Odd-frequency triplet pairing in mixed-parity superconductors

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We show that mixed-parity superconductors may exhibit equal-spin pair correlations that are odd-in-time and can be tuned by means of an applied field. The direction and the amplitude of the pair correlator in the spin space turn out to be strongly dependent on the symmetry of the order parameter, and thus provide a tool to identify different types of singlet-triplet mixed configurations. We find that odd-in-time spin-polarized pair correlations can be generated without magnetic inhomogeneities in superconducting/ferromagnetic hybrids when parity mixing is induced at the interface.

Introduction

Symmetry breaking is a central concept in physics, superconductivity being an exemplary case. In a conventional superconductor gauge symmetry is broken and Cooper pairs condense in the most symmetric configuration. The discovery of superfluid 3He started the era of unconventional superconductivity where other symmetries get broken and alternative pairing mechanisms emerge with respect to the phonon mediated one. This happens in high-temperature cuprates, f-electrons superconductors, cobaltates, ruthenates, pnictides, organics and many other superconductors [1, 2].

The issue of the gap symmetry and the superconducting mechanism has become more intriguing since the recent discovery of superconductivity in a number of materials whose lattices lack inversion symmetry 3, with important implications for the symmetry of the superconducting state. In this framework, difficulties may emerge in detecting parity mixing of Cooper pairs partly due to the fact that conventional experimental approaches utilized for the determination of parity of Cooper pairs, such as Knight shift measurements, do not provide useful information when spin-orbit coupling is larger than the pairing energy scale.

In some of the unconventional superconductors time reversal symmetry can also be broken both for spin singlets and spin triplets as well as in the cases of superconductivity coexisting with ferromagnetic long-range order 4. Concerning this symmetry, in the majority of the superconductors the order parameter is assumed to be even in the frequency domain, so that it may be even or odd in space depending on whether the Cooper pairs form spin singlets or triplets, respectively. However, if we allow for an odd-in-time dependence, more exotic types of pairings are possible, like that originally predicted in the context of liquid 3He 5. For these states the triplet pair correlation function is symmetric under the exchange of spatial and spin coordinates but antisymmetric under the exchange of time coordinates.

A significant advance in the understanding of odd-in-time pairing has been achieved since many experimental observations 6–9 have been accounted for as a manifestation of odd-in-time equal-spin (OTES) pair correlations generated at the interface between a spin singlet superconductor and a ferromagnet whose magnetization has an inhomogeneous profile both in amplitude and phase 10, 11. The interplay of magnetic non-collinearity and odd-in-time pairing emerges also in magnetically active interfaces that are able to change the spin direction of incident electrons across the junction 13, 17. Otherwise, zero-spin projection odd-in-time pair correlations take place in normal/superconductor junctions between triplet superconductors and diffusive normal metals 14 or ferromagnets 15 as well as in conventional ballistic hybrids without spin-triplet ordering 16.

The main interest in the search for odd-in-time pair correlations is motivated by the possibility of engineering spin-polarized supercurrents travelling through strong ferromagnets on distances that do not depend on the strength of the exchange field 17. The issue of functionalizing spin-polarized pair currents in superconducting/ferromagnetic hybrids is indeed a challenging task for the high potential towards innovative applications in the field of the spintronics 18 where it is the spin degree of freedom rather than the charge one to be exploited.

The aim of this letter is to demonstrate how odd-in-time equal-spin pair correlations are intimately connected to the symmetry breaking in unconventional superconductors. We show that OTES pair correlations manifest in mixed-parity superconductors and their existence is strongly dependent on the direction of an applied field in such a way to single out different types of parity mixing configurations. We also find a significant connection with the generation of spin-polarized pairs in hybrids. A different mechanism, with respect to those mentioned above, is presented for the case of a superconductor/Rashba metal/ferromagnet hybrid without requiring any inhomogeneity in the magnetic profile. Indeed, if parity mixing is yielded at the interface, i.e. via antisymmetric spin-orbit interaction, then OTES correlations are not trivial in all directions of the spin space assuming that the magnetization and the vector defining the spin-orbit interaction are not orthogonal.
**Model and results** We start by considering a generic superconducting system having an equal time order parameter, i.e., even in time, for both the spin singlet $d_{0k}$ and the triplet channel $d_{k} = \{d_{1k}, d_{2k}, d_{3k}\}$ expressed through the following matrix $\hat{\Delta}_k$:

$$
\hat{\Delta}_k = \begin{pmatrix}
-d_{1k} + id_{2k} & d_{3k} + d_{0k} \\
-d_{0k} & d_{1k} + id_{2k}
\end{pmatrix}
$$

