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Relationship between Ginzburg-Landau and BCS theory

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A generalization of the BCS ground state is suggested and leads to expectation values for the energy and the current density consistent with the Ginzburg-Landau expressions. $\Psi(R)$ describes the quantum-mechanical motion of the center of mass of the superconducting pairs, and $\Psi^*(R)\Psi(R)$ turns out to give the number of superconducting pairs per unit volume at R. Extension to finite temperatures appears to be a possibility.

I. INTRODUCTION

Inspired by the strong-coupling formulation of Eliashberg and Nambu, Gor'kov,[1] Schrieffer,[2] and others, for example Eilenberger,[3] have derived Ginzburg-Landau (GL) equations for superconductivity. Simplified treatments are worked out in the well-known textbook of de Gennes.[4] The expansion of Gor'kov has been extended to low temperatures by, for example, Werthamer.[5] In all these treatments the GL order parameter $\Psi(R)$ is identified with the spatially dependent gap function $\Delta(R)$ and found to be proportional to it. However, the form of the "kinetic energy" in GL suggests that $\Psi(R)$ has some direct relation to the motion of the center of mass of individual pairs. Discussion of electron tunneling is often done on the basis of the motion of the center of mass of the tunneling electron pair.[6] At the same time agreement with tunneling experiments can be obtained on the basis of the GL equations, with $\Psi(R)$ the order parameter.[7] In this paper a generalization of the BCS wave function is proposed, which leads by means of a natural expansion to precisely the GL equations at zero temperature. Moreover, $\Psi(R)$ describes the quantum-mechanical motion of the center of mass of the superconducting pairs, and $\Psi^*(R)\Psi(R)$ turns out to give the number of superconducting pairs per unit volume at R. Although the work is at zero temperature in order to convey the development in a relatively simple way, generalization to finite temperatures appears possible.

Of the standard derivations of the GL equation it is the simplified *ad hoc* parametrization of the BCS wave function described in de Gennes' book, already cited, which comes closest to the present approach. However, in that treatment it is not possible to give any first-principles interpretation to the coefficients $\alpha,\beta,1/(2m)$ in the GL equations. The treatment of Gor'kov[1] applies only in the neighborhood of $T=T_c$, and extensions to all temperatures give rise to equations more complicated than those of GL.[5] At the same time, it has been pointed out that GL equations appear to have some validity at lower temperatures.[8]

The requirements of a spatially inhomogeneous generalization of the BCS ground state are quite demanding. Analysis of tunneling experiments and other considerations suggest, as pointed out, that the GL function $\Psi(R)$ is actually related to the motion of the center of mass of the pairs. At the same time, $\Psi(R)$ is to be of the nature of an order parameter. The present treatment, as noted, differs from the standard derivation in the choice of expansion parameter. The familiar BCS coefficients u_k,v_k are taken as spatially independent, and identical with their choice in BCS. Ultimately, any slow inhomogeneity in a spatial coordinate R is carried in the trial function by an auxiliary function $C(R)$, which, in the absence of electromagnetic fields, becomes a constant, unity for the homogeneous BCS state, zero for the filled Fermi sea, i.e., for the normal metallic state. It is $C(R)$ which becomes the expansion parameter. In the general situation with fields, the constant of proportionality $\gamma(u_kv_k)$ by which $C(R)$ is multiplied to obtain $\Psi(R)$ leads to the interpretation of $\Psi^*(R)\Psi(R)$ as the number of superconducting pairs per unit volume, see Eqs. (28a) and (28b). At the same time, $\Psi(R)$ itself is seen to be associated with the motion of the center of mass of the electron pairs, and the kinetic-energy term in the GL equation becomes their true kinetic energy.

To obtain these physical results it is necessary to write down a first-principles wave function of, say, $2N$ electron coordinates, and separate them into center-of-mass and relative coordinates of pairs. This, incidentally, opens the possibility of including effects due to the internal motion of the pairs, which would arise for a sufficiently rapidly varying vector potential $\mathbf{A}$ or sufficiently short GL coherence length.

The separation of coordinates leads to a mixed system of bosons and fermions. In a series of papers, Girardeau has developed a formalism for such systems.[9] His work addresses a gas of atoms when both the coordinates of the nuclei and the internal coordinates of the electrons are of interest. In one of the papers he considers the application of his work to superconductivity, showing how to reduce his formalism to center-of-mass and relative coordinates for electronic pairs. This leads to a reformulation of the BCS ground state in terms of a description like that of Blatt and Matsubara, as a Bose-Einstein condensation.[10] It is interesting to note that in this sense the present paper can be viewed as an outgrowth of the Blatt-Matsubara picture; these authors pointed out that the fully condensed state needs generalization when there is a nonvanishing vector potential, with the inclusion of

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pairs $\mathbf{k}_1,\mathbf{k}_2$, for which the total quasimomentum $\mathbf{k}_1+\mathbf{k}_2$ no longer necessarily vanishes. For simplicity, and to make the paper self-contained, a direct development using from the outset relative and center-of-mass coordinates of electron pairs and without Girardeau's reformulation of the Hamiltonian is given here in Sec. III. Section II serves as an introduction, developing the suggested trial function when no fields are applied. Section IV completes the paper, treating the general case of a superconductor with a nonvanishing vector potential.

