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New class of singlet superconductors which break time reversal and parity

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A class of singlet superconductors with a gap function $\Delta(\mathbf{k},\omega_n)$ which is *odd* in both momentum and Matsubara frequency is considered. Some of the physical properties of this superconductivity are discussed and it is argued that in many cases there is no gap in the quasiparticle spectrum and these superconductors will exhibit a Meissner effect.

Some recent models of high-T_c superconductors with unusual structure of the gap function $\Delta(\mathbf{k},\omega_n)$ have introduced general questions about the possible symmetry types of the gap for singlet superconductors. For example, Mila and Abrahams[1] discussed a singlet superconductor with a gap which is an odd function in $(k-k_F)$. This form, as discussed by Anderson,[2] annihilates the effect of strong short-range repulsion.

A careful symmetry analysis leads us to the conclusion that in addition to the standard BCS-like singlet gap function, there is a new, apparently unnoticed, class of singlet superconductors, whose gap function $\Delta(\mathbf{k},\omega_n)$ and anomalous Green's function are *odd* in both Matsubara frequency ω_n and momentum $\mathbf{k}$.

Nearly two decades ago in a little-noticed article, Berezinskii[3] considered the possibility of unusual $S=1$ triplet pairing in ^{3}He. He argued that it is permissible, from the point of view of symmetry of the superconducting gap, to have a phase in which the gap function is a vector in spin space for triplet case, odd in Matsubara frequency, and even in momentum $\mathbf{k}$. Although it is now commonly believed that, in the observed phases, the gap in superfluid ^{3}He is even in frequency and odd in $\mathbf{k}$, there is no symmetry restriction which prohibits the phase proposed by Berezinskii.

We shall adapt Berezinskii's approach[3] to the singlet case. We introduce the anomalous Green's function in d dimensions,

$$F(\mathbf{k},\omega_n)=\frac{1}{2}\sum_{\alpha,\beta}\int d\mathbf{r}\int_{-\beta}^{\beta}d\tau\, e^{i\omega\tau}e^{i\mathbf{k}\cdot\mathbf{r}}\langle T_\tau\psi_\alpha(\tau,\mathbf{r})\psi_\beta(0,0)\rangle g_{\beta\alpha}\,, \tag{1}$$

with the notations $g_{\alpha\beta}=(i\sigma_y)_{\alpha\beta}$ a spin metric tensor, τ the Matsubara time, and $\beta=1/T$. Note that the anomalous Green's function is explicitly written in a general spin-singlet form; the function $F(\mathbf{k},\omega_n)$ is a true scalar: $S^+F(\mathbf{k},\omega)\equiv 0$, where $S^+=\sum S_i^+$ is the total spin-raising operator. The same discussion holds for the anomalous self-energy $W(\mathbf{k},\omega_n)$ and the gap function $\Delta(\mathbf{k},\omega_n)$.[4]

If one *assumes* that the spatial wave function for the singlet Cooper pair is an even function under $\mathbf{k}\to-\mathbf{k}$, the standard BCS expression for the gap $\Delta(\mathbf{k},\tau)\propto\langle T_\tau\psi_{\mathbf{k}\uparrow}\psi_{-\mathbf{k}\downarrow}\rangle$ is recovered. We do not want to make any assumptions at this point, so the anomalous Green's function F and anomalous self-energy W are taken in the form of the general singlet, Eq. (1). Then the *only* constraint on the possible symmetry of F and W follows from the anticommutativity of the ψ operators in F, and we immediately get, for the singlet case,[4]

$$F(\mathbf{k},\omega_n)=F(-\mathbf{k},-\omega_n)\,, \tag{2a}$$

$$\Delta(\mathbf{k},\omega_n)=\Delta(-\mathbf{k},-\omega_n)\,. \tag{2b}$$

There are two distinct ways to satisfy Eqs. (2) in terms of definite symmetry types of the gap.

(a) The standard Eliashberg-BCS singlet gap which is even both in ω_n and $\mathbf{k}$, $\Delta(\mathbf{k},\omega_n)=\Delta(-\mathbf{k},\omega_n)=\Delta(\mathbf{k},-\omega_n)$. For this kind of pairing the equal-time anomalous Green's function is nonzero, leading to the usual off-diagonal long-range order (ODLRO). Then the equal-time Cooper pair orbital wave function has to be symmetric in electron coordinates since the spin wave function is a singlet and antisymmetric.

