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On the Phase Transition of a Superconductor

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Abstract. In previous studies of the statistical mechanics of a superconductor, only the 'reduced Hamiltonian' of the BCS theory¹⁾ has been used which ignores the vast majority of the electron-electron interactions. Here, the Hamiltonian is extended by including the other interactions as perturbations up to the second order. As a preliminary step, omitting all but the first-order terms in the Hamiltonian, we derive a rigorous expression for the free energy. Then, to take account of the second-order perturbations, a variational method is used. Particular attention is paid to the behavior of the free energy near the critical temperature. Effects of the lattice periodicity are not examined in this paper.

1. Introduction

The thermal behavior of a superconductor has been theoretically studied by BARDEEN, COOPER, and SCHRIEFFER¹⁾, and by BOGOLIUBOV, ZUBAREV, and TSERKOVNIKOV²⁾. In both studies, the BCS model of a superconductor was used. This model is characterized by a 'reduced Hamiltonian' in which only pairs of electrons with opposite momenta appear coupled. As a technique of calculation, BCS used a variational approximation (minimization of the free energy), whereas BZTs were able to prove that the free energy, as calculated by BCS, is exact in the sense that the volume-proportional part of the free energy is completely and rigorously given by the BCS result. (See, however, our comments at the end of section 2.) Subject to certain conditions, the system has a phase transition of the second order (in the absence of external fields), and the specific heat vs. temperature curve shows a remarkable resemblance to the experimental curves.

The following question must be raised, however. The interaction matrix-elements contained in BCS's reduced Hamiltonian form only a very small (actually, vanishingly small) minority among all matrix-elements appearing in a more realistic Hamiltonian, e.g. in the interactions mediated by virtual phonons. Some people argue that these additional interactions, presumably, will affect the superconductive and the normal state essentially in the same manner and can therefore be

*) Most of this work was carried out while the author was visiting at Bell Telephone Laboratories, Murray Hill, New Jersey.

omitted, in a first approximation, in spite of their large number. Plausible as this argument is, it has not been substantiated.

The main purpose of the present study is to adduce some evidence in favor of this view. If one wants to take account of all (or a majority of) the additional interactions, he can do this only in some approximation. We intend to treat the additional matrix elements in the Hamiltonian by a perturbation theory up to the second order, and the results will show that this is not unreasonable as far as differences between the superconductive and normal phases are concerned. It will turn out that in our approximation the phase transition (if it exists at all) retains very nearly its second order character.

The procedure will be in two steps. We shall first simplify the BZTs method²⁾ and at the same time generalize it to allow the lowest order selfenergy of the electron gas to be included. This problem can still be treated rigorously. Then, adding the second-order perturbations, we have to resort to a variational method.

2. First-Order Hamiltonian

We consider interaction operators involving products of four free-electron absorption and emission operators

$$(a_{k_4 s'}^* a_{k_3 s'}) (a_{k_2 s}^* a_{k_1 s}) \quad (1)$$

($\mathbf{k}_2 - \mathbf{k}_1 = \mathbf{k}_3 - \mathbf{k}_4 \neq 0$). They may refer to phonon-mediated and (screened) Coulomb interactions. For the BCS pair interaction we have $\mathbf{k}_3 = -\mathbf{k}_1$, $\mathbf{k}_4 = -\mathbf{k}_2$, and $s' = -s$. We write it as

$$H_2 = -V^{-1} \sum_{kk'} J_{kk'} (a_{-k-}^* a_{k+}^*) (a_{k'+} a_{-k'-}) \quad (2)$$

where a_{k+} refers to an electron with momentum \mathbf{k} and spin *up*, while a_{-k-} refers to an electron with momentum $-\mathbf{k}$ and spin *down*. $J_{kk'} > 0$ is favorable for 'superconductivity'. In addition, we include in the first-order Hamiltonian the selfenergy term $\mathbf{k}_3 = \mathbf{k}_2$, $\mathbf{k}_4 = \mathbf{k}_1$, $s' = s$:

$$\left. \begin{aligned} H_1 &= V^{-1} \sum_{kk'} I_{kk'} \sum_s a_{ks} a_{ks}^* a_{k's}^* a_{k's} \\ &= -V^{-1} \sum_{kk'} I_{kk'} \sum_s \left(a_{ks}^* a_{ks} - \frac{1}{2} \right) \left(a_{k's}^* a_{k's} - \frac{1}{2} \right) + \\ &\quad + \frac{1}{2} V^{-1} \sum_{kk'} I_{kk'}. \end{aligned} \right\} \quad (3)$$

$I_{kk'}$ (like $J_{kk'}$) is real and symmetric ($I_{kk} = 0$). Note that, regarding Coulomb interactions, we have included in H_1 the single-electron self-energies which should really be subtracted ($a_{ks} a_{ks}^* = 1 - a_{ks}^* a_{ks} \rightarrow -a_{ks}^* a_{ks}$), but an equivalent subtraction can be made in the kinetic energy, provided a high-energy cutoff is conceded.

