Topological Properties of Time Reversal Symmetric Kitaev Chain and Applications to Organic Superconductors

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We show that the pair of Majorana modes at each end of a 1D spin triplet superconductor with total Cooper pair spin $S_z = 0$ (i.e., $\Delta_{\uparrow\uparrow} = -\Delta_{\downarrow\downarrow} = p\Delta_0$; two uncoupled time reversed copies of the Kitaev $p$-wave chain) are topologically robust to perturbations such as mixing by the $S_z = 0$ component of the order parameter $(\Delta_{\uparrow\uparrow} = \Delta_{\downarrow\downarrow})$, transverse hopping (in quasi-1D systems), non-magnetic disorder, and also, most importantly, to time reversal breaking perturbations such as applied Zeeman fields/magnetic impurities and the mixing by the $S_y = 0$ component of the triplet order parameter $(\Delta_{\uparrow\uparrow} = \Delta_{\downarrow\downarrow})$. We show that the robustness to time reversal breaking results from a hidden chiral symmetry which places the system in the BDI topological class with an integer $\mathbb{Z}$ invariant. Our work has important implications for the quasi-1D organic superconductors (TMTSF)$_2$X ($X=PF_6, ClO_4$) which have been proposed as triplet superconductors with equal spin pairing $(\Delta_{\uparrow\uparrow}, \Delta_{\downarrow\downarrow} \neq 0, \Delta_{\uparrow\downarrow} = 0)$ in applied magnetic fields.

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It was shown by Read and Green [1] that 2D spinless $p$-wave superconductors host zero energy Majorana fermion (MF) excitations (with second quantized operator $\gamma$ satisfying $\gamma\dagger = \gamma$) in order parameter defects such as vortices and edges. Kitaev showed [2] that the 1D version of the same system (henceforth called “Kitaev $p$-wave chain”) can host MFs at the chain ends which can be used for topological quantum computation (TQC) [3]. Recently, MFs have been proposed to exist in systems closely analogous to the spinless $p$-wave superconductors/superfluids such as heterostructures of topological insulators and $s$-wave superconductors [4], cold fermion systems with Rashba spin orbit coupling, Zeeman field, and an attractive $s$-wave interaction [5, 6] and also, heterostructures of spin-orbit coupled semiconductor thin films [7, 8] or nanowires [9, 10] proximity coupled with $s$-wave superconductors and a Zeeman field. There have been recent claims of experimental observation of MFs in the semiconductor heterostructure which have attracted considerable attention [11–20]. In concurrent developments recent work [21–23] has established that the quadratic Hamiltonians describing gapped topological insulators and superconductors can be classified into 10 distinct topological symmetry classes that can be characterized by certain topological invariants. The symmetry classification of a given system is important as it provides an understanding of the effects of various perturbations on the stability of the protected surface modes such as the MFs. Generally speaking, if a given perturbation breaks a symmetry, the zero energy zero modes of the corresponding symmetry protected topological state acquire non zero energy and are removed by that perturbation.

Although the 1D spinless Kitaev chain has an unphysical Hamiltonian, quasi-1D spin-triplet superconductivity has been proposed in a class of organic superconductors (TMTSF)$_2$X (Bechgaard salts, $X=PF_6, ClO_4$) in the presence of applied magnetic fields [24–27] (it has also been proposed recently in Li$_{0.5}$Mo$_6$O$_{17}$ [31]). The Bechgaard salts are quasi-one-dimensional charge transfer salts exhibiting pressure induced superconductivity with abnormally high upper critical fields $H_{c2}$ [25]. The precise form of the order parameter is not completely known, but there is evidence, at least in the presence of a magnetic field, that the superconducting state is consistent with an equal-spin-pairing (ESP) $p$-wave phase [24, 30]. Such a phase with $\Delta_{\uparrow\uparrow}, \Delta_{\downarrow\downarrow} \neq 0, \Delta_{\uparrow\downarrow} = 0$ realizes two independent copies of the Kitaev $p$-wave chain, one for each spin sector. By continuity from Kitaev’s argument [2], since the two spin sectors are uncoupled, one expects a pair of MFs (one from each spin sector) at each end of the chains. (The average spin-polarizations of the MFs are zero, however, since they are an equal superposition of particles and holes within a single spin sector.) Nevertheless, since for $\Delta_{\uparrow\uparrow} = -\Delta_{\downarrow\downarrow} = p\Delta_0$ (henceforth called the “TR-symmetric Kitaev chain”) the Hamiltonian is symmetric under time reversal, it may appear that the pair of MFs at a given end are protected by the TR symmetry, the topological class being DIII with a $\mathbb{Z}_2$ invariant. A consequence of this would be the MFs in (TMTSF)$_2$X (or in Li$_{0.5}$Mo$_6$O$_{17}$) would acquire a gap in the presence of Zeeman fields and/or magnetic impurities and would be difficult to observe experimentally.

