s+if pairing in Ising superconductors

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(Dated: February 8, 2019)

We show that an in-plane Zeeman field applied to non-centrosymmetric Ising superconductors converts singlet s-wave Cooper pairs to equal-spin triplet if pairs, leading to an enhancement of the critical transition line beyond expected from Ising spin-orbit coupling. Singlet to triplet conversion relates to a phase transformation due to spin rotation by the Zeeman field and has a geometric origin. The discussion is especially relevant, but not limited to monolayer transition metal dichalcogenides.

Introduction.— In non-centrosymmetric superconductors, the presence of momentum odd spin-orbit coupling (SOC) leads to parity-mixed Cooper pair wave functions [1–3]. The lack of an inversion center allows for the co-existence of a parity-even singlet and a parity-odd triplet pairing [4]. A Zeeman field and SOC affect singlet and triplet Cooper pairs in distinct ways. The Zeeman field breaks singlets, which is referred to as paramagnetic limiting. This is different for triplets, which might align their spin along the magnetic field avoiding paramagnetic limiting [5–7]. By contrast, SOC suppresses the inter-valley impurity scattering suppresses the critical Zeeman field. Later in Ref. [19], we showed that the interplay of Zeeman field and SOC, and mainly focus on real singlet and $S_z=\pm 1$ imaginary triplet order parameters changes sign under the rotation by $\pi/3$, and have $f$-wave symmetry. The $S_z=0$ triplet parameter is present even in the absence of Zeeman field and respects the time-reversal symmetry. The $S_z=\pm 1$ triplets are induced by the Zeeman field and break the time-reversal symmetry of the superconducting state. For this reason, the order parameter describing these triplets is purely imaginary. Here, we study the interplay of Zeeman field and SOC, and mainly focus on real singlet and $S_z=\pm 1$ imaginary triplet order parameters. The resulting superconducting state has, therefore, $s+if$ symmetry.

The findings presented here are relevant for non-centrosymmetric superconductors, where the applied magnetic field has an orthogonal component to the effective SOC field. This applies to a large class of materials [20], which besides monolayer TMDs include interface superconductivity [21] and artificial heterostructures [22].

The Hamiltonian and free energy.— The standard model of a superconductor with anti-symmetric SOC $\gamma_k = -\gamma_{-k}$ and a Zeeman field $\mathbf{B}$ is [2]

$$H = \sum_{k,s} \xi_k c_{k s}^\dagger c_{k s} + \sum_{k,s,s'} (\gamma_k - \mathbf{B} \cdot \sigma)_{ss'} c_{k s}^\dagger c_{k s'},$$

$$+ \frac{1}{2} \sum_{k,k',\{s_i\}} V_{s_1 s_2 s'_1 s'_2} (k,k') c_{k s_1}^\dagger c_{-k s_2}^\dagger c_{-k' s'_2} c_{k' s'_1}. \tag{1}$$

The normal state dispersion $\xi_k = \xi_{-k}$ includes the chemical potential. We define the average over the Fermi surface $\langle |\gamma_k| \rangle_{\text{FS}} = \Delta_0^2$. We use units where $\mathbf{B}$ absorbs usual the prefactor with the $g$-factor and the Bohr magneton $g \mu_B/2$. The interaction in the Cooper channel can
be separated into singlet and triplet parts as
\[
V_{s_1 s_2 , s'_1 s'_2} (k, k') = \sum_{\Gamma, j} (-\nu_{r, \Gamma}) \left[ \hat{\tau}_{\Gamma, r_j} \right]_{s_1 s_2} \left[ \hat{\tau}_{\Gamma', r_j} \right]_{s'_1 s'_2}^* \, \mathcal{G} \, \sum_{\Gamma, j} (-\nu_{r, \Gamma}) \left[ \hat{\tau}_{\Gamma, r_j} \right]_{s_1 s_2} \left[ \hat{\tau}_{\Gamma', r_j} \right]_{s'_1 s'_2}^* ,
\]
(2)
where \( \hat{\tau}_{\Gamma, r_j} = \hat{\psi}_{\Gamma, r_j} i \sigma_y \) and \( \hat{\tau}_{\Gamma, r_j} = d_{\Gamma, r_j} \cdot \sigma \sigma_y \). \( j \) labels the basis functions of an irreducible representation \( \Gamma \), and \( \nu_{r, \Gamma} \) are interactions in each channel and can be attractive (positive) or repulsive (negative). In a noncentrosymmetric material, singlet and triplet channels may belong to the same \( \Gamma \) and therefore are allowed to couple [8]. We do not include such terms in Eq. (2), since as we demonstrate, parity-mixing is induced primarily by the Zeeman field and does not depend on interaction channel mixing.

