

Position-Dependent Superconductivity

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A discussion is given of several methods used in generalizing the Bardeen-Cooper-Schrieffer theory of superconductivity to problems where position-dependence plays a key role. It is pointed out that the method in most common use (that of Gorkov) is inappropriate for discussing the rather long-range effects on each other (extending over distances of about 10^{-5} cm) of two metals in contact. A method appropriate for describing such effects is obtained by generalizing the Nakamura theory of position-independent superconductivity. This method leads to results qualitatively similar to those obtained previously by Parmenter using heuristic arguments. The various methods of treating position-dependent superconductivity are all different limiting forms of a very general form of theory due to Blatt, or, in an equivalent but particle-nonconserving form, due to Bogoliubov and Valatin. The saddle-point method of summing cluster expansions, used in both the Blatt and Nakamura theories, is shown to be mathematically justified, in contrast to the situation with most condensed systems.

I. INTRODUCTION

THERE is a growing body of experimental evidence¹⁻⁶ which suggests that a sufficiently thin film of superconducting metal deposited on bulk normal metal will have its superconductivity quenched by the presence of the normal metal. Conversely, a sufficiently thin film of normal metal such as copper apparently can be made superconducting by being deposited on bulk superconducting metal. In both cases, the critical film thickness is of the order of, or somewhat less than, the coherence distance of the superconductor. For homogeneous soft superconductors the critical thickness may be several thousand Angstroms.⁷ In an attempt to understand these effects, the writer⁸ has generalized the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity⁹ to the case where there is position dependence in the problem. The essential idea of the writer was to generalize the BCS expression for the energy density in a superconductor by adding a term representing the center-of-mass kinetic-energy density of the Cooper pairs. (In the BCS theory, there is no center-of-mass motion of Cooper pairs.) With the aid of this additional term, the theory was able to predict results in good qualitative agreement with experiment. The form of this additional kinetic-energy term was determined by heuristic arguments. In the present

paper we wish to replace the heuristic arguments by more precise considerations. Having done this, we will find a modification of the detailed form of the additional term. However, this leads to no qualitative changes in the theory. In particular, if we treat the order parameter ϵ_0 as being approximately independent of wave vector \mathbf{k} (as done in Refs. 8 and 9), we obtain the same form of integrodifferential equation for ϵ_0 as was obtained before. The closeness of the present form of the theory to that of Ref. 8 insures that the two forms will make similar predictions with regard to a given situation. Detailed numerical calculations will not be carried out in this paper.

The mathematical machinery necessary for carrying out our program is available in the work of Nakamura¹⁰ and Blatt.¹¹ Nakamura sought to reformulate the BCS theory so that it would be manifestly particle-conserving. Unlike BCS, Nakamura worked with many-electron wave functions that are eigenfunctions of total electron number. These wave functions are antisymmetrized products of two-electron wave functions (the same two-particle wave function for every pair of electrons). This two-particle wave function is a product of a singlet function of the spins of the two electrons times a spatial function of the distance separating the two electrons, the spin function being antisymmetric under interchange of the two-electron spin coordinates. Nakamura showed that the problem of calculating expectation values of the many-electron Hamiltonian with respect to such many-electron wave functions is very similar mathematically to that of calculating the partition function in the Mayer theory of the classical imperfect gas.¹² In both problems, the desired result can be written as a so-called cluster expansion. Using the saddle-point method¹³ of analytically summing such

¹ E. F. Burton, J. O. Wilhelm, and A. D. Misener, *Trans. Roy. Soc. Can.* **III**, 28, 65 (1934); A. D. Misener and J. O. Wilhelm, *ibid.* **29**, 5 (1935).

² H. Meissner, *Phys. Rev.* **109**, 686 (1958); **117**, 672 (1960); *Phys. Rev. Letters* **2**, 458 (1959).

³ P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, *Phys. Rev. Letters* **6**, 686 (1961).

⁴ P. Hilsch and R. Hilsch, *Naturwissenschaften* **48**, 549 (1961); *P. Hilsch, Z. Physik* **167**, 511 (1962).

⁵ A. C. Rose-Innes and B. Serin, *Phys. Rev. Letters* **7**, 278 (1961).

⁶ W. A. Simmons and D. H. Douglass, *Phys. Rev. Letters* **9**, 153 (1962).

⁷ Critical thicknesses as small as several hundred Angstroms were found by Hilsch (Ref. 4). This presumably results from a decreased coherence distance, which in turn is due to a normal-electron mean free path lowered by disorder scattering.

⁸ R. H. Parmenter, *Phys. Rev.* **118**, 1173 (1960).

⁹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

¹⁰ K. Nakamura, *Progr. Theoret. Phys. (Kyoto)* **21**, 713 (1959).

¹¹ J. M. Blatt, *Progr. Theoret. Phys. (Kyoto)* **24**, 851 (1960); *J. Australian Math. Soc.* **1**, 465 (1960).

¹² J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 13.

¹³ M. Born and K. Fuchs, *Proc. Roy. Soc. (London)* **A166**, 391 (1938).

series, Nakamura showed that the resultant expression for the energy density could be made equivalent to the BCS expression by a suitable choice of the two-electron spatial function.

Blatt¹¹ generalized the work of Nakamura by taking the spatial part of the two-electron wave function to be an arbitrary function of the positions of the two electrons, rather than simply a function of the distance between the two electrons. This arbitrariness is, of course, restricted by the requirement that the two-electron wave function be antisymmetric under interchange of electronic coordinates. Thus, with the spin portion of the wave function being antisymmetric under interchange of the two spin coordinates (i.e., a singlet state), the spatial part must be symmetric under interchange of the two-electron position coordinates. Like Nakamura, Blatt took his many-electron wave function to be an antisymmetrized product of these two-electron wave functions (the same function of position and spin coordinates of the two particles for every pair of electrons). Such many-electron wave functions are eigenfunctions of total electron number. The expectation value of the many-electron Hamiltonian with respect to this many-electron wave function can be written as a series which is analogous to a cluster expansion. Blatt also used the saddle-point method of analytically summing such series to get an expression for the energy density. This expression properly goes to the BCS expression for the energy density in the limit where there is no position dependence left in the problem.

Invoking periodic boundary conditions, we may expand the spatial part of the Blatt two-electron wave function as a double Fourier series, the coefficients of which are $f_{\mathbf{k}\mathbf{k}'}$. The BCS case corresponds to $f_{\mathbf{k}\mathbf{k}'} = f_{\mathbf{k}}\delta_{\mathbf{k},-\mathbf{k}'}$, i.e., f is diagonal in \mathbf{k} , $-\mathbf{k}'$. In addition, there are three other limiting cases of special interest. The first case corresponds to f being nearly diagonal in \mathbf{k} , $-\mathbf{k}'$ in the sense that all off-diagonal elements of f are much smaller than the diagonal elements. The second case corresponds to f being nearly diagonal in a different sense; namely that f be nonvanishing only for very small values of $(\mathbf{k}+\mathbf{k}')$, the center-of-mass wave vector of the electron pair. The third case corresponds to f being Hermitian in \mathbf{k} , $-\mathbf{k}'$ so that f may be made diagonal by a suitable unitary transformation.

The first to these three cases is appropriate for treating deviations from position independence by means of perturbation theory. Blatt made use of this case for discussing the Meissner effect in a gauge-invariant manner. The second case is to be discussed in this paper. It is the appropriate method for understanding the rather long-range effects of normal metals on superconducting metals, and vice versa. The third case is equivalent to a generalization of the usual Hartree-Fock method. A set of orthonormal one-electron orbitals is chosen. By pairing each orbital with its time-reversed mate, one can set up a many-electron

wave function similar to the BCS ground-state wave function. By minimizing the expectation value of the many-electron Hamiltonian with respect to this many-electron wave function, one finds equations for the one-electron set of orbitals which are self-consistent; i.e., those which are solutions to the one-electron Schrödinger equation containing the effective field due to all the electrons except the one occupying the given orbital. Like the Hartree-Fock method, there is a contribution to this effective field resulting from correlation between parallel-spin electrons (the exchange field). Unlike the Hartree-Fock method, there is also a contribution to the effective field resulting from correlation between antiparallel-spin electrons.

