Exact Wave Functions in Superconductivity

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The ground-state wave function and some of the excited states of the BCS reduced Hamiltonian are found. In the limit of large volume, the boundary and continuity conditions on the exact wave function lead directly to the equations which Bardeen, Cooper, and Schrieffer found by a variational technique. It is also shown in what sense the BCS trial wave function may be considered asymptotically exact in this limit. Finite-volume corrections are included in an appendix, and explicit calculations are carried out for a one-step model of the kinetic energy which has possible applications to the problem of the finite nucleus.

I. INTRODUCTION

WE wish to find the ground-state wave function and some of the elementary excited states of

$$H=\sum_{k,s}\epsilon(k,s)C_{k,s}{}^{*}C_{k,s}-v\sum_{k}\sum_{k'\neq k}C_{k\uparrow}{}^{*}C_{-k\downarrow}{}^{*}C_{-k'\downarrow}C_{k'\uparrow}. \quad (1)$$

The operators C and C^* are the usual Fermi operators and anti-commute. The sums are restricted to an immediate neighborhood of the Fermi surface, which includes $4n$ distinct states of momentum (k) and spin $(s=\uparrow$ or $\downarrow)$, and which are populated by $2n$ electrons. In other words, our eigenfunctions must be simultaneously eigenfunctions of the number operator η

$$\eta=\sum_{k,s}C_{k,s}{}^{*}C_{k,s}, \quad (2)$$

with eigenvalue $2n$.

Our Hamiltonian is the famous "reduced Hamiltonian" of the BCS theory; and for an introduction to the present work, we refer the reader to Sec. II of the BCS paper.[1] In their notation, $n=N(0)\hbar\omega$, where $N(0)=$density of states at the Fermi surface and $\hbar\omega=$typical phonon energy. As has been stated, we wish to investigate the nature of the exact solutions to this problem, and we shall see that they are very similar to what BCS found by a variational calculation.

For the purposes of finding the ground state, it is convenient to think in terms of a pseudo-Hamiltonian $\tilde{H}$ which has the same ground state as (1). First, by time-reversal symmetry, we may assume that $\epsilon(k,\uparrow)=\epsilon(-k,\downarrow)$. Second, it is clear that, in the ground state, all electrons must be paired, as in $C_{k\uparrow}{}^{*}C_{-k\downarrow}{}^{*}$, because unpaired electrons do not benefit from the attractive interaction. Following BCS, then, we define

$$b_k{}^{*}=C_{k\uparrow}{}^{*}C_{-k\downarrow}{}^{*}, \quad b_k=C_{-k\downarrow}C_{k\uparrow}, \quad (3)$$

and consequently, the ground state of the pseudo-Hamiltonian

$$\tilde{H}=2\sum\epsilon_k b_k{}^{*}b_k-v\sum_{k}\sum_{k'\neq k}b_k{}^{*}b_{k'} \quad (4)$$

coincides with the ground state of H. [We have set $\epsilon_k=\epsilon(k,\uparrow)$.] Indeed, every eigenstate of $\tilde{H}$ is a state of H, but the converse is not true. The b_k operators have mixed commutation properties and may not be regarded as Bosons for which the diagonalization of (4) would be trivial. In fact, they are a set of Pauli operators.[1]

A complete set of states for our problem consists of all possible configurations of n pairs, of which a typical member is

$$\phi_i=[\prod_{k\subseteq\{k\}^i}b_k{}^{*}]|0\rangle \quad (5)$$

where $\{k\}_i$ is a set of n different k's chosen from the $2n$ permissible values. There are $(2n)!/(n!)^2\cong 2^{2n}/(\pi n)^{\frac{1}{2}}$ different ϕ_i's. For comparison, the totality of configurations (allowing an arbitrary occupation number) is 2^{2n}. For every ϕ_i there is a corresponding amplitude, which we may write as $f_i\equiv f[S(k_1)\cdots S(k_{2n})]$, where $S(k_j)=1$ or 0 according to whether k_j is in the set $\{k\}_i$ or not. It is to be understood that f is not defined for all possible values of its arguments (of which there are 2^{2n}) but only for those values such that $\sum_j S(k_j)\equiv n$. The general eigenfunction of $\tilde{H}$ is therefore

$$\psi=\sum_{\text{config.}}f_i\phi_i. \quad (6)$$

The problem now consists of finding the ground-state amplitudes f_i and the corresponding energy. For some insight into the general problem, we first turn to the strong-coupling limit which is well understood.

II. STRONG-COUPLING LIMIT[2]

We set $\epsilon_k=0$, and the Hamiltonian is simply

$$H_{\text{s.c.}}=-v\sum_{k}\sum_{k'\neq k}b_k{}^{*}b_{k'}. \quad (7)$$

As this is purely attractive, we may safely assume that the ground-state wave function possesses all the symmetry of the Hamiltonian. The outstanding symmetry property is invariance under the interchange of any two momenta k and k'. Therefore, one may pre-

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

[2] The strong-coupling limit is generally well understood. An exhaustive treatment of this limit, including a perturbation-theoretic approach to weak coupling, is given by Wada and Fukuda, Progr. Theoret. Phys. (Kyoto) **22**, 775 (1959).

