The background image is a scenic landscape. The foreground is filled with the surface of a body of water, showing numerous bright, shimmering reflections of sunlight. In the middle ground, a city skyline is visible across the water, featuring various buildings and a prominent church spire. The background consists of a bright blue sky filled with large, fluffy white clouds.

Unconventional Superconductors with Spin-Orbit Interaction

Tatsuki Hashimoto

UNCONVENTIONAL SUPERCONDUCTORS WITH SPIN- ORBIT INTERACTION

Tatsuki Hashimoto

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UNCONVENTIONAL SUPERCONDUCTORS WITH SPIN- ORBIT INTERACTION

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof.dr. T.T.M. Palstra,
on account of the decision of the graduation committee,
to be publicly defended
on the Wednesday, 7th of March 2018 at 14:45

by

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Chapter 1

Introduction

Superconductivity is one of the most fundamental phenomena in condensed matter physics. This thesis reveals in what manner superconductivity and its transport properties may be affected by a spin-orbit interaction, which is a relativistic interaction connecting a particle's spin with its motion. Topological materials and semiconductor nanowires are the most typical examples of materials having strong and peculiar spin-orbit interactions. In this chapter, the basic knowledge and historical progress of superconductivity and topological materials are simply summarized to facilitate understanding of the main topics in subsequent chapters.

1.1 Superconductivity

1.1.1 Discovery of superconductivity and its basic properties

Until the middle of the 19th century, oxygen, hydrogen, nitrogen, and helium were believed to be incapable of liquefaction; therefore they were called "permanent gases". With the advancements in cooling technology, scientist succeeded in liquefying oxygen, hydrogen, and nitrogen successively in the late 19th century. Finally, in 1908, H. Kamerlingh Onnes succeeded in liquefying helium here in the Netherlands. The boiling point of helium is 4K, and the discovery of such a low-temperature refrigerant led to the another great discovery of the century. In the beginning of the 20th century, questions were raised regarding the resistivity of metals at a very low temperature in the society of material science. At that time, there were two hypotheses: (i) the resistivity diverges on approaching 0K since the energy of electrons also approaches zero, (ii) the resistivity would disappear since the phonon, which disturbs the movement of electrons, can be weakened by decreasing the temperature. Under these circumstances, Kamerlingh Onnes started to measure the resistivity of metals using liquid helium. When he was measuring the resistivity of mercury, he discovered that it disappeared at approximately 4.2K. After repeated verifications, Kamerlingh Onnes finally announced the discovery of "superconductivity" in 1911 [1], more than a 100 years ago.

Presently, many elementary metals, except certain magnetic metals, plus various alloys and compounds exhibit superconductivity at low temperatures, and several basic properties of superconductivity have been well interpreted physically [2, 3]. One of the most fundamental properties of superconductivity is the disappearance of electrical resistivity. Since there is no resistivity, it is possible to accommodate large current, which in turn enables us to create a large magnetic field effectively. The magnetic field derived from the superconductor is used in the medical field for magnetic resonance imaging (MRI) to check the human body. Additionally, the construction of maglev train system using superconductor magnets has begun in Japan and by 2027 the train will commute between Tokyo and Nagoya (approximately 300km) in approximately 40 minutes. In 1933, German physicists W. Meissner and R. Ochsenfeld discovered that superconductors exclude the internal magnetic field, which is another important property of superconductivity called the "Meissner effect" [4]. In general, if a magnetic field is applied to a metal, it induces an electrical current inside

the metal, and the resulting current in turn generates an opposing magnetic field. If the metal is a perfect conductor like a superconductor, the induced and applied magnetic fields completely cancel each other, which gives the impression of excluding the internal magnetic field. This may occur in an ideal perfect conductor. However, in the case of the superconductivity, the internal magnetic field abruptly excluded with the superconducting transition, which is distinct from ideal perfect conductors.

Since the discovery of superconductivity, many scientists have endeavored to understand the reason behind the occurrence of such a unique state, and certain theories, e.g., the London theory [5] and Ginzburg-Landau theory [6], succeeded in interpreting some of the phenomena occurring in superconductors. However, it took very long to construct the full microscopic theory of superconductivity because the superconductivity is a completely quantum mechanical phenomena and had to await the development of the quantum theory. In 1957, J. Bardeen, L. Cooper, and R.J. Schrieffer proposed a fully microscopic theory explaining superconductivity, which is now called the Bardeen-Cooper-Schrieffer (BCS) theory [7]. The key idea of their theory is the pairing of two electrons (Cooper pair). In general, electrons have equal negative charges, which induces repulsive forces between them. However, BCS discovered that phonons can induce effective attraction forces between the electrons with opposite momenta. Once the electrons are paired, they are considered to be Bose particles, which can share the ground state with other particles (Bose-Einstein condensation).

1.1.2 Unconventional superconductivity

Superconductors can be characterized by the total spin S and angular momentum L of a Cooper pair. Regarding the spin state, there are two choices, $S = 0$ spin singlet or $S = 1$ spin triplet. For the spin-singlet state, the sign of a pair potential changes by exchanging the electrons forming a Cooper pair. On the other hand, the spin-triplet state does not change the sign. Cooper pairs form electrons with momentum $+k$ and $-k$, which means that if the momentum dependence of a Cooper pair is even (odd), exchanging the electrons forming a Cooper pair gives a plus (minus) sign. Therefore, the momentum dependence of a Cooper pair must be even (odd) for the spin-singlet (-triplet) state to satisfy the Fermi-Dirac statistics. In other word, the total angular momentum L should be even (odd) for spin-single (-triplet) state. Cooper pairs with angular momentum $L = 1, 2, 3$ are called p -wave, d -wave, f -wave, respectively. Thus far, most of the superconductors discovered are so called "conventional s -wave

Figure 1.1: (a) Schematic picture of relationship between the d -vector and the total spin of a Cooper pair S . (b) Spin configuration of a Cooper pair with $d \parallel z$. The spin structure of the Cooper pair is antiparallel (parallel) for spin-quantization axis along the z (x and y) direction

superconductors" where the superconducting gap is isotropic, $L = 0$ and the spin state is singlet. On the other hand, some materials display superconductivity with an anisotropic superconducting gap, non-zero total angular momentum or/and spin triplet pairing. Such superconductivity cannot be simply explained by the phonon mechanism of the BCS theory, and is called "unconventional superconductivity" [8,9]. ^3He (both BW and ABM state) [10] and Sr_2RuO_4 [11,12] are considered as spin-triplet p -wave superconductors. The typical example of a spin-singlet d -wave superconductor is a cuprate superconductor, which has demonstrated the highest T_c in the absence of pressure [13]. UPT_3 has shown some evidence of spin-triplet f -wave superconductivity [14]. Note that in the absence of inversion symmetry, these classifications are not valid, and spin-singlet and triplet states are mixed.

The pair potentials for spin-triplet pairings can be described with the three components of order parameter. To represent the three components of order parameter, it is convenient to use the d -vector notation because the d -vector behaves as a three-dimensional vector for rotations of spin space, thereby enabling us to understand the spin structure of a Cooper pair schematically [15]. The d -vector can be defined as

$$\hat{\Delta}(k) = \begin{pmatrix} \Delta_{\uparrow\uparrow}(k) & \Delta_{\uparrow\downarrow}(k) \\ \Delta_{\downarrow\uparrow}(k) & \Delta_{\downarrow\downarrow}(k) \end{pmatrix} = \begin{pmatrix} -d_x(k) + id_y(k) & d_z(k) \\ d_z(k) & d_x(k) + id_y(k) \end{pmatrix}. \quad (1.1)$$

where $\uparrow(\downarrow)$ indicates spin-up (down) for the z spin-quantized axis. The direction of the d -vector is perpendicular to the total spin of a Cooper pair as shown in Fig.1.1(a).

Figure 1.2: Energy dispersion of typical Andreev bound states in unconventional superconductors (topological superconductors): Blue regions (Grey lines or regions) indicate the bulk continuum level (edge or surface mode). (NCS: non-centrosymmetric, SC: superconductor)

In other words, if we see a Cooper pair with a spin axis parallel (perpendicular) to the d -vector, the spin configuration of the Cooper pair is anti-parallel (parallel). For example, $d \parallel z$ case is shown in Fig.1.1(b). If we see this Cooper pair with $d \parallel z$ with the spin axis parallel to z (x or y), the spin configuration of the Cooper pair is antiparallel (parallel). The d -vector of Sr_2RuO_4 is parallel to the c axis of the crystal [11, 12].

1.1.3 Andreev bound state

An outstanding feature of the unconventional superconductor is the existence of the mid-gap surface (or edge) state called Andreev bound state (ABS). Depending on the symmetry of a pair potential and direction of surface one makes, the dispersion of ABS takes various forms. The energy dispersion of some typical ABSs are shown in Fig.1.2. Sr_2RuO_4 is believed to be a chiral p -wave state that breaks time-reversal symmetry. In this case, there can be a single ABS connecting the upper and lower bulk continuum levels (chiral edge mode) [16, 17]. In the absence of inversion symmetry, spin-singlet or triplet is no longer a conserved quantity, leading to the mixing of states. It is known that if the spin-triplet component is dominant, some non-centrosymmetric superconductors with Rashba spin-orbit interactions present a helical edge mode [18], as shown in Fig.1.2(b). ^3He BW phase is a spin-triplet, odd-parity superfluid. This is a three-dimensional system; if one makes a surface, it has a cone shape ABS within the superconducting gap. High- T_c cuprate superconductors are two dimensional electronic systems and their pairing symmetry is d -wave. In this

case, if one makes an edge, a flat edge mode appears between the bulk point nodes, as shown in Fig.1.2(d) [19].

Thus far, whether a system has ABS or not has been discussed considering the sign change of a pair potential on a Fermi surface. However, in the last decade, it has been revealed that a topological number, which can be calculated with a wave function in the momentum space, can predict the existence of an ABS. We shall discuss this in the following section.

1.2 Topological materials

Consider a single electron Hamiltonian $\hat{H}$ and a Schrödinger equation $\hat{H}\Psi = E\Psi$. Solving the equation gives energy eigenvalues E and their corresponding eigenvectors Ψ . A common classification of the electronic states of materials is based their energy eigenvalues (energy band structures). If the energy band is fully occupied, electrons cannot be excited by a bias voltage and electronic current does not flow. However, if the energy band is partially occupied, the electrons can be excited and current flows in the material. The materials in the former case are metals and those in the latter case are insulators, and intermediate materials are called semiconductors.

Recently, a new classification based on wave function is attracting great research interest. This classification is in terms of the shape (topology) of some quantity calculated from the wave function in momentum space and is applicable to materials with energy gaps similar to insulators and superconductors. Materials with non-trivial topological structures (non-zero topological numbers) are now called topological materials. A fundamental physical consequences of non-trivial topology is the bound state between materials (or vacuum) with different topological numbers. In the case of a topological insulator, if we make a surface, it gives a spin-polarized surface state, which is applicable to future spintronics devices. In the following, the basic feature of topological materials and superconductivities realized in topological materials are summarized.

1.2.1 Quantum Hall insulator and topological insulator

Quantum Hall insulator (QHI) is the first example of a topological material. The QHI is realized by applying a magnetic field to a two-dimensional electronic system. In the QHI, the Hall conductivity is given by $\sigma_{xy} = Ne^2/h$, where e is the electronic charge and h is the Planck's constant, and more importantly, N is a integer number, i.e., the Hall conductance of the QHI is quantized. This fact was experimentally found by K. von Klitzing *et al* in 1980 [20]. In 1982, D.J.Thouless, M. Kohmoto, M.P. Nightingale and M. den Nijs calculated the Hall conductivity by using Kubo formula, and found that the quantization of the Hall conductivity can be expressed using a quantity cal-

culated by wave function as [21,22]

$$N = \sum_n \int_{\text{BZ}} \frac{d^2\mathbf{k}}{2\pi} \left(\frac{\partial a_{n,y}}{\partial k_x} - \frac{\partial a_{n,x}}{\partial k_y} \right), \quad (1.2)$$

$$\mathbf{a}_n(\mathbf{k}) = -i \langle u_{nk} | \frac{\partial}{\partial \mathbf{k}} | u_{nk} \rangle \quad (1.3)$$

Here, $\langle u_{nk} |$ is the wave function for the n th band and $\int_{\text{BZ}}$ indicates the integral for the entire Brillouin zone. $\mathbf{a}_n(\mathbf{k})$ is the Berry curvature [23], and if this quantity has a singularity in the Brillouin zone, N becomes non-zero. This situation is indeed a twisted state (topologically non trivial state) and N is the topological number representing this situation. In the QHI, this topological number N is named TKNN number after the people who discovered this quantity.

In 1988, F.D.M. Haldane showed that quantum Hall effect occurs without Landau levels in a honeycomb lattice that has a periodic magnetic flux at K and K' site [24]. However, since it is difficult to manipulate magnetic flux in an atomic scale, the quantum Hall effect in the proposed system has not been realized yet. Thereafter, in 2005, C.L. Kane and E.J. Mele predicted that spin-orbit interaction plays the same role as magnetic flux in the Haldane model, giving rise to a similar effect [25,26]. One of most interesting feature of this system is that the quantum Hall effect occurs for the spin current [quantum spin Hall effect(QSHE)] instead of charge current because of the presence of time-reversal symmetry. Further, Kane and Mele have shown that the QSHE is associated with the Z_2 topological number that can be defined under the time-reversal symmetry. Note that although Kane and Mele first considered the QSHE in graphene, it has not been observed in this material since the spin-orbit interaction of graphene is too small to open a gap. However, in 2006, B.A. Bernevig, T.L. Hughes and S.C. Zhang predicted that QSHE occurs in the HgTe/CdTe quantum well [27]. Then, in 2007, M. König *et. al.* succeeded in observing the quantization of Hall conductivity in the system [28]. In the same year, J.E. Moore and L. Balents [29], L. Fu *et. al.* [30], and R. Roy [31] showed that Z_2 topological number can be also defined in three dimensional systems. In the following year, D. Hsieh succeeded in directly observing the surface Dirac cone by angle resolved photo emission spectroscopy (ARPES) measurements in $\text{Bi}_{1-x}\text{Sb}_x$ [32]. In three-dimensional materials, multiple channels on the two-dimensional surface prohibit the quantization of the Hall conductivity. Therefore, the three dimensional materials with non-zero Z_2 number are not called quantum spin Hall insulators (QSHIs) but "topological insulators" instead. Note that the term "topological insulator" became popular recently. Thus

class	TRS	PHS	CS	$d = 1$	2	3	$d = 1$	2	3
A	0	0	0	0	Z	0	-	IQHI	-
AIII	0	0	1	Z	0	Z	?	-	?
AI	+1	0	0	0	0	0	-	-	-
BDI	+1	+1	1	Z	0	0	Polyacetylene	-	-
D	0	+1	0	Z_2	Z	0	Majorana wire	Sr_2RuO_4	-
DIII	-1	+1	1	Z_2	Z_2	Z	?	?	$^3He(BW)$, CBS
AII	-1	0	0	0	Z_2	Z_2	-	2DTI	3DTI
CII	-1	-1	1	2Z	0	Z_2	?	-	?
C	0	-1	0	0	2Z	0	-	?	-
CI	+1	-1	1	0	0	2Z	-	-	?

Table 1.1: Topological periodic table [36–38]: Ten symmetry classes of single-electron Hamiltonian for time-reversal symmetry (TRS), particle-hole symmetry (PHS) and chiral symmetry (CS) are summarized. The first column shows the 10 classes. In the second to fourth column, the absence of the symmetries is denoted with "0", and the presence of the symmetries is denoted with "+1" or "-1", depending on the sign of the square of the symmetry operators. The fifth to seventh column show the space dimension d . The last three column show the examples that have the non-trivial topological invariant in the symmetry class. "-" stands for the class without topological phase and "?" stands for the class without any specific examples.

the two dimensional QSHI is also sometimes called a two-dimensional topological insulator.

After the discovery of $Bi_{1-x}Sb_x$, various topological insulators have been discovered, especially among Bi compounds [33]. According to Y. Ando's review paper in 2013, more the 30 materials had been already confirmed as topological insulators mainly via ARPES measurements [34]. Recently, it has been revealed that some half Heusler compounds can also be in topological insulating states by applying the strain [35] and topological insulators in new compound are being discovered continuously to date.

Z_2 topological number of the topological insulator can be defined only when time-reversal symmetry is present. This is one of the main differences between the QHI and topological insulator. In other word, the discovery of Z_2 topological insulator means that the argument on the topological structure of the wave function is extended to the case with a symmetry. Consequently, the last decade has witnessed the extension to other symmetries like particle-hole symmetry and crystalline symmetry. The classification of the Hamiltonian according to symmetry has been well discussed in

the context of random matrix theory for a disordered electronic system [39]. For a free electron fermionic system, there are ten classes under the time-reversal symmetry, particle-hole symmetry, and chiral symmetry. A.P. Schnyder *et. al.* [36, 37] and A. Kitaev [38] have summarized the possible topological phases for the ten classes, respectively, which is shown in Table 1.1. The details of the table are shown in its caption. QHI and topological insulator belong to class A and AII, respectively.

1.2.2 Topological superconductivity and Majorana fermion

The topological argument is applicable to the superconducting state since quasiparticle spectra have energy gaps. Superconductors that have a non-zero topological number are now called topological superconductors, having surface ABS (SABS) within the superconducting gap (See Fig.1.2). The research on the topological phase for superconductors and that for insulators has developed in different contexts separately. M. Stone [40] and G.E. Volovik [41] have studied the topological structure in ^3He (though it is a superfluid) since 1980s. In the 1990s, J. Goryo and K Ishikawa revealed that Hall conductance for ^3He [42] and PT violating superconductors [43] can be described by the language of topological number. In the 2000s, N. Reed and D. Green showed that zero-energy edge states appear in the two dimensional spinless chiral p -wave superconductor owing to their non-trivial topological structure [44]. Thus far, the formation of SABS has been interpreted by solving the scattering process at the interface of different materials. However, it has been revealed that the topological invariant calculated with the bulk wave function can predict the existence of SABSs without considering scattering problems. Moreover, as summarized in the Table 1.1, the topological superconductors can be considered as topological phases that can be defined under the particle-hole symmetry, which is an essential symmetry for superconductivity, in stead of/ in addition to the time-reversal symmetry. The interpretation of the existence of SABSs using a topological number is the recent progress, and the topological periodic table connects the study of the topological phases in normal state and superconducting state. Note that, hereafter, in this thesis, we use the term "topological material" for materials with non-trivial topological invariant in the normal state and "topological superconductor" for superconductors with non-trivial topology.