The particle-nonconserving analog of this third case has been developed by Gorkov,¹⁴ who introduced a version using one-electron Green's functions. It appears difficult, if not impossible, to interpret the experimental results mentioned before in terms of the picture represented by this third case. The essential difficulty lies in the fact that appreciable position dependence of the effective self-consistent potential will be restricted to regions lying within a Debye screening length ($\sim 10^{-8}$ cm) of an interface between two different metals. The modification of the one-electron wave functions near the Fermi level by this effective field will be restricted to regions lying within a Fermi wavelength ($\sim 10^{-7}$ cm) of the interface. It is only over such regions that the perturbing electric fields appearing in the self-consistent Hamiltonians for the various one-electron orbitals are large enough to appreciably modify the probability density of the orbitals, despite the fact that there is correlation between antiparallel-spin electrons extending over the Pippard coherence distance ξ_0 , orders of magnitude larger than the screening length or the Fermi wavelength. The magnetic analog of this is the screening out of a magnetic field within the penetration depth λ , which may be much less than ξ_0 . The small Fermi wavelength in a metal is directly attributable to the relatively large kinetic energies associated with conduction electrons in a metal. The larger the kinetic energy of an electron, the larger must be the electric field to appreciably modify the electron's trajectory.¹⁵

¹⁴L. P. Gorkov, *Zh. Eksperim. i Teor. Fiz.* **34**, 735 (1958) [translation: *Soviet Phys.—JETP* **7**, 505 (1958)].

¹⁵Several recent calculations using the Gorkov method [e.g., P. G. de Gennes and E. Guyon, *Phys. Letters* **3**, 168 (1963)] appear to obtain reasonable agreement with experiments on superposed films of superconductors and normal metals. This agreement seems to be reached at the expense of self-consistency of the calculations; i.e., the one-electron wave functions which upon time-reversal pairing give rise to the position-dependent pairing potential are different from those wave functions which are eigenfunctions of the one-electron Hamiltonian containing this same pairing potential. The negligible long-range effect of the pairing potential on the one-electron wave functions is consistent with the fact that the static long-wavelength longitudinal dielectric constant is indifferent to the presence or absence of the superconducting phase in a superconductive metal [see, e.g., R. E. Prange, *Phys. Rev.* **129**, 2495 (1963)].

In contrast, if we allow the electric field to modify the center-of-mass motion of the various Cooper pairs (rather than the motion of individual electrons), we have the possibility of position dependence extending much farther into the metal. Because of the very small kinetic energy (possibly even negative) of the Cooper pairs, minute electric fields can appreciably modify the probability density of the pair wave functions. In effect, we have a de Broglie wavelength for pairs which is much larger than the Fermi wavelength of the electrons. It should be noted that there is no *a priori* reason that this de Broglie wavelength be equal to the Pippard coherence distance. The discussion of the present paragraph corresponds to the second of our three cases.

A particle-nonconserving generalization of the Gorkov theory (and thus also of our third case) is due to Bogoliubov and Valatin.¹⁶ The additional generality is obtained by constructing the many-electron generalized Hartree-Fock wave function from paired *single-fermion* orbitals, rather than *single-electron* orbitals. (As long as we restrict ourselves to the case of zero current and zero magnetic field, as we are doing in this paper, it is appropriate to pair time-reversed single-fermion orbitals.) The use of single-fermion orbitals (representing part of the time an electron, part of the time a hole) rather than simply single-electron orbitals allows the Bogoliubov-Valatin formulation to be as general as that of Blatt, a fact recently pointed out by Baranger.¹⁷ By the same token, both formulations appear to be equally difficult to solve. As has already been discussed, the specialization to one-electron orbitals is too restrictive to obtain long-range effects. The more general single-fermion approach does allow the possibility of long-range effects, since a fermion built out of electrons and holes near the Fermi level may have a much smaller kinetic energy than that of an electron near the Fermi level (due to cancellation of electron and hole kinetic energies). The Gorkov formulation can be made equivalent to that of Bogoliubov-Valatin only by introducing a more general form of single-particle kinetic-energy operator than is conventionally used.

Henceforth, we will deal with the second of the three limiting cases of the Blatt theory. Rather than attempting to analyze this second case in detail by making the appropriate specialization of the Blatt theory, we shall choose the alternative of making the appropriate generalization of the Nakamura theory. Such a choice leads to greater simplicity of treatment and ease of understanding. In carrying through the analysis, we will take pains to demonstrate the applicability of the saddle-point method of summing cluster expansions,¹³ the reason being that the method is usually thought to be inapplicable to a *condensed* system, and a super-

conductor is certainly a condensed electron system. Neither Nakamura nor Blatt gave sufficient attention to this point.

II. THEORY

In the BCS theory of superconductivity, the ground-state wave function is

$$\Psi_0' = \prod_k [(1-h_k)^{1/2} + h_k^{1/2} c_{k\uparrow}^* c_{-k\downarrow}^*] \Phi_0. \quad (1)$$

Φ_0 is the vacuum-state wave function. The c_k 's are the usual electron creation and destruction operators. The parameters h_k lie in the range $0 \leq h_k \leq 1$. This ground-state wave function does not characterize a state of fixed number of electrons. That portion of Ψ_0' which represents the case of precisely $2N$ electrons being present is given by¹⁸

$$\frac{1}{N!} \prod_{k'} (1-h_{k'})^{1/2} \left[\sum_k h_k^{1/2} (1-h_k)^{-1/2} c_{k\uparrow}^* c_{-k\downarrow}^* \right]^N \Phi_0. \quad (2)$$

This is equivalent to an antisymmetrized product of N two-electron wave functions (the same two-electron wave function for each of the N pairs of electrons). Thus, we choose a many-electron wave of this type for our ground state, i.e.,

$$\Psi_0 = \sum_P (-1)^p P \{ \chi(1,2) \chi(3,4) \cdots \chi(2N-1, 2N) \}, \quad (3)$$

P being the permutation operator (of parity p) working on the $2N$ electronic coordinates, each coordinate including position r and spin σ . Corresponding to the fact that opposite spin electrons appear together in (1) and (2), the two-electron wave function χ must be a singlet, i.e.,

$$\chi(1,2) = \frac{1}{\sqrt{2}} [\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)] \psi(\mathbf{r}_1, \mathbf{r}_2), \quad (4)$$

α and β being the usual spin functions. The spatial orbital ψ must be symmetric under interchange of \mathbf{r}_1 and \mathbf{r}_2 .

We wish to calculate the expectation value, with respect to Ψ_0 , of the many-electron Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \phi_{ij}, \quad (5)$$

$p_i^2/2m$ representing the kinetic energy of the i th electron (or, in the effective-mass approximation, the

¹⁶ N. N. Bogoliubov, Usp. Fiz. Nauk **67**, 549 (1959) [translation: Soviet Phys.—Usp. **2**, 236 (1959)]; J. G. Valatin, Phys. Rev. **122**, 1012 (1961); J. G. Valatin, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience Publishers, Inc., New York, 1961), Vol. IV.

¹⁷ M. Baranger, Phys. Rev. **130**, 1244 (1963).

¹⁸ Here we are making the assumption that $h_k \neq 1$. Depending on the detailed form of the electron-electron interaction, this may or may not be the case. Certainly $h_k \rightarrow 1$ as \mathbf{k} moves deep inside the Fermi sphere in reciprocal space. For convenience, we shall continue to treat h_k as though it fails to reach unity. An alternative procedure is to redefine the vacuum state to include those electrons for which $h_k = 1$. In any case, the final results are independent of what is assumed for h_k .