sume that

$$f(\cdots S(k)\cdots S(k')\cdots)=f(\cdots S(k')\cdots S(k)\cdots), \quad (8)$$

i.e., that f is a symmetric function of its arguments. Now we make use of the property that $S(k)=0$ or 1, which is expressible as

$$S(k)=S^2(k). \quad (9)$$

Consequently,[3] the most general function which obeys Eq. (8) can be written as

$$f(S(k_1)\cdots S(k_{2n}))=f(\sum_k S(k))=f(n). \quad (10)$$

But as n is a constant, f must be constant and hence all amplitudes are equal in the strong-coupling ground state. We can check this directly:

$$(-v\sum_k\sum_{k'\neq k} b_k^*b_{k'})\cdot f(n)\sum_i\prod_{k\subseteq\{k\}_i} b_k^*|0\rangle = E_{s.c.}f(n)\sum_i\prod b_k^*|0\rangle, \quad (11)$$

with $f(n)=n!(2n!)^{-\frac{1}{2}}\cong 2^{-n}(\pi n)^{\frac{1}{4}}$ for normalization. This is the Schrodinger equation, and each complexion is connected to n^2 other complexions. Therefore,

$$E_{s.c.}=-vn^2, \quad (12)$$

a well-known result. It may be useful to recall that n and v^{-1} are both proportional to the volume (for fixed density), so that E is an extensive property of the system. Eq. (12) is in perfect agreement with the BCS result taken in the strong-coupling limit, but is in slight disagreement with the calculation of Wada and Fukuda,[2] who include a diagonal term $-v\sum b_k^*b_k$ in their interaction. There is no particular significance in their discrepancy.

III. ONE-STEP MODEL

The number of sign changes (or nodes) in the amplitudes f is a good quantum number, and by the adiabatic theorem, its value persists as ϵ_k is changed from a constant value to some arbitrary function. We make use of this to solve for the ground state of a model which is not quite so trivial as the strong-coupling limit, and which may be of interest in the nuclear problem where energy levels are discrete. We shall assume that ϵ_k is a step function—zero over half of the states and equal to a positive constant (ϵ) over the remaining states.

The ground-state amplitudes must be nodeless functions which are symmetric under the interchange of any two pairs within the same half-space. Let the occupation numbers over each half-space be,

$$n_0=\sum_{\substack{k \text{ such that}\\ \epsilon_k=0}} S_k \quad \text{and} \quad n_\epsilon=\sum_{\substack{k \text{ such that}\\ \epsilon_k=\epsilon}} S_k. \quad (13)$$

[3] This theorem was kindly pointed out to us by Dr. D. Jepsen and Dr. T. D. Schultz of this laboratory.

We can eliminate n_0 by the relation

$$n=n_0+n_\epsilon=\text{const}, \quad (14)$$

and therefore the ground-state amplitudes are a function of n_ϵ alone, and are denoted $f(n_\epsilon)$. The equations for the amplitudes are simply

$$[2\epsilon n_\epsilon-E-2vn_\epsilon(n-n_\epsilon)]f(n_\epsilon) = v(n-n_\epsilon)^2f(n_\epsilon+1)+vn_\epsilon^2f(n_\epsilon-1), \quad (15)$$

where n_ϵ assumes integer values from zero to a maximum of n. These equations are easily soluble when n is a small integer. For example, if $n=1$, there are only two amplitudes, $f(0)$ and $f(1)$, and the eigenvalue equation is the usual determinantal condition

$$\text{Det}\begin{vmatrix}-E & -v\\ -v & 2\epsilon-E\end{vmatrix}=0, \quad (16)$$

which has the solutions

$$E_\pm=\epsilon\pm(\epsilon^2+v^2)^{\frac{1}{2}}. \quad (17)$$

The lower of these E_- is the ground-state energy and belongs to the nodeless solution $f(1)/f(0)>0$, as expected.

For large n, the determinantal equation is impractical, and we now use a method for isolating the ground-state energy from all the other solutions in the limit of large volume, $n\to\infty$. Corrections in the form of an expansion in n^{-1} are discussed in the Appendix, and may be of value already for $n\geq 3$, when the determinantal method is cumbersome.

Because the amplitudes can be chosen real and positive in the ground state, we write

$$f(n_\epsilon)=\text{const}e^{nS(x)}, \quad (18)$$

where $x\equiv n_\epsilon/n$, and S is a real function. Next, we divide both sides of Eq. (15) by $nf(n_\epsilon)$ and find

$$2\epsilon x-W-2\lambda x(1-x) = \lambda[(1-x)^2p(x+1/n)+x^2/p(x)], \quad (19)$$

where

$$p(x)=\exp\{n[S(x)-S(x-1/n)]\}, \quad (20)$$

$$W\equiv E/n, \quad \text{and} \quad \lambda\equiv vn. \quad (21)$$

The variable x goes from 0 to 1 in steps of $1/n$. One can now proceed to the limit $n\to\infty$, but first one notes that

$$\lim_{n\to\infty}\exp\{n[S(x+1/n)-S(x)]\} = \lim_{n\to\infty}\exp\{+n[S(x)-S(x-1/n)]\} = \exp[\partial/\partial x S(x)], \quad (22)$$

provided $S(x)$ is a sufficiently smooth function. Therefore, to order $1/n$ if $S(x)$ is sufficiently smooth, $p(x)=p[x+(1/n)]$, and Eq. (19) turns into an algebraic

equation

$$2\epsilon x - W - 2\lambda x(1-x) = \lambda\{(1-x)^2 p(x) + x^2/p(x)\}, \quad (23)$$

