Superconductivity with Pairs in a Relative p Wave*†

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(Received 6 March 1963)

In previous treatments of superconducting systems with attractive interactions acting in odd-angular-momentum partial waves, the correlated electron pairs were formed in only two components of a spin triplet. This oversight is corrected here by a more general variational treatment, allowing all three components. In the case of a p-wave interaction, the present state is proved to give the absolute minimum of the free energy. Its rotational degeneracy is discussed. The energy spectrum is found to be isotropic (provided the normal phase is also) with the usual gap, and so to be completely equivalent thermodynamically to the BCS state. The charge-density autocorrelation is also isotropic, and the charge-current correlation vanishes. The state exhibits the conventional Meissner effect, and cannot be experimentally distinguished from the BCS state by means of electromagnetic or tunneling measurements, acoustic attenuation, or nuclear magnetic resonance (NMR) relaxation times. The paramagnetic spin susceptibility decreases with temperature from its value in the normal phase to a limiting ratio of $\frac{2}{3}$, in good agreement with results deduced from Knight shift measurements on mercury and tin, and in contrast to the BCS prediction. However, the addition of impurities is found to reduce the critical temperature sharply (again in contrast to the BCS case). Thus, the experimental observation of the p-wave pair state is expected to be difficult, and the agreement with Knight shift data is probably fortuitous. Finally, it is suggested that a similar effect in He^3 might explain why the predicted superfluid phase has not been observed.

I. INTRODUCTION

A GREAT measure of success has been achieved by the Bardeen-Cooper-Schrieffer (BSC) theory of superconductivity[1] in comprehending and correlating a large and varied body of experimental observations on superconductors. Agreement between theory and experiment[2] is in many instances so striking as to establish the validity, virtually beyond doubt, of the fundamental BCS hypothesis of correlated electron pair formation in the superconducting state. Nevertheless, certain isolated puzzles do remain,[3] one in particular which has attracted a good deal of theoretical attention being the observed Knight shifts in nuclear magnetic resonance (NMR) experiments on mercury,[4] tin,[5] and vanadium.[6] These resonance frequency shifts from free atom to metal are conventionally interpreted as reflecting the presence of an additional magnetic field at the nuclei due to a nonvanishing spin magnetization of the conduction electrons in the external field. Since according to the BCS theory pairs are in spin singlets (electron spins opposed), and since a finite energy is required to break the correlation, the theory predicts[7] that a weak uniform magnetic field cannot polarize the superconducting electron spins and, hence, that at zero temperature no shift should occur.

Observations to the contrary have stimulated a number of authors to propose possible explanations.[8,9] Although these focus primarily on the small size and impure composition of the samples,[8] among the suggestions advanced has been that the electrons might pair in a spin triplet, thereby remaining able to interact with a magnetic field and exhibiting a finite spin susceptibility even in a bulk superconductor.[9] Because the over-all wave function of a Fermion system must be antisymmetric under the interchange of any two particles, a pair of total spin $S=1$ (the symmetric spin functions) must necessarily have odd spatial parity, and hence, odd orbital angular momentum. Triplet pairing thus requires the hypothesis of an interparticle interaction attractive in at least one odd partial wave, such as the p wave.

Such interactions have already been studied in considerable detail,[10] although primarily because of a close mathematical similarity to the low-temperature super-

* Work supported in part by the U. S. Air Force Office of Scientific Research and the U. S. Atomic Energy Commission.
† Initiated while both authors were at the University of California, San Diego, La Jolla, California.
[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957); N. N. Bogoliubov, Zh. Eksperim. i Teor. Fiz. **34**, 58 (1958) [translation: Soviet Phys.—JETP **7**, 41 (1958)]; J. G. Valatin, Nuovo Cimento **7**, 843 (1958).
[2] Reviewed by J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III.
[3] J. Bardeen, IBM J. Research Develop. **6**, 3 (1962).
[4] F. Reif, Phys. Rev. **106**, 208 (1957).
[5] G. M. Androes and W. D. Knight, Phys. Rev. **121**, 779 (1961).
[6] R. J. Noer and W. D. Knight, Bull. Am. Phys. Soc. **6**, 122 (1961).
[7] K. Yosida, Phys. Rev. **110**, 769 (1958).
[8] V. Heine and A. B. Pippard, Phil. Mag. **3**, 1046 (1958); R. A. Ferrell, Phys. Rev. Letters **3**, 262 (1959); P. C. Martin and L. P. Kadanoff, *ibid.* **3**, 322 (1959); J. R. Schrieffer, *ibid.* **3**, 323 (1959); P. W. Anderson, *ibid.* **3**, 325 (1959); A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 480 (1960) [translation: Soviet Phys.—JETP **12**, 337 (1961)]; L. N. Cooper, Phys. Rev. Letters **8**, 367 (1962).
[9] For a review, see H. Suhl in *Low Temperature Physics*, edited by C. DeWitt, B. Dreyfus, and P. G. de Gennes (Gordon and Breach, New York, 1962).
[10] D. J. Thouless, Ann. Phys. (N. Y.) **10**, 553 (1960); P. W. Anderson and P. Morel, Phys. Rev. **123**, 1911 (1961).

fluid phase proposed for liquid He^3.[11] In particular, Anderson and Morel[10] (AM) have predicted for a state with p-wave attraction, many peculiar features, such as energy spectrum with anisotropic gap vanishing in certain directions, nonexponential low temperature specific heat, and surface currents, which taken together make this state physically implausible and in sharp conflict both with the BCS results and with experiment.

The present paper re-examines this question and demonstrates that the previous treatments[10] of attractive, odd-parity interactions in fact contain uniformly the same oversight. The method used to find the appropriate superconducting state was a coupling of single-electron states of parallel spin components,[12] thus allowing pairs with spin components $S_z=\pm 1$ only; it did not consider the symmetrized combination of antiparallel spins which comprises the $S_z=0$ component of the expected spin triplet. Here we propose (Sec. II) a variational state incorporating components $S_z=0$ as well as $S_z=\pm 1$; in the special case of a p-wave interaction, we select one of the solutions corresponding to stationary points of the free energy, and show that it not only has lower ground-state energy than the equal spin pairing (ESP), but more generally gives the absolute free energy minimum. The ESP must, therefore, describe some excited state.

The properties of the state with p-wave pairing are found (Sec. III and IV) to be very close in most respects to those of the BCS state with s-wave pairs, in contrast to the ESP. Assuming an isotropic normal phase, the superconducting spectrum is also completely isotropic and displays the usual gap; the state is thus thermodynamically identical to BCS. The charge-density autocorrelation function is isotropic, and the charge density–current density correlation vanishes. The spin susceptibility, on the other hand, is always finite, with a superconducting-to-normal ratio decreasing monotonically with temperature to the limiting value $\chi_s/\chi_n=\frac{2}{3}$, in good (if possibly fortuitous) agreement with the Hg and Sn data.[4,5] In such other key measurements as the acoustic attenuation and NMR relaxation, as well as the complete range of electromagnetic experiments from the Meissner effect to infrared absorption, the p-wave state is found to predict results essentially the same as the BCS state.

The effect of adding impurities to the system differs, however, from BCS, although both the theoretical and experimental situations are not entirely clear-cut. In the conclusion (Sec. V) we discuss to what extent the p-wave pair state is physically realizable in the presence of impurities, and show that it is unlikely to be a valid explanation of the existing anomalous Knight-shift phenomena.

An Appendix specifies a criterion for the existence of a ground state mixing both s- and p-wave pairs, and shows this to be unlikely for most reasonable potentials.

II. FREE-ENERGY MINIMIZATION

1. General Formalism

From the pair interaction potential

$$\mathcal{U}=\tfrac{1}{2}\sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} V_{\mathbf{k}\mathbf{k}'}a_{-\mathbf{k}\sigma'}{}^{\dagger}a_{\mathbf{k}\sigma}{}^{\dagger}a_{\mathbf{k}'\sigma}a_{-\mathbf{k}'\sigma'} \tag{1}$$

(where $a_{\mathbf{k}\sigma}{}^{\dagger}$ creates a particle of momentum $\mathbf{k}$ and third spin component $\frac{1}{2}\sigma$), the ESP retains only the terms with $\sigma=\sigma'$, which, unlike $\mathcal{U}$, are not invariant to a rotation of the spin space. It is, therefore, not surprising that this theory predicts a strong anisotropy in the ground state and the single quasiparticle excitations. In order to treat symmetrically all three components of the spin triplet which are included in the full interaction $\mathcal{U}$ of Eq. (1), we must couple electron states of opposite momenta and both same and opposite spins.

We, therefore, perform a canonical transformation[13] (conserving the momentum but not the z component of the spin)

$$a_{\mathbf{k}\sigma}=\sum_{\sigma'}(u_{\sigma\sigma'}{}^{\mathbf{k}}\alpha_{\mathbf{k}\sigma'}+v_{\sigma\sigma'}{}^{\mathbf{k}}\alpha_{-\mathbf{k}\sigma'}{}^{\dagger}), \tag{2}$$

where $\alpha^{\dagger}$ is a quasiparticle creation operator. This transformation mixes four states, and thus is more general than the usual one.[14] It proves convenient to adopt a four-component matrix notation[15]

$$a^{\mathbf{k}}\equiv\begin{pmatrix} a_{\mathbf{k}\uparrow} \\ a_{\mathbf{k}\downarrow} \\ a_{-\mathbf{k}\uparrow}{}^{\dagger} \\ a_{-\mathbf{k}\downarrow}{}^{\dagger}\end{pmatrix}, \quad \alpha^{\mathbf{k}}\equiv\begin{pmatrix} \alpha_{\mathbf{k}+} \\ \alpha_{\mathbf{k}-} \\ \alpha_{-\mathbf{k}+}{}^{\dagger} \\ \alpha_{-\mathbf{k}-}{}^{\dagger}\end{pmatrix}, \tag{3}$$

and to write the transformation (2) in the abbreviated form

$$a^{\mathbf{k}}=\begin{pmatrix} u^{\mathbf{k}} & v^{\mathbf{k}} \\ v^{-\mathbf{k}*} & u^{-\mathbf{k}*}\end{pmatrix}\equiv U^{\mathbf{k}}\alpha^{\mathbf{k}}, \tag{4}$$

where $u^{\mathbf{k}}$, $v^{\mathbf{k}}$ are 2×2 matrices and $U^{\mathbf{k}}$ is 4×4.[15] The condition that the transformation be canonical (that both a and α obey Fermion commutation relations) is then simply

$$U^{\mathbf{k}}U^{\mathbf{k}\dagger}=1, \tag{5}$$

or that $U^{\mathbf{k}}$ is unitary. From definition (4) it can be seen that $U^{\mathbf{k}}$ and $U^{-\mathbf{k}}$ are not independent; the relation between them is

$$U^{\mathbf{k}}=\begin{pmatrix} 0 & 1 \\ 1 & 0\end{pmatrix}U^{-\mathbf{k}*}\begin{pmatrix} 0 & 1 \\ 1 & 0\end{pmatrix}. \tag{6}$$

[11] K. A. Brueckner, T. Soda, P. W. Anderson, and P. Morel, Phys. Rev. **118**, 1442 (1960); V. J. Emery and A. M. Sessler, *ibid.* **119**, 43 (1960).

