already made [P. H. Smith <u>et al.</u>, Phys. Rev. Letters <u>6</u>, 686 (1961); see also L. N. Cooper, Phys. Rev. Letters <u>6</u>, 689 (1961)]. The theory discussed in the present Letter takes its simplest form if the single-particle electron states are plane waves or Bloch states. But clearly this is not necessary.

'Small effects due to the curvature of the Fermi

ling states as close to total momentum zero as possible. The device we have employed should not be elevated to the level of a universal principle; it merely provides a quick way to count the paired states.

surface have been neglected. There is no need in principle to do this. A pairing can be introduced, if

necessary, by enumeration of the states and by coup-

## $l \neq 0$ PAIRING IN SUPERCONDUCTORS

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and  $C_3$ :

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Gor'kov and Galitskii<sup>1</sup> have proposed one- and two-particle Green's functions for a superconductor whose Cooper pairs are in states of nonzero relative angular momentum. Anderson and Morel,<sup>2</sup> using BCS<sup>3</sup>-type states with parameters which depend on the direction as well as the magnitude of the momentum, start with an isotropic Hamiltonian but find an anisotropic state, with an energy gap which vanishes in certain directions in momentum space. The Gor'kov-Galitskii model, on the other hand, exhibits an isotropic energy gap; furthermore, it predicts a lower free energy than that of the Anderson-Morel states. However, attempts to construct a wave function for the isotropic state have so far been unsuccessful, which leaves unanswered the question of whether or not the above-mentioned Green's functions in fact describe the physical system. We propose to show that they do not, by demonstrating the impossibility of constructing a complete hierarchy of Green's functions, with the first two being given by those of Gor'kov and Galitskii. (Note that such a hierarchy can be constructed for the BCS case.)

We introduce the thermodynamic Green's function,<sup>4</sup>

$$G_{n}(1\cdots n, 1'\cdots n')$$

$$= (-i)^{n} \frac{\operatorname{Tr}\{e^{-\beta(H-\mu N)}T[\psi(1)\cdots\psi(n)\psi^{\dagger}(n')\cdots\psi^{\dagger}(1')]\}}{\operatorname{Tr}\{e^{-\beta(H-\mu N)}\}}$$
(1)

where  $H - \mu N$  is the reduced Hamiltonian, the indices refer to space-time points,  $\beta$  is the inverse temperature, and T is the Wick timeordering operator. We also find it useful to define the dynamical correlation functions<sup>4,5</sup>  $C_2$   $\begin{aligned} G_2(12;1'2') \\ &= G_1(11')G_1(22') - G_1(12')G_1(21') + C_2(12;1'2'), \\ G_3(123;1'2'3') \\ &= \mathfrak{C}[G_1(11')G_1(22')G_1(33')] + [C_2(12;1'2')G_1(33')] \\ &+ \text{cyclic perm. of } (123) + \text{cyclic perm. of } (1'2'3')] \\ &+ C_3(123;1'2'3'), \end{aligned}$ 

where G is the antisymmetrization operator for primed and unprimed indices separately. The interaction term in the reduced Hamiltonian is effective only for scattering pairs of opposite momenta. Thus a single-particle excitation has infinite lifetime. Then since  $G_3$  corresponds to the observation of the evolution of an odd number of excited particles, at least one of these must propagate freely, and  $C_3 = 0$ -at least at zero temperature. We note that the remaining  $G_3$  contains the properly antisymmetrized combination of each of the terms appearing. This approximation breaks off the infinite set of coupled Green's function equations of motion; we find

$$\begin{bmatrix} i \frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} \end{bmatrix} G_1(11')$$
  
=  $\delta(1-1') - \frac{i}{\Omega}(13 | V | 45)C_2(45; 1'3) + O(1/\Omega),$   
 $\begin{bmatrix} i \frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} \end{bmatrix} C_2(12; 1'2')$   
=  $\frac{i}{\Omega}(13 | V | 45)C_2(45; 1'2')G(23) + O(1/\Omega).$  (3)

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Summation (or integration) over repeated indices is implied here. We have necessarily used a nonlocal potential and have indicated the volume ( $\Omega$ ) dependence explicitly. Depending on our choice of  $C_2$ , (3) is just the set of equations obtained by Gor'kov<sup>6</sup> (for l = 0 pairing) or by Gor'kov and Galitskii.<sup>1</sup> These equations can now be used to obtain an explicit expression, correct to order  $1/\Omega$ , for the quantity

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m}\right]G_3(123;1'2'3'),$$

if we neglect  $C_3$  in the decomposition (2) of  $G_3$ . We already have another expression for this quantity, given by the equation of motion of  $G_3$ :

$$\begin{bmatrix} i \frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} \end{bmatrix} G_3(123; 1'2'3')$$
  
