Spherical Impurity in an Infinite Superconductor*

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The modifications in a superconducting medium due to a single, spherically symmetric, nonmagnetic impurity are examined using the BCS theory of superconductivity. The energy spectrum of quasiparticles has both a discrete portion (bound states) and a continuous portion (scattering states). In the scattering region ($E>\Delta$), a given energy corresponds to two distinct momentum states, one above and one below the Fermi level. The calculation of the S matrix for the impurity scattering is thus a problem of two coupled channels. The electron density $n(r)$ and the order parameter $\Delta(r)$ far from the impurity are evaluated asymptotically in terms of the eigenphase shifts and mixing parameter of the two channels. Two soluble models for the impurity are considered. With a hard-sphere, long-range spatial oscillations are found in $\Delta(r)$ as well as in $n(r)$. With a delta-shell potential, a resonant enhancement occurs in the scattering of quasiparticles with momentum near the Fermi momentum. Both the spatial oscillations and the resonant enhancement are expected to appear for more general impurity potentials.

I. INTRODUCTION

MICROSCOPIC theories of superconductivity have generally been restricted to translationally invariant systems,[1] where the theory may be greatly simplified in momentum representation. Even superconducting alloys, which are inherently nonuniform, have been rendered translationally invariant by averaging over the random positions of the impurities.[2] In contrast, the standard theory of normal metallic alloys[3] is based on the intrinsic spherical symmetry of a single impurity atom. The effect of the impurity on the normal metal is expressed in terms of a set of phase shifts, found from the solution of the Schrödinger equation.[4] This paper gives an analogous partial-wave treatment of a superconductor containing a single spherically symmetric potential (to be called an impurity for simplicity).[5] The impurity is responsible for several essentially kinematic effects, which are independent of the detailed form of the potential. The most striking results are: (1) the existence of long-range spatial oscillations in the order parameter $\Delta(r)$, and (2) a resonant enhancement of the impurity scattering of quasiparticles with momentum near the Fermi momentum.

Section II reviews the properties of a uniform superconductor using a separation in partial waves. Section III incorporates the impurity potential into the partial-wave equations, which are then rewritten in the form of the Lippmann-Schwinger equation. The S matrix element that describes the scattering of quasiparticles by the impurity is calculated from the single-particle Green's function in Sec. IV. The scattering cross section is then simplified in terms of the phase shifts, which are introduced in Sec. V. Two soluble models illustrate the most important effects of the impurity: a hard-sphere potential (Sec. VI) and a delta-shell potential (Sec. VII).

II. A UNIFORM SUPERCONDUCTOR

Thermodynamic Green's functions offer a convenient formalism for the study of many-particle systems at finite temperatures.[6,7] It is useful to introduce a matrix notation to include the anomalous correlation functions characteristic of a superconducting medium.[8,9] We therefore define a matrix single-particle Green's function

$$G_{ij}(\mathbf{r}t,\mathbf{r}'t')=-i\langle(\Psi_i(\mathbf{r}t)\Psi_j^\dagger(\mathbf{r}'t'))_+\rangle, \qquad (1)$$

where $\Psi(\mathbf{r}t)$ is a two-component vector, $\Psi_1(\mathbf{r}t)=\psi_\uparrow(\mathbf{r}t)$, $\Psi_2(\mathbf{r}t)=\psi_\downarrow^\dagger(\mathbf{r}t)$. Here the arrow represents spin up and spin down with respect to an arbitrary axis of quantization. The subscript $+$ in Eq. (1) indicates positive time ordering of the Heisenberg field operators (from right to left in ascending order) and includes an additional sign factor $(-1)^P$, where P is any permutation from the given order. The average implied by $\langle\cdots\rangle$ is taken over a grand canonical ensemble at a temperature β^{-1}.

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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[2] A. A. Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **35**, 1558 (1958) [English transl.: Soviet Phys.—JETP **8**, 1090 (1959)]. See also P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[3] J. Friedel, Phil. Mag. **43**, 153 (1952); Advan. Phys. **3**, 446 (1954); Nuovo Cimento **7**, Suppl. 2, 287 (1958); E. Daniel, J. Phys. Radium **20**, 767, 849 (1959); J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1960).
[4] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., pp. 103–114.
[5] Related work has appeared by H. Suhl, in *Low-Temperature Physics* (Gordon and Breach, Science Publishers, New York, 1962), pp. 244–258; H. Suhl, D. R. Fredkin, J. S. Langer, and B. T. Matthias, Phys. Rev. Letters **9**, 63 (1962).
[6] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959); L. P. Kadanoff and P. C. Martin, *ibid.* **124**, 670 (1961). We shall follow the notation of this reference rather than that of Ref. 7.
[7] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).
[8] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].
[9] Y. Nambu, Phys. Rev. **117**, 648 (1960).

In the BCS theory,[1,8] the single-particle Green's functions obey a matrix equation of motion

$$\{i\partial/\partial t+\tau^{(3)}[(2m)^{-1}\nabla^2+\mu]-\Delta(r)\tau^{(1)}-\mathcal{U}(r)\}G(\mathbf{r}t,\mathbf{r}'t')=\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \quad (2)$$

where $\mathcal{U}(r)$ is a 2×2 matrix of the form $\mathcal{U}(r)=\mathcal{U}_1(r)\tau^{(1)}+\mathcal{U}_3(r)\tau^{(3)}$, depending only on $r\equiv|\mathbf{r}|$. The symmetry of $\mathcal{U}$ implies that the order parameter $\Delta(r)$ is also spherically symmetric. In the absence of magnetic fields or spin-dependent interactions, $\Delta(r)$ may be taken to be real, as assumed in Eq. (2). The matrices $\tau^{(i)}$ are the standard Pauli spin matrices. The quantities μ and m are the chemical potential and electron mass, and units have been chosen such that $\hbar=1$.

An essential feature of the BCS theory is the self-consistent determination of the order parameter. In the Gorkov approximation,[7,8] which is used here for mathematical simplicity, the interelectron potential is replaced by a constant attraction for electrons with energy near the Fermi energy and zero elsewhere. The self-consistency condition then becomes

$$\Delta(r)=g\langle\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})\rangle=igG_{12}(\mathbf{r}t^+,\mathbf{r}t), \quad (3)$$

where g is a positive coupling constant, and the notation t^+ means a time infinitesimally later than t.

The thermodynamic Green's function is most easily determined by restricting the time variables to the range $0\leqq t,t'\leqq-i\beta$. In this domain, G is antiperiodic in each variable with period $-i\beta$[6,7]; this property allows an expansion in a Fourier series,

$$G_{ij}(\mathbf{r}t,\mathbf{r}'t')=i\beta^{-1}\sum_\nu e^{-i\omega_\nu(t-t')}\hat{G}_{ij}(\mathbf{r},\mathbf{r}',\omega_\nu), \quad (4)$$

where $\omega_\nu=i\pi\nu/\beta$ and ν runs over the odd integers. The equation of motion for the Fourier coefficient is easily found from Eqs. (2) and (4) to be

$$\{\omega_\nu+\tau^{(3)}[(2m)^{-1}\nabla^2+\mu]-\Delta(r)\tau^{(1)}-\mathcal{U}(r)\}\times\hat{G}(\mathbf{r},\mathbf{r}',\omega_\nu)=\delta(\mathbf{r}-\mathbf{r}'). \quad (5)$$

Equation (5) determines $\hat{G}$ only at a discrete set of points, and the full Green's function requires an analytic continuation to all values of the frequency. For this purpose, it is simplest to compute the matrix spectral function $A(\mathbf{r},\mathbf{r}',\omega')$ from the prescription

$$A(\mathbf{r},\mathbf{r}',\omega')=-i[\hat{G}(\mathbf{r},\mathbf{r}',\omega'-i\eta)-\hat{G}(\mathbf{r},\mathbf{r}',\omega'+i\eta)], \quad (6)$$

where $\eta\to0(+)$. The single-particle Green's function may then be constructed from the integral representation

$$G(\mathbf{r}t,\mathbf{r}'t')=\int\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\int\frac{d\omega'}{2\pi}A(\mathbf{r},\mathbf{r}',\omega')\times\left[\frac{1}{1+e^{-\beta\omega}}\frac{1}{\omega-\omega'+i\eta}+\frac{1}{1+e^{\beta\omega}}\frac{1}{\omega-\omega'-i\eta}\right]. \quad (7)$$

The remainder of this section is restricted to a uniform superconductor, in which the impurity potential $\mathcal{U}(r)$ vanishes. For calculations in Sec. IV, it is convenient to introduce a two-component wave function $\Phi(\mathbf{r}t)$, which satisfies the homogeneous equation corresponding to Eq. (2)

$$\{i\partial/\partial t+\tau^{(3)}[(2m)^{-1}\nabla^2+\mu]-\Delta\tau^{(1)}\}\Phi(\mathbf{r}t)=0. \quad (8)$$

Here the order parameter is a constant in the absence of the potential. Equation (8) has plane-wave solutions of the form

$$\Phi_\mathbf{k}(\mathbf{r}t)=(2\pi)^{-3/2}\mathfrak{N}_k e^{i(\mathbf{k}\cdot\mathbf{r}-Et)}, \quad (9)$$

where $\mathfrak{N}_k$ is a normalization vector. Substitution of Eq. (9) into Eq. (8) provides an eigenvalue equation for the energy E, whose solution is the BCS energy spectrum

$$E=\pm E_k=\pm[\epsilon_k^2+\Delta^2]^{1/2}. \quad (10)$$

Kinetic energy is measured relative to the Fermi surface

$$\epsilon_k=(k^2/2m)-\mu\equiv(2m)^{-1}(k^2-k_f^2), \quad (11)$$

where k_f is the Fermi momentum. The plane-wave eigenfunction for positive (negative) energy is denoted by

$$\Phi_\mathbf{k}^{(\pm)}(\mathbf{r}t)=(2\pi)^{-3/2}\mathfrak{N}_k^{(\pm)}e^{i(\mathbf{k}\cdot\mathbf{r}\mp E_kt)}. \quad (12)$$

The normalization vector may be determined from the orthonormality condition

$$\int d^3r\Phi_\mathbf{k}^{(\pm)}(\mathbf{r}t)^\dagger\Phi_{\mathbf{k}'}^{(\pm)}(\mathbf{r}t)=\delta(\mathbf{k}-\mathbf{k}'), \quad (13)$$

where either the upper or the lower signs are taken; furthermore, $\Phi_\mathbf{k}^{(+)}$ and $\Phi_\mathbf{k}^{(-)}$ are orthogonal. A matrix product is implied in the integrand of Eq. (13), and $\Phi^\dagger$ means Hermitian conjugate. It is simple to show that the resulting normalization vectors are

$$\mathfrak{N}_k^{(+)}=\begin{pmatrix}u_k\\v_k\end{pmatrix}\quad\mathfrak{N}_k^{(-)}=\tau^{(1)}\tau^{(3)}\mathfrak{N}_k^{(+)}=\begin{pmatrix}-v_k\\u_k\end{pmatrix}, \quad (14)$$

where u_k and v_k are the usual BCS coherence factors[1]

$$u_k=[\tfrac{1}{2}(1+\epsilon_k/E_k)]^{1/2}\quad v_k=[\tfrac{1}{2}(1-\epsilon_k/E_k)]^{1/2}. \quad (15)$$

The plane-wave eigenfunctions, Eq. (12), may be expanded in partial waves[10]

$$\Phi_\mathbf{k}^{(\pm)}(\mathbf{r}t)=e^{\mp iE_kt}\sum_{lm}Y_{lm}(\hat{r})Y_{lm}^*(\hat{k})\Phi_{kl}^{(\pm)}(r)=e^{\mp iE_kt}(4\pi)^{-1}\sum_l(2l+1)P_l(\hat{r}\cdot\hat{k})\Phi_{kl}^{(\pm)}(r). \quad (16)$$

In Eq. (16), the notation $Y_{lm}(\hat{r})$ has been used as an abbreviation for $Y_{lm}(\theta,\varphi)$, where (θ,φ) are the polar angles of the unit vector $\hat{r}$ with respect to the fixed coordinate axes. The addition formula for spherical harmonics[10] has been used to obtain the second line

[10] See, for example, M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), Chap. 1, Sec. 3.

above. The partial wave function is proportional to the lth spherical Bessel function,[11]

$$\Phi_{kl}^{(\pm)}(r)=(2/\pi)^{1/2}i^l\mathfrak{V}_k^{(\pm)}j_l(kr), \quad (17)$$

and obeys a simple normalization condition

$$\int_0^\infty r^2dr\Phi_{kl}^{(\pm)}(r)^\dagger\Phi_{k'l}^{(\pm)}(r)=k^{-2}\delta(k-k'). \quad (18)$$

III. A SUPERCONDUCTOR WITH ONE IMPURITY

The single-particle Green's function $\hat{G}(\mathbf{r},\mathbf{r}',\omega_\nu)$ is rotationally invariant in the presence of a spherically symmetric potential and may be expanded in partial waves

$$\hat{G}(\mathbf{r},\mathbf{r}',\omega_\nu)=\sum_{lm}Y_{lm}(\hat{r})Y_{lm}^*(\hat{r}')\hat{G}_{lm}(r,r',\omega_\nu). \quad (19)$$