which is subject to the requirement that $p(x)$ be real, positive, and continuous. The conjecture that $S(x)$ approaches a continuous limit function as $n \to \infty$, which implies that $p(x) \cong p(x+1/n)$ and satisfies Eq. (23), which in turn implies that $S(x)$ has a limit function is certainly self-consistent. But it need not be true. Equation (19) is a nonlinear difference equation, and in order to get from the point $x=0$ to the point $x=1/4$ say, we must iterate it $n/4$ times. The assertion that $p(x+1/n)$ may be replaced by $p(x)$ will result in an error of order $1/n$. But since it takes $n/4$ steps to get to $x=1/4$, we may accumulate an error or order 1, in which case $p(1/4)$ will not satisfy Eq. (23). Once $p(x)$ ceases to satisfy the quadratic equation, we see from Eq. (19) that $p(x)$ will oscillate wildly. In the Appendix we prove that the errors do not in fact accumulate in the regions $(0,m)$ and $(n,1)$ where m and n are the least and greatest points, respectively, at which the discriminant of Eq. (23) vanishes. For the ground state, the discriminant vanishes at only one point and, hence, in this case, our smoothness assumption is justified everywhere except in a small neighborhood about the vanishing point. There are three critical points: at $x=0$ and 1, and at the turning point where the discriminant vanishes.

The "boundary conditions" are as follows: at $x=0$,

$$p(0) = -W/\lambda, \quad (24)$$

which follows from Eq. (19) at $x=0$. Obviously, W will have to be negative or zero. At $x=1$,

$$p(1) = \lambda/(2\epsilon - W), \quad (25)$$

which follows from Eq. (19) at $x=1$. At intermediate points, the quadratic equation possesses two solutions

$$p(x) = \frac{2\epsilon x - W - 2\lambda x(1-x)}{2\lambda(1-x)^2} \pm \frac{1}{1-x}\left[\left(\frac{2\epsilon x - W - 2\lambda x(1-x)}{2\lambda(1-x)}\right)^2 - x^2\right]^{\frac{1}{2}}. \quad (26)$$

The boundary conditions impose the positive root near $x=0$ and the negative root near $x=1$. Therefore, at one intermediate point, the discriminant must vanish so that the transition from positive to negative root may be continuous. The reality condition is translated into the requirement that the discriminant have a minimum at this "turning point" where it vanishes. Thus, simultaneously, we require

$$D = \left[\left(\frac{2\epsilon h_\epsilon - W - 2\lambda h_\epsilon(1-h_\epsilon)}{2\lambda(1-h_\epsilon)}\right)^2 - h_\epsilon^2\right] = 0, \qquad p(h_\epsilon) = \frac{h_\epsilon}{1-h_\epsilon}, \quad (27)$$

where $x=h_\epsilon$ is the turning point (by analogy with the BCS notation) and

$$\left.\frac{\partial D}{\partial x}\right|_{h_\epsilon} = 0. \quad (28)$$

It does *not* follow, however, that

$$\left.\frac{dp(x)}{dx}\right|_{x=h_\epsilon} = \left.\frac{d}{dx}\left(\frac{x}{1-x}\right)\right|_{x=h_\epsilon}, \quad \text{and indeed} \quad \frac{dp(x)}{dx}$$

is discontinuous at the point $x=h_\epsilon$, although it always remains finite. Equations (27) and (28) possess a solution provided $\lambda \geq \epsilon/2$,

$$h_\epsilon = \frac{1}{2}\left(1 - \frac{\epsilon}{2\lambda}\right), \quad p(h_\epsilon) = \frac{1-\epsilon/2\lambda}{1+\epsilon/2\lambda}, \quad (29)$$

and

$$W = -\lambda[1-\epsilon/(2\lambda)]^2. \quad (30)$$

Recalling that $\lambda = vn$ and $E = nW$, we find for the ground energy in the one-step model:

$$E_{\text{o.s.}} = -(vn)(n)\left(1 - \frac{\epsilon}{2(vn)}\right)^2, \quad \text{for} \quad (vn) \geq \frac{\epsilon}{2}. \quad (31)$$

For $(vn) = \lambda < \frac{1}{2}\epsilon$, the turning point sticks at $h_\epsilon = 0$, and one finds that only the negative solution is required for reality and continuity, provided $W=0$. Therefore,

$$E_{\text{o.s.}} = 0 \quad \text{for} \quad (vn) \leq \tfrac{1}{2}\epsilon. \quad (32)$$

Had we used the BCS trial function, the results would have been identical. As we shall see in Secs. IV and V, this is no coincidence, even though the BCS trial function is not an eigenfunction and does not conserve particles. It may also be easily verified that these results agree with the strong-coupling theory if we set $\epsilon=0$, even as to the constancy of the amplitudes $f(n_\epsilon)$ in that limit. For the excited states, we turn back to the Hamiltonian in its original form given in Eq. (1).

The low-lying excited states are relatively easy to find in the one-step model. We break up a pair, putting one electron in an $\epsilon_k = 0$ state, and the other in an $\epsilon_k = \epsilon$ state. There are $(n-1)$ remaining pairs for which $(n-1)$ $\epsilon_k = 0$ states are accessible, and an equal number of $\epsilon_k = \epsilon$ states. The energy of the "singles" is

$$E \text{ singles} = 0 + \epsilon = \epsilon, \quad (33)$$

and the lowest possible energy for the remaining pairs is [substituting $(n-1)$ for n in our previous result]

$$E^{(n-1)} = -(v)(n-1)^2\left[1 - \frac{\epsilon}{2v(n-1)}\right]^2, \quad (34)$$

provided $v(n-1) \geq \frac{1}{2}\epsilon$, and zero otherwise. Thus, the excitation energy Δ associated with such excited states

is (calculated to leading order in the volume)

$$\Delta = E \text{ singles} + E^{(n-1)} - E^{(n)} = 2(vn), \text{ if } (vn) \geq \tfrac{1}{2}\epsilon, \quad (35)$$

and

$$\Delta = \epsilon, \text{ if } (vn) \leq \tfrac{1}{2}\epsilon. \quad (36)$$

It is interesting to note from Eq. (35) that unless ϵ exceeds a critical value, this energy of excitation is independent of ϵ, hence, is the same as for the strong-coupling limit. This shows an amazing rigidity in the ground-state wave function.

