Time- and Position-Dependent Superconductivity

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Anderson's time-dependent generalization of the BCS theory of superconductivity and Parmenter's position-dependent generalization have successfully been combined. The result is a powerful formalism which is capable of treating a number of previously intractable problems. The derived boundary conditions are consistent with but more general than the boundary conditions previously assumed by (1) Ginzburg and Landau, and (2) Parmenter. The formalism is strikingly analogous to "micromagnetics," the continuum theory of ferromagnetism in solids.

IN 1958, Anderson[1] generalized the BCS theory[2] of superconductivity to include time-dependent problems. Last year, the writer[3] generalized the BCS theory to include position-dependent problems. These two generalizations have now successfully been combined by making use of a hint supplied by the continuum theory of ferromagnetism in solids.[4] The result is a powerful formalism which allows one to solve a number of problems which have eluded previous analysis. Certain questions of principle are also resolved, in particular boundary conditions.

At $T=0$, the BCS theory[2] makes use of the Hamiltonian

$$\mathcal{H}_{\rm BCS}=2\sum_{k>k_F}\epsilon_k b_k^* b_k+2\sum_{k<k_F}|\epsilon_k|\,b_k b_k^*-\sum_{k,k'}{}' V_{kk'}b_{k'}^* b_k,$$

$$b_k=c_{-k\downarrow}c_{k\uparrow},\quad b_k^*=c_{k\uparrow}^* c_{-k\downarrow}^*.$$

(The prime on the double summation indicates that the term $\mathbf{k}=\mathbf{k}'$ is missing.) Here $V_{kk'}$ is the interaction potential, ϵ_k the one-electron energy associated with the wave vector $\mathbf{k}$ (the zero of energy being taken at the Fermi surface $k=k_F$). The b's are the Cooper pair creation and annihilation operators; the c's are the electron creation and annihilation operators. Anderson[1] pointed out that this Hamiltonian could be rewritten

$$\mathcal{H}_{\rm BCS}=-2\sum_k \epsilon_k s_{3k}-\sum_{k,k'}{}' V_{kk'}(s_{1k}s_{1k'}+s_{2k}s_{2k'})+\text{const}, \quad (1)$$

where

$$s_{1k}=\tfrac{1}{2}(b_k^*+b_k),$$
$$s_{2k}=\tfrac{1}{2}i(b_k^*-b_k), \quad (2)$$
$$s_{3k}=\tfrac{1}{2}(1-2b_k^* b_k),$$

are the x, y, and z components, respectively, of an isotopic-spin operator $\mathbf{s}_k$, spin up representing absence and spin down presence of the Cooper pair associated with wave vector $\mathbf{k}$. From the anticommutation relations satisfied by the electron creation and annihilation operators, it follows that $\mathbf{s}_k\times\mathbf{s}_{k'}=i\mathbf{s}_k\delta_{kk'}$, so that $\mathbf{s}_k$ is indeed a spin operator. In this fashion, Anderson made the BCS theory of superconductivity look like a problem in ferromagnetism. The variational derivative of $\mathcal{H}_{\rm BCS}$ with respect to $\mathbf{s}_k$ is proportional to the effective magnetic field seen by $\mathbf{s}_k$. The condition that $\mathbf{s}_k$ be parallel to this magnetic field leads directly to the BCS integral equation for the energy gap at $T=0$. The energy required to flip over $\mathbf{s}_k$ in its magnetic field corresponds to a pair excitation energy in the BSC theory. A group of spins magnetically precessing in a coherent fashion corresponds to a collective excitation.

In this fashion, Anderson was able to generalize the BCS theory to include time-dependent problems. A very natural extension will allow position-dependent problems to be handled as well. One imitates the procedure pioneered by Landau and Lifshitz[5] in extending ferromagnetism to position-dependent problems (e.g., domain walls). The Hamiltonian is

$$\mathcal{H}=\int\mathcal{H}(\mathbf{R})d^3R, \quad (3)$$

$$\mathcal{H}(\mathbf{R})=\mathcal{H}_{\rm BCS}(\mathbf{R})+\mathcal{H}_{\rm EX}(\mathbf{R}), \quad (4)$$

$$\mathcal{H}_{\rm EX}(\mathbf{R})=\frac{\hbar^2}{4m}\sum_k\{(\nabla_R s_{1k})^2+(\nabla_R s_{2k})^2+(\nabla_R s_{3k})^2\}, \quad (5)$$

where now $\mathbf{s}_k$ is a function of $\mathbf{R}$ and satisfies the commutation relation

$$\mathbf{s}_k(\mathbf{R})\times\mathbf{s}_{k'}(\mathbf{R}')=i\mathbf{s}_k(\mathbf{R})\delta_{kk'}\delta(\mathbf{R}-\mathbf{R}'). \quad (6)$$

In the continuum theory of ferromagnetism, so-called micromagnetics,[4] $\mathcal{H}_{\rm EX}$ represents the contribution of exchange to the energy density. The only difference is that here the squares of the gradients of the components of $\mathbf{s}_k$ are multiplied by $\hbar^2/4m$ rather than by a constant proportional to the exchange integral. We will later demonstrate the correctness of this procedure.

