The Quantum-Field Approach to Superconductivity Theory

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In this review, we consider the field-theoretic method in the theory of superconductivity, discuss the basic ideas of superconductivity, and present a generalization of the Ginzburg–Landau and BCS theories in the frame of many-particle quantum field theory. Quantum field theory provides the original and powerful tools for the solution of certain problems of superconductivity.

KEYWORDS: Superconductivity, Supersymmetry, Nambu Spinor, Habbard-Stratanovich Transformation, Ginzburg-Landau Theory, BCS, Green Function.

CONTENTS

1. INTRODUCTION

Studies in the field of superconductivity theory is one of the most bright, fruitful, and promising trends in the theoretical physics of condensed matter, since superconductivity remains to be one of the most interesting research areas in physics.[1–6]

The theory of superconductivity seems to be founded on the London postulate.[7] Associated with the gauge transformation, the conserved current is

$$\mathbf{j} = -\frac{i}{2}(\phi^* \nabla \phi - \phi \nabla \phi^*) - e|\phi|^2 \mathbf{A} \qquad (1)$$

The current due to the first term is called the paramagnetic current; and that due to the second, the diamagnetic current. In the superconducting state, the first term on the right-hand side changes very slightly, and sometimes the wave function is quite rigid, that only the diamagnetic current survives. In this respect, the superconductor is the perfect diamagnetic substance. The current is dominated by

$$\mathbf{j} = -k^2 \mathbf{A} \qquad (2)$$

where k is properly chosen positive constant. The Meissner effect is easily derived from the Ampére's equation,

$$\nabla \times \mathbf{B} = \mathbf{j} \qquad (3)$$

Taking rotation gives

$$\nabla^2 \mathbf{B} = k^2 \mathbf{B} \qquad (4)$$

or

$$B_x = B_0 e^{-kx} \tag{5}$$

It is important to note that $|\phi|^2$ in Eq. (1) is very large, the classic scale quantity, so that the magnetic field in Eq. (5) dumps very rapidly. This is the Meissner effect. We know similar phenomena, the screening of the Coulomb interaction, or the quark confinement.

The boson model of Cooper pairs is considerably successful. Equation (3) yields $\nabla^2 \mathbf{A} = k^2 \mathbf{A}$, which is

$$\partial^\mu A_\mu = -k^2 A_\mu \tag{6}$$

suggesting that photon is massive, that is a fundamental aspect to superconductivity.[8]

An essentially similar treatment has been presented by Ginzburg and Landau (GL).[9] The superconducting state is the macroscopic state; in other words, a thermodynamic phase. They characterized this phase by introducing the order parameter, Ψ. This looks like the Schrödinger function Ψ, and then the primitive quantum theorists got confused, saying that behind the Iron Curtain the quantum theory was different in features from that of the Western countries.

The theory is handled as the phase transition. The Lagrangian for the superconducting state is postulated as

$$F_s = F_0 + a|\Psi|^2 + \frac{1}{2}b|\Psi|^4 + \frac{1}{2m^*}\left|\left(-i\hbar\nabla + \frac{e^*\mathbf{A}}{c}\right)\right|^2 + \frac{h^2}{8\pi} \tag{7}$$

where $*$ indicates the quantities in question referred to the superconductor ($\times 2$). Note that there are $-|\Psi|^2$ and $|\Psi|^4$ terms in the potential parts. These drive the system to spontaneous symmetry breaking and lead to a phase transition for the suitable choice of constants a and b. This is now called the Higgs mechanism.[8] Certainly, the GL treatment is a few years ahead of the Nambu–Goldstone suggestion.

The GL theory is known as the macroscopic quantum mechanism, and in this sense, the big Ψ is sometimes amusingly called the cat's Ψ.

A very instructive presentation of the macroscopic quantum theory is found in *Feynman lectures on Physics*. Vol. III, Chap. 21. Various topics there, such as the Josephson junction, are quite readable.

The microscopic theory was prepared by Bardeen, Cooper and Schrieffer.[3] However, as a preliminary discussion, we present the Bogoliubov treatment. The superconductivity is a kind of many-electron problems. The most general Hamiltonian should be

$$H = \int dx \psi^+(x) h(x) \psi(x)$$
$$+ \frac{1}{2} \int dx\, dx' \psi^+(x)\psi(x)v(x, x')\psi^+(x')\psi(x') \tag{8}$$

Since the algebra of electrons is the spinor, the terms other than the above identically vanish. In other words, the three- or four-body interactions are useless. First, we specify the spin indices, and next the plane-wave representation for the spatial parts. Equation (8) is simply written as

$$H = \epsilon_k(a_k^+ + a_k) + v_{k,-k}a_k^* a_{-k}^* a_{-k}a_k \tag{9}$$

The simplification or the mean-field approximation for the two-body part is twofold—say,

$$\Delta_{k,-k}a_{k\alpha}a_{k\alpha}\langle a_{-k\beta}^+ a_{-k\beta}^+\rangle$$
$$\Delta'_{k,-k}a_{k\alpha}^+ a_{k\beta}^+\langle a_{k\alpha}a_{-k\beta}\rangle + \text{c.c.} \tag{10}$$

Sergei Kruchinin (1957)—is leading scientist of the Bogolyubov Institute for Theoretical Physics, NASU (Kiev, Ukraine). Professor of at the National Aviation University. S. P. Kruchinin has published significant original works in the fields of nuclear physics and many-particle systems, solid-state physics, superconductivity, theory of nonlinear phenomena, nanophysics. He is the author and co-author of more than 100 scientific works which have been published in leading scientific journals. He has been using advanced mathematical methods to solve the posed problems. Since the time high-temperature superconductors were discovered, S. P. Kruchinin has intensively studied their physical properties. In particular, it is worth noting the work carried out jointly with A. S. Davydov "Interlayer Effects in the Newest High-Tc Superconductors" (Physica C, 1991), where the theory of the non-monotonous dependence of the critical temperature of superconductivity on the number of cuprate layers in the elementary cell of high-temperature superconductors was developed. This work has remained up to date in connection with the search for new superconductors operating at room temperature. Kruchinin's works on superconductivity were included in the monograph "Modern aspects of Superconductivity: Theory of Superconductivity" (World Scientific, Singapore, 2010, jointly with H. Nagao) which shows the contemporary status of the problems of high-temperature superconductivity. He has published the textbook "Theory of Field. Solution of the problems" for students. Kruchinin was the organizer of seven international conferences on the current problems of high-temperature superconductivity and nanosystems. Six books in Springer and one book in World Scientific publishing houses were published under his guidance. Kruchinin Sergei is the co-editor of the following journals: "Quantum Matter" (USA), "Reviews in Theoretical Science" (USA), "Progress in Nanotechnology and Nanomaterials" (USA).

The latter looks curious, since such expectation value $\langle a_{k\alpha} a_{-k\beta}\rangle$ vanishes identically. Against this common sense, Bogoliubov put the Hamiltonian,

$$H = \epsilon_k(a_k^+ + a_k) + \Delta_k a_k^* a_{-k}^* + \Delta_k^* a_{-k} a_k \qquad (11)$$

We understand that Bogoliubov presumed the Cooper pair, and provided the effective Hamiltonian for pairs. His theory may be a shorthand treatment of the BCS theory. This Hamiltonian is diagonalized by the so-called Bogoliubov transformation which defines the quasiparticle responsible for the superconductivity as

$$\begin{pmatrix} \gamma_{k\uparrow} \\ \gamma_{-k\downarrow}^+ \end{pmatrix} = \begin{pmatrix} u_k & -v_k \\ v_k & u_k \end{pmatrix} \begin{pmatrix} c_{k\uparrow} \\ c_{-k\downarrow}^+ \end{pmatrix} \qquad (12)$$

with

$$u_k^2 - v_k^2 = 1 \qquad (13)$$

The spirit of the Bogoliubov transformation is to mix operators $c_{k\uparrow}$ and $c_{-k\downarrow}^+$, which are different in spin. The quasiparticle yields the new ground state, so that the particle pair or the hole pair arises near the chemical potential. The stabilization energy thus obtained is called the gap energy Δ_k.[3, 10]

We now follow the BCS microscopic treatment. The Green function has been effectively used by employing the Nambu spinor. This makes the unified treatment of normal and superconducting states possible. However, the temperature Green function (Matsubara function) is used from the beginning.

2. SPINORS

We start with the general many-electron Hamiltonian not restricted to the BCS Hamiltonian. The BCS state responsible for the superconducting state is easily recognized from the formal description. The simplest method of the quantum chemistry should be the Hückel theory. This consists of the single energy matrix,

$$\beta_{rs} = \int dx\, h(x) \rho_{rs}(x) \qquad (14)$$

where $h(x)$ is the single-particle quantum mechanical Hamiltonian and the electron density $\rho_{rs}(x)$ is given by the product of the single-particle (atomic) orbitals χ_r and χ_s. Note that this is the spin-less theory.

We then extend the treatment into the spin space,

$$\beta_{rs} = \begin{pmatrix} \beta_{rs}^{\uparrow\uparrow} & \beta_{rs}^{\uparrow\downarrow} \\ \beta_{rs}^{\downarrow\uparrow} & \beta_{rs}^{\downarrow\downarrow} \end{pmatrix} \qquad (15)$$

Any 2×2 matrix is expanded by the Pauli spin matrices together with the unit matrix,

$$\sigma^0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
$$\sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad (16)$$

However we employ other combinations:

$$\sigma^\uparrow = \frac{1}{2}(\sigma^0 + \sigma^3) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$
$$\sigma^\downarrow = \frac{1}{2}(\sigma^0 - \sigma^3) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$
$$\sigma^+ = \frac{1}{2}(\sigma^1 + i\sigma^2) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$
$$\sigma^- = \frac{1}{2i}(\sigma^1 - i\sigma^2) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \qquad (17)$$

We then in Eq. (24) have

$$\beta_{rs} = \beta_{rs}^\mu \sigma^\mu$$
$$\beta_{rs}^\mu = \mathrm{Tr}(\sigma^\mu \beta_{rs}) \qquad (18)$$

in detail

$$\beta_{rs}^\uparrow = \beta_{rs}^{\uparrow\uparrow} \quad \beta_{rs}^\downarrow = \beta_{rs}^{\downarrow\downarrow}$$
$$\beta_{rs}^+ = \beta_{rs}^{\downarrow\uparrow} \quad \beta_{rs}^- = \beta_{rs}^{\uparrow\downarrow} \qquad (19)$$

As to the Pauli matrices, the ordinary commutators are

$$\left.\begin{aligned} [\sigma^i, \sigma^j] &= 2i\epsilon_{ijk}\sigma^k \\ [\sigma^3, \sigma^+] &= 2\sigma^+ \\ [\sigma^3, \sigma^-] &= -2\sigma^- \\ [\sigma^+, \sigma^-] &= \sigma^3 \end{aligned}\right\} \qquad (20)$$

$$\left.\begin{aligned} [\sigma^\uparrow, \sigma^\downarrow] &= 0 \\ [\sigma^\uparrow, \sigma^+] &= \sigma^+ \\ [\sigma^\uparrow, \sigma^-] &= -\sigma- \\ [\sigma^\downarrow, \sigma^+] &= -\sigma^+ \\ [\sigma^\downarrow, \sigma^-] &= \sigma- \\ [\sigma^+, \sigma^-] &= \sigma^3 \end{aligned}\right\} \qquad (21)$$

and the anticommutators are

$$\left.\begin{aligned} [\sigma^i, \sigma^j]_+ &= 2i\delta_{ij} \\ [\sigma^+, \sigma^-]_+ &= 1 \end{aligned}\right\} \qquad (22)$$

We then express the matrix in Eq. (15) as

$$\beta_{rs} = \beta_{rs}^\mu \sigma^\mu$$
$$\beta_{rs}^\mu = \mathrm{Tr}(\sigma^\mu \beta_{rs}) \qquad (23)$$

in details

$$\beta_{rs}^\uparrow = \beta_{rs}^{\uparrow\uparrow} \quad \beta_{rs}^\downarrow = \beta_{rs}^{\downarrow\downarrow}$$
$$\beta_{rs}^+ = \beta_{rs}^{\downarrow\uparrow} \quad \beta_{rs}^- = \beta_{rs}^{\uparrow\downarrow} \qquad (24)$$

Here, if the quantum-mechanical Hamiltonian has the single-particle character without the external field causing

a rotation in the spin space, the off-diagonal elements are meaningless. The Hückel theory involves the spin diagonal terms.

However, if we take the electron–electron interaction into account, even in the mean-field approximation, the off-diagonal elements become meaningful and responsible for the superconductivity. This is what we investigate here.

2.1. Spinor

The algebra representing electrons is the spinor. The Dirac relativistic (special relativity) function describes this property well. However, the relativity seems not so important for the present problem. We now concentrate on the spinor character of the electron. The field operator has two components in the spin space:

$$\phi(x) = \begin{pmatrix} \phi_\uparrow(x) \\ \phi_\downarrow^+(x) \end{pmatrix}$$

$$\bar{\phi}(x) = \phi^+(x)\sigma^3 = \begin{pmatrix} \phi_\uparrow^+(x) & \phi_\downarrow(x) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} \phi_\uparrow^+(x) & -\phi_\downarrow(x) \end{pmatrix} \tag{25}$$

This is called Nambu representation.[11] The negative sign in front of $\phi_\downarrow$ is seen in the Dirac conjugate $\phi^+ \to \bar{\phi}$.

The field operators satisfy, of course, the anticommutators

$$[\phi_\alpha(x), \phi_\beta^+(s')]_+ = \delta_{\alpha,\beta}\delta(x - x') \tag{26}$$

where $(\alpha, \beta) = (\uparrow, \downarrow)$, and $x = (\mathbf{r}, t)$. Then for spinors (25) the matrix commutator holds:

$$[\phi(x), \bar{\phi}(x')]_+ = \left[\begin{pmatrix} \phi_\uparrow(x) \\ \phi_\downarrow^+(x) \end{pmatrix}, \begin{pmatrix} \phi_\uparrow^+(x') & -\phi_\downarrow(x') \end{pmatrix} \right]_+$$

$$= \begin{pmatrix} [\phi_\uparrow(x), \phi_\uparrow^+(x')]_+ & [\phi_\downarrow(x'), \phi_\uparrow(x)]_+ \\ [\phi_\downarrow^+(x), \phi_\uparrow^+(x')]_+ & [\phi_\downarrow(x'), \phi_\downarrow^+(x)]_+ \end{pmatrix}$$

$$= \begin{pmatrix} \delta(x - x') & 0 \\ 0 & \delta(x - x') \end{pmatrix} \tag{27}$$

2.2. Noether Theorem and Nambu–Goldstone Theorem

We seek for the meaning of the Nambu spinor.[12] Consider a global transformation of fields with the constant Λ:

$$\phi_\alpha(x) \to \phi_\alpha(x)e^{i\Lambda}$$

$$\phi_\alpha^+(x) \to \phi_\alpha(x)e^{-i\Lambda} \tag{28}$$

It is recognized that the Hamiltonian and the equation of motion are invariant under this transformation. We can see that this transformation is a rotation around the σ^3 axis with Λ:

$$\phi(x) \to e^{i\sigma^3\Lambda}\phi(x) \tag{29}$$

since

$$e^{i\sigma^3\Lambda} = \cos(\sigma^3\Lambda) + i\sin(\sigma^3\Lambda)$$

$$= 1 - \frac{(\sigma^3\Lambda)^2}{2!} + \frac{(\sigma^3\Lambda)^4}{4!}$$

$$\quad + \cdots + i\left(1 - \frac{(\sigma^3\Lambda)^3}{3!} + \frac{(\sigma^3\Lambda)^5}{5!} + \cdots\right)$$

$$= 1 - \frac{\Lambda^2}{2!} + \frac{\Lambda^4}{4!} + \cdots + i\sigma^3\left(1 - \frac{\Lambda^3}{3!} + \frac{\Lambda^5}{5!} + \cdots\right)$$

$$= \sigma^0\cos\Lambda + i\sigma^3\sin\Lambda \begin{pmatrix} e^{i\Lambda} & 0 \\ 0 & e^{-i\Lambda} \end{pmatrix}$$

Here, we discuss briefly the Noether theorem and the Nambu–Goldstone theorem. The latter makes a profound investigation possible. If the Lagrangian of the system in question is invariant under some transformation which is just the present case, we have the continuity relation. Notice that the density and the current are, in terms of the Nambu spinor,

$$j^0 = \phi^+(x)\sigma^3\phi(x)$$

$$\mathbf{j} = -i\frac{\hbar}{2m}(\phi^+(x)\nabla\phi(x) + \nabla\phi^+(x)\phi(x)) \tag{30}$$

Then the continuity relation is

$$\partial_t j_0(x) + \nabla \cdot \mathbf{j} = 0 \tag{31}$$

If the system is static, the density must be conserved:

$$\partial_t j^0 = 0 \tag{32}$$

Put

$$G = \int dx j^0(x) \tag{33}$$

and if it is found that

$$[G, \Psi'(x)] = \Psi(x) \tag{34}$$

and the expectation value of $\Psi(x)$ over the ground state does not vanish,

$$\langle 0|\Psi|0\rangle \neq 0 \tag{35}$$

i.e., if the ground state satisfying the relation (33) does not vanish, we can expect the appearance of a boson $\Psi(x)$, whose mass is zero. This boson is called a Goldstone boson, and the symmetry breaking takes place in the system. This is what the Goldstone theorem insists on. The details are in the standard book on the field theory.[8]

Now we apply this theorem to superconductivity. The invariant charge is

$$Q = \int d^3x\phi_\alpha^+(x)\phi_\alpha(x) = \int d^3x\phi^+(x)\sigma^3\phi(x) \tag{36}$$

In terms of the Nambu spinor, here σ^3 is crucial. In the commutator (33), we seek for the spin operators which do

not commute with σ^3 and find, say, $\sigma^{\pm}$. We then have the Goldstone commutator as

$$\int d^3 x' \langle [\phi^+(x')\sigma^3\phi(x'), \phi^+(x)\sigma^{\pm}\phi(x)] \rangle_{t=t'}$$

$$= \int d^3 x (\pm 2) \langle 0|\phi^+(x)\sigma^{\pm}\phi(x')|0\rangle \delta(r-r') \quad (37)$$

In details,

$$\phi^+(x)\sigma^+\phi(x) = \begin{pmatrix} \phi_{\uparrow}^+(x) & \phi_{\downarrow}(x) \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \phi_{\uparrow}(x) \\ \phi_{\downarrow}^+(x) \end{pmatrix}$$

$$= \phi_{\uparrow}^+(x)\phi_{\downarrow}^+(x) \quad (38)$$

$$\phi^+(x)\sigma^-\phi(x) = \phi_{\uparrow}(x)\phi_{\downarrow}(x)$$

Notice that here the same symbol ϕ is used for the ordinary field with spin and the Nambu spinor. The above are nothing but the Cooper pairs, and we now find the Goldstone bosons Ψ^* and Ψ. In literature, it is noted that

$$\langle 0|\phi^+(x)\sigma^{\pm}\phi(x)|0\rangle = \pm\frac{\Delta_{\pm}}{g} \neq 0 \quad (39)$$

where Δ and g are the gap and the coupling parameter, respectively. We expect the estimate

$$\Delta_+ \sim \Delta_- = \Delta$$

to be reasonable.

The Cooper pairs are now the Goldstone bosons. A comment about the Goldstone boson or the massless elementary excitation with $k = 0$ is required. Using Eq. (33), we write the Goldstone commutator (34) as

$$\int d^3 y [\langle 0|j_0(y)|n\rangle \langle n|\phi'(x)|0\rangle$$

$$- \langle 0|\phi'(x)|n\rangle \langle n|j_0(y)|0\rangle]_{x_0=y_0} \neq 0 \quad (40)$$

where $|n\rangle$ is the intermediate state, and $x_0 = y_0$ implies that this is the equal time commutator.