The present treatment can be seen to give mathematically inequivalent results when compared with the standard derivation. The expansions are carried out at every value of k, rather than after final expressions containing summations over k have been set up. This leads to inequivalent expressions for α and β compared to those in the literature.

The present treatment gives inequivalent results in another way. The standard approach is built upon an infinite family of functions of variation $v_k(R)$, one function for every value of k, whereas here, see Eqs. (15) and (17), there is only one function of variation $C(R)$. Thus, the standard method may yield superior results, if fully implemented. In any case, however, the procedure goes beyond the single parameter variation envisaged in the GL method, and, except right at $T=T_c$, leads to equations more complicated than those of GL. Further there are difficulties. For example, in the simplified treatment of de Gennes the *a priori* expansion in the gap function $\Delta(R)$ influences the values of the $v_k(R)$. This element of arbitrariness is likewise present in the standard Green's-function analysis, where the expansion parameter $\Delta(R)$ is predetermined by the equations of motion for local Green's functions, and expansions follow. The Green's function procedure introduces a conceptual difficulty, as well, in that the supercurrent, and, hence, the wave function, is in response to the overall situation, i.e., one has a true Euler variational problem rather than a local problem; any *a priori* local equation, short of the N-body Schrödinger equation, is going to have a heuristic element.

The present method is thought to be a more direct way of getting to the goal, that of deriving the GL equations. To circumvent the various difficulties the spatial dependence with fields is here carried by the single-order parameter $C(R)$ in a trial function. The functional dependence of C on R is then determined by minimizing the expectation value of the overall energy, as it then turns out, precisely by equations having the GL form.

A different requirement on a generalized BCS trial function is that a first-principles expression for the current density in terms of the center-of-mass coordinates agree with the GL expression for the current obtained in the usual way by minimizing the free energy with respect to the vector potential. Lastly, the coefficients α,β may not depend on the vector potential. All the requirements mentioned in this section will be found fulfilled.

The interpretation of the order parameter as a gap function has always seemed as physically somewhat unsatisfying. The present paper aims to make a contribution by showing that a direct interpretation of the Ginsburg-Landau order parameter $\Psi(R)$ as a true center-of-mass wave function for pairs is straightforward. With the discovery of high-T_c superconductivity there is a new interest in the fundamentals of the conductivity mechanism. For this reason, in particular, a more direct interpretation of the Ginsburg-Landau equations would be desirable.

II. THE FIELD FREE DESCRIPTION

It will be helpful first to outline the approach with no applied field, with the vector potential $\mathbf{A}=\mathbf{0}$, and with the Ginzburg-Landau "wave-function" a constant. Φ_0, the generalization of the BCS zero-temperature function is then suggested to be

$$\Phi_0=\pi_{k>k_F}[D_k u_k+Cv_k a^*_{k\uparrow}a^*_{-k\downarrow}]$$

$$\times\pi_{k<k_F}[Cu_k+D_k v_k a^*_{k\uparrow}a^*_{-k\downarrow}]|0\rangle \tag{1a}$$

$$\equiv\pi_k[\tilde{u}_k+\tilde{v}_k a^*_{k\uparrow}a^*_{-k\downarrow}]|0\rangle \tag{1b}$$

where the $a^*_{k\uparrow},a^*_{-k\downarrow}$ are electron creation operators, $|0\rangle$ the vacuum state, and the u_k,v_k assume their usual BCS values, taken as real. In Eq. (1a) the electron operators have been separated according to whether their wave vector k places them above or below the Fermi energy, E_F. For simplicity explicit vector notation will be omitted where the reader is sure to understand that vector quantities are involved. Additional parameters C and D_k have been introduced. C, associated with the "minority carrier," electrons above E_F, holes below, is taken to represent the GL order parameter; it indicates the degree of superconductivity. When C vanishes Φ_0 becomes the metallic state, when C approaches unity Φ_0 becomes the standard BCS ground state. The alternate form for Φ_0, Eq. (1b), defines when compared to Eq. (1a) the short hand coefficients $\tilde{u}_k,\tilde{v}_k$. The purpose of the coefficients D_k, taken as real, is to provide normalization:

$$D_k^2u_k^2+|C|^2v_k^2=1 \quad k>k_F\ , \tag{2a}$$

$$D_k^2v_k^2+|C|^2u_k^2=1 \quad k<k_F\ . \tag{2b}$$

In addition, for normalization, one must, in fact have,

$$|C|^2\le 1. \tag{2c}$$

With Eqs. (1a), (2a), and (2b) one can calculate the expectation of the energy as

$$U_0(C)=\langle\Phi_0(C)|H|\Phi_0(C)\rangle\ , \tag{3}$$

where the Hamiltonian H, given below, will have the BCS form. Of course the parameter C overspecifies Φ_0. If one regards the parameters u_k,v_k as known, and varies $U_0(C)$ with respect to C (after elimination of the D_k) $U_0(C)$ will have its minimum at $C=1$. (This is obvious, since with u_k,v_k fixed at BCS, any values of the scaling factor C other than 1 imply the existence of a different minimum.) Nevertheless, this variational calculation will represent the $A\to 0$ limit of the proposed calculation for finite $\mathbf{A}$, where C will be a function of space; it illustrates features of the suggested approach for bridging from the microscopic to the macroscopic.