Now introduce operators

$$A_{ks} = \left(a_{ks}^* a_{ks} - \frac{1}{2} \right) + \xi_{ks} \quad (4)$$

$$B_k = a_{k+} a_{-k-} + \eta_k \quad (5)$$

where ξ_{k+} , ξ_{k-} , and η_k are real functions which are to serve as trial functions. The 'perturbation' will comprise the terms

$$H' = -V^{-1} \sum_{kk'} (I_{kk'} \sum_s A_{ks} A_{k's} + J_{kk'} B_k^* B_{k'}) \quad (6)$$

whereas all the rest defines the unperturbed system:

$$\left. \begin{aligned} H^0 &= H_{kin} + H_1 + H_2 - H' + \text{const.} \\ &= \sum_k [(k^2 - k_0^2)/2m] \sum_s \left(a_{ks}^* a_{ks} - \frac{1}{2} \right) + \\ &+ 2 \sum_k \sum_s \Gamma_{ks} \left(a_{ks}^* a_{ks} - \frac{1}{2} \right) \\ &+ \sum_k \Delta_k (a_{k+} a_{-k-} + a_{-k-}^* a_{k+}^*) + U \end{aligned} \right\} \quad (7)$$

where

$$\Gamma_{ks} = V^{-1} \sum_{k'} I_{kk'} \xi_{k's} \quad (8)$$

$$\Delta_k = V^{-1} \sum_{k'} J_{kk'} \eta_{k'} \quad (9)$$

$$U = V^{-1} \sum_{kk'} (I_{kk'} \sum_s \xi_{ks} \xi_{k's} + J_{kk'} \eta_k \eta_{k'}) \quad (10)$$

In (7) we can replace

$$2 \sum_s \Gamma_{ks} \left(a_{ks}^* a_{ks} - \frac{1}{2} \right) \quad \text{by} \quad (\sum_{s'} \Gamma_{ks'}) \sum_s \left(a_{ks}^* a_{ks} - \frac{1}{2} \right),$$

the difference of these expressions being proportional to $\Gamma_{k+} - \Gamma_{k-}$ which will eventually vanish [see (26)]. The quantity

$$\varepsilon_k = (k^2 - k_0^2)/2m + \sum_{s'} \Gamma_{ks'} \quad (11)$$

will then play the role of a 'renormalized' kinetic energy. The constant k_0 shall be chosen such that ε_k vanishes at the Fermi surface.

H^0 is diagonalized by the quasi-particle transformation

$$\left. \begin{aligned} a_{k+} &= u_k \alpha_{k+} + v_k \alpha_{-k-}^* \\ a_{-k-} &= u_k \alpha_{-k-} - v_k \alpha_{k+}^* \end{aligned} \right\} \quad (12)$$

$$u_k^2 = \frac{1}{2} (1 + \varepsilon_k/E_k) \quad , \quad v_k^2 = \frac{1}{2} (1 - \varepsilon_k/E_k) \quad (13)$$

$$E_k = (\Delta_k^2 + \varepsilon_k^2)^{1/2} (> 0) \quad (14)$$

with the result

$$H^0 = U + \sum_k E_k n_k \quad (15)$$

where

$$n_k = \alpha_{k+}^* \alpha_{k+} + \alpha_{-k-}^* \alpha_{-k-} - 1 \quad (16)$$

n_k has the eigenvalues $-1, 0, 0, +1$. Note that H^0 depends on the trial functions through E_k [(14) with (8), (9), (11)] and U (10).