Bloch energy), and ϕ_{ij} representing the potential energy of interaction between the i th and j th electrons. Nakamura has proved that this expectation value

$$W_0 = (\Psi_0, H\Psi_0) / (\Psi_0, \Psi_0) \quad (6)$$

can be written in the form¹⁹

$$W_0 = \sum_{m_l} \mathcal{E}(\cdots m_l \cdots) \prod_l b_l^{m_l} / m_l! \times \sum_{m_l} \prod_l b_l^{m_l} / m_l! \quad (7)$$

$$\mathcal{E}(\cdots m_l \cdots) = \sum_l m_l (t_l + v_l) + \sum_{l \neq l'} m_l m_{l'} v_{ll'} + \frac{1}{2} \sum_l m_l (m_l - 1) v_{ll} \quad (8)$$

where

$$b_l = l^{-1} (-1)^{l-1} \int \psi(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_2, \mathbf{r}_3) \cdots \psi(\mathbf{r}_{2l}, \mathbf{r}_1) d^3 r^{2l} \quad (9)$$

$$t_l = l^{-1} (-1)^{l-1} b_l^{-1} \int \psi(\mathbf{r}_2, \mathbf{r}_3) \psi(\mathbf{r}_4, \mathbf{r}_5) \cdots \psi(\mathbf{r}_{2l}, \mathbf{r}_1) \times \sum_i (p_i^2 / 2m) \psi(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_3, \mathbf{r}_4) \cdots \times \psi(\mathbf{r}_{2l-1}, \mathbf{r}_{2l}) d^3 r^{2l} \quad (10)$$

$$v_l = l^{-1} (-1)^{l-1} b_l^{-1} \int \psi(\mathbf{r}_2, \mathbf{r}_3) \psi(\mathbf{r}_4, \mathbf{r}_5) \cdots \psi(\mathbf{r}_{2l}, \mathbf{r}_1) \times \frac{1}{2} \sum_{i \neq j} \phi_{ij} \psi(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_3, \mathbf{r}_4) \cdots \psi(\mathbf{r}_{2l-1}, \mathbf{r}_{2l}) d^3 r^{2l} \quad (11)$$

$$v_{ll'} = l^{-1} l'^{-1} (-1)^{l+l'} b_l^{-1} b_{l'}^{-1} \int \int \psi(\mathbf{r}_1, \mathbf{r}_2) \psi(\mathbf{r}_2, \mathbf{r}_3) \cdots \times \psi(\mathbf{r}_{2l}, \mathbf{r}_1) \frac{1}{2} \sum_{ij'} \phi_{ij'} \psi(\mathbf{r}_{1'}, \mathbf{r}_{2'}) \psi(\mathbf{r}_{2'}, \mathbf{r}_{3'}) \cdots \times \psi(\mathbf{r}_{2l'}, \mathbf{r}_{1'}) d^3 r^{2l} d^3 r^{2l'} \quad (12)$$

[Note: Since magnetic fields are of no concern in the present paper, ψ has been assumed to be a real function, i.e., not complex. A crystal of unit volume has been assumed.] The integrals appearing in b_l , t_l , v_l , and $v_{ll'}$ are the so-called cluster integrals, while the sums appearing in (7) and (8) are cluster expansions. \sum_l and \prod_l represent sums and products, respectively, over all positive integers l , there being a specified non-negative integer m_l associated with each value of l . \sum_{m_l} represents a sum over all possible ways of choosing the set of numbers m_l consistent with the restraint

$$\sum_l l m_l = N. \quad (13)$$

¹⁹ Nakamura's proof of this result is independent of the functional form of $\psi(\mathbf{r}_1, \mathbf{r}_2)$. Thus, his proof holds more generally than for the special case of interest to him, where ψ was a function only of $\mathbf{r}_1 - \mathbf{r}_2$.

Let us now consider $\psi(\mathbf{r}_1, \mathbf{r}_2)$ as a function of

$$\begin{aligned} \mathbf{R}_{12} &= \frac{1}{2} (\mathbf{r}_1 + \mathbf{r}_2), \\ \mathbf{r}_{12} &= \mathbf{r}_1 - \mathbf{r}_2, \end{aligned} \quad (14)$$

the center-of-mass position of the two electrons, and the interelectronic distance. Thus we write $\psi(\mathbf{R}_{12}, \mathbf{r}_{12})$, although it must be understood that ψ is not the same function of \mathbf{R}_{12} and \mathbf{r}_{12} that it was of \mathbf{r}_1 and \mathbf{r}_2 . (Note that ψ must be an even function of \mathbf{r}_{12} , since ψ is symmetric under interchange of \mathbf{r}_1 and \mathbf{r}_2 .) The basic assumption of the present paper is that $\psi(\mathbf{R}_{ij}, \mathbf{r}_{ij})$ is a very slowly varying function of \mathbf{R}_{ij} . (The validity of this assumption will be checked in Sec. III.) Specifically, with respect to the clusters

$$\psi(\mathbf{R}_{12}, \mathbf{r}_{12}) \psi(\mathbf{R}_{23}, \mathbf{r}_{23}) \cdots \psi(\mathbf{R}_{2l,1}, \mathbf{r}_{2l,1})$$

appearing in the integrals defining b_l , t_l , and v_l , we assume that the $2l$ distinct $\mathbf{R}_{i,i+1}$ may all be replaced by the center-of-mass coordinate of the cluster,

$$\mathbf{R} = (2l)^{-1} \sum_{i=1}^{2l} \mathbf{r}_i, \quad (15)$$

The major contribution to these integrals will come from those regions of configuration space where all $2l$ electrons lie close to one another, since $\psi(\mathbf{R}_{ij}, \mathbf{r}_{ij})$ and ϕ_{ij} are presumed to be appreciable in size only when \mathbf{r}_{ij} is not large. Thus, \mathbf{R}_{ij} will not be very different from \mathbf{R} , and the slowness of the variation of $\psi(\mathbf{R}_{ij}, \mathbf{r}_{ij})$ with \mathbf{R}_{ij} will allow the latter to be replaced by \mathbf{R} . In a similar fashion, with respect to the two clusters appearing in the integral defining $v_{ll'}$, we assume that the \mathbf{R}_{ij} may all be replaced by the center-of-mass coordinate of the $2(l+l')$ electrons composing the two clusters.

For the purposes of the present paper, ϕ_{ij} may be assumed independent of the center-of-mass coordinate \mathbf{R}_{ij} . It does, however, depend on both the position and velocity of relative motion of the two electrons. We shall Fourier-expand ϕ and ψ with respect to \mathbf{r}_{ij} i.e.,

$$\psi(\mathbf{R}, \mathbf{r}_{ij}) = \sum_k f_k(\mathbf{R}) \exp(i\mathbf{k} \cdot \mathbf{r}_{ij}), \quad (16)$$

$$V_{kk'} = \int \exp(-i\mathbf{k} \cdot \mathbf{r}_{ij}) \phi_{ij} \exp(+i\mathbf{k}' \cdot \mathbf{r}_{ij}) d^3 r_{ij}. \quad (17)$$

We obtain

$$b_l = l^{-1} (-1)^{l-1} \int d^3 R \sum_k f_k^{2l}, \quad (18)$$

$$t_l = 2(-1)^{l-1} b_l^{-1} \int d^3 R \sum_k f_k^{2(l-1)} \times [(\hbar^2 k^2 / 2m) f_k^2 + l(\hbar^2 / 8m) (\nabla_{\mathbf{R}} f_k)^2], \quad (19)$$

$$v_l = 2(-1)^{l-1} b_l^{-1} \int d^3 R \sum_{kk'} (f_k - f_{k'})^{-1} f_{k'} f_k^{2l} V_{kk'}. \quad (20)$$

In these last three equations, the \mathbf{R} dependence of f_k is understood. Equations (18) and (19) follow immediately from the previous equations; Eq. (20) is proved in Appendix C of Nakamura's paper. Equation (19) contains two terms giving, respectively, the internal kinetic energy and the center-of-mass kinetic energy of the two electrons in each Cooper pair. It is this second term that distinguishes the present theory from that of Nakamura.