The BCS Hamiltonian is

$$H=\sum_{k,\sigma}\zeta_k a_{k,\sigma}a_{k,\sigma}+W_p \ , \tag{4a}$$

$$W_p=V/2\sum_{k,l}a^*_{k\uparrow}a^*_{-k\downarrow}a_{-l\downarrow}a_{l\uparrow} \ , \tag{4b}$$

where σ is the spin, and ζ_k a one particle energy relative to E_F, and $(V/2)$ the constant potential coupling pairs. The energy per unit volume $U_0(C,D_k)$ in Eq. (3) becomes

$$U_0(C,D_k)=2\sum_{k}\zeta_k\tilde{v}_k^2+V/2\sum_{k,l}\tilde{u}_k\tilde{v}_k^*\tilde{u}_l^*\tilde{v}_l^* \ . \tag{5a}$$

Substituting expressions for $\tilde{u}_k,\tilde{v}_k$ obtained from comparing Eqs. (1a) and (1b), into Eq. (5a) one obtains:

$$U_0(C,D_k)=2\sum_{k>k_F}\zeta_k|C|^2u_k^2+2\sum_{k<k_F}\zeta_kD_k^2v_k^2+V/2\sum_{k,l}|C|^2D_kD_lv_kv_lu_ku_l \ . \tag{5b}$$

To obtain a variational expression dependent only on C one has recourse to the normalization conditions, Eqs. (2a) and (2b). An expansion in the parameter C in the spirit of the GL theory is forthcoming if for $k>k_F$ one makes the expansion:

$$D_ku_k=\sqrt{1-|C|^2v_k^2}\simeq 1-v_k^2|C|^2/2-v_k^4|C|^4/8\cdots, \quad k>k_F \ , \tag{6}$$

and a similar expansion for the "majority" term D_ku_k when $k<k_F$. Since, for $k>k_F$ the largest value of v_k^2 is (1/2) one gets rapid convergence for $|C|\geq 1$. (With only three terms, even at $C=1$, $v_k^2=1/2$, the accuracy is 98.3%.)

Substituting Eq. (6) and the corresponding equation for, say, D_lv_l when $l<k_F$ into Eq. (5b) for $U_0(C,D_k)$, one obtains

$$U_0(C)=2\sum_{k<k_F}\zeta_k+\alpha'|C|^2+(\beta'/2)|C|^4 \tag{7a}$$

with

$$\alpha'\equiv 2\sum_{k>k_F}\zeta_ku_k+2\sum_{k<k_F}(-\zeta_k)u_k^2+\alpha'' \ , \tag{7b}$$

$$a''=V/2\left[\sum_{\substack{k>k_F\\ l>k_F}}v_kv_l+2\sum_{\substack{k>k_F\\ l<k_F}}v_ku_l+\sum_{\substack{k<k_F\\ l<k_F}}u_ku_l\right] , \tag{7c}$$

$$\beta'=-V/2\left[\sum_{\substack{k>k_F\\ l>k_F}}(v_l^2+v_k^2)v_lv_k+2\sum_{\substack{k>k_F\\ l<k_F}}(v_k^2+u_l^2)v_ku_l+\sum_{\substack{k<k_F\\ l<k_F}}(u_l^2+u_k^2)u_lu_k\right] , \tag{7d}$$

where $V<0$, $\alpha'<0$, and $\beta'>0$, as usual. The first term on the right-hand side of (7a) is the kinetic energy of the normal state relative to $2NE_F$, and will be dropped. C appropriately normalized will, it is being suggested, become Ψ_∞, the GL order parameter when $\mathbf{A}=0$, and Eqs. (7) will become the corresponding result for the energy of the superconductor at zero temperature.

III. CHANGE TO CENTER OF MASS AND RELATIVE COORDINATES

For current carrying states, the general idea is to replace, for example, $Cv_ka^*_{k\uparrow}a^*_{-k\downarrow}$ when $k>k_F$ in Eq. (1a) by $\sum_Q c_Qa^*_{k+Q/2\uparrow}a^*_{-k+Q/2\downarrow}$, $\hbar Q$ being the momentum of the center of mass of the pair, and c_Q being new coefficients. However, in a BCS-like wave function undesirable annihilations could occur when an operator, $a^*_{k+Q/2\uparrow}$, say, belonging to the pair k, $-k$ would operate on a wave function component containing orbitals $k'+Q'/2$, belonging to a pair k', $-k'$, where $k'<k$. It would only be necessary for $k+Q/2$ to equal $k'+Q'/2$. To avoid this difficulty it was found convenient to make changes of variable to relative and center-of-mass coordinates for pairs, and to decompose determinantal wave functions into components corresponding to different possible pairings of electron coordinates.