In this paper we show that the pair of MFs at each end of a TR-symmetric Kitaev chain are in fact topologically robust to a large class of perturbations including mixing by the $S_z = 0$ component of the order parameter $(\Delta_{\uparrow\uparrow} = \Delta_{\downarrow\downarrow})$, transverse hopping (for quasi-1D systems), non-magnetic disorder, and also, importantly, to perturbations that explicitly break the TR symmetry such as Zeeman fields/magnetic impurities (in two orthogonal directions in spin-space) and perturbations rendering $|\Delta_{\uparrow\downarrow}| \neq |\Delta_{\downarrow\uparrow}|$ (i.e., mixing by the $S_y = 0$ component of the order parameter, $\Delta_{\uparrow\downarrow} = \Delta_{\downarrow\uparrow} = p\Delta_1$). Note that such TR-breaking perturbations are likely to be present in the experiments as the evidence for the possible spin-triplet order in Bechgaard salts is found only in the presence of magnetic fields [24–26]. We show that the topological robustness to the TR-breaking perturbations results from a hidden chiral symmetry that places the TR-symmetric Kitaev chain in the BDI topological class with an integer $\mathbb{Z}$ invariant. The integer invariant is equal to the number of MF modes at each end pro-
tected by the chiral symmetry. In quasi-1D systems with multiple coupled chains the \( \mathbb{Z} \) invariant can take arbitrary integer values equal to the number of the chains. Our work clarifies the topological properties of the doubled Kitaev chains and the related quasi-1D superconductors with a spin-triplet \( p \)-wave order parameter. Additionally, our work shows that the MFs and the resultant zero bias tunneling peak \([32, 33]\) and the fractional ac Josephson effect \([2, 34]\) should be topologically robust and experimentally observable in (TMTSF)\(_2\)X and Li\(_{0.9}\)Mo\(_{6}\)O\(_{17}\).

We begin with the 1D electronic tight binding Hamiltonian for a pair of Kitaev chains in uncoupled spin sectors,

\[
H_1 = \sum_{i,\alpha} (-\epsilon_{i\alpha} c_{i+1,\alpha}^\dagger c_{i\alpha} - \mu c_{i\alpha}^\dagger c_{i\alpha} + \Delta_{\alpha\alpha} c_{i\alpha}^\dagger c_{i+1,\alpha}^\dagger + h.c.),
\]

where \( i = 1, \ldots, N \) represents the lattice sites and \( \alpha = \uparrow, \downarrow \) is the spin index. The first term in Eq. (1) represents the kinetic energy, \( \mu \) is the chemical potential and \( \Delta_{\alpha\alpha} \) is the ESP \( p \)-wave superconducting pair potential. For a finite wire we first solve the BdG equations corresponding to Eq. (1) for the TR-symmetric case, \( \Delta_{\uparrow\downarrow} = -\Delta_{\downarrow\uparrow} = p\Delta_0 \) (see below for the TR-invariance of the doubled Kitaev chain). As shown in Fig. (1), the low-energy spectrum for this system contains a total of four zero energy modes (two on each end) separated by a finite gap on each side. The wave functions for the pair of zero modes at each end are such that the corresponding second quantized operators satisfy the Majorana condition, \( \gamma_i^\dagger = \gamma_i \).

We examine the stability of the MFs against the TR-breaking perturbation Hamiltonian \( H_2 \),

\[
H_2 = \sum_{i,\alpha,\alpha'} \left[ (\vec{V} \cdot \vec{\sigma})_{\alpha\alpha'} c_{i\alpha}^\dagger c_{i\alpha'} + J (\vec{S}_{i\uparrow} \cdot \vec{\sigma})_{\alpha\alpha'} c_{i\alpha}^\dagger c_{i\alpha'} + \Delta_1 (c_{i\uparrow}^\dagger c_{i+1,\uparrow} + c_{i\downarrow}^\dagger c_{i+1,\downarrow}) + h.c. \right].
\]

(2)

