1. Introduction

Topology is a mathematical concept to classify shapes. When two shapes can be continuously deformed into each other (like the shapes of a doughnut and a teacup), they belong to the same topological class. Similarly, when a quantum mechanical wavefunction is adiabatically connected to a different wavefunction, they may be called topologically identical. In the case of quantum many-body systems, simple combinations of atomic wavefunctions are considered to be trivial, and hence any condensed matter system whose wavefunction is adiabatically connected to the atomic limit is topologically trivial. However, when the wavefunction is adiabatically distinct from the atomic limit, such a system may be called topological. The first quantum mechanical system which was recognized to be topological was the quantum Hall system; in this case, the adiabatic continuity can be mathematically judged by an integer number called Chern number [1, 2], which will be explained in detail in the next section. In general, topological classifications are done by finding an integer number called topological invariant which characterize the topology; the Chern number is a prominent example of the topological invariant in quantum-mechanical systems.

Although the nontrivial topology in the quantum Hall system was recognized in as early as 1982 [1], topological quantum systems gained wide interest after the theoretical discovery in 2005 of the quantum spin Hall insulator phase in a two-dimensional (2D) time-reversal-invariant insulator [3], whose topology is characterized by a $Z_2$ topological invariant [4]. This topology was extended to three-dimensional (3D) systems [5–7], leading to the birth of the term topological insulators [5]. The historical perspective of topological insulators is concisely summarized in a recent review [8].

It was soon recognized that topological classifications are possible in principle for various quantum many-body systems having a gap in the energy-band spectrum to protect the occupied states. As a result, systematic topological classifications of not only insulators but also superconductors based on the symmetry properties were conducted [9, 10]. Such theories elucidated how the symmetry and dimensionality of a gapped system dictate the types of topological invariants; for example, a time-reversal-breaking superconductor can be topological in...
2D but not in 3D. In general, topological superconductors are adiabatically distinct from the Bose-Einstein condensate of Cooper pairs, which obviously forms a trivial superconducting state, like the atomic limit of an insulator.

Interestingly, before the above-mentioned developments regarding the topological quantum systems took place, nontrivial topology in superfluid helium 3 (He-3) was discussed by Volovik [11]. Also, topologically nontrivial superconductors were discussed in 2000 in a 2D model by Read and Green [12] and in a one-dimensional (1D) model by Kitaev [13]. Both models consider spinless, time-reversal-breaking p-wave pairing for the superconducting state, which gives rise to a non-Abelian Majorana zero mode in the vortex core in the 2D case or at the edge in the 1D case. In 2003, Sato proposed a 2D model to realize a similar non-Abelian Majorana zero mode even in the case of s-wave pairing [14]. These models were motivated to realize topologically-protected quantum computations that are free from decoherence. It is noteworthy that those models of topological superconductors preceded the recent developments of topological quantum systems, but concrete ideas to realize such topological superconductors emerged only after the discovery of topological insulators, which provide a con-

ments of topological quantum systems, but concrete ideas to realize topologically-protected quantum computations that are free from decoherence. It is noteworthy that those models of topological superconductors preceded the recent developments of topological quantum systems, but concrete ideas to realize such topological superconductors emerged only after

In condensed matter systems, when a quasiparticle is a super-

– are exotic in that particles are their own antiparticles [15

17]. Interestingly, before the above-mentioned developments

48x506]d. A unique function on

n n defined by

with an integer

, we need to take

n n is non-singular on

k k is the

48x518]ution, and hence there remains a gauge degree of freedom,

|u_s(k)| \to e^{i\gamma_s(k)}|u_s(k)|. \quad (3)

This leads to a gauge transformation in \( \mathcal{A}^{\alpha}(k) \) as

\[ \mathcal{A}^{\alpha}(k) \to \mathcal{A}^{\alpha}(k) - \partial_k \phi_{\alpha}(k). \quad (4) \]

Now we note that any physical quantity should be gauge invariant. A gauge-invariant quantity to be constructed from \( \mathcal{A}^{\alpha}(k) \) is the ‘field strength’ of the Berry connection,

\[ F_{ij}^{\alpha}(k) = \partial_k \mathcal{A}_j^{\alpha}(k) - \partial_j \mathcal{A}_k^{\alpha}(k), \quad (5) \]

which has a physical meaning. As we will show in the next section, the integration of the field strength over the whole Brillouin zone defines a topological invariant named Chern number.

Another gauge invariant quantity constructed from \( \mathcal{A}^{\alpha}(k) \) is the Berry phase, which is given as its line integral along a closed path \( C \) in the momentum space. We first take a gauge with which \( \mathcal{A}^{\alpha}(k) \) is non-singular on \( C \) (which is always possible), and then calculate the line integral along \( C \),

\[ \oint_C dk \cdot \mathcal{A}^{\alpha}(k). \quad (6) \]

Since various choices are possible for the gauge taken above, there remains a freedom for a non-singular gauge transformation, with \( e^{i\phi_{\alpha}(k)} \) a unique function on \( C \). Such a gauge transformation changes the line integral equation (6) as

\[ \oint_C dk \cdot \mathcal{A}^{\alpha}(k) \to \oint_C dk \cdot \mathcal{A}^{\alpha}(k) - \oint_C dk \cdot \partial_k \phi_{\alpha}(k). \quad (7) \]

The second line integral in the right hand side is easily evaluated: Due to the uniqueness of \( e^{i\phi_{\alpha}(k)} \) on \( C \), this term must give \( 2\pi N \) with an integer \( N \). Consequently, one can see that

\[ \exp [i \oint_C dk \cdot \mathcal{A}^{\alpha}(k)] \]

2. Concept of topology in quantum mechanics

We will first familiarize the readers with the concept of topology in quantum-mechanical wavefunctions, by elaborating on a simple example.

2.1. Berry phase, Berry connection, and gauge field

When a Hamiltonian depends on a certain set of parameters, its eigenstates are defined in the corresponding parameter space. The wavefunctions may have a ‘twist’ in such a parameter space, i.e. they may have a topologically nontrivial structure. The Berry phase typically characterizes such a non-trivial topology in the parameter space.

In particular, the Berry phase in the momentum space plays an important role in the topology of insulators and superconductors. Let us consider a band insulator described by a Bloch Hamiltonian \( \mathcal{H}(k) \) with the crystal momentum \( k \). The eigenstates are given by the solutions of the Bloch equation,

\[ H(k)|u_s(k)\rangle = E_s(k)|u_s(k)\rangle, \quad (1) \]

so that they contain \( k \) as a parameter of the wavefunctions. The Berry connection \( \mathcal{A}^{\alpha}(k) \) defined by

\[ \mathcal{A}^{\alpha}(k) = i\langle u_s(k)|\partial_k u_s(k)\rangle \quad (2) \]

measures the rate of change in the wavefunction \( |u_s(k)\rangle \) in the momentum space, and therefore it vanishes when \( |u_s(k)\rangle \) does not change with \( k \).

To consider the topology based on \( \mathcal{A}^{\alpha}(k) \), we need to take into account the ambiguity in the solutions of equation (1); this Bloch equation does not fix the phase factor of the solution, and hence there remains a gauge degree of freedom,

\[ |u_s(k)| \to e^{i\gamma_s(k)}|u_s(k)|. \quad (3) \]

This leads to a gauge transformation in \( \mathcal{A}^{\alpha}(k) \) as

\[ \mathcal{A}^{\alpha}(k) \to \mathcal{A}^{\alpha}(k) - \partial_k \phi_{\alpha}(k). \quad (4) \]

Now we note that any physical quantity should be gauge invariant. A gauge-invariant quantity to be constructed from \( \mathcal{A}^{\alpha}(k) \) is the ‘field strength’ of the Berry connection,

\[ F_{ij}^{\alpha}(k) = \partial_k \mathcal{A}_j^{\alpha}(k) - \partial_j \mathcal{A}_k^{\alpha}(k), \quad (5) \]

which has a physical meaning. As we will show in the next section, the integration of the field strength over the whole Brillouin zone defines a topological invariant named Chern number.

Another gauge invariant quantity constructed from \( \mathcal{A}^{\alpha}(k) \) is the Berry phase, which is given as its line integral along a closed path \( C \) in the momentum space. We first take a gauge with which \( \mathcal{A}^{\alpha}(k) \) is non-singular on \( C \) (which is always possible), and then calculate the line integral along \( C \),

\[ \oint_C dk \cdot \mathcal{A}^{\alpha}(k). \quad (6) \]

Since various choices are possible for the gauge taken above, there remains a freedom for a non-singular gauge transformation, with \( e^{i\phi_{\alpha}(k)} \) a unique function on \( C \). Such a gauge transformation changes the line integral equation (6) as

\[ \oint_C dk \cdot \mathcal{A}^{\alpha}(k) \to \oint_C dk \cdot \mathcal{A}^{\alpha}(k) - \oint_C dk \cdot \partial_k \phi_{\alpha}(k). \quad (7) \]

The second line integral in the right hand side is easily evaluated: Due to the uniqueness of \( e^{i\phi_{\alpha}(k)} \) on \( C \), this term must give \( 2\pi N \) with an integer \( N \). Consequently, one can see that

\[ \exp [i \oint_C dk \cdot \mathcal{A}^{\alpha}(k)] \]
is gauge-invariant. The phase factor of this gauge-invariant quantity is the Berry phase, which, in general, can take any real value and change continuously, and thus is not a topological invariant. Nevertheless, when a certain symmetry is imposed and a suitable $C$ is considered, the Berry phase can be quantized and give a topological invariant, as we will show later.

### 2.2. Chern number

Shortly before Berry discovered his famous phase in quantum mechanics [18], Thouless, Kohmoto, Nightingale and den Nijs introduced a topological number (TKNN integer) to characterize the quantum Hall states [1]. Soon after these works, Simon pointed out a mathematical relation between the two quantities [19] and Kohmoto derived the TKNN integer in the form of the (first) Chern number [2]. It is now generally recognized that the Chern number is one of the most fundamental topological numbers in topological phases of matter.

For a 2D system, the Chern number of the $n$th band is defined by using the field strength of the Berry connection as

$$
C_{1}^{(n)} = \frac{1}{2\pi} \int_{2\text{dBZ}} \partial_{k} \cdot \partial_{\phi} \phi_{n}(k),
$$

(9)

where the integration is performed on the 2D Brillouin zone. This integration is facilitated by using the Stokes’ theorem: Due to the periodicity of the Brillouin zone, the integral vanishes if the Berry connection $A^{(n)}(k)$ has no singularity over the Brillouin zone. On the other hand, if $A^{(n)}(k)$ has a singularity at $k_0$, one performs the gauge transformation

$$
A^{(n)}(k) = A^{(n)}(k) - \partial_{k} \phi_{n}(k)
$$

(10)

in the region $R$ including $k_0$, so that $A^{(n)}(k)$ has no singularity in $R$. From the Stokes’ theorem, the integral in equation (9) becomes the line integral of the gauge function,

$$
C_{1}^{(n)} = \frac{1}{2\pi} \int_{\partial R} \partial_{k} \cdot \partial_{\phi} \phi_{n}(k),
$$

(11)

where $\partial R$ is the boundary of $R$. Because $e^{i\phi_{n}(k)}$ is a unique function on $\partial R$, this $C_{1}^{(n)}$ must be an integer. For a 2D insulator, the total Chern number of the occupied bands

$$
C_h = \sum_{E_{\nu} < E_F} C_{1}^{(n)}(E_{\nu}),
$$

(12)

is of particular importance, because it is directly related to the Hall conductance through

$$
\sigma_{xy} = -\frac{e^2}{h} C_h.
$$

(13)

Under time-reversal, the total Berry connection of the occupied bands and its field strength transform as

$$
\sum_{E_{\nu} < E_F} A^{(n)}(k) \rightarrow \sum_{E_{\nu} < E_F} A^{(n)}(-k),
$$

$$
\sum_{E_{\nu} < E_F} F_{ij}^{(n)}(k) \rightarrow -\sum_{E_{\nu} < E_F} F_{ij}^{(n)}(-k).
$$

(14)

Therefore, if the system retains time-reversal symmetry, the total Chern number of the occupied bands satisfies

$$
C_h = \frac{1}{2\pi} \int_{2\text{dBZ}} \partial_{k} \cdot \partial_{\phi} \phi_{n}(k),
$$

$$
= -\frac{1}{2\pi} \int_{2\text{dBZ}} \partial_{k} \cdot \partial_{\phi} \phi_{n}(-k)
$$

$$
= -C_h,
$$

(15)

which leads to $C_h = 0$. This means that time-reversal breaking is necessary for realizing a quantum Hall state with a non-zero $C_h$.

### 2.3. Role of symmetry

The symmetry of the Hamiltonian plays a crucial role in determining the topology of the occupied states. Actually, if no symmetry is assumed, the only possible topological phase in up to three dimensions is the quantum Hall state with a non-zero Chern number [20]. To see this, let us consider a general Hamiltonian $H(k)$. The Hamiltonian is diagonalized by using a unitary matrix $U(k)$ as

$$
U^{(k)}H(k)U(k) = \left( \begin{array}{ccc} E_1(k) & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & E_n(k) \end{array} \right).
$$

(16)

We suppose that the Hamiltonian describes a band insulator with a band gap at the Fermi energy $E_F$. For convenience, the bands are numbered from the highest energy, with the first $m$ bands to be empty; in other words, we assume $E_i(k) > E_F$ for $i = 1, \ldots, m$, and $E_i(k) < E_F$ for $i = m + 1, \ldots, n$.

To examine the topology of this system, we perform an adiabatic deformation of the Hamiltonian. If no symmetry is imposed on $H(k)$, any deformation is allowed as long as it keeps a band gap. In particular, one can make the energies of all the occupied (empty) states to become $-1 \ (1)$ without closing the gap. Such a deformation does not change the topological property of occupied bands.

After this deformation, we have

$$
U^{(k)}H(k)U(k) = \left( \begin{array}{ccc} \text{I}_{m \times m} & 0 & 0 \\ 0 & \text{I}_{(n-m) \times (n-m)} \end{array} \right).
$$

(17)

where $\text{I}_{m \times m}$ and $\text{I}_{(n-m) \times (n-m)}$ are the $m \times m$ and $(n-m) \times (n-m)$ unit matrices, respectively. Therefore, the information of the topology is encoded in the unitary matrix $U(k)$. It should be noted here that $U(k)$ itself has a gauge redundancy. Indeed, using a $m \times m$ unitary matrix $U_{m \times m}(k)$ and another $(n-m) \times (n-m)$ unitary matrix $U_{(n-m) \times (n-m)}(k)$, one can construct the gauge transformation

$$
U(k) \rightarrow U(k) \left( \begin{array}{ccc} U_{m \times m}(k) & 0 \\ 0 & U_{(n-m) \times (n-m)}(k) \end{array} \right),
$$

(18)

which does not change $H(k)$ in equation (17). Consequently, $U(k)$ is not merely an element of the group of $n \times n$ unitary matrices, $U(n)$, but it should be regarded as an element of its coset space.
where the equivalence relation of the coset space is obtained on the basis of the gauge redundancy expressed in equation (18). As a result, the unitary matrix $U(k)$ defines a map from the Brillouin zone to the coset space $\mathcal{M}$.

Such a map can be topologically classified by the homotopy theory. In the present case, the homotopy group $\pi_d(M)$ is given by

$$\pi_d(M) = \begin{cases} 0, & d = 1, 3 \\ \mathbb{Z}, & d = 2 \end{cases}.$$ (20)

This means that a topologically non-trivial structure exists only in $d = 2$ dimensions for $d \leq 3$. The integer topological number of $\pi_d(M)$ is given by the Chern number defined in equation (12).

### 2.4. Time-reversal symmetry and $\mathbb{Z}_2$ index

The above result implies that some additional symmetry is needed to obtain topological phases other than the quantum Hall states. Indeed, in the presence of time-reversal symmetry, one can obtain new topological phases, i.e. the quantum spin Hall phase in 2D [3, 4, 21] and the topological insulator phase in 3D [5–7].

A key structure of these new topological phases is the Kramers degeneracy due to time-reversal symmetry. The time-reversal operator $T$ obeys $T^2 = -1$ for spin-$\frac{1}{2}$ electrons, and the anti-unitarity of $T$ yields

$$\langle Tu | Tv \rangle = \langle v | u \rangle,$$ (21)

for any states $|u\rangle$ and $|v\rangle$. Therefore, a state $|u\rangle$ and its time-reversal partner $T|u\rangle$ is orthogonal, i.e. $\langle u | Tu \rangle = 0$, because of the relation

$$\langle u | Tu \rangle = \langle T^2 u | Tu \rangle = -\langle u | Tu \rangle.$$ (22)

In time-reversal-invariant systems, $|u\rangle$ and $T|u\rangle$ have the same energy, and thus the above result implies that any energy eigenstate has two-fold degeneracy, which is called Kramers degeneracy.

For the Bloch Hamiltonian $H(k)$ in equation (1), time-reversal symmetry leads to

$$TH(k)T^{-1} = H(-k).$$ (23)

Thus, if we consider an eigenenergy $|u_k\rangle$ of $H(k)$, its Kramers partner $T|u_k\rangle$ is an eigenstate of $H(-k)$, which is also written as $|u_{-k}\rangle$ with a different eigenstate $|u_k\rangle$ of $H(k)$. For later convenience, we relabel the band indices of the Kramers pairs $(|u_k\rangle, |u_{-k}\rangle)$ to $(|u_1^\uparrow\rangle, |u_1^\downarrow\rangle)$ and $(|u_2^\uparrow\rangle, |u_2^\downarrow\rangle)$. Considering the phase ambiguity of the eigenstates, they satisfy

$$|u_{-k}^\uparrow\rangle = e^{i\varphi(k)} |u_1^\uparrow\rangle |u_{-k}^\downarrow\rangle,$$ (24)

where $\varphi(k)$ signifies the gauge degree of freedom.

As discovered first by Kane and Mele [4], the Kramers degeneracy makes it possible to introduce a new topological number called $\mathbb{Z}_2$ index in 2D. Originally, the $\mathbb{Z}_2$ index was provided in the form of a Pfaffian, but there are several different ways to define the same $\mathbb{Z}_2$ index [5, 7, 22]. Here, we define it as a variant of the so-called spin Chern number [23].

For a 2D system with a fixed spin orientation, say $S$, one can introduce the spin Chern number. In the diagonal basis of $S_z$, the Hamiltonian is written as

$$H(k) = \begin{pmatrix} H_{\uparrow}(k) & 0 \\ 0 & H_{\downarrow}(k) \end{pmatrix},$$ (25)

where $H_{\uparrow}(k)$ ($H_{\downarrow}(k)$) is the Hamiltonian in the $S_z = 1/2$ ($S_z = -1/2$) sector. With this separation of $H(k)$, the spin Chern number $C_{\uparrow}$ ($C_{\downarrow}$) is defined as the Chern number of $H_{\uparrow}(k)$ ($H_{\downarrow}(k)$). Since the spin flips time-reversal, each spin sector does not have time-reversal invariance. Hence, the spin Chern number can be nonzero even for a time-reversal-symmetric system, although the total Chern number always vanishes (i.e. $C_{\uparrow} + C_{\downarrow} = 0$) due to time-reversal symmetry.

In general, the spin–orbit coupling breaks spin conservation, and thus the spin Chern number is not well-defined in a spin–orbit coupled system. However, in the presence of time-reversal symmetry, one can derive an analogous topological number even for a spin–orbit coupled system in 2D. Instead of the spin eigensectors, we use Kramers pairs $(|u_1^\uparrow(k)\rangle, |u_1^\downarrow(k)\rangle)$ to divide the Hilbert space into two subspaces, and then introduce the Chern numbers in those subspaces,

$$C_{\uparrow} = \frac{1}{2\pi} \int_{2dBZ} dk_x dk_y \mathcal{F}_{xy}^{\uparrow}(k),$$

$$C_{\downarrow} = \frac{1}{2\pi} \int_{2dBZ} dk_x dk_y \mathcal{F}_{xy}^{\downarrow}(k),$$ (26)

where $\mathcal{F}_{xy}^{\uparrow}(k)$ and $\mathcal{F}_{xy}^{\downarrow}(k)$ are the field strengths of the Berry curvatures $\mathbb{A}^{\uparrow}(k)$ and $\mathbb{A}^{\downarrow}(k)$, namely,

$$\mathbb{A}^{\uparrow}(k) = i \sum_{E < E_0} \langle u_{1^\uparrow}(k) | \partial_k u_{1^\uparrow}(k) \rangle,$$

$$\mathbb{A}^{\downarrow}(k) = i \sum_{E < E_0} \langle u_{1^\downarrow}(k) | \partial_k u_{1^\downarrow}(k) \rangle.$$ (27)

These Chern numbers share the same property as the spin Chern numbers. They take integer numbers, and hence they can be exchanged; this process changes the sign of the Chern numbers, and thus the Chern numbers $C_{\uparrow}$ and $C_{\downarrow}$ cannot be unique. Nevertheless, this difficulty can be resolved by considering the parities of the Chern numbers, $(-1)^{C_{\uparrow}}$ and $(-1)^{C_{\downarrow}}$. Because of the constraint $C_{\uparrow} = -C_{\downarrow}$, these parities are always the same, making them robust against the exchange of the superscripts. As a result, we have a well-defined $\mathbb{Z}_2$ index

$$(-1)^{C_{\uparrow}} \equiv (-1)^{C_{\downarrow}} = (-1)^{C_{\downarrow}}.$$ (28)

For a spin-preserving time-reversal-invariant system, the $\mathbb{Z}_2$ index coincides with the parity of the spin Chern number. An
insulator with \((-1)^{\nu_a} = -1\) is topologically distinct from an ordinary insulator and such a system is called a quantum spin Hall insulator.

Using the time-reversal invariance, one can also introduce \(Z_2\) indices in three dimensions \([5]\). We consider the time-reversal-invariant momenta \(\Gamma_i\) in the 3D Brillouin zone, which satisfy \(-\Gamma_i = \Gamma_i + G\) for a reciprocal lattice vector \(G\). There are eight such \(\Gamma_i\)’s in 3D, which can be indexed by using three integers \(n_a (a = 1, 2, 3)\) taking the value of 0 or 1:

\[
\Gamma_i = (n_a n_b n_c) = \frac{1}{2} (n_1 b_1 + n_2 b_2 + n_3 b_3),
\]

where \(b_i\) are the primitive reciprocal lattice vectors (see figure 1). One can choose four time-reversal-invariant momenta by fixing one of the three \(n_a\)'s. For instance, by fixing \(n_1\) as \(n_1 = 0\), one obtains four time-reversal-invariant momenta \(\Gamma_i (n_0 n_2 n_3)\) with \(n_2 = 0, 1\) and \(n_3 = 0, 1\). These four time-reversal-invariant momenta can be used for specifying a distinct time-reversal-invariant plane: A time-reversal-invariant plane \(\Sigma^a\) is defined as a plane in the 3D Brillouin zone which includes those four time-reversal-invariant momenta obtained by fixing \(n_a\). One can easily see that there are six distinct time-reversal-invariant planes in the 3D Brillouin zone.

For each time-reversal-invariant plane \(\Sigma^a\), one can introduce the \(Z_2\) index \((-1)^{CH} \Sigma_a\). A total of six \(Z_2\) indices can be introduced in this manner, but there exist the following constraints \([5]\):

\[
(-1)^{CH (\Sigma^a)} = (-1)^{CH (\Sigma^b)} = (-1)^{CH (\Sigma^c)} = (-1)^{CH (\Sigma^d)}.
\]

Hence, only the following four \(Z_2\) indices,

\[
(-1)^{\nu_a} \equiv (-1)^{CH (\Sigma^a)} , \quad (a = 1, 2, 3)
\]

are independent \([5]\). The first three \(Z_2\) indices can be non-trivial (i.e. \(-1\)) even when the system is quasi-2D. Indeed, \((-1)^{\nu_a}\) becomes \(-1\) even for a \(k_z\)-independent Hamiltonian if \((-1)^{CH (\Sigma^a)} = -1\). On the other hand, the last \(Z_2\) index \((-1)^{\nu_a}\) is intrinsic to 3D, and hence this is called 3D \(Z_2\) index. An insulator having the nontrivial 3D \(Z_2\) index is called a strong topological insulator.

In the case of centrosymmetric band insulators, there is a useful formula for evaluating the \(Z_2\) indices \([24]\). The inversion operator \(P\) has the property \(P^2 = 1\) and inversion symmetry leads to

\[
PH(k)P^{-1} = H(-k).
\]

Hence, an energy eigenstate of \(H(k)\) at \(k = \Gamma_i\) is simultaneously an eigenstate of \(P\). Because \([T, P] = 0\), a Kramers pair of the energy eigenstates has a common eigenvalue \(\xi = \pm 1 \) of \(P\), namely,

\[
P|u^a_i (\Gamma_i)\rangle = \xi_i |u^a_i (\Gamma_i)\rangle,\quad P|u^b_i (\Gamma_i)\rangle = -\xi_i |u^b_i (\Gamma_i)\rangle.
\]

By using \(\xi_i\), the \(Z_2\) index in 2D is evaluated as

\[
(-1)^{\nu_a} = \prod_i \xi_i,
\]

where the product is taken for all inequivalent \(\Gamma_i\)'s in 2D. In the case of 3D, we have

\[
(-1)^{\nu_a} = \prod_{n_a = 1, n_b, n_c} \xi_i,\quad \xi_i = (n_a n_b n_c)
\]

and

\[
(-1)^{\nu_a} = \prod_i \xi_i
\]

where the product in the latter equation is taken for all eight \(\Gamma_i\) in the 3D Brillouin zone.

2.5. Topological materials

Here, we briefly summarize the recently discovered topological materials, i.e. topological insulators, Weyl semimetals, and Dirac semimetals. As we shall discuss later, upon carrier doping these materials may show topological superconductivity without the necessity of strong electron correlations.

2.5.1. Topological insulator

The spin–orbit coupling is essentially important in topological insulators. Distinct from ordinary insulators, topological insulators have gapless surface Dirac fermions with a spin-momentum-locked energy dispersion \([8, 25, 26]\). Such a nontrivial electronic structure stems from a strong spin–orbit coupling. For instance, consider a prototypical topological insulator, Bi2Se3. The bulk band near the Fermi energy consists of \(p_z\) orbitals of two inequivalent Se atoms in the unit cell, and the Hamiltonian is written as \([27]\)

\[
H_{TI} (k) = (m_0 - mk^2)\sigma_z + v_1 k_x \sigma_y + v_2 (k_y \sigma_x - k_z \sigma_y).
\]

Here, \(\sigma_i\) denotes the Pauli matrix in the orbital space where the eigenstates of \(\sigma_i\) (i.e. \(\sigma_z = \pm 1\)) correspond to two \(p_z\) orbitals, and \(s_i\) is the Pauli matrix in the spin space. Reflecting the crystal structure of Bi2Se3, \(H_{TI} (k)\) is invariant under the inversion \(P\), which exchanges the \(p_z\) orbitals:

\[
PH_{TI} (-k)P^{-1} = H_{TI} (k), \quad P = \sigma_z.
\]

As shown in the previous section, inversion symmetry leads to a simple criterion for topological insulators \([24]\). For the continuum Hamiltonian equation \((37)\), there are only two
Here it should be noted that the spin-momentum locking in the surface states originates from the spin–orbit-coupling term $\nu \sigma_z (k_x s_y - k_y s_x)$ in $H_T(k)$ (see figure 2).

2.5.2. Weyl semimetal. Weyl semimetals are 3D materials that support bulk gapless excitations described by the $2 \times 2$ Weyl Hamiltonian

$$H(k) = v(k - k_0) \cdot s,$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (46)$$

where $s$ is the Pauli matrices of (pseudo) spin [28–31]. The spin-momentum-locked nature of the Hamiltonian implies a strong spin–orbit coupling in the system.

A band structure described by the Weyl Hamiltonian is obtained as a result of band crossing between a pair of spin-non-degenerate bands. Hence, Weyl semimetals can be realized only when time-reversal or inversion symmetry is broken. Otherwise, the bands are spin-degenerate at each momentum due to the Kramers theorem, and an isolated Weyl node cannot be obtained. Weyl semimetals have the following characteristics:

1. Each Weyl point has a non-zero Chern number calculated on a sphere surrounding that point [28].
2. The summation of the Chern numbers for all the Weyl points vanishes (Nielson–Ninomiya theorem [32, 33]).
3. They host gapless metallic surface states forming a Fermi arc in the surface Brillouin zone [30].