We introduce the superconducting mean fields \( \Delta_{s_1 s_2} (k) = \sum_{k', s_1', s_2'} V_{s_1 s_2, s_1' s_2'} (k, k') (\epsilon_k' - \epsilon_k) \cdot \Delta_{s_1' s_2'} \), that are matrix elements of the gap matrix in spin-space \( \Delta_k = \langle \psi_0 | \sigma \rangle \Delta_k \). The even order parameter \( \psi_0 = \sum_{s} \left( \hat{\psi}_{s} \right) \) parametrizes singlets, and the odd \( \psi_0 = -d_{s} \) parametrizes triplets.

We use a path integral approach to obtain free energy (See Supplemental Material at [URL will be inserted by publisher] for a detailed derivation)
\[
F = -\frac{1}{2} \sum_{k, k', s_1, s_2} \Delta_{s_1 s_2}^* (k') V_{s_1 s_2, s'_1 s'_2} (k, k') \Delta_{s'_1 s'_2} (k) + \frac{1}{2} T \sum_{k, \omega_n} \sum_{l=1}^{2l} (-1)^l \langle G(k, \omega_n) \Delta_k \Delta^T (k, -\omega_n) \Delta^*_k \rangle^l,
\]
(3)
where \( \omega_n = (2n+1) \pi T \) are Matsubara frequencies, and the normal state Green’s function \( G(k, \omega_n) \) can be expressed in terms of its band projections
\[
G(k, \omega_n) = G_+ (k, \omega_n) \sigma_0 + G_- (k, \omega_n) \hat{g}_k \cdot \sigma; \quad (4)
\]
\[
G_{\pm} (k, \omega_n) = \frac{1}{2} \left[ \frac{1}{i \omega_n - \epsilon_{k,+}} \pm \frac{1}{i \omega_n - \epsilon_{k,-}} \right],
\]
(5)
where \( \epsilon_{k, \pm} = \xi_k \pm |\gamma_k - B| \) and \( \hat{g}_k = (\gamma_k - B) / |\gamma_k - B| \).

Parity-mixing by Zeeman field. — The truncation to quadratic order \( (l = 1) \) in the order parameters of Eq. (3) determines the transition line \( B_c (T) \). We introduce the short notation for the products \( G_{\pm} G_{\pm} = G_0 (k, \omega_n) G_{\pm} (k, -\omega_n) \) with \( a, b = \pm \). Choosing real \( \psi_0 \), we calculate the trace in Eq. (3) for \( l = 1 \)
\[
\frac{1}{2} \text{tr} \left[ G(k, \omega_n) \Delta_k \Delta^T (k, -\omega_n) \Delta^*_k \right] = G_+ G_+ (|\psi_0|^2 + |d_k|^2) - G_- G_- (|\psi_0|^2 \hat{g}_k \cdot \hat{g}_k + \hat{g}_k \cdot d_k \cdot \hat{g}_k) - (\hat{g}_k \cdot d_k) \cdot (\hat{g}_k \cdot d_k) + G_+ G_- (2 \psi_0 \hat{g}_k \cdot \Delta k) + G_+ G_- (2 \psi_0 \hat{g}_k \cdot \Delta k \cdot d_k)
\]
(6)
where \( \hat{g}_k = \hat{d}_k \times \hat{d}_k \). If the superconducting states respect time-reversal symmetry \( (\text{Im} d_k = 0) \), the singlet-triplet mixing occurs in \( a \neq b \) terms only. Such terms, however, are proportional to the difference of density of states of the two Fermi sheets at the Fermi level \( E_F \), \( \Delta N = N_{F, +} - N_{F, -} \), which gives a contribution of the order \( \Delta N / E_F \) [5]. Then, if \( \Delta N / E_F \ll 1 \), the singlet and triplet channels decouple at the quadratic level and can be studied separately. As the Zeeman field breaks time-reversal, singlet-triplet coupling arises via the term of Eq. (6) proportional to \( 2 \psi_0 (\hat{g}_k \cdot \hat{g}_k - \hat{g}_k \cdot d_k) \cdot \text{Im} d_k \), which is non-negligible even when \( \Delta N / E_F \ll 1 \).

