method of second quantization. We denote the interaction potential between the particles when there are electrons at positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ as $V(\boldsymbol{r}_1,\boldsymbol{r}_2)$. Since the particles are indistinguishable, $V(\boldsymbol{r}_1,\boldsymbol{r}_2)$ must satisfy the following condition:

$$V(\boldsymbol{r}_1,\boldsymbol{r}_2) = V(\boldsymbol{r}_2,\boldsymbol{r}_1). \tag{67}$$

For example, the potential of the Coulomb interaction between electrons is described by $V(\boldsymbol{r}_1,\boldsymbol{r}_2) = 1/|\boldsymbol{r}_1-\boldsymbol{r}_2|$ (with the Coulomb constant set to 1 for simplicity), and the above conditions are satisfied.

First, let's consider only the two-electron state. The Hamiltonian $\hat{V}$ representing the Coulomb interaction between electrons should satisfy the following form when acting on a position-fixed two-electron state $|\boldsymbol{r}_1\boldsymbol{r}_2\rangle$:

$$\hat{V}|\boldsymbol{r}_1\boldsymbol{r}_2\rangle = V(\boldsymbol{r}_1,\boldsymbol{r}_2)|\boldsymbol{r}_1\boldsymbol{r}_2\rangle \tag{68}$$

As it turns out, V takes the following form[15]

$$\hat{V} = \frac{1}{2}\int d^3\boldsymbol{x}d^3\boldsymbol{y}\Psi^\dagger(\boldsymbol{x})\Psi^\dagger(\boldsymbol{y})V(\boldsymbol{x},\boldsymbol{y})\Psi(\boldsymbol{y})\Psi(\boldsymbol{x}). \tag{69}$$

[15]It is most natural to follow the order of $\Psi^\dagger(\boldsymbol{x})$, $\Psi^\dagger(\boldsymbol{y})$, $\Psi(\boldsymbol{y})$, and $\Psi(\boldsymbol{x})$ for the field operators. Intuitively, one might want to line up the field operators with $\Psi^\dagger(\boldsymbol{x})$, $\Psi(\boldsymbol{x})$, $\Psi^\dagger(\boldsymbol{y})$, and $\Psi(\boldsymbol{y})$, since $\Psi^\dagger(\boldsymbol{x})\Psi(\boldsymbol{x})$ corresponds to the operator that gives the density of position $\boldsymbol{r}$. However, when this arrangement is done, the potential $\hat{V}$ will include a constant shift [2]. In particular, in the limit of $L\to\infty$, this constant becomes infinite and we need to work on removing it. I won't show it here, but I hope you will accept this ordering as a "good luck charm".

The 1/2 factor is attached to avoid double counting of the Coulomb interaction with respect to particle exchange. Let's quickly act on $|\boldsymbol{r}_1\boldsymbol{r}_2\rangle$:

$$\hat{V}|\boldsymbol{r}_1\boldsymbol{r}_2\rangle = \frac{1}{2}\int d^3\boldsymbol{x}\, d^3\boldsymbol{y}\, \Psi^\dagger(\boldsymbol{x})\Psi^\dagger(\boldsymbol{y})V(\boldsymbol{x},\boldsymbol{y})\Psi(\boldsymbol{y})\Psi(\boldsymbol{x})|\boldsymbol{r}_1\boldsymbol{r}_2\rangle. \tag{70}$$

Using the formula (59) twice, we obtain

$$\begin{aligned}
&\Psi(\boldsymbol{y})\Psi(\boldsymbol{x})|\boldsymbol{r}_1\boldsymbol{r}_2\rangle \\
&= \Psi(\boldsymbol{y})\left[\delta(\boldsymbol{x}-\boldsymbol{r}_1)|\boldsymbol{r}_2\rangle - \delta(\boldsymbol{x}-\boldsymbol{r}_2)|\boldsymbol{r}_1\rangle\right] \\
&= \delta(\boldsymbol{x}-\boldsymbol{r}_1)\delta(\boldsymbol{y}-\boldsymbol{r}_2)|\mathrm{vac}\rangle - \delta(\boldsymbol{x}-\boldsymbol{r}_2)\delta(\boldsymbol{y}-\boldsymbol{r}_1)|\mathrm{vac}\rangle.
\end{aligned} \tag{71}$$