[12] For brevity, we shall refer to this state as the ESP (equal spin pairing) solution.

[13] N. N. Bogoliubov, Doklady Akad. Nauk SSSR **119**, 244 (1958) [translation: Soviet Phys.—Doklady **3**, 292 (1958)]; J. G. Valatin, Phys. Rev. **122**, 1012 (1961).

[14] But see remark at the end of Sec. III.

[15] We adopt the convention that quantities with superscript $\mathbf{k}$ are matrices in either 2- or 4-dimensional spin space; tr will denote trace in these spaces only.

We next select for the system a trial density matrix of independent quasiparticles.

$$\rho \propto \exp[-\beta \sum_{\mathbf{k}\sigma} E_{\mathbf{k}\sigma}\alpha_{\mathbf{k}\sigma}^{\dagger}\alpha_{\mathbf{k}\sigma}], \quad \mathrm{Tr}\rho = 1, \tag{7}$$

and choose the parameters $U^{\mathbf{k}}$ and $E_{\mathbf{k}\sigma}$ so as to minimize the free energy appropriate to ρ. The variational calculation is considerably simplified, however, by making a different choice of independent variables. For this we define the 4×4 matrix

$$\langle a^{\mathbf{k}} a^{\mathbf{k}\dagger}\rangle \equiv \mathrm{Tr}\{\rho a^{\mathbf{k}} a^{\mathbf{k}\dagger}\} \equiv \frac{1}{2}\begin{pmatrix} 1+w^{\mathbf{k}} & x^{\mathbf{k}} \\ -x^{-\mathbf{k}*} & 1-w^{-\mathbf{k}*} \end{pmatrix} \equiv \tfrac{1}{2}(1+W^{\mathbf{k}}), \tag{8}$$

or in detail,

$$\begin{aligned} \langle a_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma'}^{\dagger}\rangle &= \tfrac{1}{2}(\delta_{\sigma\sigma'} + w_{\sigma\sigma'}^{\mathbf{k}}), \\ \langle a_{\mathbf{k}\sigma} a_{-\mathbf{k}\sigma'}\rangle &= \tfrac{1}{2} x_{\sigma\sigma'}^{\mathbf{k}}. \end{aligned} \tag{8'}$$

Again we find that $W^{\mathbf{k}}$ and $W^{-\mathbf{k}}$ are related: Since the exchange of operators in Eq. (8′) shows that

$$w^{\mathbf{k}} = w^{\mathbf{k}\dagger}, \quad x^{\mathbf{k}} = -\tilde{x}^{-\mathbf{k}}, \tag{9}$$

therefore, using definition (8),

$$W^{\mathbf{k}} = W^{\mathbf{k}\dagger} = -\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} W^{-\mathbf{k}*} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{10}$$

Furthermore, $W^{\mathbf{k}}$ is closely related to $U^{\mathbf{k}}$ and $E_{\mathbf{k}\sigma}$. The form (7) of the density matrix implies that

$$\begin{aligned} \langle \alpha^{\mathbf{k}} \alpha^{\mathbf{k}\dagger}\rangle &= \begin{bmatrix} 1-f(E_{\mathbf{k}+}) & & & 0 \\ & 1-f(E_{\mathbf{k}-}) & & \\ & & f(E_{-\mathbf{k}+}) & \\ 0 & & & f(E_{-\mathbf{k}-}) \end{bmatrix} \\ &\equiv \tfrac{1}{2}(1+\tanh\tfrac{1}{2}\beta E^{\mathbf{k}}), \end{aligned} \tag{11}$$

where f is the usual Fermi-Dirac distribution function, and $E^{\mathbf{k}}$ is the diagonal matrix of signature $(E_{\mathbf{k}+}, E_{\mathbf{k}-}, -E_{-\mathbf{k}+}, -E_{-\mathbf{k}-})$. Comparison of Eqs. (8) and (11) using Eqs. (4) and (5) shows that

$$W^{\mathbf{k}} = \tanh(\tfrac{1}{2}\beta U^{\mathbf{k}} E^{\mathbf{k}} U^{\mathbf{k}\dagger}). \tag{12}$$

Thus, $U^{\mathbf{k}}$ is the unitary transformation which diagonalizes the Hermitian matrix $W^{\mathbf{k}}$, whose (real) eigenvalues are functions of $E_{\mathbf{k}\sigma}$, and so the $W^{\mathbf{k}}$ are completely equivalent to the $U^{\mathbf{k}}$ plus $E^{\mathbf{k}}$ as a set of variational parameters. However, the fact that the subsidiary conditions (10) on $W^{\mathbf{k}}$ are linear, in contrast to the conditions (4) and (5) on $U^{\mathbf{k}}$, makes the minimization of the free energy with respect to the $W^{\mathbf{k}}$ much more convenient.

The free energy

$$F \equiv \langle \mathfrak{K}\rangle - TS, \tag{13}$$

may be expressed in terms of the $W^{\mathbf{k}}$. Measuring the kinetic energy ϵ_k from the chemical potential μ, the Hamiltonian of the system is

$$\mathfrak{K} \equiv \mathfrak{K}_0 - \mu\mathfrak{N} + \mathfrak{V} = \sum_{\mathbf{k}\sigma} \epsilon_k a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} + \mathfrak{V}. \tag{14}$$

The application of a generalized Wick's theorem[16] then gives[15]

$$\begin{aligned} \langle \mathfrak{K}\rangle &\equiv \mathrm{tr}(\rho\mathfrak{K}) \\ &= \tfrac{1}{2}\,\mathrm{tr}\{\sum_{\mathbf{k}} \epsilon_k(1-w^{\mathbf{k}}) + \tfrac{1}{4}\sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} x^{\mathbf{k}\dagger} x^{\mathbf{k}'}\}, \end{aligned} \tag{15}$$

and the entropy S is calculated by using Eqs. (7), (11), and (12)

$$\begin{aligned} S &\equiv -\mathrm{tr}(\rho \ln\rho) = -\sum_{\mathbf{k}\sigma}\{f(E_{\mathbf{k}\sigma}) \ln f(E_{\mathbf{k}\sigma}) \\ &\qquad + [1-f(E_{\mathbf{k}\sigma})] \ln[1-f(E_{\mathbf{k}\sigma})]\} \\ &= -\sum_{\mathbf{k}} \mathrm{tr}\{\tfrac{1}{2}(1+W^{\mathbf{k}}) \ln[\tfrac{1}{2}(1+W^{\mathbf{k}})]\} \\ &= -\sum_{\mathbf{k}} \mathrm{tr}\{\tfrac{1}{2}(1-W^{\mathbf{k}}) \ln[\tfrac{1}{2}(1-W^{\mathbf{k}})]\}. \end{aligned} \tag{16}$$

Using the fact that $W^{\mathbf{k}}$ as well as its infinitesimal variation $\delta W^{\mathbf{k}}$ must satisfy Eqs. (10), the corresponding variation δF of the free energy [given by Eqs. (13), (15), and (16)] can be cast into the form

$$\delta F = -\tfrac{1}{4}\sum_{\mathbf{k}} \delta W^{\mathbf{k}} \left[\mathcal{E}^{\mathbf{k}} - \frac{1}{\beta} \ln \frac{1+W^{\mathbf{k}}}{1-W^{\mathbf{k}}} \right], \tag{17}$$

with the definitions

$$\mathcal{E}^{\mathbf{k}} \equiv \begin{pmatrix} \epsilon_k & \Delta^{\mathbf{k}} \\ -\Delta^{-\mathbf{k}*} & -\epsilon_k \end{pmatrix}, \tag{18}$$

and

$$\Delta^{\mathbf{k}} \equiv -\tfrac{1}{2}\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} x^{\mathbf{k}'} = -\tilde{\Delta}^{-\mathbf{k}}. \tag{19}$$

Since the coefficient of $\delta W^{\mathbf{k}}$ in Eq. (17) satisfies the requirements (10), the condition for a stationary free-energy function [$\delta F = 0$ for any $\delta W^{\mathbf{k}}$ satisfying Eq. (10)] implies

$$\mathcal{E}^{\mathbf{k}} - \beta^{-1} \ln(1+W^{\mathbf{k}})/(1-W^{\mathbf{k}}) = 0,$$

or

$$W^{\mathbf{k}} = \tanh\tfrac{1}{2}\beta\mathcal{E}^{\mathbf{k}}. \tag{20}$$

By comparison with Eq. (12), it is seen that at stationary points,

$$\mathcal{E}^{\mathbf{k}} = U^{\mathbf{k}} E^{\mathbf{k}} U^{\mathbf{k}\dagger}, \tag{21}$$

so that U also diagonalizes $\mathcal{E}$ into E.