IV. SOLUTION FOR ARBITRARY FUNCTION ϵ_k

Proceeding with a knowledge of the one-step model, we can now derive the BCS equations for an arbitrary function ϵ_k. We do this by approximating ϵ_k as closely as we please by a staircase function. If we call the number of states in the step about some discrete ϵ, N_ϵ, then as $n \to \infty$, $N_\epsilon \to \infty$. Thus, no matter how "fine" the staircase, each step will always have an infinite number of states associated with it. The limit to a continuous function $\epsilon(k)$ is taken *after* the limit $n \to \infty$, but always the number of steps on the staircase is regarded as large. We shall assume that ϵ varies from a minimum value $E_F - \hbar\omega$ to a maximum of $E_F + \hbar\omega$, where E_F is the unperturbed Fermi level and $\hbar\omega$ is the energy of the typical phonons responsible for the attractive interaction v. We define the population of the portion of phase space belonging to ϵ_k in a given complexion by

$$n_\epsilon = \sum_{\substack{k \text{ such that} \\ \epsilon_k = \epsilon}} S_k. \quad (37)$$

As before, n_ϵ can vary by integer steps from zero to a maximum value N_ϵ. If we denote a sum over distinct energy shells, (i.e., a sum over the steps in the staircase) by the usual summation symbol with superscript ϵ, we recall that

$$\sum^\epsilon n_\epsilon = n, \quad (38)$$

and

$$\sum^\epsilon N_\epsilon = 2n. \quad (39)$$

The algebraic equations for the amplitudes are

$$[2\sum^\epsilon \epsilon n_\epsilon - E - v\sum^\epsilon n_\epsilon(N_\epsilon - n_\epsilon)] f(\cdots n_\epsilon \cdots n_{\epsilon'} \cdots) = V \sum^\epsilon \sum^{\epsilon' \neq \epsilon} (N_\epsilon - n_\epsilon) n_{\epsilon'} \times f(\cdots (n_\epsilon + 1) \cdots (n_{\epsilon'} - 1) \cdots). \quad (40)$$

We let

$$f(\cdots n_\epsilon \cdots n_{\epsilon'} \cdots) = \exp nS(\cdots x_\epsilon \cdots x_{\epsilon'} \cdots), \quad (41)$$

where $x_\epsilon = n_\epsilon / N_\epsilon$, and again divide both sides of the equation by the amplitude $f(\cdots n_\epsilon \cdots n_{\epsilon'} \cdots)$. One defines

$$p_{\epsilon,\epsilon'} = \frac{f(\cdots (n_\epsilon + 1) \cdots (n_\epsilon - 1) \cdots)}{f(\cdots n_\epsilon \cdots n_\epsilon \cdots)}, \quad (42)$$

from which it follows that in the limit $n \to \infty$,

$$p_{\epsilon',\epsilon} = 1/p_{\epsilon,\epsilon'}, \quad \epsilon \neq \epsilon'. \quad (43)$$

Once again we have assumed that $p_{\epsilon,\epsilon'}$ approaches a continuous limit function. If we extend this definition to include the special case $\epsilon' = \epsilon$, $p_{\epsilon,\epsilon} = (p_{\epsilon,\epsilon})^{-1} = 1$, then in our limit, Eq. (40) simplifies to

$$2\sum^\epsilon N_\epsilon \epsilon x_\epsilon - E = \tfrac{1}{2} v \sum^\epsilon N_\epsilon \sum^{\epsilon'} N_{\epsilon'} \times \{(1 - x_\epsilon) x_{\epsilon'} p_{\epsilon,\epsilon'} + (1 - x_{\epsilon'}) x_\epsilon / p_{\epsilon,\epsilon'}\}. \quad (44)$$

Each $p_{\epsilon,\epsilon'}$ is required to be real and continuous in the ground state, with respect to variations in any of the independent variables x_ϵ, or of the parameters ϵ and ϵ'. For example, we must find

$$\lim_{\epsilon' = \epsilon} p_{\epsilon,\epsilon'} = 1, \quad \text{and} \quad p_{\epsilon,\epsilon''} p_{\epsilon'',\epsilon'} = p_{\epsilon,\epsilon'}, \quad (45)$$

but these conditions will be trivially satisfied by our solution. To investigate the continuity with respect to the independent variables, we isolate an arbitrary term on the right-hand side of Eq. (44), and combine all the other terms with the left-hand side. Thus,

$$\alpha = \beta p_{\epsilon,\epsilon'} + (\gamma / p_{\epsilon,\epsilon'}), \quad (46)$$

where

$$\alpha = 2\sum^\epsilon N_\epsilon \epsilon x_\epsilon - E - \tfrac{1}{2} v \sum^{\epsilon''} N_{\epsilon'} \sum^{\epsilon'''} N_{\epsilon''} \times \left\{ (1 - x'') x''' p_{\epsilon'',\epsilon'''} + \frac{(1 - x''') x''}{p_{\epsilon'',\epsilon''}} \right\}, \quad (\epsilon'',\epsilon''') \neq (\epsilon,\epsilon'), \ \neq (\epsilon',\epsilon), \quad (46a)$$

$$\beta = \tfrac{1}{2} v N_\epsilon N_{\epsilon'} (1 - x_\epsilon) x_{\epsilon'}, \quad (46b)$$

and

$$\gamma = \tfrac{1}{2} v N_\epsilon N_{\epsilon'} (1 - x_{\epsilon'}) x_\epsilon. \quad (46c)$$

