Unconventional singlet-triplet superconductivity

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Abstract. Have you been lying awake wondering what symmetries determine whether a superconductor is spin-singlet, triplet, or both? We show that if one supplies additional degrees of freedom to BCS theory, spin-singlet can coexist with spin-triplet superconductivity. We guide the reader to the most general superconducting state using symmetry arguments. If both singlet and triplet pairing channels act, a magnetic field can convert between spin-singlet and triplet states. Two possible singlet-triplet superconductors candidates are: $CeRh_2As_2$ and bilayer-$NbSe_2$.

1. Introduction
The two key symmetries in conventional Bardeen-Cooper-Schrieffer (BCS) theory are time-reversal and inversion [1, 2]. The BCS superconducting ground state $|\psi_{\mathsf{BCS}}\rangle$ has a rigid phase, which occurs through the $U(1)$ phase symmetry breaking of the normal state. Unconventional superconductors break additional symmetries such as rotation, or the key symmetries of BCS theory. Another venue to unconventional superconducting states is examining additional degrees of freedom (DOFs), such as orbital, valley, sublattice, etc., which introduce non-trivial symmetries. Here, we introduce the superconducting state-vector of a superconductor with additional DOFs. The additional DOF leads to the possibility of having a superposition of singlet and triplet components in the state-vector. This contrasts with non-centrosymmetric superconductors, where the explicit removal of inversion symmetry is required.

2. The superconducting state-vector
Consider a superconducting order parameter $\Delta^{ab}_{s_1 s_2}(\mathbf{k}) \propto \langle c_{-\mathbf{k}s_2 b} c_{\mathbf{k}s_1 a}\rangle$, where $\mathbf{k}$ is momentum, $s_1, s_2 = \{\uparrow, \downarrow\}$ is the z-spin projection, and $a, b = \{1, 2\}$ is an additional internal DOF that could refer to orbitals, sublattice or layers. We assume that corresponding superconducting state-vectors to the order parameter can be written as

$$\left|\psi^{ab}_{sm}(\mathbf{k})\right\rangle = \phi(\mathbf{k})|\chi_{sm}\rangle \otimes |\Upsilon_{ab}\rangle, \tag{1}$$

where s is the total spin and $m = s_1 + s_2$, which is $s = m = 0$ for a singlet state and $s = 1$ for the triplet states $m = \{1, 0, -1\}$ [3]. Let us write the singlet state as $|\psi^{ab}_S(\mathbf{k})\rangle = \phi(\mathbf{k})|\chi_{00}\rangle \otimes |\Upsilon_{ab}\rangle = \phi(\mathbf{k})(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)| \otimes |\Upsilon_{ab}\rangle$ and the triplet states $|\psi^{ab}_{Tm}(\mathbf{k})\rangle = \phi(\mathbf{k})|\chi_{1,m}\rangle \otimes |\Upsilon_{ab}\rangle$, where $|\chi_{1,0}\rangle = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$, $|\chi_{1,1}\rangle = |\uparrow\uparrow\rangle$ and $|\chi_{1,-1}\rangle = |\downarrow\downarrow\rangle$. For the four possibilities of $|\Upsilon_{ab}\rangle$ we choose $|\Upsilon_{11}\rangle = |1, 1\rangle + |2, 2\rangle$, $|\Upsilon_{22}\rangle = |1, 1\rangle - |2, 2\rangle$, $|\Upsilon_{12}\rangle = |1, 2\rangle + |2, 1\rangle$ and $|\Upsilon_{21}\rangle = |1, 2\rangle - |2, 1\rangle$. The four possible spin states combined with the four possible internal DOF states give 16 possible configurations, as opposed to only 4 possibilities without the additional DOF.

2.1. Permutation and inversion symmetry

The Pauli principle enforces that under the action of the permutation operator $\mathsf{P}|\psi_{sm}^{ab}(\mathbf{k})\rangle = -|\psi_{sm}^{ab}(\mathbf{k})\rangle$. The permutation operator P takes $\mathbf{k} \to -\mathbf{k}$, $s_1 \leftrightarrow s_2$, and exchanges the particle subspaces $a \leftrightarrow b$. Then we have for singlets and triplets, respectively

$$\mathsf{P}\left|\psi_S^{ab}(\mathbf{k})\right\rangle = \mathsf{P}\left[\phi(\mathbf{k})|\chi_{00}\rangle \otimes |\Upsilon_{ab}\rangle\right] = -\phi(-\mathbf{k})|\chi_{00}\rangle \otimes |\Upsilon_{ba}\rangle \stackrel{\mathrm{Pauli}}{=} -\phi(\mathbf{k})|\chi_{00}\rangle \otimes |\Upsilon_{ab}\rangle; \quad (2)$$

$$\mathsf{P}\left|\psi_{Tm}^{ab}(\mathbf{k})\right\rangle = \mathsf{P}\left[\phi(\mathbf{k})|\chi_{1,m}\rangle \otimes |\Upsilon_{ab}\rangle\right] = \phi(-\mathbf{k})|\chi_{1,m}\rangle \otimes |\Upsilon_{ba}\rangle \stackrel{\mathrm{Pauli}}{=} -\phi(\mathbf{k})|\chi_{1,m}\rangle \otimes |\Upsilon_{ab}\rangle. \quad (3)$$