We assume that $V_{kk'}$ vanishes when $\mathbf{k}=\mathbf{k}'$. This corresponds to saying that that part of ϕ which does not scatter has been absorbed into the one-electron portions of the many-electron Hamiltonian. It is now easy to prove that

$$v_{ll'}=0. \quad (21)$$

Thus, Eq. (7) can be written more simply as

$$W_0 = \sum_l (t_l + v_l) b_l \frac{\partial}{\partial b_l} \ln Q_N, \quad (22)$$

where Q_N is defined as

$$Q_N = \sum_{m_l} \prod_l b_l^{m_l} / m_l!. \quad (23)$$

At this point we introduce the saddle-point method¹³ of evaluating Q_N . Define

$$G_v(z) = \sum_l l^v b_l z^l, \quad (24)$$

$$Q(z) = e^{G_0(z)}. \quad (25)$$

Expanding the exponent in (25), we get

$$Q(z) = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\sum_l b_l z^l \right)^N. \quad (26)$$

But

$$\left(\sum_l b_l z^l \right)^N = \sum_{m_l} N! \prod_l (b_l z^l)^{m_l} / m_l!, \quad (27)$$

where, as in (7) and (23), the summation is over all possible ways of choosing the set of non-negative integers m_l consistent with the restraint (13). Combining (11), (23), (26), and (27), we get the result²⁰

$$Q(z) = \sum_{N=0}^{\infty} z^N Q_N. \quad (28)$$

Choosing a contour of integration in the complex z plane lying within the circle of convergence of (28), we may write

$$Q_N = \frac{1}{2\pi i} \oint z^{-(N+1)} Q(z) dz. \quad (29)$$

²⁰ Here we are assuming that the power-series expansions in Eqs. (24) and (28) both have finite radii of convergence about the origin in the z plane. It will become clear that this is true provided $h_k \neq 1$, the condition mentioned in Ref. 18.

We take this contour to be a circle of radius Z centered on the origin. Thus

$$Q_N = (2\pi Z^N)^{-1} \int_{-\pi}^{+\pi} \exp[G_0(Ze^{i\theta}) - iN\theta] d\theta. \quad (30)$$

Now

$$\frac{\partial}{\partial \theta} [G_0(Ze^{i\theta}) - iN\theta] = i[G_1(Ze^{i\theta}) - N],$$

$$\frac{\partial^2}{\partial \theta^2} [G_0(Ze^{i\theta}) - iN\theta] = -G_2(Ze^{i\theta}).$$

We specify that the radius Z be such that

$$G_1(Z) = N. \quad (31)$$

From (18) and (24), we have

$$G_2(z) = \sum_k (1 + f_k^2 z)^{-2}. \quad (32)$$

Assuming $\psi(\mathbf{R}, \mathbf{r})$ to be real and to represent vanishing velocity of relative motion of the two electrons, it follows that f_k is real, so that $G_2(Z)$ is positive. Thus the point $z=Z(\theta=0)$ is a saddle point of $z^{-(N+1)}Q(z)$, a maximum with respect to variations in θ , a minimum with respect to variations in Z . Expanding $G_0(Ze^{i\theta}) - iN\theta$ as a power series in θ , keeping only the constant term and the term quadratic in θ , we get

$$Q_N = (2\pi Z^N)^{-1} e^{G_0(Z)} \int_{-\pi}^{+\pi} \exp[-\frac{1}{2}G_2(Z)\theta^2] d\theta,$$

It can be shown that $G_2(Z) \gg 1$, so that the integration limits $\pm\pi$ can be replaced by $\pm\infty$ with negligible error. Thus,

$$Q_N = Z^{-N} e^{G_0(Z)} [2\pi G_2(Z)]^{-1/2},$$

$$\ln Q_N = G_0(Z) - N \ln Z - \frac{1}{2} \ln [2\pi G_2(Z)]. \quad (33)$$

In order to evaluate Eq. (22), we need to differentiate $\ln Q_N$ with respect to b_l . In doing this, we can ignore the last term on the right-hand side of (33). From (32) we see that $G_2(Z)$ is very insensitive to the particular values of $f_k^2 Z$, since the major contribution to the sum over \mathbf{k} comes from regions of k space where f_k is effectively zero. (This is also the reason why $G_2(Z) \gg 1$.) Thus $\ln G_2(Z)$ should be insensitive to variations of b_l . In differentiating (33) with respect to b_l , we should remember that Z varies with b_l . However, we can actually ignore this, since Eq. (31) shows that the partial derivative of $G_0(Z) - N \ln Z$ with respect to Z will vanish. Thus,

$$\frac{\partial}{\partial b_l} \ln Q_N = Z^l, \quad (34)$$

so that (22) becomes

$$W_0 = \sum_l (t_l + v_l) b_l Z^l. \quad (35)$$

With the aid of Eqs. (18)-(20), this can be written

$$W_0 = \int d^3R W_0(\mathbf{R}), \tag{36}$$

where we define

$$W_0(\mathbf{R}) = 2 \sum_k (1 + f_k^2 Z)^{-1} \left[\left(\frac{\hbar^2 k^2}{2m} \right) f_k^2 Z + \frac{\hbar^2}{8m} (\nabla_R f_k)^2 Z (1 + f_k^2 Z)^{-1} \right] + 2 \sum_{kk'} \left(\frac{f_k^2 Z}{1 + f_k^2 Z} \right) V_{kk'} \left(\frac{f_{k'}}{f_k - f_{k'}} \right). \tag{37}$$

It should be understood that f_k and $f_{k'}$ are both functions of \mathbf{R} in this expression. By interchanging \mathbf{k} and \mathbf{k}' , we can write the potential-energy term in a more symmetric fashion,

$$W_0(\mathbf{R}) = 2 \sum_k (1 + f_k^2 Z)^{-1} \left[\left(\frac{\hbar^2 k^2}{2m} \right) f_k^2 Z + \frac{\hbar^2}{8m} (\nabla_R f_k)^2 Z (1 + f_k^2 Z)^{-1} \right] + \sum_{kk'} V_{kk'} \frac{f_k f_{k'} Z (1 - f_k f_{k'} Z)}{(1 + f_k^2 Z)(1 + f_{k'}^2 Z)}. \tag{38}$$

Equation (31), the defining equation for Z , becomes

$$\int d^3R \sum_k \left(\frac{f_k^2 Z}{1 + f_k^2 Z} \right) = N. \tag{39}$$

Now defining

$$h_k^{1/2} = (1 + f_k^2 Z)^{-1/2} f_k Z^{1/2}, \tag{40}$$

we transform the last two equations into

$$W_0(\mathbf{R}) = 2 \sum_k \left(\frac{\hbar^2 k^2}{2m} \right) h_k + \frac{\hbar^2}{4m} \sum_k [4h_k(1 - h_k)]^{-1} (\nabla_R h_k)^2 + \sum_{kk'} V_{kk'} [h_k(1 - h_k)h_{k'}(1 - h_{k'})]^{1/2} - \sum_{kk'} V_{kk'} h_k h_{k'}, \tag{41}$$

and

$$\int d^3R \sum_k h_k = N. \tag{42}$$

Here h_k and $h_{k'}$ are functions of \mathbf{R} .

