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Magnetism and Superconductivity

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1. Introduction

Following the establishment of the Bardeen-Cooper-Schrieffer theory of superconductivity[1] as a widely successful model for actual superconductors, considerable progress was made in accounting for their diamagnetic properties. On the other hand, spin effects in superconductors are still rather poorly understood. The reason is that the B.C.S. model requires a pairing of conduction electrons in quasi-bound states with antiparallel spins, and this requirement has so far proved extremely rigid. No really convincing alternatives to such pairing have as yet come to light. Among the effects that are very difficult to reconcile with antiparallel pairing we may list the non-vanishing of the Knight shift in some superconductors[2] as the temperature is lowered towards absolute zero, and the apparent ferromagnetism coexisting with superconductivity in some dilute alloys of the rare earths, particularly gadolinium, in lanthanum and in Yttrium-Osmium-Two[3),4)]. Some of the more plausible explanations of the finite Knight shift[5),6)] rely on spin-orbit scattering by surface or volume imperfections or impurities. The apparent coexistence of superconductivity and ferromagnetism has been ascribed to spiral spin ordering[7], or, alternatively, to non-uniformity in the phase through the material. Even where some understanding of spin effects exists, there are still divergences of opinion. For example, the initial decline of transition temperature of lanthanum when gadolinium is added can be evaluated by perturbation theory based on B.C.S. states, but it is still controversial if the reduction is due to a reduction in the energy gap or due to a change in the order of the transition of the kind involved when the magnetic field is applied to a *bulk* superconductor. It is almost certain that both effects occur simultaneously. That is to say, neglecting change of the energy gap, the free energy difference between the normal and superconducting states declines with increasing spin-impurity content; on the other hand the gap declines also. But there is disagreement as to which of these two effects causes the sample to go normal at the least impurity concentration.

What is missing in all these problems is a really intimate understanding of the effects of impurities on superconductors. Although plausible explanations for the behavior of imperfect superconductors were provided by Anderson[8] in terms of pairing of electrons in time reversed states, nothing remotely resembling our understanding of impurities in normal metals exists for superconductors.

The purpose of this paper is to suggest in outline how a detailed theory might be constructed. In the present paper we shall confine ourselves to non-magnetic impurities, or imperfections. (That is not to say that magnetic effects are thereby excluded: As is well known, the critical field of an imperfect superconductor can be higher than that of the perfect one, suggesting that imperfections might somehow 'pin' regions of superconductivity around them).

2. Generalization of the Hartree-Fock equations to superconductors

We postulate an electron gas with an interaction that will be attractive in a certain neighborhood of the Fermi surface, and repulsive elsewhere. In addition the electrons are subject to a potential V due to a distribution of impurities. The problem is to establish a Hartree-like Hamiltonian for this system, bearing in mind the innovations introduced by the B.C.S. theory. As is known, the ordinary Hartree-Fock Hamiltonian is the 'best' single particle Hamiltonian available for representing the normal electron gas. It is 'best' in the sense that the difference between it and the true Hamiltonian cannot give rise to one-particle excitations above the unperturbed ground state. That is to say, treating the difference between the true po-

tential and the Hartree-Fock potential as a perturbation, the perturbation series will not contain any excited states with only one electron-hole pair above the ground state.

It is a simple matter to find such a single particle Hamiltonian for a superconductor, remembering that one now has an additional type of c-number to consider; the creation (and the destruction) of a pair of electrons in time reversed states. Let $\Psi_\uparrow(r), \Psi_\downarrow(r)$ denote the up- and down-spin electron field operators respectively. By analogy with the Bogoliubov quasiparticles, we introduce a new set of Fermions

$$\left.\begin{aligned}\Phi_1^*(\omega)&=\int[f(r,\omega)\Psi_\uparrow^*(r)-g(r,\omega)\Psi_\downarrow(r)]dv\ ,\\ \Phi_2^*(\omega)&=\int[g(r,\omega)\Psi_\uparrow(r)+f(r,\omega)\Psi_\downarrow^*(r)]dv\ .\end{aligned}\right\}\tag{1}$$