If we ignore the internal DOF $|\Upsilon_{ab}\rangle$, the last equality in Eqs. (2) and (3) tell us that for a singlet (triplet) state the momentum structure $\phi(\mathbf{k})$ must be even (odd) [1, 2]. However, in the presence of $|\Upsilon_{ab}\rangle$, even-momentum-triplets and odd-momentum-singlets can now exist, because the Fermionic antisymmetry can now be carried by an additional DOF $|\Upsilon_{ab}\rangle$.

It is instructive to determine the inversion (parity) sectors of the superconducting state-vectors. The action of the inversion operator $\mathsf{I}\left|\psi_{sm}^{ab}(\mathbf{k})\right\rangle$ takes $\mathbf{k} \to -\mathbf{k}$, leaves the spins $\{s_1, s_2\}$ invariant, and we assume that $\mathsf{I}|\Upsilon_{ab}\rangle$ exchanges not the particle subspaces, but the DOFs $1 \leftrightarrow 2$, as would be the case when different sublattices are related by inversion. Then we have

$$\mathsf{I}\left|\psi_{sm}^{ab}(\mathbf{k})\right\rangle = \mathsf{I}\left[\phi(\mathbf{k})|\chi_{sm}\rangle \otimes |\Upsilon_{ab}\rangle\right] = \phi(-\mathbf{k})|\chi_{sm}\rangle \otimes \mathsf{I}|\Upsilon_{ab}\rangle = \phi(-\mathbf{k})|\chi_{sm}\rangle \otimes \begin{cases} |\Upsilon_{ab}\rangle, \ (a=1) \\ -|\Upsilon_{ab}\rangle, \ (a=2). \end{cases}$$
$$(4)$$

If we ignore $|\Upsilon_{ab}\rangle$, Eq. (4) tells us that singlets ($\phi(\mathbf{k}) = \phi(-\mathbf{k})$) belong to the $+1$ inversion sector, whereas triplets ($\phi(\mathbf{k}) = -\phi(-\mathbf{k})$) belong to the -1 inversion sector. Therefore, if the system is inversion symmetric, the superconducting state-vector must have a definite parity, that is, it either belongs to the parity eigenvalue sector $+1$ or -1. In this case, inversion symmetry prohibits a superposition of a singlet with a triplet state. When an inversion symmetric superconducting material lacks additional DOFs, one then knows that its superconducting state is either singlet or triplet. What if inversion symmetry lacks? Then, there is no definite parity (and no selection rule) which allows a singlet-triplet superposition in the state-vector. The main message of Eq. (4) is that in the presence of additional DOFs $|\Upsilon_{ab}\rangle$, a singlet-triplet superposition is symmetry allowed even in inversion symmetric systems.

2.2. Singlet-triplet states

As an example, consider the superposition $|\psi(\mathbf{k})\rangle = c_1|\psi_S^{11}(\mathbf{k})\rangle + c_2|\psi_{T0}^{22}(\mathbf{k})\rangle$, where c_1 and c_2 are complex coefficients. By applying the permutation operator, we obtain

$$\mathsf{P}|\psi(\mathbf{k})\rangle = c_1\mathsf{P}|\psi_S^{11}(\mathbf{k})\rangle + c_2\mathsf{P}|\psi_{T0}^{22}(\mathbf{k})\rangle = c_1\phi_1(-\mathbf{k})\left[-|\chi_{00}\rangle\right] \otimes |\Upsilon_{11}\rangle + c_2\phi_2(-\mathbf{k})|\chi_{T,0}\rangle \otimes |\Upsilon_{22}\rangle. \ (5)$$

