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Theory of the Knight Shift and Flux Quantization in Superconductors*

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Some of the consequences of a generalization of the theory of superconductivity which yields a finite Knight shift(1) are presented. In this theory, by introducing an electron-electron interaction which is not spatially invariant, the pairing of electrons with varying total momentum is made possible.(2) An expression for χ_s (the spin susceptibility in the superconducting state) is derived. In general χ_s is smaller than χ_n but is not necessarily zero. The precise magnitude of χ_s will vary from sample to sample and will depend on the non-uniformity of the samples. There should be no marked size dependence and no marked dependence on the strength of the magnetic field; this is in accord with observation.(3) The basic superconducting properties are retained, but there are modifications in the various electromagnetic and thermal properties since the electrons paired are not time reversal conjugates of one another. In particular the consequences of this generalized theory on flux quantization arguments are presented.

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A generalization of the theory of superconductivity which yields a finite Knight shift has recently been proposed.[1] In this the assumption usually made that the electron-electron interaction is spatially invariant has been relaxed; it thus becomes possible by a coherent mixing of electron pair states of different total momentum to construct a superconducting state with a finite spin susceptibility. There seems to be no reason to doubt that the variation of the electron-electron interaction required to explain the Knight shift would be present in the samples on which experiments have been done. In fact, similar variations are possible in bulk materials. Under these circumstances an exploration of the consequences on the theory of superconductivity of spatially non-invariant electron-electron interactions would be necessary even in the absence of the Knight-shift experiments. In this note we present some results obtained in such an investigation.

The idea underlying this theory could be put to a direct test by an experiment which compares the Knight shifts for several samples of similar size and construction but of varying composition. The ratio of the spin susceptibilities in the superconducting and normal states as given by Eq. (16) of reference 1 can be written

$$\frac{\chi_s}{\chi_n} = \left[1 + \tfrac{1}{2} \left| \frac{V''}{V} \right| \left(\frac{\epsilon_o}{\mathcal{E}_F^*} \right)^2 \frac{1}{N(o)V} \right]^{-1} \tag{1}$$

where $\mathcal{E}_F^* \equiv \dfrac{\hbar^2 k_F^2}{2m^*}$, m^* is the electron effective mass at the Fermi surface, and

$$V(x) = V_o + \tfrac{1}{2} V'' x^2 + \ldots \tag{2}$$

is the expansion of the scattering matrix element in powers of the average total momentum transfer in electron-electron scattering:

$$x = \left(\frac{\Delta K}{k_F}\right)_{av} = \frac{\delta k}{k_F}\ . \tag{3}$$

If, for example, the Knight shift could be measured for a sample of metal A, for a similar sample of metal B and again for a mixture of A and B [preferably a eutectic mixture—not a homogeneous alloy] then, beyond any variation due to metallic parameters, one would expect that the Knight shift would be closer to that of the normal metal for the mixture AB than for either A or B alone, since in that case the variation of the electron-electron interaction should be greater, or $\left|\frac{V''}{V}\right|$ should be smaller, and χ_s/χ_n should be closer to unity.

<u>Thermodynamic and Coherence Properties</u>

The system described above displays the usual properties of a superconductor with some modifications. The pair operators

$$\begin{aligned} b_{\underset{\sim}{k}} &= C_{-\underset{\sim}{\varkappa}}\, C_{\underset{\sim}{\varkappa}} \\ b^*_{\underset{\sim}{k}} &= C^*_{\underset{\sim}{\varkappa}}\, C^*_{-\underset{\sim}{\varkappa}} \end{aligned} \tag{4}$$

are associated with the pair occupation amplitudes $\alpha_{\varkappa}$ and $\beta_{\varkappa}$ where, for the ground state Ψ_o,