The generalization of the Hartree-Fock equations takes the form of simultaneous equations for the functions f and g:

$$\left.\begin{aligned}-\frac{\hbar^2}{2m}\nabla^2 f-\mu f+\int V(r,r')f(r',\omega)dv'\\ -\int U(r,r')g(r',\omega)dv'+V_I(r)f(r,\omega)=\omega f(r,\omega)\ ,\\ +\frac{\hbar^2}{2m}\nabla^2 g+\mu g-\int V(r,r')g(r',\omega)dv'\\ -\int U(r,r')f(r',\omega)dv'-V_I(r)g(r,\omega)=\omega g(r,\omega)\ .\end{aligned}\right\}\tag{2}$$

Here $V_I(r)$ is the impurity potential, μ is the chemical potential, $V(r,r')$ is the Hartree-Fock potential, expressed in terms of the electron-electron interaction $v(r,r')$ by

$$\begin{aligned}V(r,r')=\sum_\omega\int 2\tilde{g}(r',\omega)g(r'',\omega)v(r,r'')\delta(r-r')dv''\\ -\sum_\omega\tilde{g}(r',\omega)g(r,\omega)v(r,r')\ .\end{aligned}\tag{3}$$

Finally $U(r,r')$ is a new 'superconductive' potential given by

$$\begin{aligned}U(r,r')&=-\sum_\omega\tilde{f}(r',\omega)g(r,\omega)v(r,r')\\ &=-\sum_\omega\tilde{g}(r',\omega)f(r,\omega)v(r,r')\ .\end{aligned}\tag{4}$$

The last equality in (4) follows from one of the orthogonality relations satisfied by the f, g pairs:

$$\left.\begin{aligned}&\int[f(r,\omega)\tilde{f}(r,\omega')+g(r,\omega)\tilde{g}(r,\omega')]dv=\delta_{\omega\omega'}\ ,\\ &\int[\tilde{g}(r,\omega)f(r,\omega')-g(r,\omega')\tilde{f}(r,\omega)]dv=0\ ,\\ &\sum_\omega[\tilde{f}(r',\omega)f(r,\omega)+\tilde{g}(r',\omega)g(r,\omega)]=\delta(r-r')\ ,\\ &\sum_\omega[\tilde{f}(r',\omega)g(r,\omega)-\tilde{g}(r',\omega)f(r,\omega)]=0\ .\end{aligned}\right\}\tag{5}$$

In terms of the solutions of eqtn (2), obtained self-consistently according to (3) and (4), the energy of the system is

$$\begin{aligned}&-2\sum_\omega\int\tilde{g}(r,\omega)\frac{\hbar^2}{2m}\nabla^2 g(r,\omega)dv\\ &\quad+\frac{1}{2}\sum_\omega\int\tilde{g}(r,\omega)V(r,r')g(r',\omega)dvdv'+\sum_\omega\int\tilde{g}(r,\omega)(V_I(r)-\mu)g(r,\omega)dv\\ &\quad-\frac{1}{2}\sum_\omega\int[\tilde{f}(r,\omega)U(r,r')g(r',\omega)+\text{comp. conj.}]dvdv'\end{aligned}\tag{6}$$

in the ground-state, *i.e.*, in the vacuum of the Φ-operators.