2. A Special Class of Variational States

The coupled matrix Eqs. (19) and (20), with definitions (8) and (18), constitute a complete description of the variational states leading to a stationary free energy.

[16] C. Bloch and C. De Dominicis, Nucl. Phys. **7**, 459 (1958); M. Gaudin, *ibid.* **15**, 89 (1960).

In full generality, however, they are quite difficult to analyze, so we at first consider only a special class of solutions for which the equations simplify greatly. We will then show that this class in fact contains those solutions which correspond to the absolute minimum of the free energy, as desired. The restriction we impose is that $\Delta^{\mathbf{k}}$ be proportional to a unitary matrix:

$$\Delta^{\mathbf{k}}\Delta^{\mathbf{k}\dagger}=|\Delta_{\mathbf{k}}|^2. \tag{22}$$

This condition then implies that $(\mathcal{E}^{\mathbf{k}})^2$ is proportional to the unit matrix [from Eq. (18)] and, hence, [from (21)] that

$$(\mathcal{E}^{\mathbf{k}})^2=(E^{\mathbf{k}})^2=\epsilon_k^2+|\Delta_{\mathbf{k}}|^2\equiv E_{\mathbf{k}}^2. \tag{23}$$

Thus, $E_{\mathbf{k}\sigma}=E_{-\mathbf{k}\sigma}$ is independent of σ. A further consequence is the reduction of Eq. (20) to

$$W^{\mathbf{k}}=(\mathcal{E}^{\mathbf{k}}/E_{\mathbf{k}})\tanh\tfrac{1}{2}\beta E_{\mathbf{k}}, \tag{24}$$

which now splits into the pair of 2×2 relations

$$w^{\mathbf{k}}=(\epsilon_k/E_{\mathbf{k}})\tanh\tfrac{1}{2}\beta E_{\mathbf{k}}, \tag{24'}$$

$$x^{\mathbf{k}}=(\Delta^{\mathbf{k}}/E_{\mathbf{k}})\tanh\tfrac{1}{2}\beta E_{\mathbf{k}}. \tag{24''}$$

The latter, when combined with Eq. (19), becomes the familiar gap equation

$$\Delta^{\mathbf{k}}=-\tfrac{1}{2}\sum_{\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}(\Delta^{\mathbf{k}'}/E_{\mathbf{k}'})\tanh\tfrac{1}{2}\beta E_{\mathbf{k}'}, \tag{25}$$

where $\Delta^{\mathbf{k}}$ is now a 2×2 matrix, and $E_{\mathbf{k}}$ is given by Eqs. (22) and (23).

One type of solution of Eq. (25) corresponds to the ESP, and is characterized in the present formalism by $\Delta^{\mathbf{k}}$ being diagonal. More explicitly, if the potential is restricted to a p-wave attraction only,

$$V_{\mathbf{k}\mathbf{k}'}=-3V_1(k,k')\hat{k}\cdot\hat{k}', \tag{26}$$

AM have shown, with the assumptions of the standard model [$V_1(k,k')$ constant and nonvanishing only if k and k' lie inside a shell $|\epsilon_k|<\tilde{\omega}$ containing $4\tilde{\omega}N_0$ states] and weak coupling, that the ESP zero-temperature gap function leading to the lowest ground-state energy $\langle\mathcal{H}\rangle_{\mathrm{ESP}}$ is,

$$\Delta^{\mathbf{k}}{}_{\mathrm{ESP}}=2\tilde{\omega}\exp(-1/N_0V_1)\times(0.94)(4\pi)^{1/2}\begin{pmatrix}Y_{11}(\hat{k}) & 0\\ 0 & Y_{1,-1}(\hat{k})\end{pmatrix}^*. \tag{27}$$

However, Eqs. (25)–(26) have many other solutions; most especially, we exhibit

$$\Delta^{\mathbf{k}}{}_0=\Delta_k\begin{pmatrix}-\hat{k}_x+i\hat{k}_y & \hat{k}_z\\ \hat{k}_z & \hat{k}_x+i\hat{k}_y\end{pmatrix}=\Delta_k\left(\frac{4\pi}{3}\right)^{1/2}\begin{pmatrix}\sqrt{2}Y_{11}(\hat{k}) & Y_{10}(\hat{k})\\ Y_{10}(\hat{k}) & \sqrt{2}Y_{1,-1}(\hat{k})\end{pmatrix}^*, \tag{28}$$

[consistent with Eq. (22)] where Δ_k is now isotropic. With this ansatz, Eq. (25) reduces to

$$\Delta_k=\tfrac{1}{2}\sum_{\mathbf{k}'}V_1(k,k')(\Delta_{k'}/E_{k'})\tanh\tfrac{1}{2}\beta E_{k'}, \tag{29}$$

which with Eq. (23) are the same gap equations as in the s-wave case, the radial part $V_1(k,k')$ of the p-wave potential simply replacing the s-wave interaction. At least for the model potential used above, the corresponding ground-state energy $\langle\mathcal{H}\rangle_0$ is, in fact, lower than $\langle\mathcal{H}\rangle_{\mathrm{ESP}}$, since an explicit calculation reveals

$$\langle\mathcal{H}\rangle_{\mathrm{ESP}}-\langle\mathcal{H}\rangle_0=2N_0\tilde{\omega}^2\exp(-2/N_0V_1)[1-(0.94)^2]>0. \tag{30}$$

3. Absolute Minimum of the Free Energy

More generally, though, we can demonstrate that for any p-wave potential (26), the "isotropic" solution given by Eqs. (28)–(29) leads to the absolute minimum of the free energy corresponding to a variational state of the form (7), and is, thus, the best approximation of this form. To carry out this proof, we shall use a generalization of the method of Balian and Mehta.[17] Attaching the subscript 0 to all quantities associated with the solution (28)–(29), we obtain from Eqs. (13) and (15),

$$F-F_0=\tfrac{1}{2}\operatorname{tr}\{\sum_{\mathbf{k}}\epsilon_k(w^{\mathbf{k}}{}_0-w^{\mathbf{k}})+\tfrac{1}{4}\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}(x^{\mathbf{k}\dagger}x^{\mathbf{k}'}-x^{\mathbf{k}\dagger}{}_0x^{\mathbf{k}'}{}_0)\}+T(S_0-S). \tag{31}$$

By using Eqs. (24'), (24''), and (25) in the form

$$\epsilon_k=(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})w^{\mathbf{k}}{}_0,$$

$$\sum_{\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}x^{\mathbf{k}'}{}_0=-2(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})x^{\mathbf{k}}{}_0,$$

and again recalling definition (8), we can recast the free-energy difference (31) as

$$F-F_0=\tfrac{1}{8}\sum_{\mathbf{k}\mathbf{k}'}\operatorname{tr}\{(x^{\mathbf{k}}-x^{\mathbf{k}}{}_0)^\dagger M_{\mathbf{k}\mathbf{k}'}(x^{\mathbf{k}'}-x^{\mathbf{k}'}{}_0)\}+\tfrac{1}{4}\sum_{\mathbf{k}}(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})\operatorname{tr}\{(w^{\mathbf{k}}-w^{\mathbf{k}}{}_0)^2\}+Q-Q_0, \tag{32}$$

where

$$M_{\mathbf{k}\mathbf{k}'}\equiv2(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})\delta_{\mathbf{k}\mathbf{k}'}+V_{\mathbf{k}\mathbf{k}'}, \tag{33}$$

$$Q\equiv-\tfrac{1}{8}\sum_{\mathbf{k}}(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})\operatorname{tr}\{(W^{\mathbf{k}})^2\}-TS. \tag{34}$$

When considered as a function of the $W^{\mathbf{k}}$, the quantity Q [in which S is given by Eq. (16)] has stationary points when

$$\delta Q\equiv-\tfrac{1}{4}\sum_{\mathbf{k}}\operatorname{tr}\{\delta W^{\mathbf{k}}[(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})W^{\mathbf{k}}-\beta^{-1}\ln(1+W^{\mathbf{k}})/(1-W^{\mathbf{k}})]\}=0,$$

[17] R. Balian and M. L. Mehta, Nucl. Phys. **31**, 587 (1962).

that is, using Eqs. (24) and (20), when

$$\frac{1}{W^{\mathbf{k}}{}_0}\ln\frac{1+W^{\mathbf{k}}{}_0}{1-W^{\mathbf{k}}{}_0}=\frac{1}{W^{\mathbf{k}}}\ln\frac{1+W^{\mathbf{k}}}{1-W^{\mathbf{k}}},$$

which is equivalent to

$$(W^{\mathbf{k}})^2=(W^{\mathbf{k}}{}_0)^2.$$

Since Q depends only on $(W^{\mathbf{k}})^2$, $Q=Q_0$ at the stationary points. Moreover, the behavior of S at the boundaries of $W^{\mathbf{k}}$ (whose eigenvalues must lie between -1 and $+1$) implies that Q cannot attain its absolute minimum on the boundaries. Thus, the minimum occurs at the stationary points, so that

$$Q-Q_0\geq 0.$$

If in addition the matrix $M_{\mathbf{k}\mathbf{k}'}$ is positive semidefinite, then it is evident from Eq. (32) that $F-F_0\geq 0$, and the isotropic solution does indeed give an absolute minimum F_0 of the free energy. This positive semidefiniteness condition is exactly the same as in the s-wave case, since by saturating the matrix M with an arbitrary vector

$$\xi_{\mathbf{k}}=(4\pi)^{1/2}\sum_{lm}\xi_{klm}Y_{lm}(\hat{k}),$$

we find

$$\xi^\dagger M\xi=\sum_{\mathbf{k}\mathbf{k}'m}\xi_{k1m}{}^*[2(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})\delta_{\mathbf{k}\mathbf{k}'}-V_1(k,k')]\xi_{k'1m}+\sum_{\mathbf{k},l\neq 1,m}2(E_{k0}\coth\tfrac{1}{2}\beta E_{k0})\,|\,\xi_{klm}|^2. \quad (35)$$

For $l=1$ and for each m, the summand is identical to what would have been obtained with an s-wave potential $V_{\mathbf{k}\mathbf{k}'}=-V_1(k,k')$, as can be seen also from the gap Eq. (29). But it is proved in Ref. 17 that the matrix in the right-hand side of Eq. (35) is in general positive semidefinite (and so M also) precisely for that solution E_{k0} of Eqs. (23) and (29) which gives the lowest free energy for the state with s-wave pairing. The p-wave variational solution (28), then, is actually one of lowest free energy.