The Pauli principle then imposes that $\phi_1(\mathbf{k})$ is an even function and $\phi_2(\mathbf{k})$ must be odd. With this knowledge, we now apply the inversion operator to check the parity sectors. We obtain $\mathsf{P}|\psi_S^{11}(\mathbf{k})\rangle = (+1)|\psi_S^{11}(\mathbf{k})\rangle$ and $\mathsf{P}|\psi_{T0}^{22}(\mathbf{k})\rangle = (+1)|\psi_{T0}^{22}(\mathbf{k})\rangle$, where we used $\mathsf{I}|\Upsilon_{22}\rangle = -|\Upsilon_{22}\rangle$. Therefore, because of the additional DOF, $|\psi_S^{11}(\mathbf{k})\rangle$ singlets and $|\psi_{T0}^{22}(\mathbf{k})\rangle$ triplets belong to the same parity, which allows them to coexist in a superposition even in an inversion symmetric material. The mathematical subtlety relies on the fact that $\mathsf{P}|\Upsilon_{22}\rangle = |\Upsilon_{22}\rangle$, but $\mathsf{I}|\Upsilon_{22}\rangle = -|\Upsilon_{22}\rangle$.

The most general even and odd superpositions are

$$|\psi_{\mathsf{even}}\rangle = c_1|\psi_S^{11}\rangle + c_2|\psi_S^{12}\rangle + c_3|\psi_S^{21}\rangle + c_4|\psi_{T0}^{22}\rangle + c_5|\psi_{T,1}^{22}\rangle + c_6|\psi_{T,-1}^{22}\rangle; \quad (6)$$

$$|\psi_{\mathsf{odd}}\rangle = c_7|\psi_S^{22}\rangle + c_8|\psi_{T0}^{11}\rangle + c_9|\psi_{T0}^{12}\rangle + c_{10}|\psi_{T0}^{21}\rangle + c_{11}|\psi_{T1}^{11}\rangle + c_{12}|\psi_{T,-1}^{11}\rangle + c_{13}|\psi_{T1}^{12}\rangle + c_{14}|\psi_{T,-1}^{12}\rangle$$
$$+ c_{15}|\psi_{T1}^{21}\rangle + c_{16}|\psi_{T,-1}^{21}\rangle.$$
$$(7)$$

Here, all the 16 possible states are assigned to an even or odd sector. If the system lacks inversion, then $|\Psi\rangle = |\psi_{\text{even}}\rangle + |\psi_{\text{odd}}\rangle$. The singlet state $c_7|\psi_S^{22}\rangle$ deserves special attention since it is the only parity-odd-singlet. Suppose that the pairing mechanism of an inversion symmetric material only admits singlet instabilities. This means that because of the additional DOF, there are always mutually excluding even-singlet and odd-singlet instabilities that might *switch* depending on external parameters. This is likely to be the case in CeRh$_2$As$_2$ [4], and possibly also in few-layer NbSe$_2$ [5].

3. Effect of a Zeeman field

What are the interesting properties of the perhaps so far speculated singlet-tripled mixed superconductors? One interesting aspect is how the multicomponent superconducting state responds to a Zeeman magnetic field. It is intuitive to understand why. Heuristically, a Zeeman field applied to a singlet state $|\chi_{00}\rangle = |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$ will try to polarize the spins along the magnetic field and thus breaking up the singlet configuration. In contrast, a Zeeman field applied for instance to the triplet state $|\chi_{1,\pm1}\rangle$ only favors it. Even more, if there is an attractive pairing in both singlet and triplet channels, instead of breaking up the singlets, the Zeeman field can convert the singlet configuration to a triplet. Then, the field can control the singlet-triplet volume ratio.

Let us give a simple geometric description of the singlet-triplet conversion process. Consider a 2D superconductor with the quantization axis set perpendicularly to the 2D plane. The superconducting state at zero field is taken to be the pure singlet

$$|\Psi_0(\mathbf{k})\rangle = |\psi_S^{11}(\mathbf{k})\rangle = \phi(\mathbf{k})|\chi_{00}\rangle \otimes |\Upsilon_{11}\rangle = [|\mathbf{k}\uparrow\rangle|-\mathbf{k}\downarrow\rangle - |\mathbf{k}\downarrow\rangle|-\mathbf{k}\uparrow\rangle] \otimes |\Upsilon_{11}\rangle. \qquad (8)$$

We now apply a magnetic field along the y-axis. In the very large magnetic field limit, according to the heuristic conversion argument, we expect all singlets to convert to triplets. The action of the y-directed magnetic field on a $|\mathbf{k}\uparrow\rangle$ state can be implemented as a spin rotation around the x-axis $R_x(\theta) = \exp(-i\sigma_x\theta/2)$. In the large magnetic field limit, and taking into account that Cooper pairing occurs at opposite momenta, the action of the magnetic field B_y on an arbitrary state is $\mathsf{B}_y = R_x(\text{sgn}(\pm\mathbf{k})\pi/2)$, where the sign function determines whether the state is located at positive or negative momenta [6]. Since B_y does not act on $|\Upsilon_{11}\rangle$, we omit it in the following. We have

$$\mathsf{B}_y|\Psi_0(\mathbf{k})\rangle = R_x\left(\frac{\pi}{2}\right)|\mathbf{k}\uparrow\rangle R_x\left(-\frac{\pi}{2}\right)|-\mathbf{k}\downarrow\rangle - R_x\left(\frac{\pi}{2}\right)|\mathbf{k}\downarrow\rangle R_x\left(-\frac{\pi}{2}\right)|-\mathbf{k}\uparrow\rangle = i\left(|\psi_{T1}(\mathbf{k})\rangle - |\psi_{T,-1}(\mathbf{k})\rangle\right). \qquad (9)$$