Some superconductors like high T_c cuprate superconductors and heavy-fermion compound superconductors have both bulk gapless regions on the Fermi surface

(point nodes or line nodes) and surface states [45]. In this case, it is not possible to characterize the surface state with a global topological invariant defined in the entire Brillouin zone. However, by introducing topological numbers in lower dimensional subspaces, we can characterize the surface state. Consider a two-dimensional d_{xy} superconductor as an example. If one makes an edge for x direction, the SABS appears between the point nodes, as shown in Fig.1.2 (b). If we choose certain k_y which does not cross the point nodes for any k_x , the BdG Hamiltonian for this line belongs to the symmetry class AII since this system only has chiral symmetry. Thus we can define Z topological number (winding number) for this one-dimensional system. Between the point nodes, the winding number which is calculated by the path integral on the one-dimensional line, is non-zero, which is corresponded to the existence of the zero-energy flat surface band. In addition, the path integral on the line for fixed k_y is equivalent to that along the contour surrounding the nodal point. Thus, the nodal point itself can also be considered as a topological object.

A particle that is its own antiparticle is called the Majorana fermion, first proposed by E. Majorana [46]. Although the Majorana fermion is considered as the candidate of Neutrino and dark matter, there has been no clear experimental evidence to support the proposal. However, there have been proposals to realize the Majorana fermion in condensed matter. Moreover, it has been revealed that Majorana fermions obey non-Abelian statistics and can be used for fault tolerant quantum computation, attracting great research interest [47]. Bogoliubov quasiparticles in superconductors are described by the superposition of electrons and holes. In the superconducting state, electronic charge is no longer a conserved quantity, so the Bogoliubov quasiparticle can take any arbitrary charge, including a chargeless state. Therefore, superconductors are considered as promising platforms to realize the Majorana fermion as a quasiparticle (Majorana quasi particle). To realize the Majorana state, electron and hole components should be completely equal, which can be achieved at the middle of the superconducting gap $E = 0$ as shown in Fig.1.2. The conventional s -wave superconductors cannot reach this state because of the superconducting gap. However, SABSs in topological superconductors can access this state because the surface states connect the upper and lower bands, passing through $E = 0$. In addition, the vortex core state in a topological superconductor can also be a Majorana state. It is also possible to realize the Majorana state using s -wave superconductors by combining with other materials. M. Sato has already predicted that the Majorana quasi-particle can be realized using conventional superconductors in 2003 [48]. He has shown that the Majorana quasiparticles appear in the vortex core of a superconducting two dimensional

Dirac system. More recently, in 2009, L. Fu and C.L. Kane have shown that the Majorana quasi-particle can be realized in a more specific system: a topological insulator with proximity induced s -wave superconductivity [49]. Moreover, superconducting proximitized nanowire with strong spin-orbit interaction under a magnetic field can also host Majorana quasi-particles at the edge [50–52], which is experimentally observed as a peak structure in tunneling spectra [53].

1.2.3 Topological semimetal

Similar to the nodal superconductors, it is possible to characterize the bulk gapless point in the normal state with a certain topological number. Semimetals with non-zero topological number are now called topological semimetals. In topological semimetals, a non-trivial topological structure leads to the exotic surface states connecting bulk gapless points. In the following, we see Weyl semimetals that have doubly degenerate gapless points (Weyl points) and Dirac semimetals that have four-fold degenerate gapless points (Dirac points). Note that although there are semimetals that have gapless lines (nodal line semimetals), we do not discuss in details of these materials in this thesis.

Weyl semimetal

Weyl semimetals have non-degenerate cone-shaped dispersion (Weyl cone), and doubly degenerate gapless points (Weyl points) [54,55]. When both time-reversal symmetry and inversion symmetry are present, the energy band must be doubly degenerate. Therefore, either time-reversal symmetry or inversion symmetry must be broken to realize the Weyl semimetal.

An electronic state around a three-dimensional Weyl point is given by

$$\hat{H}_w^{3D} = -\mu\hat{\sigma}_0 \pm v(\hat{\mathbf{k}} - \hat{\mathbf{k}}_0) \cdot \hat{\boldsymbol{\sigma}}, \quad (1.4)$$

where μ is the chemical potential, v is the group velocity, $\hat{\sigma}$ is the Pauli matrix for the spin degree of freedom. An interesting feature of this system is that the Weyl point cannot be removed by changing any parameter, μ , $\mathbf{k}_0$, v . Changing the parameter μ ($\mathbf{k}_0$), or we can also say that adding a term parallel to σ_0 ($\hat{\sigma}$), means changing the energy (momentum) of the Weyl point. Changing v simply means changing the slope

Figure 1.3: Schematic picture of a Weyl semimetal in momentum space.

of the Weyl cone. On the other hand, consider a two dimensional Weyl Hamiltonian

$$\hat{H}_w^{2D} = -\mu\hat{\sigma}_0 \pm v(k_x\sigma_x + k_y\sigma_y). \quad (1.5)$$

Here we set $k_0 = 0$ for brevity. We can naturally add an additional term parallel to σ_z , e.g. $m\sigma_z$, where m is the momentum independent, breaking the gapless Weyl points. This argument is also true for a one dimensional system, hence the stable Weyl point can exist only in a three-dimensional system.

The three dimensional Weyl point is the topological object. If we look at the spin expectation value $\hat{S} = \langle \psi | \hat{\sigma} | \psi \rangle$ around the k_0 , the spin vectors are pointing outwards, having a hedgehog structure, as shown in Fig.1.3. On the other hand, the spin vectors around the $-k_0$ are pointing inwards. These structure can be removed only when the two points are merged. Indeed, the Chern numbers calculated on the sphere surrounding the Weyl points k_0 and $-k_0$ are +1 and -1, respectively. Corresponding to the non-trivial topological nature, Weyl semimetals have a surface state connecting the Weyl points with opposite Chern number as shown in Fig.1.3.

For the Weyl Hamiltonian Eq.1.4, we can add a term $v'(\mathbf{k} - \mathbf{k}_0)\sigma_0$. This term does not open the Weyl point; however, the Weyl cones can be tilted. If $v' > v$, the Weyl

Figure 1.4: Schematic picture of structural change from the normal insulator to the topological insulator or topological Dirac semimetal

points can be the touching point of electron pockets and hole pockets for $\mu = 0$; Weyl semimetals with this type of Weyl cone are now called type II Weyl semimetals [56].

Dirac semimetal

Dirac semimetals have doubly degenerate cone shaped energy dispersion (Dirac cone), and a four-fold degenerate band touching point (Dirac point). In the following, we only focus on the three-dimensional system and do not mention two-dimensional systems like graphene. In the broad sense, there are two types of Dirac semimetals, i.e. accidental ones and symmetry protected ones. The former type appears just on the topological phase transition point between a TI and a normal insulator [55,57–59]. In this case, the bulk Dirac cones are easily gapped out. This type of Dirac semimetal is realized in $\text{Bi}_{1-x}\text{Sb}_x$ [60,61] and $\text{Pd}_{1-x}\text{Sn}_x\text{Te}$ [58,62] by changing the composition x . Consider two parabolic bands with two-fold degeneracy, $vk^2 + m$ and $-vk^2 - m$. In the usual case, if the two bands cross each other $m < 0$, the touching point opens up an energy gap because of the level repulsion. However, if the band touching occurs on the 3, 4 or 6 fold rotational symmetric axis, the band touching point can remain

gapless [63,64] as schematically shown in Fig.1.4. This is because the states forming the gapless points belong to the different subspaces of the rotational symmetry. In this case, a topological number can be defined for the rotational symmetry subspace and these types of Dirac semimetals with non-zero topological numbers are called topological Dirac semimetals. Similar to the Weyl semimetals, topological Dirac semimetals have a surface state connecting two Dirac points. The Dirac points are formed by the band crossing. Therefore, the topological Dirac semimetals have two Dirac points in most cases. Note that it is also possible to use non-symmorphic symmetry (e.g. glide and screw symmetry) to characterize the topological Dirac point. In this case, a single Dirac cone appears at the time-reversal symmetric point and the surface state is absent.

To describe the four-fold degenerate Dirac point, model Hamiltonian should be at least a 4×4 matrix, meaning that it is necessary to take into account the orbital (pseudo spin) degree of freedom in addition to the spin degree of freedom. Dirac semimetals can be further classified into three types with respect to the inversion symmetry of this orbital degree of freedom [63]. The inversion operators for the three cases are given by $P = \sigma_0, \sigma_x, \sigma_z$, where the σ denotes the orbital degree of freedom. Each type of Dirac semimetals gives different spin or orbital structure on the Fermi surface, leading to unique intrinsic superconductivity and transport properties as seen in Chap. 2.

Cd_3As_2 [65–69] and Na_3Bi [70–72] are the $P = \sigma_z$ type topological Dirac semimetals. Similar to Weyl semimetals, there are type II Dirac semimetals with tilted Dirac cones; the following materials are predicted to be this type of Dirac semimetals, PdTe_2 [73], PtSe_2 [73], VAl_3 [74], and KMgBi [75]. Furthermore, ab initio calculations have predicted that $\theta\text{-TaN}$ [76], ZrTe [77], and RERh_6Ge_4 ($\text{RE}=\text{Y,La,Lu}$) [78] have triple degenerate gapless points (triple point fermion), and CoSi [79] has a six-fold degenerate point. In addition, it is predicted that Ba_3SnO has multiple Dirac points with different energies near the Fermi level [80].

1.2.4 Superconductivity in topological materials

Topological materials have characteristic spin or orbital textures on the Fermi surface. Recently, it has been revealed that the characteristic spin or orbital texture can support unconventional superconductivity. Now, topological materials are being considered

Figure 1.5: Spin structure on Fermi surfaces for (a) inversion symmetric (b) time-reversal symmetric Weyl semimetals.

as promising platforms to find unconventional superconductivity. For example, we will see the superconductivity in Weyl semimetals below; the superconductivity in Dirac semimetals is discussed in Chap.2 of this thesis. Moreover, the superconducting topological materials that have been found so far are summarized below.

superconductivity in Weyl semimetals

Weyl semimetals are materials that host non-degenerate Weyl cones. Different from the Dirac semimetals, Weyl cones are non-degenerate, which means that, at least, either time-reversal symmetry or inversion symmetry is broken. If both symmetries are broken, Cooper pairs cannot form between the electron with k and $-k$. This situation is not natural for superconductivity based on the BCS theory. Therefore, we only consider the cases where either time-reversal symmetry or inversion symmetry is broken, and the other symmetry is preserved. The following discussion is based on Sato's argument in Ref. [81].

In a periodic system, the total topological charge must be canceled (the Nilsen-Ninomiya theorem), i.e. the number of the Weyl point should be even, and half of the Weyl points must have positive charges while the other half must have negative charges. In the case of inversion symmetric Weyl semimetals, the least number of the Weyl points is two. On the other hand, in the case of time-reversal symmetric Weyl semimetals, that number is four. Once the carrier is doped, each Weyl semimetal has the Fermi surface and characteristic spin texture on it as shown in Fig.1.5. If we look at the spin structure at $\mathbf{k}$ and $-\mathbf{k}$, the spin configuration is always parallel (antiparallel) for the inversion symmetric (time-reversal symmetric) Weyl semimetals, as shown with the dotted circles and double head arrows in Fig.1.5. In time-reversal symmetric Weyl semimetals, the spin structure does not restrict the spin state (singlet or triplet). However, in the case of inversion symmetric Weyl semimetals, the spin-singlet channel (antiparallel-spin channel) is prohibited. For this reason, we can naturally expect the realization of spin triplet state in inversion symmetric Weyl semimetals.

Hereafter, we will focus on the superconductivity in inversion symmetric Weyl semimetals. A minimal model for an inversion symmetric Weyl semimetal is given by

$$H_W(\mathbf{k}) = v(\mathbf{k}\hat{\tau}_z - \mathbf{k}\hat{\tau}_0)\hat{s} - \mu\hat{\tau}_0, \quad (1.6)$$

where $\hat{\tau}_i$ and $\hat{s}_i$ ($i = 0, x, y, z$) are the Pauli matrices, respectively, and μ is a chemical potential. The inversion operation of this system is $P = \tau_x$. The BdG Hamiltonian is given by

$$\hat{H}_{\text{BdG}} = \begin{pmatrix} \hat{H}_W(\mathbf{k}) & \hat{\Delta} \\ \hat{\Delta}^\dagger & -\hat{H}_W^*(-\mathbf{k}) \end{pmatrix}. \quad (1.7)$$

For this system, we can consider six types of momentum independent pairings as

$$\Delta_0\hat{\tau}_0\hat{s}_0, \Delta_0\hat{\tau}_z\hat{s}_0, \Delta_0\hat{\tau}_x\hat{s}_0, \Delta_0\hat{\tau}_y\hat{s}_x, \Delta_0\hat{\tau}_y\hat{s}_y, \Delta_0\hat{\tau}_y\hat{s}_z \quad (1.8)$$

The detailed reasoning behind the possibility six pairings is shown in the main part, Chap.2. The first 3 pairings are spin-singlet pairings, and the latter 3 pairings are spin-triplet pairings with the d -vector oriented to the x , y and z direction, respectively. As mentioned above, if a Cooper pair does not have the center of mass, a spin-singlet state does not give rise to the superconducting gap because of the mismatch of the

spin structure. In the case of spin-triplet pairing, the spin structure of a Cooper pair depends on the space direction. As mentioned in the previous section, if we see a Cooper pair with the direction parallel to the d -vector, the spin configuration of the Cooper pair is anti-parallel. Whereas, if we see a Cooper pair with the direction normal to the d -vector, the spin configuration of the Cooper pair is parallel. For example, we focus on the possible pairing $\hat{\Delta} = \Delta_0 \hat{\tau}_y \hat{s}_z$. In this case, the d -vector is parallel to the z direction, i.e. if we look at this pairing with z (x or y) spin quantized axis, the spin configuration is anti-parallel (parallel). On the other hand, the spin structure of the Weyl semimetal on the z axis is fixed to the z direction and the spin configuration of electrons at $+k_z$ and $-k_z$ is parallel, which is conflicting to the spin structure of the Cooper pair. Therefore, the resulting superconducting gap has point node on the z axis in this case. On the Fermi surface of the Weyl semimetal, there must be points where the spin is oriented either x , y or z direction. Therefore, even if we choose other spin-triplet pairings i.e. $\Delta_0 \hat{\tau}_y \hat{s}_x$ or $\Delta_0 \hat{\tau}_y \hat{s}_y$, they also have point nodes on the Fermi surfaces. Here, we schematically discuss the superconducting gap structure of the intrinsic superconducting Weyl semimetals. It has been also shown that the superconducting gap structure can be interpreted in a mathematically rigid manner by introducing the topological invariant of this symmetry class [81].

Intrinsic superconductivity in Weyl semimetals has been theoretically studied by several groups thus far. G.Y. Cho *et. al* [82] and H. Wei *et. al.* [83] have discussed whether the spin-triplet state with point node or fully-gapped spin-singlet Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state is stable in the inversion-symmetric Weyl semimetal, where the authors use the simplest effective model (2×2 Weyl Hamiltonian). They have shown that the fully-gapped spin-singlet FFLO state is energetically favored. G. Bednik *et. al.* have also studied the spin-triplet vs FFLO state in a Weyl semimetal using a model for a Weyl semimetal realized in a topological insulator/normal insulator hetero structure [84]. In contrast to Ref. [82], their results have shown that the nodal spin-triplet state is more stable than the fully-gapped spin-singlet FFLO state. Remarkably, B. Lu *et. al.* have revealed that the superconducting Weyl semimetals host zero-energy crossed ABS, which gives rise to the pronounced zero-bias conductance peak in the tunneling spectra [85]. In addition, M. Alidoust *et. al.* have recently studied superconductivity in type II Weyl semimetals, showing that the superconducting gap structure and the SABS can be dramatically changed associated with the structural transition from the type I state to the type II state [86]. The above studies are on inversion-symmetric Weyl semimetals. The possible superconductivity in time-reversal symmetric Weyl semimetals are also studied in Ref. [87].