=  $\delta(1-1')G_2(23; 2'3') - \delta(1-2')$   
 $\times G_2(23; 1'3') + \delta(1-3')G_2(23; 1'2')$   
 $- (i/\Omega)(14|V|56)G_4(5623; 1'2'3'4).$  (4)

By comparing these two expressions, we find

$$(14 | V | 56)[G_4(5623; 1'2'3'4) - \{C_2G_1G_1\}]$$
  
=  $(14 | V | 56)[C_2(56; 1'4)C_2(23; 2'3')$   
+  $C_2(56; 2'4)C_2(23; 3'1')$   
+  $C_2(56; 3'4)C_2(23; 1'2')] + O(1/\Omega).$  (5)

Here we have indicated by  $\{C_2G_1G_1\}$  the properly antisymmetrized product of terms of the form

$$C_2(56; 1'4)G_1(22')G_1(33').$$

Equation (5) implies that

$$\begin{aligned} G_4(5623; 1'2'3'4) &= \{C_2G_1G_1\} + C_2(56; 1'4)C_2(23; 2'3') \\ &+ C_2(56; 2'4)C_2(23; 3'1') + C_2(56; 3'4)C_2(23; 1'2') \\ &+ G_4'(5623; 1'2'3'4), \end{aligned}$$

where  $G_4'$  contains only terms which give  $O(1/\Omega)$ when multiplied by  $(1/\Omega)(14|V|56)$  and summed over 5 and 6. Because of the symmetry of  $G_4$ , the right-hand side of (6) must be invariant under the permutation  $(1'2') \neq (3'4)$ . We note that for  $C_2$  factorizable,

$$C_2(12; 1'2') = f(12)\overline{f}(1'2')$$

this symmetry is obtained with any  $G_4'$  which itself exhibits it (e.g.,  $G_4'=0$ ). If this factorization cannot be made (as is true in the Gor'kov-Galitskii theory), then

$$G_{4}'(5623; 1'2'3'4)$$

$$= C_{2}(56; 3'2')C_{2}(23; 41') + C_{2}(56; 1'2')$$

$$\times C_{2}(23; 3'4') + G_{4}''(5623; 1'2'3'4), \quad (7)$$

where  $G_4''$  must have the desired symmetry. Consider

$$(14 | V | 56)[G_4'(5623; 1'2'3'4) - G_4'(5623; 3'41'2')]$$
  
=  $(14 | V | 56)[C_2(56; 3'2')C_2(23; 41')$   
 $-C_2(56; 1'4)C_2(23; 2'3')$   
 $+C_2(56; 1'2')C_2(23; 3'4)$   
 $-C_2(56; 3'4)C_2(23; 1'2')].$  (8)

If we explicitly insert Gor'kov and Galitskii's expression for  $C_2$  into Eq. (8), we find that the right-hand side is of order unity unless l = 0, when  $C_2$  becomes factorizable. But we have required  $VG_4' = O(1/\Omega)$  and the left-hand side of (8) is, therefore,  $O(1/\Omega)$ . This contradiction demonstrates the inconsistency of the Gor'kov-Galitskii decomposition.

Physically we can also point out some disturbing aspects of the Gor'kov-Galitskii theory. In the first place they suggest

$$C_{2}(12;1'2') = P_{l}(\theta)f(12)\overline{f}(1'2'), \qquad (9)$$

where  $\theta$  is the angle between  $\vec{r}_1 - \vec{r}_2$  and  $\vec{r}_1' - \vec{r}_2'$ . This implies a correlation between the direction of the angular momenta of pairs separated by an arbitrarily large amount in space-time. This feature of the correlations can be expressed in a different way. The equation for  $F_M^{\dagger} = Y_l^{-M} \vec{f}$ can be written in the form:

$$F_{M}^{\dagger}(1'2') = -iG(31')\Delta_{M}^{*}(33')G(3'2') + iF_{M}^{\dagger}(1'3)\sum\Delta_{M'}(33')F_{M'}^{\dagger}(3'2'), \quad (10)$$

where the gap  $\Delta_M$  is defined by

$$\Delta_{M}^{*}(12) = F_{M}^{\dagger}(34)(34 | V| | 12).$$
 (11)

(The asterisk denotes complex conjugate.) Thus

in every process of pair creation the system is required to remember how many pairs of each type it started with. Such considerations mitigate the initial physical attractiveness of the model due to its simplicity and help to indicate why the inconsistency described above arises.

The author would like to acknowledge helpful discussions with Professor J. Bardeen, Professor L. P. Kadanoff, and Professor J. R. Schrieffer on this and related topics.