The method used here is indeed not restricted to the p-wave case. The expression (32) is valid whenever F_0 is a stationary value of the free energy associated with a gap matrix $\Delta^{\mathbf{k}}{}_0$ satisfying Eq. (22). An application to the question of the existence of a mixture of s- and p-wave pairing[18] (when the potential $V_{\mathbf{k}\mathbf{k}'}$ contains both waves) is given in Appendix A.

III. ROTATIONAL PROPERTIES AND DEGENERACY

In the previous section, we have proved that the equation $\delta F=0$ does not have any solution of free energy lower than F_0. However, this minimum is degenerate, and other solutions besides (28) of the same energy exist. The family of minimum solutions $\Delta^{\mathbf{k}}{}_{\varphi R}$ can be deduced from Eq. (32); it is constructed by multiplying $\Delta^{\mathbf{k}}{}_0$ by a phase factor $e^{i\varphi}$ and replacing $Y_{1m}(\hat{k})$ by $Y_{1m}(R\hat{k})$, where R is a rotation in the momentum space only. Whereas the first type of degeneracy is associated as usual with the nonconservation of particle number in the canonical transformation (2) and with the invariance of $\mathcal{H}$ under the gauge group $a_{\mathbf{k}\sigma}\rightarrow a_{\mathbf{k}\sigma}e^{i\varphi/2}$, the second type is connected with the nonconservation of spin in (2) despite the invariance of $\mathcal{H}$ under rotation of the spin and momentum spaces separately. In addition to the total particle number, the total spin and orbital angular momentum of the trial system do not have well-defined values. (Expressions for the mean-square fluctuation of these quantities are presented in Sec. IV.) Nevertheless, states with a well-defined total spin and orbital angular momentum may be built by superposition of solutions with different values of R (weighted with an appropriate rotation matrix) in exactly the same way that the BCS state of fixed number of particles is obtained by mixing solutions with different values of φ.[19] These angular momentum eigenstates, although degenerate in this approximation, would appear in an exact theory as low-lying rotational collective excitations.

Additional understanding of this degeneracy may be gained by studying the rotational properties of the trial density matrix associated with the minimum solution (28). By substituting Eqs. (4), (21), (18), and (28) into (7), we can express this density matrix as

$$\rho_0\propto\exp\{-\beta[\sum_{\mathbf{k}\sigma}\epsilon_k a_{\mathbf{k}\sigma}{}^\dagger a_{\mathbf{k}\sigma}+\sum_{\mathbf{k}\sigma\sigma' m}\Delta_k(2\pi/3)^{1/2}\times\langle\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}\sigma,\tfrac{1}{2}\sigma'\,|\,1m\rangle Y_{1m}{}^*(\hat{k})a_{\mathbf{k}\sigma}{}^\dagger a_{-\mathbf{k}\sigma'}{}^\dagger+\text{H.c.}]\}. \quad (36)$$

In this form it is easy to check that ρ_0 is invariant under a full rotation, although not under rotations of the spin or momentum spaces separately. More precisely, the system is composed of bound pairs each having spin $S=1$ and orbital angular momentum $L=1$, coupled to a total angular momentum $J=0$.

These conclusions become even clearer if instead of using a basic set of electron wave functions with quantum numbers $\mathbf{k}$ and σ, we use a spherical wave basis characterized by radial wave number k, orbital angular momentum l, and total angular momentum j with projection μ. The density matrix (36) then becomes

$$\rho_0\propto\exp\{-\beta\sum_{kj\mu}[\epsilon_k\sum_{l=j\pm\frac{1}{2}}a_{klj\mu}{}^\dagger a_{klj\mu}+\Delta_k(j+\tfrac{1}{2})^{1/2}\times\langle jj\mu-\mu\,|\,00\rangle a_{k,j+\frac{1}{2},j,\mu}{}^\dagger a_{k,j-\frac{1}{2},j,-\mu}{}^\dagger+\text{H.c.}]\}, \quad (37)$$

showing that instead of the canonical transformation (2), the p-wave state could also be obtained by pairing electrons of same k and j, opposite μ, and $l=j\pm\frac{1}{2}$. The Clebsch-Gordan coefficient now reveals explicitly that for this solution each pair has zero total angular momentum.

[18] N. R. Werthamer, H. Suhl and T. Soda, Eighth International Conference on Low-Temperature Physics, London, 1962 (to be published).

[19] P. W. Anderson, Phys. Rev. 112, 1900 (1958).

Still another choice of basis which also sheds light on the rotational characteristics is the helicity representation.[20] In this representation, the spin of a particle is quantized not along the z axis, but rather along the direction of the momentum. The helicity quantum number λ is taken to be $+(-)$ when the spin projection is parallel (antiparallel) to $\mathbf{k}$. Thus, the unitary transformation between electron operators in the two bases may be taken as the spin rotation

$$\exp(-i\theta_{\mathbf{k}}\tfrac{1}{2}\sigma_y)\exp(-i\varphi_{\mathbf{k}}\tfrac{1}{2}\sigma_z),$$

or

$$\begin{aligned} a_{\mathbf{k}+} &= \cos\tfrac{1}{2}\theta_{\mathbf{k}}e^{\frac{1}{2}i\varphi_{\mathbf{k}}}a_{\mathbf{k}\uparrow}+\sin\tfrac{1}{2}\theta_{\mathbf{k}}e^{-\frac{1}{2}i\varphi_{\mathbf{k}}}a_{\mathbf{k}\downarrow}, \\ a_{\mathbf{k}-} &= -\sin\tfrac{1}{2}\theta_{\mathbf{k}}e^{\frac{1}{2}i\varphi_{\mathbf{k}}}a_{\mathbf{k}\uparrow}+\cos\tfrac{1}{2}\theta_{\mathbf{k}}e^{-\frac{1}{2}i\varphi_{\mathbf{k}}}a_{\mathbf{k}\downarrow}, \end{aligned} \tag{38}$$

where $(\theta_{\mathbf{k}},\varphi_{\mathbf{k}})$ are the polar angles of $\mathbf{k}$ with respect to the z axis. The gap matrix rewritten in the helicity formalism now takes a very simple form: In the usual BCS case,

$$\Delta_{\lambda\lambda'}{}^{\mathbf{k}}=\lambda\Delta_k\delta_{\lambda\lambda'}, \tag{39}$$

whereas in the p-wave case, Eq. (28) is equivalent to

$$\Delta_{\lambda\lambda'}{}^{\mathbf{k}}=\Delta_k\delta_{\lambda\lambda'}. \tag{39'}$$

An alternative way of forming these superconducting states is thus seen in both cases to be the pairing of electron states of opposite momenta but equal helicities; the factor of λ difference supplies the needed change of parity. The density matrix (36) transformed into the new basis is simply

$$\rho_0\propto\exp\{-\beta[\sum_{\mathbf{k}\lambda}\epsilon_k a_{\mathbf{k}\lambda}{}^{\dagger}a_{\mathbf{k}\lambda} +\tfrac{1}{2}\sum_{\mathbf{k}\lambda\lambda'}\Delta_{\lambda\lambda'}{}^{\mathbf{k}}a_{\mathbf{k}\lambda}{}^{\dagger}a_{-\mathbf{k}\lambda'}{}^{\dagger}+\text{H.c.}]\}, \tag{40}$$

and is, therefore, clearly rotationally invariant in both s- and p-wave cases. The values of the spin and orbital angular momentum of a pair follow immediately from the forms of Eqs. (39) and (39') and the work of Jacob and Wick.[20]

The previous developments apply only to the special solution ρ_0 corresponding to $\Delta^{\mathbf{k}}{}_0$ [Eq. (28)], and the physical picture of the other solutions ρ_R of the same energy is less simple. In particular, the rotation R of the momentum space with respect to the spin space decouples the spin $S=1$ of each pair from its angular momentum $L=1$, so that each pair no longer has the well-defined total angular momentum $J=0$.

It is also worth remarking that whereas the canonical transformation of plane-wave states initially proposed in Eq. (2) mixes *four* such states, the resulting superconducting system is, in fact, composed just of pairs, as seen in expressions (37) and (40) for the associated density matrix ρ_0, or in similar expressions for ρ_R. This is a special case of a general theorem[21] which states that an arbitrary canonical transformation can always be regarded as a pairing of the BCS-Bogoliubov type between single-particle states in an appropriate representation. The ESP method overlooked the fact that this appropriate representation was not the usual plane wave basis, but rather the spherical wave representation, Eq. (37), or the helicity representation, Eq. (40).

[20] M. Jacob and G. C. Wick, Ann. Phys. 1, 404 (1959).

IV. EQUILIBRIUM AND TRANSPORT PROPERTIES

1. Equilibrium Properties

The single quasiparticle excitation spectrum of the state with p-wave pairs is given by $E_k=(\epsilon_k+\Delta_k)^{1/2}$, combined with Eq. (29) to determine Δ_k, and is isotropic. Thus, the system behaves exactly as does the usual BCS state with respect to every equilibrium thermodynamic property, or other property dependent only on the spectrum or density of states. (The density of the rotational states mentioned in Sec. III is small, and just like the usual collective states, their contribution is negligible.) For example, the specific heat is exponentially small at low temperatures; there is no T^3 contribution as predicted by the ESP solution since the energy gap here has no nodes. As another item, the thin film tunneling characteristics are identical with the BCS state.