(b) Singlet superconducting pairing with a gap which is odd in both $\mathbf{k}$ and ω_n,

$$F(\mathbf{k},\omega_n)=-F(-\mathbf{k},\omega_n)=-F(\mathbf{k},-\omega_n)\,, \tag{3a}$$

$$\Delta(\mathbf{k},\omega_n)=-\Delta(-\mathbf{k},\omega_n)=-\Delta(\mathbf{k},-\omega_n)\,. \tag{3b}$$

In this paper, we shall consider this kind of singlet superconductivity. Equation (3b) implies that the spin-singlet gap is described in terms of an odd orbital function, while, at the same time, the spin function is odd. There is no violation of the Pauli principle because the equal-time gap function vanishes since the gap is odd in ω_n.[5] The physical consequences of this behavior of the gap are far reaching. For example, such a system does not exhibit conventional ODLRO which requires a nonzero equal-time anomalous correlator.

Before discussing the physical properties of such a superconductor, we consider the microscopic Eliashberg equations which lead to this kind of gap function. With standard Nambu-Eliashberg notation, the matrix Green's function has the form

$$\hat{G}(\mathbf{k},\omega_n)=\frac{i\omega_n Z_{\mathbf{k}}(\omega_n)\tau_0+W(\mathbf{k},\omega_n)\tau_1}{\omega_n^2 Z_{\mathbf{k}}^2(\omega_n)+|W(\mathbf{k},\omega_n)|^2+\epsilon_{\mathbf{k}}^2}\ . \tag{4}$$

The one-loop self-energies in the superconducting and normal channels are

$$W(\mathbf{k},\omega_n)=-T\sum_{n',\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}(\omega_n-\omega_{n'})\frac{W(\mathbf{k}',\omega_{n'})}{\omega_{n'}^2 Z_{\mathbf{k}'}^2(\omega_{n'})+\epsilon_{\mathbf{k}'}^2+|W(\mathbf{k}',\omega_{n'})|^2}\ , \tag{5a}$$

$$[1-Z_{\mathbf{k}}(\omega_n)]i\omega_n=T\sum_{n',\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}(\omega_n-\omega_{n'})\frac{i\omega_{n'}Z_{\mathbf{k}'}(\omega_{n'})}{\omega_{n'}^2 Z_{\mathbf{k}'}^2(\omega_{n'})+\epsilon_{\mathbf{k}'}^2+|W(\mathbf{k}',\omega_{n'})|^2}\ , \tag{5b}$$

where $V_{\mathbf{k}\mathbf{k}'}(\omega_n-\omega_{n'})$ is some effective interaction. These equations are written with the assumption that the same interaction enters into both Eqs. (5a) and (5b); the effect of impurities is neglected. It follows from Eqs. (3a) and (3b) that only the odd components in $\mathbf{k}$, $\mathbf{k}'$, ω_n, and $\omega_{n'}$ of the potential $V_{\mathbf{k}\mathbf{k}'}(\omega_n-\omega_{n'})$ contribute in the momentum integral and frequency sums in Eq. (5a). As indicated earlier,[4] we assume in this paper that $Z_{\mathbf{k}}(\omega_n)$ is an even function of $\mathbf{k}$ and ω_n. Other possibilities will be discussed in a subsequent paper.[6] Then only the even-in-$\mathbf{k}$ and odd-in-ω_n components of $V_{\mathbf{k}\mathbf{k}'}(\omega_n-\omega_{n'})$ enter the right-hand side of Eq. (5b). The $\mathbf{k}$ dependence of the normal self-energy near the Fermi surface is usually weak, so we shall neglect it in Eq. (5). We see that there are no intrinsic inconsistencies within the Eliashberg formulation which forbid the odd gap solution of Eq. (3b).

In what follows, we discuss how an interaction mediated by phonons can lead to the odd gap,

$$V_{\mathbf{k}\mathbf{k}'}(\Omega_m)=\alpha^2 D_{\mathbf{k}\mathbf{k}'}(\Omega_m)=\alpha^2\frac{2}{\pi}\int d\omega\frac{A_{\mathbf{k}\mathbf{k}'}(\omega)\omega}{\omega^2+\Omega_m^2}\ , \tag{6}$$

where $\Omega_m=\omega_n-\omega_{n'}$ is an even (bosonic) Matsubara frequency. Then antisymmetrization in $D_{\mathbf{k}\mathbf{k}'}(\omega_n-\omega_{n'})$ over $\omega_{n'}$ automatically implies antisymmetrization over ω_n. In the phonon case, there needs to be sufficient $\mathbf{k}$ dependence in $D_{\mathbf{k}\mathbf{k}'}(\Omega)$ to be able to produce odd-in-$\mathbf{k}$, $\mathbf{k}'$ interactions. Phonons do not contribute to the (odd) pairing kernel of Eq. (5a) if they are described in the Einstein approximation with $\mathbf{k}$-independent spectral density $A(\omega)$.