Type	Material	Topo. superconductivity	remark	Ref.
TI	Bi_2Se_3	anomalous H_{c2}	under pressure (11GPa-)	[88]
TI	$\text{Cu}_x\text{Bi}_2\text{Se}_3$	nematic SC [89–91]	most promising nematic SC	[92]
TI	$\text{Sr}_x\text{Bi}_2\text{Se}_3$	nematic SC? [93]		[94]
TI	$\text{Nb}_x\text{Bi}_2\text{Se}_3$	nematic SC? [95,96]	TRS broken? [97]	[97]
TI	$\text{Cu}_x(\text{PdSe})_5(\text{Bi}_2\text{Se}_3)_6$	nodal?(C_{6I}) [98]	2D Fermi surf. [99]	[98]
TI	Bi_2Te_3	no report	under pressure (3GPa-)	[100]
TI	$\text{Pd}_x\text{Bi}_2\text{Te}_3$	no report		[101]
TI	$\text{Tl}_x\text{Bi}_2\text{Te}_3$	no report	hole pockets	[102]
TI	Sb_2Te_3	no report	under pressure (4GPa-)	[103]
TI	Tl_5Te_3	no report	Sn doping	[104]
TI	$\alpha\text{-PdBi}$	nodal?(T_1^{-1}) [105]	NCS	[106]
TI	PdBi_2	no report	structural isomers(α, β)	[107]
TI	$\text{APtBi}(A=\text{Y},\text{Lu},\text{La})$	$A=\text{Y}$:ZBCP observed [108]	THH,NCS	[109–111]
TI	BPdBi ($B=\text{Y},\text{Lu},\text{Ho},\text{Er},\text{Tm},\text{Ce}$)	no report	THH,NCS	[112,113] [114–116]
TCI	$\text{Sn}_{1-x}\text{In}_x\text{Te}$	ZBCP observed [117]	Pd doping	[118]
DS	Cd_3As_2	ZBCP observed [119,120]	under pressure (8.5GPa-)	[119–121]
DS	Au_2Pb	ZBCP observed [122]		[123]
DS	PdTe_2	no report	TypeII DS, TypeI SC	[124]
DS	$\text{Sr}_{3-x}\text{SnO}$	no report		[125]
DS	BaMnBi_2	no report	under pressure(2.6GPa-)	[126]
WS	TaAs	ZBCP observed [127]	tip pressure induced SC [127]	[127]
WS	MoTe_2	no report	pressure enhances T_c [128,129]	[128,129]
WS	WTe_2	no report	under pressure (10.5GPa-)	[130]
NLS	PdTaSe_2	no report	NCS	[131]

Table 1.2: Topological materials that exhibit superconductivity: The right-most column shows references that report the superconductivity in the materials. (TI: topological insulator, TCI: topological crystalline insulator, DS: Dirac semimetal, WS: Weyl semimetal, NLS: nodal line semimetal, SC: superconductor(ivity), ZBCP: zero-bias-conductance peak, TRS: time reversal symmetry, NCS: non-centrosymmetric)

1.2.5 Material realization

Thus far, it has been reported that approximately twenty topological materials (and their similar compounds) possess superconducting phases. Remarkably, there are also some reports that indicate the realization of topological superconductivity. Table 1.2 shows topological materials that exhibit intrinsic superconductivity. The materials summarized in this table have bulk Fermi surfaces naturally or by carrier doping, and superconductivity that realizes only in the surface has not yet been reported.

Although there are many studies concerning superconductivity proximity induced in topological surface state, here we focus only on the intrinsic superconductivity in topological materials. The right-most column shows the references that reported the superconductivity in materials (zero resistivity and Meissner effect). The study on superconducting topological materials is a new topic that began in 2010. Therefore, superconductivity in some "topological materials" had already been discovered in different contexts before 2010. The first example of the superconducting topological material is copper doped topological insulator Bi_2Se_3 ($\text{Cu}_x\text{Bi}_2\text{Se}_3$) [92], which is now considered as the most promising candidate for the new type of topological superconductor. S. Sasaki *et.al.* first observed the zero-bias conductance peak (ZBCP) for the (111) surface by point contact spectroscopy, which suggests the existence of SABS [89]. There are two more papers reporting the observation of the ZBCP [132, 133]. However, dI/dV curve measured by scanning tunneling microscope experiments show simple U-shaped spectra that can be seen in conventional s -wave superconductor, contradicting the results of point contact measurements [134]. To solve this contradiction, Mizushima *et. al.* calculated the surface density of state self consistently where the parity mixing of pair potential at the surface is taken into account [135]. As a result, they clarified that even if the conventional s -wave pairing is realized, the anomalous spin-orbit interaction in the TI induces additional coherence peaks in the surface density of state spectrum. They also showed that the simple U-shaped spectrum can be realized even in the case of topological superconductivity if the material has two-dimensional Fermi surface. In fact, the dimensional change of the Fermi surface has been observed [136]. Therefore, it is now believed that the sample dependent Fermi surface may cause a contradiction of the surface experiments. Most recently, three bulk physical property measurements were performed to reveal the pairing symmetry in $\text{Cu}_x\text{Bi}_2\text{Se}_3$. They are spin susceptibility measurements, upper-critical field measurements, and specific heat measurements in the rotational magnetic field. All the experiments show the two-fold rotational symmetric superconducting gap around the c axis, which breaks the crystalline three fold rotational symmetry [90, 91]. In the weak correlation regime, this state can be only explained by one of the topological superconducting states [91, 137]. Since the system spontaneously breaks the three-fold rotational symmetry associated with the superconducting phase transition, and has a two-fold rotational symmetry, this superconductivity is now referred to as "nematic superconductivity". Moreover, besides the Cu doped case, upper critical field measurements indicate the nematic state in the Sr or Nb doped cases as well [94–96]

Similarly, compound topological insulators $\text{Cu}_x(\text{PdSe})_5(\text{Bi}_2\text{Se}_3)_6$ can also be in a superconducting state below $T_c = 2.85\text{K}$ [98]. ARPES measurements have shown that both bulk and surface bands cross the Fermi energy [99]. In addition, the temperature dependence of the specific heat shows linear behavior near $T = 0$, indicating the existence of line node [98]. Ideally, Bi_2Se_3 and Bi_2Te_3 are topological insulators, but in real materials, the Fermi level crosses the bulk band, being the metallic state. It has been reported that both materials can be in superconducting states under pressure [88, 100]. In particular, the upper critical field of Bi_2Se_3 cannot be interpreted by the conventional s -wave superconducting state, suggesting the possibility of some unconventional (topological) superconductivity [88]. In addition, Bi_2Te_3 can also be in a superconducting state by doping Pd or Tl instead of applying pressure [101, 102]. Superconductivity in Tl_5Te_3 has been also observed [104]. This material has surface Dirac cone stemming from the topologically non-trivial band structure. However, the band structure near the Fermi level is quite complicated. This implies that one cannot use the simple effective model around the Γ point to investigate superconductivity. Therefore, there is no theoretical study on the superconductivity of this material to date.

Bi-Pd alloy, α -PdBi and PdBi_2 have a non-zero Z_2 number and the resulting surface state [138, 139], and can be in a superconducting state [106, 107]. α -PdBi is a non-centrosymmetric material (NCS). In the NCS superconductor, spin-singlet pairing and spin triplet pairing can coexist. In general, if the triplet component is dominant, the topological superconducting state can be realized [18]. For this reason, α -PdBi is considered to be a possible candidate for topological superconductor. However, only the temperature dependence of T_1^{-1} by NMR measurements indicates the existence of nodes on the superconducting gap [105], and no additional clear evidence of topological superconductivity has reported yet. PdBi has structural isomers, α phase and β phase, and in particular superconductivity in β phase has been studied in depth. The experimental results of tunneling spectroscopy by STM/STS [140], that by point contact [141], and μ -SR [142] have indicated a fully gapped superconducting state. Moreover, the tunneling spectra (both high and low transmissivity experiments) have suggested the absence of SABS [140, 141]. Different from other Pd-Bi alloys, α -PdBi₂ has a surface state at the Fermi level. However, experimental results of London penetration depth have demonstrated conventional s -wave like behavior [143].

Half Heusler compounds APtBi ($A=\text{Y, Lu, La}$) and BPdBi ($B=\text{Y, Lu, Ho, Er, Tm, Ce}$) have a bulk gapless point at Γ point in the Brillouin zone. However, by breaking the cu-

bic symmetry by applying strain for instance, the bulk gapless point opens the gap, having the surface gapless Dirac cone. The half Heusler compound mentioned above also enters the superconducting state. In particular, for YPtBi, there are several experimental results indicating the realization of unconventional superconductivity. The temperature dependence of the upper critical field can be interpreted well by nodal superconductivity [144]. Correspondingly, the temperature dependence of the London penetration depth has indicated the existence of the line node [108]. Furthermore, point contact spectra have shown the zero-bias conductance peak, which may originate from the SABS [108].

Topological crystalline insulator In doped SnTe ($\text{Sn}_{1-x}\text{In}_x\text{Te}$) can also be in superconducting state [118]. A zero-bias conductance peak has also been observed at (001) surface in this material [117]. If one makes the (001) surface, two Fermi surfaces are projected onto the same place in the surface Brillouin zone. Theoretical calculations have shown that this Fermi surface overlap gives rise to a unique SABS provided a fully-gapped topological superconducting state is realized [145].

Next, we see the Dirac semimetals that exhibit superconductivity. Cd_3As_2 comes into superconducting state at $T_c = 2.0$ under the pressure of 8.5 GPa. [121]. Two groups have observed the ZBCP for (112) natural cleavage surface, suggesting topological superconductivity [119, 120]. Superconductivity in Cd_3As_2 is one of the main topic of this thesis, the details of which are shown in Chap.2. Au_2Pb exhibits superconductivity at $T_c = 1.2\text{K}$ [123]. This material has also shown the ZBCP in the point contact spectra [122]. The above two Dirac semimetals are type I Dirac semimetals. However, type II Dirac semimetal PdTe_2 , which has tilted Dirac cones, has also shown superconductivity [124]. Interestingly, PdTe_2 is the first example of superconducting type-II Dirac semimetal; this is also the first example of type I superconductor among the topological material based superconductors [108].

Among Weyl semimetals, superconductivity has been found in TaAs [127], MoTe_2 [128], and WTe_2 [130]. All are time-reversal symmetric Weyl semimetals. TaAs is a type I Weyl semimetals, but the others are type II Weyl semimetals with tilted Weyl cones. The superconductivity in TaAs has been discovered recently. The superconductivity has been observed only when the tunneling conductance is measured with PtIr tip, where the tip is considered to be giving pressure [127]. Furthermore, the tunneling spectra have shown the ZBCP, suggesting the existence of SABS [127]. Re-grading MoTe_2 , superconductivity has been observed with $T_c = 0.1\text{K}$. However, by giving the pressure, the T_c increases up to 8.2K at 11.7GPa [129]. WTe_2 shows super-

conductivity only under pressure greater than 10.5GPa [130]. Superconductivity has also been observed in nodal line semimetal PdTaSe₂ [131,146]. Experimental results of the London penetration depth [147] and thermal conductivity [148] have indicated fully gapped superconductivity. The peculiar doughnut-shaped Fermi surface in the nodal line semimetals may induce topological superconductivity.

As summarized in the Table.1.2, superconductivity has been observed in many topological materials. The discovery of new topological materials that show superconductivity is being reported continuously to date. Seven years have passed since the discovery of superconductivity in Cu_xBi₂Se₃ and considerable theoretical and experimental efforts have been made to reveal the superconductivity realized in this material. Now, Cu_xBi₂Se₃ is considered the most promising topological superconductor among all the topological material based superconductors. However, superconductivity in other topological materials has not yet been investigated in detail. In particular, it is difficult to conclude whether they are topological superconductors or not because the topological superconductivity is suggested only by the point contact spectra or(and) anomalous upper critical field. Further experimental and theoretical study is required. The most promising way to elucidate the topological superconductivity may be the direct observation of the SABS by ARPES measurements, as used for normal state topological materials. However, the current technology cannot reach the SABS within such small superconducting gaps.

Chapter 2

Superconductivity in doped Dirac semimetals

In this chapter, we theoretically study intrinsic superconductivity in doped Dirac semimetals. Dirac semimetals host bulk Dirac points which are formed by doubly degenerate bands, so the Hamiltonian is described by 4×4 matrix and six types of k -independent pair potential are allowed by the Fermi-Dirac statistics. We show that the unique spin-orbit coupling leads to characteristic superconducting gap structures and d -vectors on the Fermi surface and the electron-electron interaction between intra and inter orbitals gives the novel phase diagram of superconductivity. It is found that when the inter-orbital attraction is dominant, the unconventional superconducting state with point nodes appears.

2.1 Introduction

Recent theoretical studies have revealed that the doped topological materials can be promising candidates to realize unconventional superconductivity due to their unique spin-orbit interaction [149, 150] and robustness against the non-magnetic impurities [151–154], as discussed in Chap.1. In this chapter, we study superconductivity in doped rotation symmetric Dirac semimetals (DSs). DSs are materials that host bulk Dirac cones [55, 57]. Several materials have been predicted to be DSs [65, 123, 155–157], and Cd_3As_2 [67, 158–164] and Na_3Bi [165–167] have been confirmed experimentally. Recently, superconductivity has been observed in Cd_3As_2 [168–170]. Moreover, point contact experiments for Cd_3As_2 have suggested the existence of SABS [168, 169], gathering great attention as a candidate of unconventional superconductor. In addition, It have revealed that an unique orbital texture in DSs suggests unconventional pairings (Δ_2 and Δ_3 in this thesis) [150].

However, the physical properties of the superconducting states in doped DSs have not been examined systematically, and thus it has been difficult to identify the pairing symmetry experimentally. One of our purposes of this chapter is to clarify the physical property and topological structure of possible superconducting states in doped DSs. Due to the presence of time-reversal symmetry and inversion symmetry, the electronic states near the Dirac points are minimally described by a 4×4 Dirac Hamiltonian with spin and orbital degrees of freedom. For the superconducting state, doubly degenerate bands allow six types of k -independent Cooper pair and the unique orbital texture favors an equal-spin pairing, giving rise to point nodes on the Fermi surface. From this view point, the superconductivity in doped DSs can be unconventional and its physical implication deserves further exploring. Superconductivity in Dirac systems has also been studied for doped TIs, Weyl semimetals, and bilayer Rashba systems. These superconducting states also show unconventional superconductivity, but we emphasize that the crystal symmetry and spin-orbit coupling of DSs are different from them. Hence, the Cooper pairs respect different irreducible representations, implying that they can show unique superconducting gap structures and d -vectors on the Fermi surface.

To clarify these points, we derive analytical formula of possible pair potentials in band basis and reveal the superconducting gap structure and d -vector on the Fermi surface. It is found that the superconducting gap structure can be classified into four types, i.e., isotropic full gap, point node at poles, horizontal line node, and vertical

Figure 2.1: (a) The energy dispersion of the Dirac semimetal. The bulk Dirac cones appear on the k_z axis. (b) The double Fermi surface of the doped Dirac semimetal. Symmetry axis and plane focused in this paper are also shown.

line node. We also show that these superconducting gap structure can be interpreted from the orbital structure of the DS and possible pair potentials. Moreover, for the spin-triplet pairings, the direction of the d -vector is either parallel to x - y plane or parallel to z -direction. These characteristics of the superconducting states are completely different from those of other topological materials. We also solve the linearized gap equation to make a superconducting phase diagram, in which an unconventional superconducting state (Δ_2 or Δ_3 in this paper) is realized when the inter-orbital attraction is sufficiently stronger than the intra-orbital one.

This chapter is organized as follow. First, we introduce a model Hamiltonian for DSs and consider possible pair potentials in Sec. 2.2. In Sec. 2.3, by transforming the pair potentials from orbital basis to band basis, we obtain single-band descriptions of the pair potentials. We also show the superconducting gap structure and d -vector on the Fermi surface. In Sec. 2.4, we show that the superconducting gap structure can be interpreted from the orbital structure of DSs. In Sec. 2.5, we obtain the phase diagram for the superconducting state. In Sec. 2.6, we discuss the difference between superconductivity in DSs and TIs and briefly mention superconductivity in other class of Dirac semimetals. Finally, we summarize our results in Sec. 4.5.

2.2 Model

DSs have both time-reversal symmetry and inversion symmetry, which lead to doubly degenerate bands. Thus, to construct a model with four-fold degenerate Dirac points, it is necessary to take into account the orbital degrees of freedom in addition to the spin degrees of freedom. As mentioned in Chap. 1, in the broad sense, there are two types of DS, i.e., accidental ones and symmetry protected ones. Here, we consider the symmetry protected one. The representative example of the symmetry protected DS is Cd_3As_2 , where relevant orbitals are $S_{J=\frac{1}{2}}$ and $P_{J=\frac{3}{2}}$ with total angular momentum J , and bulk Dirac points are protected by the four-fold symmetry. We discuss in the following Cd_3As_2 class DSs. In the basis set of $|s, \uparrow\rangle$, $|p_x + ip_y, \uparrow\rangle$, $|s, \downarrow\rangle$, and $|p_x - ip_y, \downarrow\rangle$, the low energy effective Hamiltonian for the DSs near Γ point is described by

$$H_n(\mathbf{k}) = a(\mathbf{k})\sigma_z s_0 + b(\mathbf{k})\sigma_x s_z + c(\mathbf{k})\sigma_y s_0 + d(\mathbf{k})\sigma_x s_x + e(\mathbf{k})\sigma_x s_y, \quad (2.1)$$

where s_i and σ_i ($i = 0, x, y, z$) are the Pauli matrices in the spin and orbital space, respectively [63, 65]. As summarized in Ref. [63], the basis functions for four-fold symmetric DSs are given as

$$a(\mathbf{k}) = m_0 - m_1 k_z^2 - m_2 (k_x^2 + k_y^2), \quad (2.2)$$

$$b(\mathbf{k}) = \eta k_x, \quad (2.3)$$

$$c(\mathbf{k}) = -\eta k_y, \quad (2.4)$$

$$d(\mathbf{k}) = (\beta + \gamma)k_z(k_y^2 - k_x^2), \quad (2.5)$$

$$e(\mathbf{k}) = -2(\beta - \gamma)k_z k_x k_y, \quad (2.6)$$

where m_0 , m_1 , m_2 , η , β and γ are the material dependent parameters. The energy dispersion is shown in Fig. 2.1 (a). By tuning the chemical potential, double Fermi surfaces appear as shown in Fig. 2.1 (b).

The crystals of Cd_3As_2 belong to D_{4h} point group and thus the Hamiltonian satisfies the following symmetries.

(i) time-reversal symmetry: $\mathcal{T} = i\sigma_0 s_y \mathcal{K}$

$$\mathcal{T} H_n(\mathbf{k}) \mathcal{T}^\dagger = H_n(-\mathbf{k}), \quad (2.7)$$

(ii) inversion symmetry: $\mathcal{P} = \sigma_z s_0$,

$$\mathcal{P} H_n(\mathbf{k}) \mathcal{P}^\dagger = H_n(-\mathbf{k}), \quad (2.8)$$

(iii) four-fold rotational symmetry along z-axis: $\mathcal{C}_4 = e^{i(\pi/4)(2\sigma_0 + \sigma_z)s_z}$

$$\mathcal{C}_4 H_n(k_x, k_y, k_z) \mathcal{C}_4^\dagger = H_n(k_y, -k_x, k_z), \quad (2.9)$$

(iv) x-y mirror-reflection symmetry: $\mathcal{M}_{xy} = i\sigma_0 s_z$

$$\mathcal{M}_{xy} H_n(k_x, k_y, k_z) \mathcal{M}_{xy}^\dagger = H_n(k_x, k_y, -k_z), \quad (2.10)$$

(v) y-z mirror-reflection symmetry: $\mathcal{M}_{yz} = i\sigma_0 s_x$

$$\mathcal{M}_{yz} H_n(k_x, k_y, k_z) \mathcal{M}_{yz}^\dagger = H_n(-k_x, k_y, k_z), \quad (2.11)$$

(vi) (110) mirror-reflection symmetry: $\mathcal{M}_{(110)} = (\sigma_z s_x - i\sigma_0 s_0) / \sqrt{2}$

$$\mathcal{M}_{(110)} H_n(k_x, k_y, k_z) \mathcal{M}_{(110)}^\dagger = H_n(k_y, k_x, k_z). \quad (2.12)$$

The corresponding symmetry axis and planes are shown in Fig. 2.1 (b).