The BCS ground state is comprised of determinental components $|D\rangle$. In $|D\rangle$ one finds that for any orbital $\phi_{k\uparrow}$, a mate $\phi_{-k\downarrow}$ is also provided. Any one of the $2N$ products comprising $|D\rangle$ constitutes a particular pairing of the electron coordinates $r_1,\ldots,r_{2N}$, according to which coordinates occupy the mated orbitals. It will be convenient to refer to a particular pairing of the $2N$ coordinates (each of which, as spin is included, has four components) as an *arrangement*, reserving "pairing" for the usual mating of orbitals.

The totality of $(2n)!$ permutations comprising any determinental component $|D\rangle$ can, clearly, be split into arrangements:

$$|D\rangle\equiv n_A^{-1/2}\sum_a(-1)^a|D_a\rangle \ . \tag{8a}$$

A given arrangement differs from the next by a single interchange of partners, for example, from having r_1 paired with r_2, and r_3 with r_4, to having r_1 paired with r_3, and r_2 with r_4; this occasions a change of sign, as indicated by the factor $(-1)^a$ in Eq. (8a). The total number of arrangements with $2N$ electrons, n_A in Eq. (8a) is given by

$$n_A=(2N-1)(2N-3)\cdots(3)(1) \tag{8b}$$

$$\equiv(2N-1)!! \, . \tag{8c}$$

Given orthogonal orbitals, the various components $|D_a\rangle$ will be orthogonal, and if the $|D_a\rangle$ are normalized, $|D\rangle$ in Eq. (8a) will also be normalized.

With any given arrangement there comes a particular set of N relative coordinates r_{ij} and N center of mass coordinates R_{ij}:

$$r_{ij}=r_i-r_j \, , \tag{9a}$$

$$R_{ij}=(r_i+r_j)/2 \, . \tag{9b}$$

For this arrangement $|D_a\rangle$ becomes

$$|D_a\rangle=\frac{1}{\sqrt{N!}}|\phi_k(i,j)|_+ \, , \tag{10a}$$

$$\phi_k(i,j)\equiv 1/\sqrt{2}[e^{ikr_{ij}}\alpha(r_i)\beta(r_j)-e^{-ikr_{ij}}\alpha(r_j)\beta(r_i)] \, . \tag{10b}$$

The upright brackets in Eq. (10a) denote that $|D_a\rangle$ is the sum of all permutations of the N relative coordinates among the N orbitals $\phi_k(i,j)$ occupied in the particular BCS component $|D\rangle$. One notes that for plane-wave orbitals (to which the treatment is restricted)

$$\phi_{k\uparrow}(r_i)\phi_{-k\downarrow}(r_j)=e^{ikr_{ij}}\alpha(r_i)\beta(r_j) \tag{10c}$$

with α,β the spin-up and spin-down functions. Equation (10b), thus, is giving the orbital of a given pair. $\phi_k(ij)$ in Eq. (10b) is the antisymmetrized combination, leading to the overall antisymmetry of $|D\rangle$ in Eq. (8a). On the other hand, exchange of relative coordinates r_{ij} in $|D_a\rangle$ should not lead to a sign change, since two electrons are being exchanged simultaneously. The lower right-hand plus sign in Eq. (10a) denotes that although $|D_a\rangle$ is, as in determinental functions, the sum over all permutations, it is the symmetric sum, the terms are to be added without minus signs upon exchange.

Since there are $N!$ permutations among the N relative coordinates in $|D_a\rangle, |D_a\rangle$ will be comprised of $2^N N!$ products of simple orbitals, and can be easily normalized. It follows that the total number of products comprising $|D\rangle$ is given by

$$2^N N! n_A=(2N)! \tag{11}$$

in view of Eq. (8c), as is to be expected.

Consider now matrix elements of the BCS Hamiltonian, H, in Eq. (5). These are between components $|D_a\rangle, |D_b'\rangle$ in Eq. (8a) of the same determinental function $|D\rangle$ but corresponding to different arrangements, or between components $|D_a\rangle, |D_b\rangle$, where $|D_b'\rangle$ is in an arrangement belonging to a BCS component $|D'\rangle$ with occupations different from those in $|D\rangle$. H is comprised of one electron diagonal terms, and the pair interaction W_p in Eq. (4b). A regards the former terms, all elements involving disparate arrangements vanish, there are no exchange elements for one electron operators.

The two electron pair interaction is, in electron coordinates, the sum over all possible pair interactions $g(r_{ij})$ [see Eq. (20a)]. The BCS model Hamiltonian considers only elements in which entire pairs are scattered:

$$\langle D_a|g(r_{ij})|D_b\rangle \text{ or in } \langle D_a|g(r_{ij})|D_b'\rangle$$

$|D_b\rangle$ or $|D_b'\rangle$ must differ from $|D_a\rangle$ in the interchange of one particular pair state, $(k\leftrightarrow l)$. The pair state under consideration, k or l in the expansions of the functions $|D_a\rangle, |D_b\rangle, |D_b'\rangle$ must each depend on r_{ij}. Thus, in both $|D_a\rangle$ and in $|D_b\rangle$ or $|D_b'\rangle, r_i$ and r_j must be paired. Since the other orthogonal orbitals in the respective wave functions overlap only for components where the orbitals are occupied in the same way, $|D_a\rangle$ and $|D_b\rangle$, or $|D_a\rangle$ and $|D_b'\rangle$ must actually correspond to the same arrangement:

$$\langle D_a|g(r_{ij})|D_b\rangle=\langle D_a|g(r_{ij})|D_b'\rangle=0, \quad a\neq b \, . \tag{12}$$

Matrix elements of the BCS model Hamiltonian connecting wave function components from different arrangements vanish.