Since

$$j_0(y) = e^{-ipy} j_0(0) e^{ipy} \quad (41)$$

it is seen that

$$\int d^3 y [\langle 0|J_0(0)|n\rangle \langle n|\phi'(x)|0\rangle e^{ip_n y}$$

$$- \langle 0|\phi'(x)|n\rangle \langle n|J_0(0)|0\rangle e^{-ip_n y}]_{x_0=y_0}, \quad (p|n\rangle = p_n|n\rangle)$$

$$= \delta(\mathbf{p}_n)[\langle 0|J_0(0)|n\rangle \langle n|\phi'(0)|0\rangle e^{ip_{n0} y}$$

$$- \langle 0|\phi'(x)|n\rangle \langle n|J_0(0)|0\rangle e^{-ip_{n0} y}]_{x_0=y_0}]$$

$$= \delta(\mathbf{p}_n)[\langle 0|J_0(0)|n\rangle \langle n|\phi'(0)|0\rangle e^{iM_n y_0}$$

$$- \langle 0|\phi'(0)|n\rangle \langle n|J_0(0)|0\rangle e^{-iM_n y_0}]_{x_0=y_0}] \neq 0 \quad (42)$$

In order to obtain the first equality, spatial integration is carried out. Then, considering $p^{\mu} = (\mathbf{p}, M)$, we retain the

fourth component. In the last equation, when $M_n \neq 0$, cancellations will arise for the summation over n. We thus obtain, only for $M_n = 0$, the finite result

$$\langle 0|j_0(0)|n\rangle \langle n|\phi'(0)|0\rangle - \langle 0|\phi'(0)|n\rangle \langle n|j_0(0)|0\rangle$$

$$= \text{Im } \langle 0|j_0(0)|n\rangle \langle n|\phi'(x)|0\rangle \quad (43)$$

which is met with the requirement (34). The excitation with $M_n = 0$ implies the excitation which need not the excitation energy, suggesting the Goldstone boson.

We further note that the mass-zero excitation is the imaginary quantity. This suggests the current to be the phase current, as is seen in the Josephson effect.

Before closing this preliminary discussion, we want to make a few remarks. At the beginning, we mentioned London's postulate that the superconducting state is characterized by a statement that the wave function is rigid, so that the current is entirely the diamagnetic current due to only the vector potential $\mathbf{A}$. "Rigid" is not really rigid, but it is understood that the spatial derivative is vanishing, or the current flows along the entirely flat path, which is described in a textbook as the path going around the top of a Mexican hat. Boldly speaking, the electron in the superconducting state is massless. Also, we have pointed out that the vector potential $\mathbf{A}$, which leads to the Meissner effect, satisfies the covariant relation (6),

$$\partial_{\mu}A_{\mu} = -k^2 \quad (44)$$

so that a photon is massive in the superconductor.

In the following chapters, we develop a substantial microscopic explanation of the above assertions.

3. PROPAGATOR

In the previous section, we have found that, as is seen in Eq. (41), the superconducting state strongly concerns the gap function or the anomalous Green function. We want to deal with the solid-state substances. However, the infinite crystals described by the single band have already been fully investigated in literature, and the recent investigations were carried out on objects with multiband structure.[13, 14] The infinite system with many bands is constructed from the unit cell, which is really a chemical molecule. The atoms in this molecule give the band index of the real crystal. In this respect, we first investigate the Green function of a unit cell. The Green function is now shown in the site representation.

Corresponding to the spinors (24), we define the spinor in the site representation as

$$\mathbf{a}_r = \begin{pmatrix} a_{r\uparrow} \\ a_{r\downarrow}^+ \end{pmatrix}, \quad \bar{\mathbf{a}}_r = (a_{r\uparrow}^+ \quad -a_{r\downarrow}) \quad (45)$$

Due to this definition, it is unnecessary to insert σ^3 in the matrix $\mathbf{G}$, as is seen in the Schrieffer's book.[3]

The commutator is

$$[\mathbf{a}_r, \bar{\mathbf{a}}_s]_+ = \begin{pmatrix} [a_{r\uparrow}, a_{s\uparrow}^+]_+ & [a_{s\downarrow}, a_{r\uparrow}]_+ \\ [a_{r\downarrow}^+, a_{s\uparrow}^+]_+ & [a_{s\downarrow}, a_{r\downarrow}^+]_+ \end{pmatrix}$$

$$= \begin{pmatrix} \delta_{rs} & 0 \\ 0 & \delta_{rs} \end{pmatrix} = \delta_{rs}\mathbf{1}_{2\times 2} \qquad (46)$$

The matrix propagator is defined by

$$\mathbf{G}_{rs}(\tau) = -\langle\langle \mathbf{a}_r(\tau_1), \bar{\mathbf{a}}_s(\tau_2)\rangle\rangle$$

$$= -\begin{pmatrix} \langle\langle a_{r\uparrow}(\tau_1), a_{s\uparrow}^+(\tau_2)\rangle\rangle & -\langle\langle a_{r\uparrow}(\tau_1), a_{s\downarrow}(\tau_2)\rangle\rangle \\ \langle\langle a_{r\downarrow}^+(\tau_1), a_{s\uparrow}^+(\tau_2)\rangle\rangle & -\langle\langle a_{r\downarrow}^+(\tau_1), a_{s\downarrow}(\tau_2)\rangle\rangle \end{pmatrix}$$

$$= -\langle\theta(\tau_1-\tau_2)\mathbf{a}_r(\tau_1)\bar{\mathbf{a}}_s(\tau_2)$$
$$+ \theta(\tau_2-\tau_1)\bar{\mathbf{a}}_s(\tau_2)\mathbf{a}_r(\tau_1)\rangle \qquad (47)$$

where τ is the imaginary time, so that the propagator is the temperature Green function or the Matsubara function. In what follows, we put

$$\tau = \tau_1 - \tau_2 \qquad (48)$$

and system depends on $(\tau_1 - \tau_2)$. If we want to obtain the gap function, we consider

$$\mathrm{Tr}(\sigma^+\mathbf{G}_{rs}(\tau)) = \langle\langle a_{r\downarrow}^+(\tau_1), a_{s\uparrow}^+(\tau_2)\rangle\rangle \qquad (49)$$

and the standard procedure will be followed.

3.1. Hamiltonian
Various Hamiltonians can be written by using the charge density matrix,

$$\rho_{rs}(x) = \begin{pmatrix} \rho_{r\uparrow s\uparrow}(x) & \rho_{r\uparrow s\downarrow}(x) \\ \rho_{r\downarrow s\uparrow}(x) & \rho_{r\downarrow s\downarrow}(x) \end{pmatrix} = \sigma^\mu \rho_{rs}^\mu \qquad (50)$$

where the basis orbitals are put to be real, so that we do not need the conjugation procedure for field operators.

The Hückel Hamiltonian or the single-particle Hamiltonian has the structure

$$H^0 = h_{rs}^\mu \bar{\mathbf{a}}_r \sigma^\mu \mathbf{a}_r \qquad (51)$$

where h includes the chemical potential and can be explicitly written as

$$h_{rs} = \int \rho_{rs} h(x)$$

$$= \int dx h(x) \begin{pmatrix} \rho_{r\uparrow s\uparrow}(x) & \rho_{r\uparrow s\downarrow}(x) \\ \rho_{r\downarrow s\uparrow}(x) & \rho_{r\downarrow s\downarrow}(x) \end{pmatrix} = \sigma^\mu h_{rs}^\mu \quad (52)$$

Hereafter, we use the summation convention that repeated indices imply that the summation is carried out to facilitate manipulations. Other two-particle Hamiltonians are given in a similar way. Noting that

$$v_{rs;\,tu}^{\mu\nu} = \int dx\,dx' \rho_{rs}^\mu(x) v(x-x') \rho_{tu}^\nu(x') \qquad (53)$$

we have[28]

$$H^{\mathrm{dir}} = \frac{1}{2}(\bar{\mathbf{a}}_r \sigma^a \mathbf{a}_s) v_{rs;\,tu}^{ab}(\bar{\mathbf{a}}_t \sigma^b \mathbf{a}_u), \quad (a, b = \uparrow, \downarrow)$$

$$H^{\mathrm{ex}} = -\frac{1}{2}(\bar{\mathbf{a}}_r \sigma^a \mathbf{a}_s) v_{rs;\,ut}^{aa}(\bar{\mathbf{a}}_t \sigma^a \mathbf{a}_u), \quad (a = \uparrow, \downarrow)$$

$$H^{\mathrm{super}} = \frac{1}{2}\{(\bar{\mathbf{a}}_r \sigma^+ \mathbf{a}_s) v_{rs;\,tu}^{+-}(\bar{\mathbf{a}}_t \sigma^- \mathbf{a}_u)$$
$$+ (\bar{\mathbf{a}}_r \sigma^- \mathbf{a}_s) v_{rs;\,tu}^{-+}(\bar{\mathbf{a}}_t \sigma^+ \mathbf{a}_u)\} \qquad (54)$$

For the direct interaction, the quantum-mechanical Hamiltonian is

$$H^{\mathrm{dir}} = \int dx\,dx' \chi_{r\uparrow}^*(r)\chi_{s\uparrow}(r)(x)v(x-x')\chi_\downarrow^*(x')\chi_{u\downarrow}^*(x')$$

For the field-theoretical Hamiltonian, the wave functions are replaced by the creation.annihilation operators $a_{r\uparrow}^+$, $a_{r\uparrow}$, and so on. These are written in the spinor notation; for example,

$$a_{r\uparrow}^+ a_{s\uparrow} = (a_{r\uparrow}^+ a_{r\downarrow}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} a_{s\uparrow} \\ a_{s\downarrow}^+ \end{pmatrix}$$

$$= \mathbf{a}_r^+ \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \mathbf{a}_s = \mathbf{a}_r^+ \sigma^\uparrow \mathbf{a}_s$$

Note that H^{ex} is obtained by reversing indices $(u \leftrightarrow t)$ in $v_{rs;\,tu}$.

4. NONINTERACTING
"Noninteracting" implies that the Hamiltonian is bilinear with respect to operators so that diagonalization is always possible. It should be instructive to begin with the single-particle case, since even if we manipulate the complicated two-particle case, the procedures are almost the same when the mean-field approximation is employed.

The energy for the Hamiltonian (52) is

$$E^0 = \mathrm{Tr}(\hat{\rho}H^0) = h_{rs}\langle\bar{\mathbf{a}}_r \mathbf{a}_s\rangle \qquad (55)$$

where $\hat{\rho}$ is the statistical operator,

$$\hat{\rho} = e^{\beta(H^0-\Omega)} \qquad (56)$$

with the normalization factor Ω. We now define the temperature Green's function, in which τ is the imaginary time, $\tau = it$,[15, 16]

$$G_{rs}(\tau) = -\mathrm{Tr}\hat{\rho}[(\theta(\tau_1)\mathbf{a}_r(\tau_1)\mathbf{a}_s^+(\tau_2) - \theta(-\tau)\mathbf{a}_s^+(\tau_2)\mathbf{a}_r(\tau_1)]$$
$$= \langle\langle \mathbf{a}_r(\tau_1)\mathbf{a}_s^+(\tau_2)\rangle\rangle \qquad (57)$$

where

$$\tau = \tau_1 - \tau_2 \qquad (58)$$

and it is assumed that the system is only dependent of the relative time τ. Then we can written E^0 in terms of the temperature Green's function,

$$E^0 = \mathrm{Tr}[h_{rs}G_{sr}(\tau = 0^-)] \qquad (59)$$

Note that h_{rs} and G_{sr} are both matrices.

The equation of motion (57) for the noninteracting Hamiltonian (51) can be read as

$$\partial_{\tau_1} \langle\langle \mathbf{a}_s(\tau_1) \bar{\mathbf{a}}_r(\tau_2) \rangle\rangle$$

$$= \delta(\tau_1 - \tau_2) \langle [\mathbf{a}_s(\tau_1), \bar{\mathbf{a}}_r(\tau_2)]_+ \rangle$$

$$+ \langle [\mathbf{a}_s(\tau_1), \bar{\mathbf{a}}_{s'} \mathbf{a}_{r'} h_{s'r'}(\tau_1)]_-, \bar{\mathbf{a}}_r(\tau_2) \rangle$$

$$= \delta(\tau_1 - \tau_2) \delta_{sr} + \langle \delta_{ss'} h_{r's'}(\tau_1) \mathbf{a}_{r'}(\tau_1), \bar{\mathbf{a}}_r(\tau_2) \rangle$$

$$= \delta(\tau_1 - \tau_2) \delta_{sr} + \{h_{sr'}\} \langle\langle \mathbf{a}_{r'}(\tau_1), \bar{\mathbf{a}}_r(\tau_2) \rangle\rangle \quad (60)$$

It can be solved using the Fourier transformation[15]

$$\langle\langle \mathbf{a}_s(\tau_1) \bar{\mathbf{a}}_r(\tau_2) \rangle\rangle = \frac{1}{\beta} \sum_n e^{i\omega_n \tau} \langle\langle \mathbf{a}_s \bar{\mathbf{a}}_r; \omega_n \rangle\rangle \quad (61)$$

with

$$\omega_n = (2n+1)\pi/\beta \quad (62)$$

where the odd number indicates that particles are fermions. Then Eq. (50) becomes

$$(i\omega_n \delta_{sr'} - h_{sr'}) \langle\langle \mathbf{a}_{r'} \bar{\mathbf{a}}_r; \omega_n \rangle\rangle = \delta_{sr} \quad (63)$$

In this step, the matrix structure of the above should be carefully investigated. Let us assume that the single-particle Hamiltonian is spin-diagonal:

$$h_{sr} = \begin{pmatrix} h_{sr}^\uparrow & 0 \\ 0 & h_{sr}^\downarrow \end{pmatrix} \quad (64)$$

It is preferable to introduce the flame diagonalizing each element:

$$h_{sr}^\uparrow = (\langle s \mid i \rangle \langle i|h|i \rangle |i \rangle \langle ir \rangle)^\uparrow = \langle s \mid i \rangle^\uparrow \epsilon_{i\uparrow} \langle i \mid r \rangle^\uparrow \quad (65)$$

Then we have

$$\langle\langle \mathbf{a}_s \bar{\mathbf{a}}_r \rangle\rangle = \frac{1}{\beta} \sum_n (1)$$

$$\times \left(\begin{pmatrix} \dfrac{(\langle s \mid i \rangle \langle i \mid r \rangle)^\uparrow}{i\omega_n - \epsilon_{i\uparrow}} & 0 \\ 0 & \dfrac{(\langle s \mid i \rangle \langle i \mid r \rangle)^\downarrow}{i\omega_n - \epsilon_{i\downarrow}} \end{pmatrix} \right)^{-1}$$

$$= \frac{1}{\beta} \sum_n \begin{pmatrix} \dfrac{(\langle s \mid i \rangle \langle i \mid r \rangle)^\uparrow}{i\omega_n - \epsilon_{i\uparrow}} & 0 \\ 0 & \dfrac{(\langle s \mid i \rangle \langle i \mid r \rangle)^\downarrow}{i\omega_n - \epsilon_{i\downarrow}} \end{pmatrix}$$

$$= \begin{pmatrix} (\langle s \mid i \rangle n(\epsilon_i) \langle i \mid r \rangle)^\uparrow & 0 \\ 0 & (\langle s \mid i \rangle n(\epsilon_i) \langle i \mid r \rangle)^\downarrow \end{pmatrix}$$

$$\quad (66)$$

where

$$n(\epsilon_{i\uparrow}) = \frac{1}{1 + e^{\epsilon_{i\uparrow}/k_B T}} \quad (67)$$

Another sophisticated way starts from the decomposed Hamiltonian

$$H^0 = \bar{\mathbf{a}}_r \sigma^\mu h_{rs}^\mu \mathbf{a}_s \quad (68)$$

The commutator is evaluated as

$$[\mathbf{a}_s, \bar{\mathbf{a}}_{r'} \sigma^\mu h_{r's'}^\mu \mathbf{a}_{s'}] = \delta_{sr'} \sigma^0 \sigma^\mu h_{r's'}^\mu \mathbf{a}_{s'} = \sigma^\mu h_{ss'}^\mu \mathbf{a}_{s'} \quad (69)$$

The equation of motion

$$(i\omega_n \delta_{ss'} - \sigma^\mu h_{ss'}^\mu) \langle\langle \mathbf{a}_{s'}, \bar{\mathbf{a}}_r; \omega_n \rangle\rangle = \sigma^0 \delta_{sr} \quad (70)$$

In the matrix notation,

$$(i\omega_n - \sigma^\mu h^\mu) \langle\langle \mathbf{a}, \bar{\mathbf{a}}; \omega_n \rangle\rangle = \sigma^0$$

or

$$\langle\langle \mathbf{a}, \bar{\mathbf{a}}; \omega_n \rangle\rangle = \frac{\sigma^0}{i\omega_n - \sigma^\mu h^\mu} \quad (71)$$

In the representation that h is diagonal,

$$\langle r|h|s \rangle = \langle r \mid i \rangle \langle i|h|i \rangle \langle i \mid s \rangle = \epsilon_i \langle r \mid i \rangle \langle i \mid s \rangle \quad (72)$$

the relation (71) becomes

$$\langle\langle \mathbf{a}, \bar{\mathbf{a}}; \omega_n \rangle\rangle = \frac{(|i\rangle\langle i|)(i\omega_n + \sigma^\mu \epsilon_i^\mu)}{(i\omega_n - \sigma^\mu \epsilon_i^\mu)(i\omega_n + \sigma^\mu \epsilon_i^\mu)}$$

$$= \frac{(|i\rangle\langle i|)(i\omega_n + \sigma^\mu \epsilon_i^\mu)}{(i\omega_n)^2 - (\epsilon_i^\mu)^2} \quad (73)$$

Now

$$\frac{i\omega_n + \sigma^\mu \epsilon_i^\mu}{(i\omega_n)^2 - (\epsilon_i^\mu)^2}$$

$$= \frac{i\omega_n}{(i\omega_n)^2 - (\epsilon_i^\mu)^2} + \frac{\sigma^\mu \epsilon_i^\mu}{(i\omega_n)^2 - (\epsilon_i^\mu)^2}$$

$$= \frac{1}{2} \left(\frac{1}{i\omega_n - \epsilon_i^\mu} + \frac{1}{i\omega_n + \epsilon_i^\mu} \right)$$

$$+ \frac{\sigma^\mu}{2} \left(\frac{1}{i\omega_n - \epsilon_i^\mu} - \frac{1}{i\omega_n + \epsilon_i^\mu} \right)$$

$$= \frac{1}{2} \left(\frac{1}{i\omega_n + \epsilon_i^\mu} + \frac{1}{i\omega_n + \epsilon_i^\mu} \right)$$

(summing ω_n)

$$\to \frac{1}{2}(n(\epsilon_i^\mu) + n(-\epsilon_i^\mu)) + \frac{\sigma^\mu}{2}(n(\epsilon_i^\mu) - n(-\epsilon_i^\mu)) \quad (74)$$

We evaluate $G_{rs}^\uparrow$,

$$G_{rs}^\uparrow = \mathrm{Tr}\sigma^\uparrow \left\{ \langle r \mid i \rangle \langle i \mid s \rangle \frac{\sigma^0}{2}(n(\epsilon_i^\mu) + n(-\epsilon_i^\mu)) \right.$$

$$\left. + \frac{\sigma^\mu}{2}(n(\epsilon_i^\mu) - n(-\epsilon_i^\mu)) \right\}$$

$$= \langle r \mid i \rangle \langle i \mid s \rangle]^\uparrow n(\epsilon_i^\uparrow) \quad (75)$$

We then have

$$\frac{1}{\beta} \sum_n G_{rs}^\uparrow(0^-) = \frac{1}{\beta} \sum_n \frac{\langle r \mid i \rangle \langle i \mid s \rangle}{i\omega_n - \epsilon_i^\uparrow} = \langle r \mid i \rangle n(\epsilon_i^\uparrow) \langle i \mid s \rangle \quad (76)$$

This relation holds for both $\uparrow$ and $\uparrow$, and recover the result (66).

Along the way, we give the energy expression for Eq. (51):

$$E^0 = \mathrm{Tr}(h_{rs}G_{sr})$$

$$= \mathrm{Tr}\begin{pmatrix} h_{rs}^{\uparrow} & 0 \\ 0 & h_{rs}^{\downarrow} \end{pmatrix}$$

$$\times \begin{pmatrix} \langle s|i\rangle n(\epsilon_i^{\uparrow})\langle i|r\rangle & 0 \\ 0 & \langle s|i\rangle n(\epsilon_i^{\downarrow})\langle i|r\rangle \end{pmatrix} \quad (77)$$

It may be needless to present another illustration:

$$E^0 = \mathrm{Tr}(h_{rs}G_{sr}) = \mathrm{Tr}(\sigma^\mu h_{rs}^\mu)(\sigma^\nu G_{sr}^\nu) \quad (78)$$

The result is meaningful if $\sigma^\mu \sigma^\nu = \sigma^0$, which leads to, in the present case,

$$\sigma^\mu = \sigma^\nu = \sigma^\uparrow, \quad \text{or} \quad \sigma^\mu = \sigma^\nu = \sigma^\downarrow$$

Such manipulations will be used in the later investigation.