The free energy, at the temperature $T = 1/\beta$, of the unperturbed system can then be written

$$F^0 = U + F' \quad (17)$$

$$\left. \begin{aligned} F' &= -\beta^{-1} \sum_k \ln \sum_{n_k} \exp(-\beta E_k n_k) \\ &= -2\beta^{-1} \sum_k \ln (2 \cosh \beta E_k/2) \end{aligned} \right\} \quad (18)$$

Note that the thermal average of n_k is

$$(n_k)_{av} = \partial F' / \partial E_k = -\tanh \beta E_k/2 \equiv -\tau_k^0 \quad (19)$$

Also, from (12) and (19)

$$(a_{ks}^* a_{ks})_{av} = \frac{1}{2} (\sum_s a_{ks}^* a_{ks})_{av} = \frac{1}{2} (1 - \tau_k^0 \varepsilon_k / E_k) \quad (20)$$

$$(a_{k+} a_{-k-})_{av} = -\tau_k^0 \Delta_k / 2 E_k \quad (21)$$

Let us now minimize F^0 with regard to the trial functions, using (19) again:

$$\frac{\partial F^0}{\partial \xi_{ks}} = \frac{\partial U}{\partial \xi_{ks}} - \sum_{k'} \tau_{k'}^0 \frac{\partial E_{k'}}{\partial \xi_{ks}} = 0 \quad (22)$$

$$\frac{\partial F^0}{\partial \eta_k} = \frac{\partial U}{\partial \eta_k} - \sum_{k'} \tau_{k'}^0 \frac{\partial E_{k'}}{\partial \eta_k} = 0 \quad (23)$$

With the definitions (10) and (14) [with (8), (9), (11)] this gives

$$2 \xi_{ks} = \tau_k^0 \varepsilon_k / E_k \quad (24)$$

$$2 \eta_k = \tau_k^0 \Delta_k / E_k \quad (25)$$

This result must be compatible with (8) and (9):

$$\Gamma_{ks} = V^{-1} \sum_{k'} I_{kk'} \tau_{k'}^0 \varepsilon_{k'} / 2 E_{k'} \quad (26)$$

$$\Delta_k = V^{-1} \sum_{k'} J_{kk'} \tau_{k'}^0 \Delta_{k'} / 2 E_{k'} \quad (27)$$

Equation (27), in conjunction with (14), is the integral equation, originally derived by BCS¹⁾, which determines the 'energy gap' Δ_k as a function of the temperature [see (19)], and its solution in the 'weak coupling case' is well known. Then, inserting (26) into (11) gives the renormalized kinetic energy; the quantity

$$\frac{1}{\hbar} \frac{d\varepsilon_k}{dk} = \frac{1}{m} + \frac{2}{\hbar} \frac{d\Gamma_{ks}}{dk} = \frac{1}{m^*(k)} \quad (28)$$

defines an effective mass m^* which in turn determines the density of states in the vicinity of the Fermi surface.

It remains to be proved that F^0 , as defined by (17), (18) and minimized as described, gives the volume-proportional part of the free energy F *completely*, or in other words, that this part is not affected by the perturbation H' (6). This is a consequence of the fact that the thermal averages of the quantities A_{ks} and B_k vanish:

$$(A_{ks})_{av} = 0, \quad (B_k)_{av} = 0 \quad (29)$$

Indeed, by inserting (20), (21) and (24), (25) into (4) and (5) this is immediately verified. Then, the proof given by BZTs²⁾ for the case $I_{kk'} = 0$ can be readily generalized. Namely, writing down the m th order correction to the partition function, $Tr \exp(-\beta(H^0 + H'))$, one meets with expressions of the following type

$$V^{-m} Tr [\exp(-\beta H^0) \prod_{i=1 \dots 2m} \{\exp(\beta_i H^0) C_{k_i} \exp(-\beta_i H^0)\}]$$

where each C_{k_i} stands for one of the operators A_{ks} , B_k , B_k^* . (The β_i are integration variables.) It is easily seen that the Trace vanishes, on account of (29), if *one* momentum, say \mathbf{k}_1 , is different from all the other momenta, $\mathbf{k}_2 \dots \mathbf{k}_{2m}$, occurring in the product. In order to obtain a non-vanishing term, one has to have m pairs of equal \mathbf{k}_i 's so that, after multiplying with the appropriate factors $I_{kk'}$, $J_{kk'}$ and then summing over $\mathbf{k}_1 \dots \mathbf{k}_{2m}$, the sum runs only over m independent \mathbf{k} -vectors. If one then divides by $Tr \exp(-\beta H^0)$ and finally writes the sums as integrals (for $V \rightarrow \infty$), the factors V^{-m} and V^m cancel out and the result becomes volume-independent. Hence, up to any finite order ($m \ll N = \text{total number of particles}$):

$$\lim_{V \rightarrow \infty} \frac{Tr \exp(-\beta(H^0 + H'))}{Tr \exp(-\beta H^0)} = \text{finite},$$

and

$$\lim_{V \rightarrow \infty} V^{-1} (F - F^0) = 0, \quad q. e. d.$$

The discussion of F^0 will be postponed, but some general comments should be made at this point. While ξ_{ks} (24) and Γ_{ks} (26) have well-