The "boundary conditions" are

$$p_{\epsilon,\epsilon'} = \alpha/\beta \quad \text{when} \quad \gamma = 0, \quad (47)$$

$$p_{\epsilon,\epsilon'} = \gamma/\alpha \quad \text{when} \quad \beta = 0, \quad (48)$$

whereas the general solution is

$$p_{\epsilon,\epsilon'} = \frac{\alpha}{2\beta} \pm \left[\left(\frac{\alpha}{2\beta} \right)^2 - \frac{\gamma}{\beta} \right]^{\frac{1}{2}}. \quad (49)$$

Continuity might require that at some point $p_{\epsilon,\epsilon'}$ have a cusp. That is, the discriminant must vanish at some point, and

$$\alpha = 2(\beta\gamma)^{\frac{1}{2}}. \quad (50)$$

The reality condition requires that

$$\frac{\partial}{\partial t} \left\{ \left(\frac{\alpha}{2\beta} \right)^2 - \frac{\gamma}{\beta} \right\} = 0, \quad (51)$$

where t is representative of any variable in the problem. This is already quite similar to the one-step problem, and suggestive of the BCS equations, but the derivation is not yet complete. Anyhow, for each pair (ϵ,ϵ'), there exists a value of x_ϵ and $x_{\epsilon'}$ (which we shall denote h_ϵ and $h_{\epsilon'}$) for which

$$p_{\epsilon,\epsilon'}=\frac{\alpha}{2\beta}=\left(\frac{\gamma}{\beta}\right)^{\frac{1}{2}}=\left(\frac{(1-h_{\epsilon'})h_\epsilon}{(1-h_\epsilon)h_{\epsilon'}}\right)^{\frac{1}{2}} \tag{52}$$

by Eqs. (49) and (50). At this point, Eq. (44) reads

$$E=2\sum^{\epsilon}N_\epsilon\epsilon h_\epsilon -v\sum^{\epsilon}N_\epsilon\sum^{\epsilon'}N_{\epsilon'}[h_\epsilon h_{\epsilon'}(1-h_\epsilon)(1-h_{\epsilon'})]^{\frac{1}{2}}. \tag{53}$$

We also investigate Eq. (44) in the neighborhood of this point. Let $n_\epsilon=N_\epsilon\cdot h_\epsilon+\delta n$, $n_{\epsilon'}=N_{\epsilon'}\cdot h_\epsilon-\delta n$, and all other occupations remain fixed. For infinitesimal δn, one finds a differential equation, which after some simplification reduces to

$$2\epsilon-\frac{v}{2}\sum^{\epsilon''}N_{\epsilon''}\sum^{\epsilon'''}N_{\epsilon'''} \times\left\{(1-h'')h'''-\frac{(1-h''')h''}{p^2_{\epsilon'',\epsilon'''}}\right\}\frac{1}{N_\epsilon}\frac{d}{dx_\epsilon}p_{\epsilon'',\epsilon'''}\Big|_{x_\epsilon=h_\epsilon} -v\sum_{\epsilon''\neq\epsilon}^{\epsilon''}N_{\epsilon''}\left\{-h''p_{\epsilon,\epsilon''}+\frac{(1-h'')}{p_{\epsilon,\epsilon''}}\right\} -vN_\epsilon(1-2h_\epsilon)=\text{const.} \tag{54}$$

In general, we don't know the value of $d/dx_\epsilon(p_{\epsilon'',\epsilon'''})$, not even at the point in question. However, it is finite, and by Eq. (52), its coefficient vanishes.

$$2\epsilon-v\left(\frac{1-2h_\epsilon}{[h_\epsilon(1-h_\epsilon)]^{\frac{1}{2}}}\right) \times\sum^{\epsilon''}N_{\epsilon''}[h_{\epsilon''}(1-h_{\epsilon''})]^{\frac{1}{2}}=\text{const.} \tag{55}$$

Following BCS, this is solved by defining the gap parameter ϵ_0

$$\epsilon_0=v\sum^{\epsilon''}N_{\epsilon''}[h_{\epsilon''}(1-h_{\epsilon''})], \tag{56}$$

from which it follows that

$$h_\epsilon=\tfrac{1}{2}[1-\tilde{\epsilon}/(\tilde{\epsilon}^2+\epsilon_0^2)^{\frac{1}{2}}], \tag{57}$$

where $\tilde{\epsilon}=\epsilon-\frac{1}{2}$ const. To determine this constant, we refer back to Eqs. (38) and (39) which, upon being combined, yield the condition

$$\sum^{\epsilon}N_\epsilon\tilde{\epsilon}/(\tilde{\epsilon}^2+\epsilon_0^2)^{\frac{1}{2}}=0. \tag{58}$$

It is easy to see that this constant is the chemical potential for a pair 2μ, which is conventionally determined by the condition that the total number of particles be fixed, as here. If N_ϵ is approximately a constant function of ϵ, then Eq. (58) can be written as

$$\int_{E_F-\hbar\omega}^{E_F+\hbar\omega}d\epsilon\frac{\tilde{\epsilon}}{(\tilde{\epsilon}^2+\epsilon_0^2)^{\frac{1}{2}}}=0, \tag{59}$$

and it is seen that μ is independent of ϵ_0 and is equal to its unperturbed value which we denote by E_F. Otherwise, one defines

$$\phi(\epsilon)=N_\epsilon/N_{2\mu}, \tag{60}$$

and Eq. (58) becomes

$$\int_{E_F-\hbar\omega}^{E_F+\hbar\omega}d\epsilon\phi(\epsilon)\frac{\tilde{\epsilon}}{(\tilde{\epsilon}^2+\epsilon_0^2)^{\frac{1}{2}}}=0. \tag{61}$$

This is an implicit equation for the chemical potential and, in general, μ can be a function of ϵ_0.