5. INTERACTING

In this chapter, the electron–electron interactions are taken into account, and we will discuss how they lead to the superconducting state. The Hamiltonians given in Eq. (54) are

$$H^{\mathrm{dir}} = \frac{1}{2}(\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)v_{rs;\,tu}^{ab}(\bar{\mathbf{a}}_t\sigma^b\mathbf{a}_u), \quad (a, b = \uparrow, \downarrow)$$

$$H^{\mathrm{ex}} = -\frac{1}{2}(\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)v_{rs;\,ut}^{aa}(\bar{\mathbf{a}}_t\sigma^a\mathbf{a}_u), \quad (a = \uparrow, \downarrow)$$

$$H^{\mathrm{super}} = \frac{1}{2}\{(\bar{\mathbf{a}}_r\sigma^+\mathbf{a}_s)v_{rs;\,tu}^{+-}(\bar{\mathbf{a}}_t\sigma^-\mathbf{a}_u)$$
$$+ (\bar{\mathbf{a}}_r\sigma^-\mathbf{a}_s)v_{rs;\,tu}^{-+}(\bar{\mathbf{a}}_t\sigma^+\mathbf{a}_u)\}$$

These are written in the mean-field approximation. The estimate beyond this approximation is not the case of the present consideration. We have

$$H^0 = h_{rs}^a\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_r(a = \uparrow, \downarrow)$$

$$H^{\mathrm{dir}} = (\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)v_{rs;\,tu}^{ab}\langle\bar{\mathbf{a}}_t\sigma^b\mathbf{a}_u\rangle = (\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)D_{rs}^{a:\mathrm{dir}}$$
$$(a, b = \uparrow, \downarrow)$$

$$H^{\mathrm{ex}} = -(\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)v_{rs;\,ut}^{aa}\langle\bar{\mathbf{a}}_t\sigma^b\mathbf{a}_u\rangle = (\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)D_{rs}^{a:\mathrm{ex}}$$
$$(a = \uparrow, \downarrow)$$

$$H^{\mathrm{sup}} = (\bar{\mathbf{a}}_r\sigma^+\mathbf{a}_s)v_{rs;\,ut}^{+-}\langle\bar{\mathbf{a}}_t\sigma^-\mathbf{a}_u\rangle + (\bar{\mathbf{a}}_r\sigma^-\mathbf{a}_s)v_{rs;\,ut}^{-+}\langle\bar{\mathbf{a}}_t\sigma^+\mathbf{a}_u\rangle$$
$$= (\bar{\mathbf{a}}_r\sigma^+\mathbf{a}_s)D_{rs}^{-:\mathrm{sup}} + \bar{\mathbf{a}}_r\sigma^-\mathbf{a}_s)D_{rs}^{+:\mathrm{sup}} \quad (79)$$

where

$$D_{rs}^{a:\mathrm{dir}} = v_{rs;\,tu}^{ab}\langle\bar{\mathbf{a}}_t\sigma^b\mathbf{a}_u\rangle$$

$$D_{rs}^{a:\mathrm{ex}} = -v_{rs;\,ut}^{ab}\langle\bar{\mathbf{a}}_t\sigma^b\mathbf{a}_u\rangle\delta_{ab}$$

$$D_{rs}^{+:\mathrm{sup}} = v_{rs;\,tu}^{+-}\langle\bar{\mathbf{a}}_t\sigma^-\mathbf{a}_u\rangle \quad (80)$$

where $\langle\cdots\rangle$ implies the ground state average, actually which is obtained by wave functions in the previous step during the SCF calculations.

These Hamiltonians are classified into two kinds called modes—the normal many-electron problem and that for the superconductivity:

$$H = H^{\mathrm{norm}} + H^{\mathrm{sup}} \quad (81)$$

where

$$H^{\mathrm{norm}} = (\bar{\mathbf{a}}_r\sigma^a\mathbf{a}_s)(h_{rs}^a\delta_{rs} + D_{rs}^{a:\mathrm{dir}} + D_{rs}^{a:\mathrm{ex}})$$

$$H^{\mathrm{sup}} = \bar{\mathbf{a}}_r\sigma^{\pm}\mathbf{a}_s D_{rs}^{\mp:\mathrm{sup}} \quad (82)$$

The main difference between the two is that in the former we have the single-particle Hamiltonian, and in the latter we do not. Various D_{rs} are complicated, but they are merely the c-numbers in this treatment. The propagator in question in Eq. (57) is presented here again:

$$G_{rs}(\tau) = -\mathrm{Tr}\hat{\rho}[(\theta(\tau)\mathbf{a}_r(\tau_1)\mathbf{a}_s^+(\tau_2) - \theta(-\tau)\mathbf{a}_s^+(\tau_2)\mathbf{a}_r(\tau_1)]$$

$$= \langle\langle\mathbf{a}_r(\tau_1)\mathbf{a}_s^+(\tau_2)\rangle\rangle$$

The equation of motion can be read as

$$\partial_{\tau_1}\langle\langle\mathbf{a}_s(\tau_1)\bar{\mathbf{a}}_r(\tau_2)\rangle\rangle$$

$$= \delta(\tau_1 - \tau_2)\langle[\mathbf{a}_s(\tau_1), \bar{\mathbf{a}}_r(\tau_2)]_+\rangle$$

$$+ \langle[\mathbf{a}_s(\tau_1), \bar{\mathbf{a}}_{s'}\mathbf{a}_{r'}H_{s'r'}^a(\tau_1)]_-, \bar{\mathbf{a}}_r(\tau_2)\rangle$$

$$(a; \ \mathrm{norm}, \ \mathrm{sup})$$

$$= \delta(\tau_1 - \tau_2)\delta_{sr} + D_{sr'}^a\sigma^a\langle\langle\mathbf{a}_{r'}(\tau_1), \bar{\mathbf{a}}_r(\tau_2)\rangle\rangle \quad (83)$$

Making the Fourier transformation with respect to $\tau = \tau_2 - \tau_2$ gives

$$(i\omega_n - D_{rs'}^a\sigma^a)G_{s'r} = \delta_{sr} \quad (84)$$

or, in the matrix form,

$$G(\omega_n) = \frac{1}{i\omega_n - D^a\sigma^a} = \frac{i\omega_n + D^a\sigma^a}{(i\omega_n)^2 - (D^a)^2} \quad (85)$$

Note that D^a consists of the single-electron part and the two-electron interaction term which involves another mate ρ_{tu}^a combined with the propagator $\langle\bar{\mathbf{a}}_t\sigma^a\mathbf{a}_u\rangle$:

$$D^a(x) = h^a(x) + \int dx'v(x - x')\rho_{tu}^b(x')\sigma^b\langle\bar{\mathbf{a}}_t\mathbf{a}_t\rangle \quad (86)$$

However, the mean-field approximation makes this as if it were the single-electron interaction. A few comments will be given about the matrix character of G. This is a big matrix with site indices, and each element is a $(2, 2)$-matrix in the spin space. The index a characterizes the mode of the mean-field potential. All the modes are independent of each other and are individually diagonalized. We now introduce a flame, in which these are diagonal:

$$\langle i^a|D^a|i^a\rangle = \eta_i^a \qu(87)$$

Look at the right-hand side of Eq. (85) and remember the Einstein convention that repeated indices imply summation:

$$(D^a)^2 = (\eta^\uparrow)^2 + (\eta^\downarrow)^2 + (\eta^+)^2 + (\eta^-)^2$$
$$= (\eta^{\text{norm}})^2 + (\eta^{\text{sup}})^2 \tag{88}$$

where the second line is in a simple notation. Then we have

$$G(\omega_n) = \frac{|i^a\rangle(i\omega_n + \langle i^a|D^a|i^a\rangle\sigma^a)\langle i^a|}{\{i\omega_n - (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})\}\{i\omega_n + (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})\}}$$

$$= |i^a\rangle\frac{1}{2}\left(\frac{1}{i\omega_n - (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}\right.$$

$$\left. + \frac{1}{i\omega_n + (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}\right)\langle i^a| + |i^a\rangle$$

$$\times \frac{D_{ii}^a\sigma^a}{2(\eta_i^{\text{norm}} + \eta_i^{\text{sup}})} \times \left(\frac{1}{i\omega_n - (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}\right.$$

$$\left. - \frac{1}{i\omega_n - (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}\right)\langle i^a| \tag{89}$$

Taking the (r, s) matrix elements and the mode c, which is achieved by the operation,

$$\text{Tr}\,\sigma^c G_{rs} = G^c rs \tag{90}$$

we select the terms on the right-hand side with the mode c satisfying

$$\text{Tr}\,\sigma^c\sigma^a = 1 \tag{91}$$

Otherwise, the Tr operation leads to the vanishing result.

Carrying out the summation over ω_n, we get

$$G_{rs}^c(0^-)$$

$$= \frac{1}{\beta}\sum_n G_{rs}^c(\omega_n) = \frac{1}{\beta}\sum_n \langle r^c|i^a\rangle\frac{1}{2}$$

$$\times \left(\frac{1}{i\omega_n - (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})} + \frac{1}{i\omega_n + (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}\right)\langle i^a|s^c\rangle$$

$$+ \frac{1}{\beta}\sum_n \langle r^c|i^a\rangle\frac{D_{ii}^a}{2(\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}$$

$$\times \left(\frac{1}{i\omega_n - (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})} - \frac{1}{i\omega_n + (\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}\right)\langle i^a|s^c\rangle$$

$$= \langle r^c|i^a\rangle\frac{1}{2}(n(\eta_i^{\text{norm}} + \eta_i^{\text{sup}}) + n(-\eta_i^{\text{norm}} - \eta_i^{\text{sup}}))\langle i^a|s^c\rangle$$

$$+ \langle r^c|i^a\rangle\frac{D_{ii}^a}{2(\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}$$

$$\times (n(\eta_i^{\text{norm}} + \eta_i^{\text{sup}}) - n(-\eta_i^{\text{norm}} - \eta_i^{\text{sup}}))\langle i^a|s^c\rangle$$

$$= \frac{1}{2}\delta_{rs} - \langle r^c|i^a\rangle\frac{D_{ii}^a}{2(\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}$$

$$\times \tanh(\eta_i/2k_BT)\langle i^a|s^c\rangle \tag{92}$$

where

$$n(\eta_i^a) = \frac{1}{1 + e^{\eta_i^a/k_BT}} \tag{93}$$

and

$$n(\eta) + n(-\eta) = 1$$

$$n(\eta) - n(-\eta) = -\tanh\left(\frac{\eta}{2k_BT}\right)$$

In the estimation of matrix elements, the chemical potential which has been disregarded up to now is taken into account. Namely, the Hamiltonian has an additive term $-\mu\bar{\mathbf{a}}_r\mathbf{a}_r$, which causes

$$\eta_i^a \to \eta_i^a - \mu < 0, \quad \text{while} - \eta_i^a \to -(\eta_i^a - \mu) > 0$$

The mean-field potentials are carefully treated. In modes with $\uparrow$ and $\downarrow$, we have the nonvanishing single-particle parts, $h_{rs}^\uparrow\delta_{rs}$ and $h_{rs}^\downarrow\delta_{rs}$, which are usually negative. However, for superconducting modes, $h_{rs}^\pm = 00$, and the chemical potential is lost for the same reason. The latter may be closely related to the fact that the number of particles is not conserved in a superconductor. These circumstances are crucial for the superconducting mode.

5.1. Unrestricted Hartree–Fock (HF)

Let us review the SCF procedure. We now discuss the ordinary many electron system. As an example, the propagator with the up spin, Eq. (89), is

$$G_{rs}^\uparrow(0^-) = \frac{1}{2}\langle r^\uparrow|s^\uparrow\rangle - \langle r^\uparrow|i^a\rangle\frac{D_{ii}^a}{2(\eta_i^{\text{norm}} + \eta_i^{\text{sup}})}$$

$$\times \tanh(\eta_i^a/2k_BT)\langle i^a|s^\uparrow\rangle \tag{94}$$

where $\langle r^\uparrow|s^\uparrow\rangle$ is the overlap integral between the sites r and s and approximately vanishes, and

$$D_{ii}^a = h_{ii}^\uparrow + v_{ii;tu}^{\uparrow a}G_{tu}^a - v_{ii;tu}^{\uparrow\uparrow}G_{tu}^\uparrow$$

$$(a: \uparrow, \downarrow) \tag{95}$$

Note that

$$\tanh(\eta_i^a/2k_BT) < 0, \quad \text{since } \eta_i^a < 0 \tag{96}$$

Look at the potential of the mode $\uparrow$,

$$D^\uparrow(x) = h^\uparrow(x) + \int dx' v(x-x')\rho_{tu}^b(x')\sigma^b\langle\bar{\mathbf{a}}_t\mathbf{a}_t\rangle \tag{97}$$

In this case, there is $h^\uparrow(x)$, whose matrix element should be negative, so that even if the matrix elements of the second terms are positive, the (r, s) matrix element of $D^\uparrow(x)$ is probably negative. This is usually the case in atoms, molecules and solids. In evaluating $D^\uparrow(x)$, the propagators (wave functions) of all other modes are required. In this respect, Eq. (94) is the self-consistent relation between propagators. Usually, the self-consistent relation between

wave functions is given in a such a way that, at the beginning, the total energy is given by the potentials given in terms of tentatively approximated wave functions, and the new approximate wave functions in the next step are obtained by optimizing the total energy. This procedure is lacking in the present consideration.

5.2. Gap Equation for Superconductivity

In the case of superconductivity, since $\sigma^+(\sigma^-)$ is traceless, the first term of Eq. (92) vanishes, and also $h^+ = 0$. Now Eq. (92) can be read as

$$G_{rs}^+(0^-) = -\left\{ \langle r^+ \mid i^+ \rangle \frac{v_{ii;\,tu}^{+-} \langle \bar{\mathbf{a}}_{\mathbf{t}} \mathbf{a}_{\mathbf{u}} \rangle^-)}{2(\eta_i^{\mathrm{norm}} + \eta_i^{\mathrm{sup}})} \langle i^+ \mid s^+ \rangle \right\}$$
$$\times \tanh(\eta_i^+/2k_B T)$$
$$= -\left\{ \langle r^+ \mid i^+ \rangle \frac{v_{ii;\,tu}^{+-} G_{tu}^-}{2(\eta_i^{\mathrm{norm}} + \eta_i^{\mathrm{sup}})} \langle i^+ \mid s^+ \rangle \right\}$$
$$\times \tanh(\eta_i^+/2k_B T) \qquad (98)$$

This complicated equation gives the relation between G_{rs}^+ and G_{rs}^-, both referring to the superconductivity, and is called the gap equation. A few points should be presented. While selecting the superconducting mode, we used

$$\mathrm{Tr}(\sigma^+ \sigma^-) = \mathrm{Tr} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$
$$= \mathrm{Tr} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = 1 \qquad (99)$$

so that

$$\mathrm{Tr}(\sigma^+ v^{+a} \sigma^a) = v_{ii;\,tu}^{+-} \qquad (100)$$

The relation (98) yields

$$-\left\{ \langle r^+ \mid i^+ \rangle \frac{v_{ii;\,tu}^{+-}}{2(\eta_i^{\mathrm{norm}} + \eta_i^{\mathrm{sup}})} \langle i^+ \mid s^+ \rangle \right\} > 0 \qquad (101)$$

As has been mentioned previously, we have no chemical potential in the superconducting state, so that η_i^+ is positive, the same as $v_{ii;\,tu}^{+-}$ is. Therefore, it is required that $\langle r^+ \mid i^+ \rangle \langle i^+ \mid s^+ \rangle$ be negative so that Eq. (101) can hold. This is really possible, as will be mentioned below. Thus, we are not at all concerned with the electron–phonon coupling. Let us perform the successive approximations as

$$\langle r^+ \mid i^+ \rangle v_{ii;\,tu}^{+-} \langle i^+ \mid s^+ \rangle \tanh(\eta_i^+/2k_B T)$$
$$\approx \sum_i^{\mathrm{occ}} \langle r^+ \mid i^+ \rangle v_{ii;\,tu}^{+-} \langle i^+ \mid s^+ \rangle \qquad (T \to 0)$$
$$= q_{rs} v_{ii;\,tu}^{+-} (< 0) \qquad (102)$$

Here, $v_{ii;\,tu}^{+-}$ is the electron–electron interaction between two electron densities and is certainly positive (repulsive). However, the bond order is not necessarily so, but $q_{14} < 0$

in the following example. The last relation was usually assumed at the beginning of the superconductivity theory.

We thus obtain the condition for the superconducting state to appear; it is purely electronic and is apart from the electron–phonon coupling mechanism. Actually, for the chain molecule of four carbon atoms, called butadiene, the matrix $q_{rs}, (r, s) = (1 \sim 4)$ is

$$\{q_{rs}\} = \begin{pmatrix} 1.000 & 0.894 & 0.000 & -0.447 \\ & 1.000 & 0.447 & 0.000 \\ & & 1.000 & 0.894 \\ & & & 1.000 \end{pmatrix} \qquad (103)$$

We can clearly see that

$$v_{11;\,14}^{+-} q_{14} < 0 \qquad (104)$$

6. ILLUSTRATIVE EXAMPLE, CRITICAL TEMPERATURE

The gap Eq. (98) is, in appearance, considerably different from the usual one. We rewrite this equation in a form similar to the usual one. To this end, we adopt, as an example, a polyacene high polymer. Benzene, naphthalene, anthracene, etc. are a series of polyacene, shown in Figure 1. Here, the unit cell which is the butadiene molecule is in the dotted rectangle numbered by n. The interactions t_1 and t_2 are given for the corresponding bonds.

6.1. Bond Alternation

At the beginning, we discuss the bond alternation or the Peierls instability of these molecules. The infinite chain of acetylene, the so-called polyacetylene, has the bond alternation, i.e., the long and short bonds do not lose their memories in the limit where an infinite chain has been formed. This is popular with chemists,[19] but physicists call it Peierls distortion.[20] The bond alternation causes the gap between the conduction and valence bands. It has been said that this discontinuity prevents the superconducting phase from arising. However, this is an old-fashioned assertion and now seems sceptical.

In the Hückel theory, the interaction matrix elements are put as t_1 for the shorter bond and t_2 for the longer bond:

$$H^0 = -t_1(a_{2n}^+ a_{1n} + a_{1n}^+ a_{2n})$$
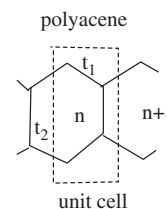$$- t_2(a_{1n+1}^+ a_{2n} + a_{2n}^+ a_{n+1}) \qquad (105)$$

Fig. 1. Polyacene.

where we consider the neighboring unit cells numbered n and $n+1$, and each cell has two kinds of bonds. The transfer integrals are parameterized as

$$t_1 = t - \delta, \quad t_2 = t + \delta, \quad (\delta > 0, \delta/t \ll 1) \qquad (106)$$

and then the Hamiltonian is easily diagonalized as

$$\epsilon_k = \pm[t^2(1 + \cos k) + \delta^2(1 - \cos k)]^{1/2} \qquad (107)$$

where $+$ and $-$ correspond to the conduction and valence bands, respectively. We are interested in the features at the zone boundary $k = \pi$:

$$\epsilon_\pi^c = 2\delta, \quad \epsilon_\pi^v = -2\delta \qquad (108)$$

Here, the superscripts c and v indicate the conduction and valence bands, respectively. When $\delta \neq 0$, certainly we have the gap, and if $\delta = 0$, the two bands continuously join into a single band called the half-filled band.