defined signs, a simultaneous change of sign in η_k and Δ_k is compatible with (25) and (27); but these two solutions are physically equivalent, and we are free to choose $\Delta_k \geq 0$. As is well known, there is always the formal solution $\eta_k = 0$, $\Delta_k = 0$; this is the so-called trivial solution. It should be pointed out, however, that it is an unacceptable solution if a non-trivial one, giving a lower free energy, exists. This follows already from the mere fact that the free energy is defined unambiguously in terms of the energy eigenvalues of the system. But it is also easy to see why the trivial solution goes wrong. Indeed, it is clear from (7) that, for $\Delta_k = 0$, H^0 reduces to the *kinetic* energy, and *all* of the interaction H_2 is then treated as a perturbation, i.e. by an expansion in powers of a coupling parameter J . This is certainly wrong for a condensed state in which some physical quantities like the energy gap behave non-analytically as J goes to zero. By the same token, the non-trivial 'rigorous' solution could be wrong too, namely, if some collective effects are hidden in H' and remain unnoticed owing to the perturbation expansion. Quite generally, it should be realized that the type of rigorous solution one obtains by the BZTs method is heavily prejudiced by the type of terms which one includes in the 'unperturbed' Hamiltonian, a choice based primarily on physical intuition.

3. Second-Order Approximation

We now want to take into account, at least approximately, the vast majority of the interaction matrix-elements (1), namely those which are not contained in (2) and (3); we call them H'' . None of them has a diagonal part in our quasi-particle representation ($\alpha_{ks}^* \alpha_{ks}$ diagonal), and it is convenient right away to diagonalize $H^0 + H''$:

$$S^{-1} (H^0 + H'') S = H^0 + h$$

(h diagonal, $\sim H''^2$). There are only three kinds of terms in the free-particle representation which can contribute to h ; apart from numerical factors and energy denominators, they involve the operators

$$O_1 = (a_\lambda^* a_\lambda) (a_\mu^* a_\mu) (a_\nu^* a_\nu) (a_\varrho^* a_\varrho) \quad (30)$$

$$O_2 = (a_\lambda^* a_\lambda) (a_\mu^* a_\mu) (a_{-k-}^* a_{k+}^*) (a_{k'+} a_{-k'-}) \quad (31)$$

$$O_3 = (a_{-k-}^* a_{k+}^*) (a_{-k'-}^* a_{k'+}^*) (a_{k''+} a_{-k''-}) (a_{k''' +} a_{-k''' -}) \quad (32)$$

(Greek indices stand for momentum and spin). For instance, O_2 can arise from a linear combination of two terms like

$$a_\lambda^* a_\mu a_{-k'-}^* a_{k+} \quad \text{and} \quad a_\lambda^* a_\mu a_{-k-}^* a_{k'+}$$

occurring in H'' , by multiplying them crosswise with their conjugates. Now, O_2 actually simulates a BCS pair coupling of the type $H_2(2)$. When treated as perturbations, the matrix-elements O_2 are 'dangerous' in the sense that they cause divergencies (for $\Delta_k \rightarrow 0$; see section 4). They are more adequately accounted for by including them in H_2 with $a_\lambda^* a_\lambda$ and $a_\mu^* a_\mu$ replaced by their thermal averages [see (20)]. This amounts to a *renormalization* of the coefficients $J_{kk'}$ in (2). As to the terms $O_3(32)$, their contribution to the free energy is so small that they are meaningless unless one goes to higher approximations in H'' . Therefore, after the renormalization of $J_{kk'}$, h can be entirely identified with the terms of the type O_1 (30). [Of course, O_1 carries a factor V^{-2} and, because only three of the four momenta are independent, h_{av} will be proportional to V .]

The corrected free energy will be written

$$F = F^0 + f, \quad (33)$$

with f given by

$$Tr \exp [\beta (F^0 - H^0) + \beta (f - h)] = 0,$$

or in lowest approximation:

$$f = Tr (h \exp \beta (F^0 - H^0)) \equiv h_{av} \quad (34)$$

H^0 and F^0 are again given by (15) and (17), (18), but in order to make optimum use of the approximation (34), we now want to minimize F instead of F^0 (3). Note that h_{av} [see (30) and (20)] depends on the trial functions only through E_k . Setting

$$\partial F / \partial \xi_{ks} = 0, \quad \partial F / \partial \eta_k = 0,$$

one sees immediately that in all Equations (22)–(27), τ_k^0 must be replaced by

$$\tau_k = - \partial (F' + f) / \partial E_k = \tau_k^0 - \partial h_{av} / \partial E_k. \quad (35)$$

