THEORY OF THE KNIGHT SHIFT IN SUPERCONDUCTORS*

Leon N. Cooper†
Department of Physics, Brown University, Providence, Rhode Island
(Received March 5, 1962; revised manuscript received April 10, 1962)

Observation of a finite Knight shift[1] in superconductors, which indicates that the electron paramagnetic spin susceptibility does not go to zero, even at $T=0$, has presented a major problem[2] for the theory[3] since an electron spin paramagnetism seems to necessitate the loss of pair correlation energy; but this pairing energy is orders of magnitude larger than the magnetic energy. Several theoretical suggestions have been made[4] depending on various effects such as possible spin-orbit interactions, or electron mean free paths, but none of these has yet produced a satisfactory consistent explanation.

In this Letter we present a generalization of the theory of superconductivity which yields a finite Knight shift, while making limited modifications in the predictions of the previous theory. This theory is expected to be valid for weak magnetic fields and for samples where the field penetration is complete. It can very likely be extended to include strong fields and those portions of a bulk specimen where there is field penetration.

The essential idea is to abandon the pairing of electrons with identical total momentum for pairings with differing total momentum. That such a theory could give a finite Knight shift has been known for some time. (Pipard and Heine[5] made this point several years ago.) The problem has been to construct a consistent theory which embodies this idea.

This we do in what follows. The restriction of all the electron pairs to the identical momentum (zero for the ground state) is necessitated by the need to couple every pair state to all others (or at least a large number of others) in order to form the coherent ground state, and by the conservation of linear momentum in the scattering of electron pairs. The first condition is the heart of the theory and must be maintained. The second condition, however, is not necessary unless one has translational invariance in the material.

In most materials, especially in the tiny specimens under the conditions which have been employed to measure the Knight shift, there are very likely sufficient strains, defects, and conglomerations of impurities so that the material is not the same from point to point. Therefore, we need not assume that the electron-electron interaction is independent of absolute position or that momentum is conserved in transitions. To get an idea of how much variation there must be, we note that the magnetic energies are of the order of 10^{-17} erg. To explain the observed Knight shift for such small energies requires changes of total momentum in electron scatterings of the order of

$$(\hbar^2/m)k_F\delta k \simeq 10^{-17} \text{ erg},$$

or

$$\delta k \simeq 10^2 \text{ cm}^{-1}. \quad (1)$$

Such changes in total momentum would be produced if the scattering interaction varied substantially over distances of 10^{-2} cm. This does not seem to be unlikely in the experimental samples.[6]

As has been done before, the pair operators,

$$b_{\vec{k}} = C_{-\vec{\kappa}} C_{\vec{\kappa}}, \quad b_{\vec{k}}^* = C_{\vec{\kappa}}^* C_{-\vec{\kappa}}^*, \quad (2)$$

are associated with the pair occupation amplitudes $\alpha_{\vec{\kappa}}$ and $\beta_{\vec{\kappa}}$ where, for the ground state Ψ_0,

$$(\Psi_0, b_{\vec{k}}^* b_{\vec{k}} \Psi_0) = |\beta_{\vec{\kappa}}|^2 = h_{\vec{k}},$$

$$|\alpha_{\vec{\kappa}}|^2 + |\beta_{\vec{\kappa}}|^2 = 1,$$

$$\alpha_{\vec{\kappa}} = \alpha_{-\vec{\kappa}} = \alpha_{\vec{\kappa}}^*, \quad \beta_{\vec{\kappa}} = -\beta_{-\vec{\kappa}}. \quad (3)$$