The first term in Eq. (2) represents an applied Zeeman field \( \vec{V} = (V_x, V_y, V_z) \), the second term represents magnetic impurities localized at site \( i \) with spin \( \vec{S}_i \) and coupling constant \( J \), and the third term \( \Delta_1 \) adds an \( S_y = 0 \) component to the triplet order parameter. All three terms break the TR symmetry (note that the term \( \Delta_1 \), added to a state with \( S_z = 0 \), makes the magnitudes of the order parameter in the two spin sectors unequal, \( |\Delta_{\uparrow\uparrow}| \neq |\Delta_{\downarrow\downarrow}| \)). Additionally, we checked the robustness of the MFs to TR-invariant perturbations such as \( (\Delta_{\uparrow\uparrow} = \Delta_{\downarrow\downarrow} = p\Delta_2) \), non-magnetic disorder, and, for multiple coupled chains, to hopping in the transverse directions. Since the spin-orbit coupling in the organic superconductors is negligible \([20]\) we have not included a Rashba spin-orbit term in the perturbation Hamiltonian.

Fig. (1b) shows the low energy BdG spectrum of the full Hamiltonian \( H = H_1 + H_2 \). The pair of MFs at each end remain protected to perturbations such as Zeeman fields and magnetic impurities along two transverse directions, and also to mixing by the \( S_y = 0 \) and \( S_z = 0 \) components of the triplet order parameter. In addition we have also found (not shown in Fig. 1) that the MFs are robust to non-magnetic disorder and to transverse hopping (in a quasi-1D system). However we find that a Zeeman field along \( x \) (or \( y \)) splits the MFs to finite energy \( \pm \) as illustrated in Fig. (1c). Nevertheless, since the MFs are robust to TR-breaking perturbations such as bulk \( V_x \) and \( V_z \) as well as magnetic impurities and mixing by the \( S_y = 0 \) component of the order parameter, the topological robustness of the MFs cannot be explained by the time reversal symmetry.

To understand the topological properties of the TR-symmetric Kitaev chain we rewrite \( H_1 \) in Eq. (1) (for \( \Delta_{\uparrow\uparrow} = -\Delta_{\downarrow\downarrow} = p\Delta_0 \)) as, \( H_1 = \sum_k \Psi_k^\dagger H_1(k) \Psi_k \), where

\[
H_1(k) = (-2t \cos(k) - \mu) \sigma_0 \tau_z + \Delta_0 \sin(k) \sigma_z \tau_x,
\]

and the perturbation Hamiltonian \( H_2 \) as \( H_2 = \sum_k \Psi_k^\dagger H_2(k) \Psi_k \) with,

\[
H_2(k) = V_x \sigma_x \tau_z + V_y \sigma_y \tau_0 + V_z \sigma_z \tau_z + \Delta_1 \sin(k) \sigma_0 \tau_x,
\]

(4)

where \( \sigma_i \) and \( \tau_i \) are the Pauli matrices in the spin and the particle-hole spaces, respectively. Here we have used the coupled spin and particle-hole basis, \( \Psi_k = (c_{k\uparrow}, c_{k\downarrow}, c_{-k\uparrow}, c_{-k\downarrow})^T \), and have replaced \( k_x \) by \( k \). Using the time reversal operator \( \Theta = i\sigma_y \tau_0 \mathcal{K} \) and the particle-hole operator \( \Xi \) \((\Xi = \sigma_0 \tau_z \mathcal{K})\) in this basis, where \( \mathcal{K} \) is the complex conjugation operator, it is easy to see that \( H_1 \) is
The anti-commutation with and the particle-hole symmetry (see Eq. (4), including non-magnetic disorder and transverse hopping, except $V_y$). Note that all the perturbations in $W$ [21, 23, 35, 36].

We see the accidental protection of the MFs. Even though the Zeeman field is still unbroken, the Zeeman field can change the value of $W$ from $2 \rightarrow 1 \rightarrow 0$, indicating a corresponding decrease of the number of MFs on a given end. Physically, the Zeeman field reduces the number of MFs by 1 by removing the Fermi surfaces in turn.