Thus

$$2 \xi_{ks} = \tau_k \varepsilon_k / E_k, \quad 2 \eta_k = \tau_k \Delta_k / E_k, \quad (36)$$

$$\left. \begin{aligned} \Gamma_{ks} &= \Gamma_k = V^{-1} \sum_{k'} I_{kk'} \tau_{k'} \varepsilon_{k'} / 2 E_{k'}, \\ \Delta_k &= V^{-1} \sum_{k'} J_{kk'} \tau_{k'} \Delta_{k'} / 2 E_{k'}. \end{aligned} \right\} \quad (37)$$

Regarding the perturbation H' (6), we observe that (29) is now no longer rigorously true. However, $(A_{ks})_{av}$ and $(B_k)_{av}$ are still small as h , and hence the contribution of H' to the free energy is small as h^2 (or even less) and must be neglected here.

Our approximation can only be meaningful if we find τ_k close to τ_k^0 . To examine whether this is so, let us look at the limiting case of low temperatures.

For $T = 0$, of course, only the ground state (all $\alpha_{ks}^* \alpha_{ks} = 0$) contributes:

$$\tau_k (T = 0) = 1 - \partial h_0 / \partial E_k \quad (38)$$

From the unperturbed ground-state or quasi-vacuum, only emission of quasi-particles is possible, hence the energy denominators in h_0 are all negative $[-(E_\lambda + E_\mu + E_\nu + E_\rho)]$, and one sees easily that the differentiation of these denominators gives the predominant contributions to $\partial h_0 / \partial E_k$. Their sign is such that $\tau_k < 1$. Equation (37) then tells us that the perturbation h_0 has the effect of replacing the pair coupling constant J ($= \overline{J_{kk'}}$) by a smaller one

$$J_{eff} = J \tau = \overline{J_{kk'} \tau_{k'}}, \quad \tau < 1 \quad (39)$$

(averages taken over an energy shell $|\varepsilon_k| < \omega$, where $\omega \gg \overline{\Delta}_k$ in the 'weak coupling case'). The usual analysis of Equation (37) then gives

$$\Delta = \overline{\Delta}_k \approx \omega \exp(-1/\gamma J \tau) \quad (40)$$

if $J \tau > 0$; otherwise the trivial solution, $\Delta_k = 0$, takes over. While $\tau < 1$ has the effect of making the 'gap' Δ smaller, it should be remembered that we are now dealing with a renormalized J and a corrected density of states γ [see (28)]. The energy difference between the superconductive and normal ground-states is given by

$$(U - \sum_k E_k + h_0) - (U - \sum_k E_k + h_0)_{\Delta_k=0} \quad (41)$$

The perturbation h_0 obviously depresses the normal state more effectively than the superconductive one.

In making order of magnitude estimates we have taken the H'' matrix-elements of the general order J/V (like H_2). In the weak coupling case ($\Delta \ll \omega$) one finds τ close to unity, namely

$$1 - \tau \sim (\gamma J)^2 \sim (\ln \omega / \Delta)^{-2}, \quad (42)$$

and also in (41), the term $h_0 - (h_0)_{\Delta_k=0}$ is by a factor $\sim (\gamma J)^2$ smaller than the other (unperturbed) terms. So far, the perturbation treatment of H'' is apparently justified. It is, of course, conceivable that H'' gives rise to collective effects which our method fails to detect, owing to the perturbational expansion. But in such a situation the whole basic pair-coupling idea of BCS would be in doubt.

Going to high temperatures, $T \rightarrow \infty$, we claim that τ_k , like τ_k^0 (19), vanishes:

$$\tau_k(T = \infty) = 0. \quad (43)$$

Indeed, h_{av} tends to zero once T has become much larger than all energy denominators occurring in h . [Rewriting h_{av} as an expression symmetrical in 'initial' and 'intermediate' states, see Equation (63) in the *Appendix*, shows this most easily.] (43) is even true to *all* orders in H'' , and presumably also to all orders in $H' + H''$. Anyway, within our approximation, τ_k must be taken as zero for $T \rightarrow \infty$, with the implication that Equation (37), at sufficiently high temperatures, admits only the trivial solution $\Delta_k = 0$.