Next, we consider the superconducting state. We assume the following pair interaction [149]:

$$H_{\text{int}}(\mathbf{x}) = -U[n_1^2(\mathbf{x}) + n_2^2(\mathbf{x})] - 2Vn_1(\mathbf{x})n_2(\mathbf{x}), \quad (2.13)$$

where U and V are intra- and inter-orbital interactions, respectively, and n_i ($i = 1, 2$) is a density operator for orbital i . Then we construct the Bogoliubov de Gennes (BdG) Hamiltonian in the mean field regime:

$$H_{MF} = \int dk \hat{c}^\dagger H_{\text{BdG}}(\mathbf{k}) \hat{c}, \quad (2.14)$$

$$H_{\text{BdG}}(\mathbf{k}) = [H_n(\mathbf{k}) - \mu] \tau_z + \Delta_i \tau_x, \quad (2.15)$$

where τ_x and τ_z are the Pauli matrices in the Nambu (particle-hole) space, μ and Δ_i denote the chemical potential and pair potential, respectively. Here, the basis is taken as $\hat{c}^\dagger = (c_{1\uparrow}^\dagger, c_{2\uparrow}^\dagger, c_{1\downarrow}^\dagger, c_{2\downarrow}^\dagger, -c_{1\downarrow}, -c_{2\downarrow}, c_{1\uparrow}, c_{2\uparrow})$. Then, we discuss possible pair potentials. For the two orbital system, there are sixteen combinations of two Pauli matrices.

Δ		spin	orb.	Rep.	$\mathcal{P}$	$\mathcal{C}_4$	$\mathcal{M}_{xy}$	$\mathcal{M}_{yz}$	$\mathcal{M}_{zx}$	$\mathcal{M}_{(110)}$
Δ_{1a}	$\sigma_0 s_0$	singlet	intra	A_{1g}	+	+	+	+	+	+
Δ_{1b}	$\sigma_z s_0$	singlet	intra	A_{1g}	+	+	+	+	+	+
Δ_2	$\sigma_y s_y$	triplet	inter	B_{1u}	-	-	-	-	-	+
Δ_3	$\sigma_y s_x$	triplet	inter	B_{2u}	-	-	-	+	+	-
Δ_{4a}	$\sigma_x s_0$	singlet	inter	E_u	-	Δ_{4b}	+	+	-	$-\Delta_{4b}$
Δ_{4b}	$\sigma_y s_z$	triplet	inter	E_u	-	Δ_{4a}	+	-	+	Δ_{4a}

Table 2.1: Possible pair potentials for the Dirac semimetals. Spin state, orbital state, irreducible representation and symmetry properties of each pairings are shown.

ces, s_i and σ_i ($i = 0, x, y, z$), but six combinations out of them satisfy the Fermi-Dirac statistic, which are described by $\Delta\sigma_0 s_0 \equiv \Delta_{1a}$, $\Delta\sigma_z s_0 \equiv \Delta_{1b}$, $\Delta\sigma_y s_y \equiv \Delta_2$, $\Delta\sigma_y s_x \equiv \Delta_3$, $\Delta\sigma_x s_0 \equiv \Delta_{4a}$, and $\Delta\sigma_y s_z \equiv \Delta_{4b}$. These pair potentials can be classified by inter- or intra-orbital in addition to the spin-singlet or triplet. Δ_{1a} and Δ_{1b} are spin-singlet intra-orbital pairings. Δ_2 , Δ_3 , and Δ_{4b} are spin-triplet inter-orbital pairings. Δ_{4a} is a spin-singlet inter-orbital pairing. Moreover, these pair potentials are classified into four irreducible representations of the D_{4h} point group : A_{1g} (Δ_{1a} and Δ_{1b}), B_{1u} (Δ_2), B_{2u} (Δ_3) and E_u (Δ_{4a} and Δ_{4b}), which are summarized in Table 5.1. Symmetry properties of the pair potentials under the inversion $\mathcal{P}$, four-fold rotation $\mathcal{C}_4$, and mirror-reflection symmetry $\mathcal{M}_{xy}$, $\mathcal{M}_{yz}$ and $\mathcal{M}_{(110)}$ are also summarized in Table 5.1. As long as we consider the k -independent pair potentials in this orbital basis, the parity of the intra- (inter-) orbital pair potentials are even (odd) under the inversion operation. It is noted that the matrix forms of the possible pair potentials are common in two orbitals or layers systems such as TIs [149], Weyl semimetals [84], and bilayer Rashba systems [171]. However, the superconductivity in the DSs is completely different from that in other materials since the normal state is different, as we see below.

2.3 Single band description of pair potentials : superconducting gap and spin structure

In this section, to understand the superconducting gap and spin structure on the Fermi surface, we derive the pair potentials in the band basis, where $H_n(\mathbf{k})$ is diagonalized [172]. Then, we extract conduction or valence band components of the

pair potential in order to obtain the single-band description. First, we diagonalize the spin part of $H_n(\mathbf{k})$. The Hamiltonian reduces to

$$H_{n\tilde{s}}(\mathbf{k}) = a(\mathbf{k})\sigma_z + c(\mathbf{k})\sigma_y + \tilde{s}L(\mathbf{k})\sigma_x, \quad (2.16)$$

where $\tilde{s} = \pm 1$ and $L(\mathbf{k}) = \sqrt{d^2(\mathbf{k}) + e^2(\mathbf{k}) + b^2(\mathbf{k})}$. The corresponding eigenvectors are given by

$$|\tilde{s}+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \cos \frac{P_k}{2} \\ \cos \frac{P_k}{2} \left(\frac{d(\mathbf{k}) + ie(\mathbf{k})}{L(\mathbf{k}) + b(\mathbf{k})} \right) \end{pmatrix}, \quad (2.17)$$

$$|\tilde{s}-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \sin \frac{P_k}{2} \\ -\sin \frac{P_k}{2} \left(\frac{d(\mathbf{k}) + ie(\mathbf{k})}{L(\mathbf{k}) - b(\mathbf{k})} \right) \end{pmatrix}, \quad (2.18)$$

where $\cos \frac{P_k}{2} = \sqrt{1 + \frac{b(\mathbf{k})}{L(\mathbf{k})}}$ and $\sin \frac{P_k}{2} = \sqrt{1 - \frac{b(\mathbf{k})}{L(\mathbf{k})}}$. By using the eigenvectors, the following relations are obtained as

$$\tilde{s}_x = -\frac{d(\mathbf{k})b(\mathbf{k})}{l(\mathbf{k})L(\mathbf{k})}s_x - \frac{e(\mathbf{k})b(\mathbf{k})}{l(\mathbf{k})L(\mathbf{k})}s_y + \frac{l(\mathbf{k})}{L(\mathbf{k})}s_z, \quad (2.19)$$

$$\tilde{s}_y = \frac{e(\mathbf{k})}{l(\mathbf{k})}s_x - \frac{d(\mathbf{k})}{l(\mathbf{k})}s_y, \quad (2.20)$$

$$\tilde{s}_z = \frac{d(\mathbf{k})}{L(\mathbf{k})}s_x + \frac{e(\mathbf{k})}{L(\mathbf{k})}s_y + \frac{b(\mathbf{k})}{L(\mathbf{k})}s_z, \quad (2.21)$$

where $l(\mathbf{k}) = \sqrt{d^2(\mathbf{k}) + e^2(\mathbf{k})}$, $\tilde{s}_i$ ($i = 0, x, y, z$) are the Pauli matrices for the spin helicity basis. Next, we diagonalize the orbital part. The eigenvalues are given by

$$E_{n\tilde{\sigma}}(\mathbf{k}) = \tilde{\sigma} \sqrt{a^2(\mathbf{k}) + b^2(\mathbf{k}) + c^2(\mathbf{k}) + d^2(\mathbf{k}) + e^2(\mathbf{k})}, \quad (2.22)$$

where $\tilde{\sigma} = \pm 1$. The corresponding eigenvectors are

$$|\tilde{s}\pm, \tilde{\sigma}+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \cos \frac{Q_k}{2} \\ \cos \frac{Q_k}{2} \left(\frac{\tilde{s}L(\mathbf{k}) + ic(\mathbf{k})}{R(\mathbf{k}) + a(\mathbf{k})} \right) \end{pmatrix}, \quad (2.23)$$

$$|\tilde{s}\pm, \tilde{\sigma}-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \sin \frac{Q_k}{2} \\ -\sin \frac{Q_k}{2} \left(\frac{\tilde{s}L(\mathbf{k}) + ic(\mathbf{k})}{R(\mathbf{k}) - a(\mathbf{k})} \right) \end{pmatrix}, \quad (2.24)$$

where $R(k) = |E_{n\tilde{\sigma}}(\mathbf{k})|$, $\cos \frac{Q_k}{2} = \sqrt{1 + \frac{a(k)}{R(k)}}$, $\sin \frac{Q_k}{2} = \sqrt{1 - \frac{a(k)}{R(k)}}$. Finally, the eigenvectors for the normal Hamiltonian are obtained as

$$|u_{\tilde{s},\tilde{\sigma}}\rangle = |\tilde{s}\pm\rangle \otimes |\tilde{s}\pm, \tilde{\sigma}\pm\rangle. \quad (2.25)$$

By using the eigenvectors $|u_{\tilde{s},\tilde{\sigma}}\rangle$, we obtain the pair potentials in the band and spin helicity basis. Then, with Eqs. (2.19) - (2.21), we transform the pair potentials from the band and spin helicity basis to the band and real spin basis:

$$\hat{c}'^\dagger = (c_{\alpha\uparrow}^\dagger, c_{\beta\uparrow}^\dagger, c_{\alpha\downarrow}^\dagger, c_{\beta\downarrow}^\dagger, -c_{\alpha\downarrow}, -c_{\beta\downarrow}, c_{\alpha\uparrow}, c_{\beta\uparrow}) \quad (2.26)$$

where α and β are band indices. The obtained results are

$$\Delta'_{1a}(\mathbf{k}) = \Delta \tilde{\sigma}_0 s_0, \quad (2.27)$$

$$\Delta'_{1b}(\mathbf{k}) = \frac{\Delta}{R(k)} (r(\mathbf{k})\tilde{\sigma}_x + a(k)\tilde{\sigma}_z) s_0, \quad (2.28)$$

$$\begin{aligned} \Delta'_2(\mathbf{k}) = & -\Delta \left[\frac{a(k)}{r(k)R(k)} \tilde{\sigma}_x (b(k)s_x + c(k)s_y - d(k)s_z) \right. \\ & \left. + \frac{e(k)}{r(k)} \tilde{\sigma}_y s_0 - \frac{1}{R(k)} \tilde{\sigma}_z (b(k)s_x + c(k)s_y - d(k)s_z) \right], \end{aligned} \quad (2.29)$$

$$\begin{aligned} \Delta'_3(\mathbf{k}) = & -\Delta \left[\frac{a(k)}{r(k)R(k)} \tilde{\sigma}_x (c(k)s_x - b(k)s_y + e(k)s_z) \right. \\ & \left. + \frac{d(k)}{r(k)} \tilde{\sigma}_y s_0 - \frac{1}{R(k)} \tilde{\sigma}_z (c(k)s_x - b(k)s_y + e(k)s_z) \right], \end{aligned} \quad (2.30)$$

$$\begin{aligned} \Delta'_{4a}(\mathbf{k}) = & -\Delta \left[\frac{a(k)}{r(k)R(k)} \tilde{\sigma}_x (d(k)s_x + e(k)s_y + b(k)s_z) \right. \\ & \left. - \frac{c(k)}{r(k)} \tilde{\sigma}_y s_0 - \frac{1}{R(k)} \tilde{\sigma}_z (d(k)s_x + e(k)s_y + b(k)s_z) \right], \end{aligned} \quad (2.31)$$

$$\begin{aligned} \Delta'_{4b}(\mathbf{k}) = & -\Delta \left[\frac{a(k)}{r(k)R(k)} \tilde{\sigma}_x (-e(k)s_x + d(k)s_y + c(k)s_z) \right. \\ & \left. + \frac{b(k)}{r(k)} \tilde{\sigma}_y s_0 - \frac{1}{R(k)} \tilde{\sigma}_z (-e(k)s_x + d(k)s_y + c(k)s_z) \right], \end{aligned} \quad (2.32)$$

where $\tilde{\sigma}_i$ ($i = 0, x, y, z$) are the Pauli matrices in the band basis and

$$r(k) = \sqrt{b^2(k) + c^2(k) + d^2(k) + e^2(k)}. \quad (2.33)$$

In the case of the DS, the Fermi surface consists of either electron or hole band. If the chemical potential is large enough compared with the magnitude of the pair potential,

$|\mu| \gg \Delta$, we can consider that the superconductivity occurs in either conduction or valence band (quasi-classical approximation). Thus inter-band and valence (or conduction) band component can be ignored. Namely, it is sufficient to consider only the (1,1) [or (2,2)] component of $\tilde{\sigma}_i$. The conduction band components of pair potentials are as follows:

$$\Delta_{1a}^c(\mathbf{k}) = \Delta s_0, \quad (2.34)$$

$$\Delta_{1b}^c(\mathbf{k}) = \frac{\Delta}{R} [m_0 - m_1 k_z^2 - m_2 (k_x^2 + k_y^2)] s_0, \quad (2.35)$$

$$\Delta_2^c(\mathbf{k}) = \Delta \left[\frac{\eta}{R} (k_x s_x - k_y s_y) + \frac{\beta + \gamma}{R} k_z (k_y^2 - k_x^2) s_z \right], \quad (2.36)$$

$$\Delta_3^c(\mathbf{k}) = -\Delta \left[\frac{\eta}{R} (k_y s_x + k_x s_y) + 2 \frac{\beta - \gamma}{R} k_x k_y k_z s_z \right], \quad (2.37)$$

$$\begin{aligned} \Delta_{4a}^c(\mathbf{k}) = & \Delta \left[\frac{\eta}{R} k_x s_z \right. \\ & \left. + \frac{\beta + \gamma}{R} k_z (k_y^2 - k_x^2) s_x - 2 \frac{\beta - \gamma}{R} k_x k_y k_z s_y \right], \end{aligned} \quad (2.38)$$

$$\begin{aligned} \Delta_{4b}^c(\mathbf{k}) = & -\Delta \left[\frac{\eta}{R} k_y s_z \right. \\ & \left. - 2 \frac{\beta - \gamma}{R} k_x k_y k_z s_x - \frac{\beta + \gamma}{R} k_z (k_y^2 - k_x^2) s_y \right]. \end{aligned} \quad (2.39)$$

It is found that, in the single-band description, Δ_{1a} and Δ_{1b} are regarded as spin-singlet even-parity pairings, and Δ_2 , Δ_3 , Δ_{4a} and Δ_{4b} are spin-triplet odd-parity pairings. In the single-band description, the spin-singlet or triplet completely corresponds to even or odd under the inversion operation for all pairings. Although Δ_{4a} is a spin-singlet inter-orbital pairing in the orbital basis, it is considered as a spin-triplet pairing in the band basis. In other words, the spin triplet component of Δ_{4a} is induced by the spin-orbit interaction. In addition, if the parameters related to the spin-orbit interaction are absent $\eta = \beta = \gamma = 0$, the odd parity pairings $\Delta_2 = \Delta_3 = 0$, which means that the spin-orbit interaction is essential to realize these unconventional superconductivity. As shown below, these single-band representations are useful to capture the bulk superconducting properties such as the heat capacity and the spin susceptibility.

2.3.1 Superconducting gap structure

In Fig. 2.2, we show the magnitude of the superconducting gap $|\Delta_i^c(\mathbf{k})|/\Delta$ plotted on the Fermi surface (a)-(f) and the bulk density of state (DOS) $N_s(E)/N_n(0)$ (g)-(h).

Figure 2.2: (a) - (f) Superconducting gap structure on the Fermi surface and (g) - (l) the bulk density of state for the possible pair potentials. The color on the Fermi surface indicates the magnitude of the energy gap $|\Delta_i^c(\mathbf{k})|/\Delta$ ($i = 1a, 1b, 2, 3, 4a, 4b$).

In the case of Δ_{1a} , the gap structure is isotropic full gap, where the DOS diverges at $E/\Delta = 1$ and there is no state in $E/\Delta < 1$. In the case of Δ_{1b} , line nodes exist in the horizontal direction. Therefore, the DOS is proportional to E and divergence at $E/\Delta = 1$ is suppressed. It should be noted that the line nodes are accidental nodes, and thus, by tuning some parameters, we can remove the nodes without any topological phase transition. For Δ_2 and Δ_3 , the superconducting gap has point nodes on k_z -axis. The DOS near $E/\Delta = 0$ is proportional to E^2 . As is seen from Fig. 2.2, the superconducting gaps of Δ_2 and Δ_3 are quite similar. This is because Δ_2 and Δ_3 are different only by k^3 terms, i.e., $d(\mathbf{k})$ and $e(\mathbf{k})$ in Eq. 2.1. For Δ_{4a} (Δ_{4b}), there are point nodes on the k_z axis. In the absence of the k^3 terms, the point nodes become the line node at $k_x = 0$ ($k_y = 0$) for Δ_{4a} (Δ_{4b}). Although the k^3 terms change the superconducting gap structure, the superconducting gap structure of Δ_{4a} can be effectively considered as line node, as is obvious from Figs. 2.2 (e) and (f), since the gap opening effect of the k^3 terms are quite small compared with k -linear terms around Γ point. Then, the DOS is proportional to E^2 at very near $E/\Delta = 0$ but the line shape is almost E linear in the wide region of $E/\Delta < 1$. The superconducting gap in the case of with and without the k^3 terms are summarized in Table 2.2.