The surface Fermi arc in a Weyl semimetal is terminated at the points in the surface Brillouin zone onto which a pair of Weyl points are projected. This is because the surface Fermi arc originates from the Weyl points; namely, the non-zero Chern numbers associated with the Weyl points give rise to the gapless surface states which connect the two singularities in the momentum space.

2.5.3. Dirac semimetal. Finally, we consider Dirac semimetals, which are 3D semimetals or metals that support spin-degenerate gapless bulk nodes [34–38]. Like Weyl semimetals, a gapless node in a Dirac semimetal is realized as a crossing point of two bands, but the difference from Weyl semimetals lies in the fact that Dirac semimetals have both time-reversal and inversion symmetries. In such a case, the Kramers theorem dictates that each energy band has two-fold spin degeneracy, and thus the band crossing point is four-fold degenerate. Therefore, a gapless node in a Dirac semimetal is described by a $4 \times 4$ matrix Hamiltonian like in the case of a Dirac fermion.

As an example, let us consider Cd$_3$As$_2$ [36, 39–42]. In this Dirac semimetal, the Dirac points for gapless excitations appear at two points in the momentum space, $k_z = \pm k_0$ on the $k_z$ axis. Near these points, the Hamiltonian to describe the gapless dispersion is given by

$$H_x(k) = v_x(\pm k_z - k_0) \sigma_0 + v_y(k_y \sigma_5 - k_y \sigma_0),$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (47)$$

where $\sigma_0$ and $\sigma_5$ are the Pauli matrices in the orbital and spin spaces, respectively. The time-reversal operator $T$ and the inversion operator $P$ are written as $T = i\sigma_0 K$ ($\sigma_0$ is the $2 \times 2$ identity matrix) and $P = \sigma_0$, and the Hamiltonian transforms as

$$TH_x(-k)T^{-1} = H_x(k), \hspace{1cm} PH_x(-k)P^{-1} = H_x(k).$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (48)$$

Hence, the system as a whole is invariant under $T$ and $P$. If we introduce the Gamma matrices $\gamma_{i=x,y,z}$ as

$$\gamma_i \gamma_j = \epsilon_{ijk} \gamma_k,$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (49)$$

where $\epsilon_{ijk}$ is the Levi-Civita symbol.
it follows that the relation $\gamma_i\gamma_j = 2\delta_{ij}$ holds and the Hamiltonian $H_{\pm}(\mathbf{k})$ can be rewritten in the form of the Dirac Hamiltonian,

$$H_{\pm}(\mathbf{k}) = vk_x\gamma_x + vk_y\gamma_y + v_c(\pm k_z - k_0)\gamma_z.$$  (50)

For Dirac semimetals, neither time-reversal nor inversion symmetry ensures the stability of gapless nodes. For instance, one can add the term $\Delta H(\mathbf{k}) = mk_2\sigma_k s_0$, which preserves both time-reversal and inversion symmetries, to the above $H_{\pm}(\mathbf{k})$. The resulting energy dispersion is

$$E_{\pm}(\mathbf{k}) = \pm \sqrt{v_c^2(k_z + k_0)^2 + m^2k_2^2 + v^2(k_x^2 + k_y^2)},$$  (51)

which is gapped. Therefore, there must be an additional symmetry to prohibit such a gap-opening term. In general, energy bands of electrons in a solid are formed by electron orbitals of the constituent atoms. If one chooses a symmetry of the crystal and consider a momentum subspace which is invariant under that symmetry, each band has a quantum number associated with the symmetry of the electron orbital. When two bands having different quantum numbers intersect, they belong to different subspaces and hence no mixing is allowed, protecting the crossing point to remain gapless. In the case of Cd$_3$As$_2$, four-fold rotation ($C_4$) symmetry around the $z$-axis forbids the gap-opening mass term [37]. To see this, we note that the $C_4$ operation transforms $H_{\pm}(\mathbf{k})$ as

$$C_4H_{\pm}(\mathbf{k}_y, -k_x, k_z)C_4^{-1} = H_{\pm}(\mathbf{k}).$$  (52)

In the $C_4$-invariant momentum subspace at $k_x = k_y = 0$, $C_4$ and $H_{\pm}(0,0,k_z)$ commute, and hence the energy band has an eigenvalue of $C_4$ as a good quantum number. In Cd$_3$As$_2$, the $\sigma_z = 1$ band and the $\sigma_z = -1$ band have different eigenvalues of $C_4$. Indeed, on the $k_z$-axis, the Hamiltonian equation (47) becomes

$$H_{\pm}(\mathbf{k}) = v_c(\pm k_z - k_0)\sigma_z s_0,$$  (53)

which includes no off-diagonal band-mixing term. Moreover, the gap-opening term $\Delta H(\mathbf{k}) = mk_2\sigma_k s_0$ mentioned above is not allowed by the $C_4$ symmetry.

3. Basics of superconductivity

3.1. Bogoliubov quasiparticles and particle-hole symmetry

We first consider a single-band description of a superconductor. With an appropriate pairing interaction in the momentum space, a general single-band effective Hamiltonian is given by

$$\mathcal{H} = \sum_{k_i, k_j} \varepsilon_{ij}(\mathbf{k})c_{k_i \sigma}^\dagger c_{k_j \sigma} + \frac{1}{2} \sum_{k_i, k_j, k_{i'}, k_{j'}} V_{ij,i'j'}(\mathbf{k}, \mathbf{k}')c_{k_i \sigma}^\dagger c_{k_{i'} \sigma}^\dagger c_{k_{j'} \sigma} c_{k_j \sigma}$$  (54)

where $c_{k \sigma}$ ($c_{k \sigma}^\dagger$) is the annihilation (creation) operator of the electron with momentum $\mathbf{k}$ and spin $\sigma$, and $\varepsilon_{ij}(\mathbf{k})$ is the band Hamiltonian to give the momentum- and spin-dependent band energy measured from the chemical potential; this can be viewed as a $2 \times 2$ matrix operator in the spin basis. Its spin dependence comes from the spin–orbit coupling. The anti-commutation relation between $c_{k \sigma}$ and $c_{k \sigma}^\dagger$ implies the following relation for the pairing interaction $V_{ij,i'j'}$: $V_{ij,i'j'}(\mathbf{k}, \mathbf{k}') = -V_{ji',j'i}(\mathbf{k}, \mathbf{k}') = -V_{ij,i'j'}(\mathbf{k}', \mathbf{k})$.

In a superconducting state, Cooper pairs form so that the two-body operator $c_{k \sigma}^\dagger c_{-k \sigma}$ has a nonzero expectation value $\langle c_{k \sigma}^\dagger c_{-k \sigma} \rangle$. By defining a pair potential

$$\Delta_{\sigma}(\mathbf{k}) = -\sum_{k_i, k_j} V_{ij,i'j'}(\mathbf{k}, \mathbf{k}') \langle c_{k_i \sigma}^\dagger c_{-k_{i'} \sigma} \rangle,$$  (56)

one can decouple the quadratic term and simplify the Hamiltonian within the mean-field approximation to

$$\mathcal{H} = \sum_{k_i, k_j} \varepsilon_{ij}(\mathbf{k})c_{k_i \sigma}^\dagger c_{k_j \sigma} + \frac{1}{2} \sum_{k_i, k_{i'}} \left[ \Delta_{\sigma}(\mathbf{k})c_{k_i \sigma}^\dagger c_{-k_{i'} \sigma} + \text{h.c.} \right].$$  (57)

It is convenient to rewrite this into a $4 \times 4$ matrix form

$$\mathcal{H} = \frac{1}{2} \sum_{k_{i', i}} \left( \varepsilon_{ij}(\mathbf{k}) - \Delta_{\sigma}(\mathbf{k}) \right) c_{k_{i'}}^\dagger c_{k_{i'}},$$  (58)

with

$$\mathcal{H}_{4 \times 4}(\mathbf{k}) = \begin{pmatrix} \varepsilon_{ij}(\mathbf{k}) & \Delta_{\sigma}(\mathbf{k}) \\ -\Delta_{\sigma}(\mathbf{-k}) & -\varepsilon_{ij}(\mathbf{-k}) \end{pmatrix}.$$  (59)

where the spin indices make $\varepsilon_{ij}(\mathbf{k})$ etc to be $2 \times 2$ matrices. Also note that $(c_{k \sigma}^\dagger, c_{-k \sigma})$ is actually a four-component vector $(c_{k \uparrow}, c_{k \downarrow}, c_{-k \uparrow}, c_{-k \downarrow})$. In the above, we have neglected constant terms since they merely shift the ground state energy.

The matrix form of the Hamiltonian equation (59) has a particular symmetry called particle-hole symmetry. To see this, we define an anti-unitary operator

$$C = \begin{pmatrix} 0 & I_{2 \times 2} \\ I_{2 \times 2} & 0 \end{pmatrix},$$  (60)

with the complex conjugation operator $K$ and the $2 \times 2$ unit matrix $I_{2 \times 2}$. This operator exchanges the particle sector with the hole sector, and it transforms $\mathcal{H}_{4 \times 4}(\mathbf{k})$ as

$$C \mathcal{H}_{4 \times 4}(\mathbf{k}) C^{-1} = -\mathcal{H}_{4 \times 4}(\mathbf{-k}),$$  (61)

which is the mathematical expression of the particle-hole symmetry. Here, one should note the relation

$$\Delta_{\sigma}(\mathbf{k}) = -\Delta_{\sigma}(\mathbf{-k}),$$  (62)

coming from the Fermi statistics of $c_{k \sigma}$. The particle-hole symmetry is associated with the redundancy in the Hamiltonian. That is, the components of the vector $(c_{k \sigma}^\dagger, c_{-k \sigma})$ in equation (58) are related by complex conjugate, and hence they
are not independent; accordingly, the matrix components of $\mathcal{H}_{4\times4}(k)$ are not independent of each other, and the particle-hole symmetry expresses this mutual dependence of the components.

The effective Hamiltonian equation (58) is diagonalized by the eigenvectors $(u_i(k), v_j^*(-k)^\dagger)$ of the eigen equation

$$\mathcal{H}_{4\times4}(k)\begin{pmatrix} u_i(k) \\ v_j^*(-k) \end{pmatrix} = E(k)\begin{pmatrix} u_i(k) \\ v_j^*(-k) \end{pmatrix}. \quad (63)$$

The particle-hole symmetry imposes a relation between the solutions of equation (63); namely, using equation (61), one can rewrite equation (63) into

$$\mathcal{H}_{4\times4}(k)C\begin{pmatrix} u_i(-k) \\ v_j^*(-k) \end{pmatrix} = -E(-k)C\begin{pmatrix} u_i(-k) \\ v_j^*(-k) \end{pmatrix}, \quad (64)$$

which implies that the eigenvalues $E(k)$ and $-E(-k)$ come in pairs. One can thus write the set of four eigenvalues of the $4\times4$ matrix $\mathcal{H}_{4\times4}(k)$ as $(E_i(k), E_2(k), -E_1(-k), -E_2(-k))$ with $E_i(k) \geq 0$. Expressing the eigenvector for $E_i(k)$ $(i = 1, 2)$ as $(u_i^{(s)}(-k), v_j^{(s)*}(-k))$, we can diagonalize $\mathcal{H}_{4\times4}(k)$ as

$$U^\dagger(k)\mathcal{H}_{4\times4}(k)U(k) = \begin{pmatrix} E_1(k) \\ E_2(k) \\ -E_1(-k) \\ -E_2(-k) \end{pmatrix}, \quad (65)$$

where the unitary matrix $U(k)$ is given by

$$U(k) = \begin{pmatrix} u_i^{(s)}(-k) \\ v_j^{(s)*}(-k) \end{pmatrix}. \quad (66)$$

Here we used the relation $C(u_i^{(s)}(-k), v_j^{(s)*}(-k)) = (v_i^{(s)}(-k), u_j^{(s)*}(-k))$. Without loss of generality, one can assume $E_i(k) \geq 0$ for any weak-pairing superconducting states. A ‘weak Cooper pair’ means that the energy scale of the pair potential $\Delta(k)$ is much smaller than that of $\varepsilon_{\sigma\varphi}(k)$ in equation (54). Thus, the pair potential can be neglected except near the Fermi surface where $\varepsilon_{\sigma\varphi}(k)$ vanishes. At the Fermi energy, the pair potential opens a gap and separates the positive energy branch from the negative one. Reflecting the spin degrees of freedom, there are two positive energy branches $E_1(k)$ and $E_2(k)$. Substituting the expression equation (65) for $\mathcal{H}_{4\times4}(k)$ into equation (58), one obtains

$$\mathcal{H} = \sum_{ki}\varepsilon_{\sigma\varphi}(k)\alpha_i^\dagger\alpha_{ki}, \quad (67)$$

with

$$\alpha_{ki} = \sum_s(u_i^{(s)}(k)c_{ki} + v_j^{(s)*}(-k)c_{-ki}^\dagger). \quad (68)$$

The operator $\alpha_{ki}$ satisfies the anti-commutation relation

$$\{\alpha_{ki}, \alpha_{kj}\} = \delta_{ij}\delta_{kk}, \quad \{\alpha_{ki}, \alpha_{kj}\} = \{\alpha_{ki}, \alpha_{kj}\}^\dagger = 0, \quad (69)$$

and it describes thermal excitations of quasiparticles called Bogoliubov quasiparticles with energy $E_i(k)$. The ground state of a superconductor is annihilated by $\alpha_{ki}$,

$$\alpha_{ki}|0\rangle = 0, \quad (70)$$

which implies that the negative energy states are fully occupied as in an insulating state.

The above properties also hold for multi-orbital (i.e. multi-band) superconductors. In a general multi-orbital system, electrons have the orbital index $\sigma = 1, \ldots, N$ as well as the spin index $s = \uparrow, \downarrow$. Expressing these internal indices with $\alpha \equiv (s, \sigma)$, the Hamiltonian is written as

$$\mathcal{H} = \frac{1}{2} \sum_{k,\alpha,\beta} c_{k\alpha}^\dagger(c_{-k\beta})^\dagger \mathcal{H}(k) c_{k\beta},$$

with the following $4N \times 4N$ Hamiltonian

$$\mathcal{H}(k) = \begin{pmatrix} \varepsilon_{\sigma\varphi}(k) & \Delta_{\sigma\varphi}(k) \\ \Delta_{\sigma\varphi}^*(k) & -\varepsilon_{\sigma\varphi}(k) \end{pmatrix}, \quad (72)$$

where $\varepsilon(k) = H(k) - \mu$ is the normal-state Bloch Hamiltonian $H(k)$ measured relative to the chemical potential $\mu$. The anti-commutation relation of $c_{k\alpha}$ implies

$$\Delta_{\sigma\varphi}(k) = -\Delta_{\sigma\varphi}(-k), \quad (73)$$

and the BdG Hamiltonian $\mathcal{H}(k)$ has the particle-hole symmetry

$$\mathcal{C} \mathcal{H}(k) \mathcal{C}^{-1} = -\mathcal{H}(-k), \quad (74)$$

in a similar manner as the single band case. The spectrum of the Bogoliubov quasiparticles in the superconducting state is determined by

$$\mathcal{H}(k)|u_\alpha(k)\rangle = E_\alpha(k)|u_\alpha(k)\rangle, \quad (76)$$

with a $4N$-component wavefunction $|u_\alpha(k)\rangle$. Because of the particle-hole symmetry, positive- and negative-energy states come in pairs, and the negative-energy states are fully occupied in the superconducting ground state.

### 3.2. Pairing symmetry

The pair potentials are often classified based on their spin angular momentum. In the simple single-band case discussed above, spin is the only internal degrees of freedom for electrons. Since a Cooper pair is formed by pairing two spin-1/2 electrons, the spin angular momentum of a pair potential is either 0 (spin-singlet) or 1 (spin-triplet). A spin-singlet pair potential is antisymmetric in the spin space, which is written as

$$\Delta_{\sigma\varphi}(k) = i\psi(k)[s_i\lambda_\sigma]. \quad (77)$$
On the other hand, a spin-triplet pair potential is symmetric in the spin space, and it can be expressed as

$$\Delta_{sr}(k) = i\psi(k) s_r + i\mathbf{d}(k) \cdot s \mathbf{s}_r, \quad (81)$$

This is the essential characteristic of noncentrosymmetric superconductors [45].

### 3.3. Bogoliubov–de Gennes equation

Equations (63) and (76) determine the quasiparticle spectrum in the bulk superconducting state. Here we generalize these equations to systems with boundaries or defects. As we will show later, the quasiparticle states localized at boundaries or defects play important roles in topological superconductors.

Below, we only discuss the single-band case for simplicity. The generalization to a multi-orbital case is straightforward.

First, to consider a system with a boundary, we replace the momentum $\mathbf{k}$ in the Hamiltonian equation (59) with its operator form $-i\mathbf{\partial}_x$. This changes the eigen equation (63) into a differential equation

$$\mathcal{H}_{4s}(−i\mathbf{\partial}_x)\begin{pmatrix} \tilde{u}_s(x) \\ \tilde{v}_s(x) \end{pmatrix} = E \begin{pmatrix} \tilde{u}_s(x) \\ \tilde{v}_s(x) \end{pmatrix}, \quad (82)$$

with $\tilde{u}_s(x) = (1/\sqrt{V}) \sum_k e^{ikx} u_k(k)$ and $\tilde{v}_s(x) = (1/\sqrt{V}) \sum_k e^{ikx} v_k(k)$. ($V$ is the system volume.)

There are several ways to introduce a boundary. The simplest way is to impose a boundary condition on the differential equation (82). For instance, to consider a system extending to the positive $x$-direction with the boundary at $x = 0$, we place the boundary condition

$$\begin{pmatrix} \tilde{u}_s(x) \\ \tilde{v}_s(x) \end{pmatrix} = 0 \quad (83)$$

at $x = 0$. At the same time, a physical wavefunction $(\tilde{u}_s(x), \tilde{v}_s(x))'$ should not diverge at anywhere with $x > 0$. The solution of equation (82) under these two requirements determines the quasiparticle spectrum of the system with the boundary at $x = 0$.

We can modify the differential equation (82) so as to mimic a real system more closely. Instead of imposing the boundary condition (83), one can add to the kinetic energy $\varepsilon_{\text{sp}}(-i\mathbf{\partial}_x)$ a confining potential $V(x)$ which blows up at $x = 0$. In a similar way, one can take into account various boundary effects such as a surface potential or a modulation of the gap function near the boundary.

Alternatively, one can use a lattice model to consider a system with a boundary. Discretization of the space $x$ and the derivative $\partial_x$ in equation (82) into sites $\mathbf{m}$ and $\mathbf{n}$ on a lattice leads to a tight-binding equation

$$\sum_{\mathbf{n}} \mathcal{H}_{4s}(\mathbf{m}, \mathbf{n}) \begin{pmatrix} \tilde{u}_s(\mathbf{m}) \\ \tilde{v}_s(\mathbf{m}) \end{pmatrix} = E \begin{pmatrix} \tilde{u}_s(\mathbf{m}) \\ \tilde{v}_s(\mathbf{m}) \end{pmatrix}, \quad (84)$$

By restricting $\mathbf{m}$ and $\mathbf{n}$ to a finite region, one can obtain the equation with a boundary, which also determines the quasiparticle spectrum in a finite region.

The influence of a defect can be taken into account in equation (82). When a defect is present, quasiparticles at different positions feel different values of the gap function. Thus, $\Delta_{\text{sp}}(-i\mathbf{\partial}_x)$ in equation (82) becomes position dependent and is replaced by $\Delta_{\text{sp}}(-i\mathbf{\partial}_x, \mathbf{x})$:

$$\begin{pmatrix} \varepsilon_{\text{sp}}(-i\mathbf{\partial}_x) & \Delta_{\text{sp}}(-i\mathbf{\partial}_x, \mathbf{x}) \\ \Delta_{\text{sp}}^\dagger(-i\mathbf{\partial}_x, \mathbf{x}) & -\varepsilon_{\text{sp}}^\dagger(i\mathbf{\partial}_x) \end{pmatrix} \begin{pmatrix} \tilde{u}_s(\mathbf{x}) \\ \tilde{v}_s(\mathbf{x}) \end{pmatrix} = E \begin{pmatrix} \tilde{u}_s(\mathbf{x}) \\ \tilde{v}_s(\mathbf{x}) \end{pmatrix}. \quad (85)$$

For instance, let us consider a vortex located at the origin in a 2D $s$-wave superconductor. In this case, $\Delta_{\text{sp}}(-i\mathbf{\partial}_x, \mathbf{x})$ is given by

$$\Delta_{\text{sp}}(-i\mathbf{\partial}_x, \mathbf{x}) = i\psi(\rho)e^{i\varphi}[s_y]_{12}, \quad (86)$$

with $\mathbf{x} = (\rho\cos\varphi, \rho\sin\varphi)$ and the Pauli matrix $s_y$ in the spin space. Here $\psi(\rho)$ is the pairing amplitude which vanishes at the origin ($\psi(0) = 0$) and approaches a constant value at $\rho = \infty$ ($\psi(\infty) = \psi_0$). For other defects, explicit forms of...
The Andreev bound states can be provided in a similar manner, although they can be more complicated. Equation (85) determines the quasiparticle spectrum in the presence of a defect.

Equations (63), (82) and (85) are called Bogoliubov–de Gennes (BdG) equation and determine the quasiparticle spectrum in a superconductor under various conditions.

4. Andreev bound states

Near a boundary or a vortex core, Cooper pairs collapse. As a result, spatially-localized in-gap states can be formed in a superconductor. For instance, a vortex in an s-wave superconductor is known to host mini-gap states bound in the vortex core [46]. Such bound states in a superconductor are generally called Andreev bound states. They are very sensitive to the phase of the superconducting wavefunctions, and thus provide useful information on the pairing symmetry [47, 48].

Whereas Andreev bound states are in general mini-gap states, for a class of superconductors they can be a gapless mode or, more drastically, they can be zero-energy (mid-gap) states, for a class of superconductors they can be a gapless states [49]. As an example, let us consider a 2D $d_{x^2-y^2}$ superconductor at $k_F$, we have the BdG equation for a semi-infinite $d_{xy}$-wave superconductor where $\varepsilon_{xy}(k)$ and $\Delta_{xy}(k)$ in equation (59) are given by

$$\varepsilon_{xy}(k) = \left( \frac{\hbar^2 k^2}{2m} - \mu \right) \delta_{xy},$$

$$\Delta_{xy}(k) = \frac{k_x k_y}{k_F^2} \left[ \epsilon_y \right]_{xy}.$$  

Here $\Delta_0$ is a positive constant, $\mu (>0)$ is the chemical potential, and $k_F = \sqrt{2m\mu / \hbar}$ is the Fermi momentum. In this case, the BdG Hamiltonian reduces to

$$\mathcal{H} = \sum_{k} \left( c_{k \uparrow}^\dagger c_{-k \downarrow} + c_{-k \uparrow}^\dagger c_{k \downarrow} \right)$$

where the $2 \times 2$ matrix Hamiltonian is given by

$$\mathcal{H}_{2 \times 2}(k) = \left( \begin{array}{cc} \epsilon(k) & \psi(k) \\ \bar{\psi}(k) & -\epsilon(k) \end{array} \right)$$

with

$$\epsilon(k) = \left( \frac{\hbar^2 k^2}{2m} - \mu \right), \quad \psi(k) = \Delta_0 \frac{k_y}{k_F^2}.$$  

Now we solve the BdG equation for a semi-infinite $d_{xy}$-wave superconductor at $x > 0$. Replacing $k_x$ with $-i\partial_x$, we have the BdG equation for a zero-energy state,

$$\mathcal{H}_{2 \times 2}(-i\partial_x, k_y)|u_0(x)\rangle = 0.$$  

For $|k_y| < k_F$, the above equation with the boundary condition $u(x = 0) = 0$ has a solution [50]

$$|u_0(x)\rangle = C \left( \frac{1}{-i\text{sgn}k_y} \right) e^{ik_y} \sin \left( \frac{k_y^2 - k_F^2}{2} x \right) e^{-it\xi}$$

for weak pairing (i.e. $m\Delta_0/\hbar^2 k_F^2 \ll 1$). Here, $C$ is a normalization constant and $\xi^{-1} \equiv m\Delta_0/k_y^2 \hbar^2 k_F^2$. The zero-energy state is localized at the boundary, which strongly affects the transport properties through the edge [52].

In the above example, the Andreev bound state has a flat dispersion with zero energy. However, there are a variety of gapless Andreev bound states in other unconventional superconductors, depending on the symmetry of the system. For example, in the time-reversal-breaking $^3$He-A phase in 2D, there appear gapless chiral edge states with a linear dispersion, while in the time-reversal-invariant $^3$He-B phase in 3D, gapless helical surface states with a linear dispersion show up [11, 49].

4. Theory of topological superconductors

4.1. General definition

As discussed in section 3.1, all negative energy states of the BdG Hamiltonian are fully-occupied in a superconducting state. Thus, like in insulators, one can define topological numbers for the occupied states. Depending on the dimension and symmetries of the system, various topological numbers can be introduced. In the broadest sense, a superconductor is regarded topological if any of such topological numbers is nonzero. Unconventional superconductors often have nodal superconducting gaps, where the nodes themselves have topological numbers. From the above definition, such unconventional superconductors are topological, and they may be called weak topological superconductors.

In a narrower sense, a fully-opened gap is required besides a nonzero topological number for topological superconductivity. In this case, no gapless bulk excitation exists and the system may be called a strong topological superconductor. Similar to the case of a quantum Hall state, the transport properties of such a system at low temperature are purely determined by topologically-protected gapless excitations localized at a boundary or at a topological defect.

4.2. Particle-hole symmetry and topological superconductor

In section 2.3, we have argued that general Hamiltonians do not have any non-trivial topological structure in one and three-dimensions. Nevertheless, as we shall discuss below, topological superconductors are possible in both one and three dimensions, as well as in two-dimensions. The key to understanding this result is the symmetry specific to superconductors. As was shown in section 3.1, superconductors are generically characterized by particle-hole symmetry. This symmetry enables us to introduce topological numbers other than the Chern number.

To see this, let us consider a 1D spinless superconductor,

$$\mathcal{H} = \frac{1}{2} \sum_k \left( \epsilon_k c_k^\dagger c_k + \text{h.c.} \right)$$

with

$$\mathcal{H}_{2 \times 2}^\dagger(k) = \left( \begin{array}{cc} \epsilon(k) & d(k) \\ d^*(k) & -\varepsilon(-k) \end{array} \right).$$

$$\mathcal{H}_{2 \times 2}(k) = \left( \begin{array}{cc} \epsilon(k) & \psi(k) \\ \bar{\psi}(k) & -\epsilon(k) \end{array} \right).$$

$$\epsilon(k) = \left( \frac{\hbar^2 k^2}{2m} - \mu \right), \quad \psi(k) = \Delta_0 \frac{k_y}{k_F^2}.$$
Here, due to the Fermi statistics (i.e. the anti-commutation relation) of \(c_i\), the term \(\hat{d}(k)\) must be an odd function of \(k\), which makes \(\mathcal{H}_2 \times \mathcal{H}(k)\) to have the particle-hole symmetry, \(\mathcal{H}_2 \times \mathcal{H}(k)\). Below, we additionally assume that \(\varepsilon(k)\) is an even function of \(k\), since otherwise fully-gapped superconductivity is not realized in general. For simplicity, the lattice constant is taken to be 1, so that the Hamiltonian is \(2\pi\)-periodic, \(\mathcal{H}_2 \times \mathcal{H}(k) = \mathcal{H}_2 \times \mathcal{H}(k + 2\pi)\).

Let us first reproduce the argument in section 2.3: Using a \(2 \times 2\) unitary matrix \(U(k)\), one can diagonalize \(\mathcal{H}_2 \times \mathcal{H}(k)\) in equation (94) as

\[
U(k) \mathcal{H}(k) U(k)^\dagger = \begin{pmatrix} E(k) & 0 \\ 0 & -E(k) \end{pmatrix} \tag{95}
\]

where \(E(k) = \sqrt{\varepsilon^2(k) + |\hat{d}(k)|^2} > 0\). Since \(U(k)\) in the above equation is not unique but has a redundancy of the gauge degree of freedom, we can generalize it to

\[
U(k) = \mathcal{U}(2) U(1) \times U(1) \tag{96}
\]

with \(U(1)\) rotations \(e^{i\theta(k)} (i = 1, 2)\). This \(U(k)\) is not merely an element of the unitary group \(U(2)\), but it should be regarded as an element of the coset space

\[
\mathcal{M} = \mathcal{U}(2)/\mathcal{U}(1) \times \mathcal{U}(1), \tag{97}
\]

which is equivalent to a 2D sphere, i.e. \(\mathcal{M} = S^2\) [53]. Since the 1D Brillouin zone is equivalent to a 1D circle \(S^1\), the image of the Brillouin zone by the map \(U(k)\) is a circle \(S^1\) on the sphere \(S^2\) of \(\mathcal{M}\). The circle \(S^1\) can smoothly shrink to a point on the sphere \(S^2\), and thus no topological constraint exists on this map, which reproduces the homotopy result \(\pi(\mathcal{M}) = 0\) in section 2.3.