The time derivative of $\mathbf{s}_k$ is given by

$$i\hbar(d\mathbf{s}_k/dt)=[\mathbf{s}_k,\mathcal{H}], \quad (7)$$

[1] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).
[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[3] R. H. Parmenter, Phys. Rev. **132**, 2490 (1963).
[4] W. F. Brown, Jr., *Micromagnetics* (Interscience Publishers, Inc., New York, 1963); S. Shtrikman and D. Treves, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, Chap. 8.
[5] L. Landau and E. Lifshitz, Phys. Z. Sowjet. 8, 153 (1935).

the right-hand side being the commutator of $\mathbf{s}_k$ and $\mathcal{H}$. With the aid of (6), this can be rewritten

$$\hbar(d\mathbf{s}_k/dt)=\mathbf{s}_k\times\mathbf{H}_k, \tag{8}$$

where

$$\begin{aligned}\mathbf{H}_k\equiv&-(\delta\mathcal{H}/\delta\mathbf{s}_k)\equiv-(\partial/\partial\mathbf{s}_k-\boldsymbol{\nabla}_R\cdot\partial/\partial\boldsymbol{\nabla}_R\mathbf{s}_k)\mathcal{H}\\&=2\hat{u}_1[(\hbar^2/4m)\nabla_R{}^2s_{1k}+\sum_{k'}{}' V_{kk'}s_{1k'}]\\&\quad+2\hat{u}_2[(\hbar^2/4m)\nabla_R{}^2s_{2k}+\sum_{k'}{}' V_{kk'}s_{2k'}]\\&\quad+2\hat{u}_3[(\hbar^2/4m)\nabla_R{}^2s_{3k}+\epsilon_k]\end{aligned} \tag{9}$$

is (in suitable units) the effective magnetic field seen by the spin vector $\mathbf{s}_k$. ($\hat{u}_i$ is a unit vector along the ith direction in isotopic-spin space.) Note that the effective magnetic field is the negative of the so-called variational derivative[6] of $\mathcal{H}$ with respect to $\mathbf{s}_k$. In calculating the commutator of $\mathcal{H}$ and $\mathbf{s}_k$, one performs a partial integration with respect to $\mathbf{R}$ of the terms $(\boldsymbol{\nabla}_R s_{ik})^2$ in order to avoid having to evaluate the commutator of s_{ik} and $\boldsymbol{\nabla}_R s_{ik}$. This partial integration[7] leads to the appearance of $\nabla_R{}^2 s_{ik}$ in $\mathbf{H}_k$.

It should also lead to a delta-function contribution to $\mathbf{H}_k$ on the surface[8] (i.e., a contribution to $\mathbf{H}_k$ which is infinite on the surface and zero everywhere else). Such a contribution appearing in (8) would lead to pathological behavior in $\mathbf{s}_k$. The requirement that this surface contribution to $\mathbf{H}_k$ vanish thus leads automatically to boundary conditions. This delta-function contribution is

$$\begin{aligned}(\delta\mathcal{H}_{\mathrm{SUR}}/\delta s_{2k})&=(\partial s_{2k}/\partial n)-(s_{2k}/s_{1k})(\partial s_{1k}/\partial n),\\(\delta\mathcal{H}_{\mathrm{SUR}}/\delta s_{3k})&=(\partial s_{3k}/\partial n)-(s_{3k}/s_{1k})(\partial s_{1k}/\partial n).\end{aligned} \tag{10}$$

Since the magnitude of $\mathbf{s}_k$ is $\frac{1}{2}$, only two of its three components can be independently varied. Because of the form of $\mathcal{H}$, one of these two must be s_{3k} (to insure the most general variation in $\mathcal{H}$). It was assumed in Eq. (10) that the other independent component is s_{2k}; it could equally well have been chosen s_{1k}. At the surface of a superconductor, (10) must be set equal to zero.[9] An obvious generalization is that (10) should be continuous as one moves along a one-electron trajectory through an interface separating two metals (or a normal-superconducting interface[10]).