The problem we shall consider concerns solutions of (2) when there is a single charged impurity whose potential, together with the screening effect of $V(r, r')$, may be replaced by a highly localized potential, which, for simplicity, will be taken to be a delta-function located at the origin. The relevant solutions of (2) are scattering solutions: linear combinations of incoming plane waves, and outgoing spherical waves. (In this connection it is to be noted that for a given eigenvalue ω there are *four* waves that satisfy (2), with wave-vectors equal and opposite in pairs). To obtain an idea of the character of the change in the gap U as a function of position in the vicinity of the impurity, we first make a very rough, non-selfconsistent calculation in which we find the functions f and g, neglecting the change in U, and use them to find the change in U. (This could then be used to recalculate f and g, and so on.) Replacing, then, the gap operator $U(r, r')$ by a constant, the scattering solutions of (2) are, with $\hbar^2/2m=1$,

$$\left.\begin{aligned} f_k &= u_k e^{ik\cdot r} + \sum_{k'} e^{ik'\cdot r}\left[\frac{(\mu-k'^2-\omega_k)f_k(0)-Ug_k(0)}{(\mu-k'^2)^2+U^2-\omega_k^2+i\delta_1}\right]V_I\frac{\Omega_0}{\Omega}, \\ g_k &= v_k e^{ik\cdot r} + \sum_{k'} e^{ik'\cdot r}\left[\frac{(\mu-k'^2+\omega_k)g_k(0)+Uf_k(0)}{(\mu-k'^2)^2+U^2-\omega_k^2+i\delta_2}\right]V_I\frac{\Omega_0}{\Omega}, \end{aligned}\right\} \tag{7}$$

where Ω is the total volume, and Ω_0 the volume occupied by the impurity. We have not troubled to write out in full the values of f and g at the origin; these values can be found by setting r equal to zero and solving. The incoming wave-pair $u_k e^{ik\cdot r}$, $v_k e^{ik\cdot r}$ forms the Bogoliubov quasi-particle, with energy $\omega_k=\sqrt{\varepsilon_k^2+U^2}$ where $\varepsilon_k=k^2-\mu$. Provided the change in U due to the impurity is not too large, the scattered waves in (7) may be simplified as follows: The terms under the summation signs have two pairs of poles

$$k'=\pm\sqrt{\mu+\sqrt{\omega_k^2-U^2}}\,; \qquad k'=\pm\sqrt{\mu-\sqrt{\omega_k^2-U^2}}\,. \tag{8}$$

The residue at one of these is of order $\hbar\omega_D/U$ larger than the residue at the other, where $\hbar\omega_D$ is the Debye energy. Hence if $\hbar\omega_D \gg U$, the contribution from the other pole may be neglected. Then (7) takes the simple form

$$\left.\begin{aligned} f_k &= \frac{1}{\Omega^{1/2}}\left[u_k e^{ik\cdot r} + V_0\frac{\Omega_0}{\Omega}\sum e^{ik'\cdot r}\frac{f_k(0)}{|\varepsilon_k|-\varepsilon_{k'}+i\delta_1}\right], \\ g_k &= \frac{1}{\Omega^{1/2}}\left[v_k e^{ik\cdot r} - V_0\frac{\Omega_0}{\Omega}\sum e^{ik'\cdot r}\frac{g_k(0)}{|\varepsilon_k|+\varepsilon_{k'}+i\delta_2}\right], \end{aligned}\right\} \tag{9}$$

where terms in U have been discarded. The infinitesimal numbers δ_1, δ_2 must have signs such that the scattered waves are outgoing.

In this approximation

$$\left.\begin{aligned} f_k(0) &= u_k\Big/\Omega^{1/2}\left(1-\frac{\Omega_0 V_0}{\Omega}\sum\frac{1}{|\varepsilon_k|-\varepsilon_{k'}+i\delta_1}\right); \\ g_k(0) &= v_k\Big/\Omega^{1/2}\left(1+\frac{\Omega_0 V_0}{\Omega}\sum\frac{1}{|\varepsilon_k|+\varepsilon_{k'}+i\delta_2}\right), \end{aligned}\right\} \tag{10}$$

which shows that if the impurity gives rise to a virtual bound state near the Fermi surface, which is the only region of interest in the construction of U, the change in U can become very large. Evaluating (9) for free particles, and neglecting the possibility of a resonance by replacing $f_k(0), g_k(0)$ by u_k, v_k respectively, we find