To illustrate, consider the weak-coupling ($Z=1$) limit of the Eliashberg equations (5). Although interaction with phonons does produce a Z-factor renormalization, we neglect it for this discussion. Our purpose here is to give a discussion based on a model interaction and not to propose an actual phonon interaction. Thus, we assume $Z=1$ and that the odd-pairing kernel arises from the odd part of an interaction mediated by acoustic phonons with

$$V_{\mathbf{k}\mathbf{k}'}(\Omega)=\alpha^2\frac{c^2(\mathbf{k}-\mathbf{k}')^2}{c^2(\mathbf{k}-\mathbf{k}')^2+\Omega^2}\ . \tag{7}$$

For $\mathbf{k}\sim\mathbf{k}'\sim k_F$ the frequency in the phonon propagator is usually small in comparison with the term containing the momenta: $|\Omega|\ll c|\mathbf{k}-\mathbf{k}'|$. This allows us to expand $V_{\mathbf{k}\mathbf{k}'}(\Omega)$ in Eq. (7). Keeping in mind that only the odd-in-$\mathbf{k}$, $\mathbf{k}'$, ω_n, and $\omega_{n'}$ components contribute to the gap equation (5a), we obtain

$$V_{\mathbf{k}\mathbf{k}',\mathrm{odd}}=4\alpha^2\frac{\mathbf{k}\cdot\mathbf{k}'\omega_n\omega_{n'}}{c^2(\mathbf{k}+\mathbf{k}')^2(\mathbf{k}-\mathbf{k}')^2}+O\left(\left[\frac{\omega_c}{ck_F}\right]^2\right),$$

where ω_c is the maximum phonon frequency. The linearized gap equation is then

$$\Delta(\mathbf{k},\omega_n)=(4\alpha^2T/c^2)\sum_{n',\mathbf{k}'}\frac{\mathbf{k}\cdot\mathbf{k}'\omega_n\omega_{n'}}{(\mathbf{k}^2+\mathbf{k}'^2)^2-4(\mathbf{k}\cdot\mathbf{k}')^2}\cdot\frac{\Delta(\mathbf{k}',\omega_{n'})}{\omega_{n'}^2+\epsilon_{\mathbf{k}'}^2}\ . \tag{8}$$

From Eq. (8), it follows that the gap has to be linear in frequency up to the cutoff ω_c. We shall use the ansatz

$$\Delta(\mathbf{k},\omega_n)=\frac{i\omega_n}{\omega_c}\frac{\mathbf{k}}{k_F}\cdot\mathbf{d}(\mathbf{k},\omega_n) \tag{9}$$

with $\mathbf{d}(\mathbf{k},\omega_n)=\mathbf{d}\Theta(\omega_c-|\omega_n|)$, where $\Theta(x)$ is a step function. Combining Eqs. (8) and (9) when $T<\omega_c$, we find that the gap equation exhibits nontrivial solutions *above* a critical temperature T_{c-}, where

$$1=\frac{\alpha^2}{\alpha_c^2}\left(1+\tfrac{3}{2}\pi^2\frac{T_{c-}}{\omega_c}\right). \tag{10}$$

Here $N_0\alpha_c^2=a(ck_F,\omega_c)^2$, where a is a positive constant of order unity.

The thermodynamics of this phase is different from the one for BCS superconductors: For intermediate couplings $\alpha^2<\alpha_c^2$, the gap equation leads to a nontrivial solution in the temperature range $T_{c+}>T>T_{c-}$, where T_{c+}, of order ω_c, is the temperature at which the smallest value of $\omega_{n'}$ in the sum of Eq. (8) exceeds the cutoff, rendering the right-hand side zero. In the region just above T_{c-}, the system is described by a Ginzburg-Landau (GL) theory with order parameter $|\mathbf{d}|\propto(T-T_{c-})^{1/2}$. At larger values of the coupling, $\alpha^2>\alpha_c^2$, the lower critical temperature T_{c-} goes to zero and the lower GL region vanishes. Berezinskii[3] found analogous results in his treatment of the odd-frequency gap for triplet pairing. Detailed analysis of the thermodynamics and GL theory of this phase will be given elsewhere.[6]

A special case of the odd gap will occur if the form of the interaction admits a solution of the form $\Delta(\mathbf{k},\omega_n)=\mathbf{k}\cdot\mathbf{d}\,\mathrm{sgn}(n)$. In this case, the T_c equation from Eq. (5a) is precisely that of a p-wave BCS superconductor and the condensed phase occurs for $T_c>T>0$. We shall not discuss this possibility further.