$$\begin{aligned} (\Psi_o, b^*_{\underset{\sim}{k}}\, b_{\underset{\sim}{k}}\, \Psi_o) &= \left|\beta_{\underset{\sim}{\varkappa}}\right|^2 = h_{\underset{\sim}{k}}, \\ \left|\alpha_{\underset{\sim}{\varkappa}}\right|^2 + \left|\beta_{\underset{\sim}{\varkappa}}\right|^2 &= 1, \\ \text{and} \qquad \alpha_{\underset{\sim}{\varkappa}} = \alpha_{-\underset{\sim}{\varkappa}} &= \alpha^*_{\underset{\sim}{\varkappa}}, \\ \beta_{\underset{\sim}{\varkappa}} &= -\beta_{-\underset{\sim}{\varkappa}}. \end{aligned} \tag{5}$$

Now, however, $\underset{\sim}{\varkappa}$ means $(\underset{\sim}{k} + \frac{\delta \underset{\sim}{k}}{2}, \uparrow)$ and $-\underset{\sim}{\varkappa}$ means $-(\underset{\sim}{k} - \frac{\delta \underset{\sim}{k}}{2}, \downarrow)$. The vectors

$\underset{\sim}{\delta k}_{\pm}$ give the deviation from the usual pairing of time reversed states and will be determined by the spatial variation of the electron-electron interaction and by the local magnetic field. A quasi-particle excitation spectrum can be defined in the usual way by

$$\xi_{\kappa} = \alpha_{\kappa} C_{\kappa} - \beta^{*}_{\kappa} C^{*}_{-\kappa} \tag{6}$$

and

$$\xi^{*}_{\kappa} = \alpha_{\kappa} C^{*}_{\kappa} - \beta_{\kappa} C_{-\kappa} ,$$

except that κ has the altered significance given above. The ξ's satisfy the usual Fermi commutation relations, and single particle excitations are separated from the ground state by the generalized energy gap, Δ, given by (9) of reference 1.

Using this the thermodynamic properties of the superconductor can be calculated. One finds, for example, small shifts in T_c and in ϵ_o. The shift of ϵ_o, for example, in the parabolic approximation used in (2) is

$$\left| \frac{\Delta\epsilon_o}{\epsilon_o} \right| = \frac{1}{4}\left(\chi_s / \chi_n \right)^2 \left(\frac{\chi_n}{\chi_s} - 1 \right) \left(\frac{\mu H}{\epsilon_o} \right)^2 . \tag{7}$$

There will also be field dependent variations of the penetration depth which may be observable. All of these effects increase with magnetic field both because μH increases and $\epsilon_o(H)$ decreases and therefore would be easiest to observe in small specimens where the critical fields are large. It unfortunately is necessary to separate the μH effects from the usual magnetic effects (which we may call orbital effects). We therefore need a theory accurate for strong magnetic fields and are pursuing this question.

Calculation of the various superconductor coherence properties proceeds in a straightforward way. The dominant terms are those usually obtained, but corrections due to the new pairing do occur. In particular the kernel for the electromagnetic response in the $q \to 0$ limit (Meissner effect) becomes:

$$J_\mu(q) = K_{\mu\nu}(q)\, A^T_\nu\,(q)$$

$$\lim_{q\to 0} K_{\mu\nu}(q) = -\delta_{\mu\nu}\frac{ne^2}{mc}\left[1 - \left(\frac{1}{4}\frac{\chi_s}{\chi_n}\,\frac{\mu H}{\mathcal{E}^*_F}\right)^2\right]. \tag{8}$$

Flux Quantization

The usual flux quantization arguments [4,5] rely on the assignment of a common total (angular) momentum to all the paired electrons in order to establish the unit of quantization as $\frac{ch}{2e}$. Since the theory described above allows pairs of different total (angular) momentum if the electron-electron interaction is not invariant under translations (rotations), the basis of the arguments for flux quantization in units of $\frac{ch}{2e}$ must be re-examined.

We find that as a consequence of the generalized pairing:

1) The flux quantization steps should be smoothed out somewhat at the edges of the jumps under experimental conditions which maximize the magnetic energy (i.e., performed near the critical field).