Next, we turn to the polyacene, whose unit cell is the butadiene molecule. In this case, we obtain four bands:

$$\epsilon_k^{c'} = \frac{1}{2}[t_3 + (t_3^2 + 4|\tilde{t}_k|^2)^{1/2}] = -\epsilon_k^{v'}$$

$$\epsilon_k^c = \frac{1}{2}[-t_3 + (t_3^2 + 4|\tilde{t}_k|^2)^{1/2}] = -\epsilon_k^v \qquad (109)$$

where

$$\tilde{t}_k = t_1 + t_2 e^{ik} \qquad (110)$$

The usual pairing property in alternant hydrocarbons is also seen in this case. Employing the parametrization (106) gives, at $k = \pi$,

$$\epsilon_\pi^v = \frac{1}{2}[t_3 + (t_3^2 + 16\delta^2)^{1/2}] \approx 4t_3(\delta/t_1)^2 \qquad (111)$$

When $\delta = 0$ (without bond alternation), we have

$$\epsilon_k^v = \frac{1}{2}\{t_3 - [t_3^2 + 8t^2(1 + \cos k)]^{1/2}\} \qquad (112)$$

Consider single-particle states. If $\delta = 0$ and $k = \pi$ we have, from Eq. (110), $\tilde{t} = 0$, so that the amplitudes at sites 2 and 5 vanish. Therefore, when $\delta = 0$, we get at $k = \pi$,

$$|\psi_k^v\rangle = \frac{1}{2}(a_{1k}^+ - a_{4k}^+)|0\rangle$$

$$|\psi_k^c\rangle = \frac{1}{2}(a_{1k}^+ + a_{4k}^+)|0\rangle \qquad (113)$$

It is seen that $|\psi_k^v\rangle$ is antisymmetric about the C_{2v} symmetry axis, and $-|\psi_k^v\rangle$ is symmetric. Thus, v and c bands are not continuous at $k = \pi$.

6.2. Deformation Energy

For these systems, let us study whether the bond alternation is energetically favorable or not. We assume that the energy gain due to the bond alternation mainly contributes to the highest valence band energy, ϵ_k^v.

The case of polyacetylene. The energy gain ΔE is

$$\Delta E = \int_0^{2\pi} \frac{dk}{2\pi}(\epsilon_k^v - \epsilon_k^v(0)) \qquad (114)$$

where the second term refers to the case without bond alternation ($\delta = 0$). In Eq. (107), we shift the integration origin from 0 to π, then approximate

$$\cos k = \cos(\pi + p) \approx -1 + p^2/2$$

For small p, we obtain

$$\Delta E = -\int_0^{2\pi} \frac{dk}{2\pi}\{\sqrt{(tp)^2 + 4\delta^2} - tp\}$$

$$= \frac{2t}{\pi}\left(\frac{\delta}{t}\right)^2 \ln\left(\frac{\delta}{\pi t}\right) \quad (<0) \qquad (115)$$

For polyacene, similar treatment of ϵ_k^v of Eq. (109) leads to

$$\epsilon_k^v = \frac{1}{2}\left(1 - \left\{1 + 16\left(\frac{\delta}{t}\right)^2 + 4p^2\left[1 - \left(\frac{\delta}{t}\right)^2\right]\right\}^{1/2}\right) \qquad (116)$$

and then the deformation energy becomes

$$\Delta E = t\left(\frac{\delta}{t}\right)^2\left(\frac{\pi}{4} - \frac{2}{\pi}\ln 4\pi\right) \approx -0.83\, t\left(\frac{\delta}{t}\right)^2 \qquad (117)$$

The bond alternation looks favorable for both cases. However, when the effect of the σ bond is taken into account, this almost cancels out the stabilization energy of the π system in the case of polyacene. On the other hand, this is not the case for polyacetylene due to the singular term in the relation (117).

Therefore, in what follows, by concentrating on polyacene, we are free from the bond alternation.

6.3. Polyacene, Gap Equation, Critical Temperature

The unit cell of polyacene is a butadiene molecule composed of four $2p\pi$ carbon atoms. The Hamiltonian in the tight-binding approximation is given as

$$H^0 = t(a_{n1}^+ a_{n2} + a_{n2}^+ a_{n3} + a_{n4}^+ a_{n3} + \text{h.c})$$
$$+ t(a_{n+1,1}^+ a_{n2} + a_{n+1,4}^+ a_{n3} + \text{h.c}) \qquad (118)$$

where the second line connects the unit cells n and $n+1$.[21]

The band structure of levels and the linear combination of atomic orbitals (LCAO) coefficients U are

$$\epsilon_1(k) = \frac{t}{2}\{1 + s(k)\}$$

$$\epsilon_2(k) = -\frac{t}{2}\{1 - s(k)\}$$

$$\epsilon_3(k) = \frac{t}{2}\{1 - s(k)\}$$

$$\epsilon_4(k) = -\frac{t}{2}\{1 + s(k)\} \qquad (119)$$

with

$$s(k) = \sqrt{9 + 8\cos\ k} \qquad (120)$$

$$U = \begin{pmatrix} N_4 & N_3 & N_2 & N_1 \\ -N_4\epsilon_4/\tilde{t}_k & -N_3\epsilon_3/\tilde{t}_k & -N_2\epsilon_2/\tilde{t}_k & -N_1\epsilon_1/\tilde{t}_k \\ N_4\epsilon_4/\tilde{t}_k & -N_3\epsilon_3/\tilde{t}_k & N_2\epsilon_2/\tilde{t}_k & -N_1\epsilon_1/\tilde{t}_k \\ -N_4 & N_3 & -N_2 & N_1 \end{pmatrix} \qquad (121)$$

where, for example,

$$N_1^2 = \frac{|\tilde{t}_k|^2}{2(|\tilde{t}_k|^2 + \epsilon_1^2)}, \quad 1/\tilde{t}_k = \frac{e^{ik/2}}{2t\cos(k/2)} \qquad (122)$$

At this stage, we have completed, in principle, the usual many-electron problem. The mean-field approximation makes the interaction problem a one-particle problem even though the SCF treatment is required at each step. In other words, from the viewpoint of the Hückel theory, the spin-diagonal parts provide the answer. On the other hand, the spin-off diagonal part, which means less in the case without electron–electron interactions, is responsible for the superconductivity.

Up to the previous chapter, the problem had been investigated in the site representation. That is to say, the system is considered to be composed of N sites. However, the real substance is formed from unit cells, so that the system is a repetition of the unit cell. The usual band theory of polyacene has thus been completed at this stage.

We turn to the onset of superconductivity. In this case, the single-particle approach is almost meaningless, but the pair state—say, the wave function of a Cooper pair—should be investigated. For this purpose, the Green function of a Cooper pair is most preferable. The gap Eq. (98) is nothing but the SCF equation for a Cooper pair.

The electronic structure of the single butadiene molecule referring to $k = 0$ is suggestive. Let the total number of sites of high polymer polyacene be N. The number of sites in the unit cell is four. Then $N = 4n$, with the number of unit cells n. The numbers 1~4 are the band indices; then we have the chemical potential between the $2n$ level and $3n$ level. The Cooper pair should be the hole pair of the $2n$ level indicated by mode $(-)$ or the particle pair of the $3n$ level. The discussion is confined to these levels in solid-state physics, even if the interaction with other bands is taken into account.

The $2n$ and $2n+1$ levels are called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These features and behaviors are not so far or qualitatively the same as those for $k = 0$.

The electronic structure of a single butadiene molecule is suggestive. The levels and the bond orders are (the unit $= t$)

$$\begin{array}{c|c} \epsilon_1 & -1.618 \\ \epsilon_2 & -0.618 \\ \epsilon_3 & 0.618 \\ \epsilon_4 & 1.618 \end{array} \qquad (123)$$

Here, ϵ_1 and ϵ_2 are occupied (valence) levels, while ϵ_3 and ϵ_4 are unoccupied (conduction) ones. Let the probability amplitude, with which the electron on level i is found at the site r, be $\langle r \mid i \rangle$, then the bond order q_{rs} is defined as (at the zero temperature)

$$q_{rs} = \sum_i^{occ} \langle r \mid i \rangle \langle i \mid s \rangle \qquad (124)$$

where the summation includes the spin state. In the determination of the attractive electron–electron interaction, the bond order is of crucial importance.

The bond orders are

Site				
1	1.000	0.894	0.000	−0.447
2	0.894	1.000	0.447	0.000
3	0.000	0.447	1.000	0.894
4	−0.447	0.000	0.894	1.000

$$(125)$$

We indicate the negative value of q_{14}. In solid-state physics, the discussion is concentrated on the highest valence band or the lowest conduction band. In the quantum-chemical language, the partial bond orders referring only to level 2, q_{rs}^H, which seem not so far from those with k, are listed as

Site				
1	0.362	0.224	−0.224	−0.362
2	0.224	0.138	−0.138	−0.224
3	−0.224	−0.138	0.138	0.224
4	−0.362	−0.224	0.224	0.362

$$(126)$$

We indicate the negative value of q_{14}^H.

If we want to look at the band structure, such as q_{rs}^H, it is multiplied by the third column of Eq. (121).

Based on these results, we may perform successive approximations or simplifications:
(1) The denominator of Eq. (98) is the sum of the ordinary Hartree–Fock energy and that of the superconducting state, and the latter is

$$\eta_i^{\text{sup}} = -v_{ii;\,tu}^{+-} G_{tu}^- \qquad (127)$$

The total energy is obtained by summing

$$\eta_i = \eta_i^{\text{norm}} + \eta_i^{\text{sup}} \qquad (128)$$

with respect to the chemical potential.

(2) Each level with η_i has really a band structure and is then written as $\eta_{i;k}$, by stressing the band structure by k with the band index i. Then i is put to be the highest occupied level, and the integration over k is carried out. The bond orders thus obtained are approximated by the partial bond orders q_{rs}^H.

(3) The electron–electron interaction, which is effectively negative due to the chemical structure of species, can be simply written for $g < 0$:

$$g = q_{rs}v_{rs;tu}^{-+} \tag{129}$$

(4) The energy interval establishing the superconductivity in the BCS theory is related to the electron–phonon interaction, $\hbar\omega_D$ (Debye frequency). In the present theory, it is replaced by the band width nearly equal to $|g|$.

(5) Assuming

$$G_{s\uparrow,r\downarrow}^+(0^-) = G_{t\uparrow,u\downarrow}^+(0^-) \tag{130}$$

in Eq. (98), we have

$$1 = gN(0)\int_0^{|g|}\frac{d\xi}{\xi+\eta^{\text{sup}}}\tanh\left(\frac{\xi+\eta^{\text{sup}}}{2k_BT}\right) \tag{131}$$

where $\xi = \eta^{\text{norm}}$. The critical temperature T_C is determined by the condition that η^{sup} vanishes at this temperature. The integration in Eq. (131) is carried out as usual. Approximating

$$\int\frac{d^3k}{(2\pi)^3} = N(0)\int d\xi$$

gives

$$\int_0^{|g|}\frac{d\xi}{\xi}\tanh\left(\frac{\xi}{2k_BT}\right) = \int_0^Z\frac{dz}{z}\tanh z, \quad z = |g|/2k_BT$$

$$= [\ln z\tanh z]_0^Z - \int_0^\infty dz\ln z\,\text{sech}^2 z \tag{132}$$

where the upper limit in the second integration is replaced by ∞, which makes it integrable:[15]

$$\int_0^\infty dz\ln z\,\text{sech}^2 z = -\ln\frac{4e^\gamma}{\pi}, \quad \gamma \text{ is the Euler constant}$$

A simple rearrangement of the result gives

$$k_BT_C = \frac{2e^\gamma}{\pi}|g|e^{-1/N(0)g} \sim 1.13|g|e^{-/N(0)g} \tag{133}$$

The result is entirely the same as the current one. However, since it is probable that

$$|g|/k_BT \sim 100 \tag{134}$$

the critical temperature is, at most, enhanced by this value, even though it is considerably reduced by the factor $e^{-1/N(0)g}$.

6.4. Conclusion

As has been presented, superconductivity is not a too-complicated phenomenon. If we employ the spinor representation, superconductivity is described in parallel with the normal electronic processes. If we find, in the copper oxide complex, the four-site unit as a butadiene molecule, it might be the origin of the superconductivity of this material. We think that it is not so difficult a problem for quantum chemists.

7. LINEAR RESPONSE MAGNETIC RESONANCE IN NORMAL AND SUPERCONDUCTING SPECIES; SPIN-LATTICE RELAXATION TIME

7.1. Introduction

The theory of linear response is one of the main topics in solid-state physics, and its application to superconductivity is also a fundamental problem. Perhaps the most important problem is the Meissner effect. However, we are now interested in the magnetic resonance, whose main theme should concern the relaxation time. Let us discuss the spin-lattice relaxation time T_1 in the nuclear magnetic resonance. An elegant theory has been provided by Kubo and Tomita,[22] and revised by us with the temperature Green function.[23]

The spin–lattice relaxation time T_1 increases remarkably in a superconductor just below the critical temperature. This is explained by the BCS pairing theory and is said to be its brilliant triumph.[3, 24, 25] The external perturbation acting on the electron is written as

$$H' = B_{k\sigma,k'\sigma'}c_{k\sigma}^+c_{k'\sigma'} \tag{135}$$

where $c_{k\sigma}^+$, $c_{k\sigma}$, etc. are the creation and annihilation operators of an electron in the normal phase, and $B_{k\sigma,k'\sigma'}$ is the matrix element of the perturbation operator between the ordinary one-electron states in the normal phase. The problem is as follows: If we rewrite it in terms of operators of a quasiparticle in the superconducting phase, what will arise?

The time reversal to the above, $B_{-k'-\sigma',-k-\sigma}$, has the same absolute value, but the phase is the same or the reverse.

It is possible to classify as:

$1_\pm$. The spin flip-flop does not arise:

$$B_{k\sigma,k'\sigma}(c_{k\sigma}^+c_{k'\sigma} \pm c_{-k'-\sigma}^+c_{-k-\sigma})$$

$2_\pm$. The spins flip-flop does arise:

$$B_{k\sigma,k'-\sigma}(c_{k\sigma}^+c_{k'-\sigma} \pm c_{-k'\sigma}^+c_{-k-\sigma})$$

As seen above, the theory implicitly assumes that the system is a perfect crystal and is described by the single wave vector k. The positive and negative signs of k indicate waves propagating from the vertex or off the vertex. Before entering into the discussion about the

relaxation time of the magnetic resonance, we briefly review the Bogoliubov theory.[3, 10, 15] The Bogoliubov transformation defines a quasiparticle responsible for the superconductivity as

$$
\begin{pmatrix} \gamma_{k\uparrow} \\ \gamma_{-k\downarrow}^+ \end{pmatrix} = \begin{pmatrix} u_k & -v_k \\ v_k & u_k \end{pmatrix} \begin{pmatrix} c_{k\uparrow} \\ c_{-k\downarrow}^+ \end{pmatrix} \tag{136}
$$

with

$$
u_k^2 - v_k^2 = 1
$$

The spirit of the Bogoliubov transformation is to mix the operators $c_{k\uparrow}$ and $c_{-k\downarrow}^+$, which are different in spin (as to the wave number, this mixing is not so serious) and not mixed in the normal situation. The quasiparticle yields the new ground state near the chemical potential. The stabilization energy thus obtained is called the gap energy, Δ_k. What we have done in Section 3 is a substantial understanding of this reason. However, if we want to make the $\pm k$ distinction meaningful, it is natural to adopt the four-component spinor—say, the extended Nambu spinor (perhaps spurious).[26] For ordinary states,

$$
\mathbf{c}_k^+ = \begin{pmatrix} c_{k\uparrow}^+ & c_{-k\downarrow} & c_{-k\uparrow} & c_{k\downarrow}^+ \end{pmatrix}, \quad \mathbf{c}_k = \begin{pmatrix} c_{k\uparrow} \\ c_{-k\downarrow}^+ \\ c_{-k\uparrow}^+ \\ c_{k\downarrow} \end{pmatrix} \tag{137}
$$

and, for the superconducting state,

$$
\boldsymbol{\gamma}_k^+ = \begin{pmatrix} \gamma_{k\uparrow}^+ & \gamma_{-k\downarrow} & \gamma_{-k\uparrow} & \gamma_{k\downarrow}^+ \end{pmatrix}, \quad \boldsymbol{\gamma}_k = \begin{pmatrix} \gamma_{k\uparrow} \\ \gamma_{-k\downarrow}^+ \\ \gamma_{-k\uparrow}^+ \\ \gamma_{k\downarrow} \end{pmatrix} \tag{138}
$$

These are connected with each other by the Bogoliubov transformation as

$$
\boldsymbol{\gamma}_k = U_k \mathbf{c}_k, \quad \boldsymbol{\gamma}_k^+ = \mathbf{c}_k U_k^+ \tag{139}
$$

where

$$
U_k = \begin{pmatrix} \mathbf{u}_k & 0 \\ 0 & \mathbf{u}_k^+ \end{pmatrix}, \quad \text{with } \mathbf{u}_k = \begin{pmatrix} u_k & v_k \\ -v_k & u_k^+ \end{pmatrix} \tag{140}
$$

Careful manipulation is instructive.
Case 1_+:

$$
(c_{k\sigma}^+ c_{k'\sigma} + c_{-k'-\sigma}^+ c_{-k-\sigma})
$$
$$
= \mathbf{c}_k^+ \Sigma^3 \mathbf{c}_{k'} = \boldsymbol{\gamma}_k^+ U_k \Sigma^3 U_{k'}^+ \boldsymbol{\gamma}_{k'} \tag{141}
$$

where

$$
\Sigma^3 = \begin{pmatrix} \sigma^3 & \\ & -\sigma^3 \end{pmatrix} \tag{142}
$$

This is the 4×4 matrix manipulation; however, it is enough to note the upper half of the result.

The upper half of Eq. (139) is

$$
\begin{pmatrix} c_{k\uparrow}^+ & c_{-k\downarrow} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} c_{k'\uparrow} \\ c_{-k'\downarrow}^+ \end{pmatrix}
$$
$$
= \begin{pmatrix} \gamma_{k\uparrow}^+ & \gamma_{-k\downarrow} \end{pmatrix} \begin{pmatrix} u & v \\ -v & u \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} u' & -v' \\ v' & u' \end{pmatrix} \begin{pmatrix} \gamma_{k'\uparrow} \\ \gamma_{-k'\downarrow}^+ \end{pmatrix}
$$
$$
= \begin{pmatrix} \gamma_{k\uparrow}^+ & \gamma_{-k\downarrow} \end{pmatrix} \begin{pmatrix} uu' - vv' & -uv' - vu' \\ -vu' - uv' & vv' - uu' \end{pmatrix} \begin{pmatrix} \gamma_{k'\uparrow} \\ \gamma_{-k'\downarrow}^+ \end{pmatrix} \tag{143}
$$

where u and v are the abbreviations of u_k and v_k, respectively, while u' and v' are those of $u_{k'}$ and $v_{k'}$.
Case 1_-:

$$
\sum_\sigma (c_{k\sigma}^+ c_{k'\sigma} - c_{-k'-\sigma}^+ c_{-k-\sigma})
$$
$$
= \mathbf{c}_k^+ \mathbf{1} \mathbf{c}_{k'} = \boldsymbol{\gamma}_k^+ U_k \mathbf{1} U_{k'}^+ \boldsymbol{\gamma}_{k'} \tag{144}
$$

The upper half of the above is

$$
\begin{pmatrix} \gamma_{k\uparrow}^+ & \gamma_{-k\downarrow} \end{pmatrix} \begin{pmatrix} uu' + vv' & -uv' + vu' \\ -vu' + uv' & vv' + uu' \end{pmatrix} \begin{pmatrix} \gamma_{k'\uparrow} \\ \gamma_{-k'\downarrow}^+ \end{pmatrix} \tag{145}
$$

As is shown clearly, the original term is transformed in the quasiparticle representation into a combination of the scattering term with the diagonal element in the $\mathbf{u}_k$ matrix and the creation or annihilation of a pair with the off-diagonal element of $\mathbf{u}$. These matrix elements are called the coherent factors.