It is appropriate to point out why the saddle-point method of summing cluster expansions worked in the present problem, despite the fact that a superconductor is a highly condensed system. Consider $G_0(z)$.

$$G_0(z) = \sum_l b_l z^l = \int d^3R \sum_k \sum_{l=1}^{\infty} l^{-1} (-1)^{l-1} (f_k^2 z)^l = \frac{1}{\Omega} \sum_{R,k} \ln(1 + f_k^2 z) = \frac{1}{\Omega} \sum_{R,k} \ln \left[1 + \left(\frac{h_k}{1 - h_k} \right) \left(\frac{z}{Z} \right) \right]. \tag{43}$$

Here we have replaced the integration over the crystal $\int d^3R$ by the corresponding summation over all atomic sites $\Omega \sum_R$, Ω being the atomic volume. This replacement is justified by the slow variation of $f_k(\mathbf{R})$ with \mathbf{R} . From the definition of $Q(z)$, we have

$$Q(z) = \left\{ \prod_{R,k} \left[1 + \left(\frac{h_k}{1 - h_k} \right) \left(\frac{z}{Z} \right) \right] \right\}^{\Omega}. \tag{44}$$

It is clear that $G_0(z)$ has singularities along the negative real axis at those points where

$$z = -Z h_k^{-1} (1 - h_k). \tag{45}$$

It will be seen presently that, independently of \mathbf{R} , $h_k(\mathbf{R})$ is less than or greater than one-half dependent on whether \mathbf{k} lies outside or inside, respectively, the Fermi surface in k space. Thus those \mathbf{k} lying inside the Fermi surface give rise to singularities lying inside the contour of integration in Eq. (29). This is a consequence of the condensed nature of the system we are studying. For most problems, singularities in G_0 would imply singularities in $Q = \exp G_0$. Singularities in Q inside the contour of integration would, of course, negate the applicability of the saddle-point method. For our particular problem, however, singularities in G_0 do not imply singularities in Q . As can be seen from (44), the singularities of G_0 correspond to zeros of Q , so that the saddle-point method is applicable despite the condensation of the system.²¹ Equation (45) shows that it is necessary to assume $h_k \neq 1$ in order that both $G_0(z)$ and $Q(z)$ have finite radii of convergence about the origin.²⁰ A further difficulty occurring in the theory of the condensed imperfect gas results from the volume dependence of the cluster integrals.²² There is no analogous problem here because the total volume occupied by the electrons is set by the dimensions of the crystal, not by the degree of condensation of the electrons.

The last term on the right-hand side of (41) is missing from the BCS theory because of truncation of the many-electron Hamiltonian in that theory. It turns out that this term is independent of \mathbf{R} , and thus may be ignored in determining the dependence of h_k on \mathbf{R} . The \mathbf{R}

²¹ This result appears to be a consequence of the type of cluster integral b_l occurring in the present theory, the so-called chain cluster integral, in contrast to the more general form of cluster integral appearing in imperfect-gas theory.

²² T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 5.

independence of this term is a consequence of the dependence on \mathbf{k} and \mathbf{k}' of $V_{kk'}/h_k h_{k'}$, as will become apparent presently. Let us redefine the zero of energy of W_0 such that this term disappears from (41) and, in addition, the first term on the right-hand side of (41) becomes $2\sum_k \epsilon_k h_k$, where

$$\epsilon_k = \frac{\hbar^2}{2m}(k^2 - k_F^2), \quad (46)$$

and k_F is the Fermi momentum (i.e., we take the one-electron energy ϵ_k to be zero at the Fermi surface).

It is instructive to rewrite the second term on the right-hand side of (41):

$$\begin{aligned} & \frac{\hbar^2}{4m} \sum_k [4h_k(1-h_k)]^{-1} (\nabla_R h_k)^2 \\ &= \frac{\hbar^2}{4m} \sum_k [(\nabla_R (h_k)^{1/2})^2 + (\nabla_R (1-h_k)^{1/2})^2]. \end{aligned} \quad (47)$$

In the writer's previous paper,⁸ it was assumed that the term $(\hbar^2/4m)(\nabla_R (h_k)^{1/2})^2$ appeared only for $k > k_F$, and the term $(\hbar^2/4m)(\nabla_R (1-h_k)^{1/2})^2$ appeared only for $k < k_F$, whereas the analysis of the present paper has demonstrated that both terms should appear for every k . Intuitively, the first term represents center-of-mass kinetic energy of a Cooper pair of electrons; the second, center-of-mass kinetic energy of a Cooper pair of holes. The inclusion of both terms will modify quantitatively, but not qualitatively, the results of the previous paper. For ϵ_k large and positive (i.e., $h_k \rightarrow 0$), only the electron term is important; for ϵ_k large and negative (i.e., $h_k \rightarrow 1$), only the hole term is important.

We now wish to find the function $h_k(\mathbf{R})$ which minimizes W_0 . This is obtained from the Euler-Lagrange equation

$$\left[\frac{\partial}{\partial h_k} - \nabla_R \frac{\partial}{\partial \nabla_R h_k} \right] W_0(\mathbf{R}) = 0. \quad (48)$$

Inserting $W_0(\mathbf{R})$, we get

$$\begin{aligned} & 2\epsilon_k - (\hbar^2/8m) \{ [h_k(1-h_k)]^{-1/2} \nabla_R \}^2 h_k + (1-2h_k) \\ & \times [h_k(1-h_k)]^{-1/2} \sum_{k'} V_{kk'} [h_{k'}(1-h_{k'})]^{+1/2} = 0. \end{aligned} \quad (49)$$

Anticipating the fact that $V_{kk'}$ is an *even* function of ϵ_k and $\epsilon_{k'}$, we can immediately infer from (49) that $(1-2h_k)$ is an *odd* function of ϵ_k . Now $h_k \rightarrow 0$ for $\epsilon_k \gg 0$, $h_k \rightarrow 1$ for $\epsilon_k \ll 0$, this holding for all \mathbf{R} . Therefore,

$$\sum_k h_k(\mathbf{R}) = N, \quad (50)$$

a stronger condition than that of Eq. (42). [It should be remembered, in comparing (42) and (50), that we are considering the crystal to have unit volume.] Equation (50), in effect, states that the density of Cooper pairs is uniform throughout the crystal (no net change density).

III. THE SUPERCONDUCTING METAL

Henceforth we shall assume

$$\begin{aligned} V_{kk'} &= \pm V \quad \text{for } |\epsilon_k|, |\epsilon_{k'}| < \hbar\omega \\ &= 0 \quad \text{otherwise,} \end{aligned} \quad (51)$$

$\hbar\omega$ being a mean phonon energy. The minus sign (attractive interaction) is to be taken for the superconducting metal to be discussed in this section; the plus sign (repulsive interaction) is to be taken for the normal metal to be discussed in the following section. We write

$$h_k = \frac{1}{2} [1 - (\epsilon_k(\epsilon_k^2 + \epsilon_{0k}^2)^{-1/2})], \quad (52)$$

so that

$$1 - 2h_k = \epsilon_k(\epsilon_k^2 + \epsilon_{0k}^2)^{-1/2}, \quad (53)$$

$$2(h_k(1-h_k))^{1/2} = \epsilon_{0k}(\epsilon_k^2 + \epsilon_{0k}^2)^{-1/2}. \quad (54)$$

Since h_k is a function of \mathbf{R} , the order parameter ϵ_{0k} also is.²³ We shall restrict ourselves to the case where h_k and ϵ_{0k} vary along one direction only in the crystal, say the x direction. Equation (49) can be rewritten

$$\begin{aligned} & \frac{1}{2} V \sum_{k'} \left(\frac{\epsilon_{0k'}}{\epsilon_{0k}} \right) (\epsilon_{k'}^2 + \epsilon_{0k'}^2)^{-1/2} \\ & - \frac{\hbar^2}{8m} \left(\frac{1}{\epsilon_{0k}} (\epsilon_k^2 + \epsilon_{0k}^2)^{1/2} \frac{d}{dx} \right)^2 (\epsilon_k^2 + \epsilon_{0k}^2)^{-1/2} = 1. \end{aligned} \quad (55)$$