The ground-state energy is simply obtained by substituting the values of h_ϵ determined by Eqs. (57) and (58) into Eq. (53), as in reference 1.

This concludes our derivation of the equations of superconductivity based on an analysis of the properties of the exact eigenfunction of the reduced Hamiltonian (1). In the following section, we conclude our verification of the BCS theory by showing that the point $\{x_\epsilon\}=\{h_\epsilon\}$ is a stationary point, in the sense that as $n\to\infty$, the contribution of the various configurations to the wave function becomes essentially a delta function centered about this point, and that, therefore, the BCS trial function (or any other trial function which is correct in the neighborhood of this point) becomes asymptotically exact in this limit, and not just the variational energy.

V. THE STATIONARY POINT

In the limit of infinite volume, only certain configurations contribute significantly to the wave-function normalization integral, and also in the calculation of matrix elements to the low-lying excited states. We have seen that the BCS equations are exact in the neighborhood of a certain point in occupation-number-space. We shall now show that this is also the stationary point, and that the BCS wave function correctly weights the relative amplitudes of different configurations in the neighborhood of this point, provided care is exercised in conserving particles.

We investigate the one-step model,[4] for which the wave-function normalization requires

$$1=\sum_{n_\epsilon=0}^{n}\left[\frac{n!}{n_\epsilon!(n-n_\epsilon)!}\right]^2 f^2(n_\epsilon). \tag{62}$$

The first factor is the number of ways we can have the occupation number n_ϵ, i.e., the number of distinct configurations belonging to the same value of n_ϵ. In

[4] The generalization to the model of Sec. IV would be repetitious and will be omitted.

the limit $n\to\infty$, both this factor and $f^2(n_\epsilon)$ are very rapidly varying functions of n_ϵ, and most of the contribution comes from a neighborhood of the point where the summand has a maximum. (The sum could be replaced by an integral at this point and evaluated by the method of steepest descents.)

Let the stationary point be at $\bar{n}_\epsilon$, and let us factor from the sum the value of the summand at this point.

$$1=\left(\frac{n!f(\bar{n}_\epsilon)}{\bar{n}_\epsilon!(n-\bar{n}_\epsilon)!}\right)^2\left(1+\frac{(n-\bar{n}_\epsilon)^2}{(\bar{n}_\epsilon+1)^2}\frac{f^2(\bar{n}_\epsilon+1)}{f^2(\bar{n}_\epsilon)}+\frac{\bar{n}_\epsilon^2}{(n-\bar{n}_\epsilon+1)}\right.$$
$$\times\frac{f^2(\bar{n}_\epsilon-1)}{f^2(\bar{n}_\epsilon)}+\frac{(n-\bar{n}_\epsilon)^2(n-\bar{n}_\epsilon-1)^2}{(\bar{n}_\epsilon+1)^2(\bar{n}_\epsilon+2)^2}\frac{f^2(\bar{n}_\epsilon+2)}{f^2(\bar{n}_\epsilon)}$$
$$\left.+\frac{\bar{n}_\epsilon^2(\bar{n}_\epsilon-1)^2}{(n-\bar{n}_\epsilon+1)^2(n-\bar{n}_\epsilon+2)^2}\frac{f^2(\bar{n}_\epsilon-2)}{f^2(\bar{n}_\epsilon)}+\cdots\right). \quad (63)$$

In our limit,

$$1=\left(\frac{n!f(\bar{n}_\epsilon)}{\bar{n}_\epsilon!(n-\bar{n}_\epsilon)!}\right)^2\left(1+\frac{(1-\bar{x}_\epsilon)^2}{\bar{x}_\epsilon^2}p^2(\bar{x}_\epsilon)-O\left(\frac{1}{n}\right)\right.$$
$$+\frac{\bar{x}_\epsilon^2}{(1-\bar{x}_\epsilon)^2}\frac{1}{p^2(\bar{x}_\epsilon)}-O\left(\frac{1}{n}\right)+\frac{(1-\bar{x}_\epsilon)^4}{\bar{x}_\epsilon^4}p^4(\bar{x}_\epsilon)$$
$$\left.-O\left(\frac{1}{n}\right)+\frac{\bar{x}_\epsilon^4}{(1-\bar{x}_\epsilon)^4}\frac{1}{p^4(\bar{x}_\epsilon)}-O\left(\frac{1}{n}\right)+\cdots\right). \quad (64)$$

To order $1/n$, all the terms in the neighborhood of $\bar{x}_\epsilon\equiv\bar{n}_\epsilon/n$ must contribute equally, therefore,

$$p(\bar{x}_\epsilon)=\bar{x}_\epsilon/(1-\bar{x}_\epsilon). \quad (65)$$

However, comparing this with Eq. (27), we see that

$$\bar{x}_\epsilon=h_\epsilon, \quad (66)$$

and indeed the stationary point is the same as the turning point at which the discriminant of Sec. III vanished. As this is the only point of interest in the calculation of the normalization integral (and of low-lying matrix elements), we must verify that the trial function has the right amplitudes at and near this point.