Let us turn to the case where the spin flip-flop is allowed.
Case 2_+:

$$
c_{k\sigma}^+ c_{k'-\sigma} + c_{-k'\sigma}^+ c_{-k-\sigma} = \mathbf{c}_k^+ \Sigma^J \mathbf{c}_{k'} = \boldsymbol{\gamma}_k^+ U_k \Sigma^J U_{k'}^+ \boldsymbol{\gamma}_{k'} \tag{146}
$$

with

$$
\Sigma^J = \begin{pmatrix} & & & 1 \\ & -1 & & \\ & & -1 & \\ 1 & & & \end{pmatrix} \tag{147}
$$

This relation connects the left half of $\boldsymbol{\gamma}_k^+$ and the lower half of $\boldsymbol{\gamma}_{k'}$, by giving

$$
\text{Eq. (147)} = \begin{pmatrix} \gamma_{k\uparrow}^+ & \gamma_{-k\downarrow} \end{pmatrix} \begin{pmatrix} uu' + vv' & uv' - vu' \\ -vu' + uv' & -vv' - uu' \end{pmatrix}
$$
$$
\times \begin{pmatrix} \gamma_{-k'\uparrow} \\ \gamma_{k'\downarrow}^+ \end{pmatrix} \tag{148}
$$

Case 2_-:

$$
c_{k\sigma}^+ c_{k'-\sigma} - c_{-k'\sigma}^+ c_{-k-\sigma} = \mathbf{c}_k^+ \mathbf{J} \mathbf{c}_{k'} = \boldsymbol{\gamma}_k^+ U_k \mathbf{J} U_{k'}^+ \boldsymbol{\gamma}_{k'} \tag{149}
$$

with

$$
\mathbf{J} = \begin{pmatrix} & & & 1 \\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix} \tag{150}
$$

This relation also connects the left half of $\boldsymbol{\gamma}_k^+$ and the lower half of $\boldsymbol{\gamma}_{k'}$, and we have

$$\text{Eq. (6.16)} = \begin{pmatrix} \gamma_{k\uparrow}^+ & \gamma_{-k\downarrow} \end{pmatrix} \begin{pmatrix} uu' - vv' & uv' + vu' \\ -vu' - uv' & -vv' + uu' \end{pmatrix}$$
$$\times \begin{pmatrix} \gamma_{-k'\uparrow} \\ \gamma_{k'\downarrow}^+ \end{pmatrix} \tag{151}$$

Note that, at present, the scattering terms are off-diagonal, and the creation and annihilation terms are diagonal.

By the use of the relations[3, 10, 15]

$$u_k^2 = \frac{1}{2}\left(1 + \frac{\epsilon_k}{E_k}\right), \quad v_k^2 = \frac{1}{2}\left(1 - \frac{\epsilon_k}{E_k}\right)$$
$$E_k^2 = \epsilon_k^2 + \Delta_k^2 \tag{152}$$

(Δ_k is the gap energy), the coherent factors are expressed substantially as

$$1_\pm. \quad (uu' \mp vv')^2 = \frac{1}{2}\left(1 + \frac{\epsilon_k \epsilon_{k'}}{E_k E_{k'}} \mp \frac{\Delta_k \Delta_{k'}}{E_k E_{k'}}\right)$$
$$2_\pm. \quad (uv' \mp vu')^2 = \frac{1}{2}\left(1 \mp \frac{\Delta_k \Delta_{k'}}{E_k E_{k'}}\right) \tag{153}$$

In case 1_+, we have the ultrasonic attenuation, while the electromagnetic interaction is in case 2_+ and the magnetic resonances are in case 2_-.

7.2. T_1 in NMR

A detailed analysis of the spin–lattice relaxation time T_1 in the nuclear magnetic resonance will be presented in the next section. Here, the results are given briefly

$$T_1 \sim \sum_{kk'} |B_{kk'}|^2 \frac{1}{2}\left(1 + \frac{\Delta_k \Delta_{k'}}{E_k E_{k'}}\right) n_k (1 - n_{k'})$$
$$\times \delta(E_k - E_{k'} - \omega) \tag{154}$$

where ω is the applied radio frequency. By converting the summation (explicitly shown) to the integration, and further by using the relation of state densities,

$$N(E)dE = N(\epsilon)d\epsilon, \quad \text{then}$$
$$\frac{N(E)}{N(\epsilon)} = \frac{d\epsilon}{dE} = \begin{cases} \dfrac{E}{(E^2 - \Delta^2)^{1/2}} & (E > \Delta) \\ 0 & (E < \Delta) \end{cases} \tag{155}$$

we rewrite Eq. (152) for $\omega \ll \Delta$ as

$$T_1 \sim |B|^2 N^2(0) \int_\Delta^\infty \frac{1}{2}\left(1 + \frac{\Delta^2}{E(E+\omega)}\right)$$
$$\times \frac{E(E+\omega)k_B T(-\partial n/\partial E)\,dE}{(E^2 - \Delta^2)^{1/2}[(E+\omega)^2 - \Delta^2]^{1/2}} \tag{156}$$

where the coupling constant and the state density are replaced by their suitable averages. This integral is divergent. Therefore, T_1 of a superconductor is strongly enhanced just below the critical temperature. This phenomenon was observed and explained by Slichter et al.[24, 25] This was said to be one of the brilliant victories of the BCS theory. However, it has been found, in the recent experiments on the high-temperature superconductors or the copper oxide superconductors, that the T_1 enhancement is lost. This phenomenon is considered deeply connected with the mechanism of the high-temperature superconductivity of these species, and it attracted the interest of many investigators.[27, 29] However, as far as we know, the theory of magnetic resonance of a superconductor has been done almost entirely under the scheme mentioned in this introduction. Then it will be preferable to develop the theory of magnetic resonance in accordance with the sophisticated recent theory of superconductivity.

7.3. Theory with Green's Function

Our idea is as follows: the algebra of electrons is related to their field operators. In the same way, we assume the field for nuclei. For example, the creation operator for a nucleus a_{KM}^+ yields the nuclear motion with K and M, which are spatial and spin quantum numbers, respectively. The energy spectrum of the propagator $\mathcal{G}_{KM}(\tau) = \langle\langle a_{KM}(\tau)a_{KM}^+\rangle\rangle$ gives the line shape of the magnetic resonance.

The nuclear propagator $\mathcal{G}_{KM}(\tau)$ sees the electron sea, followed by the electron excitation in the spin space. This gives the additional line width of the nuclear magnetic resonance. The phenomenon looks like the vacuum polarization in quantum electrodynamics. The self-energy part that has thus arisen in the nuclear energy is the source of the line shape of the nuclear magnetic resonance.[23]

The spin–lattice relaxation time of the nuclear spin I^z is given by the imaginary part of the magnetic susceptibility χ_{zz}, which is equal to $(\chi_{+-} + \chi_{-+})/2$ in the spatially homogeneous system. Here, $\pm$ correspond to $(I^x \pm iI^y)/2$, respectively. The ensemble average of a change, $\delta\langle I^+(t)\rangle$, is given by the linear response theory as

$$\delta\langle I^+(t)\rangle = i \int_{-\infty}^t dt' \, \text{Tr}\{\rho_G [H^{\text{ex}}(t'), I^+(t)]_-\} \tag{157}$$

where ρ_G is the grand canonical statistical operator. However, the chemical potential is not given explicitly, unless otherwise stated. The rotating magnetic field causing the magnetic transition is, assuming a single mode for simplicity,

$$H^{\text{ex}}(t) = H_R(I^+(t)e^{i\omega t} + I^-(t)e^{-i\omega t}) \tag{158}$$

As has been said, the spin–lattice relaxation arises from the interaction between the nuclear spin and the electron spin. In other words, the electron spins play the role of a lattice system

$$H' = \hbar\gamma g\beta_B F(R, r)\mathbf{I}\cdot\mathbf{S} \tag{159}$$

where $F(R, r)$ is a function of spatial coordinates of the nucleus, R, and that of the electron, r. The term γ is the gyromagnetic ratio of the nucleus, and g and β_B are the g factor and the Bohr magneton of the electron, respectively.

Now the second quantization of the above is carried out. First of all, the orthonormalized wave function describing the nuclear behavior, $|\xi_K(R)M\rangle$, is introduced as

$$(H_N + H_M)|\xi_K(R)M\rangle = (\epsilon_K + M)|\xi_K(R), M\rangle$$
$$= \epsilon_{KM}|\xi_K(R,)M\rangle \quad (160)$$

with

$$\epsilon_{KM} = \epsilon_K + M$$

where H_N is the spatial part and H_M is the Zeeman part. Then we have

$$I^\alpha \to \langle \xi_K(R)M|I^\alpha|\xi_{K'}(R)M'\rangle a^+_{KM} a_{K'M'}$$
$$= \langle M|I^\alpha|M'\rangle a^+_{KM} a_{K'M'}\delta_{KK'} \quad (161)$$

A similar equation is given for electrons,

$$(H_S + H_m)\phi_k(r)|m\rangle = (\epsilon_k + m)|\phi_k(r), m\rangle$$
$$= \epsilon_{km}|\phi_k(r), m\rangle \quad (162)$$

where

$$\epsilon_{km} = \epsilon_k + m$$

so that

$$H' \to h\gamma g\beta_B \langle M|I^\beta|M'\rangle\langle m|S^\alpha|m'\rangle\langle \xi_K(R)$$
$$\times \phi_k(r)|F(R, r)|\xi_{K'}(R)\phi_{k'}(r)\rangle$$
$$\times (a^+_{KM} a_{K'M'})(c^+_{km} c_{k'm'}) \quad (163)$$

If the nuclear motion is assumed to be that of a harmonic oscillator, a^+_{KM} and a_{KM} are the creation and annihilation operators of vibrational excitations. When the nuclei carry noninteger spins, these are considered to obey the Fermi statistics or satisfy the anticommutation relation

$$[a^+_{KM}, a_{K'M'}]_+ = \delta_{KK'}\delta_{MM'} \quad (164)$$

However, as will be seen in the following, this selection of the statistics is not fatal for the theory. Needless to say, the operators for electrons satisfy the anticommutation relations.

The change of I^+ in Eq. (157) can be written, in the interaction representation, as (we retain the I^- term in Eq. (158))

$$\delta\langle I^+(t)\rangle = i\gamma H_R \int_{-\infty}^{t} dt' e^{-i\omega t'}$$
$$\text{Tr}\{\rho_G \langle M-1|I^-|M\rangle\langle M|I^+|M-1\rangle$$
$$[a^+_{K, M-1}(t')a_{K, M}(t'), a^+_{K, M}(t)a_{K, M-1}(t)]_-\}$$
$$= -\gamma H_R \int_{-\infty}^{t} dt' e^{-i\omega t'} D_{K, M-1, M}(t' - t)$$

$$= -\frac{1}{2}\gamma H_R e^{-i\omega t} \int_{-\infty}^{\infty} ds e^{-i\omega s} \sum_{KM} D_{K, M-1, M}(s)$$
$$= -\frac{1}{2}\gamma H_R e^{-i\omega t} D_{K, M-1, M}(\omega) \quad (165)$$

From this result, the magnetic susceptibility of the present system is

$$\chi_{+-}(\omega) = -\frac{\gamma}{2} D_{K, M-1, M}(\omega) \quad (166)$$

In the course of derivation, the matrix elements of spin operators are put to be equal to 1, and then the Tr operation is carried out. Here, $D_{K, M-1, M}(s)$ is a retarded Green function,

$$D_{K, M-1, M}(s) = -i\theta(s)\text{Tr}\{\rho_G[a^+_{KM-1}(s)a_{KM}(s),$$
$$a^+_{KM} a_{KM-1}]_-\} \quad (167)$$

and $D_{K, M-1, M}(\omega)$ is its Fourier transform. Now our problem is to estimate this retarded function.

The retarded Green function is easily obtained by analytical continuation from the Matsubara function (or the temperature Green function with imaginary time τ) which is causal in τ,

$$\mathscr{D}_{K, M-1, M}(\tau)$$
$$= -\text{Tr}\{\rho_G T\tau[a^+_{K, M-1}(\tau)a_{K, M}(\tau)a^+_{K, M} a_{K, M-1}]\} \quad (168)$$

for which the Feynman diagram analysis is available.[15]

7.4. Noninteracting

Here, we deal with the case without the spin–lattice interaction. It might be trivial; however, it seems instructive for the later investigation. By the use of the simplified notation, $\langle \cdots \rangle = \text{Tr}(\rho_G \cdots)$, the Green function in this case is written as

$$\mathscr{D}^0_{K, M-1, M}(\tau) = \langle T\tau[a^+_{KM-1}(\tau)a_{K, M}(\tau)a^+_{KM} a_{KM-1}]\rangle$$
$$= \mathscr{G}^0_{KM}(\tau)\mathscr{G}^0_{KM-1}(-\tau) \quad (169)$$

where

$$\mathscr{G}^0_{KM}(\tau) = -\langle T\tau[a_{KM}(\tau)a^+_{KM}]\rangle \quad (170)$$

and the corresponding Fourier transform of Eq. (169) is

$$\mathscr{D}^0_{K, M-1, M}(\omega_n) = \frac{1}{\beta}\sum_{\nu_n} \mathscr{G}^0_{KM}(\nu_n)\mathscr{G}^0_{KM-1}(\nu_n - \omega_n) \quad (171)$$

where

$$\mathscr{G}^0_{KM}(\nu_n) = \frac{1}{i\nu_n - \epsilon_{KM}} \quad (172)$$

Therefore

$$\mathscr{D}^0_{K, M-1, M}(\omega_n)$$
$$= \frac{1}{\beta}\sum_{\nu_n} \frac{1}{i\nu_n - i\omega_n - \epsilon_{KM-1}} \cdot \frac{1}{i\nu_n - \epsilon_{KM}}$$
$$= \frac{1}{\beta}\sum_{\nu_n} \left(\frac{1}{i\nu_n - i\omega_n - \epsilon_{KM-1}} - \frac{1}{i\nu_n - \epsilon_{KM}}\right)$$

$$\times \frac{1}{i\omega_n + \epsilon_{KM-1} - \epsilon_{KM}}$$

$$= [n(\epsilon_{KM-1}) - n(\epsilon_{KM})]\frac{1}{i\omega_n - \epsilon_{KI}} \quad (173)$$

where

$$\epsilon_{KI} = \epsilon_{KM} - \epsilon_{KM-1}$$

and it is noted that ω_n is even, and that it does not matter in obtaining the particle number. The retarded Green function is obtained simply by replacing $i\omega_n$ with $\omega + i\eta$ (η is a positive infinitesimal). Thus, we obtain

$$\delta\langle I^+(t)\rangle = e^{-i\omega t}H_R(n(\epsilon_{K-}) - n(\epsilon_{K+}))$$

$$\times \frac{1}{\omega - \epsilon_{KI} + i\eta} \quad (174)$$

where the radio frequency stimulating the resonance is rewritten by ω^0. The magnetic susceptibility χ_{+-} thus becomes

$$\chi_{+-}(\omega) = \gamma(n(\epsilon_{K-}) - n(\epsilon_{K+}))\frac{1}{\omega - \epsilon_{KI} + i\eta}$$

$$\gamma = e^{-i\omega t}H_R \quad (175)$$

whose imaginary part is

$$\chi''_{+-}(\omega) = -\pi\gamma(n(\epsilon_{K-}) - n(\epsilon_{K+}))\delta(\omega - \epsilon_{KI}) \quad (176)$$

This gives the sharp function-type energy spectrum. We have no line width or the relaxation time, and states are stationary.

7.5. Interacting; Normal

In the interacting system, G0 in Eq. (169) has to be replaced by $\mathscr{G}$, including the interaction, which in the present case is the spin–spin interaction between nuclei and electrons, as has been given in Eq. (157),

$$\mathscr{D}_{KM-1,M}(\omega_n) = \frac{1}{\beta}\sum_{\nu_n}\mathscr{G}_{KM}(\nu_n)\mathscr{G}_{KM-1}(\nu_n - \omega_n) \quad (177)$$

where, for instance,

$$\mathscr{G}_{KM}(\nu_n) = [(\mathscr{G}^0_{KM}(\nu_n))^{-1} - \Sigma_{KM}(\omega)]^{-1} \quad (178)$$

ω being the interaction energy.

Our procedure is as follows. The two Green functions with the self-energy part are evaluated. Combining them gives the retarded Green function $\mathscr{D}$ for estimating the magnetic susceptibility.

The most important (divergent) self-energy part of this self-energy is due to the ring diagram shown in Figure 2. The problem is to examine how the energy of the nucleus propagator (unequal-dashed line) is changed by the ring diagram of the electron (full line). That is to say,

$$\mathscr{G}(\nu_n)^{-1} = \mathscr{G}(\nu_n)^0 + \Sigma(\omega)$$

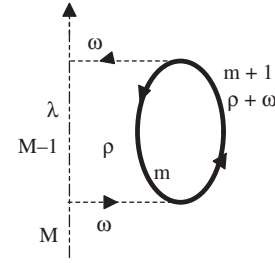$$\Sigma(\omega) = -|K|^2\mathscr{S}(\rho_n)\mathscr{S}(\rho_n + \omega) \quad (179)$$

Fig. 2. Self-energy part $\mathscr{G}(\nu_n)$.

where $\mathscr{S}$ is the electron propagator, and the minus sign is due to the fermion loop. The self-energy part includes the coupling terms, where

$$|K|^2 = \langle M|I^+|M-1\rangle\langle m-1|S^-|m\rangle|^2$$

$$\times|\langle\chi_K(R)\phi_k(r)|F(R,r)|\phi_{k'}(r)\chi_{K'}(R)\rangle|^2 \quad (180)$$

and the minus sign is due to a Fermion loop. The ring diagram is calculated as follows:

$$\mathscr{S}_{km}(\rho_n)\mathscr{S}_{km-1}(\rho_n + \omega)$$

$$= \sum_{\rho_n}\frac{1}{i\rho_n - \epsilon_{km}}\cdot\frac{1}{i\rho_n + \omega - \epsilon_{km+1}}$$

$$= \sum_{\rho_n}\left(\frac{1}{i\rho_n - \epsilon_{km}} - \frac{1}{i\rho_n + \omega - \epsilon_{km+1}}\right)\frac{1}{\omega - \epsilon_{km+1} + \epsilon_{km}}$$

$$= (n(\epsilon_{km}) - n(\epsilon_{km+1}))\frac{1}{\omega - \epsilon_{km+1} + \epsilon_{km}} \quad (181)$$

The lattice (electron) gets ω from a nucleus to lift the electron spin from m to $m+1$, and at the other vertex, the inverse process occurs. This looks like the radiation process in the photochemistry. We thus have the self-energy part of $\mathscr{G}_{K;M-1,M}$,

$$\Sigma_{K;M-1,M}(\nu_n) = |K|^2(n(\epsilon_{km}) - n(\epsilon_{km+1}))\frac{1}{\omega - \epsilon_{ks}} \quad (182)$$

where

$$\epsilon_{ks} = \epsilon_{km+1} - \epsilon_{km}$$

Another propagator $\mathscr{G}_{K;M}$, has the self-energy part $\Sigma_{K;M,M-1}(\nu_n)$. This is built by replacing $\rho_n + \omega$ with $\rho_n - \omega$ in Eq. (181) Figure 2.

$$\Sigma_{K;M,M-1}(\nu_n)$$

$$= |K|^2(n(\epsilon_{km}) - n(\epsilon_{km-1}))\frac{1}{\omega - \epsilon_{km-1} + \epsilon_{km}}$$

$$= |K|^2(n(\epsilon_{km}) - n(\epsilon_{km-1}))\frac{1}{\omega - \epsilon_{ks}}$$

$$\approx |K|^2(n(\epsilon_{km+1}) - n(\epsilon_{km}))\frac{1}{\omega - \epsilon_{ks}} \quad (183)$$

We now turn to the evaluation of the propagator $\mathscr{D}_{K;\,M-1,\,M}(\tau)$:

$$\mathscr{D}_{K;\,M-1,\,M}(\omega_n)$$

$$= \frac{1}{\beta} \sum_{\nu_n} \mathscr{G}_{KM}(\nu_n) \mathscr{G}_{KM-1}(\nu_n - \omega_n)$$

$$= \frac{1}{\beta} \sum_{\nu_n} (i\nu_n - \epsilon_{KM} - \Sigma_{KM-})^{-1}$$

$$\times (i\nu_n - i\omega_n - \epsilon_{KM-1} - \Sigma_{K;M,M-1})^{-1}$$

$$= \frac{1}{\beta} \sum_{\nu_n} \left\{ \frac{1}{i\nu_n - i\omega_n - \epsilon_{KM-1} - \Sigma_{KM-1}} - \frac{1}{i\nu_n - \epsilon_{KM} - \Sigma_{KM}} \right\}$$

$$\times \left\{ \frac{1}{i\omega_n - \epsilon_{KM-1} - \Sigma_{KM-1} + \epsilon_{KM} + \Sigma_{KM}} \right\}$$

$$= (N(\epsilon_{KM}) - N(\epsilon_{KM-1}))$$

$$\times \left\{ \frac{1}{i\omega_n - \epsilon_{KI} + \Sigma_{KM} - \Sigma_{KM-1}} \right\} \tag{184}$$

Here,

$$\epsilon_{KI} = \epsilon_{KM} - \epsilon_{KM-1}$$

and the self-energy parts are disregarded in obtaining the particle density. We can see that the additional terms in the denominator modify the line shape.