However, now $\vec{\kappa}$ means $(\vec{k}+\frac{1}{2}\delta\vec{k})\uparrow$ while $-\vec{\kappa}$ means $-(\vec{k}-\frac{1}{2}\delta\vec{k})\downarrow$. The vector $\delta\vec{k}$ is directed along $\vec{k}$ and has a magnitude, δk, which depends only on the magnetic field (which is in the direction of the up spin) and on the spatial variation of the electron-electron interaction. The amplitude for the occupation or nonoccupation of the pair states $[-(k-\frac{1}{2}\delta k)\downarrow, (k+\frac{1}{2}\delta k)\uparrow]$ are given by $\alpha_{\vec{\kappa}}$ and $\beta_{\vec{\kappa}}$. With this connection we have paired every down spin with an up spin, oppositely directed but with somewhat larger momentum.[7] This represents a departure from the usual pairing of time-reversed states. (See, for example, Anderson's paper.[4]) If the electron-electron interaction has some spatial variation, the loss in correlation energy due to the new pairing can be compensated by a gain in μH energy so that the pairing proposed above yields a lower total energy.

Due to the magnetic interaction the Fermi sphere of up spins swells by $\frac{1}{2}\delta k$ while the sphere of down spins contracts by the same amount. The relation of wave numbers at the Fermi surface is

$$k_{F\uparrow}=k_F+\tfrac{1}{2}\delta k, \quad k_{F\downarrow}=k_F-\tfrac{1}{2}\delta k. \tag{4}$$

If we now include the pairing energy, we obtain the following for the difference in energy at $T=0$ between the normal state in zero magnetic field and the superconducting state in the uniform magnetic field H. (We assume complete penetration and neglect orbital magnetic energies for the present.)

$$\begin{aligned} W_s(H)-W_n(0) = &\sum_{k>k_F} 2h_{\vec{k}}\epsilon + \sum_{k<k_F}(1-h_{\vec{k}})2|\epsilon| \\ &+\tfrac{3}{2}N\mathcal{E}_F(\delta k/k_F)^2-3\mu HN(\delta k/k_F) \\ &+\sum_{\vec{k}\vec{k}'}V_{\vec{k}',\vec{k}}(\Delta K/k_F)[h_{\vec{k}}(1-h_{\vec{k}})h_{\vec{k}'}(1-h_{\vec{k}'})]^{1/2}. \end{aligned} \tag{5}$$

The first line gives the increase in kinetic energy due to the superconducting correlation, measured from $\mathcal{E}_{F\uparrow}$ and $\mathcal{E}_{F\downarrow}$. The excitation energy of a normal pair, to a sufficient approximation, turns out to be just the same as in the absence of the field:

$$2\epsilon=(\epsilon_\uparrow+\epsilon_\downarrow)=(\mathcal{E}_\uparrow+\mathcal{E}_\downarrow-\mathcal{E}_{F\uparrow}-\mathcal{E}_{F\downarrow}). \tag{6}$$

The second line gives the increase in kinetic energy and the decrease in magnetic energy to terms of order $(\delta k/k_F)^2$ due to the shift of the up and down spheres, where N is the number of conduction electrons of one spin; the third line gives the energy due to pair correlations. The scattering matrix element, $V_{\vec{k}'\vec{k}}(\Delta K/k_F)$, is a function of the change in total momentum, ΔK, in the scattering from one pair state to another. In contrast to the usual treatment, V is not a delta function of ΔK, but is assumed to vary smoothly.

This is so because we have relaxed the assumption usually made that the electron-electron interaction is spatially invariant. For the experimental samples there is no reason to doubt that the tiny variation of the electron-electron interaction required to explain the Knight shift would be present. In fact, similar variations are not unlikely in bulk materials. Under these circumstances an exploration of the consequences on the theory of superconductivity of spatially noninvariant electron-electron interactions would be necessary even in the absence of the Knight-shift experiments.

The energy of the system is minimized with respect to $h_{\vec{k}}$ and $\delta k/k_F\equiv x$. The variation in $h_{\vec{k}}$ yields

$$h_{\vec{k}}=\tfrac{1}{2}(1-\epsilon/E_{\vec{k}}), \tag{7}$$

$$E_{\vec{k}}=(\epsilon^2+\Delta_{\vec{k}}^2)^{1/2}, \tag{8}$$

where $\Delta_{\vec{k}}$ satisfies the familiar integral equation:

$$\Delta_{\vec{k}}(\delta k/k_F)=-\tfrac{1}{2}\sum_{\vec{k}'}V_{\vec{k}'\vec{k}}(\Delta K/k_F)\frac{\Delta_{\vec{k}'}(\delta k/k_F)}{E_{\vec{k}'}}. \tag{9}$$