2) The steps themselves are not necessarily periodic in $\frac{ch}{2e}$, though they are periodic in $\frac{ch}{e}$. This is in accord with the theorem in reference 4 and is illustrated in the figure.

3) The ground state of a superconductor with a hole in some cases may be a state with non-zero current and non-zero flux in zero

external field. This does not violate any general theorems since the state is degenerate with the time reversed state of opposite current and flux.

We will sketch some of the salient points of the argument leading to the last two conclusions. Detailed calculations and a full discussion of all three statements above are left to a future publication.

At the absolute zero the energy of a superconductor with a hole(6) consists of the Fermi kinetic energy, T_F, and the correlation energy associated with the superconducting transition, W_c. Presumably W_c has its minima when the flux enclosed in the hole

$$\Phi = \frac{ch}{e}\alpha \tag{9}$$

is a unit multiple of $^{ch}/2e$ ($\alpha = 0, \pm\frac{1}{2}, \pm 1 \ldots$) since in this case there need be no angular momentum transfer in electron pair scatterings. However, as is indicated in the figure, this energy is continuous in the enclosed flux and has its maxima at $\alpha = \frac{1}{4}$. The height of the maxima are related to the Knight shift for the sample and depend on the degree of rotational symmetry of the electron-electron interaction. Thus these maxima can be lowered by making a sample of a mixture of two metals.

The variation of the Fermi energy with α can be obtained from an examination of the expression

$$T_F = A + \frac{h^2}{2mr^2}\sum_{\cdot\cdot\ell}(\ell + \alpha)^2 , \tag{10}$$

where A is a constant giving the contribution due to the radial and z momenta, and $\cdot\cdot\ell$ indicates a summation over all occupied quantum numbers, radial, z, and ℓ. In the interior of the specimen, due to the Meissner effect, the current is zero and we have

$$\sum_{\ell} \ell = - n \alpha \tag{11}$$

while the normalization implied above yields:

$$\sum_{\ell} = n. \tag{12}$$

Using these we obtain

$$T_F = A + \frac{\hbar^2}{2mr^2}\left[\sum_{\ell} \ell^2 - \alpha^2 n\right]. \tag{13}$$

Since (11) is a supplementary condition $\sum_{\ell} \ell^2$ is implicitly a function of α. As has been observed previously by Byers and Yang[4] there is a fundamental difference in the behavior of this term depending on whether the number of electrons in the line determined by a given k_z and k_r is even or odd. If it is odd, a shift of an electron from $-\ell_o$ to $\ell_o + 1$ gives a shift in the $\sum_{\ell} \ell^2$ term of $2\ell_o + 1$. If it is even, however, a shift of an electron from $-\ell_o - 1$ to $+\ell_o + 1$ gives no shift in this term. Thus if a fraction of the electrons (f_E) are in even lines, T_F is degenerate with respect to the placement of the extra electrons.[7] In this situation $T_F(\alpha)$ takes its minimum not at $\alpha = 0$ but rather at $|\alpha| = \frac{f_E}{2}$.

The total energy then is the sum of two terms one, W_c, with minima at $\alpha = 0, \pm \frac{1}{2}, \pm 1 \ldots$ and the other $T_F(\alpha)$ with minima at $\alpha = \pm {}^{f_E}/_2$, $\pm (1 \pm {}^{f_E}/_2) \ldots$. Two situations then become possible:

1) The situation, by now, expected: flux steps of ${}^{ch}/_{2e}$, ground state $\Phi = 0$. This will be the case if W_c changes more rapidly than T_F.

2) Unequal flux steps $\simeq \frac{f_E}{2}\frac{ch}{e}$, $(1 - {f_E}/{2})\frac{ch}{e}$, with an over-all periodicity in ${ch}/{e}$. In this case the ground state carries current and encloses a flux of $\sim \frac{f_E}{2}\frac{ch}{e}$. To make this second possibility more likely, the experimental sample should be non-uniform so that W_c will change less rapidly than T_F.