where $d_{0k} = d_{0,-k}$ and $d_{k} = -d_{-k}$. For the classification purposes it is useful to introduce the vector $q_k = r_k + p_k$, with $r_k = d_{0k}d_k^* + d_{0k}^*d_k$ and $p_k = id_kd_k^*$, that, for a non-vanishing amplitude, yields a non-unitary superconducting state with two non-equivalent branches in the excitation spectrum. This is a direct consequence of the product $\hat{\Delta}_k^\dagger \hat{\Delta}_k$ being not proportional to the identity matrix. The $q$-vector is decomposed into two components, one lying in the plane defined by the vectors $[d_k, d_k^*]^T$ and the other perpendicular to it. The in-plane term identifies a non-unitary state with pure mixed singlet-triplet character, while the perpendicular component is proportional to the magnetic moment of the Cooper pairs.

To describe such type of superconducting states in systems that can also lack the inversion symmetry one may use the following generalized BCS model:

$$
H = \sum_{k, s, s'} (\xi_k \sigma_0 + g_k \cdot \sigma_{s, s'} + h \cdot \sigma_{s, s'}) c_{k, s'}^\dagger c_{k, s'} + \\
\sum_{k, s, s'} (\Delta_{k, s, s'} c_{k, s'} + \Delta_{k, s, s'}^* c_{-k, s'}^\dagger)
$$

where $\sigma_0$ is the identity matrix, $\sigma$ the Pauli matrices, $\xi_k = \xi_k - \mu$ is the kinetic energy measured with respect to the chemical potential $\mu$, $\Delta_{k, s, s'}$ are the equal time components of the order parameter and $h$ is the magnetic field, respectively. $g_k$ is the antisymmetric spin-orbit term due to Rashba interaction associated with the breaking of the parity symmetry and such that $g_k = -g_{-k}$ due to time-reversal invariance. For the quantitative analysis we assume a specific tight-binding spectrum in two dimensions of the form $\xi_k = -4 \left[ \cos(k_x) + \cos(k_y) \right]$, in units of the hopping amplitude, though the results do not depend on the details of the free electron dispersion and on the dimensionality.

To search for OTES we explicitly determine for the model Hamiltonian in Eq. (1) the odd-in-time local correlator for equal-spin pairing that reads:

$$
F^{\sigma_i}(t) = \frac{1}{V} \sum_{k} \langle T_i c_{k\sigma_i}(t)c_{-k\sigma_i}(0) \rangle
$$

where $V$ is the volume system, $T_i$ is the time ordering operator, $\langle \ldots \rangle$ the thermal average and $\sigma_i = \uparrow, \downarrow$ along the direction $i = x, y, z$ in the spin space, respectively.

The results obtained are reported in the Table I where the conditions and the directions of non zero OTES are indicated. It is worth pointing out that even-in-time pair correlations are also present for all the cases associated with equal time non-trivial order parameters and they can be as well induced by an applied field.

Let us firstly consider the cases of centrosymmetric superconductors. In order to understand how odd-frequency pair correlations occur in parity mixing it is useful to start with the singlet and triplet states separately. For the pure spin singlet superconductor, the OTES correlations occur only in the presence of an applied field $h$ and with spin projections in the plane perpendicular to it. This can be understood considering that the effect of the field along a given direction, i.e., $z$, is to induce odd-in-time correlations in the $S_z = 0$ triplet channel of the Cooper pairs $^{10, 12}$. Then, due to the $SU(2)$ spin symmetry, they lead to non-zero amplitude for the equal-spin correlators at a generic angle $\theta$ in the plane perpendicular to $h$. Due to the symmetry of the ground and the excited states the correlation function is symmetric for $Z_2$ inversion along a given direction in the spin space (see Fig. 1D). On the other hand, if we consider the case of a pure spin triplet superconductor, though the spectral amplitude of the time dependent correlator is non-trivial for a given $k$-point, due to its odd in

**FIG. 1. (Color online)** Schematic representation of the non-zero components of the odd-in-time equal-spin pair correlation function for different types of mixed parity configurations. a) and b) stand for the symmetric (oval) and asymmetric (trapezoid) spectral components for the two spin projections of the odd-in-time equal-spin correlations along a given direction. c) and d) indicate direction and amplitude of the odd-in-time equal-spin correlations for a centrosymmetric mixed parity unitary and non-unitary superconductor with respect to an applied magnetic field, respectively. e) and f) depict direction and amplitude of the odd-in-time equal-spin correlations for a non-centrosymmetric mixed parity without and with applied field, respectively. The light rectangle indicates the plane perpendicular to $h$ in c) and d), while it is the plane where $g_k$ and $d_k$ lie in e) and f). See the main text for the definition of $r_k, g_k, d_0k$, and $d_k$. 