The above argument, however, is not really correct due to the particle-hole symmetry. To see this, we specify the 2D sphere \(S^2\) in a different manner. By using the Pauli matrices \(\tau\) in the Nambu space, the Hamiltonian \(\mathcal{H}(k)\) can be written as

\[
\mathcal{H}(k) = E(k) \mathbf{x}(k) \cdot \tau \tag{98}
\]

with \(\mathbf{x}(k) = (x_1(k), x_2(k), x_3(k))\) where

\[
x_1(k) = \text{Re} \frac{d(k)}{E(k)}, \quad x_2(k) = -\text{Im} \frac{d(k)}{E(k)}, \quad x_3(k) = \varepsilon(k) \frac{E(k)}{E(k)} \tag{99}
\]

Since \(x^2(k) = 1\), the space spanned by the vector \(\mathbf{x}(k)\) is the 2D sphere \(S^2\). The image of the Brillouin zone by the map \(\mathbf{x}(k)\) provides a circle \(S^1\) on \(S^2\).

Now one can see that the particle-hole symmetry imposes an additional constraint on the circle \(S^1\). Due to the particle-hole symmetry, \(d(k)\) satisfies \(d(k) = -d(-k)\), and thus \(d(k) = 0\) at \(k = 0\) and \(\pi\). This imposes a constraint on the \(S^1\) image of the Brillouin zone that it must pass a pole of the 2D sphere, i.e. \(x_1(k) = x_2(k) = 0\), at \(k = 0\) and \(k = \pi\). This constraint allows us to tell topologically distinct circles: If \(x_1(0)\) and \(x_2(\pi)\) have the same sign, \(S^1\) passes the same pole at \(k = 0\) and \(\pi\), and thus \(S^1\) can smoothly shrink to a point; on the other hand, if \(x_1(0)\) and \(x_2(\pi)\) have opposite signs, \(S^1\) passes different poles at \(k = 0\) and \(\pi\), which means that \(S^1\) cannot shrink to a point. Therefore, \(S^1\) in the former (latter) case is topologically trivial (nontrivial). Since the sign difference between \(x_1(0)\) and \(x_2(\pi)\) is specified by \(\text{sgn}[\varepsilon(0)\varepsilon(\pi)]\), the corresponding topological number \(\nu_{\text{d}}\) is a \(Z_2\) index [13]:

\[
(-1)^{\nu_{\text{d}}} = \text{sgn} \left[\varepsilon(0)\varepsilon(\pi)\right]. \tag{100}
\]

For a tight-binding model with \(\varepsilon(k) = -t \cos k - \mu (t > 0)\), the above \(Z_2\) index is evaluated as

\[
(-1)^{\nu_{\text{d}}} = -\text{sgn} \left[(t + \mu)(t - \mu)\right], \tag{101}
\]

and thus it is nontrivial when \(-t < \mu < t\). When \(\mu = t\) (\(\mu = -t\), \(E(k)\) vanishes at \(k = \pi (k = 0)\), so that the gap in the spectrum closes and the topological phase transition occurs.

In the above example, we considered the simplest \(2 \times 2\) matrix Hamiltonian, but a similar result can be obtained for a general 1D superconductor, for which the \(Z_2\) index is given in terms of the Berry phase [22] as follows: Suppose that \(\{|u_n(k)\}\) is a solution of \(\mathcal{H}(k) |u_n(k)\rangle = E_n(k) |u_n(k)\rangle\) with a positive energy \(E_n(k) > 0\). The particle-hole symmetry dictates that \(C |u_n(-k)\rangle\) is also a solution of the same equation with the energy \(E_n(-k) < 0\). When we assign a positive (negative) integer \(n\) to such \(|u_n(k)\rangle\) which gives a positive (negative) energy eigenvalue, the particle-hole symmetry allows us to set

\[
|u_{-n}(k)\rangle = C |u_n(-k)\rangle. \tag{102}
\]

To calculate the \(Z_2\) index, we introduce the gauge fields

\[
\mathcal{A}^+ = i \sum_{n>0} \langle u_n(k) | \partial_k u_n(k) \rangle, \tag{103}
\]

d and their sum \(\mathcal{A}(k) = \mathcal{A}^+ + \mathcal{A}^-(k)\). Using the particle-hole symmetry, one obtains the following relation

\[
\mathcal{A}^+(k) = \mathcal{A}^-(k). \tag{104}
\]

Writing the \(m\)th component of the eigenvector \(|u_n(k)\rangle\) as \(u_m(k)\), \(\mathcal{A}(k)\) can be recast into

\[
\mathcal{A}(k) = i \sum_{n} u_n^\dagger(k) \partial_k u_n(k) = i \text{tr} [U(k)^\dagger \partial_k U(k)], \tag{105}
\]

where \(U(k) |u_n(k)\rangle \equiv u_m(k)\). The normalization condition \(\langle u_n(k) | u_n(k) \rangle\) implies that \(U(k)\) is a unitary matrix, and the derivative in the last equation is rewritten as

\[
\text{tr} [U(k)^\dagger \partial_k U(k)] = \partial_k [\text{ln det}(U(k))] = i \partial_k \theta(k), \tag{106}
\]

where \(\theta(k)\) is the phase angle of \(\text{det}(U(k))\). Therefore, the Berry phase obtained from \(\mathcal{A}^-(k)\) along the 1D Brillouin zone

\[
\gamma = \int_{-\pi}^{\pi} dk \mathcal{A}^-(k) \tag{107}
\]

is evaluated as
corresponds to the 3D winding number in II, and this leads to the

\[ \gamma = \frac{1}{2} \int_{-\pi}^{\pi} dk A(k) \]

\[ = \frac{1}{2} \int_{-\pi}^{\pi} dk \partial_k [\ln \det U(k)] \]

\[ = -\frac{1}{2} \left[ \theta(\pi) - \theta(-\pi) \right]. \tag{108} \]

Since \( \det U(k) \) is 2\( \pi \)-periodic in \( k \), we have \( \theta(-\pi) - \theta(\pi) = 2\pi N \) with an integer \( N \). Consequently, the Berry phase is quantized as \( e^{i\nu} = e^{i\pi N} = \pm 1 \), which defines the 1D \( Z_2 \) index \((-1)^{\nu_a} \) as

\[ (-1)^{\nu_a} = e^{i\nu}. \tag{109} \]

When \((-1)^{\nu_a} = -1\), the system is topologically nontrivial. This \( Z_2 \) index can be shown to coincide with that in equation (100) for the \( 2 \times 2 \) BdG Hamiltonian equation (94).

When a superconductor preserves time-reversal symmetry, there is another constraint. The time-reversal operation flips the electron spin, which results in the two-fold Kramers degeneracy. For instance, the logical insulators, the Kramers degeneracy plays a crucial role in topological superconductors, summarizing the topological numbers discussed in this section.

### Table 1. Topological table for time-reversal-breaking (TRB) and time-reversal-invariant (TRI) superconductors (SCs).

| AZ class | TRS | PHS | 1d | 2d | 3d |
|----------|-----|-----|----|----|----|
| TRB SCs (class D) | —   | +1  | \( Z_2^{\text{CS}} \) | \( Z_2^{\text{Ch}} \) | 0 |
| TRI SCs (class DIII) | -1  | +1  | \( Z_2^{\text{CS+}} \) | \( Z_2^{\text{KM}} \) | \( Z^{(W)} \) |

which is quantized to \( \pm 1 \). The system is topologically nontrivial (trivial) when \((-1)^{\nu_a} = -1 (1)\).

In 2D, the particle-hole symmetry does not introduce a new topological structure, although this symmetry always pairs up the positive and negative energy states. Like the quantum Hall states or the quantum spin Hall states, one can define the Chern number and the Kane–Mele’s \( Z_2 \) index, respectively. \( Z^{(W)} \) corresponds to the 3D winding number in equation (118). In the middle block, +1 and -1 indicate that \( C^2 = 1 \) and \( T^2 = -1 \), respectively.

\[ A \]

\[ \Gamma \]

\[ \Gamma^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]

\[ \text{Tr}^{-1} \]

\[ \Delta \]

\[ \Delta^{-1} \]

\[ \text{Tr} \]
number. When it is interfaced with a topologically trivial state such as vacuum, there arises a mismatch of topology, which cannot be resolved without having a singularity at the boundary. The singularity is physically realized as gapless boundary states [57].

Depending on the symmetries and dimensions of the system, there exist a variety of topological numbers defining topological superconductors; correspondingly, we have a variety of gapless boundary states consistent with the symmetries and dimensions. The correspondence between a topological number and its peculiar boundary states is called bulk-boundary correspondence [9, 11, 58–61]. The bulk-boundary correspondence makes it possible to detect a definite fingerprint of topological superconductivity.

A topological superconductor may also support zero-energy states localized on topological defects. A topological defect can be considered as a sort of a boundary of the system, and thus zero-energy states appear for the same reason as the gapless boundary states [59, 62–65]. For example, let us consider a vortex in a 2D spinless chiral $p$-wave superconductor. The vortex can be considered as a small hole in the superconductor; since $|\psi\rangle = 1$ in the spinless chiral $p$-wave superconductor, the boundary of the small hole supports a gapless boundary state, which eventually becomes a zero-energy state (called ‘zero mode’) when localized in the vortex core [12, 51]. Vortices in a variety of topological superconductors may support zero modes in a similar manner [66–69].

The gapless/zero-energy states at the boundary or defects are topologically classified in a uniform manner in the mathematical framework of the K-theory [59, 65]. The classification of these gapless modes reduces to the classification of a semiclassical Hamiltonian

$$\mathcal{H}(k, r), \quad (119)$$

where $k$ is the momentum in the $d$-dimensional Brillouin zone and $r$ is the coordinate of the $D$-dimensional sphere $S^D$ surrounding a defect. Using the K-theory, one can show that the possible topological number for $\mathcal{H}(k, r)$ depends only on $\delta = d - D$. This result also implies that a defect can be considered as a boundary: Since $D$ is the defect codimension, a topological defect surrounded by $S^D$ in $d$-dimensions defines a $\delta - 1$ dimensional submanifold. (For instance, a line defect in three dimensions has $\delta = 2$ ($d = 3$, $D = 1$), and thus it defines a one-dimensional submanifold.) Therefore, the defect submanifold can be considered as a boundary of a $\delta$-dimensional insulator/superconductor [12, 65]. Consequently, the classification of the gapless modes on defects reduces to that of the $\delta$-dimensional insulators/superconductors [59].

### 4.4. Topological crystalline superconductor

Superconductors may have space-group symmetry according to their crystal structures. Like the case of topological crystalline insulators [70], such a material-based symmetry can give rise to a nontrivial topology in the superconducting state [62–66, 71–75].

To see this, let us consider mirror reflection $M_{xy}$ with respect to the $xy$ plane. When the base material has mirror-reflection symmetry, the Hamiltonian in the normal state $\mathcal{H}(k)$ obeys

$$M_{xy}\mathcal{H}(k_x, k_y, -k_z)M_{xy}^{-1} = \mathcal{H}(k). \quad (120)$$

The superconducting state keeps the mirror-reflection symmetry if the pair potential $\Delta(k)$ does not break it spontaneously. When the pair potential is invariant under mirror reflection,

$$M_{xy}\Delta(k_x, k_y, -k_z)M_{xy}^{-1} = \Delta(k), \quad (121)$$

the BdG Hamiltonian also retains the mirror-reflection symmetry, which can be expressed as

$$\tilde{M}_{xy}\mathcal{H}(k_x, k_y, -k_z)\tilde{M}_{xy}^{-1} = \mathcal{H}(k), \quad (122)$$

where $\tilde{M}_{xy}$ is the mirror-reflection operator acting on the Nambu space,

$$\tilde{M}_{xy} = \begin{pmatrix} M_{xy} & 0 \\ 0 & M_{xy}^* \end{pmatrix} \quad (123)$$

It should be noted here that the above scenario is not the only way to keep the mirror-reflection symmetry in the superconducting state. Even when the pair potential changes sign under mirror reflection,

$$M_{xy}\Delta(k_x, k_y, -k_z)M_{xy}^{-1} = -\Delta(k), \quad (124)$$

the superconducting state can still support the mirror-reflection symmetry, and the key to this scenario is the U(1) electromagnetic gauge symmetry. When a Cooper pair forms in the above pair potential, both the original mirror reflection symmetry and the U(1) gauge symmetry are spontaneously broken, but their combination can be preserved. This is because the BdG Hamiltonian has the following mirror reflection symmetry,

$$\tilde{M}_{xy}'\mathcal{H}(k_x, k_y, -k_z)\tilde{M}_{xy}'^{-1} = \mathcal{H}(k), \quad (125)$$

with

$$\tilde{M}_{xy}' = \begin{pmatrix} M_{xy} & 0 \\ 0 & -M_{xy}^* \end{pmatrix} \quad (126)$$

In general, when a crystal-symmetry operation changes the phase of the pair potential, it can be made to be retained by combining the crystal-symmetry operation with a U(1)–gauge-symmetry operation. For mirror reflection, only a sign change of the pair potential is allowed since $\mathcal{M}_{xy}^2 = -1$, and hence there are two possible realizations of the mirror reflection in the BdG Hamiltonian, which correspond to equations (123) and (126).

Now we show that mirror-reflection symmetry provides novel topological structures through the introduction of a new topological number called mirror Chern number [76]. On the mirror-invariant plane $k_z = 0$ in the Brillouin zone, the BdG Hamiltonian commutes with the mirror reflection operator,

$$[\mathcal{H}(k_x, k_y, 0), \tilde{M}_{xy}] = 0. \quad (127)$$
Therefore, an eigenstate of the BdG Hamiltonian on the mirror-invariant plane can be simultaneously an eigenstate of the mirror operator. The mirror Chern number is defined as the Chern number of each mirror eigensector. In contrast to the ordinary Chern number, the mirror Chern number can be nonzero even when the system preserves time-reversal symmetry, because the individual mirror subsector is not time-reversal invariant. Furthermore, the mirror Chern number provides a more detailed topological structure than the Kane–Mele’s $\mathbb{Z}_2$ index. For example, in the case of insulators, SnTe hosts gapless surface states ensured by a nonzero mirror Chern number, while it is trivial in the $\mathbb{Z}_2$ topology [77, 78].

The two different mirror-reflection operations for the BdG Hamiltonian discussed above leads to different properties of the topological states in superconductors [63]. While the mirror reflection-operator $\tilde{M}_{xy}$ in equation (123) commutes with the charge-conjugation operator $C$

$$[C, \tilde{M}_{xy}] = 0, \quad (128)$$

the other mirror operator $\tilde{M}'_{xy}$ in equation (126) anti-commutes

$$[C, \tilde{M}'_{xy}] = 0. \quad (129)$$

This difference gives rise to different realizations of the particle-hole symmetry in mirror subsectors. For the commuting case, the mirror subsector with the mirror eigenvalue $\tilde{M}_{xy} = i$ is interchanged with the subsector with the opposite eigenvalue $\tilde{M}_{xy} = -i$ when one applies $C$. Thus, each mirror subsector does not have its own particle-hole symmetry, although the system as a whole does. This means that the mirror subsector belongs to the same topological class as a quantum Hall state. On the other hand, in the anti-commuting case, the operator $C$ maps each mirror eigensector onto itself, and hence the mirror subsector has its own particle-hole symmetry. Moreover, the mirror subsector in the anti-commuting case effectively realizes a spinless system, since electrons with an opposite $z$-component of the spin have an opposite eigenvalue of $M_{xy}$; as a result, each subsector is topologically equivalent to a spinless superconductor, and it may support Majorana fermions of a spinless superconductor, which is discussed in the next section.

### 4.5. Topology of nodal superconductors

Unconventional superconductors often host some nodes in the bulk superconducting gap. A traditional approach to the nodal structure is based on the irreducible representation of gap functions under space-group symmetry [43]. However, it has been recognized that nodes themselves can have their own topological numbers. Such topological arguments have revealed new aspects of nodal superconductors.

From the viewpoint of group theory, stable nodes in superconductors are classified into two: those protected by crystal symmetry, and those unprotected by crystal symmetry. For both classes of nodes, one can define topological numbers.

Let us first consider nodes that are not protected by crystal symmetry. Such nodes may appear at any position on the Fermi surface, and thus, in principle, they can move freely in response to perturbations to the system. In the group theoretical approach, these nodes are called accidental nodes. It should be noted, however, that they are not necessarily unstable. They can be stable due to their intrinsic topological numbers.

The topological numbers for accidental nodes are defined on momentum-space submanifolds enclosing the nodes: A time-reversal-breaking superconductor may host an accidental point node, whose topological number is given by the Chern number on a sphere enclosing the point node. The point node is a superconducting analogue of a Weyl node in a Weyl semimetal. For this reason, a superconductor with an accidental point node is dubbed Weyl superconductor [79]. In contrast to a Weyl semimetal, which may keep time-reversal symmetry when it breaks inversion symmetry, a Weyl superconductor must always break time-reversal symmetry. This difference originates from the intrinsic symmetry of superconductors, i.e. the particle-hole symmetry. When a superconductor preserves time-reversal symmetry, it must also host chiral symmetry (which is the combination of particle-hole and time-reversal symmetries) defined in equation (117), from which one can show that the Chern number always vanishes. Hence, breaking of time-reversal symmetry is necessary for realizing a point node with a nonzero Chern number. The $^3$He A-phase in 3D supports such topologically-protected accidental point nodes at poles on the Fermi surface [11].

A superconductor may also host an accidental line node with a non-zero topological number in the presence of time-reversal symmetry [80, 81]. Such a topological number is defined on a circle $C$ enclosing the line node. Using the chiral symmetry (equation (117)), the topological number is introduced as the 1D winding number [60, 82].

$$w_{1d} = \frac{i}{4\pi} \int_C \mathbf{d} \mathbf{r} \cdot \tr \left[ \Gamma \mathcal{H}^{-1}(\mathbf{k}) \partial_\mathbf{k} \mathcal{H}(\mathbf{k}) \right]. \quad (130)$$

The line nodes in high-$T_c$ cuprates and noncentrosymmetric superconductors have non-zero values of the 1D winding number [60, 80–86].

Accidental nodes in superconductors are classified by the presence or absence of time-reversal and/or inversion symmetries. The topological classification of accidental nodes in superconductors is given in [87]. A similar classification is also discussed in [88]. In the former theory, the topological version of the Blount’s theorem [89] was employed. These classifications indicate that in addition to point and line nodes, accidental area nodes with a $\mathbb{Z}_2$ topological index are possible in even-parity, time-reversal-breaking superconductors [87, 88]. A possible realization of such area nodes in heavy-fermion superconductors was discussed recently [90].

The second class of gap nodes, which are protected by crystal symmetry, appear at high-symmetry lines or planes in the Brillouin zone. Both symmorphic symmetry (like mirror reflection) and non-symmorphic symmetry (such as glide) give rise to stable line nodes on the Brillouin-zone boundary [91–93]. Using crystal symmetry as well as particle-hole and/or time-reversal symmetries, node-protecting topological numbers can be introduced for such nodes [87, 94–98].

For both classes of nodes, the relevant topological numbers are not defined globally, but are defined only in restricted
regions in the momentum space. Hence, they are considered to be ‘weak’ topological indices. Such weak indices often lead to gapless surface states with a flat dispersion. For instance, the non-zero Chern number of Weyl superconductors gives rise to a superconducting analogue of the surface Fermi arc having a flat dispersion [11, 79, 99–104]. Also, the 1D winding number (equation (130)) for line-nodal superconductors is responsible for zero-energy surface Andreev bound states with a flat dispersion [60, 82–85, 105, 106].

For superconductors having the second class of nodes, one can introduce ‘strong’ indices, despite the fact that they are gapless in the bulk [107, 108]. This is because the nodes in this class can be easily gapped out by a local perturbation breaking the relevant crystal symmetry. By opening a gap with such a perturbation, one can define the bulk topological numbers listed in table 1. However, for an integer-valued topological number such as the Chern number in 2D Class D superconductors or the winding number in 3D Class DIII superconductors, the obtained values depend on details of the perturbation. Therefore, these integer topological numbers are not uniquely defined in this manner. Nevertheless, it has been shown that this perturbation procedure provides a unique parity of the integer topological numbers, irrespective of the details of the perturbation. As a result, for nodal superconductors of the second class, one can rigorously define mod-2 topological numbers in terms of their parity. When the mod-2 Chern number (mod-2 winding number) is non-trivial, there exists an odd number of chiral edge states (surface helical Majorana fermions) on the boundary. Concrete examples of such mod-2 gapless topological superconductors have been given in [107, 108]. Other models to yield gapless topological phases have also been discussed recently [109, 110].

5. Majorana fermions

The emergence of Majorana fermions is the most prominent characteristic of topological superconductors. Here we present phenomenological properties of Majorana fermions.

5.1. Concept of Majorana fermions

When Dirac introduced the Dirac equation to describe the relativistic motion of electrons, he found that it also predicts an antiparticle of an electron, i.e. positron. The antiparticle has the same mass and the same spin as the electron, but has an opposite charge. Whereas the Dirac equation was derived mathematically by demanding a compatibility with the special relativity in quantum mechanics, the existence of positron was verified in a cosmic ray soon after the prediction. The discovery of antiparticle was one of the great success stories in the marriage of relativity and quantum theory.

While an electron is different from a positron due to the opposite charge, a neutral particle can be identical to its antiparticle. Indeed, in 1937, Majorana found that the Dirac equation can describe a particle which is identical to its antiparticle [111]. The Dirac equation reads

$$\frac{\hbar}{c} i \partial_t \psi(x, t) = [-i \hbar \alpha \cdot \partial_x + \beta mc] \psi(x, t),$$  \hspace{1cm} (131)

where $m$ is the mass of a particle, and $\alpha$ and $\beta$ are $4 \times 4$ matrices obeying the anti-commutation relations,

$$\{\alpha_i, \alpha_j\} = 2 \delta_{ij}, \quad \{\alpha_i, \beta\} = 0, \quad \beta^2 = 1.$$  \hspace{1cm} (132)

The following $\alpha$ and $\beta$ are often used,

$$\alpha_i^D = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta^D = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$  \hspace{1cm} (133)

but this is not the only choice. Any $\alpha$ and $\beta$ satisfying equation (132) describe a relativistic fermion particle, so one can take the following $\alpha$ and $\beta$,

$$\alpha_1^M = \begin{pmatrix} 0 & \sigma_1 \\ \sigma_1 & 0 \end{pmatrix}, \quad \alpha_2^M = \begin{pmatrix} 0 & \sigma_3 \\ \sigma_3 & 0 \end{pmatrix}, \quad \alpha_3^M = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \beta^M = \begin{pmatrix} 0 & \sigma_2 \\ \sigma_2 & 0 \end{pmatrix}.$$  \hspace{1cm} (134)

which satisfy the same anti-commutation relations as equation (132). In this basis, the complex conjugate of equation (131) reads,

$$\frac{\hbar}{c} i \partial_t \psi^\ast(x, t) = [-i \hbar \alpha \cdot \partial_x + \beta mc] \psi^\ast(x, t),$$  \hspace{1cm} (135)

and thus $\psi$ and $\psi^\ast$ satisfy the same Dirac equation. This means that the reality condition $\psi = \psi^\ast$ can be imposed without contradiction. Since $\psi^\ast$ corresponds to an antiparticle of $\psi$, the obtained real field $\psi$ describes a particle identical to its antiparticle. This self-conjugate Dirac particle is today called Majorana fermion.

5.2. Majorana fermions in particle physics and in condensed matter

The neutrino in particle physics is a promising candidate of Majorana fermion. First, it is the only neutral fermion obeying the Dirac equation in the standard model of particle physics. Also, a mass term is allowed for Majorana fermions, and this so-called Majorana mass term naturally explains why neutrino is extremely light in comparison with other fermions such as electrons. However, the verification of the self-conjugate property of neutrino is very difficult, since neutrino rarely interacts with other particles. No direct experimental verification has been reported up to now.

If supersymmetry relating boson and fermion is discovered, the superpartners of gauge bosons should be Majorana fermions. Gauge bosons such as photons are described by real vector fields, so they are identical to their antiparticles. Therefore, their partner fermions called gauginos should also have the same property; namely, they are Majorana fermions. Supersymmetry is expected to be realized in high-energy particle physics and it predicts many undiscovered particles, but no such partner particle has been discovered so far.

While Majorana originally introduced his fermion to describe an elementary particle, it was recently recognized
that condensed matter systems may also support Majorana fermions [112]. In condensed matter, the constituent fermions are electrons. Since electron has a negative charge, it cannot be a Majorana fermion, as discussed above. Nevertheless, Majorana fermions may exist as emergent collective excitations of electrons. Note that the emergent Majorana fermions are distinct from the original Majorana fermions in that they do not keep the true Lorentz invariance of the Dirac equation, since they do not move with the speed of light. Nevertheless, under a proper rescaling of length and time, the emergent Majorana fermions also obey the Dirac equation. Such emergent Majorana fermions appear in boundaries of topological superconductors or in a class of spin-liquid systems.

5.3. Relationship between topological superconductivity and Majorana fermions

To be a Majorana fermion in a condensed matter systems, a collective excitation should satisfy the following two conditions: The first is that it obeys the Dirac equation. An ordinary electron in condensed matter physics has a parabolic energy dispersion obeying the non-relativistic Schrödinger equation, so it does not satisfy this condition. However, if the system supports a gapless fermionic excitation near a band crossing point, the low-energy Hamiltonian of the excitation has a matrix form with band indices and describes a linear dispersion. Therefore, the motion of the excitation naturally obeys the massless Dirac equation. The second condition is that the excitation should be its own antiparticle, which is essential for being a Majorana fermion.

These two conditions are naturally met in topological superconductors. The first condition is satisfied due to the topological nature. From the bulk-boundary correspondence, topological superconductors support gapless excitations on the boundaries, and those excitations are described by the Dirac equation. The second condition is satisfied by virtue of the fact that, as discussed in section 3.1, the electron and hole excitations are superimposed in the superconducting state so that they become indistinguishable. This makes a superconductor to obtain particle-hole symmetry, with which the topological gapless boundary excitations become Majorana fermions.

5.4. Majorana zero mode and non-Abelian statistics

Suppose that there exists a zero mode $\gamma_0$ localized in a vortex core. For instance, the vortex in a 2D chiral $p$-wave superconductor supports such a zero mode, as discussed in section 4.3. The zero mode is self-conjugate, so that it satisfies the so-called Majorana condition,

$$\gamma_0^\dagger = \gamma_0.$$  \hspace{1cm} (136)

This equation implies that a single zero mode $\gamma_0$ cannot define a creation or an annihilation operator. Indeed, if one regards $\gamma_0^\dagger$ as a creation operator of the zero mode, equation (136) requires that the annihilation operator $\gamma_0$ must be the same, which leads to a contradiction. Therefore, $\gamma_0$ cannot be considered as a creation operator.

![Figure 3. A braiding process of vortices, each of which contains a Majorana zero mode. (a) Initial configuration of vortices 1 and 2. (b) Another vortex 3 goes around vortex 2. (c) Final configuration.](image-url)

This difficulty can be resolved by considering a pair of vortices. Let us consider vortices 1 and 2, and express their Majorana zero modes as $\gamma_0^{(1)}$ and $\gamma_0^{(2)}$, which obey $\{\gamma_0^{(i)}, \gamma_0^{(j)}\} = 2\delta_{ij}$ with a suitable normalization of $\gamma_0$. When one defines the operators $c_{12}$ and $c_{12}^\dagger$ as

$$c_{12} = \frac{\gamma_0^{(1)} + i\gamma_0^{(2)}}{2}, \quad c_{12}^\dagger = \frac{\gamma_0^{(1)} - i\gamma_0^{(2)}}{2},$$  \hspace{1cm} (137)

they satisfy the conventional anticommutation relation

$$\{c_{12}, c_{12}^\dagger\} = 1.$$  \hspace{1cm} (138)

Therefore, without contradiction, one can identify $c_{12}$ and $c_{12}^\dagger$ as a creation and an annihilation operator, respectively.