Therefore, the Hamiltonian of the two-body interaction is given as

$$\begin{aligned}
\hat{V}|\boldsymbol{r}_1\boldsymbol{r}_2\rangle &= \frac{1}{2}\int d^3\boldsymbol{x}\, d^3\boldsymbol{y}\, \Psi^\dagger(\boldsymbol{x})\Psi^\dagger(\boldsymbol{y})V(\boldsymbol{x},\boldsymbol{y}) \\
&\quad\times\Big[\delta(\boldsymbol{x}-\boldsymbol{r}_1)\delta(\boldsymbol{y}-\boldsymbol{r}_2)|\mathrm{vac}\rangle - \delta(\boldsymbol{x}-\boldsymbol{r}_2)\delta(\boldsymbol{y}-\boldsymbol{r}_1)|\mathrm{vac}\rangle\Big] \\
&= \frac{1}{2}V(\boldsymbol{r}_1,\boldsymbol{r}_2)\Psi^\dagger(\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)|\mathrm{vac}\rangle - \frac{1}{2}V(\boldsymbol{r}_2,\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)\Psi^\dagger(\boldsymbol{r}_1)|\mathrm{vac}\rangle \\
&= \frac{1}{2}V(\boldsymbol{r}_1,\boldsymbol{r}_2)\Psi^\dagger(\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)|\mathrm{vac}\rangle + \frac{1}{2}V(\boldsymbol{r}_2,\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_1)\Psi^\dagger(\boldsymbol{r}_2)|\mathrm{vac}\rangle \\
&= \frac{1}{2}V(\boldsymbol{r}_1,\boldsymbol{r}_2)|\boldsymbol{r}_1\boldsymbol{r}_2\rangle + \frac{1}{2}V(\boldsymbol{r}_2,\boldsymbol{r}_1)|\boldsymbol{r}_1\boldsymbol{r}_2\rangle = V(\boldsymbol{r}_1,\boldsymbol{r}_2)|\boldsymbol{r}_1\boldsymbol{r}_2\rangle.
\end{aligned} \tag{72}$$

Thus, we can see that the present definition of $\hat{V}$ is working well (in the last line, we have used the symmetry condition (67)).

Finally, let's see if it works well when $\hat{V}$ acts on a general N-electron system. Using the formula (66) twice, we obtain

$$\begin{aligned}
&\Psi(\boldsymbol{y})\Psi(\boldsymbol{x})|\boldsymbol{r}_1\boldsymbol{r}_2\cdots\boldsymbol{r}_N\rangle \\
&= \sum_{\alpha=1}^{N}\Psi(\boldsymbol{y})(-1)^{\alpha-1}\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots\boldsymbol{r}_N\rangle \\
&= \sum_{\alpha=1}^{N}\sum_{\beta<\alpha}^{N}(-1)^{\alpha-1}(-1)^{\beta-1}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha) \\
&\qquad\qquad\times|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\beta)\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots\boldsymbol{r}_N\rangle \\
&+ \sum_{\alpha=1}^{N}\sum_{\beta>\alpha}^{N}(-1)^{\alpha-1}(-1)^{\beta-2}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha) \\
&\qquad\qquad\times|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots(\text{no }\boldsymbol{r}_\beta)\cdots\boldsymbol{r}_N\rangle.
\end{aligned} \tag{73}$$

When we continue the calculation by multiplying $\Psi^\dagger(\boldsymbol{x})\Psi^\dagger(\boldsymbol{y})$ to the above equation from the left, using the relations

$$\begin{aligned}
&|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\beta)\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots\boldsymbol{r}_N\rangle \\
&\qquad= \Psi^\dagger(\boldsymbol{r}_1)\cdots(\Psi^\dagger(\text{no }\boldsymbol{r}_\beta))\cdots(\Psi^\dagger(\text{no }\boldsymbol{r}_\alpha))\cdots\Psi^\dagger(\boldsymbol{r}_N)|\mathrm{vac}\rangle, \qquad (74)\\
&|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots(\text{no }\boldsymbol{r}_\beta)\cdots\boldsymbol{r}_N\rangle \\
&\qquad= \Psi^\dagger(\boldsymbol{r}_1)\cdots(\text{no }\Psi^\dagger(\boldsymbol{r}_\alpha))\cdots(\text{no }\Psi^\dagger(\boldsymbol{r}_\beta))\cdots\Psi^\dagger(\boldsymbol{r}_N)|\mathrm{vac}\rangle, \qquad (75)
\end{aligned}$$