Ising superconductors. — To work out a concrete example, we consider monolayer TMDs with point group symmetry \( D_{3h} \). We assume \( \Delta N / E_F \ll 1 \), which allows us to neglect the \( a \neq b \) terms in Eq. (6), and write \( \sum_k \rightarrow N_0 \int_{2 \pi} d l / 2 \int_{-\pi}^{\pi} d \epsilon_k \), where \( N_0 \) is the density of states at the Fermi level of the two Fermi sheets and \( \epsilon_k \) is a characteristic cutoff energy of the pairing interaction. We specialize to the case where \( B \parallel \gamma_k \parallel \hat{z} \), relevant for Ising superconductors in general [19]. For this special case, the band splittings at opposite momenta \( \epsilon_k \) remain the same \( |\gamma_{k, +} - B| = \sqrt{|\gamma_k|^2 + B^2} \), ensuring perfect Fermi surface nesting for Cooper pairing; see Fig. (2). Then, singlets and triplets only mix in the triple product
\[
2 \psi_0 (\hat{g}_k \times \hat{g}_k - \hat{g}_k) \cdot \text{Im} d_k \propto B \times \gamma_k \cdot \text{Im} d_k. \quad (7)
\]

Only imaginary in-plane components of the \( d \)-vector breaking time-reversal contribute to the triplet product.

We exploit the singlet and triplet order parameters of a specific \( 1 \)-dimensional irreducible representation \( \Gamma \) of \( D_{3h} \) in terms of hatted basis functions as \( \psi_{k, \Gamma} = \sum_{l=1}^{l_{\Gamma}} \psi_l \hat{\psi}_{k, \Gamma} l \), and \( d_{k, \Gamma} = \sum_{l=1}^{l_{\Gamma}} \eta_l d_{k, \Gamma} l \), where \( \psi_l \), and \( \eta_l \), serve as complex Ginzburg-Landau (GL) order parameters of the singlet and triplet component, respectively. We consider the singlet channel \( \psi_{k, A'_1} = \psi_{0, 1} \), and two channels for the triplets: \( d_{k, A'_1} = \eta_{k, \hat{z}} \gamma_k + \eta_{k, \hat{y}} \gamma_k \hat{y} \),\( \psi_{k, E'} = \eta_k \gamma_k \hat{z} + \eta_{k, \hat{y}} \gamma_k \hat{y} \); see Table I. With this decomposition into channels, we can write \( \psi_0 = \psi_{0, 1} \) and \( d_k = \gamma_k (\eta_{k, \hat{z}} \hat{y} + \eta_{k, \hat{y}} \hat{z}) \), keeping in mind that \( \{\psi_0, \eta_k\} \) belong to \( A'_1 \) and \( \{\eta_{k, \hat{z}}, \eta_{k, \hat{y}}\} \) to \( E' \).