(The prime on the summation sign indicates that k' is restricted by the condition $|\epsilon_{k'}| < \hbar\omega$.) If ϵ_{0k} were independent of x , then Eq. (55) implies that ϵ_{0k} would also be independent of k (for $|\epsilon_k| < \hbar\omega$). Since we are especially interested in the value of ϵ_{0k} at $k = k_F$, the Fermi surface, we shall solve (55) for this case, making the approximation that $(\epsilon_{0k'}/\epsilon_{0k}) = 1$ in the k' summation. Designating the value of ϵ_{0k} at the Fermi surface by ϵ_0 with no k subscript, and replacing the summation by the equivalent integration, we have

$$N(0)V \operatorname{arcsinh}(\hbar\omega/\epsilon_0) - (\hbar^2/8m)(d^2/dx^2)(1/\epsilon_0) = 1, \quad (56)$$

$N(0)$ being the density of one-electron states (of a given spin) per unit energy at the Fermi level in the metal in the normal state. Since under all conditions of interest to us $\epsilon_0 \ll \hbar\omega$, we may approximate

$$\operatorname{arcsinh}(\hbar\omega/\epsilon_0) \quad \text{by} \quad \ln(2\hbar\omega/\epsilon_0).$$

We define the constants

$$\epsilon_0(\infty) = 2\hbar\omega e^{-1/N(0)V} \quad (57)$$

$$\delta = \frac{1}{8} \left(\frac{2\hbar}{N(0)V m \omega} e^{1/N(0)V} \right)^{1/2} \quad (58)$$

and the variable

$$z(x) = \epsilon_0(\infty)/\epsilon_0(x), \quad (59)$$

²³ Unlike the position-independent case, ϵ_{0k} is not necessarily equal to the excitation energy for producing a normal carrier, a fact which will be discussed in Sec. VI.

so that Eq. (61) becomes

$$2\delta^2(d^2z/dx^2) = \ln z. \quad (60)$$

This is the same equation obtained previously by the writer.⁸ The only difference lies in the fact that the present definition of δ is a factor of $\sqrt{2}$ larger than that of Ref. 8 [a consequence of the fact that both terms appear in Eq. (47)]. As before, a first integration of (65) gives

$$\delta(dz/dx) = \pm [K + z(\ln z - 1)]^{1/2}, \quad (61)$$

a second integration giving

$$x = \pm \delta \int_{z_0}^z [K + z'(\ln z' - 1)]^{-1/2} dz', \quad (62)$$

z_0 and K being integration constants. The constant $\epsilon_0(\infty)$ is just the constant value of ϵ_0 to be found in the interior of a bulk superconductor [i.e., $\epsilon_0(\infty)$ is the BCS value of ϵ_0]. Thus, in such a bulk superconductor we want $z \rightarrow 1$ as $x \rightarrow \infty$. At the same time we want $(dz/dx) \rightarrow 0$. This means that for a bulk superconductor we must take

$$K = 1. \quad (63)$$

For this case, a plot of $1/z$ versus $\pm x/\delta$ can assume the two possible forms diagrammed in Fig. 1 of Ref. 8. The characteristic length δ can be written

$$\delta = \frac{1}{2} [2\xi_0 \lambda_F / N(0)V]^{1/2}, \quad (64)$$

where

$$\lambda_F = 2\pi/k_F \quad (65)$$

is the Fermi wavelength, and

$$\xi_0 = [\hbar v_F / \pi \epsilon_0(\infty)] \quad (66)$$

is the BCS form of the Pippard coherence distance. (v_F is the velocity of electrons at the Fermi level.) Typical values for a soft superconductor are $\lambda_F/2\pi = 10^{-8}$ cm, $\delta = 10^{-6}$ cm, $\xi_0 = 10^{-4}$ cm. It should be pointed out that critical thicknesses of metallic films (either normal on bulk superconducting material, or vice versa) are about an order of magnitude larger than δ , as was found in Ref. 8. This results from the weak dependence on z of the term $\ln z$ appearing in Eq. (60).

In the previous section, we made the basic assumption that the two-electron orbital $\psi(\mathbf{R}, \mathbf{r})$ was a much more slowly varying function of the center-of-mass coordinate \mathbf{R} than of the relative coordinate \mathbf{r} . We are now in a position to get a measure of the accuracy of this assumption. Define

$$\lambda_1 = \left[\int |\nabla_{\mathbf{r}} \psi(\mathbf{R}, \mathbf{r})|^2 d^3\mathbf{r} / \int |\psi(\mathbf{R}, \mathbf{r})|^2 d^3\mathbf{r} \right]^{-1/2}, \quad (67)$$

$$\lambda_2 = \left[\int |\nabla_{\mathbf{R}} \psi(\mathbf{R}, \mathbf{r})|^2 d^3\mathbf{r} / \int |\psi(\mathbf{R}, \mathbf{r})|^2 d^3\mathbf{r} \right]^{-1/2}. \quad (68)$$

λ_1 is a measure of the distance over which there is appreciable variation of ψ with respect to \mathbf{r} ; λ_2 is a measure of the distance over which there is appreciable variation of ψ with respect to \mathbf{R} . It is straightforward to calculate

$$\lambda_1 \cong \lambda_F / 2\pi, \quad (69)$$

$$\lambda_2 \cong \frac{d}{dR} \ln z. \quad (70)$$

We see that λ_1 is two orders of magnitude smaller than λ_2 , in agreement with our previous assumption.

IV. THE NORMAL METAL

In Ref. 8 the discussion of normal metals was restricted to the case $V_{kk'} = 0$. Here we wish to generalize to the case of repulsive electron-electron interaction, namely $V_{kk'} = +V$. Inserting such a $V_{kk'}$ into Eq. (49), we can see, by inspection, the trivial solution $h_k = 0$ for $\epsilon_k > 0$, $h_k = 1$ for $\epsilon_k < 0$, corresponding to the position-independent normal metal. In addition, however, there are nontrivial solutions which can be obtained almost as easily. The key observation is the fact that

$$f_k = [h_k / Z(1 - h_k)]^{1/2}$$

need not necessarily be a positive number, although our method of defining $h_k^{1/2}$ [Eq. (40)] might lead one to infer that $f_k \geq 0$. Actually there is no inconsistency in allowing $h_k^{1/2}$ to assume both positive and negative values. [(1 - h_k)^{1/2} will always be non-negative.] We allow the signature of $h_k^{1/2}$ to be a random function of \mathbf{k} , consistent with the condition that (1 - 2 h_k) be a continuous, odd function of ϵ_k . The potential-energy term in (49) thus becomes negligibly small (in the limit of a large crystal) and may be ignored. By allowing this random variation in the signature of $h_k^{1/2}$, we have effectively quenched the repulsive interaction.

Equation (49) now becomes

$$\epsilon_k - (\hbar^2/16m)(d^2h_k/du_k^2) = 0, \quad (71)$$

where

$$\frac{d}{du_k} \equiv (h_k(1 - h_k))^{-1/2} \frac{d}{dx}. \quad (72)$$

Thus

$$u_k^2 = (\hbar^2/8m\epsilon_k)(h_k - 1 + C_k^2),$$

where $C_k^2 - 1$ is an integration constant to be set by boundary conditions. Consider, for the moment, the case $\epsilon_k > 0$.

$$\begin{aligned} (x/\hbar)(8m\epsilon_k)^{1/2} &= \hbar^{-1}(8m\epsilon_k)^{1/2} \int [h_k(1 - h_k)]^{-1/2} du_k \\ &= \pm \frac{1}{2} \int [h_k(1 - h_k)(h_k - 1 + C_k^2)]^{-1/2} dh_k \\ &= \mp \arccdn(\pm h_k^{1/2}, C_k). \end{aligned}$$

arcdn is the inverse elliptic function (i.e., elliptic integral); C_k is the modulus of the elliptic function.

$$h_k^{1/2} = \pm \operatorname{dn} \left(\pm \frac{x}{\hbar} (8m\epsilon_k)^{1/2}, C_k \right). \quad (73)$$