A combination of Eqs. (5) and (19) gives the equation of motion for the partial-wave projection,

$$\{\omega_\nu+(2m)^{-1}\tau^{(3)}[\mathfrak{D}_l+k_f^2]-\Delta(r)\tau^{(1)}-\mathfrak{V}(r)\}\times\hat{G}_{lm}(r,r',\omega_\nu)=r^{-2}\delta(r-r'), \quad (20)$$

where $\mathfrak{D}_l$ is a differential operator

$$\mathfrak{D}_l=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{l(l+1)}{r^2}. \quad (21)$$

Equation (20) shows that $\hat{G}_{lm}$ is in fact independent of the azimuthal quantum number m. The addition theorem for spherical harmonics may then be used to simplify Eq. (19),

$$\hat{G}(\mathbf{r},\mathbf{r}',\omega_\nu)=(4\pi)^{-1}\sum_l(2l+1)P_l(\hat{r}\cdot\hat{r}')\hat{G}_l(r,r',\omega_\nu). \quad (22)$$

The spectral function defined in Eqs. (6) and (7) has a similar expansion,

$$A(\mathbf{r},\mathbf{r}',\omega')=\sum_{lm}Y_{lm}(\hat{r})Y_{lm}^*(\hat{r}')A_l(r,r',\omega')=(4\pi)^{-1}\sum_l(2l+1)P_l(\hat{r}\cdot\hat{r}')A_l(r,r',\omega'), \quad (23)$$

and it follows from Eqs. (6), (22), and (23) that

$$A_l(r,r',\omega')=-i[\hat{G}_l(r,r',\omega'-i\eta)-\hat{G}_l(r,r',\omega'+i\eta)]. \quad (24)$$

As in Sec. II, it is convenient to introduce wave functions $\mathfrak{U}_l(r)$, which satisfy the homogeneous equation derived from Eq. (20),

$$\{E+(2m)^{-1}\tau^{(3)}[\mathfrak{D}_l+k_f^2]-\Delta(r)\tau^{(1)}-\mathfrak{V}(r)\}\mathfrak{U}_l(r)=0. \quad (25)$$

Here E is the eigenvalue corresponding to the eigenfunction $\mathfrak{U}_l(r)$. Equation (25) constitutes a pair of coupled, second-order, differential equations, so that four linearly independent solutions must exist. If $r^2\mathfrak{V}(r)$ vanishes at $r=0$, it is not difficult to show that only two solutions are finite near the origin[12]; any linear combination of these two solutions behaves like

$$\mathfrak{U}_l(r)\approx\begin{pmatrix}r^l\\ r^l\end{pmatrix} \quad (26)$$

for small r.

Near infinity, Eq. (25) may be simplified considerably. If $r^2\mathfrak{V}(r)$ is finite as $r\to\infty$, both the potential and the centrifugal barrier can be neglected, and the differential equation reduces to one with constant coefficients

$$\{E+(2m)^{-1}\tau^{(3)}[\mathfrak{D}_0+k_f^2]-\Delta\tau^{(1)}\}\mathfrak{U}_l(r)=0. \quad (27)$$

Here the asymptotic value of the order parameter $\Delta(\infty)$ has been denoted by Δ. Equation (27) has solutions of the form

$$\mathfrak{U}_l(r)\sim r^{-1}e^{ikr}, \quad (28)$$

where k is a constant to be determined. Substitution of Eq. (28) into Eq. (27) yields a fourth-order algebraic equation, whose roots are

$$k_1^2=k_f^2+2m(E^2-\Delta^2)^{1/2},\qquad k_2^2=k_f^2-2m(E^2-\Delta^2)^{1/2}. \quad (29)$$

The asymptotic behavior of $\mathfrak{U}_l(r)$ clearly depends on the magnitude of E. If $E^2<\Delta^2$, all four roots are complex, and the corresponding solutions are of the form

$$r\mathfrak{U}_l(r)\sim e^{\pm ik_fr}\exp[-(k_fr/2\epsilon_f)(\Delta^2-E^2)^{1/2}],\qquad r\mathfrak{U}_l(r)\sim e^{\pm ik_fr}\exp[+(k_fr/2\epsilon_f)(\Delta^2-E^2)^{1/2}], \quad (30)$$

where the ratio Δ/ϵ_f has been assumed small. Either of the two solutions that is finite at the origin may be written as a linear combination of the four asymptotic solutions in Eq. (30). In particular, a unique acceptable solution can be constructed with the asymptotic behavior

$$r\mathfrak{U}_l(r)\sim[A_l(E)\cos(k_fr)+B_l(E)\sin(k_fr)]\times\exp[-(k_fr/2\epsilon_f)(\Delta^2-E^2)^{1/2}]+C_l(E)\cos(k_fr)\exp[(k_fr/2\epsilon_f)(\Delta^2-E^2)^{1/2}]. \quad (31)$$

Equation (31) cannot be normalized unless

$$C_l(E)=0; \quad (32)$$

this condition provides an eigenvalue equation. The eigenvalues are discrete and will be labeled by an integer n, which may take a finite or infinite set of values. The eigenfunctions are wholly analogous to the bound states of Schrödinger theory,[13] where [as in Eq.

[11] We follow the notation of *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, National Bureau of Standards, Applied Mathematics Series 55, edited by M. Abramowitz and I. A. Stegun (U. S. Government Printing Office, Washington, D. C., 1964), Chap. 10.

[12] See, for example, E. L. Ince, *Ordinary Differential Equations* (Dover Publications, Inc., New York, 1956), Chap. XVI.

[13] The problem of a superconductor in a particular two-dimensional, cylindrically symmetric potential has been examined by C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Letters **9**, 307 (1964), who discuss the bound states in detail.

(31)] the spatial range r_0 of the bound state is determined by its binding energy and is independent of the range of the potential. In a superconductor, r_0 is not less than $2\epsilon_f/k_f\Delta=k_f/m\Delta$, which is the order of the coherence length ξ_0. The state specified by Eqs. (31) and (32) describes a quasiparticle bound in the potential $\mathcal{U}(r)$; it must not be confused with the bound electron pairs, which also have a spatial extension of the order of ξ_0.

If $E^2>\Delta^2$, on the other hand, then both k_1^2 and k_2^2 are real, and all four asymptotic solutions in Eq. (28) are oscillatory. (In the energy range $E^2>\epsilon_f^2+\Delta^2$, which is not considered here, k_2 becomes imaginary; this corresponds to the attempt to create a hole inside the Fermi surface with a momentum less than zero. The same effect occurs in the normal metal, as well as in the superconductor, and is not relevant to this paper.) Both of the solutions that are finite at the origin can be normalized per unit volume. These states describe the scattering of quasiparticles by the impurity potential, similar to the scattering states of Schrödinger theory. It is important to notice that there are *two* values of the momentum ($k_1>k_f>k_2$) for a fixed value of the energy. This peculiarity is discussed in Sec. V, where it is shown that an incoming plane wave with a well-defined momentum k_1(say) leads to scattered waves with momentum k_2 as well as k_1.

The energy range $E^2\approx\Delta^2$ is also interesting, because k_1 and k_2 become degenerate as $E^2\to\Delta^2$. The four independent solutions of Eq. (27) may be written as[14]

$$\begin{aligned} &r\mathfrak{U}_l(r)\sim e^{\pm ik_1r}+e^{\pm ik_2r}, \\ &r\mathfrak{U}_l(r)\sim(k_1-k_2)^{-1}(e^{\pm ik_1r}-e^{\pm ik_2r}), \end{aligned} \tag{33}$$

which is valid for all real values of k_1 and k_2. In the limit of exact degeneracy, Eq. (33) reduces to

$$r\mathfrak{U}_l(r)\sim e^{\pm ik_fr},\ re^{\pm ik_fr}. \tag{34}$$

The last pair of solutions cannot be normalized, which gives rise to anomalous behavior in the scattering amplitudes near $E^2\approx\Delta^2(k\approx k_f)$.

The solutions to Eq. (25) must be separated into two classes, distinguished by their asymptotic form. In the bound-state region ($E^2<\Delta^2$), the eigenfunctions $\mathfrak{U}_{nl}(r)$ and eigenvalues E_{nl} are discrete, with the normalization

$$\int_0^\infty r^2dr\mathfrak{U}_{nl}(r)^\dagger\mathfrak{U}_{n'l}(r)=\delta_{nn'}. \tag{35}$$

In the continuum ($E^2>\Delta^2$), the eigenfunctions depend on a continuous parameter, which may be taken as the magnitude of the momentum k. The scattering solution that corresponds to an incoming plane wave of momentum k, with positive (negative) energy, is denoted by $\mathfrak{U}_{kl}^{(\pm)}(r)$, in analogy with Eq. (17). As k ranges from zero to infinity, all possible values of k_1 and k_2 [Eq. (29)] are included. The normalization for the scattering states is chosen to be

$$\int_0^\infty r^2dr\mathfrak{U}_{kl}^{(\pm)}(r)^\dagger\mathfrak{U}_{k'l}^{(\pm)}(r)=k^{-2}\delta(k-k'), \tag{36}$$

which should be compared with Eq. (18).

Scattering problems are generally formulated in terms of integral equations that automatically incorporate the correct boundary conditions into the wave functions. We shall therefore introduce a matrix Green's function $\mathcal{G}_l(r,r',\zeta)$ satisfying the differential equation

$$\{\zeta+(2m)^{-1}\tau^{(3)}[\mathfrak{D}_l+k_f^2]-\Delta\tau^{(1)}\}\times\mathcal{G}_l(r,r',\zeta)=r^{-2}\delta(r-r'), \tag{37}$$

where ζ is an arbitrary complex variable. The construction of $\mathcal{G}$ is straightforward, and the result can be written in either of two equivalent forms,

$$\mathcal{G}_l(r,r',\zeta)=\int_0^\infty q^2dq\left[\frac{\Phi_{ql}^{(+)}(r)\Phi_{ql}^{(+)}(r')^\dagger}{\zeta-E_q}+\frac{\Phi_{ql}^{(-)}(r)\Phi_{ql}^{(-)}(r')^\dagger}{\zeta+E_q}\right], \tag{38}$$

$$\mathcal{G}_l(r,r',\zeta)=2\pi^{-1}\int_0^\infty q^2dq\ j_l(qr)j_l(qr')\mathcal{G}(q,\zeta), \tag{39}$$

where

$$\mathcal{G}(q,\zeta)=[\zeta+\tau^{(3)}\epsilon_q+\Delta\tau^{(1)}][\zeta^2-\epsilon_q^2-\Delta^2]^{-1}. \tag{40}$$

The choice of boundary condition is discussed in Appendix A. The correct Green's function for the scattering solution is

$$\mathcal{G}_{kl}^{(\pm)}(r,r')=\mathcal{G}_l(r,r',\pm E_k+i\eta). \tag{41}$$

Here the notation $(\pm)$ refers to the sign of the energy; it must be distinguished from the $(\pm)$ of conventional scattering theory, which means outgoing or incoming waves.[15] The differential equation (25) can now be rewritten as an integral equation

$$\mathfrak{U}_{kl}^{(\pm)}=\Phi_{kl}^{(\pm)}+\mathcal{G}_{kl}^{(\pm)}\mathcal{U}'\mathfrak{U}_{kl}^{(\pm)}, \tag{42}$$

where $\mathcal{U}'$ includes the effect of the impurity on the order parameter

$$\mathcal{U}'(r)=\mathcal{U}(r)+\tau^{(1)}[\Delta(r)-\Delta]. \tag{43}$$

The first and second terms on the right side of Eq. (42) represent the incident and scattered waves, respectively.

Given the eigenfunctions of the superconductor in the presence of an impurity, it is possible to construct the Fourier coefficient $\hat{G}_l(r,r',\omega_\nu)$ of the single-particle Green's function. It can be verified by substitution into

[14] Reference 12, pp. 136–137.

[15] Reference 10, Chap. 3.

Eq. (20) that

$$\hat{G}_l(r,r',\omega_\nu)=\int_0^\infty q^2dq\Big[\frac{\mathfrak{U}_{ql}^{(+)}(r)\mathfrak{U}_{ql}^{(+)}(r')^\dagger}{\omega_\nu-E_q}+\frac{\mathfrak{U}_{ql}^{(-)}(r)\mathfrak{U}_{ql}^{(-)}(r')^\dagger}{\omega_\nu+E_q}\Big]+\sum_n\frac{\mathfrak{U}_{nl}(r)\mathfrak{U}_{nl}(r')^\dagger}{\omega_\nu-E_{nl}}. \quad (44)$$

The corresponding spectral function is obtained from Eq. (24),

$$A_l(r,r',\omega')=2\pi\int_0^\infty q^2dq[\mathfrak{U}_{ql}^{(+)}(r)\mathfrak{U}_{ql}^{(+)}(r')^\dagger\delta(\omega'-E_q)+\mathfrak{U}_{ql}^{(-)}(r)\mathfrak{U}_{ql}^{(-)}(r')^\dagger\delta(\omega'+E_q)]+2\pi\sum_n\mathfrak{U}_{nl}(r)\mathfrak{U}_{nl}(r')^\dagger\delta(\omega'-E_{nl}). \quad (45)$$

The full single-particle Green's function $G(\mathbf{r}t,\mathbf{r}'t')$ follows directly from Eqs. (7), (23), and (45).