In consequence of Eq. (12), one can evaluate the expectation of the energy while restricted to one arrangement. Further, one can conveniently build up any one wave component $|D_a\rangle$ using creation and annihilation operators b_k^*, b_k for the antisymmetric orbitals $\phi_k(i,j)$ of Eq. (10b). Here b_k^*, b_k do not correspond to either boson or fermion operators. b_k^* introduces the orbital $\phi_k(i,j)$ into the wave function, and only one orbital of a given k may appear to be sure, but the operators do not anticommute as fermions do. Their introduction is for purposes of notation, no actual calculations are carried out drawing on any properties they may have.

IV. THE GENERAL CASE, A≠0

Evidently, the BCS ground state for one particular arrangement can be written in terms of the new operators b_k^*, b_k:

$$\Phi_0=\pi_k(u_k+v_k b_k^*)|0\rangle \, . \tag{13}$$

To proceed with a generalization, one defines orbitals

$$\phi_{kQ}(i,j)\equiv\frac{1}{\sqrt{2}}[e^{ikr_{ij}}\alpha(i)\beta(j)-e^{-ikr_{ij}}\alpha(j)\beta(i)]e^{iQR_{ij}} \tag{14}$$

where R_{ij} is the center of mass coordinate, Eq. (9b). Correspondingly, one has "creation" and "annihilation" operators $b_{k,Q}^*, b_{k,Q}$. Here, $\hbar Q$ is the total momentum of the pair, which no longer needs to vanish. b_{kQ}^*, b_{kQ} add or remove orbitals $\phi_{kQ}(i,j)$ from symmetric many-body functions $1/\sqrt{N}\,|\phi_{kQ}(i,j)|_+$ defined as in Eq. (10a).

The generalization of Eq. (1a) for the BCS ground state being suggested is, in terms of the b_{kQ}^*:

$$\Phi(R)=\pi_{k>k_F}\left[D_k(R)u_k+v_k\sum_Q c_Q b^*_{kQ}\right]\pi_{k<k_F}\left[C(R)u_k+v_k\sum_Q d_{kQ}b^*_{k,Q}\right]|0\rangle \tag{15a}$$

where R is a location in the crystal. The u_k and v_k are again the standard BCS coefficients, taken to be real. Coefficients, c_Q and d_{kQ} have been introduced. For $k<k_F, d_{k0}$ is a function of R, all other coefficients are independent of R. In terms of these coefficients the functions $C(R), D_k(R)$ are given by

$$C(R)\equiv\sum_Q c_Q e^{iQR},\quad D_k(R)\equiv\sum d_{kQ}e^{iQR},\quad k>k_F \tag{15b}$$

$$\equiv d_{k0}(R)+\sum{}' d_{kQ}e^{iQR},\quad k<k_F\ , \tag{15c}$$

where in Eq. (15d) the primed sum excludes $Q=0$. Lastly,

$$d_{kQ}=c_Q(u_k/v_k),\quad k<k_F,\quad Q\neq 0\ , \tag{15d}$$

and $d_{k0}(R)$, as well as the d_{kQ} for $k>k_F$ will be defined shortly.

The functions $C(R), D_k(R)$ are the generalizations of the constant coefficients C, D_k in Eq. (1a). Eq. (15a) has been chosen to preserve the symmetry about the Fermi energy found in the field free case, with special attention to the symmetry of the current carrying terms.

The functions $D_k(R)$ are needed for normalization. They will be chosen real. Both $D_k(R)$ and $C(R)$ are presumed to vary slowly with R (the location in the crystal) on an atomic scale, i.e., on a scale of volume per electron. The idea that when one is dealing with a potential that varies slowly one can do one's quantum mechanics locally, which is here at fixed R, was first introduced by Thomas and Fermi in their statistical model of many electron atoms. The idea finds common application in semiconductor physics, when the effect of electromagnetic fields is replaced by a slowly varying Fermi energy; the model there is, therefore, one of small self-contained systems at fixed Fermi energies in series with one another. Normalization of wave functions, counting of states, etc., is in these models precisely a local affair, carried out for one subsystem at a time. This approach, it is being suggested, needs to be adopted to arrive at the macroscopic GL equations.