If we put $i\omega_n \to \omega + i\eta$, we can obtain the retarded Green function, whose imaginary part gives the line shape:

$$D(\omega) \sim \left\{ \frac{1}{\omega + i\eta - \epsilon_{KI} + \Sigma_{KM} - \Sigma_{KM-1}} \right\}$$

$$= \left\{ P\left(\frac{1}{\omega - -\Sigma_{KM-1}\epsilon_{KI}} \right) \right.$$

$$\left. - i\pi \delta(\omega - \epsilon_{KI} + \Sigma_{KM} - \Sigma_{KM-1}) \right\}$$

$$= \frac{i(\mathrm{Im})}{(\mathrm{Re})^2 + (\mathrm{Im})^2} \quad \text{(at resonance point)} \tag{185}$$

The line shape is now changed from the δ function type to the Lorentz type, as expected.

8. INTERACTING; SUPERCONDUCTOR

8.1. The Extended Nambu Spinor

Now, we investigate how the line shape obtained above is further modified in a superconductor. The electron propagators in the previous section are replaced by those in a superconductor. They have already been studied in Section 3 and are presented here in a new fashion adequate for the following investigation. As has been done by BCS, let us consider the attractive twobody potential g, which is assumed constant for simplicity, and further keep in mind the Cooper pair. The Hamiltonian

$$H_{el} = \left\{ \epsilon_{k\alpha} c_{k\alpha}^+ c_{k\alpha} + \frac{1}{2} g c_{k\alpha}^+ c_{-k\beta}^+ c_{-k\beta} c_{k\alpha} \right\} \tag{186}$$

where $\epsilon_{k\alpha}$ is the orbital energy, includes the Zeeman energy in the present case.

Now we use the extended Nambu representation of Eq. (137),

$$\mathbf{c}_k = \begin{pmatrix} c_{k\alpha} \\ c_{-k\beta}^+ \\ c_{-k\alpha}^+ \\ c_{k\beta} \end{pmatrix}, \qquad \mathbf{c}_k^+ = \begin{pmatrix} c_{k\alpha}^+ & c_{-k\beta} & c_{-k\alpha} & c_{k\beta}^+ \end{pmatrix} \tag{187}$$

with the equal-time commutator:

$$[\mathbf{c}_k, \mathbf{c}_{k'}^+]_+ = \mathbf{1}\delta_{kk'} \tag{188}$$

In these terms, the Hamiltonian is rewritten as

$$H_{el} = \boldsymbol{\epsilon}_k \mathbf{c}_k^+ \Sigma^3 \mathbf{c}_k + \frac{1}{2} g (\mathbf{c}_k^+ \Sigma^+ \mathbf{c}_k)(\mathbf{c}_{k'}^+ \Sigma^- \mathbf{c}_{k'}) \tag{189}$$

where $\boldsymbol{\epsilon}_k$ is the diagonal matrix of ϵ_γ:

$$\boldsymbol{\epsilon}_k = \begin{pmatrix} \epsilon_{k\alpha} & & & \\ & \epsilon_{-k\beta} & & \\ & & \epsilon_{-k\alpha} & \\ & & & \epsilon_{k\beta} \end{pmatrix} \tag{190}$$

Let us define

$$\Sigma^3 = \begin{pmatrix} \sigma^3 & 0 \\ 0 & -\sigma^3 \end{pmatrix}, \quad \Sigma^+ = \begin{pmatrix} \sigma^+ & 0 \\ 0 & -\sigma^- \end{pmatrix}$$

$$\Sigma^- = \begin{pmatrix} \sigma^- & 0 \\ 0 & -\sigma^+ \end{pmatrix} \tag{191}$$

with

$$\sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma^+ = \frac{1}{2}(\sigma^1 + i\sigma^2), \quad \sigma^- = \frac{1}{2}(\sigma^1 - i\sigma^2) \tag{192}$$

As for the electron–electron interaction, only those for the Cooper pairs are selected; namely, Σ^+ selects a Cooper pair in the particle state, and Σ^- in the hole state.

8.2. Green's Function

Here, the discussions done in Section 4 are repeated briefly. The above Hamiltonian is invariant under the scale transformation. Then we have a current conservation, especially the charge conservation in the static state (Noether's theorem). If we have any quantity which does not commute with this invariant charge, we can expect a phase transition (the Goldstone theorem).

The charge proportional to

$$\langle c_{k\gamma}^+ c_{k\gamma} \rangle = \sum_{k>0} \langle \mathbf{c}_k^+ \Sigma^3 \mathbf{c}_k \rangle \tag{193}$$

is invariant under the rotation about the Σ^3 axis in the space spanned by Σ^3, Σ^+ and Σ^-. Observing that

$$[\Sigma^3, \Sigma^\pm] = \pm 2\Sigma^\pm \tag{194}$$

suggests the phase transitions along the $\Sigma^\pm$ directions.

If we define

$$\bar{\mathbf{c}} = \mathbf{c}^+ \Sigma^3$$

as has been done in Section 3, the discussions parallel to those there will be possible in the following. However, this is not employed in this case.

The phase transition cannot be achieved by the perturbational approach, but the effective Hamiltonian giving the phase transition should be included at the beginning. For example, the modified Hamiltonian

$$H^0 = \mathbf{c}_k^+ (\boldsymbol{\epsilon}_k \Sigma 3 + \rho \Sigma^+ + \eta \Sigma^-) \mathbf{c}_k$$

$$H^{\text{int}} = \frac{1}{2} g \sum_{kk'} \{ (\mathbf{c}_k^+ \Sigma^+ \mathbf{c}_k) \cdot (\mathbf{c}_{k'}^+ \Sigma^- \mathbf{c}_{k'})$$

$$- \mathbf{c}_k^+ (\rho \Sigma^+ + \eta \Sigma^-) \mathbf{c}_k \} \tag{195}$$

where ρ and η are the so-called gap energies which are assumed to be independent of k for simplicity. Note that the Hamiltonian H^0 is already symmetry-broken. Here, we adopt a conventional method. In what follows, H^{int} is neglected, i.e., we start from the Green function due to the effective Hamiltonian and then take the interaction (158) into account. At this stage, we may expect the result that will be obtained in such a manner that the normal and superconducting states contribute additively.

The temperature Green function with the imaginary time τ is defined as

$$G_{kk'}^0(\tau) = -\langle T_\tau [\mathbf{c}_k(\tau) \mathbf{c}_{k'}^+] \rangle \tag{196}$$

where $\langle \cdots \rangle = \text{Tr}\{\rho_G \cdots\}$. The equation of motion of $G_{kk'}^0$ is

$$\partial_\tau G_{kk'}^0(\tau)$$

$$= -\partial_\tau [\theta(\tau) \langle \mathbf{c}_k(\tau) \mathbf{c}_{k'}^+(0) \rangle - \theta(-\tau) \langle \mathbf{c}_{k'}^+(0) \mathbf{c}_k(\tau) \rangle]$$

$$= \delta(\tau) \langle [\mathbf{c}_k(\tau), \mathbf{c}_{k'}^+(0)]_+ \rangle + \langle T\tau [\mathbf{c}_k(\tau), H^0]_-, \mathbf{c}_k^+(0) \rangle$$

$$= \delta_{kk'} + (\boldsymbol{\epsilon}_k \Sigma 3 + \rho \Sigma^+ + \eta \Sigma^-) G_{kk'}^0 \tag{197}$$

In the course of the above derivation, the commutator in Eq. (199) was used.

We make the Fourier transformation,

$$G_{kk'}^0(\tau) = \frac{1}{\beta} \sum_{\omega_n} e^{-i\omega_n \tau} G_{kk'}^0(\omega_n), \tag{198}$$

where $\beta = k_B T$ and k_B is the Boltzmann constant. Then the equation of motion becomes

$$(i\omega_n + \boldsymbol{\epsilon}_k \Sigma 3 + \rho \Sigma^+ + \eta \Sigma^-) G_{kk'}^0(\omega_n) = \delta_{kk'} \tag{199}$$

Namely,

$$G_{kk'}^0(\omega_n) = \frac{1}{i\omega_n - \boldsymbol{\epsilon}_k \Sigma 3 - \rho \Sigma^+ - \eta \Sigma^-}$$

$$= \delta_{kk'} \left\{ \frac{i\omega_n + \boldsymbol{\epsilon}_k \Sigma 3 + \rho \Sigma^+ + \eta \Sigma^-}{(i\omega_n)^2 - E_k^2} \right\} \tag{200}$$

where

$$E_k^2 = \epsilon_k^2 + \rho \eta \tag{201}$$

8.3. Spin Dynamics

The propagator in Eq. (200) is the 4×4 matrix. If we ignore ρ and η, this is reduced to the normal propagator. We have already tried this simple case.

Now we assume the terms responsible for the superconductivity as a perturbation. Namely ($\mathscr{S}$ is the electron propagator),

$$\mathscr{S}(\nu_n) = \frac{i\nu_n + \boldsymbol{\epsilon}_k \Sigma 3 + \rho \Sigma^+ + \eta \Sigma^-}{(i\nu_n)^2 - E_k^2}$$

$$= \frac{i\nu_n + \epsilon_k \Sigma 3}{(i\nu_n)^2 + \epsilon_k^2} + \frac{\rho \Sigma^+ + \eta \Sigma^-}{(i\nu_n)^2 + \epsilon_k^2} + \cdots \tag{202}$$

It is helpful to separate this relation into components and to manipulate each one individually. Noticing that

$$\sigma^0 + \sigma^3 = \sigma^\uparrow + \sigma^\downarrow$$

we have, for example by operating $\sigma^\uparrow$ followed by Tr,

$$\mathscr{S}^\uparrow(\nu_n) = \frac{i\nu_n + \boldsymbol{\epsilon}_k \Sigma 3 + \rho \Sigma^+ + \eta \Sigma^-}{(i\nu_n)^2 - E_k^2}$$

$$= \frac{1}{i\nu_n - \epsilon_{k\uparrow}} + \frac{\rho + \eta}{(i\nu_n)^2 + \epsilon_k^2} + \cdots$$

$$= \frac{1}{i\nu_n - \epsilon_{k\uparrow}} + \frac{\rho + \eta}{2\epsilon_{k\uparrow}} \left(\frac{1}{i\nu_n - \epsilon_{k\uparrow}} - \frac{1}{i\nu_n + \epsilon_{k\uparrow}} \right)$$

$$+ \cdots \tag{203}$$

In order to get the self-energy part of the nuclear propagator, we have to evaluate

$$\Sigma_{k;M-1,M}(\omega) = K^2 \frac{1}{\beta} \sum_{\nu_n} \mathscr{S}(\nu_n) \mathscr{S}(\nu_n + \omega) \tag{204}$$

The first-order term has already been evaluated in Eq. (181). Then we have to carry out the complicated manipulation due to the second term of the last line in Eq. (203). However, the combinations other than those satisfying the resonance condition $\omega \sim \epsilon_{ks}$ (see Eq. (182)) should give a small effect which is to be neglected.

We then consider that the procedures of the previous section need not be repeated, and we are allowed to multiply the results there by the factor $(\rho + \eta)/2\epsilon_{k\uparrow}$ as the perturbing correction or the superconducting effect.

8.4. Conclusion

If we review the present investigations from the viewpoints of the line shape problem in the magnetic resonance, three cases are clearly distinguished. In the noninteracting case, the line shape is written in terms of the delta function. In the interacting case of the normal phase, it is presented by the Lorentz-like function, and in the superconducting phase it is further multiplied by a coherent factor; whereas the statistical factors referring to the nuclear states never change throughout.

For a superconductor, the present theory has almost nothing to give more than the current one has done. However, the theory is not merely to reproduce the experimental result, but to predict the mechanism hidden in observations, in such a way that the manipulations reveal step by step the working mechanism inside the matter. We might be satisfied with a slightly deeper understanding of the superconductivity.

Among various opinions we give, as an example, Scalpino's.[29] He pointed out three possibilities regarding the loss of the T_1 enhancement in the copper oxide superconductor:

- The d-wave single-particle density of states has logarithmic singularities, rather than the square-root singularity for the s wave gap.
- The coherent factor for the quasiparticle scattering vanishes for $k \sim (\pi, \pi)$ for a $d_{x^2-y^2}$ gap.
- The inelastic scattering acts to suppress the peak just as for an s wave.

Scalpino had the opinion that the theory of superconductivity is already so well furnished that other fundamental ideas beyond the original BCS one are almost needless, except for some smart equipment. As the phenomena observed in the copper oxide superconductor are rather qualitative and fairly clear-cut, the explanation for them must be simple. It is expected that a quantum-chemical speculation could make this possible.

Let us address scalpino's opinion. The divergent character of Eq. (154) seems a merely mathematical problem. The difference between Eq. (185) and that (which will be obtained) for the superconducting case is the coherent factor, (203). In the case of a BCS superconductor, it holds that $E_k \gg \rho$ so that the enhancement of the spin-lattice relaxation time T_1 is observed due to this factor, which leads to the superconductivity. However, in the case of a high-temperature superconductor, $\rho, \eta \sim E_k$, as has been seen in the previous chapter, we cannot observe the sharp onset of superconductivity. Then we miss the coherent effect.

There is presumably a simpler reason why the T_1 enhancement is not observed. In copper oxide, electrons responsible for superconductivity are probably the d electrons; then we have the vanishing interaction term if it is the Fermi contact term between a nucleus and an electron—say, $F(R, r) \sim \delta(R - r)$ in Eq. (159).

9. GINZBURG–LANDAU THEORY FROM THE BCS HAMILTONIAN

The macroscopic quantum theory of superconductivity has been given by Ginzburg and Landau.[9] This looks rather phenomenological; however, since a microscopic justification has been provided by Gorkov and others,[16, 30] it has a substantial foundation. We also reviewed the GL theory, in the introduction of Section 4, from the viewpoint of Landau's general theory of phase transitions. It is crucial that the Lagrangian of the system is written as the fourth-order function of the order parameter Ψ, which is the electron field. If the coefficients of the second- and fourth-order terms are suitably chosen, the new ground state shapes a champagne bottle, or a Mexican hat is built. If electrons moves on this flat route around the top, the derivative of the orbital vanishes or the kinetic energy vanishes, which implies that the wave function is rigid. We may say that the electron mass is effectively zero. We thus have the current only due to the vector potential, i.e., the diamagnetic current. This causes the Meissner effect.

The GL theory is quite useful for applications, since the microscopic theory by itself is too complicated for manipulating large-scale problems. If we can solve the GL equation for a real problem under an appropriate boundary condition, various information on this system can be obtained.[10] The macroscopic wave function or GL order parameter Ψ is related to the gap function and is understood as the field of Cooper pairs. The parameters in the GL equation are also written in the microscopic terms or by the experimental values. In Ref. [28], the GL function Ψ is derived directly from the BCS Hamiltonian, not via the gap function or the anomalous Green function related to the gap function. The electron–electron interaction composed of the four fermion operators is changed by the Hubbard-Stratonovitch transformation to an auxiliary complex boson field ϕ, in which electrons behave as if they were free. Using the path-integral method, we can carry out the integration up to the quadratic terms of the electron operators. If we carefully analyze the resulting effective Lagrangian for the boson field, we will find that this boson field, which is described by a complex function, suggests a phase transition; the condensation arises in particles described by the real part of the boson field, while particles in the imaginary (or phase) part turn out to be massless Goldstone bosons. It is then clear that the boson field is to be the GL order parameter. In the course of analysis, the concept of supersymmetry is effectively used.

9.1. BCS Theory

We assume the classical field of an electron is described by the Grassmann algebra or the anticommuting c-number; namely, the creation and annihilation operators a_k^* and a_k are treated as anticommuting c-numbers. The BCS Hamiltonian is written as

$$H = H_0 + H_{\text{int}}$$

$$H_0 = \sum_{k\sigma} \epsilon_{k\sigma} a_{k\sigma}^* a_{k\sigma}$$

$$H_{\text{int}} = \sum_{kk'} -g_{k-k,\,-k'k'}(a_{k\uparrow}^* a_{-k\downarrow}^*)(a_{-k'\downarrow} a_{k'\uparrow})$$

$$g_{k-k,\,k'-k'} > 0 \qquad (205)$$

and

$$-g_{k-k,\,-k'k'} = \int d\mathbf{r}_1 d\mathbf{r}_2\; \chi_{k\uparrow}^*(\mathbf{r}_1)\chi_{-k\downarrow}^*(\mathbf{r}_2)v(\mathbf{r}_1,\mathbf{r}_2)$$

$$\times \chi_{-k'\downarrow}(\mathbf{r}_2)\chi_{k'\uparrow}(\mathbf{r}_1) \qquad (206)$$

where $v(\mathbf{r}_1,\mathbf{r}_2)$ is the effective coupling giving an attractive character for the electron–electron interaction. Here, the summation convention that repeated indices imply summation is used. This is helpful in facilitating the manipulation. We would consider that the BCS Hamiltonian is an attractive interaction between Cooper pairs rather than an attractive interaction between electrons, (Figs. 3 and 4). In the following, it is assumed that $\epsilon_{k\sigma}$ is independent of spin and $g_{k-k,\,k'-k'}$ is independent not only of spin but also, finally, of k and k'.

Let us investigate the partition function

$$Z = \mathrm{Tr} e^{-\beta(H_0+H_{\text{int}})} \qquad (207)$$

This is expressed by the use of the path-integral method.[31, 32] The spirit of the Feynman path-integral is sometimes written as follows: the (imaginary) time interval $0 \to \beta$ is sliced into numerous pieces, each being labeled by τ_p. Since each slice is made arbitrarily small, the quantum effect arising from the commutation relation can be neglected, so that the operators are regarded as c-numbers in each slice. Instead, this c-number function can take any value even in the small time slice. Connecting these precise values from $0 \to \beta$, we can draw all of the paths in this interval. If we count the effects from all of these paths, the quantum-mechanical result of the subject can be obtained. However, this statement seems rather misleading.