We conclude that the only criterion for a physical system to choose between odd and even gaps is the overall minimum of the free energy. From our discussion, it follows that the standard BCS s-wave superconductivity will have lower energy, at least for a weak electron-phonon interaction. However, if one takes a short-range repulsion (as in the Hubbard model) into consideration,[2] the "no-double-occupancy" constraint $\sum_{\mathbf{k},\omega}\Delta(\mathbf{k},\omega)=0$ must be obeyed in the superconducting state. This is automatically satisfied for the odd gap and in this case, odd pairing may be favored over the conventional BCS state whose energy will be raised by the repulsion.

Let us consider some of the physical properties of an odd gap superconductor. An important consequence of a gap which is odd under $\tau\rightarrow-\tau$ and under $\mathbf{r}\rightarrow-\mathbf{r}$ is that one has broken time reversal and parity. This leads to the existence of the orbital Goldstone vector $\mathbf{d}(\mathbf{k},\omega_n)$ which is analogous to the orbital momentum vector in the triplet superconductors. Below we will assume that $\mathbf{d}$ is a real vector; however, there are other possibilities.[7]

With our ansatz, the quasiparticle spectrum for such a superconductor is gapless. Indeed, if we assume the gap function has the form in Eq. (9) with a real $\mathbf{d}(\mathbf{k},\omega_n)$ which is smooth and even in ω_n and $\mathbf{k}$, then we find from the poles of the Green's function, Eq. (4) (in weak coupling, $Z\simeq 1$), that

$$\omega_k\simeq\frac{\epsilon_k}{[1+(\mathbf{k}\cdot\mathbf{d})^2/(k_F\omega_c)^2]^{1/2}}\,. \tag{11}$$

Thus quasiparticle excitations in such a superconductor are gapless; the only effect of superconducting correlations is an effective mass renormalization, $m^*_{\mathbf{k}}=m[1+(\mathbf{k}\cdot\mathbf{d})^2/(k_F\omega_c)^2]^{1/2}$. From this point of view this superconductor is essentially a normal metal with nonlocal superconducting correlations. Note that the gap vector $\mathbf{d}(\mathbf{k})$ and the mass renormalization vanish when $\mathbf{k}\perp\mathbf{d}$. The gain in free energy in the superconducting state is given by the standard BCS expression,[8]

$$\mathcal{F}_s-\mathcal{F}_n=-T\sum_{\omega_n,\mathbf{k}}\int_0^1 d\lambda\frac{|\Delta(\mathbf{k},\omega_n)|^2}{\omega_n^2+\lambda^2|\Delta(\mathbf{k},\omega_n)|^2+\epsilon_{\mathbf{k}}^2}$$
$$\simeq-\tfrac{1}{2}N_0\mathbf{d}^2\,, \tag{12}$$

where the gap is assumed to have the form of Eq. (7) with $\mathbf{d}(\mathbf{k},\omega_n)$ independent of ω_n and where N_0 is the density of states at the Fermi surface. This formula also follows from the observation that the effect of such pairing on the low-energy states is an increase of the density of states $N^*=N_0m^*/m$. This results in an energy change $\delta E=\omega_c^2(N^*-N_0)$ which is equal to the right-hand side of Eq. (12).

There is no static order parameter since $F(\mathbf{r}_1,\mathbf{r}_2;t_1,t_1)=0$. Nevertheless, the global electromagnetic U(1) group is broken because even for nonequal times t_1, t_2 and space points $\mathbf{r}_1$, $\mathbf{r}_2$, the existence of the anomalous correlator implies

$$\langle\psi_\alpha(t_1,\mathbf{r}_1)\psi_\beta(t_2,\mathbf{r}_2)\rangle\rightarrow e^{i2\phi}\langle\psi_\alpha(t_1,\mathbf{r}_1)\psi_\beta(t_2,\mathbf{r}_2)\rangle$$

under this transformation. This suggests that the electromagnetic response of these superconductors will be the same as for BCS superconductors; they will exhibit a Meissner effect. In order to calculate the kernel in linear response, we shall use standard expressions from the BCS theory,[9] and take into account the frequency and momentum dependence of the gap. Because the gap function is a scalar in our case, the correction to the gap function $\Delta(\mathbf{k},\omega_n)$ which is linear in the gauge potential $\mathbf{A}$, is proportional to div$\mathbf{A}$. In the gauge div$\mathbf{A}=0$, we can use the linear-response theory with the unperturbed gap function given by Eq. (7). This can be checked within linear-response theory directly with the use of the Peierls substitution $\mathbf{k}\rightarrow\mathbf{k}+2e\mathbf{A}$. The kernel for the static response has the form