Local normalization conditions link the coefficients C_k and d_{kQ}. Suppose one has some normalized symmetric wave function $|S_{N-1}\rangle$ or $(2N-2)$ relative and center of mass coordinates. Then, one has

$$\left\langle\sum_Q c_Q b^*_{kQ}S_{N-1}\,\middle|\,\sum_Q c_Q b^*_{kQ}S_{N-1}\right\rangle=\frac{1}{N}\sum_{i,j=1}^{N}\int C^*(R_{ij})C(R_{ij})d^3R_{ij},\quad k>k_F\ , \tag{16a}$$

$$\left\langle\sum_Q d_{kQ} b^*_{kQ}S_{N-1}\,\middle|\,\sum_Q d_{kQ} b^*_{kQ}S_{N-1}\right\rangle=\frac{1}{N}\sum_{i,j=1}^{N}\int |D_k(R_iR_{ij})|^2d^3R_{ij},\quad k<k_F\ , \tag{16b}$$

$$D_k(R,R_{ij})=d_{k0}(R)+\sum_Q{}' d_{kQ}e^{iQR_{ij}},\quad k<k_F\ , \tag{16c}$$

where evidently $D_k(R,R_{ij}=R)$ is just again $D_k(R)$, $k<k_F$. The probability of finding any one center of mass per unit volume of the local location R is given by $C^*(R)C(R)$. At the same time the probability of finding the state k, for $k<k_F$ empty at R is given by $u_k^2|C(R)|^2$. [$u_kC(R)$ is a coefficient independent of any coordinate.] Normalization of Eq. (15a) at R in unit volume becomes

$$u_k^2D_k^2(R)+v_k^2|C(R)|^2=1,\quad k>k_F\ , \tag{17a}$$

$$v_k^2D_k^2(R)+u_k^2|C(R)|^2=1,\quad k<k_F\ . \tag{17b}$$

Remembering that $D_k(R)$ is real, one sees that Eq. (17b) fixes the remaining coefficient $d_{k0}(R)$ in Eq. (15d), $k<k_F$, as well as the constant coefficients d_{kQ} in Eq. (15c), i.e., when $k>k_F$. As in the field free case for $k\gg k_F$, $V_k\rightarrow 0$, $D_k(R)\rightarrow 1$, and for $k\ll k_F$, $u_k\rightarrow 0$, $D_k(R)\rightarrow d_{k0}(R)\rightarrow 1$. $d_{k0}(R)$, associated with the k pair that carries no current, effectively becomes the normalization constant at R for $k<k_F$.

To find the expectation value of the pair interactions one begins by calculating the expectation value of the single Fourier component $e^{-iqr_{ij}}$:

$$\langle\Phi(R)|e^{-iqr_{ij}}|\Phi(R)\rangle\equiv\int d^3R_{ij}\ V_q(R_{ij}R)\ , \tag{18}$$

where $V_q(R_{ij},R)$ is obtained by integration over all coordinates, relative and center of mass other than R_{ij}. The use of Eqs. (14), (15a), (15b), and (15c) for Φ yields:

$$N[V_{-q}(R)+V_q(R)]=\sum_k D_k(R)D_{k-q}(R)C^*(R)\times C(R)v_ku_kv_{k-q}u_{k-q}\ , \tag{19a}$$

$$V_q(R)\equiv V_q(R_{ij}=R,R)\ . \tag{19b}$$

The second quantization form for the pair interaction W_p in Eq. (4b) will have the same matrix elements (barring any self-energy corrections associated with the coordinate form given here) as

$$W_p\equiv V/2\sum_{ij}{}' g(r_{ij}) \tag{20a}$$

$$=V/2\sum_{q}\sum_{i,j}{}' e^{-iqr_{ij}} , \tag{20b}$$

where the sum $\sum'_{i,j}$ includes $(2N)(2N-1)$ terms (every electron interacting with all the others with a potential V). It is to be noticed that the center of mass coordinates do not enter.

In Appendix A it is shown that when working in one particular arrangement only, as is done here,

$$W_p=V\sum_{q}\sum_{ij}e^{-iqr_{ij}} , \tag{21}$$

where the sum $\sum_{ij}$ in Eq. (21) is over the N relative coordinates of one particular arrangement. In the notation of Eqs. (18) and (19b), the expectation value in the entire crystal of the pairing interaction W_p given in Eq. (21) becomes

$$\langle \Phi | W_p | \Phi \rangle = \int d^3R \; W_p(R) \tag{22a}$$

with

$$W_p(R)=NV\sum_{q>0}V_q(R) \tag{22b}$$

where in (22b) it is recognized that all N pairs ij will yield the same integral over R_{ij} $(\equiv R)$. Combining Eqs. (19), (21), and (22b) one finally has

$$W_p(R)=V/2\sum_{q}\sum_{k,k-q}D_k(R)D_{k-q}(R)C^*(R) \times C(R)v_k u_k v_{k-q}u_{k-q} , \tag{23}$$

where the factor (1/2) allows extension to summing over all q.

Equations (17a) and (17b) are the generalizations of Eqs. (2a) and (2b). Equivalent expansions to those given in Eq. (6) are, therefore, forthcoming, D and C now being functions of R. It follows that

$$W_p(R)\equiv\alpha''|C(R)|^2+\beta'/2|C(R)|^4 \tag{24}$$

with α'',β' already defined in Eqs. (7c) and (7d), if one identifies the states $k-q$ for any q with one of the states l.