Although the effects discussed above may already have been observed,[8] it is more likely that the available evidence does not bear decisively on these points. It would clearly be of great interest to perform flux quantization experiments (especially on non-uniform samples) with special attention given to the size of the steps and to their placement about $H_{external} = 0$.

Footnotes and References

(1) L. N. Cooper, Physical Review Letters 8, 367 (1962).

(2) That such a theory could yield a finite Knight was suggested by A. B. Pippard and V. Heine, Phil. Mag. 3, 1046 (1958).

(3) F. Reif, Phys. Rev. 106, 208 (1957). G. M. Androes and W. D. Knight, Phys. Rev. 121, 779 (1961).

(4) N. Byers and C. N. Yang, Phys. Rev. Letters 7, 46 (1961).

(5) L. Onsager, Phys. Rev. Letters 7, 50 (1961).
A. Bohr and B. R. Mottelson, Phys. Rev. 125, 495 (1962).

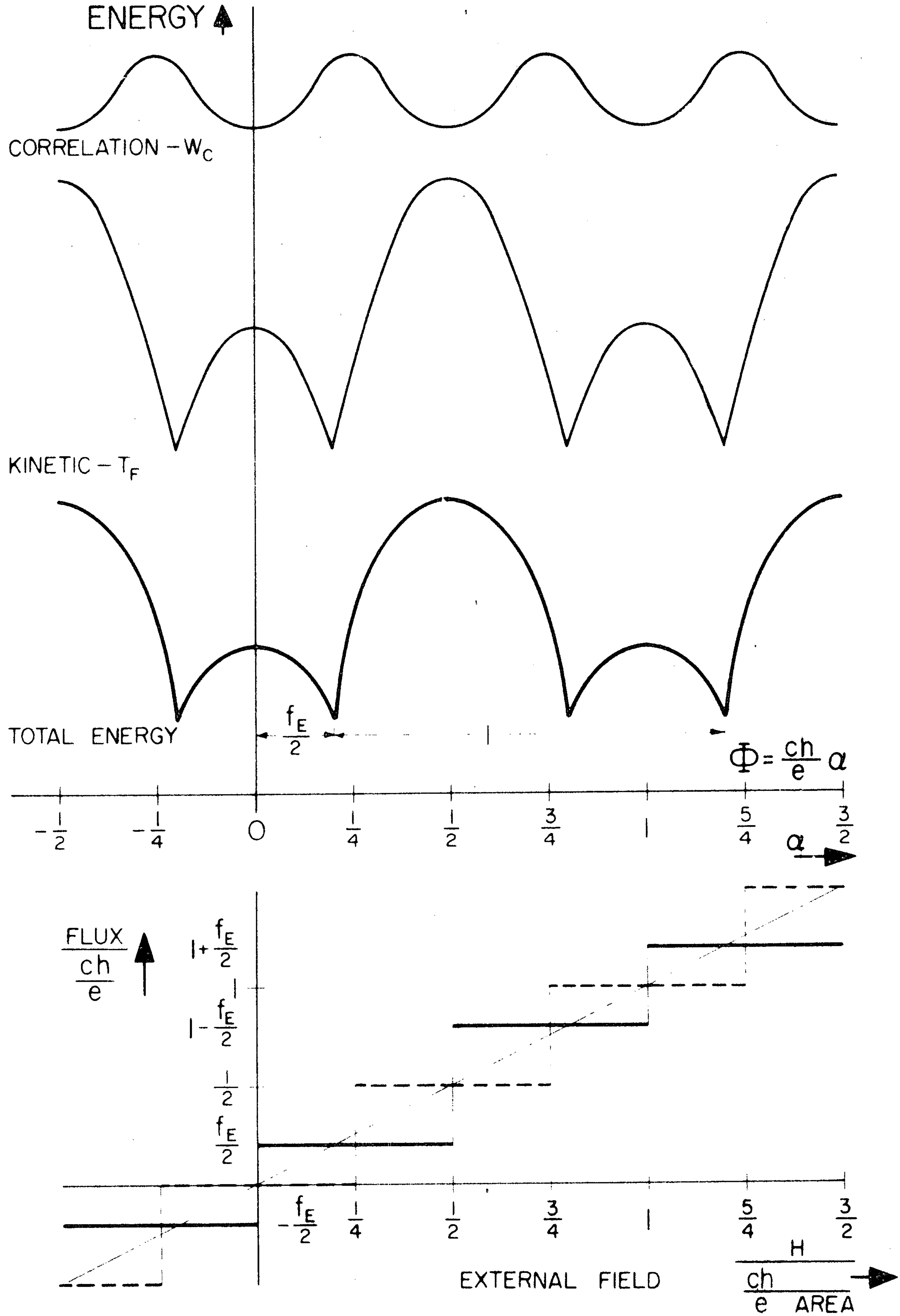
(6) We neglect both the magnetic energy and the extra kinetic energy in the thin shell in which the current is not zero since, by choice of an appropriate sample—one which is thick compared to the penetration depth and in which there is a large hole, these terms may be made arbitrarily small compared with the ones we discuss.