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space parity the average over the Brillouin zone leads to a cancellation of the odd-in-time pair correlations. This result does not depend on the unitary character of the triplet superconductor.

Taking into account the previous analysis, one can directly construct the results for centrosymmetric mixed parity superconductors. There are two relevant cases to consider with respect to the unitary nature of the ground state, corresponding to a non-zero amplitude of the vectors \( \mathbf{r} \) and \( \mathbf{p} \). If we have a unitary superconductor, OTES correlations occur in the presence of an applied field and, as for the case of the pure singlet, they are \( Z_2 \) symmetric and in the plane perpendicular to \( \mathbf{h} \) (see Fig.1b). More interesting is the case of a non-unitary parity state. For such configurations the main role is played by a non-zero amplitude of the vector \( \mathbf{r} \). This vector is non-trivial if time-reversal is broken for either the triplet or the singlet component. Indeed, for the spin triplet it can lack time reversal invariance either in the orbital or in the spin channel. The latter would imply also a non-zero amplitude for the \( \mathbf{p} \) component. Alternatively, non-unitary \( \mathbf{r} \) states can also be related to a non-trivial phase relation between the singlet and the triplet order parameter that cannot be eliminated via a global gauge transformation. For these conditions, as schematically depicted in Fig. 1c, if the applied field is not perpendicular to \( \mathbf{r} \) the OTES occur in all directions (parallel and perpendicular to \( \mathbf{h} \)) and they also break the \( Z_2 \) symmetry along a given spin projection axis (Fig. 1b). Depending on the material system and on the \( k \)-symmetry of the order parameter, if it is possible to choose a magnetic field such as \( \mathbf{h} \perp \mathbf{r} \) for all \( \mathbf{k} \) then there will be a field direction for which OTES will lie in a plane otherwise they have a finite component for any space direction. It is worth pointing out that the angular dependence of OTES correlations versus \( \mathbf{h} \) can be used to establish whether mixed parity states exhibit time reversal symmetry breaking and get insight about the \( k \)-structure of the gap amplitude. A possible application is provided by the system \( \text{Pr(Os}_{1-x}\text{Ru}_x)_{4}\text{Sb}_{12} \) where a mixed parity phase that violates time reversal symmetry \([21]\) has been proposed to interpolate between the singlet and the triplet configurations achieved at the points \( x = 0 \) and \( x = 1 \), respectively. As a general remark, the observation of OTES can be an alternative method to muon spin rotation experiments for the detection of time reversal symmetry breaking states in mixed parity configuration.

Let us consider the case of noncentrosymmetric superconductors, thus mixed-parity states in the presence of an antisymmetric Rashba type interaction. In this respect, as pointed out in Ref. \([22]\), the most convenient configuration for the triplet \( \mathbf{d}_k \) vector is such that \( \mathbf{d}_k \parallel \mathbf{g}_k \), though a possible misalignment between the two vectors is not completely prohibited. The analysis has been performed in all the possible configurations \([23]\) while the present results, due to the limited space, refer only to the physical relevant ones. In Fig.1e, we have sketched the zero-field distribution of OTES correlations in the absence of an external source of time reversal symmetry breaking. In this case, OTES are coplanar to \( \mathbf{g}_k \) and exhibit a \( Z_2 \) symmetric behaviour at any given spin direction. The application of a magnetic field modifies the distribution of OTES pair correlations in the spin space in a way that depends on the amplitude of the product \( \mathbf{h} \cdot \mathbf{g} \). Only when the field has a parallel component with respect to \( \mathbf{g} \) then OTES pair correlations occur both along the direction of \( \mathbf{h} \) and perpendicular to it. A similar behaviour can also happen if the noncentrosymmetric system is non-unitary (see Fig. 1f). In this case, the non-orthogonality of the field with respect to \( \mathbf{r} \) also leads to OTES pair correlations in all the spin directions.