Figure 2.3: d -vector on the Fermi surface for the spin-triplet pairings in the band space. In the case of Δ_2 and Δ_3 , d -vectors are almost parallel to the x - y plane. On the other hand, in the case of Δ_{4a} and Δ_{4b} , the d -vectors are almost parallel to the z -direction. Here, we show the d -vector on the Fermi surface at $k_z = \pi/4$, however, the k_z dependence of the direction of the d -vector is quite small since this is induced by k^3 terms.

It has been revealed that if the pair potential satisfies the four-fold rotational symmetry $C_4 \Delta_i C_4^\dagger = e^{-i\pi r/2} \Delta_i$ with non-zero r , the C_4 invariant Dirac points in the normal state are inherited to the superconducting state [150]. In the case of Δ_2 , Δ_3 , Δ_{4a} and Δ_{4b} , r is non-zero. Therefore, we can say that the point nodes on k_z axis in Δ_2 and Δ_3 originate from the normal state, which are topologically protected.

2.3.2 d -vector

For spin-triplet superconductors, the pair potentials can be described with d -vectors which behave like three-dimensional vectors in spin space [15]. In our basis, the d -vector $\mathbf{d}(\mathbf{k})$ is defined as

$$\Delta_i^c(\mathbf{k}) = \Delta \mathbf{d}(\mathbf{k}) \cdot \mathbf{s}, \quad (2.40)$$

	SC gap without k^3 terms	SC gap with k^3 terms	d -vector without k^3 terms	d -vector with k^3 terms
Δ_{1a}	FG	FG	none	none
Δ_{1b}	horizontal LNs	horizontal LNs	none	none
Δ_2	PNs at poles	PNs at poles	$d \parallel x\text{-}y$ plane	$x\text{-}y$ compo. is dominant
Δ_3	PNs at poles	PNs at poles	$d \parallel x\text{-}y$ plane	$x\text{-}y$ compo. is dominant
Δ_{4a}	vertical LN	PNs at poles	$d \parallel z\text{-axis}$	$z\text{-compo.}$ is dominant
Δ_{4b}	vertical LN	PNs at poles	$d \parallel z\text{-axis}$	$z\text{-compo.}$ is dominant

Table 2.2: Superconducting (SC) gap structure and d -vector for the possible pair potential. FG, PN and LN stand for full gap, point node and line node, respectively.

where $\mathbf{s} = (s_x, s_y, s_z)$. For the possible pair potentials, $\mathbf{d}(\mathbf{k})$ is easily obtained from Eqs. (2.34) - (2.39). The direction of the d -vector on the Fermi surface is important to interpret the magnetic response of the superconductivity, the details of which are mentioned in Sec. 3.2. In Fig. 2.3, we show the d -vector of the spin-triplet pair potentials in the band basis, i.e., Δ_2 , Δ_3 , Δ_{4a} and Δ_{4b} . Note that we show the d -vector for $k_z = \pi/4$, but the k_z dependence of the direction of the d -vector is negligible since it originates from the k^3 terms. In the case of Δ_2 and Δ_3 , the direction of the d -vector is almost parallel to the $x\text{-}y$ plane. Although there is the s_z component, it is much smaller than the other components since it is induced by the k^3 terms. On the other hand, in the case of Δ_{4a} and Δ_{4b} , the direction of the d -vector is almost parallel to the z -axis, and $x\text{-}y$ plane component is negligible for the same reason in the case of Δ_2 and Δ_3 .

2.4 Interpretation of superconducting gap structure with orbital texture

In this section, we interpret the superconducting gap structures from the orbital texture of DSs. In the previous letter, two of the present authors have argued how the orbital texture is consistent with Δ_2 and Δ_3 [150]. Here we generalize the argument and explain nodal structures of all the possible pairing symmetry in terms of the orbital-momentum locking. For simplicity, we ignore the k^3 terms in this section.

Figure 2.4: Orbital texture of the Dirac semimetal for spin-up and spin-down space. Single-headed arrows on the Fermi surface indicate orbital $\sigma = (\sigma_x, \sigma_y, \sigma_z)$. Orbit-momentum locking by the first term in Eq. (2.1): $a(k)\sigma_z$ plotted on the k_y - k_z plane (a). Orbit-momentum locking by the second term in Eq. (2.1): $\eta(k_x\sigma_xs_z - k_y\sigma_ys_0)$ plotted on the k_x - k_y plane at $k_z = \pm k_0$ (b). For a Cooper pair between electrons in the different spin sector, the orbit-momentum locking provides the parallel (anti-parallel) orbital configuration in the z - and x - (y -) direction, which are indicated by double-headed arrows (i) and (ii) [(iii)]. For an equal-spin Cooper pair, the orbit-momentum locking provides the parallel (anti-parallel) orbital configuration in the z - (x - and y -) direction, which is indicated by double-headed arrow (iv) [(v) and (vi)].

First, we discuss the orbit-momentum locking of DSs. Consider the Hamiltonian in Eq. (2.1). The spin is already diagonalized in Eq. (2.1), so we can divide the Hamiltonian into the spin-up and spin-down sectors as

$$H_{n\uparrow}(\mathbf{k}) = a(\mathbf{k})\sigma_z + \eta(k_x\sigma_x - k_y\sigma_y), \quad (2.41)$$

$$H_{n\downarrow}(\mathbf{k}) = a(\mathbf{k})\sigma_z - \eta(k_x\sigma_x + k_y\sigma_y). \quad (2.42)$$

These Hamiltonians have two characteristic features. First, the first terms in Eqs. (2.41) and (2.42) dominate on the k_z axis. Because of the uniaxial rotational symmetry around the z -direction in DSs, the orbital mixing second terms are not allowed on the k_z axis. Second, the orbital mixing second terms become dominant away from the k_z axis at each Dirac point. At Dirac points, both the first and the second terms vanish, but since the second terms are linear in k_i while the first ones are quadratic, the second terms are dominant except on the k_z axis. It should be noted that these two features are required by symmetry of DSs.

The above features give rise to a unique orbital texture on the Fermi surfaces surrounding Dirac points. Near poles of the Fermi surface, the first terms in Eqs. (2.41) and (2.42) are dominant, so we have the z -directed parallel orbital configuration shown in Fig. 2.4 (a). On the other hands, near the equators of the Fermi surfaces, the second terms are dominant, so we have the orbit-momentum locking structure in Fig. 2.4 (b).

Now consider the pairing states in DSs, and compare them with the orbital textures. According to the BCS theory, Cooper pairs form between electrons with opposite momenta, $-k$ and k , and, for Δ_{1a} , Δ_{1b} , Δ_{4a} , Δ_{4b} , (Δ_2, Δ_3) , they form between electrons in different (same) spin sectors. First, consider a Cooper pair between electrons in the different spin sectors. As illustrated in (i) of Fig. 2.4 (a), near poles of the Fermi surface, the Cooper pair has a parallel orbital configuration in the z -direction. On the other hand, on the equator of the Fermi surface, the Cooper pair has a parallel orbital configuration in the x -direction [(ii) in Fig. 2.4 (b)], or an anti-parallel orbital configuration in the y -direction [(iii) in Fig. 2.4 (b)]. It is found that these orbital configurations are consistent with Δ_{1a} . Note that σ_0 is diagonal on the quantization basis of σ_x or σ_z , but it is off diagonal on the quantization basis of σ_y [173]. This means that Δ_{1a} , which is proportional to σ_0 , has parallel orbital configurations in x - and z -directions but an anti-parallel one in the y -direction, which is exactly the same as the aforementioned orbital structure of Cooper pairs in DSs. On the other hand, the other gap functions, Δ_{1b} , Δ_{4a} , Δ_{4b} are not fully consistent with the orbital texture. As summarized in Table 2.3, σ_x (σ_z) indicates an anti-parallel orbital pair in the z - (x -) direction and parallel-orbital pair in other directions, and σ_y indicates an anti-parallel orbital pair in any direction. Therefore, for instance, Δ_{1b} is inconsistent with the orbital texture on the equator of the Fermi surfaces, so it has horizontal line nodes. In a similar manner, one can see that vertical line nodes of Δ_{4a} and Δ_{4b} come from the inconsistency between the pairings and the orbital texture of DSs.

For a Cooper pair between electrons in the same spin sector, the orbital texture in Fig. 2.4 (a) gives a parallel orbital configuration in the z -direction near the poles of the Fermi surface [(iv)], however, that in Fig. 2.4 (b) provides an anti-parallel orbital configuration in the x - and y - directions on the equator of the Fermi surfaces [(v), (vi)]. Since σ_y represents an anti-parallel orbital pair in any direction, these orbital configurations are consistent with Δ_2 and Δ_3 on the equator of the Fermi surface, but not consistent with them near the poles. Consequently, there arise point nodes at the poles for these gap functions.

	$\Delta_{1a}(\sigma_0)$	$\Delta_{1b}(\sigma_z)$	$\Delta_{4a}(\sigma_x)$	$\Delta_{2,3,4b}(\sigma_y)$
x	P	AP	P	AP
y	AP	P	P	AP
z	P	P	AP	AP

Table 2.3: Orbital configuration of the possible pair potentials for each direction. P (AP) stands for parallel (anti-parallel) orbital configuration.

2.5 Phase diagram

In this section, we obtain the U - V phase diagram by solving the linearized gap equation in a manner similar to the superconducting TI [149] and the bilayer Rashba system [171]. For simplicity, we ignore the k^3 terms in this section. The linearized gap equations for possible pair potentials are given by

$$\begin{vmatrix} Uq_{1a} - 1 & Uq_{1ab} \\ Uq_{1ba} & Uq_{1b} - 1 \end{vmatrix} = 0 \quad \text{for } \Delta_1, \quad (2.43)$$

$$Vq_i = 1 \quad \text{for } \Delta_2, \Delta_3, \Delta_{4a}. \quad (2.44)$$

Here, q_i ($i = 1a, 1b, 1ab, 1ba, 2, 3, 4a$) is the irreducible susceptibility:

$$q_i = -\frac{k_B T}{N} \sum_{\omega_n, \mathbf{k}} \text{Tr} \left[\frac{\Delta_i}{\Delta} G_0(\mathbf{k}) \frac{\Delta_i}{\Delta} G_0(\mathbf{k}) \right] \quad (2.45)$$

$$= -\frac{1}{N} \sum_{\mathbf{k}} \left[F_i(\mathbf{k}) \frac{\tanh \frac{E_{n+}(\mathbf{k})}{2k_B T}}{2E_{n+}(\mathbf{k})} \right], \quad (2.46)$$

where N is the number of the unit cell, k_B is the Boltzman constant, $G_0(\mathbf{k})$ is the single-particle Green's function for the normal state : $G_0(\mathbf{k}) = P_c(\mathbf{k}) / (i\omega_n - E_{n+}(\mathbf{k}))$ with the projection operator onto the conduction band $P_c(\mathbf{k}) = \sum_{\tilde{s}} |u_{\tilde{s},+}\rangle \langle u_{\tilde{s},+}| = [E_{n+}(\mathbf{k})\sigma_0 s_0 + H_n(\mathbf{k})] / 2E_{n+}(\mathbf{k})$ and $F_i(\mathbf{k})$ is the form factor originating from the orbital degrees of freedom. $F_i(\mathbf{k})$ for each pair potential is given by $F_{1a}(\mathbf{k}) = 1$, $F_{1ab}(\mathbf{k}) = F_{1ba}(\mathbf{k}) = a(\mathbf{k})/R(\mathbf{k})$, $F_{1b}(\mathbf{k}) = a^2(\mathbf{k})/R^2(\mathbf{k})$, $F_2(\mathbf{k}) = F_3(\mathbf{k}) = \eta^2(k_x^2 + k_y^2)/R^2(\mathbf{k})$, and $F_{4a}(\mathbf{k}) = \eta^2 k_x^2 / R^2(\mathbf{k})$.

The U - V phase diagram is shown in Fig. 2.5. As is obvious from the form factors, the irreducible representations satisfy the relation: $q_2 = q_3 > q_{4a}$. Therefore, the U - V

Figure 2.5: U - V phase diagram for the superconducting DS, where U (V) is the inter- (intra-) orbital attraction. The blue (green) region indicates the region where the Δ_2 and Δ_3 (Δ_1) has the highest stability.

phase diagram consists of Δ_1 , Δ_2 and Δ_3 , and Δ_{4a} (Δ_{4b}) cannot appear in the phase diagram. The phase boundary is given by

$$\frac{V}{U} = \int_{\text{FS}} d\mathbf{k} \frac{R^2(\mathbf{k}) + a^2(\mathbf{k})}{R^2(\mathbf{k}) - a^2(\mathbf{k})} \approx 2.1. \quad (2.47)$$

If the inter-orbital attraction V is sufficiently stronger than intra-orbital one U , the unconventional superconducting phase (Δ_2 or Δ_3) realizes. We can expect that the Coulomb repulsion leads to stronger V as is discussed in the superconducting TI [174]. We can also interpret this phase diagram with the orbital structure. Since all inter-orbital pairings in Table 5.1 are odd under parity, one can naturally obtain an odd-parity pairing state if V dominates. Then, among the odd-parity pairing states in Table 5.1, only Δ_2 and Δ_3 are consistent with the orbital texture on the equator of the Fermi surface. Consequently, we obtain Δ_2 and Δ_3 in the phase diagram.

2.6 Discussion

So far, we have revealed the superconductivity in DSs. Here, we briefly mention the difference between superconductivity in the DSs and that in Bi_2Se_3 type TIs focusing

Δ	Dirac semimetal	Topological insulator
$\Delta\sigma_0s_0$	FG(A_{1g})	FG(A_{1g})
$\Delta\sigma_zs_0$	LN(A_{1g})	PN(A_{2u})
$\Delta\sigma_ys_y$	PN(B_{1u})	PN(E_u)
$\Delta\sigma_ys_x$	PN(B_{2u})	PN(E_u)
$\Delta\sigma_xs_0$	LN(E_u)	FG(A_{1g})
$\Delta\sigma_ys_z$	LN(E_u)	FG(A_{1u})

Table 2.4: Possible pair potentials for two orbital models. Superconducting gap structures projected to the conduction band (the effect of the k^3 terms are ignored) of the Dirac semimetal and topological insulator and irreducible representation classified as the D_{4h} point group are shown. FG, PN and LN stand for full gap, point node and line node, respectively.

on the superconducting gap structure and the symmetry of the pair potential. In Table 2.4, we show the type of superconducting gap structure on the Fermi surface and irreducible representation of the DSs and TIs, assuming the D_{4h} crystal. The details of the superconducting gap structure of TIs are shown in Appendix. As is obvious from Table 2.4, the superconducting gap structure is totally different between DSs and TIs though the matrix forms of the pair potentials are the same. In particular, different from the superconductivity in the TIs, that in the DSs cannot be a fully-gapped topological superconductor. This difference originates from the difference of effective orbitals.

In this thesis, we have focused on Cd_3As_2 class DSs where bulk Dirac points are protected by four-fold rotational symmetry and effective orbitals are formed by s - and p -orbital. Pair potentials in the band basis for DSs protected by other discrete rotational symmetry can be easily obtained by changing the basis functions Eqs. (2.2) - (2.6) in Eqs. (2.27) - (2.32). Then, we can interpret the superconducting gap structure and d -vector. However, it should be noted that we have to reconsider surface states and stability of nodes carefully for other DSs since topological nature can be changed depending on the related discrete rotational symmetry. If the Dirac points are made of s - and d -orbitals, the different types of DSs are realized [63]. It would be interesting to explore the superconductivity in this type of DSs since the d -wave superconductivity is realized [175].

2.7 Summary

We have studied the superconductivity in Cd_3As_2 type DSs. By obtaining the single-band description of the pair potentials, we have clarified the superconducting gap structure and d -vector on the Fermi surface. It has been found that the type of the superconducting gap structure can be classified into four types: isotropic full gap, point node at poles, horizontal line node and vertical line node (effectively). For the spin-triplet case, the direction of the d -vector is classified into two types: $d \perp z$ -axis and $d \parallel z$ -axis. These characteristics of the superconducting states are completely different from those of the superconducting TIs and other topological materials. By solving the linearized gap equation, we have found that the nodal spin-triplet pairing (Δ_2 and Δ_3) can be stabilized when the inter-orbital attraction is sufficiently stronger than the intra-orbital one. Moreover, we have revealed that orbit-momentum locking in the DS plays a key role to interpret the superconducting gap structure of the possible superconducting state.

Chapter 3

Physical properties of superconducting doped Dirac semimetals

Here, we theoretically study bulk and surface physical properties of intrinsic superconductivity in doped Dirac semimetals using the model introduced in the previous chapter to verify the experimental signature of possible superconducting states. Here, we calculate the temperature dependence of bulk physical properties such as electronic specific heat and spin susceptibility and surface state. In the unconventional superconducting phase, either dispersive or flat Andreev bound states appear between point nodes, which lead to double peaks or single peak in the surface density of state, respectively. As a result, it is found that possible superconducting states can be distinguished by combining bulk and surface measurements.

3.1 Introduction

To examine whether we can distinguish the possible pair potentials experimentally, we calculate the temperature dependence of the specific heat that reflects the superconducting gap structure and spin susceptibility that reflects the Van-Vleck effect and the direction of the d -vector. Furthermore, we calculate the surface state by using the recursive Green's function method. The unconventional superconducting states show either dispersive or flat Andreev bound states on the surface depending on the parity of mirror-reflection symmetry. Using mirror-reflection symmetry, we discuss topological numbers relevant to zero-energy states. As a result, these physical implications conclude that the possible superconducting states can be distinguished by combining bulk and surface measurements. Note that the model using this section is completely the same as that used in the previous section including parameters.