4. The Phase Transition

We will then assume that a non-trivial solution of (37) exists only at temperatures below a certain critical temperature T_c . For $h = 0$, it is well known that Δ ($= \overline{\Delta_k}$), as determined by Equation (27) with (19), goes to zero at T_c as $(T_c - T)^{1/2}$. We want to show that this remains true for the perturbed system.

$$\text{Let} \quad \Delta_k = \Delta \lambda_k \quad (44)$$

where λ_k approaches a finite value (of order 1) as $\Delta \rightarrow 0$. Now (37) can be written

$$\frac{1}{2} V^{-1} \sum_k (J_{k'k} \lambda_k / \lambda_{k'}) \tau_k(E_k, T) / E_k = 1 \quad (45)$$

and, with $E_k = (\Delta^2 \lambda_k^2 + \varepsilon_k^2)^{1/2}$, this will determine Δ as a function of T . If this function goes to zero continuously as $T \rightarrow T_c$, this value T_c defines the critical temperature:

$$\frac{1}{2} V^{-1} \sum_k (J_{k'k} \lambda_k / \lambda_{k'}) \tau_k(|\varepsilon_k|, T_c) / |\varepsilon_k| = 1. \quad (46)$$

Both in (45) and (46), we transform the \mathbf{k} -sums into integrals over ε_k and then subtract (46) from (45). Since $T \approx T_c$, the factors $J_{k'k} \lambda_k / \lambda_{k'}$ in the two integrands can be taken as practically the same, and this also applies to the respective densities of states, except possibly for terms small as $[\Delta(T)]^2$. Then, the essential factor in the integrand can be expanded:

$$\begin{aligned} \tau_k(E_k, T) / E_k - \tau_k(|\varepsilon_k|, T_c) / |\varepsilon_k| &\approx \\ [(E_k^2 - \varepsilon_k^2) \partial / \partial \varepsilon_k^2 + (T - T_c) \partial / \partial T_c] \tau_k(|\varepsilon_k|, T_c) / |\varepsilon_k| \end{aligned}$$

where the two terms are proportional to Δ^2 and to $T - T_c$, respectively. So, indeed

$$\Delta^2(T) = \Theta (T_c - T) \quad \text{for} \quad T \approx T_c, \quad (47)$$

with $\Theta > 0$ [$\Delta(T)$ real for $T < T_c$].

One might object to this argument that in the region $|\varepsilon_k| \gtrsim \Delta_k$ the expansion of the integrand in powers of Δ^2 is incorrect and that the integral actually may contain terms which do not vanish as strongly as Δ^2 . We shall prove in the *Appendix*, however, that for $E_k \ll T$ [this is satisfied when $E_k \lesssim \Delta(T) \rightarrow 0$] the function $\tau_k(E_k, T)/E_k$ can be expanded into non-negative *even* powers of E_k . Then, (47) is obviously correct. It should be pointed out that the terms of type O_2 (31) which we eliminated in section 3 by renormalizing $J_{kk'}$ would have caused even an *infinity* to appear for $\Delta \rightarrow 0$. In this sense, they are 'dangerous matrix-elements' which we may not allow to occur in the perturbation \hbar .

It remains to discuss the free energy at temperatures close to T_c . Recall Equations (33) and (17):

$$F = U + F' + f \quad (48)$$

U , as given by (10), is conveniently split into two terms [see (9) and (36)]

$$\left. \begin{aligned} U &= U_1 + U_2 \\ U_1 &= \frac{1}{2} V^{-1} \sum_{kk'} I_{kk'} (\tau_k \varepsilon_k / E_k) (\tau_{k'} \varepsilon_{k'} / E_{k'}) \\ U_2 &= \sum_k \Delta_k \eta_k = \frac{1}{2} \sum_k \Delta_k^2 \tau_k / E_k \end{aligned} \right\} \quad (49)$$

Let us define a function ϕ of T and Δ [see (44)] which becomes F if T and Δ are linked by Equations (37) or (45) but, *if this equation is disregarded*, has T and Δ as two *independent* variables:

$$\phi(T, \Delta(T)) = F(T), \quad (50)$$

$$\phi(T, \Delta) = U + F' + f. \quad (51)$$

Here, each term is meant to depend on T only through the Boltzmann factors [see (18), (34), (35)], and on Δ through Δ_k (44), as specified by all preceding equations *except* (45). Then, the validity of (50) is obvious. On the other hand substituting into (51) the 'trivial solution' $\Delta = 0$, one obtains the free energy of the 'normal state' (which is a fictitious state for $T < T_c$):

$$\phi(T, 0) = F_n(T). \quad (52)$$

However, since we want to compare (50) and (52) for the same system, i.e. for a fixed total number of electrons, we have to admit an explicit Δ -dependence of $k_0^2/2m$ in ε_k (11):

$$k_0^2/2m = \mu(T, \Delta), \quad (53)$$

such that $\mu(T, \Delta(T))$ and $\mu(T, 0)$ are the correct chemical potentials of the two states:

$$\varepsilon_k = \hbar^2/2m - \mu(T, \Delta) + V^{-1} \sum_{k'} I_{kk'} (\tau_{k'} \varepsilon_{k'}/E_{k'}). \quad (54)$$