(7) In general there should always be a few electrons sprinkled over the Fermi surface of a metal whose position on that surface is irrelevant to the energy. Thus a state of current is degenerate with the state of no current. Since these currents are microscopic one normally would ignore them. However, in the multiply connected superconductor the flux associated with the placement of these degenerate electrons can be a finite fraction of $\frac{ch}{2e}$.

(8) B. S. Deaver, Jr. and W. M. Fairbank, Phys. Rev. Letters 7, 43 (1961).
R. Doll and M. Näbauer, Phys. Rev. Letters 7, 51 (1961).

Figure Caption

Fig. 1. These graphs illustrate the situation (2) mentioned in the text: Unequal flux steps $\simeq \frac{f_E}{2} \frac{ch}{e}$, $(1 - \frac{f_E}{2}) \frac{ch}{e}$, with over-all periodicity in $^{ch}/e$. The upper graph plots the correlation energy W_c, kinetic energy T_F and their sum, the total energy, as a function of enclosed flux $\Phi = \frac{ch}{e}\alpha$. The correlation energy is a symmetric even function with energy minima at $\alpha = 0, \pm \frac{1}{2}, \ldots$ and maxima at $\alpha = \pm \frac{1}{4}, \pm 3/4 \ldots$. The kinetic energy is dependent on the fraction of electrons in even lines in the sample. It is an even function with minima at $\alpha = \pm \frac{f_E}{2}, \pm (1 \pm \frac{f_E}{2}) \ldots$, and maxima, parabolic in shape, which occur at $\alpha = 0, \pm \frac{1}{2} \ldots$. In the case that the correlation energy variation is small relative to that of the kinetic energy, the total energy exhibits the behavior shown above. In the lower graph the solid line gives the flux quantization which results in this case; the dotted line shows the usual flux quantization (case 1) for comparison.



ENERGY
CORRELATION $-W_C$
KINETIC $-T_F$
TOTAL ENERGY
$\frac{f_E}{2}$
$\Phi = \frac{ch}{e}\alpha$
$-\frac{1}{2}$ $-\frac{1}{4}$ 0 $\frac{1}{4}$ $\frac{1}{2}$ $\frac{3}{4}$ 1 $\frac{5}{4}$ $\frac{3}{2}$
α
$\frac{FLUX}{\frac{ch}{e}}$
$1+\frac{f_E}{2}$
1
$1-\frac{f_E}{2}$
$\frac{1}{2}$
$\frac{f_E}{2}$
$-\frac{f_E}{2}$ $\frac{1}{4}$ $\frac{1}{2}$ $\frac{3}{4}$ 1 $\frac{5}{4}$ $\frac{3}{2}$
EXTERNAL FIELD
$\frac{H}{\frac{ch}{e\ AREA}}$