Next we consider the Hamiltonian in Eq. (1) with $\Delta_{\uparrow\uparrow} = \Delta_{\downarrow\downarrow}$ (ESP phase with $S_y = 0$). In this phase, as we show in Fig. (3a), the winding number $W = 0$ (red curve). Although $W = 0$, since the two spin sectors are uncoupled and each sector hosts a single MF, the system has a total of 2 MFs on a single end. However, in this case, the pair of MFs are not topologically protected by $S$. We see the absence of the topological protection in Fig. (3b) where a small Zeeman field $V_y$, even though it respects the symmetry under $S$ (see Eq. (3)), still removes the MFs from the chain ends. Fig. (3c,d) illustrate the fact that in the $S_y = 0$ phase, a field $V_y > \mu$ can remove one of the Fermi surfaces, resulting in the winding number increasing from 0 to 1 (Fig. (3c)), which is
then protected by the chiral symmetry $S$. We note in passing that the pair of MFs in the $S_y = 0$ phase are also protected to $V_z$, but this protection is provided by a different chiral symmetry $S = \sigma_0 \tau_y$. The topological properties of a general 1D spinful $p$-wave superconductor are beyond the scope of the present paper and will be taken up in a future publication.

To illustrate the possibility for higher integer values of $W$ (and, correspondingly, higher number of protected MFs per end) we now consider multiple chains coupled in the transverse directions by hopping parameters $t_y, t_z$. Since in the Begagaard salts $t_z : t_y : t_z = 1 : 0.1 : 0.03$ we consider only the effects of $t_y$. In the limiting case $t_y \to 0$ there exist a set of degenerate 1D chains each hosting 2 MFs at each end. A small hopping between the chains $t_y \ll t_z$ breaks this degeneracy. Despite the degeneracy breaking, the additional terms in the Hamiltonian do not break the chiral symmetry and the multi-chain problem is still described by the winding number $W$ (suitably defined for a larger dimensional $H$).

Then, the strength of $t_y$ increases the confinement energy lifts the energy of the bands above $\mu$ such that they are no longer occupied. Thus the number of MFs localized at an end (and the value of $W$) goes down in pairs. As shown in Fig. (4), at each jump of the value of $W$, the superconducting quasiparticle gap closes and the system passes through a topological quantum phase transition (TQPT).

FIG. 4. (a) Low energy BdG spectrum of four parallel chains coupled by transverse hopping $t_y$. $t_y/t_x = 0.2, 0.75, 1.5$ correspond to 8 (red circles), 6 (blue circles), and 4 (green diamonds) MFs at each end. (b) Quasiparticle gap closing and TQPT (separating phases with different number of MFs) tuned by the transverse hopping. Panels (c, d) show the bulk energy-momentum dispersion in the gapped regime with 8 MFs and as the bulk gap closes leading to the regime with 6 MFs at each end.

FIG. 5. (a) Low energy ABS spectrum as a function of $\phi$ for TR-symmetric Kitaev chain with parameters as in Fig. 1. Each red curve is twofold degenerate. (b) TR-breaking bulk Zeeman fields $V_y, V_z = 0.25$ meV lift the degeneracy but preserves the $4\pi$ periodicity of the spectrum. (c) Adding the order parameter component with $\Delta_{+1} = \Delta_{-1} = 0.5\Delta_0$, although it breaks the TR symmetry, preserves the $4\pi$ periodicity (d) The spectrum with $V_z = 1$ meV added to the junction breaks chiral symmetry and results in a conventional $2\pi$ Josephson effect.

The MFs in 1D chiral symmetric topological superconductors can be probed by differential tunneling conductance from the ends. In a butt-to-butt Josephson set up between two 1D chiral TS there exists a stable Majorana quartet (two MFs on each side of the junction). The energy levels of the junction plotted as a function of the phase difference $\phi$ is $4\pi$ periodic, giving rise to a $4\pi$ periodic Josephson effect (see Fig. 5a). As shown in Figs. (5b, 5c), the topological robustness due to chiral symmetry ensures that the single crossing of the $E$ vs. $\phi$ curves at $\phi = \pi$ is stable to perturbations including those breaking TR symmetry. In Fig. 5d we show that the $4\pi$ periodicity of the curves is broken only by adding a Zeeman field $V_z$ that breaks the chiral symmetry $S$.

In summary we show that the pair of MFs at each end of a 1D TR symmetric Kitaev $p$-wave chain are topologically robust to a large number of perturbations including those breaking TR symmetry. We identify the appropriate topological class to be BDI with an integer ($\mathbb{Z}$) invariant the value of which gives the number of topologically protected MFs at each end. In addition to the topological properties of the TR-symmetric Kitaev chains, our results establish the organic superconductors (TMTSF)$_2X$ ($X=PF_6, ClO_4$) and Li$_4$Mo$_6$O$_{17}$, which have been proposed to be quasi-1D equal-spin-pairing $p$-wave superconductors, as suitable platforms for experimental studies of MFs.

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