(The two choices of sign in this expression are independent of each other.) In the limit $h_k \ll 1$.

$$\begin{aligned} (x/\hbar)(8m\epsilon_k)^{1/2} &= \pm \frac{1}{2} \int [h_k(h_k - 1 + C_k^2)]^{-1/2} dh_k \\ &= \pm \operatorname{arccosh} \pm [h_k/(1 - C_k^2)]^{1/2}, \quad C_k^2 < 1 \\ &= \pm \operatorname{arcsinh} \pm [h_k/(C_k^2 - 1)]^{1/2}, \quad C_k^2 > 1 \end{aligned}$$

or

$$\pm h_k^{1/2} = \operatorname{const} \times \frac{\cosh \left(\frac{x}{\hbar} (8m\epsilon_k)^{1/2} \right)}{\sinh \left(\frac{x}{\hbar} (8m\epsilon_k)^{1/2} \right)}. \quad (74)$$

This is the solution obtained in Ref. 8. In the opposite limit $h_k \rightarrow \frac{1}{2}$, Eq. (74) should be modified by replacing $(8m\epsilon_k)^{1/2}$ by $(4m\epsilon_k)^{1/2}$. We have thus far been considering the case $\epsilon_k > 0$. Expressions analogous to (73) and (74) hold for the case $\epsilon_k < 0$ [$(1 - h_k)^{1/2}$ replacing $(h_k)^{1/2}$, and $|\epsilon_k|$ replacing ϵ_k].

V. BOUNDARY CONDITIONS

Before we can apply the results obtained thus far to problems involving two different metals in contact, we must discuss boundary conditions. We are immediately confronted with the difficulty that the true boundary conditions for any pair of electrons are not separable in terms of internal and center-of-mass coordinates. Thus, we are forced to replace the true boundary conditions by approximate ones which are separable.²⁴ Specifically, we assume that the two-electron orbital $\psi(\mathbf{R}_{12}, \mathbf{r}_{12})$ satisfies periodic boundary conditions with respect to the internal coordinate \mathbf{r}_{12} , while there is continuity, as a function of the center-of-mass coordinate \mathbf{R}_{12} , of both $\psi^*\psi$ and $\psi^*\nabla_R\psi$. It should be noted that not only are we assuming separability of boundary conditions, but in addition a possible loss of phase coherence of the center-of-mass motion at the boundary. (This follows from specifying that $\psi^*\psi$ and $\psi^*\nabla_R\psi$ be continuous with respect to \mathbf{R}_{12} , rather than ψ and $\nabla_R\psi$ alone.) Because of lack of geometrical perfection, on the atomic scale, of most interfaces experimentally realizable (epitaxially grown interfaces being a possible exception), it seems reasonable to assume that Cooper pairs passing through the interface will be "diffusely refracted" with consequent loss of phase. It should be added that there will be no phase coherence between two electrons on opposite sides of the interface (that is, two such electrons cannot form a Cooper pair) because of

the lack of conservation of total momentum during virtual exchanges of phonons between the two electrons. In passing from one electron to the other, a virtual phonon is refracted at the interface (with consequent change of its momentum) because of the difference in elastic properties of the two metals forming the interface.²⁵

To simplify the discussion, we shall restrict ourselves to interfaces between two metals which differ in the strength of the electron-electron interaction, while having the same one-electron energy levels. Under such conditions, the boundary conditions on ψ are equivalent to continuity of $h_k(\mathbf{R})$ and $\nabla_R h_k(\mathbf{R})$ at the interface, but not necessarily continuity of $(h_k(\mathbf{R}))^{1/2}$. With regard to the interface between a superconductor and a normal metal, it is clear that $h_k^{1/2}$ cannot be both continuous and nonvanishing at the interface, because of the fact that $h_k^{1/2}$ is positive in the superconductor but negative (for some values of k) in the normal metal.

In practice, it appears difficult, if not impossible, to get continuity of both h_k and $\nabla_R h_k$ because of the necessity for making approximations in solving Eq. (49) for a superconductor (e.g., the approximation that the order parameter ϵ_{0k} is independent of \mathbf{k}). In effect, any reasonable approximation for solving the nonlinear integro-differential equation for h_k is incompatible with the boundary conditions. This impasse can be resolved by relaxing the boundary conditions in the following manner: h_k is made continuous as before; but rather than having continuity of $\nabla_R h_k$ for all \mathbf{k} , we require only continuity of a suitably weighted average of $\nabla_R h_k$, the averaging being over values of \mathbf{k} . On physical grounds we shall assume that such a suitably weighted average is the surface-energy density associated with any discontinuities in $\nabla_R h_k$ at the surface of a crystal. We shall now calculate this surface energy. Consider that portion of W_0 due to center-of-mass kinetic energy of electron pairs, which, from Eq. (37), can be seen to be

$$W_0' = (\hbar^2/4m) \int d^3R \sum_k (1 + f_k^2 Z)^{-2} (\nabla_R f_k)^2 Z. \quad (75)$$

Note that each term in the k summation is invariant to replacement of $f_k Z^{1/2}$ by its reciprocal. We make this replacement for all $k < k_F$. Next, we expand each term $k < k_F$ as a power series in $f_k^{-1} Z^{-1/2}$,

$$\begin{aligned} W_0' &= \sum_{k > k_F} \sum_l (-1)^{l-1} Z^l \int d^3R \left(\frac{\hbar^2}{4ml} \right) (\nabla_R f_k^l)^2 \\ &+ \sum_{k < k_F} \sum_l (-1)^{l-1} Z^{-l} \int d^3R \left(\frac{\hbar^2}{4ml} \right) (\nabla_R f_k^{-l})^2. \end{aligned} \quad (76)$$

This is a cluster expansion in terms of electrons lying outside the Fermi surface and holes lying inside the Fermi

²⁴ A similar use of separable, approximate boundary conditions, with regard to a two-electron example of ferromagnetism, has been made by J. C. Slater, H. Statz, and G. F. Koster, Phys. Rev. **91**, 1323 (1953).

²⁵ This is the reason the effective electron-electron potential V can be taken to change discontinuously at an interface between two metals, V being position-independent elsewhere.

surface. Each term in the l summations can be recognized as center-of-mass kinetic energy of a cluster of $2l$ electrons for $k > k_F$, a cluster of $2l$ holes for $k < k_F$, the former cluster being represented by the wave function f_k^l , the latter cluster by the wave function f_k^{-l} . Here the kinetic energy is written as the positive square of the gradient of the wave function; a more conventional way of writing such an energy is in terms of the negative of the second derivative of the wave function, i.e.,

$$W_0'' = \sum_{k > k_F} \sum_l (-1)^{l-1} Z^l \int d^3R f_k^l \left(-\frac{\hbar^2}{4ml} \nabla_R^2 f_k^l \right) + \sum_{k < k_F} \sum_l (-1)^{l-1} Z^l \int d^3R f_k^{-l} \left(-\frac{\hbar^2}{4ml} \nabla_R^2 f_k^{-l} \right). \quad (77)$$

W_0'' differs from W_0' by a surface integral, i.e.,

$$W_0' = W_0'' + \int d^2R W_{S0}(\mathbf{R}), \quad (78)$$

where

$$W_{S0}(\mathbf{R}) = \frac{\hbar^2}{4m} \sum_{k > k_F} \sum_l (-1)^{l-1} Z^l l^{-1} f_k^l \mathbf{n} \cdot \nabla_R f_k^l + \frac{\hbar^2}{4m} \sum_{k < k_F} \sum_l (-1)^{l-1} Z^l l^{-1} f_k^{-l} \mathbf{n} \cdot \nabla_R f_k^{-l} \quad (79)$$

is the desired surface-energy density. Here \mathbf{n} is the unit vector normal to the surface. By analytically summing the l series, and rewriting f_k in terms of h_k , we get

$$W_{S0}(\mathbf{R}) = \frac{\hbar^2}{8m} \mathbf{n} \cdot \left[\sum_{k > k_F} (1-h_k)^{-1} \nabla_R h_k + \sum_{k < k_F} h_k^{-1} \nabla_R (1-h_k) \right]. \quad (80)$$