It should be noted here that a pair of separated vortices are necessary for defining the creation and annihilation operators. This nonlocality leads to a nonlocal quantum correlation between the vortices, which results in a drastic change in their statistical nature [12, 113].

To examine the statistics of the vortices, let us consider the process illustrated in figure 3. Initially, only vortices 1 and 2 exist as in figure 3(a). Later, another vortex 3 comes and it moves around vortex 2 (see figure 3(b)). Finally, vortex 3 goes far way, and vortices 1 and 2 remain in the same initial configuration. In terms of the number of vortex exchange, the process in figure 3(b) is equivalent to a process of exchanging vortex 2 and vortex 3 twice. Hence, if the vortices obey the conventional boson or fermi statistics, the finial state remains the same as the initial one. However, in a 2D chiral $p$-wave superconductor, due to the existence of the Majorana zero mode, the wavefunction of the final state is different from that of the initial state, as we show below.

To see this, let us first examine what happens in a quantum state when a particle moves around a vortex. A vortex in a superconductor contains a flux quantum $\Phi_0 = hc/2e$, therefore, when an electron moves around a vortex, the state acquires the phase factor

$$e^{-i\Phi_0/2hc} = -1$$  \hspace{1cm} (139)

due to the Aharonov–Bohm effect. In the same manner, when a hole moves around a vortex, the state obtains the same phase factor

$$e^{i\Phi_0/2hc} = -1.$$  \hspace{1cm} (140)
Consequently, a quasiparticle in the superconductor, which is a superposition of an electron and a hole, acquires the same factor $-1$. In particular, a Majorana zero mode $\gamma_0$ changes its phase as

$$\gamma_0 \rightarrow -\gamma_0$$  

(141)
after moving around a vortex.

Now we suppose that the initial state $|i\rangle$ in the vortex configuration of figure 3(a) is given by the state $|0\rangle$ annihilated by $c_{12}$ in equation (137):

$$|i\rangle = |0\rangle, \quad c_{12}|0\rangle = 0.$$  

(142)
If one considers the process in figure 3(b), the Majorana zero mode localized in vortex 3 changes sign as discussed above. At the same time, $\gamma_0^{(2)}$ also changes sign,

$$\gamma_0^{(2)} \rightarrow -\gamma_0^{(2)},$$  

(143)
because vortex 2 goes around vortex 3 in the coordinate system moving with vortex 3. Therefore, in the process of figure 3(b), the operator changes as

$$c_{12} = \frac{\gamma_0^{(1)} - i\gamma_0^{(2)}}{2} \rightarrow c_{12}^{\dagger} = \frac{\gamma_0^{(1)} + i\gamma_0^{(2)}}{2},$$  

(144)
so the final state $|f\rangle$ in figure 3(c) satisfies

$$c_{12}^{\dagger}|f\rangle = 0,$$  

(145)
instead of equation (142). In other words, the final state $|f\rangle$ become a state annihilated by $c_{12}^{\dagger}$, $|1\rangle \equiv c_{12}^{\dagger}|0\rangle$, which is orthogonal to the initial state $|i\rangle$,

$$\langle i|f\rangle = 0.$$  

(146)
This means that vortices are neither bosons nor fermions, since the braiding to provide a new state should be represented in a matrix form. The statistics expressed in a matrix form is called non-Abelian statistics, and particles obeying non-Abelian statistics are dubbed non-Abelian anyons.

In general, as discussed by Ivanov [113], an exchange of the Majorana zero modes $\gamma_0^{(i)}$ and $\gamma_0^{(j)}$ is represented by the unitary transformation

$$U_{ij} = \exp\left(-\frac{i\pi}{4}\gamma_0^{(i)}\gamma_0^{(j)}\right),$$  

(147)
from which one obtains

$$U_{ij}\gamma_0^{(i)}U_{ij}^{\dagger} = \gamma_0^{(j)}, \quad U_{ij}\gamma_0^{(j)}U_{ij}^{\dagger} = -\gamma_0^{(i)}.$$  

(148)
In the process of figure 3, where $\gamma_0^{(2)}$ and $\gamma_0^{(3)}$ are exchanged twice, one has

$$(U_{23})^2\gamma_0^{(2)}(U_{23}^\dagger)^2 = -\gamma_0^{(2)},$$

$$(U_{23})^2\gamma_0^{(3)}(U_{23}^\dagger)^2 = -\gamma_0^{(3)},$$

(149)
which reproduces equation (143). $U_{23}$ and $U_{12}$ do not commute with each other

$$U_{12}U_{23} = U_{23}U_{12},$$  

(150)
and thus the exchange process is actually non-Abelian.

In the above example, we assumed that the initial state $|i\rangle$ is given by $|0\rangle$, but one can also consider the case with $|i\rangle = |1\rangle \equiv c_{12}^\dagger|0\rangle$ in a similar manner. In this case, after the process in figure 3, the state becomes $|0\rangle$. After all, the process in figure 3 exchanges $|0\rangle$ and $|1\rangle$, which is given by the Pauli matrix $\sigma_z$,

$$\begin{pmatrix} |0\rangle \\ |1\rangle \end{pmatrix} \rightarrow \begin{pmatrix} |1\rangle \\ |0\rangle \end{pmatrix} = \sigma_z \begin{pmatrix} |0\rangle \\ |1\rangle \end{pmatrix}. $$  

(151)
An isolated Majorana zero mode also appears at each end point of a 1D topological superconductor [13]. One can exchange such Majorana zero modes in a network of 1D topological superconductors [114–123]. Again, the exchange operators of those Majorana zero modes are given by $U_{ij}$ in equation (147), and the Majorana zero mode at the end point is also a non-Abelian anyon.

The non-Abelian anyon is expected to have an application in quantum computing [124, 125], because the states $|0\rangle$ and $|1\rangle$ defined by a pair of Majorana zero modes work as a nonlocal qubit. In general, if there are $2N$ Majorana zero modes, one can define $N$ independent creation operators, which define $N$ qubits. Equation (151) implies that the process in figure 3 gives a NOT gate for the qubits.

6. Routes to topological superconductivity

Recently, much efforts have been paid to find ways to realize topological superconductivity. Here we summarize possible routes to topological superconductivity.

6.1. Odd-parity superconductors

A promising ground for topological superconductivity is the spin-triplet (or more precisely, odd-parity) pairing state. For instance, 2D spinless chiral $p$-wave superconductors have a nonzero bulk Chern number, $C_h = 1$ (or $C_h = -1$), supporting a gapless chiral Majorana edge mode on the boundary [12]. Their vortices host a single Majorana zero mode in the core, which obeys the non-Abelian statistics [12]. Also, the spin-triplet $^3$He-B phase is known to be a 3D topological superfluid hosting gapless helical Majorana fermions on its surface [49, 126–128].

In general, to clarify topological superconductivity, one needs to either evaluate topological numbers or examine the boundary states. However, in the case of odd-parity superconductors, one can judge the topological nature just from the information of the Fermi surface, independently of the details of gap functions. This result follows from the following theorem [129–131].

- An odd-parity superconductor is a topological superconductor if the Fermi surface encloses an odd number of time-reversal-invariant momenta in the Brillouin zone.
- The number of Fermi surfaces are counted as follows: For a time-reversal-invariant superconductor, the spin-degeneracy of the Fermi surfaces is neglected. Each spin-degenerate Fermi surface is counted as a single...
Fermi surface. On the other hand, for a time-reversal-breaking superconductor, a spin-degenerate Fermi surface is counted as a pair of Fermi surfaces.

Here the time-reversal-invariant momentum \( \mathbf{k} = \Gamma_i \) is defined as a momentum satisfying \( \Gamma_i = -\Gamma_i + \mathbf{G} \) with a reciprocal lattice vector \( \mathbf{G} \). The \( \Gamma_i \)'s in two and three dimensions are illustrated in figure 1.

This theorem is a consequence of the relations between the parity of topological numbers and the sign of the eigenvalues of the normal-state Hamiltonian [130]. For time-reversal-breaking superconductors, the relations in \( d \)-dimensions are

\[
(-1)^{y_{\alpha}} = \prod_{\alpha=1,2} \mathrm{sgn} \quad \epsilon_{\alpha}(\Gamma), \quad (\text{for } d = 1),
\]
\[
(-1)^{y_{\alpha^2}} = \prod_{\alpha=1,2,3,4} \mathrm{sgn} \quad \epsilon_{\alpha}(\Gamma), \quad (\text{for } d = 2),
\]
\[
(-1)^{y_{\alpha^3}} = \prod_{\alpha=1,2,3,4} \mathrm{sgn} \quad \epsilon_{\alpha}(\Gamma), \quad (\text{for } d = 3),
\]

where \( \epsilon_{\alpha}(\mathbf{k}) \) is the \( \alpha \)th eigenvalue of the normal-state Hamiltonian \( \mathcal{E}(\mathbf{k}) \) in equation (72), and the product in the right hand side with the running variable \( (\alpha, i) \) is taken for all eigenvalues of \( \mathcal{E}(\mathbf{k}) \) and all time-reversal-invariant momenta in each dimension. There are similar relations for time-reversal-invariant superconductors,

\[
(-1)^{y_{\alpha^2}} = \prod_{\alpha=1,2} \mathrm{sgn} \quad \epsilon_{\alpha}(\Gamma), \quad (\text{for } d = 1),
\]
\[
(-1)^{y_{\alpha^2}} = \prod_{\alpha=1,2,3,4} \mathrm{sgn} \quad \epsilon_{\alpha}(\Gamma), \quad (\text{for } d = 2),
\]
\[
(-1)^{y_{\alpha^3}} = \prod_{\alpha=1,2,3,4} \mathrm{sgn} \quad \epsilon_{\alpha}(\Gamma), \quad (\text{for } d = 3),
\]

where the product of the eigenvalues of \( \mathcal{E}(\mathbf{k}) \) is taken only for one of each Kramers pair \((\epsilon_{\alpha^2}(\mathbf{k}), \epsilon_{\alpha^2}(\mathbf{k}))\).

Since the Fermi surface of the \( \alpha \)th band is a surface on which the momentum \( \mathbf{k} \) satisfies \( \epsilon_{\alpha}(\mathbf{k}) = 0 \) (or \( \epsilon_{\alpha^2}(\mathbf{k}) = 0 \)), when the Fermi surface encloses \( \Gamma_i \), \( \epsilon_{\alpha}(\Gamma_i) \) (or \( \epsilon_{\alpha^2}(\Gamma_i) \)) is negative. Therefore, if the Fermi surface encloses an odd number of time-reversal-invariant momenta in the Brillouin zone, the right hand side of equation (152) or (153) becomes negative. As a result, the corresponding topological number in the left hand side becomes non-zero, which implies the realization of topological superconductivity.

Since a topological phase transition may occur only when the gap of the system closes, the above theorem implies that there arises a gap closing when the number of the Fermi surfaces enclosing \( \Gamma_i \) changes. This situation can be confirmed directly in a single-band superconductor described by the \( 4 \times 4 \) Hamiltonian equation (59). As shown in section 3.2, an odd-parity pair potential in a single-band superconductor is spin-triplet, \( \Delta(\mathbf{k}) = i\Delta_{0}d(\mathbf{k}) \cdot s_{z}y_{s} \), which vanishes at \( \Gamma_i \). Thus, at \( \Gamma_i \), the Hamiltonian becomes

\[
\mathcal{H}_{4 \times 4}(\mathbf{k}) = \begin{pmatrix} \epsilon(\Gamma) & 0 \\ 0 & -\epsilon(\Gamma) \end{pmatrix},
\]

and hence the quasiparticle spectrum reduces to that of the normal-state Hamiltonian \( \epsilon(\Gamma) \). Therefore, when the number of the Fermi surfaces enclosing \( \Gamma_i \) changes, a gap closing occurs at \( \Gamma_i \).

To appreciate the above theorem, let us consider a Fermi surface surrounding the \( \Gamma \) point in figure 4(a). If the normal state preserves both time-reversal and inversion symmetries, the Fermi surface is spin-degenerate due to the Kramers theorem. From the above theorem, one can judge that any time-reversal-invariant odd-parity superconductivity realized on this Fermi surface is topological, irrespective of the details of the pair potential. Indeed, assuming the gap function of the \( ^{3}\text{He}-\text{B} \) phase, one can confirm the existence of a gapless surface state as evidence for topological superconductivity [129]. Furthermore, even for the nodal pair potential of the planar phase of \( ^{3}\text{He} \), one obtains a topologically protected gapless mode. The latter property is ensured by the mod-2 winding number discussed in section 4.5.

Next, we consider a quasi-2D Fermi surface illustrated in figure 4(b). In this case, the Fermi surface encloses two time-reversal-invariant momenta, and hence the theorem tells us nothing about the topology in 3D. However, one can argue for weak topological superconductivity defined in lower dimensions. If one considers the 2D Brillouin zones defined by \( k_{x} = 0 \) and \( k_{z} = \pi \) in figure 4(b), the Fermi surface encloses a single time-reversal-invariant momentum in each 2D Brillouin zone. Thus, if a time-reversal-invariant odd-parity pairing is realized on the Fermi surface, the theorem tells us that the system is at least a weak topological superconductor.

When an odd-parity Cooper pair breaks time-reversal symmetry, a spin-degenerate Fermi surface is counted as two different Fermi surfaces in the theorem. Since the Fermi surfaces in ordinary superconductors are spin-degenerate, they always surround the time-reversal invariant momenta even times, and the above theorem alone is not useful for judging the topological nature. In many cases, however, one can examine the topology by employing additional symmetry considerations. For instance, when the spin–orbit coupling is so small that a superconductor has an approximate uniaxial spin-rotation symmetry with respect to, say, the \( z \)-axis, one can use it for examining the topology. In this case, upon evaluating a topological number, one can completely neglect the spin–orbit coupling which breaks uniaxial spin-rotation symmetry, because such a small perturbation does not change the topological nature. After neglecting the spin–orbit coupling, the BdG Hamiltonian commutes with the spin operator \( S_{z} \), so that it becomes block-diagonal in the eigen basis of \( S_{z} \). As a result, the spin-degenerate Fermi surface is decomposed.

**Figure 4.** Time-reversal-invariant momenta enclosed by a Fermi surface. (a) 3D Fermi surface. (b) Quasi-2D Fermi surface. Blue dots mark the time-reversal-invariant momenta.
into a nondegenerate Fermi surface in each spin sector. For the Fermi surface in figure 4(a), each spin sector has a single Fermi surface enclosing the \( \Gamma \) point, and one can identify topological superconductivity. Actually, the spin-Chern number on the \( k_z = 0 \) plane can be evaluated as

\[
(-1)^{C_{\chi}} = \prod_{\alpha, \sigma} \varepsilon_{\alpha}^{\sigma}(\Gamma), \quad (-1)^{C_{\chi}} = \prod_{\alpha, \sigma} \varepsilon_{\alpha}^{\sigma}(\Gamma),
\]

(155)

where \( \varepsilon_{\alpha}^{\sigma}(\Gamma) \) is the \( \alpha \)th eigenvalue of the normal-state Hamiltonian in the \( S_{z} = 1 \) (\( S_{z} = -1 \)) sector, and the products with respect to \( i \) are taken for all four time-reversal-invariant momenta on the \( k_z = 0 \) plane.

For a superconductor with a strong spin–orbit coupling, one can use mirror-reflection symmetry instead of spin-rotation symmetry. On a mirror-invariant plane in the momentum space, the mirror symmetric BdG Hamiltonian commutes with the mirror operator, so that it becomes block-diagonal in the eigen basis of the mirror operator. In such a situation, the mirror Chern number can be defined for each mirror eigensector. Since the spin degeneracy of the Fermi surface is now decomposed into two different mirror eigensectors, one can use the Fermi surface criterion to evaluate the mirror Chern number: By replacing the spin Chern number and the spin sector with the mirror Chern number and the mirror eigensector, one can use the Fermi surface criterion to evaluate the mirror Chern number: By replacing the spin Chern number and the spin sector with the mirror Chern number and the mirror eigensector in equation (155), one obtains the corresponding formulas for the mirror Chern numbers on the \( k_z = 0 \) plane. For the Fermi surface in figure 4(a), there is only a single Fermi surface enclosing the \( \Gamma \) point in each mirror eigensector on the mirror invariant plane at \( k_z = 0 \), and thus the mirror Chern numbers are found to be nonzero.

The above examples imply that odd-parity superconductors are intrinsically topological. Unless no Fermi surface encloses \( \Gamma \), or each Fermi surface reduces to an \( s \)-wave pairing state as illustrated in figure 5, an odd-parity pairing state leads to topological superconductivity.

6.2. Superconducting topological materials

Traditionally, spin-triplet or odd-parity superconductivity has been explored in strongly correlated electron systems [43]. However, it has been discussed recently that systems with a strong spin–orbit coupling tend to realize odd-parity pairing states. Here we show the mechanism of odd-parity pairing due to spin–orbit coupling.

6.2.1. Topological insulators. In section 2.5.1, we have considered the prototypical topological insulator Bi\(_2\)Se\(_3\) having the bulk Hamiltonian

\[
H_{TI}(k) = (m_0 - m_2 k_z^2)\sigma_z + v \mathbf{k} \cdot \mathbf{\sigma} + v \mathbf{k} \cdot \mathbf{\sigma} \times (k_z \mathbf{\sigma}_z - k_x \mathbf{\sigma}_x),
\]

(156)

Let us now consider possible superconducting states of this material [131]. Since an insulator cannot superconduct, we should first dope carriers and make the system a metal. Correspondingly, we have a non-zero chemical potential \( \mu \) in \( \mathcal{E}(k) \),

\[
H_{TI}(k) \rightarrow \mathcal{E}(k) = H_{TI}(k) - \mu,
\]

(157)

which enters the BdG Hamiltonian equation (72),

\[
\mathcal{H}(k) \equiv \begin{pmatrix} \mathcal{E}(k) & \Delta(k) \\ \Delta(k)^\dagger & -\mathcal{E}(-k) \end{pmatrix}.
\]

(158)

The doping gives rise to a Fermi surface surrounding the \( \Gamma \) point. Note that the strong spin–orbit coupling in topological insulators induce a spin texture on the Fermi surface, as shown in figure 2 for \( k_z = 0 \) plane. The spin–orbit coupling term \( v \mathbf{k} \cdot \mathbf{\sigma} \times (k_z \mathbf{\sigma}_z - k_x \mathbf{\sigma}_x) \) is similar to the Rashba term, and hence it results in a helical spin structure. However, since the system as a whole preserves inversion symmetry, the two orbitals (specified by \( \sigma_z \)) have opposite helicity. As we will see below, this structure makes it possible to host odd-parity pairing states, without relying on spin-mediated pairing interactions.

If the attractive interaction is the strongest between electrons in the same orbital, Cooper pairs are formed between electrons having antiparallel spins, as illustrated in figure 6(a); this means that an ordinary spin-singlet \( s \)-wave pairing state is realized. On the other hand, if the attractive interaction is the strongest between electrons in different orbitals, Cooper pairs will have a parallel spin structure as shown in figure 6(b); in this case a spin-triplet pairing state is realized, although the pairing interaction itself is independent of the spin. For the carrier-doped Bi\(_2\)Se\(_3\), one can reasonably assume that the attractive interaction is momentum-independent, since there is no strong electron correlations. Under this assumption, the possible pair potentials are classified into four types of irreducible representations of the \( D_{3h} \) point group relevant to Bi\(_2\)Se\(_3\). The matrix forms of the possible pairings \( \Delta_1, \Delta_2, \Delta_3, \) and \( \Delta_4 \), as well as their properties, are summarized in table 2. Among them, spin-triplet Cooper pairs are realized in \( \Delta_2 \) and \( \Delta_4 \), both of which are odd-parity pairings.

Early microscopic calculations based on the simple model Hamiltonian equation (156) supported the pair potential \( \Delta_2 \) [131, 132] rather than \( \Delta_4 \), but later the possibility of \( \Delta_4 \) was also pointed out [133]. Whereas the model Hamiltonian equation (156) is fully uniaxial symmetric along the \( z \)-axis, the

\begin{figure}

![Figure 5](image)

**Figure 5.** A topologically trivial odd-parity superconductor. Each Fermi surface realizes an \( s \)-wave pairing state.

\end{figure}
Electrons connected by the dotted lines form Cooper pairs. This term makes the spin texture of the Rashba systems may be fabricated in pairs naturally lead to odd-parity superconductivity. Such orbit coupling term in equation (156), interlayer Cooper pairs must be formed between electrons with parallel spins. In particular, the Cooper pairs cannot be in a spin-singlet s-wave pairing state.

To better understand the situation, let us consider the simplest gap functions with a constant amplitude \( \Delta_\alpha \). From the Fermi surface due to the spin–orbit coupling. In figure 7, we illustrate the spin texture obtained from equation (162). From this structure, we find the following important feature.

II:

If the total momentum of a Cooper pair is zero, the Cooper pairs must be broken to realize Weyl semimetals. At the same time, however, at least one of them must be preserved to realize a bulk superconducting state—if both are broken, electrons with momenta \( k \) and \(-k\) are not at the same energy, and thus they cannot form a Cooper pair. Therefore, in the following we assume that either time-reversal or inversion symmetry is preserved.

Time-reversal-breaking Weyl semimetals. We first consider time-reversal-breaking Weyl semimetals which preserve inversion symmetry. For a finite chemical potential, a Weyl node is described by

\[
H_W(k) = \nu(k - k_0) \cdot s - \mu. \tag{160}
\]

By performing space inversion on equation (160), we obtain an anti-Weyl node described by

\[
H_W(k) = -\nu(k + k_0) \cdot s - \mu. \tag{161}
\]

The anti-Weyl node has an opposite Chern number as the Weyl node described by equation (160), so the total Chern number is zero. Thus, they form a minimal set of Weyl points satisfying the Nilsen–Ninomiya theorem. Expressing the Weyl (anti-Weyl) node with \( \sigma_1 = 1 \) (\( \sigma_1 = -1 \)), the sum of the Hamiltonians equations (160) and (161) becomes

\[
H_{W+\overline{W}}(k) = \nu(k_1 - k_0\sigma_0) \cdot s - \mu\sigma_0, \tag{162}
\]

which transforms under inversion \( P \) as

\[
PH_{W+\overline{W}}(-k)P^{-1} = H_{W+\overline{W}}(k), \quad P = \sigma_\epsilon. \tag{163}
\]

Now we examine what kind of superconducting state naturally arises in the above system. First, it should be noted that a spin texture appears on the Fermi surface due to the spin–orbit coupling.
As long as the Cooper pairs of a time-reversal-breaking Weyl semimetal do not have any finite momentum to break the translational symmetry, the superconducting state must realize an odd-parity, spin-triplet gap function with point nodes.

One might wonder if the above two properties are specific to the simple model considered here; in this regard, they actually represent general properties derived from the topological nature of Weyl semimetals. For example, the fact that an $s$-wave pairing cannot be realized in a time-reversal-breaking Weyl semimetal is a natural consequence of the following property of superconductors:

II:

It is impossible to form an even-parity Cooper pair on any spin-nondegenerate Fermi surface if the Cooper pair keeps the (lattice) translational symmetry

This property can be derived by using a topological argument combining inversion and particle-hole symmetries. Consider an inversion-symmetric system

$$P\mathcal{E}(-k)P^{-1} = \mathcal{E}(k)$$

and its BdG Hamiltonian having the (lattice) translation symmetry

$$\mathcal{H}(k) = \begin{pmatrix} \mathcal{E}(k) & \Delta(k) \\ \Delta^*(k) & -\mathcal{E}'(-k) \end{pmatrix}. $$

If the gap function $\Delta(k)$ is even under inversion,

$$P\Delta(-k)P^\prime = \Delta(k),$$

then the inversion operator for the BdG Hamiltonian is defined as

$$\tilde{P} = \begin{pmatrix} P & 0 \\ 0 & P^\prime \end{pmatrix},$$

and the inversion symmetry reads $\tilde{P}\mathcal{H}(-k)\tilde{P}^{-1} = \mathcal{H}(k)$. The particle-hole symmetry is expressed by using the charge conjugation operator $\mathcal{C}$ as

$$\mathcal{C}\mathcal{H}(k)\mathcal{C}^{-1} = -\mathcal{H}(k),$$

where $K$ is the complex conjugate operator. Combining these two symmetries, we obtain

$$\tilde{P}\mathcal{C}\mathcal{H}(k)\mathcal{C}^{-1}\tilde{P}^{-1} = \mathcal{H}(k).$$

Note that there is an identity $[\tilde{P}, \mathcal{C}]^2 = 1$, because $[\tilde{P}, \mathcal{C}] = 0$ and $\tilde{P}^2 = \mathcal{C}^2 = 1$. One can interpret equation (172) to mean that the BdG Hamiltonian $\mathcal{H}(k)$ has zero-dimensional (0D) class D particle-hole symmetry at each momentum $k$. Hence, one can
define the 0D $\mathbb{Z}_2$ index for each momentum. This can be done in the following steps: First, we note that $P = P_1$, since $P_0^2 = 1$ and $P$ is unitary. Second, we use equation (172) to prove that the matrix $\mathcal{H}(k)P\tau_z$ is antisymmetric, i.e.

$$ (P\tau_z)\mathcal{H}(k) = -\mathcal{H}(k)P\tau_z, \quad (173) $$

which allows us to define the Pfaffian of $\mathcal{H}(k)P\tau_z$. Finally, the 0D $\mathbb{Z}_2$ index is invariant defined as

$$ (-1)^{\nu_{\text{odd}}(k)} = \text{sgn} \left[ \frac{\text{Pf}(\mathcal{H}(k)P\tau_z)}{\text{Pf}(\mathcal{H}(0)P\tau_z)} \right], \quad (174) $$

where $k_0$ is a reference momentum which can be taken to be the $\Gamma$ point, for instance.

Now we evaluate the $\mathbb{Z}_2$ index $(-1)^{\nu_{\text{odd}}(k)}$ at $k$ other than on the Fermi surface. Since the superconducting gap is usually much smaller than the Fermi energy, one can neglect the gap function $\Delta(k)$ except on the Fermi surface, and thus the 0D $\mathbb{Z}_2$ index is evaluated as

$$ (-1)^{\nu_{\text{odd}}(k)} = \text{sgn} \left[ \frac{\text{det}(\mathcal{E}(k)P)}{\text{det}(\mathcal{E}(0)P)} \right]. \quad (175) $$

Physically, $\text{det} \mathcal{E}(k)$ is a product of all band energies (measured from the chemical potential) at $k$. Since we are considering a spin-non-degenerate system, upon crossing the Fermi surface the energy of only one band changes from negative to positive, and hence $\text{det} \mathcal{E}(k)$ must change sign across the Fermi surface. Therefore, the $\mathbb{Z}_2$ index $(-1)^{\nu_{\text{odd}}(k)}$ is different between inside and outside the Fermi surface. Since the topological number changes only when the gap of the system closes, this means that there must be a gapless surface separating inside and outside the Fermi surface. In other words, the Fermi surface must remain gapless, and thus no superconducting state is realized for any even-parity gap function. When applied to Weyl semimetals which always have spin-non-degenerate Fermi surfaces, the above result dictates that an even-parity superconducting state cannot be realized in Weyl semimetals.

It should be noted here that the above constraint does not apply to an odd-parity gap function $\Delta(k)$, which transforms non-trivially under inversion,

$$ P\Delta(-k)P^\dagger = -\Delta(k). \quad (176) $$

However, combining $P$ with a U(1) gauge rotation, one can eliminate the minus sign in the right hand side of equation (176). This means that the inversion symmetry is effectively restored under the combination of the original inversion and a U(1) gauge rotation. The BdG Hamiltonian is invariant under this modified inversion $\tilde{P}'$, i.e. $\tilde{P}'\mathcal{H}(-k)\tilde{P}'^{-1} = \mathcal{H}(k)$, with $\tilde{P}'$ given by

$$ \tilde{P}' = \begin{pmatrix} P & 0 \\ 0 & -P \end{pmatrix}. \quad (177) $$

Therefore, in a manner similar to the case of an even-parity gap function, one obtains

$$ (\tilde{P}'\tau_z)\mathcal{H}(k) = \mathcal{H}(k)(\tilde{P}'\tau_z), \quad (179) $$

so that $\mathcal{H}(k)(\tilde{P}'\tau_z)$ is symmetric. Hence, one cannot define the Pfaffian of $\mathcal{H}(k)(\tilde{P}'\tau_z)$ nor the $\mathbb{Z}_2$ index. Since there is no topological number to protect the system from gap opening in this case, an odd-parity superconducting gap is allowed by symmetry.