A relevant aspect for getting OTES in all spin directions is related to the structure of the excitations spectra. Indeed, the spectra at each \( k \)-point in the Brillouin zone can have four eigenvalues that fulfill or lack the mirror symmetry when turning \( E \) into \(-E\). The most

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TABLE I. Cases with non-trivial odd-in-time equal-spin triplet pair correlations. \( Y \) and \( N \) indicates non-zero and null amplitude of the corresponding variable, respectively. \( d_{0k} \) and \( d_k \) indicate the spin singlet and triplet part of the order parameter. \( r_k \) and \( g_k \) are the vectors associated with the non-unitary parity mixing component of the \( q_k \)-vector and the Rashba interaction in non-centrosymmetric system, respectively. \( \mathbf{h} \) is the applied field. \( F^{\sigma} \) is the odd-in-time correlator for pairs with equal-spin \( \sigma \) along a given direction. \( \mathbf{g}_k \) indicates the directions coplanar to the \( g_k \)-vector.

| Inversion | Magnetic field | Order parameter | OTES correlator |
|-----------|----------------|-----------------|-----------------|
| I         | \( \mathbf{h} \cdot \mathbf{r}_k \) | \( \mathbf{h} \cdot \mathbf{g}_k \) | \( d_{0k} \) | \( d_k \) | \( F^{\sigma} \) | \( F^{\sigma} \perp \mathbf{h} \) | \( F^{\sigma} \perp \mathbf{g}_k \) | \( F^{\sigma} \perp \mathbf{g}_k \) |
| Y         | Y              | N               | Y               | N               | Y               | N               | Y               | N               |
| Y         | Y              | N               | N               | Y               | Y               | Y               | N               | N               |
| Y         | Y              | Y               | Y               | Y               | Y               | Y               | N               | N               |
| N         | N              | N               | N               | Y               | Y               | Y               | N               | N               |
| N         | Y              | N               | N               | Y               | Y               | Y               | N               | N               |
| N         | Y              | Y               | Y               | Y               | Y               | Y               | Y               | Y               |
general conditions for which \( H_k \), i.e. the \( k \)-component of the \( H \) matrix, has two couples of opposite eigenvalues are given by a vanishing value for the linear and the cubic coefficients of the characteristic polynomial \( P_k = \text{Det}(H_k - \lambda I) = a_{0k} + a_{1k} \lambda + \xi \lambda^2 + a_{3k} \lambda^3 + a_{4k} \lambda^4 \), with \( a_{0k} = -Tr H_k = 0 \) and \( a_{1k} = 4(h \cdot r_k + 2u h \cdot g_k + P_k \cdot 8k) \). If \( a_{0k} \) and \( a_{1k} \) are both zero, one can exactly demonstrate, by means of symmetry arguments only, that the longitudinal component of \( F^\sigma \)\( h(t) \) \( (F^\sigma \cdot g(t)) \) with respect to the field (\( g \)-vector) is identically zero [23]. It is thus the removal of mirror symmetry in the energy spectrum together with the parity of the OTES \( k \)-component to yield missing cancellation for the longitudinal part with respect to the field when averaging in momentum space.

**Conclusions** We have shown that OTES pair correlations can occur in superconductors with parity mixing. For centrosymmetric systems this requires the presence of an applied magnetic field and can lead to an asymmetric distribution for opposite spin projections depending on the field orientation with respect to the mixed parity non-unitary component. In materials that lack inversion symmetry, OTES can occur in zero field with components coplanar to the \( g_k \)-vector or along all spin directions when a magnetic field not orthogonal to the \( g_k \)-vector is applied. Due to the intrinsic differences of the OTES correlations depending on the magnetic field direction, it is possible to distinguish between various types of mixed parity superconducting states. We find that the removal of quasi-particle degeneracy under parity and time symmetry is a key aspect for avoiding cancellation in the momentum space and get OTES pair correlations in all spin directions.

We point out that a possible way to detect OTES is by setting up an experiment where spin-polarized long range Josephson current is observed across a diffusive half-metallic ferromagnet at different uniform orientations of the magnetization. For the cases discussed in the paper there is no need to have an inhomogeneous profile of the magnetic pattern or spin active interfaces. The direction of the magnetization is used as an effective field to generate OTES along a given direction and at the same time as a filter to select the OTES pair correlations along a given spin direction. In particular for the case where OTES are longitudinal to the applied field it is possible to have spin-polarized pairs crossing the ferromagnet without the need of inhomogeneous profile in the magnetization.

This result can lead to a significant advance in the context of hybrid systems where the occurrence of mixed parity and subdominant components close to the interface can be the sources for time and parity symmetry breaking in the energy spectra and in turn for equal-spin odd-frequency pair correlations even without magnetic inhomogeneities. This observation can be used to engineer solutions where long range pairing currents can be induced by including sources of parity mixing at the interface between singlet superconductors and ferromagnets, especially in the form of Rashba type junctions, and by properly selecting the magnetization direction. Since this parity mixing mechanism works for a uniform magnetic profile it can also account for the persistence of the long range supercurrents in hybrids even when the applied magnetic field is such that no magnetic domains are present in the ferromagnet. We acknowledge useful discussions with I. Vekhter and J. Aarts. The research leading to these results has received funding from the FP7/2007-2013 under the grant agreement No. 264098 - MAMA.

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