Since $(1-2h_k)$ is an odd function of ϵ_k , it follows that the two summations, $\sum_{k > k_F}$ and $\sum_{k < k_F}$, make equal contributions to $W_{S0}(\mathbf{R})$. Thus,

$$W_{S0}(\mathbf{R}) = -\frac{\hbar^2}{4m} \mathbf{n} \cdot \nabla_R \sum_{k > k_F} \ln(1-h_k). \quad (81)$$

Rewriting h_k in terms of the order parameter ϵ_{0k} as given by Eq. (52), assuming ϵ_{0k} to be independent of \mathbf{k} , and replacing the summation by the equivalent integration, we get

$$W_{S0}(\mathbf{R}) = -(\hbar^2/4m) \mathbf{n} \cdot \nabla_R N(0) \int_0^\infty \ln \frac{1}{2} \left[1 + \frac{\epsilon}{(\epsilon^2 + \epsilon_0^2)^{1/2}} \right] d\epsilon = -(\hbar^2/8m) (\pi-2) N(0) \epsilon_0^2 \mathbf{n} \cdot \nabla_R (1/\epsilon_0). \quad (82)$$

This expression differs from the corresponding expres-

sion in Ref. 8 only by the additional factor $(\pi-2)$. Equation (80) differs from the expression of Ref. 8 through the factor $(1-h_k)^{-1}$ for $\epsilon_k > 0$, the factor h_k^{-1} for $\epsilon_k < 0$.

VI. EXCITED STATES

In principle, the mathematical formalism of the present paper is unsuitable for a rigorous calculation of single-particle excited states of the superconductor. The difficulty stems from the fact that our many-electron wave function is an antisymmetrized product of two-electron wave functions, rather than an antisymmetrized product of one-electron wave functions. In practice, we can visualize a single-particle excited state in the following fashion. In addition to the $2N$ electrons we have been considering thus far, we introduce a $(2N+1)$ st electron which occupies with unit probability a given one-electron Bloch state of wave vector \mathbf{k} and spin s . In the limit of slow variation of the two-electron wave function $\psi(\mathbf{R}, \mathbf{r})$ with \mathbf{R} , the exclusion principle now forces the \mathbf{k} term to be removed from every one of the wave-vector summations of Sec. II; i.e., the $2N$ ground-state electrons cannot occupy the single-particle orbital already filled by the additional electron. The total energy of the system will be ϵ_k , the Bloch energy of the occupied orbital, plus the energy given by the \mathbf{R} integration of Eq. (41) after removing the terms indexed by the wave vector \mathbf{k} . The single-particle excitation energy W_k will be this total energy minus the energy before the $(2N+1)$ st electron was introduced, i.e.,

$$W_k = \int d^3R W_k(\mathbf{R}), \quad (83)$$

where

$$W_k(\mathbf{R}) = \epsilon_k (1-2h_k) - \frac{\hbar^2}{4m} [4h_k(1-h_k)]^{-1} (\nabla_R h_k)^2 - 2(h_k(1-h_k))^{1/2} \sum_{k'} V_{kk'} (h_{k'}(1-h_{k'}))^{1/2}. \quad (84)$$

[It should be recalled that the last term on the right-hand side of (41) has been removed by a redefinition of the energy.] In the case of a bulk superconductor, the order parameter ϵ_{0k} equals $\epsilon_0(\infty)$, the BCS value, over the predominant portion of the material not too close to a surface, from which it follows that

$$W_k = (\epsilon_k^2 + \epsilon_0^2(\infty))^{1/2} \quad (85)$$

just as in the BCS theory.

We see that the excitation energy W_k is not a function of position, despite the fact that the order parameter ϵ_{0k} may be.²⁶ This is a consequence of our assumption that the additional electron occupies a single-particle

²⁶ In the case of a strongly disordered superconducting alloy, a position-dependent excitation energy is possible. The value of the excitation energy at any point is a weighted average of $W_k(\mathbf{R})$ over a region surrounding the point, this region being of the size of the normal-electron mean free path in the alloy.

orbital extending throughout the crystal, rather than one localized to the surface of the crystal, for example. The reasonableness of this assumption can be inferred from the discussion of Sec. I, where it was pointed out that the electric fields which are modifying the Cooper pair wave functions hundreds of Angstroms from a surface will have a negligible effect on single-particle orbitals more than a few Angstroms from the surface. (It will be recalled that this behavior depends on the low center-of-mass kinetic energy of the Cooper pairs in comparison with that of an individual electron.) For all practical purposes, an individual electron sees a field-free crystal.

For the case of two different metals in contact at an interface, it seems appropriate to consider distinct excited states for the two metals. The Bloch orbital occupied in forming an excited state is an orbital which spreads only over the metal with which the excited state is associated. This is consistent with the loss of phase of the wave function in crossing the interface, discussed in the previous section. Consider the problem where Bloch orbital \mathbf{k} in metal A is occupied, thereby forcing $h_{\mathbf{k}}$ to vanish in A . The continuity of $h_{\mathbf{k}}$ and $\nabla_{\mathbf{R}}h_{\mathbf{k}}$ at the interface thereby forces $h_{\mathbf{k}}$ in metal B , over a region near the interface, to be smaller than it would be in the absence of any excited electron in A . This means that the excitation energy in A is, in part, due to a change in $W_0(\mathbf{R})$ in B . Such an effect is crucial for understanding the possibility of a finite energy gap in a normal metal, when that normal metal consists of a sufficiently thin film on a bulk superconductor. The absence of any attractive electron-electron interaction in the normal

metal means that changes in $W_0(\mathbf{R})$ in the normal metal itself are incapable of explaining a finite energy gap; changes in $W_0(\mathbf{R})$ in the superconductor near the interface can, however, give rise to the finite gap.

The presence or absence of a finite energy gap in the excitation spectrum can be determined without actually calculating what this excitation spectrum is. One makes use of a theorem by Migdal.²⁷ Let $h_{\mathbf{k}}$ represent the probability of occurrence of one-electron state \mathbf{k} in the many-electron ground state of a metal. (This definition of $h_{\mathbf{k}}$ is consistent with the present paper in the limit of slow variation of $h_{\mathbf{k}}$ with \mathbf{R} .) The presence of a discontinuity in $h_{\mathbf{k}}$ (as a function of $\epsilon_{\mathbf{k}}$) at the Fermi level implies the absence of an energy gap in the single-particle excitation spectrum; the absence of a discontinuity in $h_{\mathbf{k}}$ implies the presence of an energy gap. An examination of Eq. (52) indicates that the former situation corresponds to $\epsilon_{0\mathbf{k}}$ vanishing with $\epsilon_{\mathbf{k}}$; the latter situation corresponds to $\epsilon_{0\mathbf{k}}$ staying finite as $\epsilon_{\mathbf{k}} \rightarrow 0$. Thus, the vanishing energy gap goes with vanishing order parameter $\epsilon_{0\mathbf{k}}$ at the Fermi level; finite energy gap goes with finite order parameter at the Fermi level. With regard to Eq. (73), the form of $h_{\mathbf{k}}$ appropriate to the normal metal, it is easy to see that the integration constant $C_k^2 < 1$ corresponds to finite $\epsilon_{0\mathbf{k}}(k \rightarrow k_F)$, while $C_k^2 > 1$ corresponds to vanishing $\epsilon_{0\mathbf{k}}(k \rightarrow k_F)$. As was indicated in Ref. 8, a sufficiently thin film of normal metal on bulk superconductor will require the former case.

²⁷A. B. Migdal, Zh. Eksperim. i Teor. Fiz. **32**, 399 (1957) [translation: Soviet Phys.—JETP **5**, 333 (1957)]; see also J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).