As for the generality of the conclusions we obtained for the simple model, the following property can also be derived by using a topological argument.

III:

If a superconducting state preserving translational symmetry is realized in an inversion-symmetric Weyl semimetal, it must have an odd-parity gap function with point nodes. Also, the superconducting state hosts gapless Andreev bound states forming Fermi arcs.

We first show that the Fermi arcs of the Weyl semimetals remain gapless in the superconducting state [104]. In the case of a time-reversal-breaking Weyl semimetal, inversion symmetry must be preserved for Cooper pairs to from. However, inversion symmetry is explicitly broken at the surface where the Fermi arcs reside. Hence, on a general surface which does not have an accidental two-fold rotation symmetry, an electronic state in the Fermi arc does not have a partner state with opposite momentum to form a Cooper pair at the same energy (see figure 8). This means that the constituent electrons of the Fermi arc cannot form Cooper pairs with zero.
total momentum, and therefore the Fermi arc remains gapless even in the superconducting state. The redundancy in the BdG Hamiltonian for electron and hole sectors leads to the appearance of a pair of gapless Fermi arcs of Bogoliubov quasiparticles on the surface.

The same conclusion can be obtained by calculating the Chern number in the superconducting state [104]. In a Weyl semimetal illustrated in figure 9, one can evaluate the Chern number on two different planes $S_1$ and $S_2$ in the momentum space ($S_1$ and $S_2$ should not intersect the Fermi surfaces around the Weyl points). As already mentioned, except on the Fermi surfaces, one can neglect the gap function without changing the topological numbers; therefore, the Chern number on $S_i$ ($i = 1, 2$) can be evaluated for the following Hamiltonian

$$\begin{pmatrix}
\mathcal{E}(k) & 0 \\
0 & -\mathcal{E}(-k)
\end{pmatrix}$$

Since $\mathcal{E}(k)$ gives the Chern number of the original Weyl semimetal and the hole part $\mathcal{E}(-k)$ gives the same Chern number as its electron counterpart, the Chern number for the BdG Hamiltonian is twice the original Chern number which is non-zero for either $i = 1$ or 2. Such a topological character of the bulk superconducting state guarantees the existence of gapless surface states consisting of Fermi arcs of electrons and holes.

The analysis of the Chern number also gives us an insight into why the superconducting state has point nodes [104, 146, 147]. When a Weyl point is located in-between the planes $S_1$ and $S_2$ as illustrated in figure 9, the Chern number calculated on $S_1$ is different from that on $S_2$, and the difference is given by the Chern number associated with the Weyl point. Therefore, the Chern number of the BdG Hamiltonian is also different between $S_1$ and $S_2$, which means that there must be gapless points in the region between $S_1$ and $S_2$, resulting in point nodes in the superconducting state. This argument also tells us that the number of point nodes in the superconducting state coincides with twice the Chern number associated with the Weyl point.

**Time-reversal-invariant Weyl semimetals.** Now we consider superconducting states in doped time-reversal-invariant Weyl semimetals, which must break inversion symmetry. In contrast to inversion-symmetric Weyl semimetals, here we find no special reason to expect unconventional superconducting states.

This difference comes from the fact that spin transforms differently under inversion and time reversal. On one hand, spin does not change under inversion, and hence a Cooper pair formed between an electron and its inversion partner must take parallel spins; this means that a spin-singlet $s$-wave pairing does not occur in the inversion-symmetric case, as we have already seen. On the other hand, spin flips under time reversal, and hence a Cooper pair formed between an electron and its time-reversal partner takes anti-parallel spins, which allows for conventional $s$-wave pairing.

It is prudent to mention that if the pairing interaction is spin-dependent, one may have spin-triplet Cooper pairs or other unconventional superconducting states even in the time-reversal-invariant case. However, such a spin-dependent pairing interaction has been known only for heavy-fermion systems with strong electron correlations. Therefore, it is fair to say that time-reversal-invariant Weyl semimetals may become an unconventional superconductor only when electron correlations are strong.

**6.2.3. Dirac semimetals.** Dirac semimetals are also an interesting platform for topological superconductivity [148, 149]. Upon carrier doping, Dirac semimetals host Fermi surfaces surrounding Dirac points. As discussed in section 2.5.3, a gapless Dirac dispersion in a Dirac semimetal originates from bands (or orbitals) with different quantum numbers associated with a certain crystal symmetry. While no orbital mixing is permitted in the symmetry-invariant momentum subspace (which includes the Dirac point), the Fermi surface at a finite doping does not coincide with such an invariant subspace, and hence an orbital mixing is allowed on the Fermi surface. As a result, Cooper pairing between electrons with different quantum numbers is possible. In general, such an inter-orbital Cooper pair is unconventional.

As an example, we consider Cd$_3$As$_2$ mentioned in section 2.5.3. In the model Hamiltonian for this material, equation (47), there are orbital mixing terms proportional to $\sigma_\alpha$ or $\sigma_\sigma$, except on the $k_z$-axis. Therefore, the Fermi surfaces around the Dirac points naturally exhibit an orbital mixing, and Cooper pairing between different orbitals are allowed. Since the inversion operator is given by $P = \sigma_z$, such orbital-mixed Cooper pairs should have odd parity. Indeed, it was shown theoretically [148, 149] that an odd-parity pairing can be realized in Cd$_3$As$_2$ depending on the parameters of the attractive interactions given in the form

$$H_{\text{int}}(x) = -U [n_s^2(x) + n_p^2(x)] - 2V n_\alpha(x)n_\beta(x),$$

where $U$ and $V$ are the intra- and inter-orbital interactions, respectively, and $n_\alpha$ ($\alpha = s, p$) is the density operator for the $\alpha$-orbital. The obtained phase diagram is shown figure 10.

Since the Fermi surfaces in Cd$_3$As$_2$ do not enclose any time-reversal-invariant momentum, one cannot apply the criterion in section 6.1 to identify topological superconductivity. Nevertheless, the odd-parity superconducting state in this material is at least a topological crystalline superconductor.
This can be seen by considering a combination of two-fold rotation (which is twice the $C_4$ rotation responsible for stabilizing the Dirac points) and inversion, which is equivalent to mirror reflection with respect to the $xy$-plane; since Cd$_3$As$_2$ is both $C_4$ and inversion symmetric, it also has a mirror symmetry and one can define a mirror Chern number. It has been shown that its odd-parity superconducting state has a non-zero mirror Chern number and hence is topological [148, 149].

A recent experiment found that Cd$_3$As$_2$ shows a superconducting transition under pressure [150]. Also, two experimental groups reported that even in ambient pressure, the region beneath a pressurized point-contact tip develops a superconducting gap with a zero-bias peak in the conductance spectrum [151, 152]. Correspondingly, theoretical analyses showed [149] that the odd-parity superconducting states expected in Cd$_3$As$_2$ would present a peak structure in the surface density of state.

6.3. Spin-singlet pairing with spin–orbit coupling

6.3.1. s-wave pairing in 2D Dirac fermions. While an odd-parity pairing state is guaranteed to be topological when the Fermi surfaces satisfy the condition in section 6.1, most superconducting materials realize even-parity $s$-wave pairing states. Since ordinary $s$-wave superconductors do not host any gapless Andreev boundary state, it was believed that they cannot be topological. Consequently, it was also believed that non-Abelian anyons, which may appear in topological superconductors, cannot be realized in an $s$-wave pairing state.

In particular, it is usually considered that time-reversal-symmetry breaking is necessary for non-Abelian anyons; when there are two non-Abelian anyons, their clockwise exchange gives a final state which is different from that of the time-reversed counterclockwise exchange, and this explicitly shows that time-reversal symmetry is broken. Indeed, all platforms for non-Abelian anyons known in the early stage of the field, such as the $\nu = 5/2$ fractional quantum Hall state [153] or the spinless chiral $p$-wave superconductor, break time-reversal symmetry. In contrast, an $s$-wave pairing state preserves time-reversal symmetry, which seems to disqualify it as a host for non-Abelian anyons.

Nevertheless, it was theoretically discovered in 2003 that an $s$-wave pairing state can support non-Abelian anyon excitations if the pairing is realized in 2D Dirac fermions [14]. To understand its mechanism, let us consider the BdG Hamiltonian for 2D Dirac fermions coupled to an $s$-wave superconducting condensate $\Phi$:

$$H(k) = \begin{pmatrix} s_x k_x + s_y k_y & \Phi^* \\ \Phi & -s_x k_x - s_y k_y \end{pmatrix}. \quad (182)$$

This $H(k)$ has the following particle-hole symmetry,

$$C H(k) C^{-1} = -H(-k), \quad C = \begin{pmatrix} 0 & i x_y \\ -i x_y & 0 \end{pmatrix}. \quad (183)$$

In the ground state, the $s$-wave condensate $\Phi$ is uniform and can be taken as a real constant, and thus the system preserves time-reversal symmetry as follows:

$$TH(k)T^{-1} = H(-k), \quad T = \begin{pmatrix} i x_y & 0 \\ 0 & i x_y \end{pmatrix}. \quad (184)$$

Therefore, the Chern number is zero and it cannot be used for judging the topology. However, for the Dirac system one can employ the so-called index theorem to see the existence of Majorana zero modes in vortices: For the Dirac system, Majorana zero modes are introduced as solutions of $H(-i\partial)|\psi_{0}^{\pm}(x)| = 0$, where

$$H(-i\partial) = \begin{pmatrix} -i s_y \partial_x - i s_x \partial_y & \Phi(x) \\ \Phi(x) & i s_y \partial_x + i s_x \partial_y \end{pmatrix}. \quad (185)$$

This solution $|\psi_{0}^{\pm}(x)|$ also satisfies the equation

$$\left( s_x 0 \right) |\psi_{0}^{\pm}(x)| = \pm |\psi_{0}^{\pm}(x)| \quad (186)$$

at the same time. The index theorem relates the number $N_{k}$ of such zero modes to the vorticity of the condensate $\Phi(x)$ in equation (185) as [154]

$$N_{k} - N_{-k} = -\frac{1}{4\pi} \oint_{C} d\ell \frac{\langle \Phi \partial_{\ell} \Phi - \Phi \partial_{\ell} \Phi^* \rangle}{|\Phi|^2}. \quad (187)$$

Note that the right hand side in equation (187) counts the number of vortices in the system ($C$ is a contour around vortices).

The above theorem implies that a single vortex hosts an odd number of Majorana zero modes, and an explicit analysis of the zero modes indeed shows that the number of the zero modes is one [155, 156]. Therefore, like a spinless chiral $p$-wave superconductor, a vortex obeys the non-Abelian anyon statistics. The ground state of the present model keeps time-reversal symmetry, but the vortex state breaks time-reversal symmetry. This local time-reversal breaking at vortices allows the $s$-wave pairing state to host non-Abelian anyons without contradiction.
It is important to note that only a 2D system with an odd number of bulk Dirac nodes can realize non-Abelian anyons in this manner. Otherwise, a vortex hosts an even number of Majorana zero modes, which are equivalent to Dirac zero modes and the non-Abelian nature is lost. While no such condensed matter system was known in 2003, Fu and Kane explicitly demonstrated in 2008 that Majorana zero modes can be realized in the surface states of a topological insulator with proximity-induced s-wave pairing [157]; this was actually a realization of the above scenario. The s-wave pairing state in the surface Dirac fermions hosting Majorana zero modes in vortices can be viewed as a non-Abelian topological superconductor [157–160].

Note that this superconducting state in the 2D Dirac fermion system effectively realizes a spinless superconductor [157]. This is because Dirac fermions in 2D do not have spin degeneracy in the energy spectrum, unlike conventional electrons obeying the Schrödinger equation. The absence of spin degeneracy in the spectrum is the essential prerequisite for obtaining a non-Abelian Majorana zero mode in the s-wave pairing state.

6.3.2. s-wave Rashba superconductor with Zeeman field. Following the ground-breaking proposal by Fu and Kane in 2008 [157], it was shown in 2009 that even for ordinary Schrödinger electrons having a parabolic energy dispersion, a clever use of Rashba spin splitting makes it possible to realize topological superconductivity hosting Majorana zero modes [161].

To understand the basic idea, we consider electrons with the Rashba spin–orbit coupling,

\[ \varepsilon(k) = \frac{k_x^2 + k_y^2}{2m} + v(k_x s_y - k_y s_x) - \mu. \]  

(188)

This is motivated by the success of the Dirac system, because the Rashba term \( v(k_x s_y - k_y s_x) \) mimics the Dirac Hamiltonian. However, considering this term alone is not sufficient for realizing non-Abelian anyons: On one hand, the index theorem (equation (187)) is not applicable in the presence of the first term in equation (188); on the other hand, the Chern number to guarantee the Majorana zero mode vanishes due to time-reversal symmetry. Therefore, to obtain a nonzero Chern number, one introduces the time-reversal-breaking Zeeman field, i.e. apply a magnetic field in the z-direction. It can be shown that the s-wave superconducting state of the Rashba electrons in equation (188) becomes a topological superconductor with \( |C_H| = 1 \) when the Zeeman field \( H_z \) is larger than the critical value \( H^c_z \) [161–163],

\[ H_z \gg \sqrt{\mu^2 + \Delta_0^2}/|\mu_B| \equiv H^c_z, \]  

(189)

where \( \Delta_0 \) is the s-wave pair potential and \( \mu_B \) is the magnetic moment of electron. As a result, a vortex in this system becomes a non-Abelian anyon with a Majorana zero mode in the core.

Like the case of 2D Dirac fermions, the present system realizes an effectively spinless situation under the condition of equation (189). In the presence of the Zeeman term \( \mu_B H^c_z \), the eigenvalues \( \varepsilon_\pm(k) \) of the normal-state Hamiltonian equation (188) are given by

\[ \varepsilon_\pm(k) = \frac{k_x^2 + k_y^2}{2m} \pm \sqrt{v^2(k_x^2 + k_y^2) + (\mu_B H_z)^2 - \mu}, \]  

(190)

and the upper band \( \varepsilon_+(k) \) is always positive under the condition of equation (189). This means that the Fermi surface consists only of the spin-nondegenerate lower band \( \varepsilon_-(k) \) when equation (189) is satisfied, realizing an effectively spinless Fermi surface. This property allows the Majorana zero mode to appear in the vortex core in the s-wave pairing state, just like the case of a spinless chiral \( p \)-wave superconductor.

The system considered above is 2D, but the same idea can also be applied to a 1D Rashba system [164, 165]. By putting \( k_y = 0 \) in equation (188), one obtains

\[ \varepsilon(k) = \frac{k_x^2}{2m} + v k_x s_y - \mu, \]  

(191)

which gives a model of the Rashba electrons in a 1D nanowire. When a Zeeman field is applied in the z-direction, the spectrum becomes effectively spinless and an s-wave pairing state becomes a topological superconductor under the condition of equation (189). In this case, the 1D \( Z_2 \) index is non-trivial, \((-1)^{\nu_{sc}} = -1\), which guarantees the appearance of a Majorana zero mode at each end of the nanowire.

The two types of systems considered in this section, 2D Dirac fermions and Rashba electrons, are both characterized by a strong (or inherent) spin–orbit coupling. By now, the spin–orbit coupling is recognized to be the key to realizing topological superconductivity. There have been already many proposals for similar topological superconductors realized in an s-wave pairings state [15–17, 26, 57].

6.3.3. d-wave pairing with spin–orbit coupling. Instead of s-wave pairing, one can consider \( d_{x^2-y^2} \)-wave or \( d_{xy} \)-wave pairing for the realization of topological superconductivity. It has been shown that the surface Dirac fermions in topological insulators host topological superconductivity when proximity-coupled to a d-wave superconductor [166]. Also, 2D d-wave superconductors with the Rashba spin–orbit coupling can be topological in the presence of Zeeman fields [107]. In this regard, it was recently shown that a nodal d-wave Rashba superconductor can become a fully-gapped topological superconductor in the presence of the Zeeman field, because the breaking of inversion and time-reversal symmetries conspire to lift the node [167]. In 1D, \( d_{x^2-y^2} \)-wave superconductors with the Rashba spin–orbit coupling can be topological even in the absence of Zeeman fields [168].

As for non-Abelian anyons, their appearance has been investigated in 2D chiral d-wave superconductors [162, 169–171].

6.4. Spin-rotation breaking and Majorana fermion. It is useful to understand why the spin–orbit coupling or the spin-triplet pairing is important for realizing topological superconductivity. To see the reason, examination of the
topological periodic table is helpful [9, 10]. Such a table summarizes possible topological numbers in various dimensions with or without general non-spatial symmetries, namely, time-reversal, particle-hole, and chiral symmetries [9, 10]. Based on these non-spatial symmetries, Hamiltonians are classified into ten Altland–Zirnbauer (AZ) classes [172]. Time-reversal-breaking superconductors having particle-hole symmetry belong to class D in the AZ scheme, and time-reversal-invariant superconductors having additional particle-hole symmetry belong to class DIII. In table 3, we show the topological periodic table [9, 10] relevant to superconductors (a part of this table was already shown in table 1). Corresponding to different topological numbers in table 3, various types of Majorana fermions are conceived. For instance, the $Z_2$ index in the 1D class D system corresponds to a Majorana zero mode at the end of superconducting nanowires [13].

Now let us see what happens if there is no term to break the SU(2) spin-rotation symmetry, such as the spin–orbit coupling or the spin-triple pairing interaction. Such a situation corresponds to ordinary s-wave superconductors. In this case, the additional SU(2) rotation symmetry doubles the possible topological numbers (in up to three dimensions); namely, integer topological numbers become even numbers, and $Z_2$ indices become trivial. (In terms of the AZ scheme, class D and DIII becomes class C and CI, respectively, in the presence of the additional SU(2) spin-rotation symmetry.) One can see these changes in the topological numbers in the topological periodic table shown in table 3.

7. Materials realizations

There are broadly two categories of topological superconductors, intrinsic ones and artificially engineered ones. Intrinsic topological superconductors are those in which a topologically-nontrivial gap function naturally shows up. As already discussed, superconductors having odd-parity pairing are in most cases topological. Also, noncentrosymmetric superconductors, in which parity is not well-defined, can be topological when the spin-triplet component is strong. We will discuss concrete examples of such intrinsic topological insulators in this sections. One can also artificially engineer topological superconductivity in hybrid system consisting of a metal or semiconductor proximitized with a conventional s-wave superconductor. This category of topological superconductors is currently attracting significant attention due to its potential as a building block of Majorana-based qubit for topological quantum computation. In section 7.2, we will discuss the essence of such hybrid topological superconductors.

7.1. Candidates of intrinsic topological superconductors

7.1.1. Sr$_2$RuO$_4$. The superconductor Sr$_2$RuO$_4$, discovered in 1994 [173], initially attracted attention because it is isostructural to the prototypical high-temperature cuprate superconductor La$_2$–Sr$_x$CuO$_4$. This material is arguably the first superconductor in which the realization of a topological state is seriously discussed. Because of the tendency of ruthenium oxides to become ferromagnetic, spin-triplet pairing was theoretically proposed for this material [174]. Nuclear magnetic resonance (NMR) experiments found that the Knight shift, which reflects the spin susceptibility, does not change across the superconducting transition temperature $T_c$, which supports spin-triplet pairing [175]. Furthermore, muon spin rotation ($\mu$SR) experiments detected the appearance of internal magnetic field below $T_c$, pointing to time-reversal-symmetry breaking [176]. These experiments led to the expectation that a spin-triplet superconductivity with a definite chirality, often called chiral $p$-wave superconductivity [177], is realized in Sr$_2$RuO$_4$. However, there are unresolved issues, such as the fact that the chiral domains have never been observed, which have been preventing the consensus on the chiral $p$-wave superconductivity. The situation is well summarized in recent review articles [177, 178].

Whereas the realization of chiral $p$-wave superconductivity in Sr$_2$RuO$_4$ is still under debate, the spin-triplet pairing dictates that the orbital part of the gap function must have odd parity, which guarantees the topological nature of the superconductivity [180–183]. Indeed, surface Andreev bound state, which is naturally expected to accompany a topological bulk state, has been detected by a tunnel junction experiment (see figure 11) [179]. One should note, however, that in the classifications of possible topological states of matter [9, 10], time-reversal-symmetry breaking superconductor can be topological in 1D and 2D, but not in 3D. Actually, Sr$_2$RuO$_4$ is a quasi-2D material with warped cylindrical Fermi surfaces [184], and hence it harbors an essentially 2D topological superconductivity. This means that the surface Andreev bound
states to be expected as topological boundary states will be present only on the side surfaces.

The expectation for Majorana fermions in Sr$_2$RuO$_4$ is a little complex. Since spin–orbit coupling is not strong in this material, the topological surface states preserve spin degeneracy and hence the Bogoliubov quasiparticle on the surface are spin degenerate. In such a case, the two spin subspaces are not independent from each other and, even if one defines a Majorana operator in each subspace, they can mix to form an ordinary fermion [63]. This means that Majorana fermions are not expected on the surface of Sr$_2$RuO$_4$.

Nevertheless, if the Bogoliubov quasiparticles in the two spin subspaces cannot mix, they can be considered as two independent modes of Majorana fermions. It has been theoretically proposed [63] that, due to the mirror symmetry of the Sr$_2$RuO$_4$ crystal structure, there may be a magnetic-field-induced topological phase transition into a topological crystalline superconductor phase, in which two Majorana modes are each protected by symmetry.

In addition, it has been documented that half-quantized vortices show up in Sr$_2$RuO$_4$ in oblique magnetic fields [185]. Such a half-quantized vortex is expected to harbor a Majorana zero-mode in the core, because the spin degeneracy is lifted there [186]. The resulting Majorana zero-mode is non-Abelian and is in principle useful for quantum computation.

Figure 11. Differential-conductance spectrum obtained from a tunnel junction made on a side surface of Sr$_2$RuO$_4$; theoretically calculated spectrum for the side surface containing Andreev bound states is also shown with red dotted line. Bias voltage is normalized by the superconducting gap. Reprinted with permission from [179]; copyright (2011) by the American Physical Society.

7.1.2. Cu$_x$Bi$_2$Se$_3$. The superconductivity in Cu$_x$Bi$_2$Se$_3$ with $T_c$ up to $\sim$4 K was discovered in 2010 [187]. This was a first material to show superconductivity upon doping charge carriers into a topological insulator. Such a superconductor is a promising ground to look for topological superconductivity, because of the following reasons: Since the topological surface states are present in topological insulators even when carriers are doped (as long the doping is not too heavy), one would expect that the superconductivity in the bulk would lead to proximity-induced superconductivity of the surface, where 2D topological superconductivity should be found. In this respect, ARPES experiments on Cu$_x$Bi$_2$Se$_3$ confirmed that at the doping level necessary for superconductivity ($\sim$2 x $10^{20}$ cm$^{-3}$), the topological surface states are still well separated from the bulk states in the momentum space [188].

Already in 2010, a more exotic possibility was proposed for Cu$_x$Bi$_2$Se$_3$ by Fu and Berg [131]. Due to the strong spin–orbit coupling, the effective low-energy Hamiltonian of Cu$_x$Bi$_2$Se$_3$ becomes a massive Dirac Hamiltonian discussed in section 6.2.1. The four-component basis set of this Hamiltonian consists of two $p$-orbitals with opposite parities. Fu and Berg noticed that, if pairing occurs between such orbitals with opposite parities, the resulting gap function naturally obtains odd parity. In this case, since Cu$_x$Bi$_2$Se$_3$ has only one bulk Fermi surface which encircles the $\Gamma$ point [188], the Fermi surface criterion [129–131] in section 6.1 is sufficient for concluding that the bulk superconducting state is topological.

When the bulk of Cu$_x$Bi$_2$Se$_3$ is in such a topological superconducting state, helical Majorana fermions show up on the surface [131]. They are gapless and dispersive Andreev bound states having the Majorana nature. Expected dispersion of the helical Majorana fermions depends on the symmetry of the gap function and the height of the chemical potential, as has been calculated in [108, 137–139].

The crystal symmetry of Cu$_x$Bi$_2$Se$_3$ belongs to $D_{3d}$ point group. According to the symmetry classifications, there are four possible types of gap functions, $\Delta_1$ to $\Delta_4$ in table 2, that are classified based on the irreducible representations of the $D_{3d}$ point group, $A_{1g}, A_{1u}, A_{2u}$, and $E_u$, respectively [131, 189]. Among them, $\Delta_1$ is conventional even-parity type, while other three are all odd-parity and hence are topological. Note that due to the strong spin–orbit coupling, spin is no longer a good quantum number in Cu$_x$Bi$_2$Se$_3$ and the notions of spin singlet and triplet are only approximately valid.

The synthesis of superconducting Cu$_x$Bi$_2$Se$_3$ is difficult. With a simple melt-growth method in which one melts all the constituent elements together and lets them crystallize by slowly cooling across the melting point, only a low volume fraction of the superconducting phase up to 30% is available [187]. This is because Cu atoms can occupy both the Bi sites as substitutional impurities and the intercalation sites in the van der Waals gap as intercalants; in the melt-growth method, one has little control over where the Cu atoms will go. To address this problem, a new synthesis method to employ electrochemical intercalation has been developed [190], and an improved volume fraction of the superconducting phase up to 80% has been obtained; in this method, annealing the Cu-intercalated crystals at a high temperature just below the melting temperature is necessary for obtaining superconductivity. The exact role of this annealing is not known. In fact, the precise positions of the Cu atoms in the superconducting phase of the crystals have not been elucidated. This is because the superconducting phase of Cu$_x$Bi$_2$Se$_3$ is fragile against mechanical stress, which makes it difficult to prepare samples for precise crystal structure analysis. The fragility of the superconducting phase is a serious problem in making devices of Cu$_x$Bi$_2$Se$_3$ for tunnel-junction or Josephson-junction experiments; for example, after exfoliation into thin flakes, Cu$_x$Bi$_2$Se$_3$ always loses superconductivity.
Figure 12. Zero-bias conductance peak observed in Cu$_{0.3}$Bi$_2$Se$_3$ via point-contact spectroscopy. The data shown were taken in 0 T at various temperatures. Vertical dashed lines mark the superconducting gap energy. Adapted from [108]; copyright (2011) by the American Physical Society.

Nevertheless, experiments made on best available samples have already given evidence for topological superconductivity. The first indication came in 2011 from conductance spectroscopy experiments made on the surface. By using a soft-point-contact technique to minimize mechanical stress, Sasaki et al found a pronounced zero-bias peak in the differential conductance (figure 12), whose origin was scrutinized in their experiment to be intrinsic [108]. The shape of the spectra, which present clear minima at the gap energy, is in good qualitative agreement with theoretical calculations [138] of point-contact spectra for the topological cases, all of which are accompanied by surface Majorana fermions.

Recently, NMR measurements of the Knight shift, which allows one to probe the spin susceptibility in the superconducting state, found that the spin-rotation symmetry is spontaneously broken in the superconducting state of Cu$_{0.3}$Bi$_2$Se$_3$ [191]. Specifically, when the applied magnetic field is rotated in the basal plane, the Knight shift showed pronounced minima which are two-fold symmetric (figure 13). Since the crystal structure is three-fold symmetric, the two-fold symmetry must be a result of spontaneously ordering of the electronic system to break spin-rotation symmetry [134, 136]. The most natural interpretation of this result is that the superconductivity occurs through pseudo-spin-triplet odd-parity pairing, and the spin angular momentum is pinned to a particular axis in the crystal, whose origin is not very clear at the moment; possible factors to play a role in the pinning are sample edges, some uniaxial strain, or some weak superstructure associated with intercalated Cu atoms, etc. In any case, the NMR result gave direct bulk evidence for topological superconductivity in Cu$_{0.3}$Bi$_2$Se$_3$.