In principle, all physical information about the system is contained in $G(\mathbf{r}t,\mathbf{r}'t')$; simple examples of interest are the electron density $n(r)$ and order parameter $\Delta(r)$, given respectively by

$$n(r)=-2iG_{11}(\mathbf{r}t,\mathbf{r}t^+) \quad (46)$$

and the self-consistency condition, Eq. (3). The factor 2 in Eq. (46) arises from a summation over the two spin states. An elementary calculation yields

$$n(r)=\sum_l\frac{(2l+1)}{2\pi}\times\Big\{\int_0^\infty k^2dk\Big[\frac{|u_{kl}^{(+)}(r)|^2}{1+\exp(\beta E_k)}+\frac{|v_{kl}^{(+)}(r)|^2}{1+\exp(-\beta E_k)}\Big]+\sum_n\frac{|u_{nl}(r)|^2}{1+\exp(\beta E_{nl})}\Big\}, \quad (47)$$

$$\Delta(r)=g(4\pi)^{-1}\sum_l(2l+1)\times\Big\{\int k^2dk u_{kl}^{(+)}(r)v_{kl}^{(+)}(r)^*\tanh\tfrac{1}{2}\beta E_k+\sum_n u_{nl}(r)v_{nl}(r)^*[1+\exp(-\beta E_{nl})]^{-1}\Big\}. \quad (48)$$

The upper and lower components of $\mathfrak{U}_{kl}^{(\pm)}(r)$ have been denoted by $u_{kl}^{(\pm)}(r)$ and $v_{kl}^{(\pm)}(r)$. The relation (Appendix A)

$$\mathfrak{U}_{kl}^{(-)}(r)=(-1)^l\tau^{(1)}\tau^{(3)}[\mathfrak{U}_{kl}^{(+)}(r)]^* \quad (49)$$

has been used in the derivation of both Eqs. (47) and (48). The integral in Eq. (48) is divergent and must be cut off (as usual) at the Debye frequency $\epsilon_k\approx\omega_D$.[1]

For a uniform medium, there are no bound states, and Eqs. (47) and (48) can be reduced to the usual form[1] using the eigenfunctions from Eq. (17) and the theorem[11]

$$\sum_l(2l+1)[j_l(kr)]^2=1. \quad (50)$$

The constant density n and order parameter Δ are then given by

$$n=(2\pi^2)^{-1}\int_0^\infty k^2dk[1-(\epsilon_k/E_k)\tanh\tfrac{1}{2}\beta E_k], \quad (51)$$

$$\Delta=(2\pi^2)^{-1}gmk_f\int_0^{\omega_D}d\epsilon\,\Delta(\epsilon^2+\Delta^2)^{-1/2}\times\tanh[\tfrac{1}{2}\beta(\epsilon^2+\Delta^2)^{1/2}], \quad (52)$$

where the cutoff has been introduced explicitly in Eq. (52).

IV. THE S MATRIX

The single-particle Green's function describes the propagation of an excitation through the medium, following the addition or subtraction of one quasiparticle.[16] This interpretation has been used extensively in calculating the transition amplitude corresponding to various physical processes.[17,18] The S-matrix element S_{21} for the impurity scattering of a quasiparticle (of positive energy) from an initial momentum $\mathbf{k}_1$ to a final momentum $\mathbf{k}_2$ is

$$S_{21}=\lim_{t\to\infty,t'\to-\infty}i\int d^3rd^3r'\times\Phi_{\mathbf{k}_2}^{(+)}(\mathbf{r}t)^\dagger G(\mathbf{r}t,\mathbf{r}'t')\Phi_{\mathbf{k}_1}^{(+)}(\mathbf{r}'t'). \quad (53)$$

Equation (53) may be evaluated with the spectral representation for G. Since $t>t'$, the integration over ω in Eq. (7) can be performed with a contour closed in the lower half-plane. The S matrix for this problem is rotationally invariant and has an expansion in partial waves,

$$S_{21}=(4\pi)^{-1}\sum_l(2l+1)P_l(\hat{k}_2\cdot\hat{k}_1)\langle k_2|S_l|k_1\rangle. \quad (54)$$

With Eqs. (16) and (23), the lth partial-wave projection

[16] The material in this section is similar to that in a previous paper on vortices in an imperfect Bose gas [A. L. Fetter, Phys. Rev. **140**, A452 (1965)]. The present formulas differ because of the change in statistics (fermions instead of bosons) and spatial symmetry (spherical instead of cylindrical).

[17] R. P. Feynman, Phys. Rev. **76**, 749 and 769 (1949).

[18] J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1964), Chap. 6.

may be written as

$$\langle k_2|S_l|k_1\rangle=\lim_{t\to\infty,t'\to-\infty}\int\frac{d\omega'}{2\pi}\frac{e^{i(E_2-\omega')t}e^{i(\omega'-E_1)t'}}{1+e^{-\beta\omega'}}\langle k_2|\Xi_l(\omega')|k_1\rangle, \tag{55}$$

where

$$\langle k_2|\Xi_l(\omega')|k_1\rangle=\int_0^\infty r^2dr\,r'^2dr'\,\Phi_{k_2l}^{(+)}(r)^\dagger A_l(r,r',\omega')\Phi_{k_1l}^{(+)}(r')$$

$$=2\pi\int_0^\infty k^2dk[(\Phi_{k_2l}^{(+)},\mathfrak{U}_{kl}^{(+)})(\mathfrak{U}_{kl}^{(+)},\Phi_{k_1l}^{(+)})\delta(\omega'-E_k)$$

$$+(\Phi_{k_2l}^{(+)},\mathfrak{U}_{kl}^{(-)})(\mathfrak{U}_{kl}^{(-)},\Phi_{k_1l}^{(+)})\delta(\omega'+E_k)]+2\pi\sum_n(\Phi_{k_2l}^{(+)},\mathfrak{U}_{nl})(\mathfrak{U}_{nl},\Phi_{k_1l}^{(+)})\delta(\omega'-E_{nl}). \tag{56}$$

The following scalar-product notation has been used in Eq. (56):

$$(\Phi,\mathfrak{U})=\int_0^\infty r^2dr\,\Phi(r)^\dagger\mathfrak{U}(r). \tag{57}$$

The integral equation (42) for the scattering eigenfunctions allows a simplification of the individual scalar products in Eq. (56). As an example, we consider

$$(\Phi_{k_2l}^{(+)},\mathfrak{U}_{kl}^{(+)})=(\Phi_{k_2l}^{(+)},\Phi_{kl}^{(+)})+(\Phi_{k_2l}^{(+)},\mathcal{G}_{kl}^{(+)}\mathcal{V}'\mathfrak{U}_{kl}^{(+)})=k^{-2}\delta(k-k_2)+(E_k-E_{k_2}+i\eta)^{-1}(\Phi_{k_2l}^{(+)},\mathcal{V}'\mathfrak{U}_{kl}^{(+)}). \tag{58}$$

Equations (18) and (38) have been used in the derivation of the last step of Eq. (58). The remaining factors in Eq. (56) are treated in the same manner. In evaluating the limiting process in Eq. (55) it is necessary to use[19]

$$\lim_{t\to-\infty}\frac{e^{iEt}}{E-i\eta}=0;\quad\lim_{t\to\infty}\frac{e^{iEt}}{E-i\eta}=2\pi i\delta(E). \tag{59}$$

The S-matrix element now follows from a combination of Eqs. (55)–(59),

$$\langle k_2|S_l|k_1\rangle=(1+e^{-\beta E_2})^{-1}[k_2^{-2}\delta(k_2-k_1)$$

$$-2\pi i\delta(E_2-E_1)\langle k_2|T_l|k_1\rangle], \tag{60}$$

where the lth partial-wave projection of the T matrix on the energy shell is defined as

$$\langle k_2|T_l|k_1\rangle=(\Phi_{k_2l}^{(+)},\mathcal{V}'\mathfrak{U}_{k_1l}^{(+)}). \tag{61}$$

Only the positive energy states appear in Eq. (60) because the quasiparticle scattering is elastic.

The full S-matrix element is obtained by summing Eq. (60) over partial waves,

$$S_{21}=(1+e^{-\beta E_2})^{-1}[\delta(\mathbf{k}_2-\mathbf{k}_1)$$

$$-2\pi i\delta(E_2-E_1)\langle\mathbf{k}_2|T|\mathbf{k}_1\rangle], \tag{62}$$

where

$$\langle\mathbf{k}_2|T|\mathbf{k}_1\rangle=(4\pi)^{-1}\sum_l(2l+1)P_l(\hat{k}_2\cdot\hat{k}_1)\langle k_2|T_l|k_1\rangle. \tag{63}$$

The single-particle Green's function describes both the creation and propagation of a quasiparticle. These two properties appear clearly in the structure of Eq. (62). The temperature factor can be rewritten as $(1+e^{-\beta E})^{-1}=1-(1+e^{\beta E})^{-1}=1-\langle n\rangle$, which is the Fermi factor associated with the creation of the quasiparticle. The remaining part of Eq. (62) (in square brackets) describes the scattering of the quasiparticle and is the only effect of interest here. In the subsequent work, the temperature factor will therefore be ignored.[20]

The transition probability w per unit time for scattering into a solid angle $d\Omega_2$ is obtained from $|\langle\mathbf{k}_2|S|\mathbf{k}_1\rangle|^2$. It is conventional to interpret the squared delta function as[21]

$$[2\pi\delta(E_2-E_1)]^2=2\pi T\delta(E_2-E_1), \tag{64}$$

where T is the time duration of the experiment. From Eqs. (62) and (64), we find

$$w\,d\Omega_2=T^{-1}\int d^3k_2|S_{21}|^2$$

$$=2\pi\int k_2^2dk_2\,\delta(E_{k_2}-E_{k_1})|\langle\mathbf{k}_2|T|\mathbf{k}_1\rangle|^2d\Omega_2. \tag{65}$$

In contrast to the usual theory of scattering, the energy restriction can be satisfied at *two* values of the momentum, one above and one below the Fermi surface. The transition probability becomes

$$w=2\pi\rho_k|\langle\mathbf{k}_2|T|\mathbf{k}_1\rangle|^2+2\pi\rho_{k'}|\langle\mathbf{k}_2'|T|\mathbf{k}_1\rangle|^2. \tag{66}$$

Here $\mathbf{k}_2$ and $\mathbf{k}_2'$ are both parallel to $\hat{k}_2$, but they have different magnitudes, $k_2^2=k_1^2\equiv k^2$, and $(k_2')^2=2k_f^2-k_1^2$

[19] S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Row, Peterson and Company, Evanston, Illinois, 1961), p. 321.

[20] The temperature factor would never appear if the S matrix [Eq. (53)] were defined in terms of the retarded Green's function, discussed in detail in Ref. 7, pp. 144–153. The present derivation of the S matrix from the thermodynamic Green's function avoids the necessity of introducing yet another (and irrelevant) Green's function.

[21] Reference 18, p. 101.

$\equiv (k')^2$. The phase-space factor ρ_k is defined by

$$\rho_k = |k^2 dk/dE_k| . \tag{67}$$

The scattered wave contains momentum components both above and below the Fermi momentum, as has been noted previously, and the additional momentum is provided (as in the Schrödinger theory of potential scattering) by the impurity.

The differential cross section $d\sigma/d\Omega_2$ is defined as the transition probability w per unit incident flux F. With the continuum normalization used in Eq. (18), the flux is given by $F=(2\pi)^{-3}v$, where v is the incident velocity of the quasiparticle,

$$v = |dE_k/dk| = k^2/\rho_k . \tag{68}$$

The differential cross section is

$$d\sigma/d\Omega_2 = (2\pi)^4 k^{-2}[\rho_k{}^2 |\langle \mathbf{k}_2|T|\mathbf{k}_1\rangle|^2 + \rho_k \rho_{k'} |\langle \mathbf{k}_2'|T|\mathbf{k}_1\rangle|^2] . \tag{69}$$

Equation (69) appears to diverge near the Fermi momentum since

$$\rho_k = kmE_k/|\epsilon_k| = 2km^2 E_k/|k^2 - k_f{}^2| . \tag{70}$$

It is shown in Sec. V, however, that unitarity is preserved even at $k=k_f$.

V. THE PHASE SHIFTS

The scattering cross section can be simplified with the introduction of the phase shifts. Quasiparticle scattering in a superconductor is more complicated than scattering in potential theory because of the existence of two momentum states with the same energy. The present situation is essentially one of scattering in two coupled channels,[22] and the reaction matrix formalism,[23] which was developed for multichannel problems, is directly applicable here.