For other values of Δ , ϕ has no specific physical meaning and, to be sure, it is *not* the quantity F which we have minimized (as a functional of ξ_{ks}, η_k). Nevertheless, for small values of Δ , ϕ can be expanded into powers of Δ , and in particular, for temperatures just below T_c where $\Delta(T)$ is small, we obtain from (50) and (52):

$$F(T) - F_n(T) = \sum_{j>0} \frac{1}{j!} \left(\frac{\partial^j \phi(\tau, \Delta)}{\partial \Delta^j} \right)_{\Delta=0} [\Delta(T)]^j \quad (55)$$

while $F(T) = F_n(T)$ for $T \geq T_c$.

Now examine the first derivative

$$\partial \phi(T, \Delta)/\partial \Delta = \sum_k \lambda_k \partial \phi / \partial \Delta_k. \quad (56)$$

In application to functions of the $E_{k'}$ alone, like $(F' + f)$ or $\tau_k/E_{k'}$, we have*)

$$\partial / \partial \Delta_k = \sum_{k'} E_{k'}^{-1} (\Delta_k \delta_{kk'} + \varepsilon_{k'} \partial \varepsilon_{k'} / \partial \Delta_k) \partial / \partial E_{k'}. \quad (57)$$

If one then writes down $\partial(F' + f)/\partial \Delta_k$ using (35), several terms are seen to be cancelled by corresponding terms coming from $\partial U_1 / \partial \Delta_k$ and $\partial U_2 / \partial \Delta_k$ in (56). But two terms remain:

$$\left. \begin{aligned} \partial \phi(T, \Delta) / \partial \Delta &= X_1 + X_2 \\ X_1 &= (\sum_k \tau_k \varepsilon_k / E_k) \partial \mu(T, \Delta) / \partial \Delta \\ X_2 &= \frac{1}{2} \sum_k \Delta_k^2 \partial (\tau_k / E_k) / \partial \Delta \end{aligned} \right\} \quad (58)$$

With (44) and (57), one sees easily that X_2 is proportional to Δ^3 and therefore leads to a term $j = 4$ in the expansion (55). Indeed, the pre-dominant term in X_2 is

$$X_2 = \Delta^3 \frac{1}{2} \sum_k \lambda_k^4 E_k^{-1} \partial (\tau_k / E_k) / \partial E_k + \cdots (< 0) \quad (59)$$

The integral appearing here converges for $\Delta \rightarrow 0$ against a finite value, including the contribution of the region $|\varepsilon_k| \gtrsim \Delta_k$, by the same argument as was invoked above (*Appendix*). Thus, if the term X_1 in (58) could be ignored, $F(T) - F_n(T)$ would be proportional to $[\Delta(T)]^4$ or $(T_c - T)^2$, for T approaching T_c from below, and this would characterize the phase transition as one of the second order ($\partial F / \partial T$ continuous, $\partial^2 F / \partial T^2$ discontinuous at T_c).

*) Note that, at this point a \hbar -sum is not yet considered as an integral over ε_k . This makes it easier to take account of the Δ -dependence of the density of states. (Clarifying comments by Dr. Y. NAMBU are gratefully acknowledged.)

However, the term X_1 , which originates in the rigorous treatment of the selfenergy H_1 , may give rise to a term $j = 2$ in (55), thereby changing the order of the transition from second to *first*. Moreover, the \mathbf{k} -sum in X_1 (58) is cut-off dependent, and we have to invoke a new physical argument, outside the scope of our approximation, to specify the cut-off. Here we want to exploit the observation made by BARDEEN⁴) that the coherent superposition of electron wave functions which is implied in the quasi-particle transformation (12) and in all subsequent equations based on (12), is meaningful only if the lifetime of the corresponding excited electron states $\pm k$ is long enough to allow the particles to travel through the coherence distance. Since the decay rate (imaginary part of E_k) increases with $|\varepsilon_k|$, there will be a limited 'zone of coherence', say $k_1 < k < k_2$, in the vicinity of the Fermi surface ($k = k_F$), where the coherent electron pairing takes place as described, whereas outside of this zone our approximation is insufficient, and the best we can do is to set $\Delta_k = 0$ there. This provides the necessary cut-off prescription, e.g. in (57) and (58). Then, we have approximately, for T approaching T_c from below:

$$F(T) - F_n(T) = \sum_{(k_1 < k < k_2)} (\tau_k \varepsilon_k / E_k)_{\Delta=0} [\mu(T, \Delta(T)) - \mu(T, 0)] + \dots \quad (60)$$

This may contain a term *linear* in $T_c - T$ which then determines the 'heat of condensation', W .