2. Computation of Nonequilibrium Properties

The nonequilibrium behavior of the system, on the other hand, does exhibit certain significant differences from that of the BCS state. These properties, such as driven responses and absorptions, correlations and fluctuations, are described in a convenient and unified manner as special cases of double-time Green's functions.[22] If $\mathfrak{A}(t)$ and $\mathfrak{B}(t)$ are Heisenberg operators corresponding to observables, then we define the function

$$G(t-t')\equiv -i\langle T\{\mathfrak{B}(t)\mathfrak{A}(t')\}\rangle+i\langle\mathfrak{B}\rangle\langle\mathfrak{A}\rangle, \tag{41}$$

where T is the time-ordering operator. When $\mathfrak{A}$ and $\mathfrak{B}$ are both one-particle operators of the form

$$\mathfrak{A}=\sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'}A_{\sigma\sigma'}{}^{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}\sigma}{}^{\dagger}a_{\mathbf{k}'\sigma'}, \tag{42}$$

then G is closely related to the usual two-particle Green's function. It is shown in Appendix B that for a superconductor with a spin pairing restricted only by the unitary requirement (22) on $\Delta^{\mathbf{k}}$ and the form (42) for $\mathfrak{A}$ and $\mathfrak{B}$,

[21] C. Bloch and A. Messiah, Nucl. Phys. **39**, 95 (1962); B. Zumino, J. Math. Phys. **3**, 1055 (1962).

[22] See, for example, the review article of D. N. Zubarev, Uspekhi Fiz. Nauk **71**, 71 (1960) [translation: Soviet Phys.—Uspekhi **3**, 320 (1960)], and the included references.

G is given by

$$G(t)\equiv(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\, e^{-i\omega t}G(\omega)\,, \tag{43}$$

$$G(\omega)=\tfrac{1}{4}\sum_{\mathbf{k}\mathbf{k}'}\mathrm{tr}\left\{\left[B^{\mathbf{k}'\mathbf{k}}\left(1+\frac{\epsilon_k}{E_{\mathbf{k}}}\right)A^{\mathbf{k}\mathbf{k}'}\left(1+\frac{\epsilon_{k'}}{E_{\mathbf{k}'}}\right)-B^{\mathbf{k}'\mathbf{k}}\frac{\Delta^{\mathbf{k}}}{E_{\mathbf{k}}}\bar{A}^{-\mathbf{k}',-\mathbf{k}}\frac{\Delta^{\mathbf{k}'\dagger}}{E_{\mathbf{k}'}}\right]\left[\frac{f(E_{\mathbf{k}'})(1-f(E_{\mathbf{k}}))}{\omega+E_{\mathbf{k}'}-E_{\mathbf{k}}+i\eta}-\frac{f(E_{\mathbf{k}})(1-f(E_{\mathbf{k}'}))}{\omega+E_{\mathbf{k}'}-E_{\mathbf{k}}-i\eta}\right]\right.$$
$$\left.+[E_{\mathbf{k}}\to-E_{\mathbf{k}}]+[E_{\mathbf{k}'}\to-E_{\mathbf{k}'}]+[E_{\mathbf{k}}\to-E_{\mathbf{k}},E_{\mathbf{k}'}\to-E_{\mathbf{k}'}]\right\}. \tag{44}$$

The linear driven response function is readily obtained from $G(\omega)$. To define this function,[22] we consider applying to the system an externally driven time-dependent perturbation, of the form

$$\mathcal{H}'(t)=\lambda(t)\mathcal{A}. \tag{45}$$

We then inquire as to the average value at the time t of any other observable $\mathcal{B}$. The linear response is defined as the first-order change in the measured quantity due to the presence of the (weak) perturbation

$$R(t-t')\equiv\delta\langle\mathcal{B}(t)\rangle/\delta\lambda(t')\,|_{\lambda=0}$$
$$=-i\langle[\mathcal{B}(t),\mathcal{A}(t')]\rangle\Theta(t-t'). \tag{46}$$

A straightforward comparison of spectral representations[22] shows that $R(\omega)$ is obtained from the form (44) of $G(\omega)$ by the simple recipe of replacing $\omega-i\eta$ everywhere it occurs by $\omega+i\eta$.[23]

3. Spin Susceptibility

The linear response most characteristic of the state with p-wave pairs is the spin susceptibility tensor χ_{ij}. In this case the perturbation is a uniform static magnetic field in the direction j assumed to interact only with the electron spins, and the response is the total induced spin magnetization in the direction i. Thus, $B^{\mathbf{k}\mathbf{k}'}\equiv\mu_0\sigma_i\delta_{\mathbf{k}\mathbf{k}'}$, where the σ_i are the Pauli matrices, $A^{\mathbf{k}\mathbf{k}'}$ has the same form, and

$$\chi_{ij}=R(\omega=0)=\mathrm{Re}G(\omega=0). \tag{47}$$

Now the most general matrix $\Delta^{\mathbf{k}}$ can always be written in the form

$$\Delta^{\mathbf{k}}=\textstyle\sum_\nu d_{\mathbf{k}\nu}\sigma_\nu\sigma_2\,,\quad \nu=0,1,2,3\,, \tag{48}$$

where $\sigma_0\equiv\sigma_1\sigma_2\sigma_3=i$. It proves more convenient at this point to characterize the gap matrix by the $d_{\mathbf{k}\nu}$ than by the actual elements of $\Delta^{\mathbf{k}}$ itself. By referring to Eq. (19), it may easily be seen that $d_{\mathbf{k}0}$ is even in $\mathbf{k}$, while $\mathbf{d}_{\mathbf{k}}$ ($\nu=1,2,3$) is odd. Thus, $d_{\mathbf{k}0}$ is the part of the gap matrix associated with the even-parity part of the potential (e.g., the s-wave BCS part), whereas $\mathbf{d}_{\mathbf{k}}$ is associated with the odd-partial waves (such as the p-wave part). Inspection of Eq. (28) shows that the isotropic p-wave pair solution $\Delta^{\mathbf{k}}{}_0$ is expressed in this notation as simply $\mathbf{d}_{\mathbf{k}}=\Delta_k\hat{k}$, $d_{\mathbf{k}0}=0$, while the BCS solution is $d_{\mathbf{k}0}=\Delta_k$, $\mathbf{d}_{\mathbf{k}}=0$.[24]

Substituting Eqs. (44) and (48) into (47), we may evaluate the spin trace and obtain

$$\chi_{ij}=2\mu_0{}^2\sum_{\mathbf{k}}\left\{\frac{\partial f(E)}{\partial E}\delta_{ij}+\frac{1}{E^2}\left[\frac{\partial f(E)}{\partial E}+\frac{1-2f(E)}{2E}\right]\right.$$
$$\left.\times\mathrm{Re}(d_id_j{}^*-\epsilon_{ijl}d_0d_l{}^*-\mathbf{d}\cdot\mathbf{d}^*\delta_{ij})\right\}, \tag{49}$$

where we have dropped the indices $\mathbf{k}$. It is interesting to note that in general the susceptibility has full tensor character, and the induced magnetization is not the same for all directions of the applied field; this is true of the ESP solution, for instance. The isotropic p-wave solution, $\Delta^{\mathbf{k}}{}_0$ or $\Delta^{\mathbf{k}}{}_R$, on the other hand, leads to a scalar susceptibility, $\chi_{ij}=\chi\delta_{ij}$. When the standard model potential is used, its ratio to the normal Pauli susceptibility is given by

$$\chi_s/\chi_n=\tfrac{2}{3}+\tfrac{1}{3}Y\,, \tag{50}$$

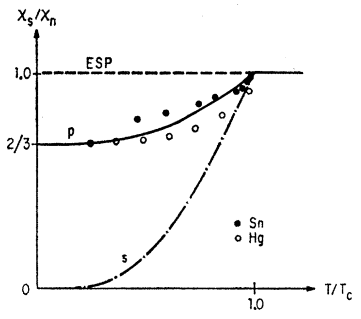

FIG. 1. Ratio of the superconducting to normal paramagnetic spin susceptibility, as a function of reduced temperature. The dash-dotted, solid, and dashed curves give the theoretical predictions for the s-wave, p-wave, and equal spin-pairing states, respectively. The experimental points are taken from the Knight shift measurements of Refs. 4 and 5.

[23] As defined here, the linear response does not include the effect of collective excitations, as would for example a treatment using the random phase approximation (see Ref. 19). The collective excitations may be restored in the Green's function context by the procedure of G. Baym and L. P. Kadanoff, Phys. Rev. **124**, 287 (1961), applied especially to the superconducting gauge-invariant electromagnetic response by V. Ambegaokar and L. P. Kadanoff, Nuovo Cimento **22**, 914 (1961). The conclusions of the present paper would not be affected.

[24] Also in this notation the ESP solution has $\mathbf{d}_{\mathbf{k}}=\hat{k}\times\hat{z}\Delta_k$, $d_{\mathbf{k}0}=0$. The degeneracy under rotation of the spin space studied in Sec. III is connected with rotations of the vector $\mathbf{d}_{\mathbf{k}}$.

with Y being the ratio previously calculated by Yosida[7] for the BCS state,

$$Y\equiv\tfrac{1}{2}\beta\int_0^\infty d\epsilon\,\mathrm{sech}^2[\tfrac{1}{2}\beta(\epsilon^2+\Delta^2)^{1/2}]. \tag{51}$$

These quantities are plotted in Fig. 1 as a function of temperature.

It is curious to note the good agreement between the prediction (50) and the experimental values obtained from Knight-shift measurements on mercury[4] and tin.[5] To regard the data as indicative of a p-wave pair state actually occurring in these elements is quite tempting. In fact, although the effective electron interaction derived in the BCS theory is an s-wave attraction, AM[10] have conjectured that the crystalline structure of some elements might tend to favor the p wave. In order to confirm this hypothesis, however, one not only must verify that the p-wave state in no way contradicts any other existing measurement on Sn and Hg, but also must consider whether a Knight-shift measurement does in fact provide information on the electronic spin susceptibility. On both counts considerable ambiguity exists: As will be discussed in the following, the state is not altogether physically acceptable, but yet cannot be ruled out entirely. Furthermore, recent NMR experiments on the hard superconductor V_3Ga have shown[25] that in this instance much, if not all, of the Knight shift can be attributed to orbital paramagnetism. These authors also present arguments for a similar situation occurring in pure vanadium[6]; the implications for the experiments on Sn and Hg are not as yet clear. We return to these questions again in the concluding section.