A complex scattering Green's function $\mathcal{G}_{kl}{}^{(+)}(r,r')$ [Eq. (41)] has been the basis of the development in Secs. III and IV. It is now convenient to introduce in addition a real Green's function

$$\mathcal{G}_{kl}{}^{(0)}(r,r') = \tfrac{1}{2}[\mathcal{G}_l(r,r',E_k+i\eta)+\mathcal{G}_l(r,r',E_k-i\eta)] , \tag{71}$$

and a corresponding real plane wave

$$\mathcal{J}_{kl}(r) = (2/\pi)^{1/2} \mathcal{R}_k{}^{(+)} j_l(kr) . \tag{72}$$

Equations (71) and (72) can be used to define a real standing-wave solution $\mathcal{W}_{kl}(r)$ to Eq. (25), in terms of a real integral equation

$$\mathcal{W}_{kl} = \mathcal{J}_{kl} + \mathcal{G}_{kl}{}^{(0)} \mathcal{V}' \mathcal{W}_{kl} . \tag{73}$$

The superscript (+) has been omitted in Eqs. (71)–(73), since only the positive energy states are of interest. The lth partial-wave projection of the reaction matrix (R matrix) is then defined on the energy shell as

$$\langle k|R_l|k'\rangle = (\mathcal{J}_{kl}, \mathcal{V}' \mathcal{W}_{k'l}) . \tag{74}$$

For a fixed energy, k and k' each assume two values, so that $\langle k|R_l|k'\rangle$ is really a 2×2 matrix. We shall consistently use the following notation for the R matrix

$$R = \begin{pmatrix} R_{kk} & R_{k\bar{k}} \\ R_{\bar{k}k} & R_{\bar{k}\bar{k}} \end{pmatrix} , \tag{75}$$

where the subscript l has been suppressed, and the momenta k and $\bar{k}$ are defined by

$$k > k_f > \bar{k} , \quad E_k = E_{\bar{k}} . \tag{76}$$

The values of k and $\bar{k}$ are related by $k^2+\bar{k}^2=2k_f{}^2$.

In a similar way, the T matrix on the energy shell is written as

$$T = \begin{pmatrix} T_{kk} & T_{k\bar{k}} \\ T_{\bar{k}k} & T_{\bar{k}\bar{k}} \end{pmatrix} , \tag{77}$$

where T is defined in Eq. (61). The derivation of the Heitler equation,[23] which relates T and R, is somewhat complicated and is relegated to Appendix B. The resulting (algebraic) equation has a simple structure

$$T_{mn} = R_{mn} - i\pi \textstyle\sum_j R_{mj} \rho_j T_{jn} , \tag{78}$$

where j, m, and n run over the two values k and $\bar{k}$. The phase-space factors ρ_k and $\rho_{\bar{k}}$ have been defined in Eq. (67). The solution of Eq. (78) for T is

$$T = X^{-1} \begin{pmatrix} R_{kk} + i\pi\rho_{\bar{k}} \det R & R_{k\bar{k}} \\ R_{\bar{k}k} & R_{\bar{k}\bar{k}} + i\pi\rho_k \det R \end{pmatrix} , \tag{79}$$

where

$$X = (1+i\pi\rho_k R_{kk})(1+i\pi\rho_{\bar{k}} R_{\bar{k}\bar{k}}) + \pi^2 \rho_k \rho_{\bar{k}} R_{k\bar{k}} R_{\bar{k}k}$$

$$\det R = R_{kk} R_{\bar{k}\bar{k}} - R_{k\bar{k}} R_{\bar{k}k} . \tag{80}$$

Equation (79) represents a substantial simplification for it expresses the (complex) T matrix in terms of the (real) R matrix.

For further analysis, it is important to show that the 2×2 R matrix is symmetric as well as real. The proof is not difficult:

$$\begin{aligned} R_{k\bar{k}} &\equiv (\mathcal{J}_{kl}, \mathcal{V}' \mathcal{W}_{\bar{k}l}) \\ &= (\mathcal{J}_{kl}, \mathcal{V}' \mathcal{J}_{\bar{k}l}) + (\mathcal{J}_{kl}, \mathcal{V}' \mathcal{G}_{\bar{k}l}{}^{(0)} \mathcal{V}' \mathcal{J}_{\bar{k}l}) + \cdots \\ &= (\mathcal{J}_{kl}, \mathcal{V}' \mathcal{J}_{\bar{k}l}) + (\mathcal{J}_{kl}, \mathcal{V}' \mathcal{G}_{kl}{}^{(0)} \mathcal{V}' \mathcal{J}_{\bar{k}l}) + \cdots \\ &= (\mathcal{J}_{kl} \mathcal{V}', \mathcal{J}_{\bar{k}l}) + (\mathcal{J}_{kl} \mathcal{V}' \mathcal{G}_{kl}{}^{(0)} \mathcal{V}', \mathcal{J}_{\bar{k}l}) + \cdots \\ &= (\mathcal{W}_{kl} \mathcal{V}', \mathcal{J}_{\bar{k}l}) \equiv R_{\bar{k}k} . \end{aligned} \tag{81}$$

The third line of Eq. (81) has been derived using the relation

$$\mathcal{G}_{kl}{}^{(0)}(r,r') = \mathcal{G}_{\bar{k}l}{}^{(0)}(r,r') , \tag{82}$$

which follows from Eqs. (71) and (76). The fourth and fifth lines depend on the symmetric character of the matrices $\mathcal{V}'$ [which is assumed below Eq. (2)] and

[22] Reference 10, Chap. 4, Sec. 1.

[23] W. Heitler, Proc. Cambridge Phil. Soc. **37**, 291 (1941); E. P. Wigner, Phys. Rev. **70**, 15 (1946); Ref. 10, Chap. 5, Sec. 6, and Chap. 7.

$\mathcal{G}_{kl}^{(0)}$ [which is obvious from the integral representation, Eq. (40)].

The structure of the Heitler equation can be clarified by a simple transformation of the R and T matrices,

$$\bar{R}_{mn}=(\rho_m)^{1/2}R_{mn}(\rho_n)^{1/2},$$
$$\bar{T}_{mn}=(\rho_m)^{1/2}T_{mn}(\rho_n)^{1/2}. \tag{83}$$

If Eq. (78) is multiplied by $(\rho_m\rho_n)^{1/2}$, the phase-space factors combine to form a matrix equation relating $\bar{T}$ and $\bar{R}$,

$$\bar{T}=\bar{R}-i\pi\bar{R}\bar{T}. \tag{84}$$

$\bar{R}$ is a real symmetric matrix, according to Eqs. (81) and (83), and it can be diagonalized by a real, orthogonal transformation matrix O.[24] Hence, there exists a diagonal matrix $\hat{R}$ such that

$$\bar{R}=O\hat{R}O^{-1}, \quad \hat{R}=O^{-1}\bar{R}O; \tag{85}$$

the diagonal elements of $\hat{R}$ are the eigenvalues of the reaction matrix $\bar{R}$, and it is useful to write $\hat{R}$ in the following form

$$\hat{R}=\begin{pmatrix}-\pi^{-1}\tan\delta_1 & 0\\ 0 & -\pi^{-1}\tan\delta_2\end{pmatrix}, \tag{86}$$

which defines the eigenphase shifts δ_1 and δ_2. Equation (86) involves no additional assumption because any real number can be represented as the tangent of an angle. The real orthogonal 2×2 matrix O depends on only a single parameter, and it may be written as

$$O=\begin{pmatrix}\cos\chi & -\sin\chi\\ \sin\chi & \cos\chi\end{pmatrix}. \tag{87}$$

χ is here called the mixing parameter, as in nucleon-nucleon scattering theory.[25] A combination of Eqs. (85)–(87) expresses the reaction matrix $\bar{R}$ in terms of three real parameters δ_1, δ_2, and χ,

$$-\pi\bar{R}=\begin{pmatrix}\cos^2\chi\tan\delta_1+\sin^2\chi\tan\delta_2 & \cos\chi\sin\chi(\tan\delta_1-\tan\delta_2)\\ \cos\chi\sin\chi(\tan\delta_1-\tan\delta_2) & \sin^2\chi\tan\delta_1+\cos^2\chi\tan\delta_2\end{pmatrix}. \tag{88}$$

The Heitler equation (84) may be rewritten in terms of $\hat{R}$ as

$$\hat{T}=\hat{R}-i\pi\hat{R}\hat{T}, \tag{89}$$

where

$$\hat{T}=O^{-1}\bar{T}O. \tag{90}$$

Direct solution of Eq. (89) shows that $\hat{T}$ is also diagonal, of the form

$$-\pi\hat{T}=\begin{pmatrix}e^{i\delta_1}\sin\delta_1 & 0\\ 0 & e^{i\delta_2}\sin\delta_2\end{pmatrix}. \tag{91}$$

The expression for $\bar{T}$ is obtained from the inverse of Eq. (90),

$$-\pi\bar{T}=\begin{pmatrix}\cos^2\chi e^{i\delta_1}\sin\delta_1+\sin^2\chi e^{i\delta_2}\sin\delta_2 & \cos\chi\sin\chi(e^{i\delta_1}\sin\delta_1-e^{i\delta_2}\sin\delta_2)\\ \cos\chi\sin\chi(e^{i\delta_1}\sin\delta_1-e^{i\delta_2}\sin\delta_2) & \sin^2\chi e^{i\delta_1}\sin\delta_1+\cos^2\chi e^{i\delta_2}\sin\delta_2\end{pmatrix}. \tag{92}$$

With Eq. (92), it is now possible to demonstrate the unitarity of the S matrix, which is equivalent to the partial-wave condition[25]

$$\int_0^\infty (k')^2dk'\langle k''|S_l^*|k'\rangle\langle k'|S_l|k\rangle=k^{-2}\delta(k-k''). \tag{93}$$

The relevant matrix elements have already been evaluated in Eq. (60) (omitting the temperature factors), and Eq. (93) can be reduced to the on-energy-shell equation

$$(2i)^{-1}[T_{mn}-T_{mn}^*]=-\pi\textstyle\sum_j T_{mj}^*\rho_jT_{jn}, \tag{94}$$

where j,m, and n run over the values k and $\bar{k}$. Multiplication of Eq. (94) by $(\rho_m\rho_n)^{1/2}$ produces a matrix equation for $\bar{T}$,

$$(2i)^{-1}(\bar{T}-\bar{T}^*)=-\pi\bar{T}^*\bar{T}, \tag{95}$$

which is reducible by an orthogonal transformation [Eq. (90)] to the diagonal equation

$$(2i)^{-1}(\hat{T}-\hat{T}^*)=-\pi\hat{T}^*\hat{T}. \tag{96}$$

Verification of Eq. (96) is trivial using the explicit form of $\hat{T}$ given in Eq. (91). This proof confirms the earlier statement that the divergence of ρ_k near the Fermi surface does not violate unitarity.

The total cross section σ_T may be written compactly in terms of the eigenphase shifts and mixing parameter.

[24] See, for example, H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, Cambridge, 1956), 3rd ed., pp. 123–124.

[25] Reference 10, pp. 344–352 and 384–398.

If Eq. (69) is integrated over angles, we obtain

$$\sigma_T = 4\pi^3 k^{-2} \sum_l (2l+1) \sum_m \bar{T}_{km}{}^* \bar{T}_{mk}$$
$$= 4\pi k^{-2} \sum_l (2l+1) \{\cos^2\chi \sin^2\delta_1 + \sin^2\chi \sin^2\delta_2\}, \quad (97)$$

which is correct for an incident momentum above the Fermi momentum. The corresponding result for a momentum below the Fermi momentum is obtained by interchanging δ_1 and δ_2. Here, δ_1, δ_2, and χ depend on l, but this has been suppressed for notational simplicity. Equation (97) reduces to the standard single-channel expression[4] if χ vanishes identically for all l.

The eigenphase shifts can also be used to study the electron density and order parameter far from the impurity. It is shown in Appendix B that the scattering wave function $\mathfrak{U}_{kl}{}^{(+)}(r)$ has the following asymptotic behavior for an incident momentum $k > k_f$

$$\mathfrak{U}_{kl}{}^{(+)}(r) \to \Phi_{kl}{}^{(+)}(r) - i\pi\rho_k T_{kk} i^l (2/\pi)^{1/2} \mathfrak{V}_k{}^{(+)} h_l{}^{(1)}(kr)$$
$$- i\pi\rho_{\bar{k}} T_{\bar{k}k} i^l (2/\pi)^{1/2} \mathfrak{V}_{\bar{k}}{}^{(+)} h_l{}^{(2)}(\bar{k}r), \quad (98)$$

where the notation of Eqs. (76) and (77) has been used. The other possibility (an incident momentum $\bar{k} < k_f$) is obtained with the substitutions

$$\Phi_{kl}{}^{(+)} \to \Phi_{\bar{k}l}{}^{(+)}, \quad T_{kk} \to T_{k\bar{k}}, \quad T_{\bar{k}k} \to T_{\bar{k}\bar{k}}.$$

Equation (98) shows that the scattered wave has outgoing components $[\sim\exp(ikr - iE_k t)]$ above the Fermi surface and incoming components $[\sim\exp(-i\bar{k}r - iE_{\bar{k}}t)]$ below the Fermi surface. The origin of this peculiar behavior for $\bar{k} < k_f$ is the function $h_l{}^{(2)}$, which arises from our choice of boundary condition for the scattering Green's function in Eq. (41). Although other boundary conditions are possible [for example, $\zeta \to \pm E_k + i\eta\,\mathrm{sgn}(k - k_f)$], the corresponding expression for the S-matrix element cannot be interpreted consistently.