The action of B_y converted $|\psi_S(\mathbf{k})\rangle$ to $\pm i|\psi_{T,\pm1}(\mathbf{k})\rangle$. Such a Zeeman induced singlet to triplet conversion can occur in inversion symmetric superconductors with additional DOFs [7] or in non-centrosymmetric materials where no additional DOF is necessary [6, 8, 7].

4. Locally non-centrosymmetric superconductors

Materials that have an inversion center can exhibit properties of non-centrosymmetric materials. This can occur in layered crystals, where each layer alone lacks inversion, but when combined with the other layers, inversion symmetry is restored [9, 7].

4.1. CeRh$_2$As$_2$

We now apply the general ideas discussed above to the new two-phase superconductor CeRh$_2$As$_2$. The magnetic field – temperature phase diagram of CeRh$_2$As$_2$ displays a low and high field phase [4]. From crystal structure, one expects that the in-plane Rashba SOC components $\{\gamma_x, \gamma_y\}$ are larger than the perpendicular Ising component γ_z [9]. Therefore, as a first approximation, we can consider the magnetic field $\mathbf{B} \perp \boldsymbol{\gamma}$.

A superconducting instability analysis shows that the state-vector c_1 in Eq. (6) has the highest critical temperature at zero field [9]. Since the crystal contains the inversion element, all odd states in Eq. (7) are prohibited to coexist with the even states in Eq. (6). However, an odd state-vector might switch with the initially dominant even state at high Zeeman fields. The odd-singlet c_7 state becomes energetically favorable at high magnetic fields. This happens because the c_7 states accommodates better to the joint presence of magnetic field, spin-orbit coupling and inter-sublattice hoppings. This is a universal property of locally non-centrosymmetric superconductors, and perhaps one can speculate more discoveries of dominant c_7 states soon.

Because of the joint presence of spin-orbit coupling $\boldsymbol{\gamma}$ and magnetic field $\mathbf{B} \perp \boldsymbol{\gamma}$, if there is (even small) attraction in the triplet channels, the field converts c_7 singlets to equal spin $\{c_{11}, c_{12}\}$ triplets. But this is not all. In the odd-phase, an additional conversion mechanism due to the joint presence of inter-sublattice hoppings and magnetic field also converts the c_7 singlets to inter-sublattice $\{c_{13}, c_{14}, c_{15}, c_{16}\}$ triplets. The zero-field $\{c_9, c_{10}\}$ triplets would require an intrinsic parity-mixed channel in the pairing interaction.

4.2. Bilayer-NbSe₂

Transition metal dichalcogenide bilayers with D_{3d} crystal symmetry are described by the same model as for CeRh₂As₂, but instead of Rashba SOC, one now has Ising SOC $\boldsymbol{\gamma}(\mathbf{k}) = (0, 0, \gamma_z(\mathbf{k}), 0)$. Since γ_z locks the spins in the z-direction, these so called *Ising superconductors* are robust against in-plane fields $\mathbf{B} \perp \boldsymbol{\gamma}$. The dominant superconducting component at zero field is very likely to be the c_1 state in Eq. (6) [5]. For in-plane fields, the same superconducting solutions found for CeRh₂As₂ for e perpendicular magnetic field apply to bilayer-TMDs. Also, because of the thin bilayer, an in-plane magnetic field couples dominantly to the spin degrees of freedom, such that orbital effects are expected to be very small. This makes bilayer-NbSe₂ a strong candidate for the c_7 odd-singlet state at high in-plane fields. It is possible that recent high field measurements already hint the c_7 state [5], but more high-field experimental data is needed.

5. Conclusion

If additional DOFs lack, singlet-triplet superconductivity can only occur via parity-mixing, which requires broken inversion symmetry. With additional DOFs, singlet-triplet pairing can occur within the same parity sector. The odd-parity sector contains only one singlet state. It is a universal property of locally non-centrosymmetric superconductors that the odd-parity singlet becomes favorable at high magnetic fields. If subleading pairing channels exist, the magnetic field converts the odd-singlets to both inter-sublattice triplets and intra-sublattice equal spin-triplets.

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