3.2 Bulk physical property

3.2.1 Specific heat

First, we calculate the temperature dependence of the electronic specific heat for the superconducting states. The temperature dependence of the specific heat reflects the superconducting gap structure [8], which has been considered as useful information to determine the symmetry of pair potential experimentally [137, 176–179]. The specific heat in the superconducting state C_s is given by

$$C_s = \frac{2\beta}{N} \sum_{\mathbf{k}} \left(E_{ij}^2(\mathbf{k}) + \beta E_{ij}(\mathbf{k}) \frac{\partial \Delta}{\partial \beta} \frac{\partial E_{ij}(\mathbf{k})}{\partial \Delta} \right) \left(-\frac{\partial f(E_{ij}(\mathbf{k}))}{\partial E_{ij}(\mathbf{k})} \right), \quad (3.1)$$

where $\beta = 1/k_B T$ and E_{ij} is the eigenvalue for the BdG Hamiltonian Eq. (2.15) given as

$$E_{1j}(\mathbf{k}) = \sqrt{\xi^2(\mathbf{k}) + 2\sqrt{f^2(\mathbf{k})g^2(\mathbf{k}) + \Delta^2\zeta_j^2(\mathbf{k})}}, \quad (3.2)$$

$$E_{2j}(\mathbf{k}) = \sqrt{\xi^2(\mathbf{k}) - 2\sqrt{f^2(\mathbf{k})g^2(\mathbf{k}) + \Delta^2\zeta_j^2(\mathbf{k})}}, \quad (3.3)$$

$$E_{3j}(\mathbf{k}) = -\sqrt{\xi^2(\mathbf{k}) - 2\sqrt{f^2(\mathbf{k})g^2(\mathbf{k}) + \Delta^2\zeta_j^2(\mathbf{k})}}, \quad (3.4)$$

Figure 3.1: Temperature dependence of the specific heat for (a) Δ_{1a} (blue solid line) and Δ_{1b} (green dashed line), and (b) Δ_2 (cyan solid line), Δ_3 (purple dotted line) and Δ_{4a} (light green dashed line).

$$E_{4j}(\mathbf{k}) = -\sqrt{\zeta^2(\mathbf{k}) + 2\sqrt{f^2(\mathbf{k})g^2(\mathbf{k}) + \Delta^2\zeta_j^2(\mathbf{k})}}. \quad (3.5)$$

Here,

$$\zeta^2(\mathbf{k}) = f^2(\mathbf{k}) + g^2(\mathbf{k}) + \Delta^2, \quad (3.6)$$

and $\zeta_j(\mathbf{k})$ ($j = 1a, 1b, 2, 3, 4a, 4b$) for each pair potential is

$$\zeta_{1a}^2(\mathbf{k}) = 0, \quad (3.7)$$

$$\zeta_{1b}^2(\mathbf{k}) = b^2(\mathbf{k}) + c^2(\mathbf{k}) + d^2(\mathbf{k}) + e^2(\mathbf{k}), \quad (3.8)$$

$$\zeta_2^2(\mathbf{k}) = a^2(\mathbf{k}) + e^2(\mathbf{k}), \quad (3.9)$$

$$\zeta_3^2(\mathbf{k}) = a^2(\mathbf{k}) + d^2(\mathbf{k}), \quad (3.10)$$

$$\zeta_{4a}^2(\mathbf{k}) = a^2(\mathbf{k}) + c^2(\mathbf{k}), \quad (3.11)$$

$$\zeta_{4b}^2(\mathbf{k}) = a^2(\mathbf{k}) + b^2(\mathbf{k}). \quad (3.12)$$

We assume that the superconducting gap has the following phenomenological temperature dependence obtained from the BCS theory:

$$\Delta(T) = 1.76k_B T_c \tanh(1.74\sqrt{T_c/T - 1}) \quad (3.13)$$

where T_c is the superconducting critical temperature.

In Fig. 3.1, we show the temperature dependence of the specific heat C_s/T as a function of the temperature T . In the case of Δ_{1a} , C_s/T has the exponential behavior near $T/T_c = 0$, and the magnitude of the specific heat jump at T_c is largest among the possible pair potentials. On the other hand, in the case of Δ_{1b} , the superconducting gap has line nodes, which leads to the linear behavior of C_s/T around $T/T_c = 0$. To satisfy the entropy balance, $\int_0^{T_c} dT [C_s(T) - C_n(T)]/T = 0$, the magnitude of the specific heat jump becomes smaller compared with Δ_{1a} . Moreover, the line shape of C_s/T for Δ_{1b} is convex upward. The superconducting gap of Δ_2 and Δ_3 are different only by the k^3 term. Therefore, as is seen from Fig. 3.1 (b), the temperature dependence of C_s/T for Δ_2 and Δ_3 are almost the same. In this case, C_s/T has T^2 -behavior at low temperature since the superconducting gap has the point nodes. In the case of Δ_3 , as is mentioned in Sec. 2.3, the superconducting gap is quite similar to that for line nodal one. For this reason, although we can see the T^2 behavior of C_s/T very near $T/T_c = 0$, the line shape of C_s/T is almost the same as line nodal one such as Δ_{1b} .

We have seen the wide variation of the temperature dependence of the specific heat for the superconducting state. However, it should be worth mentioning that Δ_{1a} and Δ_{1b} can be mixed with each other since they belong to the same irreducible representation. Hence, depending on the ratio of the mixture, the line shape of the specific heat can be similar to those of other pair potentials. Nevertheless, behaviors of the spin susceptibility of Δ_{1a} and Δ_{1b} are different from others, as we show below.

3.2.2 Spin susceptibility

In this subsection, we calculate the temperature dependence of the spin susceptibility for the possible pair potentials. From the temperature dependence of the spin susceptibility, we can see the spin structure, i.e. d -vector, on the Fermi surface [12, 15]. For spin-singlet superconductors, the spin susceptibility decreases with decreasing temperature for any direction and becomes zero at $T = 0$. On the other hand, for spin-triplet superconductors, the temperature dependence of the spin susceptibility depends on the relation between the direction of applied magnetic field and the direction of the d -vector. If the magnetic field is parallel to the d -vector, the spin susceptibility decreases with decreasing T . In contrast, the magnetic field is perpendicular to the d -vector, spin susceptibility does not depend on T . The effect of the Van-Vleck susceptibility, which originates from inter-band scattering, is also important to under-

stand the temperature dependence of the spin susceptibility. If the Van-Vleck effect is strong, the spin susceptibility has a finite value at $T = 0$ even for the spin-singlet pairing.

For the DSs, the Zeeman terms h_i ($i = x, y, z$), which express the coupling between electronic spin and magnetic field $\mathbf{H} = (H_x, H_y, H_z)$, are given by

$$h_x = \frac{1}{2}\mu_B H_x(\sigma_0 + \sigma_z)s_x, \quad (3.14)$$

$$h_y = \frac{1}{2}\mu_B H_y(\sigma_0 + \sigma_z)s_y, \quad (3.15)$$

$$h_z = \mu_B H_z \sigma_0 s_z, \quad (3.16)$$

where μ_B is the Bohr magneton and g factor is taken as 2 for simplicity. The in-plane Zeeman effect for the p -orbital is absent since $|p_x + ip_y\rangle$ and $|p_x - ip_y\rangle$ are orthogonal each other. From the linear response theory, the spin susceptibility is given by

$$\chi_i = -\lim_{q \rightarrow 0} \frac{1}{N} \sum_{\mathbf{k}, \alpha, \beta} \frac{f(E_\alpha(\mathbf{k})) - f(E_\beta(\mathbf{k} + \mathbf{q}))}{E_\alpha(\mathbf{k}) - E_\beta(\mathbf{k} + \mathbf{q})} |\langle \alpha | h_i | \beta \rangle|^2, \quad (3.17)$$

where α and β are the band indices.

In Fig. 3.2 (a), we show the temperature dependence of spin susceptibility for Δ_{1a} and Δ_{1b} . In the case of Δ_{1a} and Δ_{1b} , the spin susceptibility for any direction decreases with decreasing T . However, χ_x and χ_y have finite value at $T = 0$ in contrast to χ_z . To examine this anisotropy, we obtain the Zeeman term in the band basis:

$$\begin{aligned} \tilde{h}_x = & -\frac{\eta^2}{r^2} \tilde{\sigma}_0 \left(\frac{k_x^2 - k_y^2}{2} s_x - k_x k_y s_y \right) + \frac{m\eta^2}{r^2 R} \tilde{\sigma}_z \left(\frac{k_x^2 - k_y^2}{2} s_x - k_x k_y s_y \right) \\ & + \frac{\eta^2}{rR} \tilde{\sigma}_x \left(\frac{k_x^2 - k_y^2}{2} s_x - k_x k_y s_y \right), \end{aligned} \quad (3.18)$$

$$\begin{aligned} \tilde{h}_y = & -\frac{\eta^2}{r^2} \tilde{\sigma}_0 \left(k_x k_y s_x + \frac{k_x^2 - k_y^2}{2} s_y \right) + \frac{m\eta^2}{r^2 R} \tilde{\sigma}_z \left(k_x k_y s_x + \frac{k_x^2 - k_y^2}{2} s_y \right) \\ & + \frac{\eta^2}{rR} \tilde{\sigma}_x \left(k_x k_y s_x + \frac{k_x^2 - k_y^2}{2} s_y \right), \end{aligned} \quad (3.19)$$

$$\tilde{h}_z = \tilde{\sigma}_0 s_z, \quad (3.20)$$

where we ignore the k^3 terms for simplicity. It is found that $\tilde{h}_x$ and $\tilde{h}_y$ have inter-band component $\tilde{\sigma}_x$, which leads to the Van-Vleck susceptibility. However, $\tilde{h}_z$ has only intra-band component. In addition, the intra-band component of $\tilde{h}_{x(y)}$ is k -

Figure 3.2: Calculated results of spin susceptibility for possible pair potentials. (a) Temperature dependence of the spin susceptibility for Δ_{1a} and Δ_{1b} . Cyan solid line (light green dashed line) indicates χ_x and χ_y (χ_z) for Δ_{1a} . Blue dotted line (green dashed-dotted line) indicates χ_x and χ_y (χ_z) for Δ_{1b} . (b) Temperature dependence of the spin susceptibility for Δ_2 and Δ_3 . Cyan solid line (light green solid line) indicates χ_x and χ_y (χ_z) for Δ_2 . Blue dotted line (green dotted line) indicates χ_x and χ_y (χ_z) for Δ_3 . (c) Temperature dependence of the spin susceptibility for Δ_{4a} . Cyan solid line, blue dotted line and light green dashed line indicate χ_x , χ_y and χ_z for Δ_2 , respectively. (d) Azimuthal-angle dependence of the spin susceptibility at $T/T_c = 0.4$, where $\theta/2\pi = 0$ ($1/4$) indicates the x (y) direction. Black dashed line, blue dotted line, cyan solid line, green dashed-dashed-dotted line, solid purple line and green dashed-dotted-dotted line indicates the spin susceptibility for Δ_{1a} , Δ_{1b} , Δ_2 , Δ_3 , Δ_{4a} and Δ_{4b} , respectively.

dependent, while that of $\tilde{h}_z$ is not. Therefore, there is an anisotropy between $\chi_{x(y)}$ and χ_z . Moreover, the inter-band component is proportional to η^2 which is a parameter related to the spin-orbit interaction. Therefore, the anisotropy can be tuned by η . It is noted that the anisotropy stemming from the spin-orbit interaction can be seen in superconducting doped TIs [137], non-centrosymmetric superconductors [180] and locally non-centrosymmetric superconductors [181]. χ_i for Δ_{1a} has exponential behavior since the superconducting gap is fully gapped. On the other hand, the line shape of χ_i for Δ_{1b} is almost linear since the superconducting gap has line nodes. Although there are the anisotropic Van-Vleck effect and the effect from the superconducting gap structure, the spin susceptibility for both Δ_{1a} and Δ_{1b} decreases enough around $T = 0$.

In Fig. 3.2 (b), we show the temperature dependence of the spin susceptibility χ_i for Δ_2 and Δ_3 . As is mentioned in Sec. 2.3, the d -vector of Δ_2 and Δ_3 is almost parallel to x - y plane. Therefore, χ_z is T independent and $\chi_{x(y)}$ decreases with decreasing T . If the Van-Vleck effect is absent, $\chi_{x(y)}(0)/\chi_{x(y)}(T_c) = 0.5$ at $T = 0$ since the d -vector is completely polarized in the x - y plane.

In Fig. 3.2 (c), we show the temperature dependence of the spin susceptibility χ_i in the case of Δ_4 . The d -vector for Δ_4 is almost parallel to the z -axis. Consequently, $\chi_{x(y)}$ is T -independent and χ_z decreases with decreasing T . The line shape of χ_z is almost linear because the superconducting gap is a line node like structure.

The azimuthal-angle dependence of the spin susceptibility at $T/T_c = 0.4$ is shown in Fig. 3.2 (d). For Δ_{1a} , Δ_{1b} , Δ_2 and Δ_3 , there is no angle dependence of spin susceptibility. On the other hand, for Δ_{4a} and Δ_{4b} , the k^3 terms lead to the in-plane anisotropy as can be seen from the analytical formula of the d -vector. However, due to the fact that the effect of the k^3 terms is small compared with the k -linear terms, no angle dependence is seen in the calculated results in Fig. 3.2 (d). We note that this behavior is different from the case of the superconducting doped TIs. For superconducting doped TIs, such as $\text{Cu}_x\text{Bi}_2\text{Se}_3$, we can see azimuthal-angle dependence in the case of E_u pair potential since the d -vector parallel to the y - z or z - x plane [137], which has been also observed experimentally [90].

In summary of this subsection, we have revealed that there are wide variations of the temperature dependence of the spin susceptibility. In particular, at low temperature, the combinations of the spin susceptibility for three directions are completely different among Δ_1 , Δ_2 (Δ_3) and Δ_{4a} (Δ_{4b}). It is worth mentioning that even if Δ_{1a}

Figure 3.3: (a) (010) and (110) surface Brillouin zones, and the projected Fermi surface. (b) [(c)] Surface spectral function of the normal state for the (010) [(110)] surface along the $\bar{Z}_1-\bar{\Gamma}_1-\bar{X}_1$ ($\bar{Z}_2-\bar{\Gamma}_2-\bar{X}_2$) line. The isolated branches indicate the surface states. White dotted lines indicate $E = 0.07 \text{ eV}$. (d) [(e)] Surface spectral function of the normal state for the (010) [(110)] surface at $E = 0.07 \text{ eV}$.

and Δ_{1b} are mixed, χ_i for any direction is small enough at low temperature, which is different from the cases with other pair potentials. In addition, we have clarified that the line shape of the temperature dependence of spin susceptibility is useful to reveal the superconductivity in the doped DSs. We conclude that it is possible to distinguish the superconducting states, except the difference between Δ_2 and Δ_3 , by measuring x - y plane and z -direction Knight shift.

3.3 Surface physical properties

It has been well known that unconventional superconductors host exotic SABSs [182–185]. In this section, we reveal the SABSs of the superconducting DSs using the recursive Green’s function method [186]. We also interpret the calculated results with topological numbers.

First of all, we briefly review the surface state in the normal state [156]. In Fig. 3.3, we show the surface Brillouin zone and spectral function for the (010) and (110) surface. For the DSs, the mirror Chern number with respect to the x - y mirror plane is

Figure 3.4: Surface Andreev bound state on the (010) (a)-(d) and (110) (e)-(h) surface for the possible pair potentials.

1. Here, the mirror Chern number is defined as

$$n_{\mathcal{M}} = \frac{n_{+i} - n_{-i}}{2}, \quad (3.21)$$

where $n_{\pm i}$ is the Chern number for mirror subsectors labeled with mirror eigenvalues $\pm i$. The non-zero mirror Chern number ensures the existence of surface states as shown in Figs. 3.3 (b) and (c). Along the direction of $\bar{\Gamma}_1$ - $\bar{Z}_1$, the surface state has the form connecting the $\bar{\Gamma}$ and the bulk Dirac point. On the other hand, along the $\bar{\Gamma}_1$ - $\bar{X}_1$ ($\bar{\Gamma}_2$ - $\bar{X}_2$) direction, it looks like cone shape. The spectral functions at $E = 0.07$ eV are shown in Figs. 3.3 (d) and (e). At $E = 0.07$, there are both bulk and surface state.

3.3.1 Surface Andreev bound state

In Fig. 3.4, we show our calculated results of surface spectral function for the (010) and (110) surfaces in the superconducting state. Here, we focus on Δ_2 , Δ_3 and Δ_{4a} (Δ_{4b}) pairings and ignore Δ_1 pairings since there is no SABS in the case of Δ_1 . It is noted that, in the case of Δ_4 , the (010) surface for Δ_{4a} corresponds to the (100) surface for Δ_{4b} , and vice versa, since Δ_4 is the two-dimensional representation.

First, we would like to mention the surface state along the $\bar{\Gamma}_1$ - $\bar{Z}_1$ ($\bar{\Gamma}_2$ - $\bar{Z}_2$) direction for the (010) [(110)] surface. As can be seen from the upper column of Fig. 3.4, Δ_2 and Δ_{4a} have dispersive SABSs and Δ_3 has flat SABSs along the $\bar{\Gamma}_1$ - $\bar{Z}_1$ direction between

the point nodes. On the other hand, as is seen from the lower column of Fig. 3.4, Δ_2 has flat SABs, and Δ_3 , Δ_{4a} and Δ_{4b} have dispersive SABs along the $\bar{\Gamma}_2$ - $\bar{Z}_2$ line between the point nodes.

To interpret the surface states, we see the topological nature of the system. Since the unconventional pair potentials, Δ_2 , Δ_3 and Δ_4 , support nodes in the bulk superconducting gaps, bulk topological numbers are defined within lower dimensional subspaces in the Brillouin zone. In time-reversal-invariant odd-parity superconductors, the stability of point nodes are ensured by a one-dimensional winding number with the aid of mirror-reflection symmetry [187]. From the topological classification of nodes, the non-trivial winding number exists only if the pair potential is even under the mirror-reflection operation and predicts flat SABs between the point nodes as long as we make the surface perpendicular to the mirror invariant plane. Note that, although the point nodes in the DS with Δ_2 , Δ_3 , Δ_{4a} and Δ_{4b} are protected by the C_4 rotational symmetry, it is necessary to consider mirror-reflection symmetry to understand flat SABs. This is because the C_4 rotational symmetry cannot survive when we make the surface normal to the rotational axis.