Equation (98) can be substituted into Eqs. (47) and (48) to obtain the scattering contribution to the asymptotic form of $n(r)$ and $\Delta(r)$. Judicious use of Eq. (95) simplifies the algebra considerably, but the details are tedious and will be omitted here. The electron density and the order parameter are, respectively,

$$n(r) \to n + (2\pi^2 r^2)^{-1} \sum_l (2l+1)(-1)^l \left\{ -\int_0^{k_f} d\bar{k}\, Z_1 [1 - (\epsilon_{\bar{k}}/E_{\bar{k}}) \tanh\tfrac{1}{2}\beta E_{\bar{k}}] + \int_{k_f}^{\infty} dk\, Z_2 [1 - (\epsilon_k/E_k) \tanh\tfrac{1}{2}\beta E_k] \right\}$$
$$- (\pi r)^{-2} \sum_l (2l+1) \int_0^{k_f} d\bar{k} (\bar{k}/k)^{1/2} Z_3 [\Delta/E_{\bar{k}}], \quad (99a)$$

$$\Delta(r) \to \Delta + (g/4\pi^2 r^2) \sum_l (2l+1)(-1)^l \left\{ -\int_0^{k_f} d\bar{k} Z_1 [(\Delta/E_{\bar{k}}) \tanh\tfrac{1}{2}\beta E_{\bar{k}}] + \int_{k_f}^{\infty} dk Z_2 [(\Delta/E_k) \tanh\tfrac{1}{2}\beta E_k] \right\}$$
$$- (g/2\pi^2 r^2) \sum_l (2l+1) \int_0^{k_f} d\bar{k} (\bar{k}/k)^{1/2} Z_3 \tanh\tfrac{1}{2}\beta E_{\bar{k}}, \quad (99b)$$

where

$$Z_1 = \sin^2\chi \sin\delta_1 \sin(2\bar{k}r - \delta_1) + \cos^2\chi \sin\delta_2 \sin(2\bar{k}r - \delta_2)$$
$$Z_2 = \cos^2\chi \sin\delta_1 \sin(2kr + \delta_1) + \sin^2\chi \sin\delta_2 \sin(2kr + \delta_2) \quad (100)$$
$$Z_3 = \sin\chi \cos\chi [\sin\delta_1 \sin(kr - \bar{k}r + \delta_1) - \sin\delta_2 \sin(kr - \bar{k}r + \delta_2)].$$

Here n and Δ are the values appropriate for the uniform system, given in Eqs. (51) and (52). No cutoff is required for the convergent integrals in Eq. (99b). Only the constant term in the expression for $\Delta(r)$ remains finite for large r, so that is is self-consistent to use $\Delta(r) \approx \Delta$ in evaluating the correction terms far from the impurity.

The bound-state contribution, which has been omitted from Eq. (99) for simplicity, is negligible only for $r \gg \xi_0 \approx 10^4$ Å. It is shown in Sec. VI, however, that the scattering contributions to $n(r)$ and $\Delta(r)$ also vanish exponentially for $r \gg \xi_0$, so that the corrections to the constant values are wholly negligible in this region. For $r \ll \xi_0$, which is the interesting range in practice, both the scattering states and the bound states must be included.

In a normal metal, the order parameter and the mixing parameter vanish. Equation (99a) then reduces to the usual result[3,26] that $n(r)$ has long-range spatial oscillations of the form

$$n(r) - n \sim (2\pi^2 r^3)^{-1} \cos(2k_f r). \quad (101)$$

Similar behavior in $\Delta(r)$ as well as $n(r)$ is found with a simple impurity model in a superconductor, as we shall see in the next section.

VI. A HARD-SPHERE IMPURITY

The scattering by a spherical square-well potential is one of the standard soluble problems in Schrödinger

[26] Our derivation is similar to that of J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, 1964), pp. 135–138.

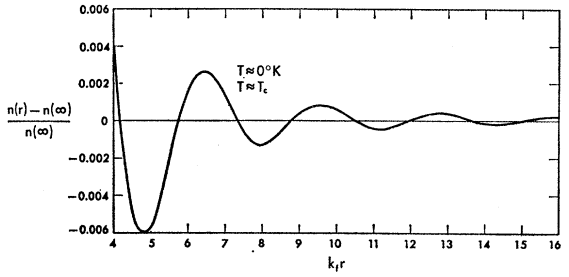

FIG. 1. The asymptotic behavior of the electron density [Eqs. (110a) and (111a)] far from a hard-sphere impurity. The numerical value of the parameters is taken from Eq. (114).

theory.[4] Such a potential also allows a complete solution of Eq. (25) for the wave function, but the algebraic complexity is formidable. The solution becomes relatively simple in the special limiting case of a hard-sphere potential, which will now be considered. The boundary conditions require that the wave functions vanish at the surface of the sphere ($r=a$). In addition, we shall assume that the order parameter is constant for $r>a$. This approximation is inadequate near the impurity, where the self-consistency condition [Eqs. (3) and (48)] is very complicated; far from the impurity, however, the difference $[\Delta(r)/\Delta(\infty)]-1$ is small and the approximation of constant order parameter is permissible.

It is simpler to calculate the real standing-wave solutions $\mathfrak{W}$, from which the scattering solutions $\mathfrak{U}$ are then derived. For the hard sphere, the eigenfunction equation (25) in the region $r>a$ is identical with the free quasiparticle equation,

$$\{E_k+(2m)^{-1}\tau^{(3)}[\mathfrak{D}_l+k_f^2]-\Delta\tau^{(1)}\}\mathfrak{W}_{kl}(r)=0, \quad (102)$$

and the wave function satisfies the additional boundary condition

$$\mathfrak{W}_{kl}(a)=0. \quad (103)$$

The solution for all k is

$$\mathfrak{W}_{kl}(r)=(2/\pi)^{1/2}\mathfrak{N}_k^{(+)} \times\{j_l(kr)-[j_l(ka)/y_l(ka)]y_l(kr)\}, \quad (104)$$

where $y_l(kr)$ is the spherical Neumann function.[11] Equation (104) is to be compared with the general asymptotic form derived in Appendix B,

$$\mathfrak{W}_{kl}(r)\rightarrow(2/\pi)^{1/2}\mathfrak{N}_k^{(+)}[j_l(kr)+\pi\rho_k R_{kk}y_l(kr)] -(2/\pi)^{1/2}\mathfrak{N}_{\bar{k}}^{(+)}y_l(\bar{k}r)\pi\rho_{\bar{k}}R_{\bar{k}k} \quad (k>k_f),$$
$$\mathfrak{W}_{\bar{k}l}(r)\rightarrow(2/\pi)^{1/2}\mathfrak{N}_{\bar{k}}^{(+)}[j_l(\bar{k}r)-\pi\rho_{\bar{k}}R_{\bar{k}\bar{k}}y_l(\bar{k}r)] +(2/\pi)^{1/2}\mathfrak{N}_k^{(+)}y_l(kr)\pi\rho_k R_{k\bar{k}} \quad (\bar{k}<k_f). \quad (105)$$

The special feature of the hard sphere is the identical vanishing of the mixing parameter—the incident and scattered waves have the same momentum. Equations (104) and (105) show that $R_{k\bar{k}}$ and $R_{\bar{k}k}$ vanish, while

$$\pi\bar{R}_{kk}=\pi\rho_k R_{kk}=-j_l(ka)/y_l(ka)=-\tan\delta_1,$$
$$\pi\bar{R}_{\bar{k}\bar{k}}=\pi\rho_{\bar{k}}R_{\bar{k}\bar{k}}=j_l(\bar{k}a)/y_l(\bar{k}a)=-\tan\delta_2. \quad (106)$$

The matrix $\bar{T}$ is also diagonal and may be found from Eq. (92) by setting $\chi=0$. The change in sign of the phase shift at $k=k_f$ is understandable in terms of Eq. (98), which has outgoing scattered waves for $k>k_f$ and incoming scattered waves for $k<k_f$.

The differential cross section for scattering of quasiparticles can be evaluated from Eq. (69); the resulting expression is identical with the scattering cross section for a hard sphere in Schrödinger theory.[27] Since only $|T|^2$ appears in Eq. (69), the observed scattering is unaffected by the sign reversal of the phase shift at $k=k_f$. The cross section is therefore a smooth function of momentum near the Fermi surface.

The simple form of the T matrix for the hard sphere means that it is possible to complete the asymptotic evaluation of $n(r)$ and $\Delta(r)$, started in Eqs. (99) and (100). Since χ is zero, these equations may be simplified to

$$n(r)-n=(2\pi^2r^2)^{-1}\sum_l(2l+1)(-1)^l \times\int_0^\infty dk[1-(\epsilon_k/E_k)\tanh\tfrac{1}{2}\beta E_k] \times\sin\delta_l\sin(2kr+\delta_l), \quad (107)$$

$$\Delta(r)-\Delta=(g/4\pi^2r^2)\sum_l(2l+1)(-1)^l \times\int_0^\infty dk(\Delta/E_k)\tanh\tfrac{1}{2}\beta E_k\sin\delta_l\sin(2kr+\delta_l), \quad (108)$$

where δ_l is defined for all k as

$$\tan\delta_l=j_l(ka)/y_l(ka). \quad (109)$$

The order parameter in Eqs. (107) and (108) depends on the temperature,[1] being finite at $T=0$, and vanishing at the critical temperature $T_c=\beta_c^{-1}$. The momentum integrals are calculated in Appendix C in two limiting cases. For $\beta\Delta\gg1$ ($T\approx0$) we find

$$[n(r)/n]-1=-\tfrac{3}{2}(k_fr)^{-3} \times\sum_l(2l+1)(-1)^l\sin\delta_l\cos(2k_fr+\delta_l) \times[1+(k_fr\Delta/\epsilon_f)]\exp(-k_fr\Delta/\epsilon_f), \quad (110a)$$

$$[\Delta(r)/\Delta]-1=(gmk_f/4\pi^2)(k_fr)^{-2}\sum_l(2l+1)(-1)^l\sin\delta_l \times\{(k_fr)^{-1}\cos\delta_l+2\sin(2k_fr+\delta_l) \times[\exp(-k_fr\Delta/\epsilon_f) +E_1(k_fr\Delta/\epsilon_f)]\}; \quad (110b)$$

for $\beta\Delta\ll1$ ($T\approx T_c$) we find

$$[n(r)/n]-1=-\tfrac{3}{2}(k_fr)^{-3}\sum_l(2l+1)(-1)^l\sin\delta_l \times\cos(2k_fr+\delta_l)\exp(-\pi k_fr/\beta\epsilon_f), \quad (111a)$$

$$[\Delta(r)/\Delta]-1=(gmk_f/4\pi^2)(k_fr)^{-2}\sum_l(2l+1)(-1)^l\sin\delta_l \times\{(k_fr)^{-1}\cos\delta_l+2\sin(2k_fr+\delta_l) \times E_1(\pi k_fr/\beta\epsilon_f)\}. \quad (111b)$$

[27] A complete discussion may be found in P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Part II, pp. 1483–1486.

In these equations, the phase shift δ_l is evaluated at $k=k_f$, and Δ means the self-consistent value of the order parameter at the temperature β^{-1}. The exponential integral $E_1(x)$ is defined as[28]

$$E_1(x)=\int_x^\infty dt\, t^{-1}e^{-t}. \tag{112}$$

Equations (110) and (111) have several very interesting features. Although both the electron density and the order parameter display long-range spatial oscillations, the two expressions are not proportional[29]; $n(r)$ falls off like r^{-3}, while $\Delta(r)$ falls off like r^{-2}. The different powers of k_fr mean that the oscillations in $\Delta(r)$ extend to larger distances. An additional enhancement occurs in the oscillations in the order parameter because of the logarithmic behavior of $E_1(x)$ for small values of its argument,[28]

$$E_1(x)\approx-\gamma-\ln x+\cdots, \tag{113}$$

where γ is Euler's constant, $\gamma=0.5772\cdots$. In the range $1\ll k_fr\ll\epsilon_f/\Delta\approx10^4$, the factor $E_1(k_fr\Delta/\epsilon_f)$ is of the order of $\ln10^4\approx9.2$. The corresponding factor in $n(r)$ is $\exp(-k_fr\Delta/\epsilon_f)\approx1$. Thus the amplitude of the oscillations in $\Delta(r)$ is about 10 times that in $n(r)$.