4. Electromagnetic Response

Complementary in structure to the spin susceptibility is the electromagnetic response,[26] including such important experimental tests of the superconducting state as the Meissner effect, infrared reflection and transmission, and microwave surface impedance. Here, the perturbation is an applied vector potential $\mathbf{A}(\mathbf{r})e^{-i\omega t}$, with the induced current density at the point $\mathbf{r}$ as the observable of interest. If we consider only the paramagnetic part of the current, then we take

$$-A^{\mathbf{k}\mathbf{k}'}=B^{\mathbf{k}\mathbf{k}'}=(e/2m\Omega)(\mathbf{k}+\mathbf{k}')e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}, \tag{52}$$

with Ω the volume, and the response tensor is

$$R(\mathbf{r},\mathbf{r}';\omega)=\frac{1}{2}\left(\frac{e}{2m}\right)^2\int\frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3}(\mathbf{k}+\mathbf{k}')(\mathbf{k}+\mathbf{k}')e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{r}')}\left\{\left[\left(1+\frac{\epsilon}{E}\right)\left(1+\frac{\epsilon'}{E'}\right)+\frac{d_0d_0'^*+\mathbf{d}\cdot\mathbf{d}'^*}{EE'}\right]\right.$$
$$\left.\times\frac{f(E)-f(E')}{\omega+E'-E+i\eta}+[E\to-E]+[E'\to-E']+[E\to-E,E'\to-E']\right\}. \tag{53}$$

Since all reasonable perturbations $\mathbf{A}(\mathbf{r})$ vary slowly over distances comparable to a lattice spacing, so that $|\mathbf{k}-\mathbf{k}'|\ll k_F$, we can replace $d_0d_0'^*+\mathbf{d}\cdot\mathbf{d}'^*$ in Eq. (53) by $|\Delta_k|^2$; thus the s-wave and p-wave pair states lead to identical expressions and are electromagnetically indistinguishable.

5. Correlation Functions and Fluctuations

A set of quantities closely related to the response functions, not readily measured in a superconductor but still useful for visualizing the nature of the state, are the correlation functions. These are defined as

$$C(\mathcal{B},\mathcal{A})\equiv\langle\mathcal{B}\mathcal{A}\rangle-\langle\mathcal{B}\rangle\langle\mathcal{A}\rangle, \tag{54}$$

and are seen to be just the equal-time Green's functions,

$$C(\mathcal{B},\mathcal{A})=i\lim_{t'\to t-}G(t-t'). \tag{55}$$

Substituting Eqs. (43) and (44), closing the ω contour in the lower half-plane, and using Eq. (24), the expression reduces to

$$C(\mathcal{B},\mathcal{A})=\tfrac{1}{4}\sum_{\mathbf{k}\mathbf{k}'}\mathrm{tr}\{B^{\mathbf{k}'\mathbf{k}}(1+w^{\mathbf{k}})A^{\mathbf{k}\mathbf{k}'}(1-w^{\mathbf{k}'})$$
$$+B^{\mathbf{k}'\mathbf{k}}x^{\mathbf{k}}\bar{A}^{-\mathbf{k}'-\mathbf{k}}x^{\mathbf{k}'\dagger}\}. \tag{56}$$

The density-density correlation in particular, computed by AM for the ESP solution and found to be anisotropic, here becomes (for $\mathbf{r}\neq\mathbf{r}'$)

$$C(\rho_\sigma(\mathbf{r}),\rho_{\sigma'}(\mathbf{r}'))=-|\tfrac{1}{2}w_{\sigma\sigma'}(\mathbf{r}-\mathbf{r}')|^2$$
$$+|\tfrac{1}{2}x_{\sigma\sigma'}(\mathbf{r}-\mathbf{r}')|^2, \tag{57}$$

where $w_{\sigma\sigma'}(\mathbf{r})$ is the Fourier transform of $w_{\sigma\sigma'}{}^{\mathbf{k}}$. The first term represents the negative correlation associated with repulsion of particles of like spin due to the Pauli principle; the positive second term represents the attraction of correlated (or bound) pairs. For the p-wave solution,

$$C(\rho_\sigma(r,\theta),\rho_{\sigma'}(0))=-\delta_{\sigma\sigma'}\left|\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}j_0(kr)\frac{\epsilon_k}{E_k}\tanh\tfrac{1}{2}\beta E_k\right|^2+\begin{pmatrix}\sin^2\theta & \cos^2\theta\\ \cos^2\theta & \sin^2\theta\end{pmatrix}\left|\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}j_1(kr)\frac{\Delta_k}{E_k}\tanh\tfrac{1}{2}\beta E_k\right|^2. \tag{58}$$

[25] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).
[26] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958); A. A. Abrikosov, L. P. Gor'kov, and I. M. Khalatnikov, Zh. Eksperim. i Teor. Fiz. **35**, 265 (1958); **37**, 187 (1959) [translations: Soviet Phys.—JETP **8**, 182 (1959); **10**, 132 (1960)].

Although the correlations of densities of like and unlike spins separately are anisotropic, averaging over spins leads to a completely isotropic result. Because of the first-order spherical Bessel function in the second term instead of the j_0 found in the corresponding BCS expression, the correlation $C(\rho,\rho)$ does have different radial dependence in the two states; the difference only occurs for small r, however, and is masked by the Pauli exclusion term.

The density-current correlation was also computed by AM, and for the ESP was found by them to be nonvanishing. In general, this correlation is

$$C(\mathbf{j}_\sigma(\mathbf{r}),\rho_{\sigma'}(\mathbf{r}'))=(1/m)\times|\tfrac{1}{2}x_{\sigma\sigma'}(\mathbf{r}-\mathbf{r}')|^2\nabla\arg x_{\sigma\sigma'}(\mathbf{r}-\mathbf{r}'),\quad(59)$$

which for the isotropic p-wave solution of Eq. (28) reduces to

$$C(\mathbf{j}_\sigma(r,\theta),\rho_{\sigma'}(0))=\frac{\hat{\varphi}}{mr}\sin^2\theta\begin{pmatrix}1&0\\0&-1\end{pmatrix}\times\left|\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}j_1(kr)\frac{\Delta_k}{E_k}\tanh\tfrac{1}{2}\beta E_k\right|^2.\quad(60)$$

Thus, there is an equatorial current about a fixed point with a distinguished spin direction, although upon averaging over spins this current correlation vanishes. It follows that no observable surface currents are to be expected here, contrary to the ESP case. It is also interesting to note that Eq. (60) gives just the correlation to be expected for two otherwise isolated spin-$\frac{1}{2}$ particles bound into an $L=1$, $S=1$, $J=0$ state. For the degenerate p-wave solutions, ρ_R, of Sec. III, the correlation pattern is less simple, since the spins must be rotated by R.

Expression (56) is also useful for computing the fluctuations of observables from their mean. By substituting appropriately for A and B, we find for particle number $\mathfrak{N}$ and total spin $\mathbf{S}$,

$$\langle\mathfrak{N}^2\rangle-\langle\mathfrak{N}\rangle^2=\sum_{\mathbf{k}}[\tfrac{1}{2}\operatorname{sech}^2(\tfrac{1}{2}\beta E_{\mathbf{k}})+|\Delta_{\mathbf{k}}/E_{\mathbf{k}}|^2\tanh^2(\tfrac{1}{2}\beta E_{\mathbf{k}})],\quad(61)$$

$$\langle\mathbf{S}^2\rangle-\langle\mathbf{S}\rangle^2=\tfrac{3}{4}\sum_{\mathbf{k}}[\tfrac{1}{2}\operatorname{sech}^2(\tfrac{1}{2}\beta E_{\mathbf{k}})+\tfrac{2}{3}|\mathbf{d}_{\mathbf{k}}/E_{\mathbf{k}}|^2\tanh^2(\tfrac{1}{2}\beta E_{\mathbf{k}})].\quad(62)$$

The first terms in these expressions represent the statistical fluctuations in the thermally excited normal electrons, while the second terms give the uncertainties due to the trial density matrix failing to conserve these quantum numbers, as discussed previously in Sec. III. The mean square fluctuation in particle number is the same for both s-wave and p-wave states, whereas in the case of total spin, it is just the pairs of parallel spins which contribute to the indefiniteness.

6. Absorptions

In addition to the real response, a second characteristic property of a driven system is the absorption. The two most significant measurements of this type in a superconductor are acoustic attenuation and NMR relaxation; the temperature dependences of the ratio of these quantities to their values in the normal state have been of great importance in verifying the electron pairing hypothesis of BCS. In order to compare the predictions of the p-wave pair state proposed here to the successful BCS formulas, we note that the relevant absorption coefficient or relaxation time is derived in a standard manner from the probability P for transition between suitably weighted initial and final electronic states, due to the application of the weak perturbation

$$\mathfrak{IC}'(t)=\lambda e^{-i\omega t}\mathfrak{A}+\text{H.c.}$$

This transition rate is given by the usual Golden Rule formula, which in turn is related through the spectral representation to the retarded Green's function via

$$P=-2\lambda^2\,\mathrm{Im}R(\omega),\quad(63)$$

where R is computed for $\mathfrak{B}=\mathfrak{A}^\dagger$.

In the case of the acoustic attenuation,[27] the perturbation is an effective potential with wave number $\mathbf{q}$ and frequency ω obeying the phonon-dispersion law, $\omega/q=$sound velocity. This potential couples to the electron charge density, so that $A^{\mathbf{k}\mathbf{k}'}=\delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}}$, and

$$P=\pi\lambda^2\sum_{\mathbf{k}\mathbf{k}'}\delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}}\left\{\left[\left(1+\frac{\epsilon}{E}\right)\left(1+\frac{\epsilon'}{E'}\right)-\frac{d_0d_0'^*+\mathbf{d}\cdot\mathbf{d}'^*}{EE'}\right]\times[f(E')-f(E)]\delta(\omega-E+E')+[E'\to-E']+[E\to-E,E'\to-E']\right\}.\quad(64)$$

In the long-wavelength limit, for $q\ll k_F$, the p-wave state leads to precisely the same result for the transition probability as does the usual BCS state. The acoustic attenuation in both cases measures the isotropic gap in the energy spectrum, Δ_k.