In the case of the DS, there are two mirror planes parallel to z -axis, i.e., y - z (z - x) plane and the (110) plane. As is summarized in Table 5.1, Δ_2 is even under the (110) mirror operation but odd under the y - z mirror operation. Conversely, Δ_3 is even under the y - z mirror operation but odd under the (110) mirror operation. On the other hand, Δ_{4a} (Δ_{4b}) is even under the y - z (z - x) mirror operation but odd under the z - x (y - z) mirror operation and does not have the (110) mirror-reflection symmetry.

To examine the stability of the flat SABs, we numerically calculate the one-dimensional winding number on the mirror-even plane for each pair potential. Here, we focus on the y - z plane in the case of Δ_3 . For the BdG Hamiltonian, the y - z mirror operator, time-reversal operator, and particle-hole operator are given by

$$\mathcal{M}'_{yz} = \begin{pmatrix} \mathcal{M}_{yz} & 0 \\ 0 & \mathcal{M}_{yz}^* \end{pmatrix}, \quad (3.22)$$

$$\mathcal{T}' = \mathcal{T}\tau_0, \quad (3.23)$$

$$\mathcal{C} = \sigma_0 s_0 \tau_x \mathcal{K}. \quad (3.24)$$

Combining these operators, we can define the mirror-chiral operator:

$$\Gamma_{\mathcal{M}} = \mathcal{M}'_{yz} \mathcal{T}' \mathcal{C}, \quad (3.25)$$

which satisfies

$$\Gamma_{\mathcal{M}} H_{\text{BdG}}(k_x, k_y, k_z) \Gamma_{\mathcal{M}}^\dagger = -H_{\text{BdG}}(-k_x, k_y, k_z). \quad (3.26)$$

With this mirror-chiral operator, we can define the one-dimensional winding number for a fixed k_z :

$$W = -\frac{1}{4\pi i} \int_{-\pi}^{\pi} dk_y \text{Tr}(\Gamma_{\mathcal{M}} H_{\text{BdG}}^{-1} \partial_{k_y} H_{\text{BdG}}). \quad (3.27)$$

To evaluate Eq. (3.27), we follow the method in Ref. [45]. As a result, we find that the winding number W is

$$W = \begin{cases} 2 & (k_{d1} < k_z < k_{d2}, k_{d3} < k_z < k_{d4}) \\ 0 & \text{otherwise} \end{cases}, \quad (3.28)$$

where k_{di} ($i = 1, 2, 3, 4$) are the momentum of the disconnected Fermi surfaces around the Dirac points as shown in Fig. 3.5. Therefore, the existence of the zero-energy flat SABSs at $k_{d1} < k_z < k_{d2}$ and $k_{d3} < k_z < k_{d4}$ is ensured by the non-zero winding number. As the same manner, we can easily interpret the zero-energy flat SABSs for the (110) surface in the case of Δ_2 with the winding number.

In the case of Δ_{4a} , the gap function is odd under the y - z mirror operation, and hence there are dispersive SABSs between the point nodes along the $\bar{\Gamma}_1$ - $\bar{Z}_1$ direction for the (010) surface. On the other hand, in the case of Δ_{4b} , the gap function is even under the y - z mirror operation, where we can define the one-dimensional winding number. However, the winding number is zero for any k_z . Correspondingly, there is no SABS along the $\bar{\Gamma}_1$ - $\bar{Z}_1$ direction as shown in Fig. 3.4 (d). For the (110) surface, both Δ_{4a} and Δ_{4b} do not have mirror-reflection symmetry, hosting the dispersive SABSs between the point nodes.

Next, we refer to the surface state along the $\bar{\Gamma}_1$ - $\bar{X}_1$ ($\bar{\Gamma}_2$ - $\bar{X}_2$) direction for the (010) [(110)] surface. As is seen from Figs. 3.3 (d) and (e), there are surface states but no bulk states at the Fermi level in the normal state. In the superconducting state, as shown in Fig. 3.4, there are zero-energy SABSs for the (010) surface in the case of

Δ_2 , Δ_3 and Δ_{4a} , and for the (110) surface in the case of Δ_2 and Δ_3 . These zero-energy SABSs are formed by the remaining surface states in the normal state. Hereafter, we call this type of zero-energy SABS as remaining zero-energy SABS.

We can understand whether the normal surface states remain gapless or not in the superconducting state with the parity of the pair potential under the mirror operation $\mathcal{M}_{xy}$ [188]. In the superconducting state, the hole band $\varepsilon^h(k)$ appears, where the relation between electron band and hole band is $\varepsilon^h(k) = -\varepsilon^e(-k)$. If the pair potential is even (odd) under the mirror operation $\mathcal{M}_{xy}$, the BdG Hamiltonian commutes with a mirror operator $\mathcal{M}_{xy}^{\eta_{\mathcal{M}}} = \text{diag}[\mathcal{M}_{xy}, \eta_{\mathcal{M}} \mathcal{M}_{xy}^*]$ where $\eta_{\mathcal{M}} = + (-)$. Then the BdG Hamiltonian can be block diagonalized by the eigenvectors of $\mathcal{M}_{xy}^{\eta_{\mathcal{M}}}$, where each block diagonalized part is labeled with mirror eigenvalue, $+i$ or $-i$. If the parity of the pair potential under the mirror operation is even, the particle-hole symmetry exists between the different mirror eigensectors, which can be schematically shown in Fig. 3.5 (b). In this case, the band with the same mirror eigensector crosses at $E = 0$, namely, $\varepsilon_{+i}^e(-k') = \varepsilon_{+i}^h(-k')$ and $\varepsilon_{-i}^e(k') = \varepsilon_{-i}^h(k')$ at $E = 0$, and hence it becomes gapped. On the other hand, if the parity of the pair potential under the mirror operation is odd, each mirror eigensector has the particle-hole symmetry. Then, the bands with opposite mirror eigenvalues cross each other at $E = 0$, namely, $\varepsilon_{+i}^e(-k') = \varepsilon_{-i}^h(-k')$ and $\varepsilon_{-i}^e(k') = \varepsilon_{+i}^h(k')$ at $E = 0$ as shown in Fig. 3.5 (b). In this case, the crossed bands cannot mix with each other and remain gapless. For these reasons, the remaining zero-energy SABSs appear on the $\bar{\Gamma}_1$ - $\bar{X}_1$ and $\bar{\Gamma}_2$ - $\bar{X}_2$ line in the case of Δ_2 and Δ_3 . It should be noted that the mirror Chern number $n'_{\mathcal{M}}$ defined with $\mathcal{M}_{xy}^-$ is 2 in the case of Δ_2 and Δ_3 , which corresponds to the zero-energy states.

The remaining zero-energy SABS on the $\bar{\Gamma}_1$ - $\bar{X}_1$ for the (010) surface in the case of Δ_{4a} is protected by a different reason. In this case, the zero-energy state can be interpreted with a zero-dimensional topological number that is defined by combining the y - z mirror operator $\mathcal{M}'_{yz}$ and the chiral operator $\mathcal{T}'\mathcal{C}$ [150]. The zero-dimensional topological number for each k_x is given by

$$\rho(k_x) = \text{sgn} \left\{ \text{Pf}[H_{\text{BdG}}^{\text{SS}}(0, k_x) i s_z \tau_x] \right\}, \quad (3.29)$$

Figure 3.5: (a) Fermi surface on the y - z mirror plane and one-dimensional winding number W for Δ_3 at a fixed k_z . Blue dots indicate the position of the point node at $k_z = k_{di}$ ($i = 1, 2, 3, 4$). For $k_{d1} < k_z < k_{d2}$ and $k_{d3} < k_z < k_{d4}$, the winding number takes $W = 2$, and otherwise $W = 0$. (b) [(c)] Schematic picture of surface electron and hole band when the parity of pair potential under the mirror operation is even (odd).

with the surface BdG Hamiltonian and surface normal Hamiltonian:

$$H_{\text{BdG}}^{\text{SS}}(k_z, k_x) = [H^{\text{SS}}(k_z, k_x) - \mu]\tau_z + \Delta^{\text{surf}}\tau_x, \quad (3.30)$$

$$H^{\text{SS}}(k_z, k_x) = v(k_z s_x - k_x s_z). \quad (3.31)$$

By changing k_x , $\rho(k_x)$ changes its sign when k_x passes through the momentum of the zero-energy surface state, which means that the surface state is protected topologically. This zero-dimensional topological number can be defined when the parity of the pair potentials under the relevant mirror operation is odd. Therefore, we can also explain the remaining zero-energy SABS on the $\bar{\Gamma}_1$ - $\bar{X}_1$ for the (010) surface in the case of Δ_2 [the $\bar{\Gamma}_2$ - $\bar{X}_2$ for the (110) surface in the case of Δ_3] with the zero-dimensional topological number for the y - z [(110)] mirror plane in addition to the mirror Chern number for the x - y mirror plane. For more details and derivation of the zero-dimensional topological number $\rho(k_x)$, see the supplemental material in Ref. [150].

Here, we make a comment on the previous work [150]. In the previous work, the minimal required symmetries of the DSs, namely time-reversal, inversion, and

Topo. No.	zero-energy SABS	pair potential and surface
W	flat	$\Delta_2(110), \Delta_3(010)$
$n'_{\mathcal{M}}$	remaining	$\Delta_2[(010), (110)], \Delta_3[(010), (110)]$
$\rho(k_x)$	remaining	$\Delta_2(010), \Delta_3(110), \Delta_{4a}(010)$

Table 3.1: Zero-energy SABS and relevant topological number. First column shows the type of topological number: one-dimensional winding number W , mirror Chern number $n'_{\mathcal{M}}$ and zero-dimensional topological number $\rho(k_x)$. Second column shows the type of zero-energy SABS and third one shows the pair potentials and surface orientations that host the zero-energy SABS characterized with the topological number.

four-fold rotational symmetries, have been assumed. Under this assumption, surface Majorana quartet has been predicted when four-fold rotation symmetry is broken into two-fold one. On the other hand, in the present paper, full D_{4h} crystal symmetries have been taken into account, which enables us to realize different surface states such as the flat surface state. It should be noted that the Majorana quartet appears even in our model in the case of Δ_2 and Δ_3 by breaking the four-fold rotational symmetry.

In summary of this subsection, we have found that wide variation of exotic SABSs appear depending on the pair potentials and surface direction. We have revealed that the zero-energy SABSs can be interpreted with three topological numbers: one-dimensional winding number, two-dimensional-mirror Chern number, and zero-dimensional topological number. The mirror-reflection symmetry plays an essential role to protect SABSs in this system. The zero-energy SABS and relevant topological number are summarized in Table 3.1.

3.3.2 Surface density of state

In this subsection, we calculate the surface density of state (SDOS) by integrating the spectral function with respect to the wave number k obtained in the previous subsection. In Fig. 3.6, we show the normalized SDOS $D_s(E)/D_n(0)$ as a function of normalized energy E/Δ for the (010) surface in the case of Δ_2 and Δ_3 , which corresponds to the case of the dispersive SABSs and flat SABSs, respectively. In the case of dispersive SABSs, double peaks appear around $E/\Delta=0.5$ and the spectra look like V shape. The double peaks originate from saddle points on the top (bottom) of the arc

Figure 3.6: SDOS as a function of normalized energy for the (010) surface. Black dashed line (blue solid line) indicates the SDOS for Δ_2 (Δ_3) which corresponds to the dispersive (flat) SABSs case.

in $E > 0$ ($E < 0$). On the other hand, the flat SABS leads to a single peak at $E/\Delta = 0$ in the SDOS. These results suggest that we can distinguish Δ_2 and Δ_3 by conductance measurement with low transmissivity realized in scanning tunneling spectroscopy.

We briefly mention the experimental results of point contact spectra for Cd_3As_2 [168,169]. The experiments have been done for the (112) natural cleavage surface and the zero-energy conductance peak has been observed. In general, one of the promising explanations of a zero-energy conductance peak in the superconducting state is the existence of a zero-energy flat band. When we see the (112) surface of Cd_3As_2 , the (110) mirror-reflection symmetry is preserved. Therefore, Δ_2 that has a flat band for this direction can explain the observed zero-energy conductance peak. Besides the topologically protected flat band, the accidental flat band stemming from the remaining normal surface state also leads to a zero-energy conductance peak. It has been revealed that, in the superconducting doped TIs with fully-gapped odd-parity pairing, the dispersion of SABSs has the structural transition from simple cone shape to twisted shape [189–191]. At the transition point, the zero-energy flat like band appears, leading to the zero-energy conductance peak. In the case of the superconducting DSs, the SABSs exist between the point nodes along Γ_2 - Z_2 . Therefore, as long as the point nodes are protected, the SABSs cannot mix with the remaining surface state, which means the SABSs cannot change their structure. For further discussion of the experiments, it is necessary to calculate conductance with high transmissivity.

3.4 Summary

We have studied the superconductivity in Cd_3As_2 type DSs. We have calculated the bulk and surface physical properties of the possible pair potentials. Our calculation results of the bulk physical properties, especially the spin susceptibility, is useful to reveal the pairing symmetry. Moreover, we have shown that the exotic SABSs exist in Δ_2 , Δ_3 , Δ_{4a} , and Δ_{4b} , and interpreted each SABS with three types topological numbers. We have concluded that it is possible to distinguish the possible superconducting states by combining the bulk and surface measurements.

Chapter 4

Andreev bound states in Zeeman split Josephson junctions

4.1 Introduction

The Josephson effect is the fundamental phenomenon in superconductor junctions [192]. Since the discovery of this effect, various types of structure have been studied. In particular, the superconductor/ferromagnet/superconductor (S/F/S) junction has attracted much research interest because of its high tunability of the supercurrent [193–195]. In S/F/S junctions, the so called π phase, where the direction of the critical current is reversed compared with 0 phase, is realized by changing the strength of the exchange field or thickness of the ferromagnetic region [196, 197].

In recent years, superconductors with spin-split energy bands, so called Zeeman-split superconductors (ZSs), have also been studied widely owing to their potential application to the superconducting spintronics [198, 199]. The homogeneous spin splitting in the superconductor can be realized in the systems such as thin F/S junctions [200, 201] or thin superconductor films under the application of an in-plane magnetic field [202]. It has been shown that N/ZS junctions, where N stands for a normal metal, can generate highly spin-polarized current [203–206]. Josephson junctions with spin-split superconductors have been also studied in various types of structures. In ZS/N/ZS junctions, the spin degeneracy of the Andreev level is lifted and the magnitude of the spin splitting can be controlled by changing either the magnitude or relative direction of the Zeeman field in the superconducting leads [207–210]. ZS/N/ZS junctions with unconventional superconducting pairing such as p - or d -wave pairing, have also been studied and the tunability of the Andreev level by changing the relative direction of the Zeeman field and superconducting d -vector have been demonstrated [211–214].

The magnetic tunability of the Andreev levels and the resulting supercurrent has been shown in the previous studies as mentioned above. However, the electric tunability of these levels has not been discovered yet in the ZS junctions, even though the electric tunability tends to have advantages for nano-device applications. To realize the electric tunability, the most promising way is introducing the Rashba spin-orbit interaction (RSOI) in a system, which is tunable by the gate voltage [215, 216]. Recently, there has been a growing interest in a one-dimensional Rashba wire, especially after the proposal to use it as a platform for Majorana fermions [50–52]. The Rashba wire has a characteristic band structure, where the spin degeneracy is lifted and the direction of spin and momentum is locked (spin-momentum locking). More

Figure 4.1: (a) Schematic illustration of the Zeeman-split superconductor/Rashba wire/Zeeman-split superconductor junction. $\hat{n}_\eta = (\cos \theta_\eta \cos \zeta_\eta, \cos \theta_\eta \sin \zeta_\eta, \sin \theta_\eta)$ is a unit vector representing the direction of Zeeman field in the left ($\eta = L$) and right ($\eta = R$) superconductor. (b) Schematic band structure of a Rashba wire. (c) Schematic band structure of a Zeeman-split superconductor. Black solid (blue dotted) lines show the spin-up (spin-down) band.

importantly, because of the pseudomagnetic effect of the RSOI, the spin precession takes place while an electron or hole is traveling in the Rashba wire.

Another motivation for this work is that although the effect of the exchange field in the nanowire is often taken into account in recent literature considering the prospect of Majorana fermions in spin-orbit coupled Josephson junctions with externally applied magnetic field, the fact that even a very small exchange field h induced in the superconducting region (in the case where these are thin enough to permit this) may affect the physical properties of the system remains virtually unexplored in this context. Despite the fact that a nanowire made of a material such as InAs is likely to have a higher g -factor than the materials used for the superconducting regions, even a small exchange field $h \ll \Delta$ induced in the superconductors is sufficient to induce qualitatively new physics such as considerable thermoelectric effects [217–219]. Our study is therefore also of relevance with regard to Majorana experiments utilizing sufficiently thin superconducting regions that an in-plane field may induce a small exchange splitting in them.

In this chapter, we theoretically study Andreev reflection and the formation of Andreev levels in Zeeman-split superconductor/Rashba wire/ Zeeman-split superconductor (ZS/RW/ZS) junction to reveal how the electric tunable RSOI in the wire and the Zeeman field in the superconductors affects the Andreev level. We first study Andreev and normal reflections at the boundary of the RW/ZS bilayer, since these processes are of fundamental relevance to the formation of bound states in a Josephson geometry. We then calculate the Andreev level energies in the ZS/RW/ZS Josephson junction. We find that the Andreev levels can be controlled by the strength of the RSOI λ , the length of the Rashba wire l and the direction of the Zeeman field though the tunneling conductance is not so affected by the RSOI. It is found that the magnitude of the band splitting of the Andreev level oscillates as a function of the strength of the RSOI λ and the length of the Rashba metal l with a certain period. We also find that the Andreev level can be dramatically altered by changing the direction of the Zeeman field relative to the vector characterizing the RSOI. In particular, if the Zeeman field has a component along the junction (x component in this chapter), the Andreev level becomes asymmetric in the superconducting phase difference ϕ and provides a finite supercurrent even at zero phase-bias $\phi = 0$.