In the normal metal, the long-range oscillations are caused by the sharp Fermi surface. In a superconductor at zero temperature, the Fermi surface is "smeared out" in a narrow range $|\epsilon_k|\leqq\Delta$, which appears in Eqs. (110) as an exponential cutoff for $k_fr\gg\epsilon_f/\Delta\approx10^4$. Hence the oscillations are restricted to the range $r\lesssim k_f/m\Delta$, which is the order of the coherence length ξ_0. In an average superconductor, $k_f\approx10^8$ cm^{-1}, while $\xi_0\approx10^{-4}$ cm, so that the amplitude of the oscillations is already vanishingly small at distances much less than the coherence length because of the inverse power of (k_fr). At finite temperatures, the Fermi surface is "smeared out" in a range $|\epsilon_k|\leqq\beta^{-1}$ even in normal metals, which is the origin of the cutoff in Eq. (111) for $k_fr\gg\pi^{-1}\beta\epsilon_f$. The order parameter vanishes in normal metals, in which case Eq. (110a) is identical with the usual expression,[3,26] while Eq. (111a) provides a generalization to finite temperatures.

Figures 1 and 2 are graphical illustrations of Eqs. (110) ($T\approx0$) and (111) ($T\approx T_c$) for $n(r)$ and $\Delta(r)$, with the specific values:

$$\begin{aligned}&k_f=10^8\text{ cm}^{-1},\quad \beta_c\epsilon_f=10^4,\quad T_c=4.42^\circ\text{K},\\ &\Delta(T=0)/\epsilon_f=1.76\times10^{-4},\quad gmk_f/2\pi^2=\tfrac{1}{3},\\ &k_fa=\tfrac{1}{2}.\end{aligned} \tag{114}$$

Here the BCS relation[1,7] $\Delta(T=0)\beta_c=\pi e^{-\gamma}\approx1.76$ has been used, where γ is again Euler's constant. The dimensionless number $gmk_f/2\pi^2$ is the same as the quantity $N(0)V$ defined in Ref. 1. Only the s state ($l=0$) is included in Figs. 1 and 2, since the partial waves for $l\geqq1$ are negligible. The oscillations in the order parameter are somewhat sensitive to temperature, while those in $n(r)$ are wholly insensitive. Figures 1 and 2 show that the amplitude of the oscillations decreases more rapidly in $n(r)$ than in $\Delta(r)$.

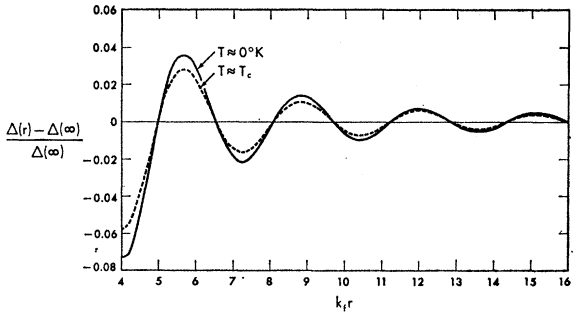

FIG. 2. The asymptotic behavior of the order parameter [Eqs. (110b) and (111b)] far from a hard-sphere impurity. The numerical value of the parameters is taken from Eq. (114).

VII. A DELTA-SHELL POTENTIAL

A delta-shell potential[30] provides another simple model of an impurity. The potential is given by

$$\mathcal{U}(r)=(2ma)^{-1}\delta(r-a)\Lambda, \tag{115}$$

where Λ is a dimensionless 2×2 matrix

$$\Lambda=\lambda_1\tau^{(1)}+\lambda_3\tau^{(3)}. \tag{116}$$

Here λ_3 is a measure of the strength of the impurity potential, while λ_1 represents the effect of the impurity on the order parameter. The magnitude of λ_1 may be estimated as follows: The spatial integral of the $\tau^{(1)}$ component of $\mathcal{U}$ should be approximately equal to $(4/3)\pi a^3\Delta$. If $k_fa\approx1$, this condition yields $\lambda_1\approx\frac{1}{3}(\Delta/\epsilon_f)\ll1$.

The integral equation (73) can be solved exactly for this potential using the coordinate representation of the standing-wave Green's function derived in Appendix B. The real wave function for $r>a$ is

$$\begin{aligned}\mathfrak{W}_{kl}(r)=\mathcal{J}_{kl}(r)&+(\pi\rho_ka/2m)[\mathcal{J}_{kl}(a)^\dagger\Lambda\mathfrak{W}_{kl}(a)]\mathcal{Y}_{kl}(r)\\&-(\pi\rho_{\bar{k}}a/2m)[\mathcal{J}_{\bar{k}l}(a)^\dagger\Lambda\mathfrak{W}_{kl}(a)]\mathcal{Y}_{\bar{k}l}(r),\end{aligned} \tag{117}$$

where k and $\bar{k}$ are defined in Eq. (76) ($k>k_f>\bar{k}$). Here,

$$\mathcal{Y}_{kl}(r)=(2/\pi)^{1/2}\mathfrak{N}_k^{(+)}y_l(kr), \tag{118}$$

which is analogous to $\mathcal{J}_{kl}$ defined in Eq. (72). In the second and third terms of Eq. (117), a matrix product

[28] We follow the notation of Ref. 11, p. 228.

[29] This result disagrees with that of C. Caroli, P. G. de Gennes, and J. Matricon, in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963), Chap. XXIII.

[30] The delta-shell potential is well known as a simple soluble model, although it appears infrequently. The approach used here is based on K. Gottfried, mimeographed lecture notes on quantum mechanics, Harvard University, 1963 (unpublished); and to be published.

is implied in the factor within square brackets. The similar solution for $\mathcal{W}_{\bar{k}l}(r)\,(r>a)$ is

$$\mathcal{W}_{\bar{k}l}(r)=\mathcal{J}_{\bar{k}l}(r)+(\pi\rho_{\bar{k}}a/2m)[\mathcal{J}_{kl}(a)^{\dagger}\Lambda\mathcal{W}_{\bar{k}l}(a)]\mathcal{Y}_{kl}(r)$$
$$-(\pi\rho_{\bar{k}}a/2m)[\mathcal{J}_{\bar{k}l}(a)^{\dagger}\Lambda\mathcal{W}_{\bar{k}l}(a)]\mathcal{Y}_{\bar{k}l}(r). \quad (119)$$

If the scalar product [defined in Eq. (57)] of Eqs. (117) and (119) is taken successively with $\mathcal{J}_{kl}(r)\mathcal{U}(r)$ and $\mathcal{J}_{\bar{k}l}(r)\mathcal{U}(r)$, four coupled algebraic equations are obtained, relating the four elements of the reaction matrix on the energy shell. The solution is straightforward,

$$M\bar{R}=\begin{pmatrix}\bar{R}_{kk}{}^{B}+\pi(\bar{R}_{kk}{}^{B}\bar{Q}_{k\bar{k}}-\bar{Q}_{k\bar{k}}\bar{R}_{\bar{k}k}{}^{B}) & \bar{R}_{k\bar{k}}{}^{B}\\ \bar{R}_{\bar{k}k}{}^{B} & \bar{R}_{\bar{k}\bar{k}}{}^{B}-\pi(\bar{Q}_{kk}\bar{R}_{\bar{k}\bar{k}}{}^{B}-\bar{R}_{k\bar{k}}{}^{B}\bar{Q}_{\bar{k}k})\end{pmatrix}, \quad (120)$$

where $\bar{R}^{B}$ is the Born approximation to $\bar{R}$,

$$\bar{R}_{jn}{}^{B}=(\rho_j\rho_n)^{1/2}(a/2m)[\mathcal{J}_{jl}(a)^{\dagger}\Lambda\mathcal{J}_{nl}(a)], \quad (121)$$

and

$$\bar{Q}_{jn}=(\rho_j\rho_n)^{1/2}(a/2m)[\mathcal{J}_{jl}(a)^{\dagger}\Lambda\mathcal{Y}_{nl}(a)]. \quad (122)$$

The indices j and n take the values k and $\bar{k}$, and

$$M=(1-\pi\bar{Q}_{kk})(1+\pi\bar{Q}_{\bar{k}\bar{k}})+\pi^2\bar{Q}_{k\bar{k}}\bar{Q}_{\bar{k}k}. \quad (123)$$

The T matrix can be calculated in a similar way, either directly from Eq. (42) or with the Heitler equation [Eqs. (79) and (80)].

The evaluation of the matrix elements for $\bar{R}$ is not difficult,

$$\bar{R}_{kk}=(\pi M)^{-1}ka[j_l(ka)]^2$$
$$\times\{\lambda_3+(\Delta\lambda_1/|\epsilon|)-X(\bar{k}a)(\lambda_1{}^2+\lambda_3{}^2)\}, \quad (124a)$$

$$\bar{R}_{\bar{k}\bar{k}}=(\pi M)^{-1}\bar{k}a[j_l(\bar{k}a)]^2$$
$$\times\{-\lambda_3+(\Delta\lambda_1/|\epsilon|)+X(ka)(\lambda_1{}^2+\lambda_3{}^2)\}, \quad (124b)$$

$$\bar{R}_{k\bar{k}}=\bar{R}_{\bar{k}k}=(\pi M)^{-1}(k\bar{k})^{1/2}$$
$$\times aj_l(ka)j_l(\bar{k}a)(E\lambda_1/|\epsilon|), \quad (124c)$$

where

$$X(x)=xj_l(x)y_l(x) \quad (125)$$

and the subscript has been suppressed on E and $|\epsilon|$ because $E_k=E_{\bar{k}}$ and $|\epsilon_k|=|\epsilon_{\bar{k}}|$. The common coefficient in Eqs. (124) is

$$M=1-X(ka)[\lambda_3+(\Delta\lambda_1/|\epsilon|)]-X(\bar{k}a)[\lambda_3-(\Delta\lambda_1/|\epsilon|)]$$
$$+X(ka)X(\bar{k}a)(\lambda_1{}^2+\lambda_3{}^2). \quad (126)$$

These relatively complicated expressions can be simplified in limiting cases. For a normal metal, $\bar{R}$ is diagonal since Δ and λ_1 vanish. Even in a superconductor, where $\lambda_1\approx\Delta/\epsilon_f$, the off-diagonal elements (124c) are negligible unless $|\epsilon|\ll\Delta$. Thus, the mixing between k and $\bar{k}$ is important only near the Fermi surface, where the superconducting and normal states differ appreciably. Equation (126) approaches a finite limit as $k\to k_f$,

$$M\to M_f\approx[1-\lambda_3X(k_fa)]^2. \quad (127)$$

In contrast, Eqs. (124) diverge, and the R matrix becomes

$$\pi\bar{R}\to\frac{\gamma_l\Delta}{|\epsilon|}\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}, \quad (128)$$

where

$$\gamma_l=\lambda_1M_f{}^{-1}k_fa[j_l(k_fa)]^2. \quad (129)$$

Equation (128) is valid only in the immediate vicinity of the Fermi surface, $|\epsilon|\lesssim\Delta^2/\epsilon_f$. In this region, the mixing parameter χ is $\frac{1}{4}\pi$, and the eigenphases are

$$\tan\delta_1=-2\Delta\gamma_l/|\epsilon|, \quad \tan\delta_2=0. \quad (130)$$

The T matrix can be found from Eq. (92),

$$\pi\bar{T}=\frac{\Delta\gamma_l}{|\epsilon|+2i\Delta\gamma_l}\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}, \quad (131)$$

which exhibits a typicalr esonant form[31] in all partial waves simultaneously. These *kinematic* resonances, which occur at the minimum in the energy-momentum relation, are different from the usual *dynamical* scattering resonances, which are generally confined to a single partial wave. Equation (131) implies singular scattering properties at $k=k_f$, where the scattering amplitude is proportional to a delta function in the scattering angle, and the total cross section is infinite. These singularities are essentially mathematical in origin and do not appear in actual experiments since the measured cross section represents an average over some momentum resolution width $2K$. Near the Fermi surface, the total cross section is a sum of resonant terms,

$$\sigma_T(k)=(2\pi/k_f{}^2)\textstyle\sum_l(2l+1)(2\Delta\gamma_l)^2$$
$$\times[\epsilon_k{}^2+(2\Delta\gamma_l)^2]^{-1}. \quad (132)$$

Hence the observed (average) value is

$$\langle\sigma_T\rangle\equiv(2K)^{-1}\int_{k_f-K}^{k_f+K}dk'\,\sigma_T(k')$$
$$=(2\pi/k_f{}^2)\textstyle\sum_l(2l+1)\varphi_l\tan^{-1}(\varphi_l{}^{-1}), \quad (133)$$

where

$$\varphi_l=(2m\Delta\gamma_l/Kk_f). \quad (134)$$

This series converges rapidly, so that the measured total cross section is finite near k_f, which is to be expected from physical considerations.

As a simple example, the momentum cutoff may be taken as $K=2\pi/L$, where L is a typical linear dimension of the sample. With the numerical values in Eq. (114) and $L\approx1$ cm, we find

$$\langle\sigma_T\rangle\approx0.135\pi k_f{}^{-2}\approx0.54\pi a^2. \quad (135)$$

[31] See, for example, A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), Vol. I, pp. 396–401.

The resonant width is small compared to the resolution width, even for $l=0$, and the observed total cross section at resonance is only about half of the geometrical cross section.