$$f_k=\frac{u_k}{\Omega^{1/2}}\left[e^{ik\cdot r}+C\frac{e^{iF(k)r}}{r}\right]; \qquad g_k=\frac{v_k}{\Omega^{1/2}}\left[e^{ik\cdot r}+C\frac{e^{iG(k)r}}{r}\right], \tag{11}$$

where

$$\begin{aligned} F(k)&=k & k>k_f\,, \qquad G(k)&=\sqrt{2k_f^2-k^2} & k>k_f\,, \\ &=\sqrt{2k_f^2-k^2} & k<k_f\,, \qquad &=k & k<k_f\,, \end{aligned} \tag{12}$$

$$C=\frac{(4\pi)^{-1}V_0\Omega_0}{\hbar^2/2m}\,,$$

u and v are found in the usual way. Without the impurity the equations for f and g become (disregarding V)

$$\begin{aligned} \varepsilon_k u_k - U_k v_k &= \omega u_k \,, \\ -\varepsilon_k v_k - U_k u_k &= \omega v_k \,, \end{aligned} \qquad U_k = -V_k \sum u_{k'} v_{k'} \,, \tag{13}$$

where $V_k = \int v(r) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} dv$ and where we have assumed for simplicity that v depends on $r-r'$ only. Finally, we neglect the dependence of V_k on its subscript altogether and, in the usual way, restrict the summation over k' to a narrow range, of order of the Debye energy, around the Fermi surface, in which range v is attractive, equal to $-w$, say. Then u and v are given by

$$u_k = \cos\varphi_k/2 \,; \quad v_k = \sin\varphi_k/2 \,; \quad \tan\varphi_k/2 = e^{-\theta_k} \,; \quad \varepsilon_k = U \sinh\theta_k \,, \tag{14}$$

and the self-consistent equation for U is $1 = V\sum 1/\sqrt{\varepsilon_k^2 + U^2}$. ($U$ is now independent of k).

We are now in a position to write down the change in U due to the scattering. To obtain simple results, we sometimes will assume that v is very short range, so that the non-local character of U can be disregarded. This is a rather serious deficiency, since the range of the attractive part of v is not necessarily very short. It would be safer to say that we are looking at the diagonal elements of U in a position representation, but that in an actual calculation of the ground state energy the off-diagonal elements must be considered as well. From (11) and (12) we find, then, that the fractional change in the diagonal elements of U consists of two distinct parts: the part due to interference of the incident part of f with the scattered part of g, and a part due to the interference of the scattered parts of f and g. The portion due to the interference of incoming and reflected parts is proportional to the scattering potential, but varies very rapidly with position. The portion due to interference of the scattered f and g waves varies rather slowly with position, and is quadratic in the impurity potential. Making use of the fact that the summations are confined to a small neighborhood of the Fermi surface, the change in the diagonal element of the gap operator may be written:

$$\frac{\Delta U(r,r)}{U} = \frac{C}{r} \frac{2\left[\int u_k v_k k dk\right] \sin 2k_f r + O\left(\frac{U^2}{\mu^2}\right)}{\int u_k v_k k^2 dk} + \frac{C^2}{r^2} \frac{\int u_k v_k \cos\{[\sqrt{2k_f^2 - k^2} - k]r\} k^2 dk}{\int u_k v_k k^2 dk} \,. \tag{15}$$

For the evaluation of the energy, we need the general off-diagonal element. The change in this element due to the impurity is

$$\begin{aligned} \frac{\Delta U(r,r')}{U} = \frac{C}{2r} \sum u_k v_k e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} [e^{i(G(k)r - \boldsymbol{k}\cdot\boldsymbol{r})} + e^{i(F(k)r - \boldsymbol{k}\cdot\boldsymbol{r})}] \\ + \text{comp. conj. with } r \text{ and } r' \text{ reversed} \\ + \frac{C^2}{2r^2} \sum u_k v_k [e^{-iF(k)r' + iG(k)r} + \text{comp. conj. with } r, r' \text{ reversed}] \,. \end{aligned} \tag{16}$$