For the case of the NMR longitudinal relaxation time, T_1,[28] on the other hand, the perturbation is the hyperfine interaction of nuclear and electron spins. Thus

$$P_{m\to n}=-2(1-e^{-\beta\omega_{nm}})^{-1}\times\sum_{\nu\nu'}\langle n|\mathbf{I}_\nu|m\rangle\,\mathrm{Im}R(\mathbf{r}_\nu,\mathbf{r}_{\nu'};\omega_{nm})\langle m|\mathbf{I}_{\nu'}|n\rangle,\quad(65)$$

where n and m are states of the nuclear system differing in energy by ω_{nm}, $\mathbf{I}_\nu$ is the nuclear spin at the site ν, and

[27] T. Tsuneto, Phys. Rev. **121**, 402 (1961), and references given therein.

[28] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959); L. C. Hebel, *ibid.* **116**, 79 (1959).

R is a tensor to be computed for $\mathbf{A}^{\mathbf{k}\mathbf{k}'}=\frac{1}{2}\boldsymbol{\sigma}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_{\nu'}}$, $\mathbf{B}^{\mathbf{k}\mathbf{k}'}$ the same with $\nu'\rightarrow\nu$. Since the interaction of one nuclear spin $\mathbf{I}_\nu$ with another $\mathbf{I}_{\nu'}$ is not significant, we have $\nu=\nu'$ in Eq. (65). Also, since the energies of the nuclear transitions are small compared to the gap, and since the nuclear spins are disordered, to a good approximation only

$$\operatorname{Im}\sum_i R_{ii}(\mathbf{r},\mathbf{r};\omega)$$
$$=\tfrac{1}{2}\pi\lambda^2\sum_{\mathbf{k}\mathbf{k}'}\{\operatorname{Re}[3(EE'+\epsilon\epsilon'+d_0d_0'^*)-\mathbf{d}\cdot\mathbf{d}'^*]/EE'\}$$
$$\times[f(E)-f(E')]\delta(E-E'-\omega) \quad (66)$$

is needed for computing P. Since $\mathbf{d}_\mathbf{k}$ is odd in $\mathbf{k}$, the $\mathbf{d}\cdot\mathbf{d}'^*$ term drops out; the $\epsilon\epsilon'$ term vanishes by reason of symmetry about the Fermi surface. The coherence factor $1+\operatorname{Re}(d_0d_0'^*/EE')$ differs for the s- and p-wave solutions, although at most by a factor of 2. But, in any event, the result for P is formally infinite, due to the uncompensated infinity in the superconducting density of states at the gap edge; an artificial level broadening must be introduced to obtain sensible results. The amount of broadening is customarily determined by fitting the experimental data at one point, so that only a relative temperature dependence of T_1 is obtained. In the absence of reliable estimates of this broadening from first principles, the experiment is entirely insensitive to an over-all numerical factor. Here again, both the BCS and p-wave pair states are consistent with observation.

V. EFFECT OF IMPURITIES: CONCLUSIONS

Upon surveying the above calculations comparing the theoretical predictions in various experimental situations of the BCS state with the alternative system of p-wave pairs, an over-all picture emerges. The only mathematical distinction between the two systems occurs in the coherence factors (the matrix elements between electronic states). For those perturbations which are spin-independent, the BCS term $\Delta_k\Delta_{k'}$ is replaced in the latter state by $\Delta_k\Delta_{k'}\hat{k}\cdot\hat{k}'$. But in two of the examples of this type [electromagnetic response, Eq. (53), and acoustic attenuation, Eq. (64)] the perturbation is of long wavelength, thus requiring the momentum transfer $\mathbf{k}-\mathbf{k}'$ to be small; the additional factor $\hat{k}\cdot\hat{k}'$ has little or no effect on the response to such perturbations. In the third example [density-density correlation, Eq. (58)], short wavelengths are involved; however, the effect of the factor $\hat{k}\cdot\hat{k}'$ in the term containing Δ_k is masked by the main Pauli exclusion term. On the other hand, when the perturbation is spin-dependent as in Eqs. (49) and (66), the analogous BCS term in the (tensor) coherence factor, $\Delta_k\Delta_{k'}\delta_{ij}$, is replaced by $\Delta_k\Delta_{k'}[\frac{1}{2}(\hat{k}_i\hat{k}_j'+\hat{k}_i'\hat{k}_j)+\hat{k}\cdot\hat{k}'\delta_{ij}]$. These two terms are always different no matter what the momentum transfer, and the resulting responses indeed differ; as examples, we have computed the spin susceptibility [long wavelength, Eq. (49)] and the NMR relaxation time [short wavelength, Eq. (66)]. However, we have seen that neither of the corresponding measurements is a sufficiently direct and unambiguous test of the theory to make a decisive choice between the two states, although we have found some indication from the spin susceptibility that the p-wave state is preferable. To make the experimental distinction clear-cut, a spin-independent perturbation of short wavelength is required.

The addition of dilute, random impurities to a pure superconducting sample satisfies these criteria. The effect on the critical temperature of such alloying, both by nonmagnetic and paramagnetic impurities, has been previously calculated in the BCS context by Suhl and Matthias,[29] and by Abrikosov and Gor'kov.[30] These authors predict that T_c is strongly depressed by magnetic impurities, while affected very much less, if at all, by nonmagnetic impurities. This is precisely the experimental situation at small concentrations: Matthias *et al.*[31] find T_c drops almost to zero with the addition of less than 1% paramagnetic rare earth in superconducting lanthanum, while Lynton *et al.*[32] measure changes of T_c due to nonmagnetic impurities in millidegrees over a similar concentration range.

To estimate the corresponding results expected from the p-wave state, it is easier to follow here the perturbation theory approach of Suhl and Matthias,[29] than the more elaborate treatment of Abrikosov and Gor'kov,[30] which yields qualitatively similar conclusions. The former authors compute the change in the free-energy difference between normal and superconducting phases, and then invoke the law of corresponding states to relate this to the change in T_c. To second order, the change in free energy due to a time-independent perturbation $\mathcal{H}'$ is

$$\delta F=\langle\mathcal{H}'\rangle+\tfrac{1}{2}R(\omega=0), \quad (67)$$

where the Green's function is computed for $\mathcal{A}=\mathcal{B}=\mathcal{H}'$; for impurities at sites ν, $\mathcal{H}'$ is just the sum of contributions from each impurity separately,

$$A^{\mathbf{k}\mathbf{k}'}=\sum_\nu\lambda(\mathbf{k}-\mathbf{k}')e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_\nu}, \quad \text{nonmagnetic},$$
$$=[I(I+1)]^{-1/2}\sum_\nu\lambda(\mathbf{k}-\mathbf{k}')e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_\nu}\boldsymbol{\sigma}\cdot\mathbf{I}_\nu,$$
$$\text{magnetic}. \quad (68)$$

Substituting Eq. (44), and averaging over random impurity configurations (and in the case of magnetic impurities, over random impurity spin orientations as well), we obtain per unit volume and to first order in the

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[32] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

impurity concentration, ξ,

$$\delta\bar{F}=\tfrac{1}{2}\xi\sum_{\mathbf{k}\mathbf{k}'}|\lambda(\mathbf{k}-\mathbf{k}')|^2\left\{\left[\frac{EE'+\epsilon\epsilon'-\gamma\Delta\Delta'}{EE'}\,\frac{f(E)-f(E')}{E-E'}\right]+[E\rightarrow -E]\right\}. \quad (69)$$

We have defined

$$\gamma\equiv\begin{array}{lll} s\ wave & p\ wave & \\ +1 & \hat{k}\cdot\hat{k}' & \text{nonmagnetic} \\ -1 & \tfrac{1}{3}\hat{k}\cdot\hat{k}' & \text{magnetic.}\end{array}$$

Proceeding through the integration of Eq. (69) step by step with Suhl and Matthias, we find to lowest order in $\Delta/\tilde{\omega}$

$$\delta(\bar{F}_s-\bar{F}_n)\cong\tfrac{1}{32}\xi N_0{}^2\Delta\int d\hat{k}d\hat{k}'|\lambda(\mathbf{k}-\mathbf{k}')|^2(1-\gamma), \quad (70)$$

the integrations to be an average over the Fermi surface; we have used the fact that $\lambda(\mathbf{k}-\mathbf{k}')$ is a slowly varying function of $|\mathbf{k}|$. We recover the result[29,30] that in the BCS state nonmagnetic impurities have no effect (in this approximation) on the free-energy difference, while the exchange scattering of paramagnetic impurities forces the superconducting and normal phases closer in free energy, linearly with the concentration.

These conclusions are not, in general, true for the p-wave pair state. Since the interaction between the conduction electrons and an impurity is short ranged, probably localized to the immediate vicinity of the impurity site itself, the perturbation extends only over a distance comparable to the lattice spacing, and as we remarked earlier very large momentum transfers of order $2k_F$ are allowed. In fact, $|\lambda(\mathbf{k}-\mathbf{k}')|^2$ is certainly not such as to restrict $\hat{k}$ to the vicinity of $\hat{k}'$ in Eq. (70). The exact cancellation of the two last terms, therefore, occurs only for $\gamma=1$, that is for an s-wave state with nonmagnetic impurities. The prediction for the p-wave pair state, then, is that magnetic impurities would tend to depress the transition temperature to roughly the same degree as for the BCS state, and that in an equivalent concentration nonmagnetic impurities would lower T_c even more, since λ^2 is likely to be a good deal larger in this case.