and the anti-commutation relation, and noting that $\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)\Psi^\dagger(\boldsymbol{x}) = \delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)\Psi^\dagger(\boldsymbol{r}_\alpha)$, we obtain

$$
\begin{aligned}
&\Psi^\dagger(\boldsymbol{x})\Psi^\dagger(\boldsymbol{y})\Psi(\boldsymbol{y})\Psi(\boldsymbol{x})|\boldsymbol{r}_1\boldsymbol{r}_2\cdots\boldsymbol{r}_N\rangle \\
&= \sum_{\alpha=1}^{N}\sum_{\beta<\alpha}^{N}(-1)^{\alpha-1}(-1)^{\beta-1}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)\Psi^\dagger(\boldsymbol{r}_\alpha)\Psi^\dagger(\boldsymbol{r}_\beta) \\
&\qquad\qquad \times|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\beta)\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots\boldsymbol{r}_N\rangle \\
&+ \sum_{\alpha=1}^{N}\sum_{\beta>\alpha}^{N}(-1)^{\alpha-1}(-1)^{\beta-2}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)\Psi^\dagger(\boldsymbol{r}_\alpha)\Psi^\dagger(\boldsymbol{r}_\beta) \\
&\qquad\qquad \times|\boldsymbol{r}_1\cdots(\text{no }\boldsymbol{r}_\beta)\cdots(\text{no }\boldsymbol{r}_\alpha)\cdots\boldsymbol{r}_N\rangle \\
&= \sum_{\alpha=1}^{N}\sum_{\beta<\alpha}^{N}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle \\
&+ \sum_{\alpha=1}^{N}\sum_{\beta>\alpha}^{N}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle
\end{aligned}
\tag{76}
$$

Therefore, we conclude

$$
\begin{aligned}
&\hat{V}|\boldsymbol{r}_1\boldsymbol{r}_2\cdots\boldsymbol{r}_N\rangle \\
&= \frac{1}{2}\int d^3\boldsymbol{x}d^3\boldsymbol{y}V(\boldsymbol{x},\boldsymbol{y})\Psi^\dagger(\boldsymbol{x})\Psi^\dagger(\boldsymbol{y})\Psi(\boldsymbol{y})\Psi(\boldsymbol{x})|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle \\
&= \frac{1}{2}\int d^3\boldsymbol{x}d^3\boldsymbol{y}V(\boldsymbol{x},\boldsymbol{y})\left[\sum_{\alpha=1}^{N}\sum_{\beta<\alpha}^{N}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle\right. \\
&\qquad\left.+\sum_{\alpha=1}^{N}\sum_{\beta>\alpha}^{N}\delta(\boldsymbol{y}-\boldsymbol{r}_\beta)\delta(\boldsymbol{x}-\boldsymbol{r}_\alpha)|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle\right] \\
&= \left(\frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta<\alpha}^{N}V(\boldsymbol{r}_\alpha,\boldsymbol{r}_\beta)+\frac{1}{2}\sum_{\alpha=1}^{N}\sum_{\beta>\alpha}^{N}V(\boldsymbol{r}_\alpha,\boldsymbol{r}_\beta)\right)|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle \\
&= \sum_{\beta<\alpha}V(\boldsymbol{r}_\alpha,\boldsymbol{r}_\beta)|\boldsymbol{r}_1\cdots\boldsymbol{r}_N\rangle.
\end{aligned}
\tag{77}
$$

In the last equation, we used the symmetry condition (67) after exchanging the summing variables α and β. The last equation shows that the operator $\hat{V}$ representing the inter-electron potential has an eigenvalue of the sum of the potentials $V(\boldsymbol{r}_\alpha,\boldsymbol{r}_\beta)$ for every particle combination $(\boldsymbol{r}_\alpha,\boldsymbol{r}_\beta)$ when the operator $\hat{V}$ acts on a position-fixed N-electron state. That is, even for N electronic states, we can see that the operator $\hat{V}$ defined by the expression (69) adequately describes the sum of the interactions between electrons.