Quite obviously, because of the presence of rapidly oscillating terms, the contribution to the energy from the change in U is second order in the scattering potential, even though the change in U contains a term of first order in V. Formulae (15) and (16) apply to the case of resonant scattering also, if the term linear in V is multiplied by

$$\left[\left\{1 - \frac{1}{\Omega}\sum \frac{\Omega_0 V}{|\varepsilon_k| - \varepsilon_{k'} + i\delta_1}\right\}^{-1} + \left\{1 + \frac{1}{\Omega}\sum \frac{\Omega_0 V}{|\varepsilon_k| + \varepsilon_{k'} - i\delta_2}\right\}^{-1}\right] ,$$

and the term quadratic in V by

$$\left\{1-\frac{1}{\Omega}\Sigma\right\}^{-1}\left\{1+\frac{1}{\Omega}\Sigma\right\}^{-1}.$$

In that case the sums in the denominators must be evaluated paying heed to the band structure; for a free electron gas they would diverge.

3. 'Pinning' of superconducting regions in a non-superconducting matrix

So far we have found the first approximation to the change in the energy gap operator U due to an impurity. We now turn to the more speculative question if it is possible for an impurity to trap a superconducting region around it, even if the sample as a whole has become normal for one reason or other, such as an applied magnetic field in excess of the critical field.

There are now two obvious types of solution: In one of these there is no incident f-wave, and the incident g-wave is $v_k e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$, where $v_k=1$ $k<k_f$, $v_k=0$ elsewhere*. The energy gap is zero everywhere, except in the immediate vicinity of the impurity, where we denote it by ΔU. To solve the scattering problem without the need for considering extremely complicated non-linear integral equations, we are forced to make an extremely drastic assumption, namely that ΔU has δ-function character. Accordingly we write

$$\Delta U=\frac{\Omega_0}{2}w\sum_k\left\{\tilde{f}_k(0)g_k(0)+\text{comp. conj.}\right\} \tag{17}$$
$$=\Omega_0\Delta U_1,\ \text{say}\,.$$

The scattering solutions, in the two cases, are

$$\left.\begin{aligned} g_k(r)&=\begin{Bmatrix} v_k e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \\ 0 \end{Bmatrix}-\frac{\Omega_0}{\Omega}\sum_{k'}\frac{e^{i\boldsymbol{k}'\cdot\boldsymbol{r}'}}{\varepsilon_{k'}-\varepsilon_k+i\delta_1}\left[Vg_k(0)+\Delta U_1 f_k(0)\right], \\ f_k(r)&=\begin{Bmatrix} 0 \\ u_k e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \end{Bmatrix}-\frac{\Omega_0}{\Omega}\sum_{k'}\frac{e^{i\boldsymbol{k}'\cdot\boldsymbol{r}'}}{\varepsilon_{k'}+\varepsilon_k+i\delta_2}\left[Vf_k(0)-\Delta U_1 g_k(0)\right], \end{aligned}\right\} \tag{18}$$

in terms of the values of f and g at the origin. Setting r equal to zero and solving for these values, we find, in one of the two cases

$$\left.\begin{aligned} g_k(0)&=(1+VB_k)/[1+V(A_k+B_k)+(V^2+\Delta U_1^2)A_kB_k] \\ f_k(0)&=\Delta U_1 B_k/[1+V(A_k+B_k)+(V^2+\Delta U_1^2)A_kB_k] \\ A_k&=\sum\frac{1}{\varepsilon_{k'}-\varepsilon_k+i\delta_1}\frac{\Omega_0}{\Omega} \\ B_k&=\sum\frac{1}{\varepsilon_{k'}+\varepsilon_k+i\delta_2}\frac{\Omega_0}{\Omega} \end{aligned}\right\} \tag{19}$$