The triplet product in Eq. (7) mixes the \( A'_1 \) singlet (\( s \)-wave) and the \( E' \) triplet (\( i f \)-wave) channels. The resultant parity-mixed superconducting state is referred to as \( s + if \). Therefore, because of the interaction in the \( E' \) channel, the Zeeman field induces equal-spin triplets.

| Irrep | Singlet \( \psi_0 \) | Triplet \( d_k \) | Order parameter | Limited by | Zeeman field |
|-------|-----------------|-------------|-----------------|----------|-------------|
| \( A'_1 \) (s) | \( \gamma_k \hat{z} \) | \( \psi_0 \) | \( \eta_k \) | \( \eta_{k, \hat{z}} \) | Ising SOC |
| \( E' \) (if) | \( \gamma_k \hat{x} \) | \( \gamma_k \hat{y} \) | \( \eta_{k, \hat{x}} \) | \( \eta_{k, \hat{y}} \) | Ising SOC |

| \( d_k \) = \( i d_k \times d_k \). If the superconducting states respect time-reversal symmetry (Im \( d_k \) = 0), the singlet-triplet mixing occurs in \( a \neq b \) terms only. Such terms, however, are proportional to the difference of density of states of the two Fermi sheets at the Fermi level \( E_F \), \( \Delta N = N_{F, +} - N_{F, -} \), which gives a contribution of the order \( \Delta N / E_F \) [5]. Then, if \( \Delta N / E_F \ll 1 \), the singlet and triplet channels decouple at the quadratic level and can be studied separately. As the Zeeman field breaks time-reversal, singlet-triplet coupling arises via the term of Eq. (6) proportional to \( 2 \psi_0 (\hat{g}_k \times \hat{g}_k - \hat{g}_k \cdot d_k) \cdot \text{Im} d_k \), which is non-negligible even when \( \Delta N / E_F \ll 1 \).
Without loss of generality, we can fix the direction of $\mathbf{B} = B \hat{e}_z$, such that we rewrite $d_{\mathbf{k}} = \gamma_{\mathbf{k}}(0, i\eta_y, \eta_z)$, where $\eta_y$ and $\eta_z$ are now real. In the limit $\Delta_{so}/E_F \ll 1$, $\eta_z$ decouples from the $\{\psi_0, \eta_y\}$ subsystem at the quadratic level. The decoupled triplet $d_{\mathbf{k}, A} \parallel \gamma_{\mathbf{k}}$ is protected from both the Zeeman field and SOC, and for this reason, we focus on the $\{\psi_0, \eta_y\}$ subsystem. The main point is: although the basis functions of $A_1$ and $E'$ are orthogonal, they mix due to the Zeeman field in Eq. (7).

The $B_c(T)$ transition.—We now obtain the continuous superconducting to normal state transition lines $B_c(T)$ using Eq. (3) with $l = 1$. The energy integrals followed by the Matsubara summation can be performed to obtain (See Supplemental Material at [URL will be inserted by publisher] for details)

$$T \sum_{\omega_n} \int d\xi G_+ G_+ = \log[2e^2 \epsilon_c/(\pi T)] - C(\rho_k)/2;$$  

$$T \sum_{\omega_n} \int d\xi G_- G_- = C(\rho_k)/2;$$

$$C(\rho_k) = \text{Re} \left\{ \psi \left( \frac{1}{2} + \frac{i\rho_k}{2} \right) - \psi \left( \frac{1}{2} \right) \right\} \geq 0,$$

where $\psi(z)$ is the digamma function, $\rho_k = \sqrt{|\gamma_k|^2 + B^2}/(\pi T)$, and $\gamma$ is Euler’s constant.

From Eqs. (8,9,10) and the trace (6), we obtain the quadratic free energy

$$\frac{1}{2N_0} F_{T,B}^{(t=1)} [\psi_0, \eta_y] = \alpha_s(T, B) \psi_0^2 + \alpha_t(T, B) \eta_y^2 + 2\alpha_{st}(T, B) \psi_0 \eta_y,$$

with the coefficients defined as

$$\alpha_s(T, B) = \ln \left( \frac{T}{T_{cs}} \right) + C(\rho) \frac{B^2}{\Delta_{so}^2 + B^2};$$  