Of interest next is the kinetic energy T. With relative and center of mass coordinates as given by Eqs. (9), again for a given arrangement, the kinetic energy separates:

$$T=T_1+T_2 , \tag{25a}$$

$$T_1=\frac{-\hbar^2}{m}\sum_{ij}\frac{\partial^2}{\partial r_{ij}^2} , \tag{25b}$$

$$T_2=\frac{-\hbar^2}{4m}\sum_{ij}\frac{\partial^2}{\partial R_{ij}^2} , \tag{25c}$$

when the sums in Eqs. (25b) and (25c) are over the N pairs ij in the chosen arrangement. For T_q one gets:

$$\langle T_1 \rangle = \int \Phi^*(R)T_1\Phi(R)\pi_{ij}[d^3r_{ij}d^3R_{ij}] \tag{26a}$$

$$= \sum_{k>k-F}2\zeta_k v_k^2|C(R)|^2+\sum_{k<k_F}2\zeta_k v_k^2 D^2(R) \tag{26b}$$

$$=2\sum_{k\le k_F}\zeta_k+2\left[\sum_{k>k_F}\zeta_k v_k^2 + \sum_{k<k_F}(-\zeta_k)u_k^2\right]|C(R)|^2 \tag{26c}$$

where the result in Eq. (26b) is obtained with the help of Eq. (15a) for $\Phi(R)$. ζ_k is again measured with respect to the Fermi energy. Equation (26c) was obtained with the help of the normalizing condition, Eq. (17b). The effect of adding in $\langle T_1 \rangle$ is, therefore, to change α'' in Eq. (24) for the pairing energy to α' in any expression for the total energy, in the same way as in the field free case. On the other hand, again using Eq. (15a) for $\Phi(R)$ the local expectation value of T_2 at R per unit volume will be given by

$$\langle T_2 \rangle = \langle T_2 \rangle' + \langle T_2 \rangle'' , \tag{27a}$$

$$\langle T_2 \rangle' = \sum_{k<k_F} v_k^2 \sum_{QQ'} c_{Q'}^*\hbar^2Q^2/(4m)c_Q e^{-i(Q'-Q)R} , \tag{27b}$$

$$\langle T_2 \rangle'' = \sum_{k<k_F} v_k^2 \sum_{QQ'} d_{kQ'}\hbar^2Q^2/(4m)d_{kQ} e^{-i(Q'-Q)R} , \tag{27c}$$

where again any coordinate R_{ij} was taken to have its local value R after the differentiation, and $\Phi(R)$ is the wave function per unit volume at R.

Equation (27c) can be written in terms of coefficients c_Q, using Eq. (15e) to eliminate the coefficient d_{kQ}. Equations (27a)–(27c) then yield the kinetic energy in the GL form if $\Psi(R)$ is defined as

$$\Psi(R)\equiv\gamma C(R) , \tag{28a}$$

$$\gamma\equiv\left[\sum_{k>k_F}v_k^2+\sum_{k<k_F}u_k^2\right]^{1/2} . \tag{28b}$$

Equations (28a) and (28b) are essentially consistent with the suggestion in GL that $\Psi^*(R)\Psi(R)$ represents the number of superconducting electrons per unit volume at R. [$\Phi(R)$ has been normalized to unit volume. $C(R)$ is the "degree of superconductivity," $C=1$ yielding BCS, see Sec. II. Thus, $\Psi^*\Psi$ represents the number of superconducting pairs per unit volume, the supercurrent originating with the minority carriers.]

The vector potential associated with electron r_i is $\mathbf{A}(r_i=R_{ij}+r_{ij}/2)$, see Eqs. (9a) and (9b). The necessary approximation is to assume that $\mathbf{A}$ is a constant over the excursion r_{ij} of the relative coordinate of the pair (coherence length). In this case $\mathbf{A}$ will be grouped with R_{ij} rather than r_{ij} in the final kinetic energy.

The final result, drawing particularly on Eqs. (27b), (28a), and (28b) is that

$$\langle T_2\rangle=\frac{1}{4m}\int\Psi^*(R)\left[\frac{\hbar}{i}\frac{\partial}{\partial R}-2eA(R)\right]^2\Psi(R)d^3R\ . \tag{29}$$

Combining now Eq. (24) for W_p with Eq. (29), and including the effect of the kinetic energy $\langle T_1\rangle$, Eqs. (27) and (26c), one gets for the total-energy expectation per unit volume at R the GL form:

$$U[\Psi(r)]=\frac{1}{4m}\Psi^*(R)\left[\frac{\hbar}{i}\frac{\partial}{\partial R}-2eA(R)\right]^2\Psi(R)$$
$$+\alpha|\Psi(R)|^2+\frac{\beta}{2}|\Psi(R)|^4\ , \tag{30a}$$

where, from Eqs. (24) and (28a)

$$\alpha=\alpha'/\gamma^2\ , \tag{30b}$$

$$\beta=\beta'/\gamma^4\ . \tag{30c}$$

The current is obtained in GL theory by minimizing the free energy with respect to $\mathbf{A}$, and setting $\nabla^2\mathbf{A}$ equal to minus the current. Given a microscopic description it becomes possible to check for consistency by direct evaluation. The current $j(R)$ at a point R is given by the expectation value,