whence we derive, with the help of (17), the self-consistency condition for the energy gap:

$$1=w\sum_{k<k_f}\frac{\mathrm{Re}\,\{B_k(1+VB_k)\}}{|1+V(A_k+B_k)+(V^2+\Delta U_1^2)A_kB_k|^2}-w\sum_{k>k_f}\frac{\mathrm{Re}\,\{A_k(1+VA_k)\}}{|1+V(A_k+B_k)+(V^2+\Delta U_1^2)A_kB_k|^2}\,. \tag{20}$$

If for some value of V the simpler equation

$$1=w\sum_{k<k_f}\frac{\mathrm{Re}\,\{B_k(1+VB_k)\}}{|1+VA_k|^2|1+VB_k|^2}-w\sum_{k>k_f}\frac{\mathrm{Re}\,\{A_k(1+VA_k)\}}{|1+VA_k|^2|1+VB_k|^2}\,, \tag{21}$$

can hold, then for a certain V, equation (20) will be satisfied with a slightly different value of V, (or for a slightly different density of states curve). It is sufficient therefore to consider (21). Quite clearly, the positions of the resonances, as well as the *strength* of the resonances (*i.e.*, the smallness of the density of states at the resonances) will be the decisive factor. Of course V, the total self-consistent impurity potential, is not arbitrary, but might be derived, in simple cases from the Friedel sum-rule.

* In the other solution $g_{\text{inc}}=0$ and $f_{\text{inc}}=u_k e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$, with $u_k=1$ $k>k_f$, $u_k=0$ $k<k_f$.

The fact that the resonance factors can have either sign forces us to indulge in one final speculation: Can impurities bring about superconductivity, when the resonances are strong, but when the electron-electron interaction is always repulsive? The answer is most probably no. The region of momentum space that is most critical is presumably that near the Fermi-surface. But close to the Fermi surface, the poles of the integrands of A_k, B_k, which are also the points at which these quantities change sign, are very close together. Therefore only an extremely rapid variation in the density of states near the Fermi surface could allow the two factors to have unequal signs.

4. Multiple scattering

The question remains if, granted some 'pinning' of the superconductivity at impurity sites, the medium as a whole shows the characteristic properties of superconductors. Within the so called 'multiple scattering approximation' this seems to be the case. It is necessary only to replace the potential V by the forward scattering matrix element T_{kk} of a suitably defined scattering matrix, and similarly to replace U by the forward element of another matrix S. Of course, at the end of the previous chapter we took ΔU to have δ-function character, and that makes it difficult to see how a continuous superconducting medium is established. It must be remembered, however, that the next approximation to ΔU will involve the product of f and g at positions other than the origin, giving a spread in the energy gap. (In fact, because of the finite range of the f and g functions, it is not certain that the δ-function approximation is really a good starting approximation).

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DISCUSSION

P. G. de GENNES: There is, I believe, one complication in this one impurity problem: If you solve the self-consistent equation for the gap operator Δ, at least in the vicinity of the transition point of the pure matrix, you find that this gap is of the form

$$\Delta(r)=\Delta_0\left(1+\frac{\alpha}{r}e^{-\lambda r/\xi_0}\right),$$

where ξ_0 is the coherence length, and $\lambda\sim\sqrt{(T-T_c)/T_c}$. So the perturbation of Δ extends very far (at least to distances of order ξ_0) and the resulting 'long range potential' may alter noticeably the quasi-particle scattering.

H. SUHL: You are quite right; to assume a δ-function for the energy gap operator is incorrect, because the f and g functions derived from a δ-function potential spread out and fall off rather slowly. To be consistent, one should calculate the energy gap operator, and then re-determine f and g.