$$Q(\mathbf{k})=1+\tfrac{3}{4}T\sum_\omega\int_0^\pi d\theta\sin^3\theta\int_{-\infty}^{\infty}d\xi\frac{(i\omega+\xi_-)(i\omega+\xi_+)+\Delta_-\Delta_+^*}{(\omega^2+\xi_-^2\,|\Delta_-|^2)(\omega^2+\xi_+^2+|\Delta_+|^2)}\,, \tag{13}$$

where $\xi_\pm=\xi\pm\frac{1}{2}\mathbf{k}\cdot\mathbf{v}$ and analogous notations for the gap. From Eq. (13), we can find the asymptotic kernel for small momenta, assuming that the gap $\Delta(\mathbf{k},\omega_n)$ is essentially linear in momentum and frequency as in Eq. (7),

$$Q(k\rightarrow 0)\simeq\frac{\pi}{2}\ln\frac{\omega_c}{T}\frac{(\mathbf{d}/\omega_c)^2}{[1+(\mathbf{d}/\omega_c)^2]^{3/2}}\,. \tag{14}$$

The fact that the kernel is logarithmically divergent means that this particular type of superconductor is of the Pippard type at low enough temperatures (the temperature has to be very small because of the weak logarithmic divergence). In the vicinity of the critical temperature, however, the temperature dependence of the penetration depth is that of the gap squared,

$$\lambda^2=\frac{2m}{Ne^2\pi}\frac{[1+(\mathbf{d}/\omega_c)^2]^{3/2}}{(\mathbf{d}/\omega_c)^2}\sim\frac{1}{\mathbf{d}^2}\,. \tag{15}$$

This makes this superconductor of the London type in the vicinity of T_{c-}. If we assume that the gap as a function of frequency has larger power than unity, we can obtain a penetration depth which is finite in the whole range of temperature.

In conclusion we found a class of singlet superconductors with a gap which is *odd* in both momentum and frequency and we showed that there is no symmetry restriction which prohibits this kind of gap function. The physical properties of these superconductors are rather unusual. Parity and time-reversal symmetries are broken; this leads to Goldstone modes and makes these singlet superconductors analogous to superfluid ^{3}He. There is no gap in the quasiparticle spectrum, and the equal-time anomalous (pair) correlator vanishes. Hence, there is no ODLRO in the usual sense but we find that there is a Meissner effect. Static impurity scattering will be pair breaking, as is usual for anisotropic superconductors. At moderate coupling, the normal phase reenters below T_{c-}. The coherent state appears to be a result of pairing among the thermally excited quasiparticles which are present at nonzero temperature. All these nontrivial properties deserve further investigation.

Note added in proof. The calculations reported here are only illustrative—they are designed to elucidate some general properties of odd-gap superconductivity. In the acoustic-phonon case discussed above, the Z-factor renormalization actually renders the condition of Eq. (10) impossible to satisfy. It was brought to the authors' attention[10] that due to the positivity of the square of the effective coupling, the structure of any kernel $V_{\mathbf{kk'}}(\Omega)$ which arises from a boson exchange process is such that a simultaneous solution of the two Eliashberg equations, Eqs. (5a) and (5b) is improbable. This issue and the consideration of other effective couplings for the odd-gap case will be treated in a forthcoming publication.[11]

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[4]Recall, W and Δ are related by $\Delta = W/Z$, where Z is the self-energy in the normal channel, which in this paper we shall take to be even in $\mathbf{k},\omega_n$.

[5]Note also that the odd gap *cannot* be obtained within the weak coupling BCS approximation which assumes no frequency dependence of the gap $\Delta(\mathbf{k},\omega_n)$.

[6]E. Abrahams and A. V. Balatsky (unpublished).

[7]In principle $\mathbf{d}(\mathbf{k},\omega)$ can be a complex vector, say $\mathbf{d} \propto \mathbf{e}_x + i\mathbf{e}_y$ as in ^{3}He-A. In this case the gap will have nodes at $\mathbf{k} \perp \mathbf{d}$ at two points on the Fermi surface. The broken time-reversal and parity symmetries lead to the existence of an intrinsic orbital momentum $\mathbf{L}_0 \| \mathbf{d}$ of the order of $(\mathbf{d}/E_F)^2$. The Goldstone modes associated with the motion of the $\mathbf{d}$ vector are additional low-lying modes which also distinguish this superconductor from the usual BCS singlet superconductor.

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