The BCS function is

$$\psi=\prod_k([1-h(\epsilon_k)]^{\frac{1}{2}}+[h(\epsilon_k)]^{\frac{1}{2}}b_k^+)\,|\,0\rangle, \quad (67)$$

and is evidently normalized. For the one-step model ($\epsilon_k=0$ or ϵ), h_ϵ is the same as in our Eq. (29), and $h_0=1-h_\epsilon$. Decomposing the function (67) into configurations of distinct n_0 and n_ϵ, we find that the trial amplitudes do correctly depend only on these parameters, but that

$$n_0+n_\epsilon\neq n, \quad (68)$$

so that the trial function does not conserve pairs, as has already been noted. For any fixed value of n_0+n_ϵ, the ratio of the trial amplitude for the configuration (n_0+n_ϵ) to the trial amplitude corresponding to $(n_0+q, n_\epsilon-q)$ is

$$\text{BCS ratio of amplitudes}=(h_\epsilon/[1-h_\epsilon])^q, \quad (69)$$

and is correct for any finite positive or negative integer q (in the limit $n\to\infty$). Moreover, the *average* value of n_0+n_ϵ in the trial function is n; therefore, such quantities as the energy, which are insensitive to the exact number of particles, can be accurately computed with the trial function, as we have already discovered in the preceding sections. This ratio is incorrect for very large values of such that $q/n\neq 0$, except in strong-coupling, where the ratio is correctly given as unity for all q. This suggests that the trial function (or the equivalent Bogoliubov transformation) be handled with some care; but because it is correct at the stationary point, this function does asymptotically, and on the average, approach the exact eigenfunction of the problem as $n\to\infty$. Many investigators have already shown that the variational ground-state energy of the reduced Hamiltonian is exact in an asymptotic sense,[5–7] but as the variational theorem does not imply an equivalent accuracy in the wave function, the present analysis has not been in any sense redundant.

APPENDIX

This section is rather mathematical and concerns the intrinsic error in approximating the nonlinear difference equation for the p functions by a quadratic equation such as (23) or (46). Once we establish that the error is of order n^{-1}, we can calculate this error to leading order to see the effect of finite-volume corrections on the theory.

The error analysis proceeds in several steps. We shall show that:

(a) $p(x)$ approaches a limit function as $n\to\infty$ and that this limit function obeys the correct boundary conditions provided the discriminant vanishes at least at one point in the interval (0,1).

(b) The lowest energy is such that the discriminant vanishes only at one point, the "critical point."

(c) The limit function which $p(x)$ approaches is the solution to the quadratic equation, except in the neighborhood of the critical point.

Let the primitive equation be (for simplicity, we depart slightly from the notation in the text)

$$a(y)p(y)p(y+1/n)-2b(y)p(y)+c(y)=0, \quad 0\leq y\leq 1, \quad (A.1)$$

where this equation holds for all $y=\text{integer}/n$ in the interval; and let $g(y)$ be the solution to the quadratic

[5] P. W. Anderson, Phys. Rev. 112, 1900 (1958).
[6] J. Bardeen and G. Rickayzen, Phys. Rev. 118, 936 (1960).
[7] N. N. Bogoliubov, D. N. Zubarev, and Yu. A. Tserkovnikov, Soviet Phys.-JETP 12, 88 (1960).

equation

$$a(y)g^2(y)-2b(y)g(y)+c(y)=0. \tag{A.2}$$

The coefficients have the properties, $c(0)=a(1)=0$, $b(y)\neq 0$. First, we show that if y_0 and y_1 are, respectively, the least and the greatest points at which the discriminant $D(y)$ vanishes,

$$D\equiv b^2-ac=0, \tag{A.3}$$

then $p(y)$ approaches a continuous limit function as $n\rightarrow\infty$, in the regions $(0,y_0)$ and $(y_1,1)$. The proof for the first region is as follows: let

$$g(y+1/n)\equiv g(y)+(1/n)\Omega(y), \tag{A.4}$$

and

$$p(y)\equiv g(y)+(1/n)S(y). \tag{A.5}$$

If we choose the correct solution to (A.2) in this region, namely,

$$g(y)=\frac{b(y)+[D(y)]^{\frac{1}{2}}}{a(y)}, \tag{A.6}$$

it can be directly verified that $S(y)$ is of order unity in the immediate neighborhood of the point $y=0$. We must now show that this function remains finite on the interval $(0,y_0)$. The function $\Omega(y)$ can be obviously calculated and is of order unity if we exclude a neighborhood of the point y_0. It is also of order unity in that neighborhood if

$$\frac{\partial}{\partial y}D\bigg|_{y=y_0}=0 \text{ (as in the ground state).}$$

Now, we calculate $p(y+1/n)$ by two different methods. Using Eqs. (A.4) and (A.5),

$$p(y+1/n)=g(y)+(1/n)[\Omega(y)+S(y+1/n)], \tag{A.7}$$

and using the primitive equation

$$p\left(y+\frac{1}{n}\right)=\frac{2b(y)}{a(y)}-\frac{c(y)}{a(y)p(y)}. \tag{A.8}$$

Eliminating $p(y)$ by Eq. (A.5), we also assume that $S(y)$ is of order unity, and, therefore,

$$p\left(y+\frac{1}{n}\right)=\frac{2b(y)}{a(y)}-\frac{c(y)}{a(y)g(y)[1+S(y)/n\cdot g(y)]}$$

$$=g(y)+\frac{1}{n}\frac{c(y)S(y)}{a(y)g^2(y)}+O\left(\frac{1}{n^2}\right). \tag{A.9}$$