Such a situation appears to be contradictory to the behavior of real materials, including Sn and Hg. Experiments have generally shown that for equivalent concentrations, magnetic impurities tend to depress the critical temperature much more than nonmagnetic ones. The hypothesis of a p-wave attraction for Sn and Hg, which we introduced in order to explain the finite value of the spin susceptibility would, therefore, be justified only if it were found that both kinds of impurities have effects of the same order of magnitude for these materials. Unfortunately, only the effects of nonmagnetic impurities in Sn have been studied,[32] but since they do not appear to be anomalously large, such an eventuality would seem unlikely. Therefore, even if the Knight shift experiments are a measure of the spin susceptibility of the conduction electrons,[25] the agreement of the data on Sn and Hg with the predictions of a p-wave pairing theory is probably a coincidence.

More generally, the possibility that a p-wave pair state might be observed in some materials has already been considered by AM.[10] We have seen that it is a very delicate question to distinguish experimentally such a state from the usual BCS state: Only a direct and unambiguous measurement of the spin susceptibility in a bulk sample (experimentally unfeasible, if not impossible), or an anomalously large effect of nonmagnetic impurities would be decisive tests. Moreover, real materials always contain at least a slight concentration of nonmagnetic impurities; while they do not dramatically affect a BCS state, they considerably increase the free energy of a p-wave pair state. Superconducting transitions of the p-wave type, if they exist, would therefore have to be looked for only in extremely pure samples.

A similar situation arises in the cases of a d-wave attraction, and in particular in the problem of the proposed low-temperature superfluid phase of liquid He^3.[11] Although here the impurities are not fixed scattering centers, their effect is expected to be much stronger than in the BCS theory, and might explain why the proposed superfluid phase has not been observed.

ACKNOWLEDGMENTS

We wish to thank Professor H. Suhl for having initially stimulated our interest in this problem, and for continued encouragement during the course of the work. It is a pleasure to acknowledge helpful and enlightening discussions with Dr. P. W. Anderson and Professor W. Kohn, and to thank Dr. J. des Cloizeaux, Dr. L. C. Hebel, and Dr. K. Sawada for valuable conversations.

APPENDIX A: MIXTURE OF DIFFERENT PARTIAL WAVES

In the body of the text we have considered an interaction in a pure angular momentum state, either only s wave or only p wave. The question naturally arises whether, if the interparticle potential is attractive in both partial waves, it might not be energetically favorable to form a state containing both s- and p-wave pairs simultaneously. An indication was gained,[18] from direct computation with a simplified model, that states of mixed angular momenta are possible, but only for special and quite restrictive potential shapes. However, some general statements on this problem can be made, using the positive-definiteness criterion on the matrix M of Sec. II.

If the potential $V_{\mathbf{k}\mathbf{k}'}$ is resolved into s- and p-wave parts, $V=V^s+V^p$, and quasiparticle energies $E_k{}^s$ and $E_k{}^p$ are found which, respectively, minimize the free energy computed with each of the potentials separately,

then

$$M_{\mathbf{k}\mathbf{k}'}{}^{ss}\equiv 2(E_k{}^s \coth\tfrac{1}{2}\beta E_k{}^s)\delta_{\mathbf{k}\mathbf{k}'}+V_{\mathbf{k}\mathbf{k}'}{}^s \quad \text{(A1)}$$

and

$$M_{\mathbf{k}\mathbf{k}'}{}^{pp}\equiv 2(E_k{}^p \coth\tfrac{1}{2}\beta E_k{}^p)\delta_{\mathbf{k}\mathbf{k}'}+V_{\mathbf{k}\mathbf{k}'}{}^p \quad \text{(A2)}$$

are both positive-definite matrices. If, on the other hand, we also find the matrix

$$M^{ps}\equiv\|2E^p \coth\tfrac{1}{2}\beta E^p+V^s\| \quad \text{(A3)}$$

to be positive definite, then it will be true from (A2) and (A3) that $\|2E^p \coth\frac{1}{2}\beta E^p+V\|\geq 0$, and Eq. (32) then implies that the solution of lowest free energy with the combined potential is the pure p-wave state. Similarly, if $M^{sp}\geq 0$, then the pure s-wave state minimizes the combined problem. Thus, a solution with s and p pairs occurring simultaneously can exist and lead to a minimum free energy only if the potentials are such that

$$M^{ss} \text{ and } M^{pp}\geq 0, \quad M^{sp} \text{ and } M^{ps}\gtrless 0. \quad \text{(A4)}$$

In particular, Eqs. (A4) cannot all be satisfied if V^s and V^p both have the same radial shape, and as was the conclusion of Ref. 18, a mixed solution is then not possible. Also, for the standard model potential, the inequalities (A4) at $T=0$ become[18]

$$\frac{\exp(1/N_0V^p)}{\exp(1/N_0V^s)}\gtrless\frac{\tilde{\omega}_p}{\tilde{\omega}_s}\gtrless\frac{\sinh(1/N_0V^p)}{\sinh(1/N_0V^s)}. \quad \text{(A5)}$$

In the weak-coupling limit, these inequalities reduce to the equality $\tilde{\omega}_s \exp(-1/N_0V^s)=\tilde{\omega}_p \exp(-1/N_0V^p)$; the existence of a potential producing a mixture of s- and p-wave pairs is, therefore, mathematically possible, but physically quite unlikely.

It is interesting to point out the connection between these results and the work of Bardasis and Schrieffer[33] on the collective excitations of a system in a pure s-wave state, but with a potential also containing some attractive p wave. These authors showed that the s-wave state becomes unstable with respect to the formation of excitons when $V^p>V^s$ (for $\tilde{\omega}_p=\tilde{\omega}_s$ and in the weak-coupling limit), implying that there exists some solution of the variational equations of energy lower than the s-wave solution. But on the other hand, AM found that the energy of the ESP state was higher than that of the s-wave state unless $(0.94)\exp(-1/N_0V^p)>\exp(-1/N_0V^s)$. Therefore, at least in the region $V^s<V^p<V^s/[1+N_0V^s\ln(0.94)]$, neither the s wave nor the ESP solutions can be the state of lowest energy. In fact, the isotropic p-wave solution studied here is just the state toward which the instability of Bardasis and Schrieffer is tending.

It may also be noted that if there is a dominant s- (or p-) wave potential, then a weaker potential of higher angular momentum but roughly the same radial shape does not produce any admixture of pairs with that l: if $M^{ss}\geq 0$, and if V^l has sufficiently near the same radial shape as V^s so that $M^{sl}\geq 0$ also, then $\|2E^s \coth\frac{1}{2}\beta E^s+V^s+V^l\|\geq 0$ as well, and the minimum for the combined interaction is pure s.

APPENDIX B: PROOF OF EQUATION (44)

To prove Eq. (44), we first substitute Eq. (42) into (41), which gives

$$G(t-t')=-i\sum B_{\sigma'''\sigma''}{}^{\mathbf{k}'''\mathbf{k}''}A_{\sigma\sigma'}{}^{\mathbf{k}\mathbf{k}'}[\langle T\{a_{\mathbf{k}''\sigma''}(t)a_{\mathbf{k}'\sigma'}(t')a_{\mathbf{k}\sigma}{}^\dagger(t'+)a_{\mathbf{k}'''\sigma'''}{}^\dagger(t+)\}\rangle-\langle a_{\mathbf{k}'''\sigma'''}{}^\dagger a_{\mathbf{k}''\sigma''}\rangle\langle a_{\mathbf{k}\sigma}{}^\dagger a_{\mathbf{k}'\sigma'}\rangle]. \quad \text{(B1)}$$

Applying the generalized Wick's theorem in the Heisenberg picture, we obtain

$$G(t-t')=i\sum_{\mathbf{k}\mathbf{k}'}\mathrm{tr}[B^{\mathbf{k}'\mathbf{k}}\langle T\{a_{\mathbf{k}}(t)a_{\mathbf{k}}{}^\dagger(t')\}\rangle A^{\mathbf{k}\mathbf{k}'}\langle T\{a_{\mathbf{k}'}(t')a_{\mathbf{k}'}{}^\dagger(t)\}\rangle$$
$$-B^{\mathbf{k}'\mathbf{k}}\langle T\{a_{\mathbf{k}}(t)a_{-\mathbf{k}}(t')\}\rangle\tilde{A}^{-\mathbf{k}',-\mathbf{k}}\langle T\{a_{-\mathbf{k}'}{}^\dagger(t')a_{\mathbf{k}'}{}^\dagger(t)\}\rangle], \quad \text{(B2)}$$

where

$$a^{\mathbf{k}}(t)=\exp\{-i\mathcal{E}^{\mathbf{k}}t\}a^{\mathbf{k}}. \quad \text{(B3)}$$

But by adopting a spectral representation, and noting Eqs. (B3), (8), and (20), we find

$$\langle T\{a^{\mathbf{k}}(t)a^{\mathbf{k}\dagger}(t')\}\rangle=i\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\int_{-\infty}^{\infty}dZ\,\delta(Z-\mathcal{E}^{\mathbf{k}})\left[\frac{1-f(Z)}{\omega-Z+i\eta}+\frac{f(Z)}{\omega-Z-i\eta}\right]. \quad \text{(B4)}$$

Requiring, in addition, solutions that satisfy Eq. (22), so that $(\mathcal{E}^{\mathbf{k}})^2=E_{\mathbf{k}}{}^2$, implies that

$$\delta(Z-\mathcal{E}^{\mathbf{k}})=\frac{1}{2}\left(1+\frac{\mathcal{E}^{\mathbf{k}}}{E_{\mathbf{k}}}\right)\delta(Z-E_{\mathbf{k}})+\frac{1}{2}\left(1-\frac{\mathcal{E}^{\mathbf{k}}}{E_{\mathbf{k}}}\right)\delta(Z+E_{\mathbf{k}}). \quad \text{(B5)}$$

Substituting Eqs. (B4) and (B5) into (B2), and the resulting expression into Eq. (43), the t and ω integrations may be performed. Finally, carrying out the remaining Z integrations leads directly to Eq. (44) as desired.

[33] A. Bardasis and J. R. Schrieffer, Phys. Rev. **121**, 1050 (1961).