$$\alpha_t(T, B) = \ln \left( \frac{T}{T_{ct}} \right) + C(\rho) \frac{\Delta_{so}^2}{\Delta_{so}^2 + B^2};$$

$$\alpha_{st}(B) = -C(\rho) \frac{B \Delta_{so}}{\Delta_{so}^2 + B^2};$$

where $T_{cs}(T_{ct})$ is the singlet (triplet) critical transition temperature determined by $(N_0 \nu_{s,A_1})^{-1} = \ln[2e \epsilon_c/(\pi T_{cs})]$ and $(N_0 \nu_{s,E'})^{-1} = \ln[2e \epsilon_c/(\pi T_{ct})]$, and $\rho = \sqrt{\Delta_{so}^2 + B^2}/(\pi T)$. Eq. (11) clearly shows the limiting mechanisms acting on the singlet and triplet components. Positive terms in Eq. (11) suppress the superconducting state and negative terms stabilize it. $\alpha_s$ shows that the Zeeman field limits the s-wave singlets $\psi_0$. By contrast, $\alpha_t$ shows that SOC limits the i-f-wave triplets $\eta_y$. With different limiting mechanisms (Zeeman field and SOC) affecting different order parameters ($\psi_0$ and $\eta_y$), their mixing via $\alpha_{st}$ can be interpreted as a conversion of s-wave singlets to equal-spin i-f-wave triplet Cooper pairs by the Zeeman field. Interestingly, $\alpha_{st}(T, B)$ vanishes in purely triplet superconductors, where anti-symmetric SOC vanishes.

Minimization of the free energy Eq. (11) yields the pair-breaking equation $\alpha_s(T, B) \alpha_t(T, B) = \alpha_{st}^2(B)$ that determines $B_c(T)$. If the attraction exists only in the s-wave singlet channel, the above condition reduces to the pair-breaking equation $\alpha_s(T, B) = 0$, which is found in Refs. [5, 18, 21]. We plot $B_c(T)$ in Fig. 1a, which is very sensitive to if components.

![Figure 1](image-url)
The Ginzburg-Landau (GL) regime.— To obtain the order parameters \( \{ \psi_0, \eta_0 \} \) in the superconducting phase, we keep the quartic terms \( (l = 2) \) in the GL expansion (3) near \( T = T_{cs} \),

\[
\frac{1}{2N_0} F_{T,B}[\psi_0, \eta_0] = \alpha_s(T_{cs}, B) \psi_0^2 + \alpha_t(T_{cs}, B) \eta_0^2 \\
+ 2\alpha_{st}(B) \psi_0 \eta_0 + \beta_1(B) (B \psi_0 - \Delta_{so} \eta_0)^2 (\Delta_{so} \psi_0 + B \eta_0)^2 \\
+ \beta_2(B) (B \psi_0 - \Delta_{so} \eta_0)^4 + \beta_3(B) (\Delta_{so} \psi_0 + B \eta_0)^4, 
\]

where the coefficients of the quadratic terms are defined in Eq. (12) and the coefficients of the quartic terms are

\begin{align}
\beta_1(B) &= \frac{\text{Im } \psi^{(1)}}{2\pi T_{cs} (\Delta_{so}^2 + B^2)^{3/2}} - \frac{C(\rho_{cs})}{(\Delta_{so}^2 + B^2)^3}; \\
\beta_2(B) &= -\frac{\text{Re } \psi^{(2)}}{16\pi^2 T_{cs}^2 (\Delta_{so}^2 + B^2)^2}; \\
\beta_3(B) &= \frac{7\zeta(3)}{8\pi^2 T_{cs}^2 (\Delta_{so}^2 + B^2)^2},
\end{align}

with \( \rho_{cs} = \rho(T_{cs}) \), and the poly-gamma functions are defined as \( \psi^{(m)} = \frac{d^m}{dz^m} \psi(z) \). In Fig. 1(b-d) we show the order parameters in the superconducting phase obtained by minimizing the free energy, Eq. (13).