VIII. DISCUSSION

The wave functions for a superconductor are drastically modified when the metal contains a single spherical impurity. The essential feature is the existence of a minimum in the energy-momentum relation. Two values of the momentum correspond to a single energy, and the coupling between the two channels must be included to achieve a consistent description. Near the minimum energy, the density of states [Eq. (67)] diverges, which leads to resonant behavior in the quasiparticle scattering. A related aspect is that the usual approximation methods, such as the Born approximation, fail completely in this momentum range. Finally, the sharpness of the Fermi surface gives rise to long-range spatial oscillations, not only in the electron density, but also in the order parameter. A natural question is whether these oscillations also appear as a change in the energy gap (as in an energy-absorption experiment). This problem will be considered in a future publication.

It is important to emphasize the purely kinematic nature of these effects, which are in no way restricted to three dimensions. An interesting two-dimensional situation is quantized flux line in a type-II superconductor, which can be formulated as a cylindrically symmetric l-dependent potential.[13] Similar effects to those noted above should appear. Unfortunately the calculation of the R matrix for the flux line is much more difficult than for the simple models treated in Secs. VI and VII. Another mathematically similar (but physically different) circumstance occurs in liquid He II, near the roton minimum in the energy-momentum relation. The inadequacy of the Born approximation in calculating the cross section for roton scattering by a vortex has long been recognized.[32] An improved treatment should include the coupling in the two different momentum channels, for which the present formalism might prove useful.

ACKNOWLEDGMENTS

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APPENDIX A

The relation between the states with positive and negative energy is best understood in terms of the symmetry of the matrix single-particle Green's function $G_{ij}(\mathbf{r}t,\mathbf{r}'t')$.[33] It follows from Eq. (1) that

$$G_{11}(\mathbf{r}t,\mathbf{r}'t')=-G_{22}(\mathbf{r}'t',\mathbf{r}t) \tag{A1}$$

in the absence of spin-dependent interactions. Equations (A1), (7), and (23) show that the spectral functions are similarly related

$$A_{11}(\mathbf{r},\mathbf{r}',\omega')=A_{22}(\mathbf{r}',\mathbf{r},-\omega'), \tag{A2}$$

$$[A_l(r,r',\omega')]_{11}=[A_l(r',r,-\omega')]_{22}. \tag{A3}$$

The exact spectral function in the presence of a single impurity is given in Eq. (45), and a direct comparison with Eq. (A3) yields

$$v_{kl}^{(\pm)}(r')v_{kl}^{(\pm)}(r)^*=u_{kl}^{(\mp)}(r)u_{kl}^{(\mp)}(r')^*, \tag{A4}$$

where u and v are the upper and lower components of the scattering wave function $\mathfrak{U}_{kl}^{(\pm)}(r)$. Equation (A4) is an identity for all r, r', and l, which can be valid only if the positive and negative energy eigenfunctions are related by

$$\mathfrak{U}_{kl}^{(-)}(r)=(-1)^l\tau^{(1)}\tau^{(3)}[\mathfrak{U}_{kl}^{(+)}(r)]^*. \tag{A5}$$

Both $\mathfrak{U}_{kl}^{(+)}$ and $\mathfrak{U}_{kl}^{(-)}$ satisfy an integral equation

$$\mathfrak{U}_{kl}^{(\pm)}=\Phi_{kl}^{(\pm)}+\mathcal{G}_{kl}^{(\pm)}\mathcal{V}'\mathfrak{U}_{kl}^{(\pm)}, \tag{A6}$$

and it is not difficult to show [using Eqs. (14) and (17)] that the incident wave in Eq. (A6) already obeys the condition (A5). The scattered-wave contribution to Eq. (A6) also satisfies the condition (A5) if

$$\mathcal{G}_{kl}^{(-)}\mathcal{V}'=\tau^{(1)}\tau^{(3)}[\mathcal{G}_{kl}^{(+)}\mathcal{V}']^*\tau^{(3)}\tau^{(1)}, \tag{A7}$$

and the explicit form of $\mathcal{V}$ [given below Eq. (2)] reduces Eq. (A7) to

$$\mathcal{G}_{kl}^{(-)}=-\tau^{(1)}\tau^{(3)}[\mathcal{G}_{kl}^{(+)}]^*\tau^{(3)}\tau^{(1)}. \tag{A8}$$

The Green's function for outgoing scattered waves of positive energy is

$$\mathcal{G}_{kl}^{(+)}(r,r')=\mathcal{G}_l(r,r',E_k+i\eta). \tag{A9}$$

Equations (40), (A8), and (A9) can then be used to verify that

$$\mathcal{G}_{kl}^{(-)}(r,r')=\mathcal{G}_l(r,r',-E_k+i\eta), \tag{A10}$$

which is Eq. (41).

APPENDIX B

The coordinate representation of the scattering Green's function has been given in Eqs. (39)–(41) as

$$\mathcal{G}_{kl}^{(+)}(r,r')=2\pi^{-1}\int_0^\infty q^2dq\; j_l(qr)j_l(qr')$$

$$\times[E_k+\tau^{(3)}\epsilon_q+\tau^{(1)}\Delta][(E_k+i\eta)^2-\epsilon_q{}^2-\Delta^2]^{-1}. \tag{B1}$$

[32] H. E. Hall and W. F. Vinen, Proc. Roy. Soc. (London) **A238**, 204 and 215 (1956); E. M. Lifshitz and L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. **33**, 535 (1957)[English transl.: Soviet Phys.—JETP **6**, 418 (1957)].

[33] The material presented here is similar to that in Appendix A of Ref. 16, which contains a fuller discussion.

It is necessary to treat separately the cases of incident momentum above and below the Fermi momentum. The notation of Eq. (76) will be used here ($k>k_f>\bar{k}$, $E_k=E_{\bar{k}}$). The integrand of Eq. (B1) may be resolved into partial fractions, and the integration over q is then performed with the standard formula[34]

$$\int_0^\infty q^2dq\frac{j_l(qr)j_l(qr')}{q^2-k^2-i\eta}=\tfrac{1}{2}\pi ki\, j_l(kr_<)h_l^{(1)}(kr_>), \quad \text{(B2)}$$

where $r_<$ and $r_>$ are the smaller and larger of r and r'. The explicit coordinate representation is

$$\begin{aligned}\mathcal{G}_{kl}^{(+)}(r,r')&=\mathcal{G}_{\bar{k}l}^{(+)}(r,r')\\&=-2i\rho_k\mathfrak{U}_k^{(+)}\mathfrak{U}_k^{(+)\dagger}j_l(kr_<)h_l^{(1)}(kr_>)\\&\quad-2i\rho_{\bar{k}}\mathfrak{U}_{\bar{k}}^{(+)}\mathfrak{U}_{\bar{k}}^{(+)\dagger}j_l(\bar{k}r_<)h_l^{(2)}(\bar{k}r_>), \quad \text{(B3)}\end{aligned}$$

where Eqs. (14), (15), and (70) have been used. The equality of $\mathcal{G}_{kl}^{(+)}$ and $\mathcal{G}_{\bar{k}l}^{(+)}$ is expected from the definition, Eq. (41), because $E_k=E_{\bar{k}}$. Substitution of Eq. (B3) into the integral equation (42) for the scattering solution then yields the asymptotic expression valid for $r\to\infty$,

$$\begin{aligned}\mathfrak{U}_{kl}^{(+)}(r)\to\Phi_{kl}^{(+)}(r)&-i\pi\rho_k\mathfrak{U}_k^{(+)}i^l(2/\pi)^{1/2}h_l^{(1)}(kr)T_{kk}\\&-i\pi\rho_{\bar{k}}\mathfrak{U}_{\bar{k}}^{(+)}i^l(2/\pi)^{1/2}h_l^{(2)}(\bar{k}r)T_{\bar{k}k}, \quad \text{(B4a)}\end{aligned}$$

$$\begin{aligned}\mathfrak{U}_{\bar{k}l}^{(+)}(r)\to\Phi_{\bar{k}l}^{(+)}(r)&-i\pi\rho_k\mathfrak{U}_k^{(+)}i^l(2/\pi)^{1/2}h_l^{(1)}(kr)T_{k\bar{k}}\\&-i\pi\rho_{\bar{k}}\mathfrak{U}_{\bar{k}}^{(+)}i^l(2/\pi)^{1/2}h_l^{(2)}(\bar{k}r)T_{\bar{k}\bar{k}}, \quad \text{(B4b)}\end{aligned}$$

where the definition of the T matrices [Eqs. (61) and (77)] has been used.

The corresponding real Green's function $\mathcal{G}_{kl}^{(0)}$ is simply the real part of Eq. (B3),

$$\begin{aligned}\mathcal{G}_{kl}^{(0)}(r,r')=\mathcal{G}_{\bar{k}l}^{(0)}(r,r')&=2\rho_k\mathfrak{U}_k^{(+)}\mathfrak{U}_k^{(+)\dagger}j_l(kr_<)y_l(kr_>)\\&\quad-2\rho_{\bar{k}}\mathfrak{U}_{\bar{k}}^{(+)}\mathfrak{U}_{\bar{k}}^{(+)\dagger}j_l(\bar{k}r_<)y_l(\bar{k}r_>). \quad \text{(B5)}\end{aligned}$$

The integral equation (73) then provides the asymptotic form of the real standing-wave solutions

$$\begin{aligned}\mathfrak{W}_{kl}(r)\to\mathcal{J}_{kl}(r)&+\pi\rho_k\mathfrak{U}_k^{(+)}(2/\pi)^{1/2}y_l(kr)R_{kk}\\&-\pi\rho_{\bar{k}}\mathfrak{U}_{\bar{k}}^{(+)}(2/\pi)^{1/2}y_l(\bar{k}r)R_{\bar{k}k}, \quad \text{(B6a)}\end{aligned}$$

$$\begin{aligned}\mathfrak{W}_{\bar{k}l}(r)\to\mathcal{J}_{\bar{k}l}(r)&+\pi\rho_k\mathfrak{U}_k^{(+)}(2/\pi)^{1/2}y_l(kr)R_{k\bar{k}}\\&-\pi\rho_{\bar{k}}\mathfrak{U}_{\bar{k}}^{(+)}(2/\pi)^{1/2}y_l(\bar{k}r)R_{\bar{k}\bar{k}}, \quad \text{(B6b)}\end{aligned}$$

where the R matrix is defined in Eqs. (74) and (75).

To derive the Heitler equation, we shall use the relation between $\mathcal{G}_{kl}^{(+)}$ and $\mathcal{G}_{kl}^{(0)}$, which follows from the integral representation, Eq. (38),

$$\begin{aligned}\mathcal{G}_{kl}^{(+)}(r,r')=\mathcal{G}_{kl}^{(0)}(r,r')&-i\pi\rho_k\Phi_{kl}^{(+)}(r)\Phi_{kl}^{(+)}(r')^\dagger\\&-i\pi\rho_{\bar{k}}\Phi_{\bar{k}l}^{(+)}(r)\Phi_{\bar{k}l}^{(+)}(r')^\dagger. \quad \text{(B7)}\end{aligned}$$

The integral equation for $\mathfrak{U}_{kl}^{(+)}$ and $\mathfrak{U}_{\bar{k}l}^{(+)}$ can be rewritten as

$$\begin{aligned}\mathfrak{U}_{kl}^{(+)}&=\Phi_{kl}^{(+)}+\mathcal{G}_{kl}^{(0)}\mathcal{V}'\mathfrak{U}_{kl}^{(+)}\\&\quad-i\pi\rho_k\Phi_{kl}^{(+)}T_{kk}-i\pi\rho_{\bar{k}}\Phi_{\bar{k}l}^{(+)}T_{\bar{k}k},\\\mathfrak{U}_{\bar{k}l}^{(+)}&=\Phi_{\bar{k}l}^{(+)}+\mathcal{G}_{\bar{k}l}^{(0)}\mathcal{V}'\mathfrak{U}_{\bar{k}l}^{(+)}\\&\quad-i\pi\rho_k\Phi_{kl}^{(+)}T_{k\bar{k}}-i\pi\rho_{\bar{k}}\Phi_{\bar{k}l}^{(+)}T_{\bar{k}\bar{k}}. \quad \text{(B8)}\end{aligned}$$

Addition and subtraction of the two Eqs. (B8) gives

$$\begin{aligned}\mathfrak{U}_{kl}^{(+)}&\pm\mathfrak{U}_{\bar{k}l}^{(+)}=\Phi_{kl}^{(+)}\pm\Phi_{\bar{k}l}^{(+)}\\&+\mathcal{G}_{kl}^{(0)}\mathcal{V}'(\mathfrak{U}_{kl}^{(+)}\pm\mathfrak{U}_{\bar{k}l}^{(+)})\\&-i\pi\rho_k\Phi_{kl}^{(+)}(T_{kk}\pm T_{k\bar{k}})-i\pi\rho_{\bar{k}}\Phi_{\bar{k}l}^{(+)}(T_{\bar{k}k}\pm T_{\bar{k}\bar{k}}). \quad \text{(B9)}\end{aligned}$$

The real solutions obey a similar equation

$$\mathfrak{W}_{kl}\pm\mathfrak{W}_{\bar{k}l}=\mathcal{J}_{kl}\pm\mathcal{J}_{\bar{k}l}+\mathcal{G}_{kl}^{(0)}\mathcal{V}'(\mathfrak{W}_{kl}\pm\mathfrak{W}_{\bar{k}l}). \quad \text{(B10)}$$