Consider the static solution to Eq. (8) where $d\mathbf{s}_k/dt=0$. Assume that $\mathbf{s}_k$ lies in the xz plane of isospin space, i.e.,

$$\begin{aligned}s_{1k}&=\tfrac{1}{2}\sin\theta_k,\\s_{2k}&=0,\\s_{3k}&=\tfrac{1}{2}\cos\theta_k.\end{aligned} \tag{11}$$

Thus

$$\begin{aligned}H_{1k}&=+(\hbar^2/4m)[\cos\theta_k\nabla_R{}^2\theta_k-\sin\theta_k(\boldsymbol{\nabla}_R\theta_k)^2]+2\Delta_k,\\H_{2k}&=0,\\H_{3k}&=-(\hbar^2/4m)[\sin\theta_k\nabla_R{}^2\theta_k+\cos\theta_k(\boldsymbol{\nabla}_R\theta_k)^2]+2\epsilon_k,\end{aligned} \tag{12}$$

where, by definition,

$$\Delta_k\equiv\tfrac{1}{2}\sum_{k'}{}' V_{kk'}\sin\theta_{k'}. \tag{13}$$

Thus, $\mathbf{s}_k\times\mathbf{H}_k=0$ becomes

$$(\hbar^2/8m)\nabla_R{}^2\theta_k=\epsilon_k\sin\theta_k-\Delta_k\cos\theta_k. \tag{14}$$

Making the substitution

$$\theta_k=\arctan\left\{\frac{2[h_k(1-h_k)]^{1/2}}{1-2h_k}\right\}, \tag{15}$$

Eq. (14) becomes

$$\begin{aligned}&2\epsilon_k-(\hbar^2/8m)\{[h_k(1-h_k)]^{-1/2}\boldsymbol{\nabla}_R\}^2h_k\\&\quad=(1-2h_k)[h_k(1-h_k)]^{-1/2}\sum_{k'}{}' V_{kk'}[h_{k'}(1-h_{k'})]^{1/2}.\end{aligned} \tag{16}$$

This is precisely the equation previously obtained by the writer[3] using a completely different method of generalizing the BCS theory to position-dependent problems. This check demonstrates the validity of generalizing Anderson's theory by introducing $\mathcal{H}_{\mathrm{EX}}(\mathbf{R})$, which represents center-of-mass kinetic energy density of Cooper pairs ($\mathbf{R}$ is the center-of-mass coordinate of a Cooper pair).

Substitution of Eqs. (11) and (15) into (10) results in precisely the boundary conditions assumed in Ref. 3, namely, continuity of h_k and $\partial h_k/\partial n$ at an interface between two metals while allowing for the possibility of a discontinuous change in signature of $h_k{}^{1/2}$ at the interface, a possibility crucial for quenching of repulsive $V_{kk'}$ on the normal-metal side of a superconductor-normal-metal sandwich. In the isotopic-spin picture, the two independently varied components of $\mathbf{s}_k$, namely s_{2k} and s_{3k}, are continuous at the interface, while the remaining component s_{1k} may suffer a discontinuous change in signature. At a free surface of a superconductor, Eq. (10) implies that $\partial h_k/\partial n$ vanish. In their most general form, the boundary conditions of the present paper are consistent with, but more general than, the boundary conditions previously assumed either by the writer[3] or by Ginzburg and Landau[11] in their phenomenological theory of superconductivity.

Position-dependent collective and pair excitations (but not single-particle excitations) can be studied by solving Eq. (7) for characteristic precessional fre-

[6] See, e. g., H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1950), p. 353.

[7] An analogous procedure is used in the second-quantization of Schrödinger's equation. See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 338.

[8] The idea of a delta-function surface magnetic field in micromagnetics was introduced by C. Kittel and C. Herring, Phys. Rev. **77**, 725 (1950).

[9] This boundary condition was first derived for micromagnetics by W. F. Brown, Jr., Phys. Rev. **58**, 736 (1940).

[10] R. H. Parmenter (to be published).

[11] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

quencies, just as was done by Anderson for the position-independent case. A possible example is a pair excitation localized and bound near the surface of a superconductor. (The word "bound" implies that the excitation energy lies in the energy gap of the superconductor.) Such a localized pair excitation could occur in the absence of localized single-particle excitations, the position-dependent pairing potential $\Delta_k(\mathbf{R})$ being capable of binding the former but not the latter.[12]

A second type of dynamic problem solvable with the present formalism is that of the inertia or effective mass associated with a moving normal-superconducting interface. Just as in the analogous ferromagnetic problem of a moving domain wall,[13] the kinetic energy of the interface results from the additional effective magnetic field required to cause $\mathbf{s}_k(\mathbf{R})$ to precess as the interface passes through $\mathbf{R}$.