More recently, specific heat measurements of Cu$_{0.3}$Bi$_2$Se$_3$ in applied magnetic fields have also found clear two-fold symmetry when the magnetic field is rotated in the basal plane (figure 14) [192]. Not only the magnetic-field-induced specific heat value in the superconducting state, but also the upper critical field $H_{c2}$ present the same two-fold symmetry. This result indicates that the superconducting gap amplitude has two-fold-symmetric minima in the momentum space, so that the number of quasiparticles induced by vortices becomes maximal when the magnetic-field orientation is perpendicular to the line connecting the two gap minima (figure 14). Such an in-plane anisotropy in the gap amplitude is only consistent with the $\Delta_4$ state among the four possibilities allowed for Cu$_{0.3}$Bi$_2$Se$_3$ [134]. Since this $\Delta_4$ state generates a subsidiary nematic order specified by a two-component order parameter, it has been called nematic superconducting state [133]. Note that the $\Delta_4$ state has nodes in the simplest theory, but these nodes are not protected by any symmetry and hence they can be easily lifted by additional interactions [133]. Therefore, the $\Delta_4$ state can be consistent with the specific-heat data [193] which point to the absence of any node.

It is prudent to mention that the experimental situation on Cu$_{0.3}$Bi$_2$Se$_3$ was controversial until the NMR result came about. A prominent example was the STM experiment which claimed conventional $s$-wave superconductivity based on the shape of the spectra, which fitted well to a BCS-based model [194]; however, there were puzzling features in the STM data, such as the extracted gap of 0.4 meV which is much smaller than the gap size of 0.7 meV obtained from the specific-heat jump [193]. Since the $T_c$ and $H_{c2}$ were essentially the same between specific heat and STM experiments, the small gap suggested by the STM data was difficult to understand. Potential sources of the controversy have been theoretically discussed [141], and it could be due to the quasi-2D nature of the Fermi surface [195] or simply the difficulty in preparing homogeneous and well-characterized samples. In any case, in view of the recent confirmations of the $\Delta_4$ state by bulk measurements, the zero-bias conductance peak found in Cu$_{0.3}$Bi$_2$Se$_3$ was likely to be the first experimental observation of Majorana fermions in a solid-state system.

Alongside the discovery of nematic superconductivity in Cu$_{0.3}$Bi$_2$Se$_3$ [191, 192], essentially the same two-fold symmetry has been observed in similar superconductors derived from Bi$_2$Se$_3$. In Sr$_{1-x}$Bi$_2$Se$_3$ [196], $H_{c2}$ presents clear two-fold in-plane anisotropy [197–199]. Also, Nb$_x$Bi$_2$Se$_3$ [200] presents two-fold in-plane anisotropy in the magnetization hysteresis loops [201]. Hence, it becomes increasingly clear that the topological $\Delta_4$ state generically shows up when Bi$_2$Se$_3$ is doped to become a superconductor.

7.1.3. Sn$_{1-x}$In$_x$Te. SnTe is a topological crystalline insulator characterized by a nontrivial mirror Chern number [77, 78, 189], and it becomes a superconductor upon substituting 2% or more of Sn with In, which introduces hole carriers [202, 203]. While the hole density increases linearly with the In content $x$, the $T_c$ versus $x$ phase diagram is complex (figure 15), presenting a minimum in $T_c$ at $x \approx 0.04$, where the structural transition from rhombohedral to cubic phase takes place; $T_c$ is a little higher ($\sim$1.6 K) in the rhombohedral phase with $x < 0.038$, and it is reduced to 1.2 K in the cubic phase at $x \approx 0.04$ [202]; increasing the x value in the cubic phase leads to an almost linear increase in $T_c$ up to 4.6 K at $x = 0.45$ [204]. Intriguingly, Sn$_{1-x}$In$_x$Te is the cleanest (i.e. presents the
lowest residual resistivity) in samples showing the lowest $T_c$ in the cubic phase [202]. It is exactly in those clean samples with $x \approx 0.04$ where a pronounced zero-bias conductance peak similar to that in Cu$_{0.3}$Bi$_2$Se$_3$ has been observed by point-contact spectroscopy [205], which points to the existence of surface Andreev bound states. Note that in Sn$_{1-x}$In$_x$Te, non-magnetic impurities raise the $T_c$ through an enhancement in the density of states at the Fermi energy [202], as discussed theoretically by Martin and Phillips [206], which is contrary to most other superconductors.

The low-energy effective Hamiltonian of SnTe is essentially the same as that for Cu$_{0.3}$Bi$_2$Se$_3$, besides the fact that the Fermi surfaces are located at the Brillouin-zone boundary, surrounding the four $L$ points [189]. This reduces the possible irreducible representations of the gap functions to $A_{1g}$, $A_{1u}$, and $A_{2u}$, corresponding respectively to the $\Delta_1$, $\Delta_2$, and $\Delta_3$ states defined for Cu$_{0.3}$Bi$_2$Se$_3$. Among them, $\Delta_2$ and $\Delta_3$ states are odd-parity with nonzero topological invariants, even though the Fermi surfaces are now surrounding four time-reversal-invariant momenta [205]. Hence, the zero-bias conductance peak observed in the point-contact spectroscopy is likely due to helical surface Majorana fermions associated with $\Delta_2$ or $\Delta_3$ states.

High-quality single crystals of Sn$_{1-x}$In$_x$Te with 100% superconducting volume fraction can be grown by a vapor transport method, but the In content is difficult to control in this method. Point-contact spectroscopy experiments performed on many Sn$_{1-x}$In$_x$Te samples found that the zero-bias conductance peak is observed only in the cleanest samples with $x \approx 0.04$ [202], suggesting that the conventional $\Delta_1$ state is competing with unconventional $\Delta_2$ or $\Delta_3$ states and disorder can easily flip the competition. This makes the studies of topological superconductivity in Sn$_{1-x}$In$_x$Te difficult. Nevertheless, availability of superconducting nanoplates [207] suitable for device fabrications gives good prospects for detailed investigations of this material.

---

**Figure 13.** Change in the NMR Knight shift between 3 K (> $T_c$ in 0.7 T) and 1.4 K (< $T_c$) measured on Cu$_{0.3}$Bi$_2$Se$_3$ in 0.7 T as a function of the magnetic-field angle which is rotated within the basal plane as depicted in the inset. These data give direct evidence that the spin susceptibility is anisotropic and hence the spin-rotation symmetry is spontaneously broken in the superconducting state. Adapted by permission from Macmillan Publishers Ltd: Nature Physics [191], Copyright (2016).

**Figure 14.** Change in the specific heat of Cu$_{0.3}$Bi$_2$Se$_3$ upon rotating the magnetic-field orientation within the basal plane, measured in 0.3 T at 0.6 K; $x$ and $y$ axes are defined in the inset. Adapted with permission from [192], Copyright (2016) by the American Physical Society.

**Figure 15.** Phase diagram of Sn$_{1-x}$In$_x$Te showing how $T_c$ changes with In doping $x_{\text{ref}}$; the latter is calculated from the measured hole density $p$. Vertical dashed line divides the ferroelectric rhombohedral phase from the cubic phase; solid straight line is a guide to the eyes to mark the linear increase in $T_c$ with $x$ in the cubic phase. Adapted with permission from [202], Copyright (2013) by the American Physical Society.
When the bulk of Sn$_{1-x}$In$_x$Te is in the conventional $\Delta$ state, it is expected that the topological surface states harbor a proximity-induced topological superconductivity. The ARPES experiments performed on Sn$_{1-x}$In$_x$Te at $x = 0.045$ confirmed that the topological surface state remains intact after In doping [208]. Since the parent material SnTe is a topological crystalline insulator, the topological surface states consist of four spin-nondegenerate Dirac cones and their locations in the surface Brillouin zone depends on the surface orientation [209]. It has been theoretically proposed that the four Dirac cones give rise to four Majorana fermions at the end of the vortex core, but only two of them are symmetry protected to robustly remain at zero energy [210]. The properties of such vortices binding a pair of Majorana zero-modes is an interesting subject to be pursued in Sn$_{1-x}$In$_x$Te in the conventional bulk superconducting state.

7.1.4. Noncentrosymmetric superconductors. In noncentrosymmetric superconductors where inversion symmetry is broken, parity is ill-defined and hence mixing of s-wave (spin-singlet) and p-wave (spin-triplet) states is allowed. Also, broken inversion symmetry allows Rashba and Dreszahaus spin–orbit couplings, which lift the spin degeneracy and split the Fermi surface. It has been shown [54, 55] that 2D noncentrosymmetric superconductors are topological when the p-wave gap is larger than the s-wave gap. In such a topological state, if it preserves time-reversal symmetry, helical Majorana fermions show up at the edge [54].

The first superconductor identified to be noncentrosymmetric was probably BiPd, which was discovered in 1952 [211]; unfortunately, this material does not present any peculiar property that is ascribable to the noncentrosymmetric nature [212]. In this regard, CePt$_3$Si [213] was the first noncentrosymmetric superconductor which presented a signature of unconventional superconductivity possibly related to the lack of inversion symmetry. This is a heavy-fermion system with strong electron interactions, which means that there is a strong on-site repulsion to favor unconventional superconductivity. Indeed, CePt$_3$Si has a line node, which is a hallmark of unconventional superconductivity [214]. The node could be a result of $s$ + $p$-wave pairing, because in such a case, the superconducting gap may be written as $\Delta = \Delta_s - \Delta_p \sin \theta$ ($\Delta_s$ and $\Delta_p$ are the gap sizes of the s- and p-wave components, respectively), which shows a sign change when $\Delta_s < \Delta_p$. However, the node could also be due to the effect of coexisting antiferromagnetic order [215]. To date, the origin of the node is not well understood. The topological nature of 3D noncentrosymmetric superconductors has been analyzed [80, 81, 85] and it was predicted that surface flat bands of topological origin should show up as a result of non-trivial bulk topology [60, 82].

Li$_3$(Pd$_{1-x}$Pt$_x$)$_3$B [216] is also a noncentrosymmetric superconductor presenting evidence for line nodes at Pt-rich compositions [217]. Contrary to CePt$_3$Si, this material has only weak electron correlations, which makes the $s$ + $p$-wave pairing as likely origin of the line nodes. Intriguingly, nodes are present in Li$_3$Pt$_3$B but not in Li$_3$Pd$_3$B, which suggests that the source of the different pairing state lies in the difference in the strength of spin–orbit coupling. In fact, it was theoretically shown that strong spin–orbit coupling enhances $p$-wave component [215]. Unfortunately, the difficulty in growing single crystals of Li$_3$Pt$_3$B has been a hindrance for detailed studies of this interesting material.

To search for a topological superconductor, 2D or quasi-2D superconductors with broken inversion symmetry would also be a fertile ground. In this regard, superconductivity induced at the surface of an insulator such as SrTiO$_3$ or KTaO$_3$ by ionic-liquid gating [218] is interesting. However, so far no evidence for $p$-wave components have been reported for these 2D superconductors.

7.1.5. Nodal topological superconductors. As mentioned in section 4.1, superconductors need not be fully gapped in order to be topological. As long as a nontrivial topological invariant is defined for the occupied states, nodal superconductors can be called topological. For example, the $\Delta_3$ and $\Delta_4$ states of Cu$_3$Bi$_2$Se$_3$ have nodes, but an explicit $Z_2$ topological invariant has been found to characterize their topological nature [108]. Similarly, concrete topological invariants have been found for 3D noncentrosymmetric superconductors [85].

An interesting superconductor related to Cu$_3$Bi$_2$Se$_3$ is Cu$_4$(PbSe)$_5$(Bi$_2$Se$_3$)$_6$. This superconductor was discovered in 2014 [219] and its specific-heat behavior strongly suggests the existence of line nodes (figure 16). A good news is that it is possible to synthesize 100% superconducting sample of this material at $x \approx 1.5$ [219]. The crystal structure of the parent material (PbSe)$_5$(Bi$_2$Se$_3$)$_6$ can be viewed as a naturally-formed heterostructure, in which a bilayer of PbSe and two quintuple-layers of Bi$_2$Se$_3$ alternate [220–222]. Since PbSe is an ordinary insulator, this natural heterostructure realizes a situation in which topological insulator units are separated by an ordinary insulator unit. Intriguingly, the ARPES study of (PbSe)$_5$(Bi$_2$Se$_3$)$_6$ found evidence that topological interface states are present at every interface between PbSe and Bi$_2$Se$_3$ units [221]. (PbSe)$_5$(Bi$_2$Se$_3$)$_6$ has a van der Waals gap in the middle of the two-quintuple-layer Bi$_2$Se$_3$ unit, and when Cu atoms

![Figure 16](image-url)
are intercalated into this van der Waals gap, the resulting Cu$_x$(PbSe)$_5$(Bi$_2$Se$_3$)$_6$ is a superconductor with $T_c = 2.85$ K [219]. Hence, the essential building blocks for superconductivity in Cu$_x$(PbSe)$_5$(Bi$_2$Se$_3$)$_6$ and Cu$_3$Bi$_2$Se$_3$ are basically the same, and the mechanism of superconductivity is also expected to be the same, although Cu$_x$(PbSe)$_5$(Bi$_2$Se$_3$)$_6$ is strongly quasi-2D due to its crystal structure. The Fu-Berg theory for Cu$_3$Bi$_2$Se$_3$ has been extended to the case of quasi-2D Fermi surface [135], and it was shown that the $\Delta_4$ state has a pair of line nodes in the quasi-2D case, while other three possible states are all fully gapped. Therefore, it is most likely that the odd-parity $\Delta_4$ state is realized not only in Cu$_3$Bi$_2$Se$_3$ but also in Cu$_x$(PbSe)$_5$(Bi$_2$Se$_3$)$_6$. Probably the higher-order effect to lift the nodes in the $\Delta_4$ state is weak or absent in the latter, leading to different specific-heat behaviors (i.e. fully-gapped versus nodal) in the two compounds.

UPt$_3$ is an unconventional heavy-fermion superconductor discovered in 1984 [223]. It has a complex $B$ versus $T$ phase diagram, with three distinct superconducting phases A (high-$T$, low-$B$), B (low-$T$, low-$B$), and C (low-$T$, high-$B$). Gap nodes are present in all three phases and the pairing is most likely spin triplet; however, the nature of each phase as well as the pairing mechanism are still under debate [224, 225]. Recently, topological crystalline superconductivity was proposed theoretically for the B-phase, based on the assumption that UPt$_3$ is a spin-triplet $f$-wave superconductor [66]. In this putative phase, two linearly dispersing Majorana modes appear at the edge of the $ab$ plane, and the two modes do not mix because they are protected by mirror chiral symmetry. Topological nodal structures in UPt$_3$ were also studied theoretically [97, 226].

YPbBi is a relatively new superconductor [227] which is noncentrosymmetric and presents evidence for line nodes [228]. It has a very low carrier density of only $2 \times 10^{18}$ cm$^{-3}$, which cannot afford its $T_c$ of 0.78 K within the BCS theory [229]. (In this regard, the $T_c$ of up to 4 K with the low carrier density of $2 \times 10^{20}$ cm$^{-3}$ in Cu$_3$Bi$_2$Se$_3$ is also too high to be explained within the BCS theory.) It has been proposed that in YPbBi, pairing of $j = 3/2$ fermions may be taking place, which allows Cooper pairs to have quintet or septet total angular momentum [230]. The topological nature of such a novel superconductor should be investigated in future.

72. Artificial topological superconductors

Artificially engineered topological superconductivity in hybrid structures are currently attracting significant attention, because they offer exciting opportunities to create and manipulate non-Abelian Majorana zero modes [15, 16]. The essential ingredients for such hybrid structures are spin-nondegenerate metal and proximity-induced $s$-wave superconductivity. The original idea came from Fu and Kane [157], who showed that if $s$-wave pairing is imposed on the topological surface states of a 3D topological insulator through superconducting proximity effect, due to the helical spin polarization of the surface states, the resulting superconducting state can be effectively viewed as a 2D $p$-wave superconductor harboring a Majorana zero mode in the vortex core.

To see this mechanism, let us consider the BdG equation $H = \sum_k \Psi(k) \bar{H}(k) \Psi(k)/2$ with the BdG Hamiltonian

$$\Psi(k) = \left( \begin{array}{c} \psi - kx \mu \\ \psi \Delta kx + \mu \end{array} \right).$$

(192)

where $\Delta$ is the proximity-induced $s$-wave pairing amplitude, $s$ is the Pauli matrix of spin, and $s \cdot k = s_kx + s_ky$. The normal-state Hamiltonian describes the spin-helical surface state. For the field operator $\Psi$, we take the Nambu representation $\Psi = (c_1, \bar{c}_1, c_1', -c_1')$.

When one creates a vortex in the condensate given by the above Hamiltonian, such a vortex hosts a Majorana zero mode and it obeys the non-Abelian anyon statistics. This result was originally derived [14] for $\mu = 0$ by using the index theorem as discussed in section 6.3.1, but a more intuitive argument can be done for $\mu \gg |\Delta|$ [157]: In the weak coupling case, the superconducting state is well-described by the single band near the Fermi energy. The wavefunction of the single-band electron can be written as $(1, e^{i\theta}/\sqrt{2}$ with $e^{i\theta} = (k_x + ik_y)/k$, and in this basis the single-band BdG Hamiltonian is transformed as

$$\left( \begin{array}{c} 1, e^{-i\theta} \\\n e^{i\theta}, 1 \end{array} \right) \tilde{H}(k) \left( \begin{array}{c} 1 \\ n \end{array} \right) = \left( \begin{array}{c} 1, e^{-i\theta} \\ e^{i\theta}, 1 \end{array} \right) \tilde{H}(k) \left( \begin{array}{c} 1 \\ n \end{array} \right) \left( \begin{array}{c} 1 \\ n \end{array} \right) \tilde{H}(k) \left( \begin{array}{c} 1 \\ n \end{array} \right)$$

(193)

It should be noted that this transformed BdG Hamiltonian describes a spinless chiral $p$-wave pairing, although it is singular at $k = 0$. Because of the non-analyticity, this single-band Hamiltonian does not have a well-defined Chern number, which is consistent with the time-reversal invariance of the original Hamiltonian equation (192); however, once a time-reversal-breaking vortex or a magnetic boundary is introduced, the singularity is smeared out and Majorana modes appear as in the case of a true spinless chiral $p$-wave superconductor [157].

Later, it was recognized that a spin-nondegenerate 2D metal similar to the surface states of 3D topological insulators can be obtained by considering the combination of Rashba spin–orbit coupling and Zeeman effect in a 2D metal: Rashba spin–orbit coupling splits a spin degenerate band into a pair of spin nondegenerate bands, and Zeeman effect will open a gap at the crossing point of these two bands; when the chemical potential is tuned into this Zeeman gap, there is only one Fermi surface which has a helical spin polarization [54]. Therefore, if $s$-wave pairing is induced in such a state by using proximity effect, it also realizes an effective $p$-wave superconductor [54, 162, 163, 231].

A drawback of the above scheme to turn a Rashba-split 2D metal into a topological superconductor is that the size of the Zeeman splitting must be larger than the size of the induced superconducting gap. This condition is difficult to meet in ordinary 2D metals due to the orbital pair-breaking effect, and one needs to devise a way to go around this problem. Possible solutions are to use semiconductors with a large
g factor, to utilize exchange coupling for Zeeman effect, or to apply magnetic fields parallel to the 2D plane [162, 163, 231].

With the same basic mechanism, it is possible to engineer a 1D topological superconductor. Inducing s-wave pairing in the 1D helical edge states of a 2D topological insulators gives rise to effective spinless 1D d-wave superconductivity, which was treated in the celebrated 1D Kitaev model [13]. Nanowires of semiconductors having strong Rashba spin–orbit coupling (such as InAs or InSb) placed in magnetic fields can also serve as a platform to engineer 1D topological superconductivity [164, 165]. Those engineered 1D topological superconductors are accompanied by localized Majorana zero-mode at the edge. Since the edge of a 1D wire is much easier to access than a vortex in the middle of a 2D system, the engineered 1D topological superconductor is generally considered to be most practically useful.

Experimentally, proximity-induced superconductivity on the surface of 3D topological insulators has been studied by many groups and there is accumulating evidence that superconductivity can indeed be induced in the topological surface states [232–239]. While it has been difficult to elucidate the topological nature of the induced 2D superconductivity, recent observation [240] of 4π-periodic Josephson supercurrent in 3D HgTe topological insulator is encouraging. The experimental situation for induced 1D superconductivity in the topological edge states of the 2D topological insulator HgTe is probably more promising; for example, it has been shown that proximity-induced superconductivity is clearly established in the 1D helical edge states [241] and the recent observation of half-frequency Josephson radiation gave reasonably strong evidence for the existence of Majorana fermions [242].

Regarding the semiconductors with Rashba-split bands, there has been no experiment on a 2D system, and efforts are focused on 1D nanowires of InAs or InSb. Initial experiments based on point-contact spectroscopy on the edges of such nanowires proximitized by Al or Nb-based superconductor found zero-bias conductance peaks in finite magnetic fields [243–245]. While this was an encouraging observation, zero-bias conductance peak in a junction made on a mesoscopic superconductor can be of various origins [246], and it was difficult to conclusively nail down the Majorana nature. This was particularly so when the junction shows a ‘soft’ gap, in which a lot of sub-gap excitations are present. However, recent experiment on InAs nanowire with epitaxially-grown Al superconductor add-layer, which realizes much cleaner proximity-induced superconductivity with a ‘hard’ gap, found convincing evidence for Majorana fermions at the edges of the nanowire through observation of the Majorana teleportation phenomenon [247].

On a different route, by putting a 1D chain of ferromagnetically-ordered atoms on top of an s-wave superconductor having strong spin–orbit coupling, one can locally create 1D topological superconductivity in the portion of the superconductor beneath the atomic chains [248]. STM experiments have been perform on Pb(110) surface decorated with Fe atomic chains, and reasonably convincing evidence for a Majorana zero-mode localized at the edge has been reported [249].

Finally, there is a very different avenue for artificially realizing a topological superconductor based on graphene. It has been proposed [250] that chiral d-wave superconductivity with a $d_{x^2−y^2}±id_{xy}$ gap structure may be realized if monolayer graphene is heavily doped to the vicinity of van Hove singularity, which lies at the doping level of ±1/8 from the pristine half-filled level. Such a state would be a time-reversal-symmetry breaking 2D topological superconductor with Majorana zero-modes in the vortex core.

8. Properties of topological superconductors

8.1. Zero-bias conductance peak

Topological superconductors are without exception accompanied by gapless surface/edge modes because of the bulk-edge correspondence of topological systems. These boundary modes can be observed as in-gap states in STM or tunnel-junction experiments, which probe the surface density of states. Also, existence of boundary modes affects the Andreev reflection at the boundary, which leaves a signature in point-contact spectra; note that, depending on the transparency of the point contact, the spectral signature varies in point-contact spectroscopy [138, 251]. In both Cu$_2$Bi$_2$Se$_3$ [108] and InSb nanowire [243], a zero-bias conductance peak in the point-contact spectra was the first signature of Majorana fermions.

The tunneling conductance spectra of topological superconductors depend on their dimensions and symmetries. In one-dimensional time-reversal-breaking topological superconductors, there exist an isolated single Majorana zero mode at each end. The tunneling conductance due to the isolated Majorana zero mode is given by

$$\frac{dI}{dV} = \frac{2e^2}{h} \left(1 + \frac{eV/2\Gamma}{1 + (eV/2\Gamma)^2}\right)^2,$$  \hspace{1cm} (194)

where $I$ is the tunneling current, $V$ is the bias voltage, and $\Gamma$ is the width of the spectrum. It shows a zero-bias differential conductance peak of height $2e^2/h$ [252–254]. If the single Majorana zero mode is coupled with another Majorana zero mode at the other end, the tunneling conductance is modified to [253],

$$\frac{dI}{dV} = \frac{2e^2}{h} \frac{1}{1 + (eV/2\Gamma - 2\epsilon/2\Gamma)^2},$$  \hspace{1cm} (195)

where $\epsilon$ is the coupling between the Majorana zero modes at different ends. When $\epsilon/\Gamma$ is negligibly small, equation (195) almost reproduces equation (194) [254], but when the mixing is substantial, the tunneling conductance shows a dip rather than a peak. In the latter case, the zero-bias conductance becomes zero.

If the system has an additional symmetry, the quantized values of the zero-bias conductance can be multiplied by an integer. For example, in one-dimensional time-reversal-invariant superconductors, the zero-bias conductance peak is doubled [35],

$$\left. \frac{dI}{dV} \right|_{eV=0} = \frac{4e^2}{h},$$  \hspace{1cm} (196)
due to the Kramers degeneracy. Because of time-reversal symmetry, they host a Kramers pair of Majorana end states, each of which induces resonant Andreev reflections of the quantized zero-bias conductance $2e^2/h$. Furthermore, if the system has chiral symmetry, the zero-bias peak can be $2Ne^2/h$ with an integer $N$ [255].

In two dimensions, topological superconductors have gapless Majorana edge modes with linear dispersion

$$E \sim \nu k_x$$  \hspace{1cm} (197)$$
in the time-reversal-breaking case, and

$$E \sim \pm \nu k_x$$  \hspace{1cm} (198)$$
in the time-reversal-invariant case. Such Majorana edge modes have a tendency to give rise to a broad zero-bias peak, not a sharp one, in the tunneling conductance. Although the actual tunneling spectra can be complicated by multi-band effects [183], in the case of simple chiral $p_x + ip_y$-wave superconductors [180, 256] and helical $p_x \pm ip_y$-wave superconductors [55], theoretical calculations found bell-shaped broad tunneling spectra.

In three-dimensional topological superconductors, the manifestations of surface Majorana fermions in the zero-bias conductance of tunneling spectroscopy would be subtle. For example, in the tunneling limit, the zero-bias conductance shows a zero-bias dip even in the presence of gapless surface helical Majorana fermions [138, 257]. The tunneling conductance through a two-dimensional interface between a metal and a superconductor is given in the form

$$\frac{dI}{dV} \bigg|_{V=0} = \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \theta T(k_x, k_y)|_{V=0},$$  \hspace{1cm} (199)$$

where $(k_x, k_y, k_z) = (k_F \sin \theta \cos \phi, k_F \sin \theta \sin \phi, k_F \cos \theta)$ is the momentum of an incident electron in the metal. The interface is taken to be normal to the $z$-axis, and the metal (superconductor) is in the negative (positive) $z$ side. Taking the momentum average of incident electrons results in the volume factor $\sin \theta \mathrm{d}\phi \mathrm{d}\theta$ in the integral. In the tunneling limit, there is no direct coupling between electrons in the metal and Cooper pairs in the superconductor, and hence surface bound states are needed to mediate the Andreev reflections. Therefore, the tunneling rate $T(k_x, k_y)$ at zero-bias is proportional to the momentum-resolved surface density of state $N(k_x, k_y, E)$ at zero energy,

$$T(k_x, k_y)|_{V=0} \propto N(k_x, k_y, E = 0).$$  \hspace{1cm} (200)$$

In the case of three-dimensional time-reversal-invariant topological superconductors, the surface states are helical Majorana fermions with the following energy dispersion

$$E \sim \nu \sqrt{k_x^2 + k_y^2},$$  \hspace{1cm} (201)$$

which give a non-zero value of $N(k_x, k_y, E = 0)$ only when $\sin \theta = 0$. Therefore, from the $\sin \theta$ factor in equation (199), the zero-bias conductance becomes zero in the tunneling limit. We illustrate the behavior of the tunneling conductance

![Figure 17. Normalized tunneling conductance $G/G_N$ as a function of bias voltage for the Balian–Werthamer (BW) phase, which is a fully-gapped three-dimensional time-reversal-invariant topological superconducting phase accompanied by surface helical Majorana fermions [9, 129]. Here, the transmissivity (represented by $Z$) is continuously varied and the tunneling limit corresponds to $Z \to \infty$. Adapted with permission from [138], Copyright (2012) by the American Physical Society.](image)

of a typical three-dimensional topological superconductor in figure 17.

Despite the general behavior discussed above, the actual tunneling conductance of three-dimensional topological superconductors may present zero-bias peaks for several reasons [138, 139]: (i) When the tunneling barrier of the tunnel junction is low or the transmissivity of the tunneling interface is high, the above argument does not hold and a zero-bias peak can appear; see figure 18(a). (ii) In the case of superconducting topological insulators, surface Majorana fermions may have a twisted energy dispersion due to the existence of surface Dirac fermions in the normal state. Such a twisted dispersion enhances the surface density of states near zero energy, leading to a zero-bias peak structure in the tunneling conductance; see figure 18(b). (iii) If the bulk superconducting gap has nodes or deep minima, the energy dispersion of surface Majorana fermions can become almost flat along the path connecting the projected bulk nodes in the surface Brillouin zone. The flat dispersion enhances the surface density of states at zero energy, resulting in a zero-bias peak in the tunneling conductance; see figures 18(c) and (d). (iv) At finite temperature, the zero-bias dip may be smeared by thermal broadening [139].