The relation $\mathcal{G}_{kl}^{(0)}=\mathcal{G}_{\bar{k}l}^{(0)}$ has been used in both Eqs. (B9) and (B10). These two equations can be combined to express $\mathfrak{U}$ in terms of $\mathfrak{W}$,

$$\begin{aligned}\mathfrak{U}_{kl}^{(+)}\pm\mathfrak{U}_{\bar{k}l}^{(+)}=i^l[&\mathfrak{W}_{kl}\pm\mathfrak{W}_{\bar{k}l}-i\pi\rho_k\mathfrak{W}_{kl}(T_{kk}\pm T_{k\bar{k}})\\&-i\pi\rho_{\bar{k}}\mathfrak{W}_{\bar{k}l}(T_{\bar{k}k}\pm T_{\bar{k}\bar{k}})], \quad \text{(B11)}\end{aligned}$$

which may be verified by substitution of Eq. (B11) into Eq. (B9).[35] The successive scalar product of Eq. (B11) with $\Phi_{kl}^{(+)}\mathcal{V}'$ and $\Phi_{\bar{k}l}^{(+)}\mathcal{V}'$ yields four coupled equations relating the elements of R and T. These are easily simplified to the Heitler equation

$$T_{mn}=R_{mn}-i\pi\textstyle\sum_j R_{mj}\rho_j T_{jn}. \quad \text{(B12)}$$

APPENDIX C

The momentum integrals in Eqs. (107) and (108) are evaluated in this appendix. It is somewhat simpler to consider first the integral appearing in the order parameter

$$\int_0^\infty dk(\Delta/E_k)\tanh\tfrac{1}{2}\beta E_k\sin\delta_l\sin(2kr+\delta_l). \quad \text{(C1)}$$

The integrand is sharply peaked near $k=k_f$ and it is permissible to evaluate the smooth function δ_l at $k=k_f$. Equation (C1) then becomes $\sin\delta_l I_l(r)$, where

$$\begin{aligned}I_l(r)&=\int_0^\infty dk(\Delta/E_k)\tanh\tfrac{1}{2}\beta E_k\sin(2kr+\delta_l)\\&=\mathrm{Im}e^{i\delta_l}\int_0^\infty dk(\Delta/E_k)\tanh\tfrac{1}{2}\beta E_k\,e^{2ikr}. \quad \text{(C2)}\end{aligned}$$

Here Im means imaginary part. The hyperbolic tangent is a meromorphic function and may be expanded as[36]

$$z^{-1}\tanh z=8\textstyle\sum_n[\pi^2(2n+1)^2+4z^2]^{-1}, \quad \text{(C3)}$$

[34] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, England, 1962), 2nd ed., p. 429, 13.53 (4).

[35] See Ref. 10, Chap. 5, Sec. 6, for the details of this standard proof.

[36] See, for example, Ref. 24, p. 386.

where the sum is over all positive integers from zero to infinity. Substitution of Eq. (C3) into Eq. (C2) yields

$$I_l(r)=4\beta\Delta\ \mathrm{Im}e^{i\delta_l}\sum_n\int_0^\infty dk\frac{e^{2ikr}}{\pi^2(2n+1)^2+\beta^2\Delta^2+\beta^2\epsilon_k{}^2}. \tag{C4}$$

Equation (C4) can be considered as a contour integral along the real axis from zero to infinity. The contour can then be deformed into the upper half-plane by Jordan's lemma[37]; an equivalent contour is the positive imaginary axis plus small circles about any poles in the first quadrant (there are no branch points).

The integral along the imaginary axis can be estimated as follows:

$$i\int_0^\infty d\kappa\ e^{-2\kappa r}[\pi^2(2n+1)^2+\beta^2\Delta^2+(\beta/2m)^2(k_f{}^2+\kappa^2)^2]^{-1}$$
$$\leqq(i/2r)[\pi^2(2n+1)^2+\beta^2\Delta^2+\beta^2\epsilon_f{}^2]^{-1}, \tag{C5}$$

since the denominator has been replaced by a smaller quantity. Equations (C3) and (C4) show that the total contribution to I_l from the integral along the imaginary axis is not greater than

$$(\Delta/2\epsilon_f r)\cos\delta_l\tanh\tfrac{1}{2}\beta\epsilon_f\approx(\Delta/2\epsilon_f r)\cos\delta_l$$

since $\beta\epsilon_f\gg1$. This expression is in fact the first term in an asymptotic expansion for large r. Hence Eq. (C2) reduces to

$$I_l(r)-(\Delta/2\epsilon_f r)\cos\delta_l=4\beta\Delta\sum_n\mathrm{Im}e^{i\delta_l}2\pi i[\mathrm{Res}], \tag{C6}$$

where [Res] is an abbreviation for the sum of the residues at the poles in the first quadrant. The poles of the integrand occur at

$$k=k_n e^{\pm i\varphi_n},\ -k_n e^{\pm i\varphi_n}, \tag{C7}$$

where

$$(2m)^{-1}\beta k_n{}^2=[(\beta\epsilon_f)^2+x_n{}^4]^{1/2},$$
$$x_n{}^4=\pi^2(2n+1)^2+\beta^2\Delta^2, \tag{C8}$$
$$\tan2\varphi_n=(\beta\epsilon_f)^{-1}x_n{}^2.$$

Only a single pole is included in the contour, so that Eq. (C6) becomes

$$I_l(r)-(\Delta/2\epsilon_f r)\cos\delta_l$$
$$=4\pi\Delta m\sum_n(k_n x_n{}^2)^{-1}\exp(-2k_n r\sin\varphi_n)$$
$$\times\sin(2k_n r\cos\varphi_n-\varphi_n+\delta_l). \tag{C9}$$

The summation may be separated into several partial sums. If $\pi(2n+1)\ll\beta\Delta$, the nth term is

$$(4\pi m/k_f\beta)\exp(-k_f r\Delta/\epsilon_f)\sin(2k_f r+\delta_l), \tag{C10a}$$

while if $\beta\Delta\ll\pi(2n+1)\ll\beta\epsilon_f$, the nth term is

$$4\Delta m k_f{}^{-1}(2n+1)^{-1}\exp[-k_f r\pi(2n+1)/\beta\epsilon_f]$$
$$\times\sin(2k_f r+\delta_l). \tag{C10b}$$

For $\beta\epsilon_f\ll\pi(2n+1)$, the terms are exponentially small [like $\exp(-k_f r)\ll1$] and may be neglected. The approximate evaluation of Eq. (C9) for $\beta\Delta\gg1$ proceeds as follows:

$$I_l(r)-\frac{\Delta}{2\epsilon_f r}\cos\delta_l\approx4\pi m\Delta\sin(2k_f r+\delta_l)$$
$$\times\left\{\sum_{n=0}^{\beta\Delta/2\pi}\frac{\exp(-k_f r\Delta/\epsilon_f)}{\beta\Delta k_f}\right.$$
$$\left.+\sum_{n=\beta\Delta/2\pi}^{\infty}\frac{\exp[-k_f r\pi(2n+1)/\beta\epsilon_f]}{k_f\pi(2n+1)}\right\}. \tag{C11}$$

The first summation is trivial, and the second can be approximated by an integral. The final result for $\beta\Delta\gg1$ is

$$I_l(r)\approx(\Delta/2\epsilon_f r)\cos\delta_l+(2\Delta m/k_f)\sin(2k_f r+\delta_l)$$
$$\times[\exp(-k_f r\Delta/\epsilon_f)+E_1(k_f r\Delta/\epsilon_f)], \tag{C12}$$

where $E_1(x)$ has been defined in Eq. (112). The opposite limit ($\beta\Delta\ll1$) is obtained from Eq. (C11) by omitting the first summation and setting the lower limit equal to zero in the second. We then find for $\beta\Delta\ll1$

$$I_l(r)\approx(\Delta/2\epsilon_f r)\cos\delta_l+(2\Delta m/k_f)\sin(2k_f r+\delta_l)$$
$$\times E_1(\pi k_f r/\beta\epsilon_f). \tag{C13}$$

Equations (C12) and (C13) can be combined with Eq. (108) to give the asymptotic form of the order parameter, Eqs. (110b) and (111b).

The momentum integral that appears in the asymptotic evaluation of $n(r)$ is

$$\int_0^\infty dk[1-(\epsilon_k/E_k)\tanh\tfrac{1}{2}\beta E_k]\sin\delta_l\sin(2kr+\delta_l). \tag{C14}$$

The quantity in square brackets is a "smeared" step function, and it is convenient to integrate by parts.[38] With the definition

$$s(k)=\int_0^k dk'\sin[\delta_l(k')]\sin[2k'r+\delta_l(k')], \tag{C15}$$

Eq. (C14) is easily written as

$$\int_0^\infty dk\ s(k)(d/dk)[(\epsilon_k/E_k)\tanh\tfrac{1}{2}\beta E_k], \tag{C16}$$

[37] See, for example, E. T. Copson, *An Introduction to the Theory of Functions of a Complex Variable* (Oxford University Press, London, 1957), pp. 136–137.

[38] This approach is standard in the theory of degenerate Fermi systems and may be found, for example, in Ref. 26, pp. 116–119.

where the integrated part vanishes at both limits. If $\delta_l(k)$ is a sufficiently smooth function, the dominant term in $s(k)$ arises from the integration of the oscillatory factor,

$$s(k)\approx-(2r)^{-1}\sin[\delta_l(k)]\cos[2kr+\delta_l(k)], \quad \text{(C17)}$$

where is is assumed that the phase shift vanishes at zero energy.[39] A rigorous proof of Eq. (C17) can also be given, if Eq. (C15) is considered as the Fourier transform of a function that vanishes for $k'>k$. Equation (C17) then emerges as the first term in an asymptotic expansion for large r.[40]

The integrand of Eq. (C16) is sharply peaked at the Fermi momentum, so that the phase shift δ_l may be evaluated at $k=k_f$. We shall write (C16) as

$$-(2r)^{-1}\sin\delta_l M_l(r); \quad \text{(C18)}$$

Equation (C3) is then used to obtain

$$M_l(r)=(4\beta/m)\,\mathrm{Re}e^{i\delta_l}\sum_n\int_0^\infty kdk\,e^{2ikr}\times\{[\pi^2(2n+1)^2+\beta^2\Delta^2+\beta^2\epsilon_k{}^2]^{-1}-2\beta^2\epsilon_k{}^2[\pi^2(2n+1)^2+\beta^2\Delta^2+\beta^2\epsilon_k{}^2]^{-2}\}, \quad \text{(C19)}$$

where Re means real part. The double poles of the integrand make a direct calculation laborious, and the following mathematical device will be used instead. We define a function $K_\lambda(r)$, depending on a parameter λ,

$$K_\lambda(r)=\mathrm{Re}e^{i\delta_l}\sum_n\int_0^\infty kdk\times e^{2ikr}[\pi^2(2n+1)^2+\beta^2\Delta^2+\beta^2\lambda^2\epsilon_k{}^2]^{-1}. \quad \text{(C20)}$$

It is easy to verify that

$$M_l(r)=(4\beta/m)\{(\partial/\partial\lambda)[\lambda K_\lambda(r)]\}\,|_{\lambda=1}, \quad \text{(C21)}$$

which reduces the calculation to one involving only simple poles. The λ dependence in Eq. (C20) is wholly equivalent to the substitution $m\rightarrow m'=\lambda^{-1}m$, and the evaluation of Eq. (C20) is almost identical with that of Eq. (C4). The contour can be deformed to the positive imaginary axis plus circles about the poles in the first quadrant. The contribution from the imaginary axis is negligible, and we find

$$K_\lambda(r)=(\pi m'/\beta)\sum_n x_n{}^{-2}\exp(-2k_n r\sin\varphi_n)\times\cos(2k_n r\cos\varphi_n+\delta_l). \quad \text{(C22)}$$

The notation of Eq. (C8) has been used here, except that m' appears everywhere instead of m.

The summation over n is approximated as in Eqs. (C10) and (C11), so that $K_\lambda(r)$ may be written in closed form for both limiting cases, $\beta\Delta\gg1$ and $\beta\Delta\ll1$. The differentiation with respect to λ is straightforward:

$$M_l(r)\approx2\cos(2k_f r+\delta_l)[1+(k_f r\Delta/\epsilon_f)]\times\exp(-k_f r\Delta/\epsilon_f) \quad (\beta\Delta\gg1) \quad \text{(C23a)}$$

$$M_l(r)\approx2\cos(2k_f r+\delta_l)\exp(-\pi k_f r/\beta\epsilon_f) \quad (\beta\Delta\ll1). \quad \text{(C23b)}$$

Equations (C23a) and (C23b) can be combined with Eqs. (C18) and (107) to yield the asymptotic form of $n(r)$, given in Eqs. (110a) and (111a).

[39] This assumption is valid for a very wide class of potentials. See, for example, Ref. 10, pp. 285–286.

[40] The evaluation is straightforward using the formulas and tables provided in M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, England, 1960), Chaps. 3 and 4.