Feynman's path-integral is the third method of quantization.[33] We begin with the classical treatment, and then if we apply the path-integral procedure to it, the quantum effect is certainly taken into account. This corresponds to the conceptual development from the geometric optics to the physical optics. The Bose system (in the quantum-mechanical sense) is written by an ordinary c-number, but
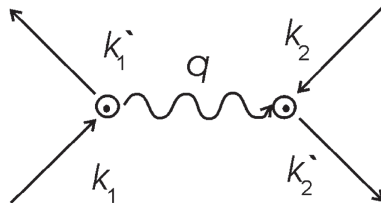
Fig. 3. In the BCS model, superconductivity arises due to the attractive electron–electron interaction which appears owing to the scattering by phonons.
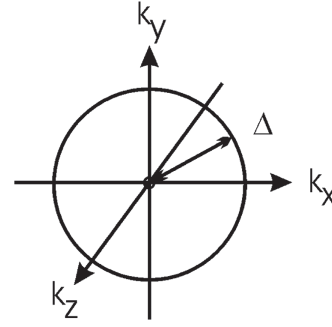
Fig. 4. Excitation of the ground state of a Cooper pair demonstrates the presence of the energy gap Δ, which is (very approximately) isotropic in the momentum space.

the Fermi system should be described by a Grassmann number. Thus, we do not worry about the commutation relations of field operators and obtain

$$Z = \mathrm{Tr}\; e^{-\beta\hat{H}}$$

$$= \lim_{N\to\infty} \int \prod_{p=1}^{N} da^*(\tau_p)da(\tau_p)$$

$$\times \exp\sum_p [\epsilon(\dot{a}^*(\tau_p)a(\tau_p)-H(\tau_p)], \quad \epsilon=\beta/N$$

$$= \int \mathscr{D}a^*(\tau)\mathscr{D}a(\tau)\exp \int_0^\beta d\tau\{a_{k\sigma}^*(\tau)(-\partial_\tau-\epsilon_{k\sigma})a_{k\sigma}(\tau)$$

$$+ g_{k-k,\,-k'k'}a_{k\uparrow}^*(\tau)a_{-k\downarrow}^*(\tau)a_{-k'\downarrow}(\tau)a_{k'\uparrow}(\tau)\} \qquad (208)$$

where

$$\mathscr{D}a^*(\tau)\mathscr{D}a(\tau) = \prod_{p=1}^{\infty} da_{k\sigma}^*(\tau_p)da_{k\sigma}(\tau_p) \qquad (209)$$

9.2. Hubbard-Stratonovitch Transformation

Difficulty lies in the quartic term of the electron–electron interaction. Let us define

$$B_\alpha^* = a_{k\uparrow}^* a_{-k\downarrow}^* \quad \text{and} \quad B_{\alpha'} = a_{-k'\downarrow}a_{k'\uparrow} \qquad (210)$$

so as to write, in each time slice,

$$g_{k-k,\,-k'k'}a_{k\uparrow}^* a_{-k\downarrow}^* a_{-k'\downarrow}a_{k'\uparrow} = g_{\alpha\alpha'}B_\alpha^* B_{\alpha'} \qquad (211)$$

This is simplified by using the identity called the Hubbard.Stratonovitch transformation.[34] We introduce a complex boson field ϕ, since $(B_\alpha)^* \neq B_\alpha$:

$$1 = \int_{-\infty}^{\infty} d\phi^* \, d\phi e^{-\pi\phi^*\phi}$$

$$= \int_{-\infty}^{\infty} d\phi^* \, d\phi e^{-\pi(\phi^*-i\sqrt{g/\pi}B^*)(\phi+i\sqrt{g/\pi}B)}$$

$$= \int_{-\infty}^{\infty} d\phi^* \, d\phi e^{-\pi\phi^*\phi+i\sqrt{g\pi}(B^*\phi-B\phi^*)}e^{-gB^*B}$$

namely

$$\int_{-\infty}^{\infty} d\phi^* \, d\phi e^{-\pi\phi^*\phi+i\sqrt{g\pi}(B^*\phi-B\phi^*)} = e^{gB^*B} \qquad (212)$$

where we have the definition

$$d\phi^* d\phi = d(\mathrm{Re}\phi)d(\mathrm{Im}\phi)^a \tag{213}$$

We cannot apply this identity for the quantum-mechanical partition function because of the noncommutativity of the operators involved, but now we have no trouble since, in the present path-integral treatment, operators turn out to be c-numbers. Then Eq. (208) becomes

$$Z = \int \int \mathcal{D}a^*(\tau)\mathcal{D}a(\tau)\,d\phi^*(\tau)\,d\phi(\tau)$$

$$\times \exp \int_0^\beta d\tau \{ -a_{k\sigma}^*(\tau)\Delta_{k\sigma}^{-1}(\tau)a_{k\sigma}(\tau) - \pi\phi_\alpha^*(\tau)\phi_{\alpha'}(\tau)$$

$$+ i\sqrt{\pi}g_{k-k,\alpha'}a_{k\uparrow}^*(\tau)a_{-k\downarrow}^*(\tau)\phi_{\alpha'}(\tau)$$

$$- i\sqrt{\pi}g_{\alpha,-k'k'}a_{-k'\downarrow}(\tau)a_{k'\uparrow}(\tau)\phi_\alpha^*(\tau)\} \tag{214}$$

with

$$\Delta_{k\sigma}^{-1}(\tau) = -\partial_\tau - \epsilon_{k\sigma}$$

The essential feature of this expression is that the operator appearing in the exponent in Eq. (214) is quadratic only in a_k and a_k^*, so that the evaluation with respect to the fermion variables is similar to the evaluation for the noninteracting system, in which particles are moving in an effective boson field ϕ_k. Equation (214) shows that, inside the exponent, Z is a weighted average of the second and third terms over the field ϕ_α.

9.3. Fourier Transform

The Fourier transformation with respect to τ is performed as

$$a_k(\tau) = \sum_{\omega_n} e^{i\omega_n \tau} a_k(\omega_n), \quad \phi_\alpha(\tau) = \sum_{\nu_n} e^{i\nu_n \tau}\phi_\alpha(\nu_n)$$

$$\omega_n = (2n+1)\pi/\beta, \quad \nu_n = 2n\pi/\beta \tag{215}$$

Note that ω_n refers to a fermion, and ν_n to a boson.

Using the above and the relation

$$\int_0^\beta d\tau\, e^{i(\omega_n - \omega_m)\tau} = \beta\delta_{nm} \tag{216}$$

we have

$$Z = \int \mathcal{D}a^*(\omega_n)\mathcal{D}a(\omega_n)\mathcal{D}\phi^*(\nu_n)\mathcal{D}\phi(\nu_n)$$

$$\times \exp \sum_{\omega_n \nu_n} \{ -\beta a_{k\sigma}^*(\omega_n)\Delta_{k\sigma}(i\omega_n)^{-1}a_{k\sigma}(\omega_n)$$

$$- \beta\pi\phi_\alpha^*(\nu_n)\phi_{\alpha'}(\nu_n)$$

$$+ i\sqrt{\pi}g_{k-k,\alpha'}a_{k\uparrow}^*(\omega_n + \nu_n)a_{-k\downarrow}^*(\omega)\phi_{\alpha'}(\nu_n)$$

$$- i\sqrt{\pi}g_{\alpha,-k'k'}a_{k'\downarrow}(\omega_n)a_{-k'\uparrow}(\omega_n + \nu_n)\phi_\alpha^*(\nu_n)\} \tag{217}$$

---

^{a}Actually, $d\phi^R d\phi^I = 1/2i d\phi^* d\phi$. The constants are adsorbed in the normalization factor.

where $\Delta_{k\sigma}(i\omega_n)$ is Green's function, given as

$$\Delta_{k\sigma}(i\omega_n) = \frac{1}{i\omega_n - \epsilon_{k\sigma}} \tag{218}$$

We can observe the following in Eq. (217): the third line tells us that, at the vertex indicated by the coupling $g_{k-k,\alpha'}$, the boson field $\phi_{\alpha'}$ sinks, and then the particle pair $a_{k\uparrow}^* a_{-k\downarrow}^*$ arises. The last line displays the reverse phenomenon. Note the energy conservations at vertices.

9.4. Nambu Spinor

At this stage, we would rather use a spinor notation due to Nambu[11] that is very useful for investigating the superconductivity:

$$\mathbf{a}_k = \begin{pmatrix} a_{k\uparrow} \\ a_{-k\downarrow}^* \end{pmatrix}, \quad \mathbf{a}_k^* = (a_{k\uparrow}^* \quad a_{-k\downarrow})$$

$$\mathbf{a}_{-k} = \begin{pmatrix} a_{-k\downarrow} \\ a_{k\uparrow}^* \end{pmatrix}, \quad \mathbf{a}_{-k}^* = (a_{-k\downarrow}^* \quad a_{k\uparrow}) \tag{219}$$

It is instructive to manipulate the complicated last line in (217) in the present language: it has a structure such that

$$\phi_{\alpha'}a_{k\uparrow}^* a_{-k\downarrow}^* - \phi_\alpha^* a_{-k'\downarrow}a_{k'\uparrow}$$

$$= \phi_{\alpha'}(a_{k\uparrow}^* \quad a_{-k\downarrow})\begin{pmatrix} 1 \\ 0 \end{pmatrix}(0 \quad 1)\begin{pmatrix} a_{k\uparrow} \\ a_{-k\downarrow}^* \end{pmatrix}$$

$$- \phi_\alpha^*(a_{-k'\downarrow}^* \quad a_{k'\uparrow})\begin{pmatrix} 0 \\ 1 \end{pmatrix}(1 \quad 0)\begin{pmatrix} a_{-k'\downarrow} \\ a_{k'\uparrow}^* \end{pmatrix}$$

$$= \phi_{\alpha'}\,\mathbf{a}_k^*\sigma^+\mathbf{a}_k + \phi_\alpha^*\mathbf{a}_{-k'}^*\sigma^-\mathbf{a}_{-k'}$$

The positive sign in the second term is due to the Grassmann character of $a_{k\uparrow}$ and $a_{-k\downarrow}$. Also,

$$a_{k\sigma}^*\epsilon_k a_{k\sigma} = \mathbf{a}^*\sigma_k^3\epsilon_k\mathbf{a}_k \tag{220}$$

since $\epsilon_k = \epsilon_{-k}$.

In the above, the Pauli matrices and related ones are rewritten as

$$\sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma^+ = \frac{1}{2}(\sigma^1 + i\sigma^2) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\sigma^- = \frac{1}{2}(\sigma^1 - i\sigma^2) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{221}$$

Equation (217) is now written as

$$Z = \iint \mathcal{D}\mathbf{a}^*\mathcal{D}\mathbf{a}\mathcal{D}\boldsymbol{\phi}^*\mathcal{D}\boldsymbol{\phi} \exp \sum_{\omega_n \nu_n} \{ -\beta\pi\phi_\alpha^*(\nu)\phi_\alpha(\nu)$$

$$+ \beta\mathbf{a}_k^*(\omega_n)(i\omega_n - \epsilon_k\sigma^3)\mathbf{a}_k(\omega_n)$$

$$+i\beta\sqrt{\pi g_{\alpha,k'-k'}}\phi_\alpha(\nu_n)\mathbf{a}_{k'}^*(\omega_n+\nu_n)\sigma^+\mathbf{a}_{k'}(\omega_n)$$

$$+i\beta\sqrt{\pi g_{\alpha',k-k}}\phi_{\alpha'}^*(\nu_n)\mathbf{a}_{-k}^*(\omega_n)$$

$$\times \sigma^-\mathbf{a}_{-k}(\omega_n+\nu_n)\} \tag{222}$$

We can integrate with respect to fermion variables: note that[31]

$$\int dz^*dz e^{(z^*Az)} = \det A \quad \text{for fermion}$$

$$\int dz^*dz e^{(z^*Az)} = (\det A)^{-1} \quad \text{for boson} \tag{223}$$

Using the upper one, we can immediately obtain

$$Z = \int \mathscr{D}\boldsymbol{\phi}^*\mathscr{D}\boldsymbol{\phi}\exp\sum_{\nu_n}\left\{-\beta\pi\phi_\alpha^*(\nu)\phi_\alpha(\nu)\right.$$

$$+\det\left\|\sum_{\omega_n}\beta(i\omega_n-\epsilon_k\sigma^3)+i\beta\sqrt{\pi g_{\alpha,k'-k'}}(\phi_\alpha(\nu_n)\sigma^+\right.$$

$$\left.+\phi_{\alpha'}^*(\nu_n)\sigma^-)\Big\|\right\} \tag{224}$$

where we have made use of a symmetry property, $g_{\alpha,k'-k'} = g_{\alpha',k-k}$, and $\|\cdots\|$ stands for a matrix. This can be also rewritten as

$$Z = \int \mathscr{D}\phi^*\mathscr{D}\phi\exp^{-\beta W(\phi)} \tag{225}$$

with the effective action for the boson field

$$W(\phi) = \pi\sum_{\nu_n}\phi_\alpha^*(\nu_n)\phi_\alpha(\nu_n) - \frac{1}{\beta}\sum_{\omega_n}\text{Tr}\log\beta$$

$$\times\left\{(i\omega_n-\epsilon_k\sigma^3)+i\sum_{\nu_n}\sqrt{u_{\alpha,k}}(\phi_\alpha(\nu_n)\sigma^+\right.$$

$$\left.+\phi_\alpha^*(\nu_n)\sigma^-)\right\} \tag{226}$$

where the relation $\log\cdot\det = \text{Tr}\cdot\log$ and the simplified notation

$$u_{\alpha,k} = \pi g_{\alpha,k'-k'} = \pi g_{\alpha',k-k} \tag{227}$$

have been used.

By employing the steepest descent method, we can obtain a particular ϕ, by optimizing $W(\phi)$, which will be denoted as $\bar{\phi}$. For example, by differentiating $W(\phi)$ with respect to $\phi_\delta^*(\nu_n)$, we have

$$\frac{\partial W(\phi)}{\partial \phi_\delta^*} = \pi\phi_\alpha - \frac{1}{\beta}\sum_{\omega_n}\text{Tr}$$

$$\times\frac{i\sqrt{u_{\delta,k}}\sigma^-}{(i\omega_n-\epsilon_k\sigma^3)+i\sqrt{u_{\alpha,k}}(\phi_\alpha(\nu_n)\sigma^++\phi_\alpha^*(\nu_n)\sigma^-)} = 0 \tag{228}$$

We thus obtain

$$\pi\bar{\phi}_\delta(\nu_n) = \frac{1}{\beta}\sum_{i\omega_n}\frac{\sqrt{(u_{\delta,k}u_{\alpha,k})}\cdot\bar{\phi}_\alpha}{(i\omega_n)^2-E_k^2} \tag{229}$$

where

$$E_k^2(\nu) = \epsilon_k^2 + \sqrt{(u_{\alpha,k}u_{\alpha',k})}\bar{\phi}_\alpha^*(\nu_n)\bar{\phi}_{\alpha'}(\nu_n) \tag{230}$$

Note that the field strength $\phi_\alpha^*(\nu_n)\phi_{\alpha'}(\nu_n)$ has the dimension of energy. In obtaining Eq. (229), we first rationalize the denominator, and then the Tr operation on σ's is carried out. The numerator that remains is the coefficient of $\text{Tr}\sigma^+\sigma^- = 1$. A similar equation is obtained for ϕ^*. Equation (229) corresponds to the gap equation.

Now we employ an approximation in the rest of this study where, as was mentioned at the beginning, $u_{\alpha,k} = u$ (a positive constant). Thus, to the first approximation, ϕ is nearly constant:

$$\frac{\pi}{u} = \frac{1}{\beta}\sum_{\omega_n}\frac{1}{(i\omega_n)^2-E_k^2} \tag{231}$$

Doing the frequency sum, we get

$$\frac{1}{\beta}\sum_{\omega_n}\frac{1}{i\omega_n-x} = \pm n(x) \tag{232}$$

where $n(x)$ is the Fermi or Bose function according to whether ω_n is odd or even, respectively, and we obtain (for fermions)

$$\frac{\pi}{u} = \frac{n(E_k)-n(-E_k)}{2E_k} = \frac{\tanh(\beta E_k/2)}{2E_k} \tag{233}$$

From the above relation combined with Eq. (229), we can estimate $\bar{\phi}$, which corresponds to the gap energy.

9.5. Critical Temperature

It is straightforward to obtain the critical temperature, T_c, for the superconductivity from Eq. (233).[15] Here, it is repeated for completeness. In the limit $T \to T_c$, the gap, or ϕ_α in the present case, disappears. The summation over k is approximately replaced by the integration

$$\frac{2\pi}{uN(0)} = \int_0^{\omega_D}\frac{d\epsilon}{\epsilon}\tanh\frac{\epsilon}{2k_BT_c} \tag{234}$$

where $N(0)$ is the state density at the Fermi surface, and the cutoff parameter ω_D is, in the case of the BCS theory, the Debye frequency of phonons associated with the attractive interaction between electrons.

The integration in Eq. (241) proceeds as follows:

$$\int_0^{\omega_D}\frac{d\epsilon}{\epsilon}\tanh\frac{\epsilon}{2k_BT_c}$$

$$= \int_0^{\beta_C\omega_D/2}\frac{dz}{z}\tanh z \quad (z = \epsilon\beta_c/2)$$

$$= \log z\tanh z]_0^{\beta_c\omega_D/2} - \int_0^{\beta_c\omega_D/2}dz\log z\,\text{sech}^2 z$$

$$\approx \log\frac{\beta_c\omega_D}{2} - \int_0^\infty dz\log z\,\text{sech}^2 z\left(\tanh\frac{\beta_c\omega_D}{2}\approx 1\right)$$

$$= \log\frac{\beta_c\omega_D}{2} + \log\frac{4e^\gamma}{\pi} \tag{235}$$

Combined with (233), this yields

$$\log \frac{\beta_c \omega_D}{2} = \frac{2\pi}{uN(0)} - \log \frac{4e^\gamma}{\pi} \tag{236}$$

where $\gamma = 0.5772$ is Euler's constant. This relation will be used in the next section. Simple rearrangements yield

$$T_c \approx 1.13 \omega_D e^{-2\pi/N(0)u} \tag{237}$$

9.6. Temperature Dependence of ϕ

For the later investigation, we derive a temperature dependence of ϕ_α near the critical temperature.[16] Coming back to (231) and restoring the hidden summation with respect to k, we can rewrite this as

$$\frac{2\pi}{uN(0)} = \frac{1}{\beta} \sum_{\omega_n} \int_0^{\omega_D} d\epsilon \frac{1}{(i\omega_n)^2 - (\epsilon^2 + u|\phi_\alpha|^2)} \tag{238}$$

Considering that $|\phi_\alpha|^2 \ll 1$ near the critical temperature, we expand the above as

$$\frac{2\pi}{uN(0)} = \frac{1}{\beta} \sum_{\omega_n} \int_0^{\omega_D} d\epsilon \left\{ \frac{1}{(i\omega_n)^2 - \epsilon^2} + \frac{u|\phi_\alpha|^2}{((i\omega_n)^2 - \epsilon^2)^2} \right.$$
$$\left. + \frac{(u|\phi_\alpha|^2))^2}{((i\omega_n)^2 - \epsilon^2)^3} + \cdots \right\} \tag{239}$$

For the convergent integrals which are the second and third terms, the integration limit is extended to infinity, and then we obtain (putting $\epsilon = \omega \tan \theta$)

$$\frac{2\pi}{uN(0)} = \int_0^{\omega_D} \frac{d\epsilon}{\epsilon} \tanh \frac{\beta \epsilon}{2} + \frac{1}{\beta} \frac{\pi}{4} u|\phi_\alpha|^2 \sum \frac{1}{\omega_n^3}$$
$$+ \frac{1}{\beta} \frac{3\pi}{16} (u|\phi_\alpha|^2)^2 \sum \frac{1}{\omega_n^5} + \cdots \tag{240}$$

The integration of the first term on the right-hand side, which is similar to (235), has β instead of β_c. Then, using (236), we have, in the lowest approximation,

$$\log \frac{\beta_c}{\beta} = \frac{1}{\beta} \frac{\pi}{4} u|\phi_\alpha|^2 \sum \frac{1}{\omega_n^3} + \cdots \tag{241}$$

Using

$$\sum_0^\infty \frac{1}{(2n+1)^p} = \frac{2^p - 1}{2^p} \zeta(p) \tag{242}$$

in (7.36), we have the temperature dependence of ϕ_α,

$$\sqrt{u|\phi_\alpha|^2} = \pi k_B T_c \sqrt{\frac{16}{7\zeta(3)}} \sqrt{1 - \frac{T}{T_c}} \qquad \zeta(3) = 1.202 \tag{243}$$

which is the same as that of the energy gap.[15]

9.7. Dynamics of the Boson Field; Symmetry Breaking

The boson field $\phi_\alpha(\nu_n)$, which satisfies (227), is written as $\bar{\phi}_\alpha$, so that

$$\phi_\alpha(\nu_n) = \bar{\phi}_\alpha + (\phi_\alpha - \bar{\phi}_\alpha) = \bar{\phi}_\alpha + \Phi_\alpha(\nu_n) \tag{244}$$

Now $\Phi_\alpha(\nu_n)$ becomes a physical or fluctuation component in solid-state physics. Our aim is to find the effective Lagrangian or Hamiltonian for it.

In order to find the terms proportional to $\Phi_\alpha(\nu_n)$ in (244), we first observe that

$$\phi_\alpha(\nu_n)\tau^+ + \phi_\alpha^*(\nu_n)\tau^-$$
$$\equiv \phi_\alpha(\nu_n) \cdot \tau = \phi_\alpha^{(a)}(\nu_n)\tau^{(a)} \quad a = 1, 2$$
$$= \bar{\phi}_\alpha(\nu_n) \cdot \tau + \Phi_\alpha(\nu_n) \cdot \tau \tag{245}$$

Expanding $W(\phi)$ in (226) in $\Phi_\alpha(\nu_n)$ and noticing that, upon the Tr operation, the odd terms with respect to τ will vanish. We have

$$W(\phi^*, \phi)$$
$$= \pi \sum_{\nu_n} \phi_\alpha^* \phi_\alpha - \frac{1}{\beta} \sum_{\omega_n} \text{Tr} \log \beta(i\omega_n - \epsilon \tau^3 - i\sqrt{u}(\bar{\phi}_\alpha \cdot \tau)$$
$$- \frac{1}{\beta} \sum_{\omega_n \nu_n} \sum_n^{even} \frac{1}{n} \text{Tr}[\Delta(\omega_n) i\sqrt{u}(\Phi_\alpha(\nu_n) \cdot \tau)]^n \tag{246}$$

where

$$\Delta_k(\omega_n) = \frac{i\omega_n + \epsilon_k \tau^3 + i\sqrt{u}(\bar{\phi}_\alpha \cdot \tau)}{(i\omega_n)^2 - E_k^2} \tag{247}$$

Note that now the propagator includes the mean-field effect. What we are interested in is the second line of Eq. (246).