\*National Science Foundation Predoctoral Fellow. <sup>1</sup>L. P. Gor'kov and V. M. Galitskii, J. Exptl. Theoret. Phys. U.S.S.R. <u>40</u>, 1124 (1961) [translation: Soviet Phys. - JETP 13, 792 (1961)].

<sup>2</sup>P. W. Anderson and P. Morel, Phys. Rev. <u>123</u>,

1911 (1961). See also V. J. Emery and A. M. Sessler, Phys. Rev. <u>119</u>, 43 (1960).

<sup>3</sup>J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. <u>108</u>, 1175 (1957).

<sup>4</sup>P. C. Martin and J. Schwinger, Phys. Rev. <u>115</u>, 1342 (1959).

<sup>5</sup>A discussion of these with reference to their applicability to the problem of superconductivity is given by A. Klein, Proceedings of the 1961 Midwest Conference on Theoretical Physics (unpublished), p. 148.

<sup>6</sup>L. P. Gor'kov, J. Exptl. Theoret. Phys. U.S.S.R. <u>34</u>, 735 (1958) [translation: Soviet Phys. - JETP <u>7</u>, 505 (1958)].

DIFFICULTY IN THE METHOD OF GREEN'S FUNCTIONS FOR A MANY-BODY SYSTEM\*

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In the last few years, the method of Green's functions,<sup>1</sup> based on the infinite set (S) of coupled equations (with boundary conditions) satisfied by the sequence of n-particle Green's functions, has been used extensively $2^{-6}$  in the theory of superconductivity.<sup>7</sup> While (S) is a consequence of the Schrödinger equation, it is often believed, although not proved, that the converse is also true. In fact, we have shown, by solving an example exactly, that (S) may possess spurious solutions, some of which lead to an energy lower than the true ground-state energy, and so do not correspond to any state wave function. Thus the Green's function method as usually formulated is not a complete dynamical description of the system, and requires in addition some criterion to distinguish these extraneous solutions from the correct one.

This work was developed in order to choose between two contradictory theories<sup>8-10</sup> of the possible superfluid phase of He<sup>3</sup>. These theories can be discussed in terms of the truncated pair Hamiltonian

$$H = \sum_{\vec{k}\sigma} (\epsilon_{\vec{k}} - \mu) a_{\vec{k}\sigma}^{\dagger} a_{\vec{k}\sigma}^{\dagger} + \Omega^{-1} \sum_{\vec{k}\vec{k}'} V_{\vec{k}\vec{k}'} a_{\vec{k}}^{\dagger} a_{\vec{k}}^{\dagger} a_{\vec{k}'}^{\dagger} a_{\vec{k$$

where  $a_{k\sigma}^{\dagger}$  t creates a plane wave of momentum

 $\vec{k}$  and spin  $\sigma$  in the volume  $\Omega$ . A model potential is chosen which vanishes unless  $\vec{k}$  and  $\vec{k}'$  lie inside a thin spherical shell centered on the Fermi surface, in which case

$$\Omega^{-1}V_{\vec{k}\vec{k}'} = -4\pi\lambda \sum_{m} Y_{2m}^{*}(\hat{k})Y_{2m}(\hat{k}').$$
(2)

For the pair Hamiltonian (1), asymptotically exact solutions<sup>5,6</sup> of (S) can be found for which all correlation functions<sup>3,6</sup> of third and higher order vanish like  $\Omega^{-1}$ . Two types of such solutions have been studied: One is the BCS type,<sup>7-9</sup> for which the second order correlation function is

$$C_{2}(\vec{k}^{\dagger} t_{1}, -\vec{k}^{\dagger} t_{2}; \vec{k}'^{\dagger} t_{1}', -\vec{k}'^{\dagger} t_{2}') = F(\vec{k}, t_{1} - t_{2})F^{+}(\vec{k}', t_{1}' - t_{2}'); \qquad (3)$$

the other, recently given by Gor'kov and Galitskii,<sup>10</sup> is based on the more general nonseparable form

$$C_{2} = \sum_{m} F_{m}(\mathbf{k}, t_{1} - t_{2}) F_{m}^{+}(\mathbf{k}', t_{1}' - t_{2}'), \qquad (4)$$

where  $F_m(\vec{k}, t)$  is proportional to  $Y_{2m}(\hat{k})$ . The BCS approach yields a ground state and an excitation spectrum which are anisotropic<sup>8,9</sup>; in contrast, the GG method leads to an isotropic system. Furthermore, the ground-state energy per unit volume  $W_{\text{GG}}$  obtained by GG is lower than  $W_{\text{BCS}}$ .