In order to make a rough calculation we assume that $V_{\vec{k}'\vec{k}}(\Delta K/k_F)$ varies slowly in $\Delta K/k_F$ near $\Delta K/k_F=0$, and replace $\Delta K/k_F$ by an average value of total momentum transfer:

$$\langle\Delta K/k_F\rangle_{\rm av}=\delta k/k_F=x. \tag{10}$$

We make the usual further assumption that the interaction is a constant in an interaction region $|\epsilon|,\ |\epsilon'|\leq(\hbar\omega)_{\rm av}$. Then $V_{\vec{k}'\vec{k}}(\Delta K/k_F)$ can be replaced by

$$\begin{aligned} V_{\vec{k}'\vec{k}}(\Delta K/k_F)&=-V(x)\,|\epsilon|,\quad |\epsilon'|\leq(\hbar\omega)_{\rm av} \\ &=0 \text{ otherwise.} \end{aligned} \tag{11}$$

If we now neglect small differences in the densities of states at the two Fermi surfaces, we obtain formulas analogous to those of BCS. In particular (in the weak-coupling limit)

$$\epsilon_0(x)=2(\hbar\omega)_{\rm av}\exp\left(\frac{-1}{N(0)V(x)}\right). \tag{12}$$

The variation in x yields

$$0=3N\mathcal{E}_Fx-3\mu HN+\sum_{\vec{k}\vec{k}'}\left[\frac{\partial}{\partial x}(-V(x))\right][h_{\vec{k}}(1-h_{\vec{k}})h_{\vec{k}'}(1-h_{\vec{k}'})]^{1/2}. \tag{13}$$

The last term is just the variation in pair correlation energy with change of average total momentum transfer; a parabolic approximation for small x gives

$$\sum_{\vec{k}\vec{k}'}\left[\frac{\partial}{\partial x}(-V)\right][h_{\vec{k}}(1-h_{\vec{k}})h_{\vec{k}'}(1-h_{\vec{k}'})]^{1/2}=a(H)x. \tag{14}$$

We thus obtain

$$x=\frac{\mu H}{\mathcal{E}_F}\bigg/\left(1+\frac{a(H)}{3N\mathcal{E}_F}\right). \tag{15}$$

This gives an electron spin susceptibility in the superconducting state:

$$\chi_s/\chi_n=1\bigg/\left(1+\frac{a(H)}{3N\mathcal{E}_F}\right). \tag{16}$$

Since it is presumed that the interaction energy is a minimum when $x=0$, $a(H)$ must be positive. We therefore find that the spin susceptibility is decreased in the superconductor but is not necessarily zero.

An expression for $a(H)$ can be derived. It depends on the second derivative of $\epsilon_0(x)$ with respect to x. If this should be zero (no variation in the interaction energy with the average total momentum change x), then the spin susceptibility in the superconductor will be the same as that in the normal metal. The precise magnitude of χ_s will vary from sample to sample and will depend on the nonuniformity of the materials. There should be no marked size dependence and, assuming $a(H)$ does not vary rapidly in H, no marked dependence on the strength of the magnetic field. This is in accord with the observations of Androes and Knight.[1] There should be a relation between the Knight shift and small shifts in T_c.

As to the other properties of superconductors, a quasi-particle spectrum can be defined; single-particle excitations will be separated from the ground state by the energy gap Δ; and the thermodynamic properties should be quite similar to previous theory. There will be alterations in the coherence properties, but it seems that these will yield quantitative rather than qualitative changes. In the absence of magnetic fields (if the scattering matrix elements are a maximum for zero change of total momentum, which is likely) the usual BCS state is the ground state. Thus these considerations apply primarily to small specimens, thin films, or to the region in bulk specimens where magnetic fields penetrate.