The difficulty in computing W stems from the fact that it is the *dissymmetry* in the properties of excitations with $k > k_F$ and $k < k_F$ which governs the quantities in Equation (60), indeed not only the \mathbf{k} -sum appearing explicitly but also similar sums occurring in μ [see (54)]. One would have to know the *difference* in the lifetimes of 'electrons' and 'holes' at about equal distance from the Fermi surface! On the other hand, just because only the dissymmetries contribute, we can expect W to be small (compared with the area under the specific-heat curve) if the zone of coherence is sufficiently narrow ($k_2 - k_1 \ll k_F$). Nevertheless, there seems to be no obvious reason for W to vanish *exactly* (even for the 'unperturbed' system: $H'' = 0$). We must therefore anticipate that there exists a non-vanishing latent heat, though it may be too small to be easily measurable.

Appendix

Labeling the eigenstates of H^0 by a suffix N , we have

$$h_N = \sum_{N'} |(N' | H'' | N)|^2 (H_N^0 - H_{N'}^0)^{-1}. \quad (61)$$

Each virtual process $N \rightarrow N'$ consists of the emission or absorption of 4 quasi-particles. In view of (35), we are interested in those terms of h where one of those 4 quasi-particles is either $k+$ or $k-$. This part of h will be called h_k ; it is volume-independent ($V \rightarrow \infty$). Furthermore, in

each term of h_k , we are interested only in those factors which depend on E_k . Remembering that only terms of the type O_1 (30) were to be retained in h , such factors all originate in $a_{ks}^* a_{ks}$ and the energy denominators. From (12) it follows that the E_k dependence of an individual term in (61) is given by

$$u_k^2 \alpha_{ks}^* \alpha_{ks} (E_k - Q)^{-1} + v_k^2 \alpha_{-k-s} \alpha_{-k-s}^* (-E_k - Q)^{-1}$$

where Q is the energy change of the other 3 quasi-particles participating in the special virtual process. Adding the $k+$ and $-k-$ contributions and inserting (13) and (16), one obtains

$$(E_k^2 - Q^2)^{-1} [(Q + \varepsilon_k) + (E_k + Q\varepsilon_k/E_k) n_k]. \quad (62)$$

In the corresponding term in the free energy (34), the thermal average (19) is to be taken. Then, for $E_k \ll T$ and $Q \gg E_k$, the result can be expanded into non-negative *even* powers of E_k .

As to the contributions $Q \lesssim E_k$, we avoid the singularity in (62) by symmetrizing $(h_k)_{av}$ in initial and intermediate states:

$$\sum_N h_N \exp(-\beta H_N^0) = \frac{1}{2} \sum_{NN'} \frac{|(N' | H'' | N)|^2}{H_N^0 - H_{N'}^0} [\exp(-\beta H_N^0) - \exp(-\beta H_{N'}^0)] \quad (63)$$

In other words, whereas in (62) we have already summed over N' for each N , we here go back and first symmetrize in every pair of states N, N' . Now, in the terms with $Q \lesssim E_k \ll T$, (63) can be expanded in powers of both βE_k and βQ , and the denominators can be cancelled out. Then one sees easily that the *odd* powers of E_k appear always multiplied either with $(n_k n'_k)$ which vanishes identically, or with odd powers of n_k or n'_k which vanish in the average (to be taken with $\beta = 0$).

This proves that, whatever the value of Q , all terms contributing to $f_k = (h_k)_{av}$ can be expanded into non-negative *even* powers of E_k . Then, however, the same is true for the functions

$$\tau_k/E_k = -E_k^{-1} \partial(F' + f)/\partial E_k \quad \text{and} \quad E_k^{-1} \partial(\tau_k/E_k)/\partial E_k.$$

This justifies the statements made in section 4, in the discussion of the Equations (47) and (59).

References

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- 4) J. BARDEEN, Cambridge Conference on Superconductivity, June-July 1959 (unpublished).