In summary, the Hamiltonian of the interacting electron system is given as

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{78}$$

$$\hat{H}_0 = \int d^3\boldsymbol{r}\Psi^\dagger(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla^2+v(\boldsymbol{r})\right)\Psi(\boldsymbol{r})$$

$$\hat{V} = \frac{1}{2}\int d^3\boldsymbol{r}d^3\boldsymbol{r}'\Psi^\dagger(\boldsymbol{r})\Psi^\dagger(\boldsymbol{r}')V(\boldsymbol{r},\boldsymbol{r}')\Psi(\boldsymbol{r}')\Psi(\boldsymbol{r}). \tag{79}$$

($\boldsymbol{x}$, $\boldsymbol{y}$ has been replaced with $\boldsymbol{r}$, $\boldsymbol{r}'$.)

9 Application: Coulomb interaction in the wavenumber basis

One of the advantages of the second quantization description method is that the interaction between electrons can be described as a scattering process between electrons clearly. We consider the Coulomb interaction $V(\boldsymbol{r},\boldsymbol{r}') = 1/|\boldsymbol{r}-\boldsymbol{r}'|$, and introduce its Fourier transformation

$$\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} = \frac{1}{V}\sum_{\boldsymbol{q}} v_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}, \tag{80}$$

with the Fourier coefficient $v_{\boldsymbol{q}}$.[16] Let us rewrite $\hat{V}$ using Eqs. (32) and (80):

$$\begin{aligned}
\hat{V} &= \frac{1}{2}\int d^3\boldsymbol{r} d^3\boldsymbol{r}' \Psi^\dagger(\boldsymbol{r})\Psi^\dagger(\boldsymbol{r}')\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\Psi(\boldsymbol{r}')\Psi(\boldsymbol{r}) \\
&= \frac{1}{2}\int d^3\boldsymbol{r} d^3\boldsymbol{r}' \sum_{\boldsymbol{k}_1}\frac{e^{-i\boldsymbol{k}_1\cdot\boldsymbol{r}}}{\sqrt{V}}c^\dagger_{\boldsymbol{k}_1}\sum_{\boldsymbol{k}_2}\frac{e^{-i\boldsymbol{k}_2\cdot\boldsymbol{r}'}}{\sqrt{V}}c^\dagger_{\boldsymbol{k}_2}\sum_{\boldsymbol{q}}\frac{e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{V}v_{\boldsymbol{q}}\sum_{\boldsymbol{k}_3}\frac{e^{i\boldsymbol{k}_3\cdot\boldsymbol{r}'}}{\sqrt{V}}c_{\boldsymbol{k}_3}\sum_{\boldsymbol{k}_4}\frac{e^{i\boldsymbol{k}_4\cdot\boldsymbol{r}}}{\sqrt{V}}c_{\boldsymbol{k}_4}, \\
&= \frac{1}{2V^3}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3,\boldsymbol{k}_4,\boldsymbol{q}} v_{\boldsymbol{q}} c^\dagger_{\boldsymbol{k}_1}c^\dagger_{\boldsymbol{k}_2}c_{\boldsymbol{k}_3}c_{\boldsymbol{k}_4}\int d^3\boldsymbol{r} e^{i(\boldsymbol{k}_4-\boldsymbol{k}_1+\boldsymbol{q})\cdot\boldsymbol{r}}\int d^3\boldsymbol{r}' e^{i(\boldsymbol{k}_3-\boldsymbol{k}_2-\boldsymbol{q})\cdot\boldsymbol{r}'}.
\end{aligned} \tag{81}$$

Now, we use the formula

$$\int d^3\boldsymbol{r} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = V\delta_{\boldsymbol{k},\boldsymbol{0}}. \tag{82}$$