Comparing Eqs. (A.7) and (A.9), we find

$$S(y+1/n)=M(y)S(y)-\Omega'(y), \tag{A.10}$$

where

$$0<M(y)=\frac{c(y)}{a(y)g^2(y)}<1 \quad \text{for} \quad y<y_0, \tag{A.11a}$$

and

$$\Omega'(y)=\Omega(y)+\text{order } 1/n. \tag{A.11b}$$

This difference equation is far simpler than the original equation (A.1). Now, we want to show that $S(y+1/n)$ is finite. An upper limit to S is $\bar{S}$,

$$\bar{S}(y+1/n)=M(y)\bar{S}(y)+\omega, \tag{A.12}$$

where $\omega=Max|\Omega'(y)|$, and is known to be finite. The solution to this equation is

$$\bar{S}(y+1/n)$$
$$=\omega(1+M(y)+M(y)M(y-1/n)$$
$$+M(y)M(y-1/n)M(y-2/n)+\cdots), \tag{A.13}$$

and if $\bar{M}(y)$ is the maximum value of M in $(0,y)$,

$$\bar{S}(y+1/n)<\omega/1-\bar{M}(y), \tag{A.14}$$

and is always finite for $y<y_0$.

A similar proof goes through for the other interval, except that one chooses the other root of the quadratic equation to make p and g agree at $y=1$.

Now, if we use the fact that $b(y)$ decreases monotonically with the energy eigenvalue, then we see that, if the energy is too low, the discriminant can never vanish in $(0,1)$; and both boundary conditions cannot be obeyed by a continuous function [which we have shown $p(y)$ to be]. The lowest value of the energy for which $D(y)=0$ in the interval is such that $y_0=y_1$, i.e., the discriminant vanishes only at one point. Then we have shown that as $n\rightarrow\infty$.

$$p(y)=g(y)=\frac{b(y)+[D(y)]^{\frac{1}{2}}}{a(y)} \quad y<y_0, \tag{A.15}$$

and

$$p(y)=g(y)=\frac{b(y)-[D(y)]^{\frac{1}{2}}}{a(y)} \quad y>y_0. \tag{A.16}$$

Our analysis does not include the immediate neighborhood of y_0. If one wished, he could investigate this critical region (which would involve an analysis similar to that of the WKB approximation at a turning point), and would undoubtedly find that a limit function does not exist here. But as this region can be chosen as small as we please, there is no real point to such an analysis. Nevertheless, we should satisfy ourselves that nothing untoward happens in this region, namely, that our assumption is justified that the lowest energy is that which gives one critical point. As we have mentioned, below this energy there is no solution (to order $1/n$) and, hence, our assumption yields a lower bound; but it agrees asymptotically with the BCS variational solution, which is an upper bound. Hence, it is correct asymptotically, and it must indeed be possible to continue our solution for $p(x)$ through the critical region.

Finally, we should like to calculate the lowest-order correction to the energy. We recall

$$p(y)=\exp\left\{n\left[S(y)-S\left(y-\frac{1}{n}\right)\right]\right\}$$
$$=\exp\left(\frac{\partial S}{\partial y}-\frac{1}{2n}\frac{\partial^2 S}{\partial y^2}+\cdots\right), \quad \text{(A.17)}$$

and

$$p\left(y+\frac{1}{n}\right)=\exp\left\{n\left[S\left(y+\frac{1}{n}\right)-S(y)\right]\right\}$$
$$=\exp\left(\frac{\partial S}{\partial y}+\frac{1}{2n}\frac{\partial^2 S}{\partial y^2}+\cdots\right).$$

Define

$$\exp\partial S/\partial y=\tilde{g}(y)\cong g(y), \quad \text{(A.18)}$$

and to order n^{-2},

$$\exp\left(\frac{1}{2n}\frac{\partial^2 S}{\partial y^2}\right)=\exp\left(\frac{1}{2n}\frac{\partial}{\partial y}\lng(y)\right), \quad \text{(A.19)}$$

where $g(y)$ is given in Eqs. (A.15) and (A.16).

With these substitutions, the primitive equation becomes

$$\left(a\exp\left[\frac{1}{2n}\frac{\partial}{\partial y}\lng(y)\right]\right)\tilde{g}^2(y)-2b\tilde{g}(y)$$
$$+\left(c\exp\left[\frac{1}{2n}\frac{\partial}{\partial y}\lng(y)\right]\right)=0, \quad \text{(A.20)}$$

and if we note that both a and c are proportioned to the interaction v, we see that the interactions off the energy shell have been increased from a strength v to an effective strength

$$\tilde{v}\equiv v\exp\left[\frac{1}{2n}\frac{\partial}{\partial y}\lng(y)\right]\approx v\left[1+\frac{1}{2n}\frac{\partial}{\partial y}\lng(y)\right], \quad \text{(A.21)}$$

which is greater than v because, in the important region near y_0,

$$(d/dy)\lng(y)>0, \quad y\approx y_0. \quad \text{(A.22)}$$

Consequently, the ground-state energy divided by the number of particles actually must increase as the volume is decreased (always at fixed density). For $n\gg 1$, this correction is quite negligible, and it always vanishes in the strong-coupling limit (in which $g(y)=1$, $\partial/\partial y[\lng(y)]=0$). In the weak-coupling limit, or for the one-step model, this correction has the effect of slightly increasing the critical temperature for very small volume crystals.