8.2. Thermal conductivity and spin current

The gapless surface/edge modes can also be probed by transport experiments. Although dc charge transport measurements are not useful because of the zero-resistivity nature of the superconducting state, one can employ thermal transport or spin transport for studying quasiparticles in the superconducting states [9]. Note that Cooper pairs do not carry heat and phonons die away following the $T^3$ law, making gapless Majorana modes to be the only heat carriers at low temperature. Therefore, a finite surface/edge thermal conductivity in a fully-gapped superconductor gives strong evidence for dispersive Majorana fermions. Also, when the surface/edge modes have a helical spin polarization as in the case of Cu$_3$Bi$_2$Se$_3$, a heat current is at the same time a spin current.
Intriguingly, if the C-shaped part of such a ring is twisted, which transforms to a ring, which means with integer boundaries may present unusual properties because the phase

device that Cu

Figure 18. Theoretically calculated tunneling spectra in three-dimensional time-reversal-invariant topological superconductors for various types of dispersions of the helical Majorana fermions at the surface: (a) conventional X-shaped energy dispersion, (b) twisted energy dispersion, and ((c), (d)) flat energy dispersions. Different colors indicate different transmissivities of the tunneling interface. The transmissivity is high for red lines, intermediate for green lines, and low for blue lines. Adapted with permission from [138], Copyright (2012) by the American Physical Society.

Measurements of the heat-current-induced spin polarization on the surface or edge of a topological superconductor gives further evidence for Majorana fermions.

8.3. Quantized thermal Hall conductivity

For 3D time-reversal-invariant topological superconductors, an interesting prediction for quantization of the thermal Hall effect has been made [258–260]. To observe this phenomenon, one needs to cover the whole surface with an s-wave superconductor to open a gap at the Dirac point of the helical Majorana-fermion dispersion. The predicted thermal Hall conductivity is \( \kappa_{\text{th}}/T = \pi^2 k_B^2 / (12h) \).

8.4. Nematicity

As already mentioned in section 7.1.2, there is strong evidence that CuBi2Se3 realizes the \( \Delta_4 \) state which can be termed a nematic superconductor [133]. The nematicity has so far been detected through uniaxial anisotropy in the Knight shift [191], specific heat [192], and upper critical field [192], in their dependencies on the orientation of the applied in-plane magnetic field. The occurrence of nematicity is also confirmed in similar superconductors, SrBi2Se3 [197–199] and NbBi2Se3 [201]. The nematicity should manifest itself in various other properties, such as thermal conductivity, penetration depth, elastic constants, sound velocity, etc. The nematicity would also give rise to a formation of nematic domains, and the domain boundaries may present unusual properties because the phase factor changes across the boundary. In fact, the physics of nematic domain boundaries would be a fertile ground for new discoveries.

8.5. Anomalous Josephson effects

Josephson junctions between a time-reversal-invariant topological superconductor and an s-wave superconductor contain surface/edge Majorana modes in the junction, which leads to an anomalous current-phase relationship. This is essentially because the Majorana mode remains gapless for the phase difference \( \theta \) of 0 or \( \pi \), but becomes gapped for \( \theta \neq 0, \pi \), which leads to a half-period Fraunhofer pattern [261]. For similar reasons, when one inserts a 3D time-reversal-invariant topological superconductor into the gap of a C-shaped s-wave superconductor to make a continuous ring, the flux quantization in the ring is predicted to occur in units of half the flux quantum, \( \frac{\pi}{4} \) [131]. Intriguingly, if the C-shaped part of such a ring is replaced by a d-wave superconductor, the flux quantization will take the value \( \frac{\hbar}{2e} (n + \frac{1}{2}) \) with integer \( n \) [131]. Signatures of topological phase transitions in terms of a discontinuity in the Josephson current-phase relation was recently discussed [262].

The Josephson current-phase relation is also sensitive to the symmetry of the system [263]. The Josephson current can be generally decomposed into a harmonic series,

\[
J(\theta) = \sum_{n=1} J_n \sin(n\theta + \phi_n),
\]

where \( J_n \) and \( I_n \) diminish as \( n \) increases. Under time-reversal operation, \( J(\theta) \) transforms to \( -J(\theta) \), which means \( I_n = 0 \) in the case of time-reversal-invariant junctions. If the junction preserves mirror-reflection symmetry as well, the current-phase relationship depends also on the mirror parity of the gap function. When we consider a junction between a mirror-odd superconductor and a conventional s-wave superconductor, mirror-reflection symmetry implies \( J(\theta + \pi) = J(\theta) \), which leads to \( J_{2n+1} = 0 \). (Note also that \( I_n = 0 \) as mentioned above.) As a result, one obtains a Josephson current with an anomalous current-phase relationship \( J(\theta) \sim \sin 2\theta \). Such an anomalous relation is useful for identifying the bulk pairing symmetry of topological superconductors.

8.6. Odd-frequency Cooper pairs

The presence of surface Majorana fermions gives rise to odd-frequency Cooper pairs at the interfaces [264]. Odd-frequency Cooper pairs are stable against disorders, which results in anomalous proximity effects in normal-metal/superconductor and superconductor/normal-metal/superconductor junctions [265–269]. For more details about the relation between topological superconductivity and odd-frequency Cooper pairs, see a recent review [57].

8.7. Majorana fermions in hybrid systems

For artificial topological superconductors engineered in hybrid systems, various predictions have been made for their
peculiar properties to reflect the existence of Majorana fermions. Most prominent predictions are half-integer conductance quantization at a ballistic NS point-contact junction, $4\pi$-periodic Josephson effect, Majorana teleportation, interference effect around an island containing a Majorana fermion, and braiding phenomena associated with Majorana exchange. We refer interested readers to the reviews dedicated to Majorana zero-modes for detailed discussions of these effects [15–17].

9. Outlook

While the concept of topological superconductivity has been prominent in theoretical physics since 2000 [12], their experimental investigations are still in its infancy. With the recent confirmations of the topological $\Delta_4$ state in Cu$_2$Bi$_2$Se$_3$ [191, 192], Majorana teleportation in InAs/Al nanowire [247], and the $4\pi$-periodic Josephson effect in HgTe/Nb junction [242], concrete platforms for exploring the physics of topological superconductivity are being established. It is foreseeable that Majorana fermions in solid-state systems will soon become a well-grounded paradigm.

In intrinsic topological superconductors, investigations of novel phenomena associated with surface/edge Majorana fermions will be an important subject. The first step would be to study heat and spin transport properties, for which Majorana fermions will be responsible. Also, the quantization of thermal Hall conductivity would be intriguing as a novel manifestation of topology. In future, conceiving a Majorana qubit based on intrinsic topological superconductors for quantum computation would be an interesting and potentially important direction. Needless to say, discoveries of new types of intrinsic topological superconductors to widen our knowledge of topological materials remain important.

In hybrid systems, since the possibility to engineer topological superconductivity has already been confirmed, the interest is shifting toward controlling and reading the occupation of a Majorana zero-mode, which is the basis of qubit operation. The most exciting prospect is the demonstration of non-Abelian statistics associated with a Majorana zero-mode [12]. Such an experiment requires braiding operation involving at least four Majorana fermions [113] and confirmation of the flipping of a qubit. This is technically very demanding, but already concrete setups and protocols have been proposed [270]. Another exciting prospect of the hybrid systems is the potential to implement the ‘surface code’ [271, 272], a protocol to realize scalable quantum computation with built-in error corrections. The surface code can in principle be realized by using non-topological quantum states, but it has been argued that using Majorana fermions will make it much simpler to realize the surface code [273–276].

Regarding the theory of topological superconductors, one of the important remaining problems is the complete understanding of topological crystalline superconductivity. Real materials have a variety of crystal symmetries, which could enrich their topological structures. For instance, it was revealed recently that nonsymmorphic space group symmetry such as glide reflection and screw rotation makes it possible to have novel $\mathbb{Z}_2$ and $\mathbb{Z}_4$ topological phases with Möbius-twisted surface states [75]. To clarify if other exotic topological surfaces may exist or not, more systematic studies are needed. Furthermore, disorder and interaction effects on topological crystalline superconductors have not been well understood yet. A naive anticipation that topological crystalline phases are easily washed out by weak disorders is found to be incorrect, and numerical studies have suggested that they could be stable against disorders [277–280]. Also, in the presence of a magnetic point group symmetry, symmetry-protected Majorana modes present the so-called Majorana Ising property, by which the coupling between the Majorana modes and disorders is strongly suppressed [65, 71, 126, 128]. Another interesting problem in topological crystalline superconductors is to study their topological quantum phase transitions; intriguingly, it has been predicted that some space supersymmetry appears at such a topological phase transition point [281, 282].

To facilitate the hunt for new topological superconductors, further understanding of topological nodal superconductors is desirable. Most discovered unconventional superconductors including high-$T_c$ cuprates are nodal, and they also have topologically non-trivial properties. Some of them have globally-defined bulk topological numbers, which implies that the nodal topological phase can be stable in the presence of disorder. Moreover, like Weyl semimetals, gapless bulk nodes could be a source of anomaly-related quantum phenomena.

Regarding the mechanism of topological superconductivity, a promising direction is to study orbital fluctuations in the presence of strong spin–orbit coupling. As was shown in section 6, inter-orbital pairing interactions can lead to spin-triplet topological superconductivity even without spin-dependent pairing interactions. In this regard, identifying the microscopic mechanism of odd-parity Cooper pairs in Sr$_2$RuO$_4$ and Cu$_2$Bi$_2$Se$_3$ would be important.

Finally, revealing hitherto-unknown topological phenomena is of particular interest. In this regard, a systematic search based on general frameworks such as topological quantum field theories might give universal and tractable predictions for novel topological phenomena.

Acknowledgments

The authors acknowledges Kouji Segawa, Alexey Taskin, Satoshi Sasaki, Zhi Ren, Markus Kriener, Mario Novak, Fan Yang, Kazuma Eto, Takaunmi Sato, Seigo Souma, Takashi Takahashi, Keiji Yada, Ai Yamakage, Shingo Kobayashi, Tatsuki Hashimoto, Satoshi Fujimoto, Takeshi Mizushima, Ken Shiozaki, Kyionori Gomi, Yoichi Yanase, Takehito Yokoyama and Yukio Tanaka for collaborations. This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas ‘Topological Materials Science’ (KAKENHI Grant Nos. JP15H05855 and JP15H05853) from JSPS of Japan. The work of MS was performed in part at the Aspen Center for Physics, which is supported by National Science Foundation grant PHY-1066293. YA is supported by DFG through CRC1238 ‘Control and Dynamics of Quantum Materials’, Project A04.
References

[1] Thouless D J, Kohmoto M, Nightingale M P and Dennijs M 1982 Quantized Hall conductance in a two-dimensional periodic potential Phys. Rev. Lett. 49 405–8
[2] Kohmoto M 1985 Topological invariant and the quantization of the Hall conductance Ann. Phys. 160 343
[3] Kane C L and Mele E J 2005 Quantum spin Hall effect in graphene Phys. Rev. Lett. 95 226801
[4] Kane C L and Mele E J 2005 Z2 topological order and the quantum spin Hall effect Phys. Rev. Lett. 95 146802
[5] Moore J E and Balents L 2007 Topological invariants of time-reversal-invariant band structures Phys. Rev. B 75 121306
[6] Fu L, Kane C L and Mele E J 2007 Topological insulators in three dimensions Phys. Rev. Lett. 98 106803
[7] Roy R 2009 Topological phases and the quantum spin Hall effect in three dimensions Phys. Rev. B 79 195322
[8] Ando Y 2013 Topological insulator materials J. Phys. Soc. Japan 82 102001
[9] Schnyder A P, Ryu S, Furusaki A and Ludwig A W W 2008 Classification of topological insulators and superconductors in three spatial dimensions Phys. Rev. B 78 195125
[10] Kitaev A 2009 Periodic table for topological insulators and superconductors AIP Conf. Proc. 1134 22–30
[11] Volovik G E 2003 The Universe in a Helium Droplet (Oxford: Oxford University Press)
[12] Read N and Green D 2000 Paired states of fermions in two dimensions with breaking of parity and time-reversal symmetries and the fractional quantum Hall effect Phys. Rev. B 61 10267–97
[13] Kitaev A Y 2001 Unpaired Majorana fermions in quantum wires Phys.—Usp. 44 131
[14] Sato M 2003 Non-abelian statistics of axion strings Phys. Lett. B 575 126–30
[15] Alicea J 2012 New directions in the pursuit of Majorana fermions in solid state systems Rep. Prog. Phys. 75 076501
[16] Beenakker C W J 2013 Search for Majorana fermions in superconductors Annu. Rev. Condens. Matter Phys. 4 113–36
[17] Sato M and Fujimoto S 2016 Majorana fermions and topology in superconductors J. Phys. Soc. Japan 85 072001
[18] Berry M 1984 Quantum phase factors accompanying adiabatic changes Proc. R. Soc. Lond. A 392 45
[19] Simon B 1983 Holonomy, the quantum adiabatic theorem and Berry’s phase Phys. Rev. Lett. 51 2167–70
[20] Avron J E, Seiler R and Simon B 1983 Homotopy and quantization in condensed matter physics Phys. Rev. Lett. 51 51–3
[21] Kane B A and Zhang S-C 2006 Quantum spin Hall effect Phys. Rev. Lett. 96 106802
[22] Qi X-L, Hughes T L and Zhang S-C 2008 Topological field theory of time-reversal invariant insulators Phys. Rev. B 78 195424
[23] Sheng D N, Weng Z Y, Sheng L and Haldane F D M 2006 Quantum spin Hall effect and topologically invariant Chern numbers Phys. Rev. Lett. 97 036808
[24] Fu L and Kane C L 2007 Topological insulators with inversion symmetry Phys. Rev. B 76 045302
[25] Hasan M Z and Kane C L 2010 Colloquium: topological insulators Rev. Mod. Phys. 82 3045–67
[26] Qi X-L and Zhang S-C 2011 Topological insulators and superconductors Rev. Mod. Phys. 83 1057–110
[27] Zhang H, Liu C-X, Qi X L, Dai X, Fang Z and Zhang S-C 2009 Topological insulators in Bi2Se3, Bi2Te3 and Sb2Te3 with a single Dirac cone on the surface Nat. Phys. 5 438.
[28] Nielsen H B and Ninomiya M 1983 The Adler–Bell–Jackiw anomaly and Weyl fermions in a crystal Phys. Lett. B 130 389–96
[29] Murakami S 2007 Phase transition between the quantum spin Hall and insulator phases in 3d: emergence of a topological gapless phase New J. Phys. 9 356
[30] Wan X, Turner A M, Vishwanath A and Savrasov S Y 2011 Topological semimetal and fermi-arc surface states in the electronic structure of pyrochlore iridates Phys. Rev. B 83 205101
[31] Burkov A A and Balents L 2011 Weyl semimetal in a topological insulator multilayer Phys. Rev. Lett. 107 127205
[32] Nielsen H B and Ninomiya M 1981 Absence of neutrinos on a lattice. (I). Proof by homotopy theory Nucl. Phys. B 185 20
[33] Nielsen H B and Ninomiya M 1981 Absence of neutrinos on a lattice. (II). Intuitive topological proof Nucl. Phys. B 193 173.
[34] Young S M, Zaheer S, Teo J C Y, Kane C L, Mele E J and Rappe A M 2012 Dirac semimetal in three dimensions Phys. Rev. Lett. 108 140405
[35] Wang Z, Sun Y, Chen X-Q, Franchini C, Xu G, Weng H, Dai X and Fang Z 2012 Dirac semimetal and topological phase transitions in A3Bi (A = Na, K Rb) Phys. Rev. B 85 195320
[36] Wang Z, Weng H, Wu Q, Dai X and Fang Z 2013 Three-dimensional Dirac semimetal and quantum transport in Cd3As2 Phys. Rev. B 88 125427
[37] Yang B-J and Nagaosa N 2014 Classification of stable three-dimensional Dirac semimetals with nontrivial topology Nat. Commun. 5 4891
[38] Novak M, Sasaki S, Segawa K and Ando Y 2015 Large linear magnetoresistance in the dirac semimetal TIBi5Se8 Phys. Rev. B 91 041203
[39] Neupane M et al 2014 Observation of a three-dimensional topological Dirac semimetal phase in high-mobility Cd3As2 Nat. Commun. 5 3786
[40] Borisenko S, Gibson Q, Evtushinsky D, Zabolotnyy V, Yi H et al 2014 A stable three-dimensional topological Dirac semimetal Phys. Rev. Lett. 113 027603
[41] Liu Z K et al 2014 A stable three-dimensional Dirac semimetal Cd3As2 Nat. Mater. 13 677–81
[42] Yi H et al 2014 Evidence of topological surface state in three-dimensional Dirac semimetal Cd3As2 Sci. Rep. 4 6106
[43] Sigrist M and Ueda K 1991 Phenomenological theory of unconventional superconductivity Rev. Mod. Phys. 63 239–311
[44] Frigeri P A, Agterberg D F, Koga A and Sigrist M 2004 Superconductivity without inversion symmetry: Mnsi versus CePt3Si Phys. Rev. Lett. 92 097001
[45] Bauer E and Ed M S 2012 Non-Centrosymmetric Superconductors Introduction and Overview (Berlin: Springer)
[46] Caroli C, De Gennes P G and Matricon J 1964 Bound Fermion states on a vortex line in a type II superconductor Phys. Lett. 9 307–9
[47] Kashiwaya S and Tanaka Y 2000 Tunnelling effects on surface bound states in unconventional superconductors Rep. Prog. Phys. 63 1641
[48] Lofwander T, Shumeiko V S and Wendin G 2001 Andreev bound states in high-Tc superconducting junctions Supercond. Sci. Technol. 14 R53
[49] Hara J and Nagaui K 1986 A polar state in a slab as a soluble model of unconventional superconductivity Phys. Rev. Lett. 57 1953–58
[50] Kopnin N B and Saloman M 1991 Mutual friction in unconventional superconductors Phys. Rev. Lett. 66 3898–901
[51] Kopnin N B 1994 Mutual friction in unconventional superconductors Supercond. Sci. Technol. 7 422–32
[52] Kopnin N B and Saloman M 1991 Mutual friction in unconventional superconductors Phys. Rev. Lett. 67 2284–7
[52] Tanaka Y and Kashiyawa S 1995 Theory of tunneling spectroscopy of d-wave superconductors Phys. Rev. Lett. 74 3451–4
[53] Manton N and Sutcliffe P 2004 Topological Solitons (Cambridge: Cambridge University Press)
[54] Sato M and Fujimoto S 2009 Topological phases of noncentrosymmetric superconductors: edge states, Majorana fermions and non-abelian statistics Phys. Rev. B 79 094504
[55] Tanaka Y, Yokoyama T, Balatsky A V and Nagao N 2009 Theory of topological spin current in noncentrosymmetric superconductors Phys. Rev. B 79 060505
[56] Grinevich P G and Volovich I G 1988 Topology of gap nodes in superfluid 3He: $\pi_2$ homotopy group for 3He-B disclination J. Low Temp. Phys. 72 371–80
[57] Tanaka Y, Sato M and Nagaosa N 2012 Symmetry and topology in superconductors ’odd-frequency pairing and edge states’ J. Phys. Soc. Japan 81 011013
[58] Hatsugai Y 1993 Chern number and edge states in the integer quantum Hall effect Phys. Rev. Lett. 71 3697–700
[59] Teo J C Y and Kane C L 2010 Topological defects and gapless modes in insulators and superconductors Phys. Rev. B 82 115120
[60] Sato M, Tanaka Y, Yada K and Yokoyama T 2011 Topology of Andreev bound states with flat dispersion Phys. Rev. B 83 245111
[61] Essin A M and Guraire V 2011 Bulk-boundary correspondence of topological insulators from their respective Green’s functions Phys. Rev. B 84 125132
[62] Teo J C Y and Hughes T L 2013 Existence of Majorana-fermion bound states on disclinations and the classification of topological crystalline superconductors in two dimensions Phys. Rev. Lett. 111 047006
[63] Ueno Y, Yamakage A, Tanaka Y and Sato M 2013 Symmetry-protected Majorana fermions in topological crystalline superconductors: theory and application to Sr$_2$RuO$_4$ Phys. Rev. Lett. 111 018702
[64] Benalcazar W A, Teo J C Y and Hughes T L 2014 Classification of two-dimensional topological crystalline superconductors and Majorana bound states at disclinations Phys. Rev. B 89 224503
[65] Shiozaki K and Sato M 2014 Theory of crystalline insulators and superconductors Phys. Rev. B 90 165114
[66] Tsutsumi Y, Ishikawa M, Kawakami T, Mitzushima T, Sato M, Ichioka M and Machida K 2013 UPt$_3$ as a topological crystalline superconductor J. Phys. Soc. Japan 82 113707
[67] Chang P-Y, Matsuura S, Schnyder A P and Ryu S 2014 Majorana vortex-bound states in three-dimensional nodal noncentrosymmetric superconductors Phys. Rev. B 90 174504
[68] Lee D and Schnyder A P 2016 Structure of vortex-bound states in spin-singlet chiral superconductors Phys. Rev. B 93 064522
[69] Tsutsumi Y, Kawakami T, Shiozaki K, Sato M and Machida K 2015 Symmetry-protected vortex bound state in superfluid $^3$He-$B$ phase Phys. Rev. B 91 144504
[70] Fu L 2011 Topological crystalline insulators Phys. Rev. Lett. 106 106802
[71] Mizushima T, Sato M and Machida K 2012 Symmetry protected topological order and spin susceptibility in superfluid $^3$He-$B$ Phys. Rev. Lett. 109 165301
[72] Zhang F, Kane C L and Mele E J 2013 Topological mirror superconductivity Phys. Rev. Lett. 110 056403
[73] Chiu C-K, Yao H and Ryu S 2013 Classification of topological insulators and superconductors in the presence of reflection symmetry Phys. Rev. B 88 075142
[74] Morimoto T and Furusaki A 2013 Topological classification with additional symmetries from Clifford algebras Phys. Rev. B 88 125120
[75] Shiozaki K, Sato M and Gomi K 2016 Topology of nonsymmetric crystalline insulators and superconductors Phys. Rev. B 93 195413
[76] Teo J C Y, Fu L and Kane C L 2008 Surface states and topological invariants in three-dimensional topological insulators: application to Bi$_2$Se$_3$/Sb$_2$ Phys. Rev. B 78 045426
[77] Hsieh T H, Lin H, Liu J, Duan W, Bansil A and Fu L 2012 Topological crystalline insulators in the siten material class Nat. Commun. 3 992
[78] Tanaka Y, Ren Z, Sato T, Nakayama K, Souma S, Takahashi T, Segawa K and Ando Y 2012 Experimental realization of a topological crystalline insulator in SnTe Nat. Phys. 8 800–3
[79] Meng T and Balents L 2012 Weyl superconductors Phys. Rev. B 86 045054
[80] Sato M 2006 Nodal structure of superconductors with time-reversal invariance and $\mathbb{Z}_2$ topological number Phys. Rev. B 73 214502
[81] Beri B 2010 Topologically stable gapless phases of time-reversal-invariant superconductors Phys. Rev. B 81 134515
[82] Schnyder A P and Ryu S 2011 Topological phases and surface flat bands in superconductors without inversion symmetry Phys. Rev. B 84 060504
[83] Tanaka Y, Mizuno Y, Yokoyama T, Yada K and Sato M 2010 Anomalous Andreev bound state in noncentrosymmetric superconductors Phys. Rev. Lett. 105 097002
[84] Yada K, Sato M, Tanaka Y and Yokoyama T 2011 Surface density of states and edge states in noncentrosymmetric superconductors Phys. Rev. B 83 064505
[85] Schnyder A P, Brydon P M R and Timm C 2012 Types of topological surface states in nodal noncentrosymmetric superconductors Phys. Rev. B 85 024522
[86] Ikegaya S, Suzuki S-I, Tanaka Y and Asano Y 2016 Quantization of conductance minimum and index theorem Phys. Rev. B 94 054512
[87] Kobayashi S, Shiozaki K, Tanaka Y and Sato M 2014 Topological Blount’s theorem of odd-parity superconductors Phys. Rev. B 90 024516
[88] Zhao Y X, Schnyder A P and Wang Z D 2016 Unified theory of PT and CP invariant topological metals and nodal superconductors Phys. Rev. Lett. 116 156402
[89] Blount E I 1985 Symmetry properties of triplet superconductors Phys. Rev. B 32 2935–44
[90] Agterberg D F, Brydon P M R and Timm C 2017 Inflated nodes in superconductors with broken time-reversal symmetry Phys. Rev. Lett. 118 127001
[91] Norman M R 1995 Odd parity and line nodes in heavy-fermion superconductors Phys. Rev. B 52 15093–4
[92] Micklitz T and Norman M R 2009 Odd parity and line nodes in nonsymmorphic superconductors Phys. Rev. B 80 100506
[93] Nomoto T and Ikeda H 2017 Symmetry protected line nodes in non-symmorphic magnetic space groups: applications to UCoGe and UPd$_2$Al$_3$, J. Phys. Soc. Japan 86 023703
[94] Yang S A, Pan H and Zhang F 2014 Dirac and Weyl superconductors in three dimensions Phys. Rev. Lett. 113 046401
[95] Chiu C-K and Schnyder A P 2014 Classification of reflection-symmetry-protected topological semimetals and nodal superconductors Phys. Rev. B 90 205136
[96] Kobayashi S, Tanaka Y and Sato M 2015 Fragile superconductors in three-dimensional chiral superconductors Phys. Rev. B 92 214514
[97] Kobayashi S, Yama S and Sato M 2016 Topologically stable gapless phases in nonsymmorphic superconductors Phys. Rev. B 94 134512
[98] Micklitz T and Norman M R 2016 Nodal-line superconductors and band-sticking (arXiv:1611.07590)
[99] Mizushima T, Tsutsumi Y, Kawakami T, Sato M, Ichioka M and Machida K 2016 Symmetry-protected topological superfluids and superconductors—from the basics to $^3$He J. Phys. Soc. Japan 85 022001
through spin relaxation

Silaev M A and V olovik G E 2012 Topological fermi arcs in superfluid 3He Phys. Rev. B 86 214511

[101] Goswami P and Balicas L 2013 Topological properties of possible Weyl superconducting states of URu2Si2 (arXiv:1312.3632)

[102] Fischer M H, Neupert T, Platt C, Schnyder A P, Hanke W, Goryo J, Thomale R and Sigrist M 2014 Chiral d-wave superconductivity in srptas Phys. Rev. B 89 020509

[103] Goswami P and Nevidomskyy A H 2013 Manipulating Majorana fermions in 1D nanowires Phys. Rev. Lett. 110 096804

[104] Chiu C-K, Vazifeh M M and Franz M 2015 Majorana fermion exchange in strictly one-dimensional structures Europhys. Lett. 110 10001

[105] Amorim C S, Ebihara K, Yamakage A, Tanaka Y and Sato M 2015 Majorana braiding dynamics in nanowires Phys. Rev. B 91 174505

[106] Chiu C-K, Vazifeh M M and Franz M 2015 Majorana fermion exchange in strictly one-dimensional structures Europhys. Lett. 110 10001

[107] Amorim C S, Ebihara K, Yamakage A, Tanaka Y and Sato M 2015 Majorana braiding dynamics in nanowires Phys. Rev. B 91 174505

[108] Kitaev A 2003 Fault-tolerant quantum computation by anyons Ann. Phys. 303 2–30

[109] Noack K, Simon S H, Stern A, Freedman M and Das Sarma S 2008 Non-abelian anyons and topological quantum computation Rev. Mod. Phys. 80 1083–159

[110] Nagato Y, Higashitani S and Nagai K 2009 Strong anisotropy in spin susceptibility of superfluid 3He-B film caused by surface bound states J. Phys. Soc. Japan 78 123603

[111] Shindou R, Furusaki A and Nagaosa N 2010 Quantum impurity spin in Majorana edge fermions Phys. Rev. B 82 180505

[112] Sato M 2009 Topological properties of spin-triplet superconductors and fermi surface topology in the normal state Phys. Rev. B 79 214526

[113] Sato M 2010 Topological odd-parity superconductors Phys. Rev. B 81 220504

[114] Fu L and Berg E 2010 Odd-parity topological superconductors: theory and application to CuBi2Se3, Phys. Rev. Lett. 105 097001