[12] For closely related discussions, see Secs. I and VI of Ref. 3.

[13] C. Kittel and J. K. Galt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3.

In addition to the *effective* magnetic fields discussed thus far, the presence of a *real* magnetic field in a superconductor can be included in the equations of motion by replacing ∇_R by $\nabla_R - i(2e/\hbar c)\mathbf{A}(\mathbf{R})$, $\mathbf{A}(\mathbf{R})$ being the magnetic vector potential at $\mathbf{R}$. This procedure, completely analogous to that used by Ginzburg and Landau,[11] takes account of the effect of the real magnetic field on the center-of-mass motion of the Cooper pairs, but does not properly describe magnetic effects on the internal motion of the Cooper pairs.

Note added in proof. By returning to the methods of Ref. 3, it can be shown that ∇_R should be replaced by $\nabla_R - i(2e/\hbar c)\mathbf{A}(\mathbf{R})$ only in the terms of $\mathcal{H}_{EX}$ containing s_{1k} and s_{2k}, not in those containing s_{3k}. (For the latter terms, ∇_R should remain unchanged.) Furthermore, only the so-called transverse portion of $\mathbf{A}$ should be included in this replacement. Any longitudinal component of $\mathbf{A}$, corresponding to center-of-mass momentum of Cooper pairs, should be introduced as an additional kinetic energy in $\mathcal{H}_{BCS}$, having the form $(1/4m)(2e\mathbf{A}_l/c)^2 \sum_k (\frac{1}{2} - s_{3k})$.

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Spin-Wave Analysis of the Sublattice Magnetization Behavior of Antiferromagnetic and Ferromagnetic $CrCl_3$†

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The temperature and magnetic-field dependences of the sublattice magnetization in the hexagonal layer-type compound $CrCl_3$ ($T_N = 16.8$°K) have been deduced from the ^{53}Cr nuclear magnetic resonance (NMR) for $0.4 \leq T \leq 8.1$°K and $0 \leq H \leq 10$ kOe. The observed zero-field data can be accounted for over the whole temperature range by a renormalized spin-wave model based on isotropic ferromagnetic (J_T) intralayer and antiferromagnetic (J_L) interlayer exchange interactions in the presence of a weak effective anisotropy field (H_A). Appropriate renormalized spin-wave dispersion relations are given for the four-sublattice antiferromagnetic (weak-field) and two-sublattice ferromagnetic (strong-field) equilibrium spin configurations. The validity of the two-dimensional approximation to these states is examined in detail for $k_B T > 2|J_L| z_L S$ and $|J_L| \ll J_T$. It is shown that under these conditions the sublattice magnetizations for $J_L < 0$ and $J_L > 0$ are identical. The three-dimensional zero-field spin-wave fit gives $J_T/k_B = 5.25$°K, $H_A(0) = 650$ Oe and a 0°K, zero-field ^{53}Cr frequency $\nu(0) = 63.318$ Mc/sec. Parallel magnetic susceptibilities calculated with these parameters in the range $0.4 < T \leq 8.1$°K are in quantitative agreement with experimental values based on measured splittings of the ^{53}Cr NMR in weak fields ($H \leq 100$ Oe). The interlayer constant, $J_L/k_B = -0.018$°K, used in the spin-wave calculations was obtained from single-crystal bulk magnetization measurements ($\chi_\perp = 9.9$ emu/mole for $T \leq 4$°K), corrected for demagnetizing effects. These measurements show that the net anisotropy in the ferromagnetic state (i.e., $H \geq 1.68$ kOe) is zero, presumably because of a cancellation of dipolar and single-ion contributions. The sublattice magnetization behavior in the ferromagnetic state appears to be strongly influenced by long-range dipolar interactions, as evidenced by significantly lower values of $M(T,H)/M(0)$ for $\mathbf{M} \| c$ than for $\mathbf{M} \perp c$.

I. INTRODUCTION

THE application of spin-wave theory to the measured sublattice magnetizations of $CrCl_3$[1,2] and $CrBr_3$[3,4] has provided considerable insight into the unusual magnetic properties of these isomorphous hexagonal, layer-type compounds. The exchange interactions in both cases are characterized by relatively

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