$$\mathbf{j}(R)=\langle\Phi|\mathbf{j}(R)|\Phi\rangle \tag{31a}$$

with

$$\mathbf{j}(R)=\frac{e}{2m}\sum_i[\mathbf{p}_i\delta(r_i-R)+\delta(r_i-R)\mathbf{p}_i]$$
$$-\frac{e^2}{m}\sum_i\mathbf{A}(r_i)\delta(r_i-R) \tag{31b}$$

and

$$\mathbf{p}_i=(\hbar/i)\nabla_{r_i}\ . \tag{31c}$$

Consider now for the pair r_1,r_2, the operator $\mathbf{J}_1(r_1,r_2|R)$, where

$$\begin{aligned}2m_i/(e\hbar)J_1(r_1,r_2|R)&\equiv\delta(r_1-R)\partial/\partial r_1+\delta(r_2-R)\partial/\partial r_2\\&=\delta(R_{12}+r_{12}/2-R)\left[\frac{\partial}{\partial r_{12}}+\frac{1}{2}\frac{\partial}{\partial R_{12}}\right]+\delta(R_{12}-r_{12}/2-R)\left[\frac{-\partial}{\partial r_{12}}+\frac{1}{2}\frac{\partial}{\partial R_{12}}\right] &&(32a)\\&\simeq\delta(R_{12}-R)\partial/\partial R_{12}\ . &&(32b)\end{aligned}$$

The differentiation in Eq. (32a) is with respect to one of the cartesian components, and the change to the relative coordinate r_{12} and the center-of-mass coordinate R_{12} of Eqs. (9) is being carried out. Again, the assumption of limited electron pair size leads to the approximation shown in Eq. (32b).

Going back to Eq. (15a) for Φ, one finds

$$\langle\Phi|J_1(r_1r_2|R|\Phi\rangle=\frac{1}{N}\gamma^2\sum_{Q,Q'}c_{Q'}^*c_Q\int e^{-Q'R_{12}}\frac{e\hbar}{2mi}\delta(R_{12}-R)\frac{\partial}{\partial R_{12}}e^{iQR_{12}}d^3R_{12}\ . \tag{33}$$

Proceeding in this way, recollecting also Eq. (15b), and Eqs. (28a) and (28b) one does find:

$$\mathbf{j}(R)=e\hbar/(2mi)[\Psi^*(R)\nabla\Psi(R)-\Psi(R)\nabla\Psi^*(R)]-(e^2/m)\Psi^*(R)\Psi(R)\mathbf{A}(R)\ . \tag{34}$$

There are, of course, ways of modifying the trial function Eq. (15a). The symmetry about E_F embodied in Eqs. (15) defining the trial function $\Phi(R)$ is designed to maximize the absolute value of the pairing interaction, again as in the field free situation. The $d_{kQ},Q\neq0$, were chosen, according to Eq. (15e), to equalize the contribution of electrons and "holes" to the supercurrent. Given a fixed value for the current, this choice will minimize the ensuing kinetic energy. These considerations preempt the choice as regards constants. A remarkable feature of the GL free energy is that the coefficients α,β do not depend in any way on the vector potential; they stay put all the way down to zero applied field. It is difficult to see how any modification of the symmetry in Eq. (15a) could leave this result intact. Extension to finite temperatures represents a hitherto unmet challenge.

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APPENDIX

Here we wish to show that

$$\langle D_a|(W_p)_{\text{new}}|D_a\rangle=\langle D|(W_p)_{\text{actual}}|D\rangle\ , \tag{A1}$$

where $(W_p)_{\text{actual}}$ is given in Eq. (20b), and $(W_p)_{\text{new}}$ is given in Eq. (21). The expectation value $\overline{V}_{ij}$ for one particular interaction in the arrangement a is given by

$$\overline{V}_{ijq}=\langle D_a|V/2e^{-qr_{ij}}|D_a\rangle\ , \tag{A2}$$

whereas, going back to Eq. (8a) for $|D_a\rangle$, one has

$$\overline{\overline{\overline{V}}}_{ijq} = \langle D|V/2e^{iqr_{ij}}|D\rangle = n_A^{-1}(2N-3)!!\overline{V}_{ij} \tag{A3}$$

because for the $(2N-1)!!$ possible arrangements, in only $(2N-3)!!$ arrangements are r_i and r_j paired. Further, from Eq. (20b)

$$(W_p)_{\text{actual}} = (2N-1)V\sum_{i,j}^{(a)} e^{-iqr_{ij}} , \tag{A4}$$

where $\sum_{i,j}^{(a)}$ is over the N relative coordinates in a, i.e., there are only $(2N)(2N-1)/2$ terms in Eq. (A4). From Eqs. (21) and (A2)

$$\langle D_a|(W_p)_{\text{new}}|D_a\rangle = \sum_q 2N\overline{V}_{ijq} , \tag{A5}$$

whereas from Eqs. (8c), (20b), and (A3),

$$\begin{aligned}\langle D|(W_p)_{\text{actual}}|D\rangle &= \sum_q (2N)(2N-1)\overline{\overline{\overline{V}}}_{ijq} \\ &= \sum_q (2N)(2N-1)\frac{(2N-3)!!}{(2N-1)!!}\overline{V}_{ijq} .\end{aligned} \tag{A6}$$

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