The term with $n = 2$ is precisely written as

$$\frac{-1}{2\beta} \sum_{\omega_n \nu_n} \text{Tr} u \Delta_k(\omega_n)(\Phi_\alpha^{(a)}(\nu_n)\tau^{(a)})\Delta_{k+\alpha}(\omega_n + \nu_n)$$
$$\times (\Phi_\alpha^{*(a')}(\nu_n)\tau^{(a')})$$
$$= \sum_{\nu_n} u|\Phi_\alpha(\nu_n)|^2 P_\alpha(\nu_n) \tag{248}$$

where careful manipulations about τ's are required. Except for the explicit ones combined with Φ's, we have τ's inside Δ's. Let us call the terms with $a = a' = 1$ and $a = a' = 2$ the direct interactions, and the terms with $a = 1$, $a' = 2$ and $a = 2$, $a' = 1$ the cross interactions. We then have

$$P_\alpha(\nu_n) = \frac{-2}{\beta} \sum_{\omega_n} \frac{i\omega_n(i\omega_n + i\nu_n) - \epsilon_k \epsilon_{k+\alpha} + u\bar{\phi}^* \cdot \bar{\phi}}{[(i\omega_n)^2 - E_k^2][(i\omega_n + i\nu_n)^2 - E_{k+\alpha}^2]} \tag{249}$$

where the first two terms in the numerator arise from the direct interaction and the third from the cross interaction. Here, use has been made of the fact that $\text{Tr } \tau^3 \tau^+ \tau^3 \tau^- = -1$. Employing (231), we can carry out a lengthy but not difficult calculation of $P_\alpha(\nu_n)$. Note that an even frequency ν_n has nothing to do with obtaining the Fermi functions. The result is

$$P_\alpha(\nu_n) = -n(E_k)(1 - n(E_{k+\alpha})) \frac{E_{k+\alpha} - E_k}{(i\nu)^2 - (E_{k+\alpha} - E_k)^2}$$
$$\times \left[\frac{E_{k+\alpha} E_k - \epsilon_{k+\alpha} \epsilon_k + u(\bar{\phi}^* \cdot \bar{\phi})}{E_{k+\alpha} E_k} \right] \tag{250}$$

Here, we again note that, in the square brackets, the first two terms are obtained from the direct interaction and the third term from the cross interaction.

It might be convenient, for the later investigation, to do the frequency sum for $P_\alpha(\nu_n)$:

$$\sum_{\nu_n} \frac{E_{k+\alpha} - E_k}{(i\nu_n)^2 - (E_{k+\alpha} - E_k)^2}$$

$$= \beta \frac{1}{\beta} \sum_{\nu_n} \frac{1}{2}\left[\frac{1}{i\nu_n - (E_{k+\alpha} - E_k)} - \frac{1}{i\nu_n + (E_{k+\alpha} - E_k)}\right]$$

$$= \frac{\beta}{2}[-n_B(E_{k+\alpha} - E_k) + n_B(-E_{k+\alpha} + E_k)]$$

$$= \frac{-\beta}{2}\coth\left[\frac{\beta(E_{k+\alpha} - E_k)}{2}\right]$$

where n_B is the Bose function, and use of Eq. (232) has been made for the even frequency ν_n. Then Eq. (250) becomes

$$\sum_{\nu_n} P_\gamma(\nu_n) = n(E_\alpha)(1 - n(E_{\alpha+\gamma}))\frac{\beta}{2}\coth\left[\frac{\beta(E_{\alpha+\gamma} - E_\alpha)}{2}\right]$$

$$\times \left[\frac{E_{\alpha+\gamma}E_\alpha - \epsilon_{\alpha+\gamma}\epsilon_\alpha + u(\bar{\phi}^* \cdot \phi)}{E_{\alpha+\gamma}E_\alpha}\right] \qquad (251)$$

We then obtain the effective action for ϕ up to the second order in Φ, as follows:

$$W_\alpha(\phi^*, \phi)$$

$$= \pi \sum_{\nu_n} \phi_\alpha^*(\nu_n)\phi_\alpha(\nu_n) - \frac{1}{\beta}\sum_{\omega_n\nu_n} \mathrm{Tr}$$

$$\times \log\{-\beta(i\omega_n - \epsilon_k\tau^3 - \sqrt{u}\bar{\phi}_\alpha(\nu_n)\cdot\tau)\}$$

$$- n(E_\alpha)(1 - n(E_{\alpha+\gamma}))\sum_{\nu_n} \frac{E_{k+\alpha} - E_k}{(i\nu)^2 - (E_{k+\alpha} - E_k)^2}$$

$$\times \left[\frac{E_{k+\alpha}E_k - \epsilon_{k+\alpha}\epsilon_k + u(\bar{\phi}^* \cdot \bar{\phi})}{E_{k+\alpha}E_k}\right] \qquad (252)$$

9.8. Instability

In order to discuss the dynamics of $\Phi_\alpha(\nu_n)$, we must obtain an expression for the action of $\Phi_\alpha(\nu_n)$ similar to that for $a_\alpha(\omega_n)$ given in the exponent of Eq. (208). Since we are interested in the energy region much lower than that for the electronic excitation $(E_{\alpha+\gamma} - E_\alpha)$, the denominator of $P_\alpha(\nu_n)$ in Eq. (250) is expanded as

$$\frac{1}{(i\nu)^2 - (E_{k+\alpha} - E_k)^2}$$

$$= \frac{-1}{(E_{k+\alpha} - E_k)^2}\left[1 + \frac{(i\nu_n)^2}{(E_{k+\alpha} - E_k)^2} + \cdots\right] \qquad (253)$$

Substituting this into $P_\alpha(\nu_n)$ in Eq. (250) and taking up the terms of the order of $(i\nu)^2$ in the above, we have

$$(i\nu_n)^2 + u(\bar{\phi}^*\bar{\phi})\frac{(E_{k+\alpha} - E_\gamma)^2}{E_{k+\alpha}E_k} + \cdots \qquad (254)$$

The second term is a small and complicated, but positive quantity. We thus obtain the effective Lagrangian for Φ up to the second order of $\Phi^*\Phi$:

$$\mathscr{L}_B \sim \Phi^*(i\nu_n)^2\Phi + \eta\Phi^*\Phi + \cdots, \quad \eta > 0 \qquad (255)$$

In the above, $i\nu_n$ is replaced by $\partial/\partial\tau$ in the future. At this stage, the details of η are immaterial except that this is positive.

To put forward the problem, we need the term proportional to $\Phi^*\Phi^*\Phi\Phi$. This is obtainable from the term with $n = 4$ in Eq. (246). Without any detailed calculation, we may presume a positive quantity for this, noted by Λ^2. Then the total Lagrangian of the boson field becomes

$$\mathscr{L}_B \sim \Phi^*(i\nu_n)^2\Phi + \eta\Phi^*\Phi - \Lambda^2\Phi^*\Phi^*\Phi\Phi \qquad (256)$$

This looks like the Lagrangian that Ginzburg and Landau have used for investigating the superconductivity. We thus expect a kind of phase transition. Let us optimize, with respect to Φ^*, the potential part of Eq. (256):

$$\mathscr{V} = -\eta\Phi^*\Phi + \Lambda^2\Phi^*\Phi^*\Phi\Phi \qquad (257)$$

$$\frac{\partial\mathscr{V}}{\partial\Phi^*} = -\eta\Phi + 2\Lambda^2\Phi^*\Phi\Phi$$

$$= (-\eta + 2\Lambda^2\Phi^*\Phi)\Phi = 0 \qquad (258)$$

If $\Phi = 0$, nothing happens; while, in the case of $\Phi \neq 0$, it is possible that

$$\overline{\Phi^*\Phi} = \frac{\eta}{2\Lambda^2} \equiv \bar{a}^2 \qquad (259)$$

We now put

$$\Phi = (\rho + \bar{a})e^{i\theta} \qquad (260)$$

Namely, only the radial part is affected. This choice is allowed in the spirit of the unitary gauge. If we insert this into (257), it follows that

$$\mathscr{V} = \Lambda^2[(\rho + \bar{a})^2 - \bar{a}^2]^2 - \Lambda^2\bar{a}^4$$

$$= \Lambda^2[\Phi^*\Phi - \bar{a}^2]^2 - \Lambda^2\bar{a}^4 \qquad (261)$$

Observing the final result, we realize that the potential becomes minimum at $|\Phi| = \bar{a}$; namely, at this position apart from the origin, $|\Phi| = 0$, which corresponds to the HF state. The mass of the field Φ is given by the coefficient of $\Phi^*\Phi$, which is $4\Lambda^2\bar{a}^2$ for a particle of the ρ field, while the term involving θ is completely lost. That is to say, the particle in the θ field is massless, and it is called the Goldstone boson. This is due to the occurrence of the infinite degeneracies along the direction perpendicular to the ρ coordinate.

9.9. Supersymmetry

The total Lagrangian of the system is

$$\mathscr{L}_{\text{tot}} = \mathscr{L}_e + \mathscr{L}_B + \mathscr{L}_{\text{int}} \tag{262}$$

where

$$\mathscr{L}_e = \mathbf{a}_i^*(i\omega_n - \epsilon_i\tau^3)\mathbf{a}_i$$

$$\mathscr{L}_B = -\dot{\Phi}^*\dot{\Phi} - \Lambda^2[\Phi^*\Phi - \bar{a}^2]^2$$

$$\mathscr{L}_{\text{int}} = -i\sqrt{u}(\Phi\mathbf{a}^*\tau^+\mathbf{a} + \Phi^*\mathbf{a}^*\tau^-\mathbf{a}) \tag{263}$$

In the above, the second line is obtained from Eqs. (256) and (261), and then the third line from Eq. (245) supplied by necessary terms, and a compact notation is used, and the immaterial constant terms are omitted. The $\mathscr{L}$ in the above is, strictly speaking, the Lagrangian density, and the action which we are interested in is the space–time integral of the Lagrangian density, so that the partial integration with respect to τ (after the replacement $i\nu_n \to \partial_\tau$) gives the first term with the minus sign. If we define the momentum conjugate to Φ,

$$\Pi = \frac{\partial\mathscr{L}_{\text{tot}}}{\partial\dot{\Phi}} = -\dot{\Phi}^* \quad \Pi^* = \frac{\partial\mathscr{L}_{\text{tot}}}{\partial\dot{\Phi}^*} = -\dot{\Phi} \tag{264}$$

the total Hamiltonian for the boson field is obtained as

$$\mathscr{H}_{\text{tot}} = \Pi^*\dot{\Phi} + \Pi\dot{\Phi}^* - \mathscr{L}$$
$$= \Pi^*\Pi + i\sqrt{u}(\mathbf{a}^*\Phi\tau^+\mathbf{a} + \mathbf{a}^*\Phi^*\tau^-\mathbf{a})$$
$$+ \Lambda^2[\Phi^*\Phi - \bar{a}^2]^2 \tag{265}$$

The momenta, Π^* and Π conjugate to Φ^* and Φ respectively, have the properties

$$[\Pi, f(\Phi^*, \Phi)]_- = \frac{\partial}{\partial\Phi}f(\Phi^*, \Phi)$$

$$[\Pi^*, f(\Phi^*, \Phi)]_- = \frac{\partial}{\partial\Phi^*}f(\Phi^*, \Phi) \tag{266}$$

since we are now dealing with the classical operators in the framework of the path-integral formalism.

Let us turn to a supersymmetric treatment.[35–37] The fermionic composite charge operators are defined as

$$Q^* = \Pi^*\mathbf{a}^* - i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\mathbf{a}^*\tau^-$$

$$Q = \Pi\mathbf{a} + i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\tau^+\mathbf{a} \tag{267}$$

First of all, we have to manipulate the commutator

$$[Q^*, Q]_+ = [\Pi^*\mathbf{a}^* - i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\mathbf{a}^*\tau^-$$
$$\times \Pi\mathbf{a} + i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\tau^+\mathbf{a}]_+ \tag{268}$$

Straightforward calculations give

$$[\Pi^*\mathbf{a}^*, \Pi\mathbf{a}]_+ = [\Pi^*\mathbf{a}^*, \mathbf{a}]_+\Pi - \mathbf{a}[\Pi, \Pi^*\mathbf{a}^*]_+$$
$$= \Pi^*[\mathbf{a}^*, \mathbf{a}]_+\Pi - \mathbf{a}[\Pi, \Pi^*]_+\mathbf{a}^* = \Pi^*\Pi$$

Here, for the Grassmann numbers, use has been made of the relation

$$[\mathbf{a}^*, \mathbf{a}]_+ = \frac{\partial}{\partial\mathbf{a}}\mathbf{a} - \mathbf{a}\frac{\partial}{\partial\mathbf{a}} = \frac{\partial\mathbf{a}}{\partial\mathbf{a}} + \mathbf{a}\frac{\partial}{\partial\mathbf{a}} - \mathbf{a}\frac{\partial}{\partial\mathbf{a}} = 1$$

Further,

$$[\Pi^*\mathbf{a}^*, i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\tau^+\mathbf{a}]_+$$
$$= [\Pi^*\mathbf{a}^*, i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)]_-\tau^+\mathbf{a}$$
$$- i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)[\tau^+\mathbf{a}, \Pi^*\mathbf{a}^*]_+$$
$$= [\Pi^*, i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)]_-\mathbf{a}^*\tau^+\mathbf{a}$$
$$- i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\tau^-\Pi^*[\mathbf{a}, \mathbf{a}^*]_+$$
$$= i\sqrt{u}\Phi\mathbf{a}^*\tau^+\mathbf{a}$$

and

$$[i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\mathbf{a}^*\tau^-, \Pi\mathbf{a}]_+$$
$$= [\Pi\mathbf{a}, i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)]_-\mathbf{a}^*\tau^-$$
$$- i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)[\mathbf{a}^*\tau^-, \Pi\mathbf{a}]_+$$
$$= [\Pi, i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)]_-\mathbf{a}\mathbf{a}^*\tau^-$$
$$- i\sqrt{u}(\Phi^*\Phi - \bar{a}^2)\tau^-\Pi[\mathbf{a}^*, \mathbf{a}]_+$$
$$= i\sqrt{u}\Phi^*\mathbf{a}\mathbf{a}^*\tau^- = -i\sqrt{u}\Phi^*\mathbf{a}^*\tau^-\mathbf{a}$$

The final term must be symmetrized:

$$[\mathbf{a}^*\tau^+, \tau^-\mathbf{a}]_+ \to \frac{1}{2}\{[\mathbf{a}^*\tau^+, \tau^-\mathbf{a}]_+ + [\mathbf{a}^*\tau^-, \tau^+\mathbf{a}]_+\} \tag{269}$$

$$= \frac{1}{2}\{[(0, a^*), (0, a)]_+ + [(b, 0), (b^*, 0)]_+\}$$

$$= \frac{1}{2}\begin{pmatrix} [b, b^*]_+ & 0 \\ 0 & [a^*, a]_+ \end{pmatrix} \tag{270}$$

$$= \frac{1}{2}\mathbf{1} \tag{271}$$

In the second line, b and b^*, which are used in literature, are defined.

We thus obtain the fundamental relation in the supersymmetric quantum mechanics,

$$\mathscr{H} = [Q, Q^*]_+ \tag{272}$$

if we endow, to the constant Λ^2 in (264), a specified value,

$$\Lambda^2 = 2u \tag{273}$$

which is reasonable.[37] However, as mentioned before, this had to be obtained analytically from the term with $n = 4$ in Eq. (252). If it is assumed that the present system is the case of supersymmetry, we can avoid this tedious calculation.

The nilpotency of the charge operators,

$$Q^2 = 0, \qquad (Q^*)^2 = 0 \tag{274}$$

is clearly preserved from $\mathbf{a}^2 = 0$ and $(\mathbf{a}^*)^2 = 0$. We have thus completed a supersymmetric analysis.

9.10. Towards the Ginzburg–Landau Equation

Now we can think about the GL equation. Since it concerns only the static part of the condensed boson field, we keep the first and third terms of Eq. (265). The first term is the kinetic part, while the last term is the potential part:

$$\mathscr{H}_{GL} = \Pi^*\Pi - \eta\Phi^*\Phi + \Lambda^2(\Phi^*\Phi)^2 \qquad (275)$$

with

$$\eta = u(\bar{\phi}^*\bar{\phi})\frac{(E_{k+\alpha} - E_\gamma)^2}{E_{k+\alpha}E_k}$$

As usual, the coefficients of $\Phi^*\Phi$ and $(\Phi^*\Phi)^2$ in the GL equation are a and b, respectively. It is crucial that a is negative, which is given by $-\eta$ in the present consideration. The temperature dependence of η is found through $u(\bar{\phi}^*\bar{\phi})$, as in Eq. (265). This is exactly the same as that obtained by Gorkov.[30]

9.11. Discussion

Some people seemed to be puzzled by the curious look of the GL equation when it was published: the superconductivity being a macroscopic, thermodynamically stable phase—why is it predicted by a Schrödinger-like wave function, to which the microscopic phenomena are subjected? Several years later, the microscopic theory was established by BCS, and soon Abrikosov had successfully correlated these two treatments. He made clear that the GL function is deeply concerned with the gap function characteristic of the superconductivity and is a wave function describing the condensed Cooper pairs.

The superconducting state is certainly a stable thermodynamical state, and a phase transition from the normal state to the superconducting state is interpreted as a long-distance correlation between the Cooper pairs. Yang[38] developed a unified treatment of the phase transition in terms of the density matrix. According to his treatment, the onset of the superconductivity is understood in such a way that the off-diagonal long-range order (ODLRO) of the second-order density matrix has a nonvanishing value. This concept is clearly related to London's rigid function, the quasiboson condensation being widely seen as a powerful model of superconductivity and the variational wave function tried by BCS.[3] Recently, Dunne et al.[39] applied the concept of ODLRO to argue the high-temperature superconductivity in copper oxide, where the attractive interaction between electrons is assumed to have originated from Friedel oscillations in the screened potential.

However, the previous presentation of Abrikosov looks to be a detour, a complicated and tedious procedure in which the condensed pair is characterized by an anomalous temperature Green function which is difficult to manipulate for beginners. Therefore, the direct way to reach the GL theory from the BCS Hamiltonian should be preferable. What we have done in the present investigation is the following: the auxiliary boson field driven by the Hubbard–Stratonovitch transformation to eliminate the quartic term of electron operators is just the GL function.

In conclusion, from the treatments used so far, the conditions which are necessary for the occurrence of superconductivity are:
(1) The wave function which means the ground-state average of operators of a Cooper pair must be complex or two-dimensional. If one of these two degrees of freedom gets a new stable structure, the other degree of freedom, whose direction is perpendicular to the former, offers the infinite degeneracy. In the Nambu theory, the first refers to the σ^1 direction, and the second to σ^2 in the fictitious spin space.
(2) The electron·electron interaction should be attractive, otherwise the negative coefficient of $\Phi^*\Phi$ in Eq. (275) cannot be obtained. In the present consideration, we have observed that this condition is established in the effective electron.electron interaction of the system involving the multiband structure.

However, we will discuss a little more the normal state under the usual condition. In the normal species, the coupling constant between electrons is intrinsically positive. However, if we are interested in the exchange interaction, i.e., the so-called Fock term with negative coupling, this is met by condition 2. This is a short range interaction, while the direct coupling is so strong as to overwhelm the exchange interaction.

Let us turn to the behavior of the quartic electron operators. It is unexpected that these are grouped into the pair operators of particle–particle and hole–hole, which do not conserve the particle number. Thus, it is natural to group them into a couple of particle–hole pairs. This choice makes the auxiliary boson function real.

The Hamiltonian which satisfies the above two conditions, looking like the BCS Hamiltonian, is the one with the dipole–dipole interaction. The simplest case is that of the intermolecular interaction due to the induced dipole–dipole interaction with a coupling constant-d:

$$H_d = -d\ a_r^* b_r^* b_s a_s \qquad (276)$$

where, for example, a_r^* and b_r^* are the creation operators for a particle and a hole, respectively. If the electron.electron interaction is screened sufficiently, this may be another possibility for the superconductivity of a molecular complex.

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