A more detailed investigation of the consequences of this generalized theory on the various properties of superconductors: coherence effects, flux quantization, etc., is being carried out.

A final word might be said concerning the deep mystery in the theory of superconductivity, the pairing condition; this is somewhat clarified (or perhaps obscured) by what has been done above. It seems clear now that the choice of singlet spin states which is due to the nature of the electron-electron potential, and the choice of identical total momentum for each pair which is due to translational invariance, are not essential. What is left is the isolation of the interaction to a subset of pairs—or the strong correlation of pairs of specially chosen electrons. I believe this is intrinsically related only to the Fermi statistics which the individual electrons satisfy and is due to the fact that these statistics seem to prevent, under the conditions of the problem (weak interaction over a small shell surrounding the Fermi surface), any further correlation than that of pairs; triplets or larger combinations seem to be excluded, and the correlation between pairs is apparently very weak compared to the pair correlation. A simple model which seems, in fact, to display these properties will be presented in the future.

The author would like to thank Professor J. R. Schrieffer for directing his attention to a missing factor of one-half in the second line of Eq. (5). He also wishes to express his appreciation to H. J. Lee, B. Schwartz, and W. Silvert for many helpful conversations.

---

*This work was supported in part by ARPA (Advanced Research Projects Agency) and the U. S. Atomic Energy Commission.

†Alfred P. Sloan Research Fellow.

[1]F. Reif, Phys. Rev. 106, 208 (1957); G. M. Androes and W. D. Knight, Phys. Rev. Letters 2, 385 (1959); Phys. Rev. 121, 779 (1961).

[2]K. Yosida, Phys. Rev. 110, 769 (1958).

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

[4]R. A. Ferrell, Phys. Rev. Letters 3, 262 (1959); P. C. Martin and L. P. Kadanoff, Phys. Rev. Letters 3, 322 (1959); J. R. Schrieffer, Phys. Rev. Letters 3, 323 (1959); P. W. Anderson, Phys. Rev. Letters 3, 325 (1959).

[5]A. B. Pippard and V. Heine, Phil. Mag. 3, 1046 (1958).

[6]It should be emphasized that, in contrast to some previous attempts to explain the Knight shift which have relied on modifications of the single-particle states, due presumably to the small sample size, we here explore the consequences of an electron-electron interaction which is not spatially invariant. Thus momentum is not conserved in transitions and an electron pair in an eigenstate of total momentum can scatter into a pair with different total momentum.

That the properties of superconductors are affected by electron-electron interactions which vary in space seems to be a direct consequence of observations already made [P. H. Smith et al., Phys. Rev. Letters 6, 686 (1961); see also L. N. Cooper, Phys. Rev. Letters 6, 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.

[7]Small effects due to the curvature of the Fermi 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 coupling 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.

$l \neq 0$ PAIRING IN SUPERCONDUCTORS

Daniel Hone*
Department of Physics, University of Illinois, Urbana, Illinois
(Received March 15, 1962)

Gor'kov and Galitskii[1] 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,[2] using BCS[3]-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,[4]

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

where $H-\mu N$ is the reduced Hamiltonian, the indices refer to space-time points, β is the inverse temperature, and T is the Wick time-ordering operator. We also find it useful to define the dynamical correlation functions[4,5] C_2 and C_3:

$$G_2(12;1'2') = G_1(11')G_1(22') - G_1(12')G_1(21') + C_2(12;1'2'),$$

$$G_3(123;1'2'3') = \mathcal{A}[G_1(11')G_1(22')G_1(33')] + [C_2(12;1'2')G_1(33') + \text{cyclic perm. of }(123) + \text{cyclic perm. of }(1'2'3')] + C_3(123;1'2'3'), \tag{2}$$

where $\mathcal{A}$ 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

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m}\right]G_1(11') = \delta(1-1') - \frac{i}{\Omega}(13|V|45)C_2(45;1'3) + O(1/\Omega),$$

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m}\right]C_2(12;1'2') = \frac{i}{\Omega}(13|V|45)C_2(45;1'2')G(23) + O(1/\Omega). \tag{3}$$