Then, only the part of $\boldsymbol{k}_1 = \boldsymbol{k}_4 + \boldsymbol{q}$, $\boldsymbol{k}_2 = \boldsymbol{k}_3 - \boldsymbol{q}$ is nonzero in the sum. By replacing $\boldsymbol{k}_3$, $\boldsymbol{k}_4$ with $\boldsymbol{k}'$ and $\boldsymbol{k}_4 = \boldsymbol{k}$ respectively, we obtain

$$\hat{V} = \frac{1}{2V}\sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} v_{\boldsymbol{q}} c^\dagger_{\boldsymbol{k}+\boldsymbol{q}}c^\dagger_{\boldsymbol{k}'-\boldsymbol{q}}c_{\boldsymbol{k}'}c_{\boldsymbol{k}}. \tag{83}$$

From this equation, the Coulomb interaction can be viewed in wave number space as a process of exchanging momentum, as represented by Fig. 2.

In the actual calculation, it is necessary to take into account the electron spin degrees of freedom. In this case, the field operator is written as $\Psi_\sigma(\boldsymbol{r})$. This is an annihilation operator that erases the electrons of the spin $\sigma(=\uparrow,\downarrow)$ at position $\boldsymbol{r}$. Similarly, $\Psi^\dagger_\sigma(\boldsymbol{r})$ is a generative operator that adds an electron of spin σ to position $\boldsymbol{r}$. The Hamiltonian is written in real space as follows:

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{84}$$

$$\begin{aligned}
\hat{H}_0 &= \sum_\sigma \int d^3\boldsymbol{r}\Psi^\dagger_\sigma(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)\Psi_\sigma(\boldsymbol{r}) \\
\hat{V} &= \frac{1}{2}\sum_{\sigma\sigma'}\int d^3\boldsymbol{r} d^3\boldsymbol{r}'\Psi^\dagger_\sigma(\boldsymbol{r})\Psi^\dagger_{\sigma'}(\boldsymbol{r}')\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\Psi_{\sigma'}(\boldsymbol{r}')\Psi_\sigma(\boldsymbol{r}).
\end{aligned} \tag{85}$$

[16] Now, we do not show the explicit form of $v_{\boldsymbol{q}}$. But it is not difficult to show $v_{\boldsymbol{q}} = 4\pi/\boldsymbol{q}^2$ in the limit of $L\to\infty$ using $\frac{1}{V}\sum_{\boldsymbol{q}}(4\pi/\boldsymbol{q}^2)e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')} \to (2\pi)^{-3}\int d^3\boldsymbol{q}\,(4\pi/\boldsymbol{q}^2)e^{i\boldsymbol{q}\cdot(\boldsymbol{r}-\boldsymbol{r}')}$, and employing the polar coordinate. We use $\int_0^\infty dx\ \sin x/x = \pi/2$ at last.

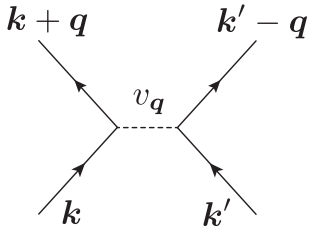

Figure 2: Electron scattering process by the Coulomb interaction.

The field operator is written in wavenumber space as

$$\Psi_\sigma(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} c_{\boldsymbol{k}\sigma}, \tag{86}$$

$$\Psi_\sigma^\dagger(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} c_{\boldsymbol{k}\sigma}^\dagger. \tag{87}$$

($c_{\boldsymbol{k}\sigma}^\dagger$, $c_{\boldsymbol{k}\sigma}$ are creation and annihilation operators of the wavenumber-fixed state) Then, the Hamiltonian is rewritten as

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{88}$$

$$\hat{H}_0 = \sum_{\boldsymbol{k}\sigma} \epsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}^\dagger c_{\boldsymbol{k}\sigma} \tag{89}$$

$$\hat{V} = \frac{1}{2V} \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\sigma,\sigma'} v_{\boldsymbol{q}} c_{\boldsymbol{k}+\boldsymbol{q}\sigma}^\dagger c_{\boldsymbol{k}'-\boldsymbol{q}\sigma'}^\dagger c_{\boldsymbol{k}'\sigma'} c_{\boldsymbol{k}\sigma}. \tag{90}$$

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