Discussion and conclusion.— The singlet to triplet conversion has a transparent geometrical interpretation, see Fig. 2. At \( B = 0 \), SOC polarizes the electron states out of the plane so that the spin-up and spin-down Fermi lines cross, Fig. 2(a,b). The Cooper pair is singlet formed by the two spin states at momenta \( \pm k \), \( \Psi_s = |k, \uparrow; -k, \downarrow\rangle - |k, \downarrow; -k, \uparrow\rangle \), where \( |m; n\rangle \) denotes the two-fermion state with \( m \) and \( n \) being the quantum numbers for each of the occupied states.

Consider the transformation of \( \Psi_s \) induced by strong Zeeman field \( B \gg \Delta_{so}; \) Fig. 2(b). In this limit, all the coefficients of the quadratic terms are defined

\[
\psi_T = |k, U_B^{\uparrow}; -k, U_B^{\downarrow}; -k, U_B^{\uparrow}; -k, U_B^{\downarrow}; \rangle, 
\]

where \( U_B^{\uparrow} \) is the operator of spinor rotation around an axis along \( n \) by an angle \( \varphi \). Since \( |\downarrow\rangle = |U_B^{\uparrow}\rangle \) and the geometrical phase \( U_{2\pi} = -1 \), Eq. (15) reduces to

\[
\Psi_t = |k, \uparrow; -k, \uparrow\rangle + |k, \downarrow; -k, \downarrow\rangle. 
\]

As expected, the Zeeman field converts the singlet \( \Psi_s \) into a \( S_z = \pm 1 \) triplet state Eq. (16). This state is odd under time-reversal \( T \) thanks to the geometric phase and is parameterized by \( \Im [\text{dk}_B] \neq 0 \). Being triplet, it is also odd in \( k \). The only combination that satisfies the above requirements is \( \text{dk}_B \propto i \gamma_k \times B \), see Fig. 2(a).

We now discuss the dependence of the singlet-to-triplet conversion on SOC. The Zeeman field is effective only if it couples occupied and unoccupied states split by SOC. Therefore, when SOC is smaller than the superconducting gap, the spin-triplet conversion is negligible. In the opposite limit, the phase space available for a converted pairs scales with the spin splitting \( \sqrt{\Delta_{so}^2 + B^2} \). This is the reason for the logarithmic enhancement of the spin-triplet mixing terms in Eq. (12), \( \alpha_{s,t,st} \propto C(\rho) \approx \ln(\sqrt{\Delta_{so}^2 + B^2}) \) in the strong SOC limit.

As shown in Fig. 1a, a weak attraction has a strong effect on \( B_c(T) \) while the effect of repulsion is less pronounced. Close to \( T_{cs} \), the enhancement of the critical field can be obtained from the pair-breaking equation in the limit \( \Delta_{so}/T_{cs} \gg 1 \), which gives

\[
\frac{B_c^2(T)}{\Delta_{so}^2} = \left( \frac{\ln \Delta_{so}}{\ln \Delta_{cs}} \right)^2 \left( \frac{1 - \frac{T}{T_c}}{\frac{T}{T_c}} \right), 
\]

where \( \Delta_{cs(ct)} = (\pi/2e^2)T_{cs(ct)} \). The term in parentheses gives the enhancement due to the presence of triplets.

According to Eq. (17) for \( \Delta_{ct} \lessgtr \Delta_{so} \) the critical field is enhanced by a factor of \( \propto \ln(\Delta_{so}/\Delta_{ct}) \), which can be substantial as in TMDs the SOC may exceed the superconducting gap by more than three order of magnitudes [12]. In summary, the conversion of \( s \)-wave singlets to \( if \) triplets by the Zeeman field is of importance both theoretically and for interpreting the experimental data.

We thank G. Blumberg, T. Dvir, and H. Steinberg for enlightening discussions. We acknowledge the financial support by the Israel Science Foundation, Grant No. 1287/15 and D.M. also acknowledges the support from the Swiss National Science Foundation, Project No. 184050.
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