[115] Bryanton P M R, Das Sarma S, Hui H-Y and Sau J D 2014 Odd-parity superconductivity from phonon-mediated pairing; application to CuBi2Se3 Phys. Rev. B 90 184512

[116] Fu L 2014 Odd-parity topological superconductor with nematic order: application to CuBi2Se3 Phys. Rev. B 90 100505

[117] Hashimoto T, Yada K, Yamakage A, Sato M and Tanaka Y 2013 Bulk electronic state of superconducting topological insulator J. Phys. Soc. Japan 82 044704

[118] Hashimoto T, Yada K, Yamakage A, Sato M and Tanaka Y 2014 Effect of fermi surface evolution on superconducting gap in superconducting topological insulator Supercond. Sci. Technol. 27 104002

[119] Nakai Y, Nakamura H and Machida M 2012 Rotational isotropy breaking as proof for spin-polarized Cooper pairs in the topological superconductor CuBi2Se3 Phys. Rev. B 86 094507

[120] Hao L and Lee T K 2011 Surface spectral function in the superconducting state of a topological insulator Phys. Rev. B 83 134516

[121] Yamakage A, Yada K, Sato M and Tanaka Y 2012 Theory of tunneling conductance and surface-state transition in superconducting topological insulators Phys. Rev. B 85 180509

[122] Hsieh T H and Fu L 2012 Majorana fermions and exotic surface Andreev bound states in topological superconductors: application to CuBi2Se3 Phys. Rev. Lett. 108 107005

[123] Takaki S, Yada K, Yamakage A, Sato M and Tanaka Y 2014 Quasi-classical theory of tunneling spectroscopy in superconducting topological insulator J. Phys. Soc. Japan 83 064705

[124] Mizushima T, Yamakage A, Sato M and Ando Y 2011 Topological superconductivity in Bi2Se3 Phys. Rev. Lett. 107 217001

[125] Brydon P M R, Das Sarma S, Hui H-Y and Sau J D 2014 Odd-parity superconductivity from phonon-mediated pairing; application to CuBi2Se3 Phys. Rev. B 90 184512

[126] Fu L 2014 Odd-parity topological superconductor with nematic order: application to CuBi2Se3 Phys. Rev. B 90 100505

[127] Hashimoto T, Yada K, Yamakage A, Sato M and Tanaka Y 2013 Bulk electronic state of superconducting topological insulator J. Phys. Soc. Japan 82 044704

[128] Hashimoto T, Yada K, Yamakage A, Sato M and Tanaka Y 2014 Effect of fermi surface evolution on superconducting gap in superconducting topological insulator Supercond. Sci. Technol. 27 104002

[129] Nakai Y, Nakamura H and Machida M 2012 Rotational isotropy breaking as proof for spin-polarized Cooper pairs in the topological superconductor CuBi2Se3 Phys. Rev. B 86 094507

[130] Hao L and Lee T K 2011 Surface spectral function in the superconducting state of a topological insulator Phys. Rev. B 83 134516

[131] Yamakage A, Yada K, Sato M and Tanaka Y 2012 Theory of tunneling conductance and surface-state transition in superconducting topological insulators Phys. Rev. B 85 180509

[132] Hsieh T H and Fu L 2012 Majorana fermions and exotic surface Andreev bound states in topological superconductors: application to CuBi2Se3 Phys. Rev. Lett. 108 107005

[133] Takaki S, Yada K, Yamakage A, Sato M and Tanaka Y 2014 Quasi-classical theory of tunneling spectroscopy in superconducting topological insulator J. Phys. Soc. Japan 83 064705

[134] Mizushima T, Yamakage A, Sato M and Ando Y 2011 Topological superconductivity in Bi2Se3 Phys. Rev. Lett. 107 217001

[135] Brydon P M R, Das Sarma S, Hui H-Y and Sau J D 2014 Odd-parity superconductivity from phonon-mediated pairing; application to CuBi2Se3 Phys. Rev. B 90 184512

[136] Fu L 2014 Odd-parity topological superconductor with nematic order: application to CuBi2Se3 Phys. Rev. B 90 100505
finite-momentum pairing and electronic analog of the He-A phase Phys. Rev. B 86 214514

[144] Bednik G, Zyzkin A A and Burkov A A 2015 Superconductivity in Weyl metals Phys. Rev. B 92 035153

[145] Zhou T, Gao Y and Wang Z D 2016 Superconductivity in doped inversion-symmetric Weyl semimetals Phys. Rev. B 93 094517

[146] Murakami S and Nagaosa N 2003 Berry phase in magnetic superconductors Phys. Rev. Lett. 90 057002

[147] Li Y and Haldane D M 2015 Topological nodal Cooper pairing in doped Weyl metals (arXiv:1510.01730)

[148] Kobayashi S and Sato M 2015 Topological superconductivity in Dirac semimetals Phys. Rev. Lett. 115 187001

[149] Hashimoto T, Kobayashi S, Tanaka Y and Sato M 2016 Superconductivity in doped Dirac semimetals Phys. Rev. B 94 014510

[150] He L P, Jia Y T, Zhang S J, Hong X C, Jin C Q and Li S Y 2016 Pressure-induced superconductivity in the three-dimensional Dirac semimetal Cd3As2 NPJ Quantum Mater. 1 16014

[151] Aggarwal L, Gaurav A, Thakur G S, Haque A K and Sheet G 2016 Unconventional superconductivity at mesoscopic point contacts on the 3D Dirac semimetal Cd3As2 Nat. Mater. 15 32–7

[152] Wang H, Wang H, Liu H, Lu H, Yang W, Jia S, Liu X-J, Xie X C, Wei J and Wang J 2016 Observation of superconductivity induced by a point contact on 3D Dirac semimetal Cd3As2 crystals Nat. Mater. 15 38–42

[153] Moore G W and Read N 1991 Nonabelions in the fractional quantum Hall effect Nucl. Phys. B 360 362–96

[154] Weinberg E J 1981 Index calculations for the fermion-vortex system Phys. Rev. D 24 2669

[155] Jackiw R and Rossi P 1981 Zero modes of the vortex-fermion system Nucl. Phys. B 190 681–91

[156] Callan C G Jr and Harvey J A 1985 Anomalies and fermion zero modes on strings and domain walls Nucl. Phys. B 250 427–36

[157] Fu L and Kane C L 2008 Superconducting proximity effect and Majorana fermions at the surface of a topological insulator Phys. Rev. Lett. 100 096407

[158] Fukui T and Fujiwara T 2010 Topological stability of Majorana zero modes in superconductor-topological insulator systems J. Phys. Soc. Japan 79 033701

[159] Fukui T 2010 Majorana zero modes bound to a vortex line in a topological superconductor Phys. Rev. B 81 214516

[160] Parente V, Campagnano G, Giuliano D, Tagliaacozzo A and Guinea F 2014 Topological defects in topological insulators and bound states at topological superconductor vortices Materials 7 1652–86

[161] Sato M, Takahashi Y and Fujimoto S 2009 Non-abelian topological order in s-wave superfluids of ultracold fermionic atoms Phys. Rev. Lett. 103 020404

[162] Sato M, Takahashi Y and Fujimoto S 2010 Non-abelian topological orders and Majorana fermions in spin-singlet superconductors Phys. Rev. B 82 134521

[163] Sau J D, Lutchyn R M, Tewari S and Das Sarma S 2010 Generic new platform for topological quantum computation using semiconductor heterostructures Phys. Rev. Lett. 104 040502

[164] Lutchyn R M, Sau J D and Das Sarma S 2010 Majorana fermions and a topological phase transition in semiconductor-superconductor heterostructures Phys. Rev. Lett. 105 077001

[165] Oreg Y, Refael G and von Oppen F 2010 Helical liquids and Majorana bound states in quantum wires Phys. Rev. Lett. 105 177002

[166] Linder J, Tanaka Y, Yokoyama T, Sudbo A and Nagaosa N 2010 Unconventional superconductivity on a topological insulator Phys. Rev. Lett. 104 067001

[167] Daido A and Yanase Y 2016 Paramagnetically induced gapful topological superconductors Phys. Rev. B 94 054519

[168] Wong C L M and Law K T 2012 Majorana kramers doublets in d,1/2,− wave superconductors with Rashba spin–orbit coupling Phys. Rev. B 86 184516

[169] Black-Schaffer A M 2012 Edge properties and Majorana fermions in the proposed chiral d-wave superconducting state of doped graphene Phys. Rev. Lett. 109 197001

[170] Farrell A and Perez-Barena T 2013 Topological superconductivity without proximity effect Phys. Rev. B 87 214517

[171] Sun S-J, Chung C-H, Chang Y-Y, Tsai W-F and Zhang F-C 2016 Helical Majorana fermions in d,1/2,− + id,− wave topological superconductivity of doped correlated quantum spin Hall insulators Sci. Rep. 6 24102

[172] Altland A and Zirnbauer M R 1997 Nonstandard symmetry classes in mesoscopic normal-superconducting hybrid structures Phys. Rev. B 55 1142–61

[173] Maeno Y, Hashimoto H, Yoshioka K, Nishizaki S, Fujita T, Bednorz J G and Lichtenberg F 1994 Superconductivity in a layered perovskite without copper Nature 372 532–4

[174] Rice T M and Sgirst M 1995 Sr3RuO4: an electronic analogue of ‘He’ J. Phys.: Condens. Matter. 7 L643

[175] Ishida K, Mukuda H, Kitaoka Y, Asayama K, Mao Z Q, Mori Y and Maeno Y 1998 Spin-triplet superconductivity in Sr3RuO4 and identified by 17O knight shift Nature 396 658–60

[176] Luke G M et al 1998 Time-reversal symmetry-breaking superconductivity in Sr3RuO4 Nature 394 558–61

[177] Catherine K and John B 2016 Chiral superconductors Rep. Prog. Phys. 79 054502

[178] Maeno Y, Katibaka S, Nomura T, Yonezawa S and Ishida K 2012 Evaluation of spin-triplet superconductivity in Sr3RuO4 identified by 17O knight shift Nature 496 658–60

[179] Kashiwaya S, Kashiwaya H, Kambara H, Furuta T, Yaguchi H, Tanaka Y and Maeno Y 2011 Edge states of Sr3RuO4 detected by in-plane tunneling spectroscopy Phys. Rev. Lett. 107 077003

[180] Yamashiro M, Tanaka Y and Kashiwaya S 1997 Theory of tunneling spectroscopy in superconducting Sr3RuO4 Phys. Rev. B 56 7847–50

[181] Furusaki A, Matsumoto M and Sigrist M 2001 Spontaneous Hall effect in a chiral p-wave superconductor Phys. Rev. B 64 054514

[182] Stone M and Roy R 2004 Edge modes, edge currents and gauge invariance in p0 +ipq superfluids and superconductors Phys. Rev. B 69 184511

[183] Yada K, Golubov A A, Tanaka Y and Kashiwaya S 2014 Microscopic theory of tunneling spectroscopy in Sr2RuO4 J. Phys. Soc. Japan 83 074706

[184] Mackenzie A P and Maeno Y 2003 The superconductivity of Sr3RuO4 and the physics of spin-triplet pairing Rev. Mod. Phys. 75 657–712

[185] Jang J, Ferguson D G, Vakaryuk V, Budakian R, Chung S B, Goldbart P M and Maeno Y 2011 Observation of half-height magnetization steps in Sr3RuO4 Science 331 186–8

[186] Tewari S, Das Sarma S, Nayak C, Zhang C and Zoller P 2007 Quantum computation using vortices and Majorana zero modes of a φ0 + ip0 superfluid of fermionic cold atoms Phys. Rev. Lett. 98 010506

[187] Hor Y S, Williams A J, Checkelsky J G, Roushan P, Seo J, Xu Q, Zandbergen H W, Yazdani A, Ong N P and Cava R J 2010 Superconductivity in Cu3Bi2Se4 and its implications for pairing in the undoped topological insulator Phys. Rev. Lett. 104 087001

[188] Wray L A, Xu S-Y, Xia Y, Hor S Y, Qian D, Fedorov A V, Lin H, Bansil A, Cava R J and Hasan M Z 2010
Observation of topological order in a superconducting doped topological insulator Nat. Phys. 6 855–9

[189] Ando Y and Fu L 2015 Topological crystalline insulators and topological superconductors: from concepts to materials Annu. Rev. Condens. Matter Phys. 6 361–81

[190] Kriener M, Segawa K, Ren Z, Sasaki S, Wada S, Kuwabata S and Ando Y 2011 Electrochemical synthesis and superconducting phase diagram of Cu2Bi2Se3 Phys. Rev. B 84 054513

[191] Matano K, Kriener M, Segawa K, Ando Y and Zheng G-q 2016 Spin–rotation symmetry breaking in the superconducting state of Cu2Bi2Se3 Nat. Phys. 12 852–4

[192] Yonezawa S, Tajiri K, Nakata S, Nagai Y, Wang Z, Segawa K, Ando Y and Maeno Y 2017 Thermodynamic evidence for nematic superconductivity in Cu2Bi2Se3 Nat. Phys. 13 123–6

[193] Kriener M, Segawa K, Ren Z, Sasaki S and Ando Y 2011 Bulk superconducting phase with a full energy gap in the doped topological insulator Cu2Bi2Se3 Phys. Rev. Lett. 106 127004

[194] Levy N, Zhang T, Ha J, Sharifi F, Talin A A, Kuk Y and Pan Y, Nikitin A M, Araizi G K, Huang Y K, Matsushita Y, Novak M, Sasaki S, Kriener M, Segawa K and Ando Y 2015 Topological crystalline insulators and superconductivity Sci. Rep. 5 84

[195] Erickson A S, Chu J H, Toney M F, Geballe T H and Kriener M, Segawa K, Ren Z, Sasaki S, Wada S, Kuwabata S and Ando Y 2011 Local pairing at upper-critical field experiments Phys. Rev. B 84 020505

[196] Martin I and Phillips P 1997 Local pairing at u impurities in bcs superconductors can enhance Tc Phys. Rev. B 56 14650–4

[197] Sasaki S and Ando Y 2015 Superconducting Sn1-xInxTe nanofilms Cryst. Growth Des. 15 2748–52

[198] Sato T, Tanaka Y, Nakayama K, Souma S, Takahashi T, Sasaki S, Ren Z, Taskin A A, Segawa K and Ando Y 2013 Fermiology of the strongly spin–orbit coupled superconductor Sn1-xInxTe: implications for topological superconductivity Phys. Rev. Lett. 110 206804

[199] Tanaka Y, Shoman T, Nakayama K, Souma S, Sato T, Takahashi T, Novak M, Segawa K and Ando Y 2013 Two types of Dirac-cone surface states on the (1 1 1) surface of the topological crystalline insulator SrTe Phys. Rev. B 88 235126

[200] Fang C, Gilbert M J and Bernevig B A 2014 New class of topological superconductors protected by magnetic group symmetries Phys. Rev. Lett. 112 106401

[201] Alekseevskii N E 1952 Sverkhprovodimost soedinenii sistemy Bi-Pd Zh. Eksp. Teor. Fiz. 23 484

[202] Peets D C, Maldonado A, Enayat M, Sun Z, Wahl P and Schuyder A P 2016 Upper critical field of the noncentrosymmetric superconductor BiPd Phys. Rev. B 93 174504

[203] Bauer E, Hilscher G, Michor H, Paul C, Scheidt E W, Gribanov A, Seropogin Y, Noël H, Sigrist M and Roegl P 2004 Heavy fermion superconductivity and magnetic order in noncentrosymmetric CePt3Si Phys. Rev. Lett. 92 027003

[204] Bauer E, Kaldar H, Prokofiev A, Royontant E, Amato A, Sereni J, Brner-Escamilla W and Bonalde I 2007 Heavy fermion superconductivity and antiferromagnetic ordering in CePt3Si without inversion symmetry J. Phys. Soc. Japan 76 051009

[205] Fujimoto S 2007 Electron correlation and pairing states in superconductors without inversion symmetry J. Phys. Soc. Japan 76 051008

[206] Badica P, Kondo T and Togano K 2005 Superconductivity in a new pseudo-binary Li3–xBixPt3Si (x = 0–1) boride system J. Phys. Soc. Japan 74 10149–4

[207] Nishiyama M, Inada Y and Zheng G-Q 2007 Spin triplet superconducting state due to broken inversion symmetry in LiPt3B Phys. Rev. Lett. 98 047002

[208] Ueno K, Shimotani H, Yuan H, Ye J, Kawasaki M and Iwasa Y 2014 Field-induced superconductivity in electric double layer transistors J. Phys. Soc. Japan 83 032001

[209] Sasaki S, Segawa K and Ando Y 2014 Superconductor derived from a topological insulator heterostructure Phys. Rev. B 90 220504

[210] Kanatzidis M G 2004 Structural evolution and phase homologies for design and prediction of solid-state compounds Acc. Chem. Res. 38 359–68

[211] Nakayama K, Eto K, Tanaka Y, Sato T, Souma S, Takahashi T, Segawa K and Ando Y 2012 Manipulation of topological states and the bulk band gap using natural heterostructures of a topological insulator Phys. Rev. Lett. 109 236804

[212] Segawa K, Taskin A A and Ando Y 2015 PbSi2B4Se41: a new member of the homologous series forming topological insulator heterostructures J. Solid State Chem. 221 196–201

[213] Stewart G R and Brandt B L 1984 High-field specific heats of A15 NbSi and NbSn Phys. Rev. B 29 3908–12

[214] Joynt R and Taillefer L 2002 The superconducting phases of UPt3 Mod. Phys. Lett. 23 1745–94

[215] Machida Y, Itoh A, So Y, Izawa K, Haga Y, Yamamoto E, Nishiyama M, Inada Y and Zheng G Q 2007 Spin triplet superconductivity in Sr3–xBixBi2Se3 single crystals using a scanning tunneling microscope Phys. Rev. B 75 144516

[216] Du G, Li Y, Schneelech J, Zhong R D, Gu G, Yang H, Lin H and Wen H H 2017 Superconductivity with two-fold symmetry in topological superconductor SrBi2Se3 probed by upper critical field experiments Sci. Rep. 6 26836

[217] Qiu Y, Nocona Sanders K, Dai J, Medvedeva J E, Wu L, Ghaemi P, Vojta T and San Hor Y 2015 Time reversal symmetry breaking superconductivity in topological materials (arXiv:1512.03519)

[218] Asaba T, Lawson B J, Tinsman C, Chen L, Corbae P, Li G, Qiu Y, Hor Y S, Fu L and Li L 2017 Rotational symmetry breaking in a trigonal superconductor Nb-doped Bi2Se3 Phys. Rev. X 7 011009

[219] Novak M, Sasaki S, Kriener M, Segawa K and Ando Y 2013 Unusual nature of fully gapped superconductivity in In-doped SnTe Phys. Rev. B 88 140502

[220] Erickson A S, Chu J H, Toney M F, Geballe T H and Fisher R I 2009 Enhanced superconducting pairing interaction in indium-doped tin telluride Phys. Rev. B 79 024520

[221] Zhong R D, Schneelech J A, Shi X Y, Xu Z J, Zhang C, Tranquada J M, Li Q and Gu G D 2013 Optimizing the superconducting transition temperature and upper critical field of Sn1–xInxTe Phys. Rev. B 88 020505

[222] Sasaki S, Ren Z, Taskin A A, Segawa K, Fu L and Ando Y 2012 Odd-parity pairing and topological superconductivity in a strongly spin–orbit coupled semiconductor Phys. Rev. Lett. 109 217004

[223] Martin I and Phillips P 1997 Local pairing at u impurities in bcs superconductors can enhance Tc Phys. Rev. B 56 14650–4

[224] Sasaki S and Ando Y 2015 Superconducting Sn1–xInxTe nanofilms Cryst. Growth Des. 15 2748–52

[225] Sato T, Tanaka Y, Nakayama K, Souma S, Takahashi T, Sasaki S, Ren Z, Taskin A A, Segawa K and Ando Y 2013 Fermiology of the strongly spin–orbit coupled superconductor Sn1–xInxTe: implications for topological superconductivity Phys. Rev. Lett. 110 206804

[226] Tanaka Y, Shoman T, Nakayama K, Souma S, Sato T, Takahashi T, Novak M, Segawa K and Ando Y 2013 Two types of Dirac-cone surface states on the (1 1 1) surface of the topological crystalline insulator SrTe Phys. Rev. B 88 235126

[227] Fang C, Gilbert M J and Bernevig B A 2014 New class of topological superconductors protected by magnetic group symmetries Phys. Rev. Lett. 112 106401

[228] Alekseevskii N E 1952 Sverkhprovodimost soedinenii sistemy Bi-Pd Zh. Eksp. Teor. Fiz. 23 484
[228] Kim H et al 2016 Beyond spin-triplet: nodal topological superconductivity in a noncentrosymmetric semimetal (arXiv:1603.03375)

[229] Meineit M 2016 Unconventional superconductivity in YPBi and related topological semimetals Phys. Rev. Lett. 116 137001

[230] Brydson P M R, Wang L, Weinert M and Agterberg D F 2016 Pairing of $f = 3/2$ fermions in half-heusler superconductors Phys. Rev. Lett. 116 177001

[231] Alicea J 2010 Majorana fermions in a tunable semiconductor device Phys. Rev. B 81 125318

[232] Williams J R, Bestwick A J, Gallagher P, Hong S S, Cui Y, Bleich A S, Analysis J G, Fisher I R and Goldhaber-Gordon D 2012 Unconventional Josephson effect in hybrid superconductor-topological insulator devices Phys. Rev. Lett. 109 056803

[233] Wang M-X et al 2012 The coexistence of superconductivity and topological order in the Bi$_2$Se$_3$ thin films Science 336 52–5

[234] Yang F et al 2012 Proximity-effect-induced superconducting phase in the topological insulator Bi$_2$Se$_3$ Phys. Rev. B 86 134504

[235] Wang E et al 2013 Fully gapped topological surface states in Bi$_2$Se$_3$ films induced by a $d$-wave high-temperature superconductor Nat. Phys. 9 621–5

[236] Cho S, Dellabetta B, Yang A, Schnelloch J, Xu Z, Valla T, Gu G, Gilbert M J and Mason N 2013 Symmetry protected Josephson supercurrents in three-dimensional topological insulators Nat. Commun. 4 1689

[237] Oostinga J B, Maier L, Schäffelgen P, Knott D, Ames C, Hart S, Ren H, Wagner T, Leubner P, Muhlbauer M, Brune C, Deacon R S, Wiedenmann J, Bocquillon E, Klapwijk T M, Mourik V, Zuo K, Frolov S M, Plissard S R, Bakkers E P and Deng M T, Yu C L, Huang G Y, Larsson M, Caroff P and Albrecht S M, Higginbotham A P, Madsen M, Kuemmeth F, Jespersen T S, Nyg J, Kroghstrup P and Marcus C M 2016 Exponential protection of zero modes in Majorana islands Nature 531 206–9

[238] Nadj-Perge S, Drozdov I K, Bernevig B A and Yazdani A 2013 Proposal for realizing Majorana fermions in chains of magnetic atoms on a superconductor Phys. Rev. B 88 020407

[239] Nadj-Perge S, Drozdov I K, Li J, Chen H, Jeon S, Seo J, MacDonald A H, Bernevig B A and Yazdani A 2014 Observation of Majorana fermions in ferromagnetic atomic chains on a superconductor Science 346 602–7

[240] Nandkishore R, Levitov L S and Chubukov A V 2012 Chiral superconductivity from repulsive interactions in doped graphene Nat. Phys. 8 158–63

[241] Blonder G E, Tinkham M and Klapwijk T M 1982 Transition from metallic to tunneling regimes in superconducting microconstrictions: excess current, charge imbalance and supercurrent conversion Phys. Rev. B 25 4515–32

[242] Law K T, Lee P A and Ng T K 2009 Majorana fermion induced resonant Andreev reflection Phys. Rev. Lett. 103 237001

[243] Flensberg K 2010 Tunneling characteristics of a chain of Majorana bound states Phys. Rev. B 82 180516

[244] Joselevich P A and Feigel’man V M 2013 Tunneling conductance due to a discrete spectrum of Andreev states New J. Phys. 15 055011

[245] Yamakage A and Sato M 2014 Interference of Majorana fermions in NS junctions Physica E 55 13–9

[246] Tanaka Y, Yokokawa T and Nagaosa N 2009 Manipulation of the Majorana fermion, Andreev reflection and Josephson current on topological insulators Phys. Rev. Lett. 103 107002

[247] Asano Y, Tanaka Y, Matsuda Y and Kashiwaya S 2003 A theoretical study of tunneling conductance in PrOs$_8$Sb$_{12}$ superconducting junctions Phys. Rev. B 68 184506

[248] Wang Z, Qi X-L and Zhang S-C 2011 Topological field theory and thermal responses of interacting topological superconductors Phys. Rev. B 84 014527

[249] Nomura K, Ryu S, Furusaki A and Nagaosa N 2012 Cross-correlated responses of topological superconductors and superfluids Phys. Rev. Lett. 108 026802

[250] Shiuzaki K and Fujimoto S 2013 Electromagnetic and thermal responses of Z topological insulators and superconductors in odd spatial dimensions Phys. Rev. Lett. 110 076804

[251] Chung S B, Horowitz J and Mason N 2013 Anomalous Josephson effect between even- and odd-frequency superconductors Phys. Rev. Lett. 110 076804

[252] Marra P, Citro R and Braggio A 2016 Signatures of topological phase transitions in Josephson current-phase discontinuities Phys. Rev. B 93 220507

[253] Yamakage A, Sato M, Yada K, Kashiwaya S and Tanaka Y 2013 Anomalous Josephson current in superconducting topological insulator Phys. Rev. B 87 100510

[254] Asano Y and Tanaka Y 2013 Majorana fermions and odd-frequency Cooper pairs in a normal-metal nanowire proximity-coupled to a topological superconductor Phys. Rev. B 87 104513

[255] Tanaka Y and Kashiwaya S 2004 Anomalous charge transport in triplet superconductor junctions Phys. Rev. B 70 012507

[256] Tanaka Y, Kashiwaya S and Yokoyama T 2005 Theory of enhanced proximity effect by midgap Andreev resonant state in diffusive normal-metal/triplet superconductor junctions Phys. Rev. B 71 094513

[257] Tanaka Y, Asano Y, Golubov A A and Kashiwaya S 2005 Anomalous features of the proximity effect in triplet superconductors Phys. Rev. B 72 140501

[258] Tanaka Y, Golubov A A, Kashiwaya S and Ueda M 2007 Anomalous Josephson effect between even- and odd-frequency superconductors Phys. Rev. Lett. 99 037005
Dr Masatoshi Sato was born in Shimane, Japan, in 1967. He obtained BSc (1991), MSc (1993), and PhD (1996) degrees from Kyoto University. He was a postdoc at Yukawa Institute for Theoretical Physics, Kyoto University (1996–1997) and at the University of Tokyo (1997–1999), and then became a research associate and later an assistant professor at Institute for Solid State Physics, the University of Tokyo (1999–2012). He became an associate professor at Nagoya University in 2012, and in 2015 he moved to Yukawa Institute for Theoretical Physics, Kyoto University as a full professor. For his seminal contributions in the field of topological superconductivity, he received ISSP Young Scientist Medal in 2010 and Superconductivity Science and Technology Award in 2013. He has been a core member of Topological Quantum Phenomena and Topological Materials Science Projects in Japan since 2010.

Dr Yoichi Ando was born in Tokyo, Japan, in 1964. He obtained BSc (1987), MSc (1989), and PhD (1994) degrees from the University of Tokyo. He was a postdoc at Bell Laboratories in the US (1994–1996), and then led a research group at Central Research Institute of Electric Power Industry in Tokyo (1996–2007), where he eventually became a department head. He was appointed to a full professor in 2007 at Osaka University, and in 2015 he moved to the University of Cologne as a W3 professor of experimental physics. According to the Web of Science, his h-index is currently 62. For his seminal contributions to the fields of high-temperature superconductivity and topological materials, he received Japan Society for the Promotion of Science (JSPS) Prize in 2006, Superconductivity Science and Technology Award in 2003 (for high-Tc cuprates) and in 2013 (for topological superconductors), Inoue Prize for Science in 2014, and Osaka Science Prize in 2014. He is one of the Highly Cited Researchers in Physics selected by Thomson Reuters in 2014, and he obtained the prestigious ERC Advanced Grant in 2017.