This chapter is organized as follows. In Sec.4.2, we first introduce a model Hamiltonian for a junction consisting of the ZS and Rashba wire. In Sec.4.3, calculation results of the Andreev reflection and the tunneling conductance are discussed. In

Sec.4.4.1, we review the Andreev level in the absence of RSOI. Then we move to the main results: Andreev level in the presence of RSOI in Sec.4.4.2. Finally, we summarize our results in Sec.4.5.

4.2 Formulation

Figure 4.1(a) shows the schematic picture of the ZS/RW/ZS junction. In this chapter, we consider a short ballistic junction that satisfies $l \ll \xi$, where l is the length of the Rashba wire and ξ is the ballistic superconducting coherence length. The Bogoliubov-de Gennes (BdG) Hamiltonian for this system is described by,

$$\begin{pmatrix} \hat{H}_0(r) & \hat{\Delta}(x) \\ -\hat{\Delta}^*(x) & -\hat{H}_0^*(r) \end{pmatrix} \hat{\psi}_i(r) = \varepsilon \hat{\psi}_i(r), \quad (4.1)$$

with

$$\hat{H}_0(r) = \left[-\frac{\hbar^2}{2m} \nabla^2 - \mu + Z(x) \right] \hat{\sigma}_0 - \hat{\lambda}(x) - \hat{h}(x), \quad (4.2)$$

$$Z(x) = Z[\delta(x) + \delta(x-l)], \quad (4.3)$$

$$\hat{\lambda}(x) = \{k_x, \lambda \Theta(x) \Theta(l-x)\} \hat{\sigma}_y \quad (4.4)$$

$$\hat{h}(x) = h_L \Theta(-x) \hat{n}_L \cdot \hat{\sigma} + h_R \Theta(x-l) \hat{n}_R \cdot \hat{\sigma}, \quad (4.5)$$

$$\hat{\Delta}(x) = \Delta [e^{i\phi_L} \Theta(-x) + e^{i\phi_R} \Theta(x-l)] (i\hat{\sigma}_y), \quad (4.6)$$

where the basis is set as $(c_\uparrow, c_\downarrow, c_\uparrow^\dagger, c_\downarrow^\dagger)$ and $\hat{\sigma}$ is the Pauli matrix for the spin space. Here, $Z(x)$ denotes the barrier potential at the boundaries, $\hat{\lambda}(x)$ is the Rashba spin-orbit interaction in the normal region, $\hat{h}(x)$ is the exchange field in the superconducting region and $\hat{\Delta}(x)$ is the superconducting pair potential, where $\delta(x)$ and $\Theta(x)$ are the δ function and step function, respectively. To satisfy the Hermiticity of the Hamiltonian at the boundaries, we adopt $\{k_x, \lambda \Theta(x) \Theta(l-x)\} \hat{\sigma}_y$ as a Rashba spin-orbit interaction term instead of $\lambda k_x \hat{\sigma}_y$. In addition, $\hat{n}_\eta = (\cos \theta_\eta \cos \zeta_\eta, \cos \theta_\eta \sin \zeta_\eta, \sin \theta_\eta)$ is a unit vector representing the direction of the Zeeman field in the left ($\eta = L$) and right ($\eta = R$) superconductors. In this chapter, we focus on the conventional s -wave superconductivity, hence we assume that the magnitude of the superconducting gap Δ is constant and positive value. The band structure of the Rashba wire and

Zeeman-split superconductor are shown in Figs.4.1 (b) and (c), where the systems are considered as infinite.

By diagonalizing the model Hamiltonian, one can obtain the wave function in the superconducting region under the plane-wave assumption as

$$\begin{aligned}
\hat{\psi}_L(x) = & a_L e^{-iq_{\uparrow}^+ x} [u_1 \cos \frac{\theta_L}{2} e^{i\phi_L/2}, u_1 \sin \frac{\theta_L}{2} e^{i(\zeta_L + \phi_L/2)}, \\
& -v_1 \sin \frac{\theta_L}{2} e^{i(\zeta_L - \phi_L/2)}, v_1 \cos \frac{\theta_L}{2} e^{-i\phi_L/2}]^T \\
& + b_L e^{-iq_{\downarrow}^+ x} [u_2 \sin \frac{\theta_L}{2} e^{-i(\zeta_L - \phi_L/2)}, -u_2 \cos \frac{\theta_L}{2} e^{i\phi_L/2}, \\
& v_2 \cos \frac{\theta_L}{2} e^{-i\phi_L/2}, v_2 \sin \frac{\theta_L}{2} e^{-i(\zeta_L + \phi_L/2)}]^T \\
& + c_L e^{iq_{\uparrow}^- x} [v_1 \cos \frac{\theta_L}{2} e^{i\phi_L/2}, v_1 \sin \frac{\theta_L}{2} e^{i(\zeta_L + \phi_L/2)}, \\
& -u_1 \sin \frac{\theta_L}{2} e^{i(\zeta_L - \phi_L/2)}, u_1 \cos \frac{\theta_L}{2} e^{-i\phi_L/2}]^T \\
& + d_L e^{iq_{\downarrow}^- x} [v_2 \sin \frac{\theta_L}{2} e^{-i(\zeta_L - \phi_L/2)}, -v_2 \cos \frac{\theta_L}{2} e^{i\phi_L/2}, \\
& u_2 \cos \frac{\theta_L}{2} e^{-i\phi_L/2}, u_2 \sin \frac{\theta_L}{2} e^{-i(\zeta_L + \phi_L/2)}]^T, \tag{4.7}
\end{aligned}$$

$$\begin{aligned}
\hat{\psi}_R(x) = & a_R e^{iq_{\uparrow}^+ x} [u_1 \cos \frac{\theta_R}{2} e^{i\phi_R/2}, u_1 \sin \frac{\theta_R}{2} e^{i(\zeta_R + \phi_R/2)}, \\
& -v_1 \sin \frac{\theta_R}{2} e^{i(\zeta_R - \phi_R/2)}, v_1 \cos \frac{\theta_R}{2} e^{-i\phi_R/2}]^T \\
& + b_R e^{iq_{\downarrow}^+ x} [u_2 \sin \frac{\theta_R}{2} e^{-i(\zeta_R - \phi_R/2)}, -u_2 \cos \frac{\theta_R}{2} e^{i\phi_R/2}, \\
& v_2 \cos \frac{\theta_R}{2} e^{-i\phi_R/2}, v_2 \sin \frac{\theta_R}{2} e^{-i(\zeta_R + \phi_R/2)}]^T \\
& + c_R e^{-iq_{\uparrow}^- x} [v_1 \cos \frac{\theta_R}{2} e^{i\phi_R/2}, v_1 \sin \frac{\theta_R}{2} e^{i(\zeta_R + \phi_R/2)}, \\
& -u_1 \sin \frac{\theta_R}{2} e^{i(\zeta_R - \phi_R/2)}, u_1 \cos \frac{\theta_R}{2} e^{-i\phi_R/2}]^T \\
& + d_R e^{-iq_{\downarrow}^- x} [v_2 \sin \frac{\theta_R}{2} e^{-i(\zeta_R - \phi_R/2)}, -v_2 \cos \frac{\theta_R}{2} e^{i\phi_R/2}, \\
& u_2 \cos \frac{\theta_R}{2} e^{-i\phi_R/2}, u_2 \sin \frac{\theta_R}{2} e^{-i(\zeta_R + \phi_R/2)}]^T, \tag{4.8}
\end{aligned}$$

where a_j , b_j , c_j and d_j with $j = L, R$ are the coefficients of electron-like quasiparticles with spin- $\uparrow$, hole-like quasiparticles with spin- $\uparrow$, electron-like quasiparticles with

spin- $\downarrow$, and hole like quasiparticles with spin- $\downarrow$, respectively. Moreover, we define

$$u_{1(2)} = \sqrt{\frac{1}{2} \left(1 + \frac{\sqrt{[\varepsilon + (-)h]^2 - \Delta^2}}{\varepsilon + (-)h} \right)} \quad (4.9)$$

$$v_{1(2)} = \sqrt{\frac{1}{2} \left(1 - \frac{\sqrt{[\varepsilon + (-)h]^2 - \Delta^2}}{\varepsilon + (-)h} \right)}. \quad (4.10)$$

The wave vectors $q_{\uparrow,\downarrow}^{\pm}$ are represented as

$$q_{\uparrow,\downarrow}^{\pm} = \sqrt{(2m/\hbar^2)(\varepsilon_F^S \pm \Omega_{\uparrow,\downarrow})}, \quad (4.11)$$

$$\Omega_{\uparrow(\downarrow)} = \sqrt{[\varepsilon + (-)h]^2 - \Delta^2}. \quad (4.12)$$

We assume $\varepsilon_F^S \gg |\Omega|$ so that the wave-vectors can be treated as $q_{\uparrow}^+ = q_{\downarrow}^+ = q_{\uparrow}^- = q_{\downarrow}^- \equiv q_F$. In a similar manner, the total wave-function in the normal region is described by

$$\begin{aligned} \hat{\psi}_N(x) = & \frac{1}{\sqrt{2}} [a_1 e^{ik_1 x} (i, 1, 0, 0)^T + a_2 e^{ik_2 x} (-i, 1, 0, 0)^T \\ & + b_1 e^{-ik_1 x} (-i, 1, 0, 0)^T + b_2 e^{-ik_2 x} (i, 1, 0, 0)^T \\ & + c_1 e^{-ik_1 x} (0, 0, -i, 1)^T + c_2 e^{-ik_2 x} (0, 0, i, 1)^T \\ & + d_1 e^{ik_1 x} (0, 0, i, 1)^T + d_2 e^{ik_2 x} (0, 0, -i, 1)^T], \end{aligned} \quad (4.13)$$

with

$$k_1 = -\lambda + \sqrt{\lambda^2 + k_F^2}, \quad (4.14)$$

$$k_2 = \lambda + \sqrt{\lambda^2 + k_F^2}, \quad (4.15)$$

where a_j , b_j , c_j and d_j are coefficients of a right-moving electron, a left-moving electron, a right-moving hole, and a left-moving hole with wave number k_j ($j = 1, 2$). Here, we set $\hbar = m = 1$ for brevity. The boundary conditions for the wave functions are given by

$$\hat{\psi}_L(0) - \hat{\psi}_N(0) = 0, \quad (4.16)$$

$$\hat{\psi}_N(l) - \hat{\psi}_R(l) = 0, \quad (4.17)$$

$$\left. \frac{\partial \hat{\psi}_L(x)}{\partial x} \right|_{x=0} - \left. \frac{\partial \hat{\psi}_N(x)}{\partial x} \right|_{x=0} = (Z\hat{I} + \lambda\hat{\tau})\hat{\psi}_N(0), \quad (4.18)$$

$$\left. \frac{\partial \hat{\psi}_N(x)}{\partial x} \right|_{x=l} - \left. \frac{\partial \hat{\psi}_R(x)}{\partial x} \right|_{x=l} = (Z\hat{I} - \lambda\hat{\tau})\hat{\psi}_N(l), \quad (4.19)$$

where $\hat{I}$ is the 4×4 identity matrix and

$$\hat{\tau} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}. \quad (4.20)$$

By matching the wave-functions in the different regions by using the boundary conditions, we obtain a system of equations described as $\hat{A}\hat{x} = 0$ where $\hat{A}$ is a 16×16 matrix and $\hat{x} = (a_1, a_2, b_1, b_2, c_1, c_2, d_1, d_2, a_R, b_R, c_R, d_R, a_L, b_L, c_L, d_L)^T$. Then, the Andreev level is determined by the condition $\det(A) = 0$.

Hereafter, we assume that $k_F = q_F \equiv k$ and $|h_L| = |h_R| \equiv h$, and fix the direction of the Zeeman field in the left superconductor $\theta_L = 0$ for simplicity. In the numerical calculations, we set $h = 0.2\Delta$. Such a magnitude of the exchange splitting is experimentally well within reach using sub-Tesla magnetic fields [202].

4.3 Andreev reflection and tunneling conductance

We begin with the Andreev reflection process at the interface, since this process is of fundamental importance with regard to the formation of the Andreev levels we will later consider in a Josephson setup. Here, we consider only the right interface and set $l = 0$. Then we obtain the reflection coefficients b_1, b_2, d_1 and d_2 .

In the presence of RSOI, the spin and momentum are locked and the right moving electron with wave number k_1 (k_2) is a spin-up (-down) eigenstate for the y quantization axis in our model, which is shown in Fig.4.1 (b). Note that the left moving electron has the opposite spin compared with the right moving one. The reflection probability of a particle with k_j ($j = 1, 2$) for an electron with k_i ($i = 1, 2$) injected case is defined as $B_j^{(i)} = |b_j^{(i)}|^2$ and $D_j^{(i)} = |d_j^{(i)}|^2$. Here $B_j^{(i)}$ and $C_j^{(i)}$ are normal and

Figure 4.2: Normal $B_j^{(i)}$ and Andreev $D_j^{(i)}$ reflection probability of the Rashba wire/Zeeman-split superconductor junction as a function of energy E at $\zeta_R = \pi/2$ for $\theta_R = 0$ (black solid line), $\theta_R = \pi/4$ (blue dashed line) and $\theta_R = \pi/2$ (green dotted line). The left (right) panels show the reflection probability for the electron with k_1 (k_2) injected case. Here, the parameters are set as $Z = 0.5$ and $\lambda/k = 1$.

Andreev reflection probabilities, respectively. (See Appendix for more information regarding $b_j^{(i)}$ and $d_j^{(i)}$)

In Fig.4.2, we show numerical results of the normal and Andreev reflection probability at the interface for various orientations of the Zeeman field. The left (right) panels show the reflection probability for an electron with wave number k_1 (k_2) injected case. Let us start with the case where the orientation of the Zeeman field $\hat{n}_R$ is parallel to the z direction. In this case, the spin-dependent reflection has taken place at the interface, and thus all reflection probabilities for both k_1 and k_2 electron injected case are finite. Since the energy band in the superconducting region is lifted as shown in Fig.4.1 (c), there are double kink points at $E = \Delta \pm |h|$. As can be seen in Fig.4.2 (black line), the reflection probability for the electron with a k_1 injected case is fully consistent with that for the electron with k_2 injected case (though the spin is opposite), namely, $B_1^{(1)} = B_2^{(2)}$, $B_2^{(1)} = B_1^{(2)}$, $D_1^{(1)} = D_2^{(2)}$, and $D_1^{(2)} = D_2^{(1)}$. With increasing θ_R for $\zeta_R = \pi/2$, $B_1^{(1)}$, $D_2^{(1)}$, $B_2^{(1)}$, and $D_1^{(2)}$ are suppressed, and when $\hat{n}_R \parallel y$ ($\theta_R = \pi/2$), $B_1^{(1)}$, $D_2^{(1)}$, $B_2^{(2)}$ and $D_1^{(2)}$ become zero, since left- and right- moving particles with the same wave number have the opposite spin and there is no spin dependent scattering at the interface. The reflection probability $B_2^{(1)}$, $D_1^{(1)}$, $B_1^{(2)}$, and $D_2^{(2)}$ are also changed by tuning θ_R as shown in Fig.4.2. At $\theta_R = \pi/2$, there is single kink point at $E = \Delta + h$ for $B_2^{(1)}$ and $D_1^{(1)}$, and at $E = \Delta - h$ for $B_1^{(2)}$ and $D_2^{(2)}$, since the spin-up and -down processes occurs separately. Note that here we vary the direction of the Zeeman field in the z - y plane, but the same results can be obtained if we change the direction of the Zeeman field in the x - y plane. For more information, the analytical formulas for the reflection coefficients for $\hat{n}_R \parallel z$ (or x) and y are shown in Appendix A.

Next, we calculate the tunneling conductance σ_s at zero temperature given by [220–222]

$$\sigma_s = \sum_{i=1,2} (1 - B_1^{(i)} - B_2^{(i)} + D_1^{(i)} + D_2^{(i)}). \quad (4.21)$$

Figure 4.3 (a) [(b)] shows the numerical results of the tunneling conductance in the case of $\hat{n}_R \parallel z$ ($\hat{n}_R \parallel y$). In these figures, the back solid lines show the observable tunneling conductance. Blue dashed and green dotted lines are the contribution from electrons with the k_1 and k_2 injected case, respectively. Although the contribution from the k_1 or k_2 injected case depends on the orientation of the Zeeman field when the fields are in the z - y plane, the total observable tunneling conductance does not depend on the direction. This is because the contributions from the k_1 injected case

Figure 4.3: Tunneling conductance of a Rashba wire/Z Zeeman-split superconductor junction as a function of bias voltage for (a) $\hat{n}_R \parallel z$ and (b) $\hat{n}_R \parallel y$. Black solid lines show the observable tunneling conductance. Blue dashed and green dotted lines are the contribution from the electron with k_1 and k_2 injected case, respectively. The total observable tunneling conductance does not depend on the orientation of the Zeeman field.

and k_2 case completely compensate each other. Figure 4.4 (a) shows the tunneling conductance as a function of the bias voltage for various λ , and Fig.4.4(b) shows it as a function of λ at zero bias voltage for various strengths of the barrier potential Z . As can be seen in the figures, the tunneling conductance is weakly affected by the RSOI, similarly to the results for two-dimensional electron gas with RSOI/superconductor junctions obtained by Yokoyama *et. al* [221]. Nevertheless, the Andreev levels in the ZS/RW/ZS trilayer are dramatically affected by the RSOI as shown below.

4.4 Andreev levels in Josephson junctions

4.4.1 In the absence of Rashba spin-orbit interaction

Before we move to the main results of the Andreev level in the presence of RSOI, we briefly review the case without RSOI [207]. In the absence of the RSOI, the Andreev bound state changes depending on the relative direction of the Zeeman field in two superconductors. When the Zeeman fields in two superconductors are parallel, the

Figure 4.4: (a) Tunneling conductance of Rashba wire/Z Zeeman split superconductor junction as a function of bias voltage at $Z = 0.5$ for $\lambda/k = 0$ (black solid line), $\lambda/k = 0.5$ (blue dashed line) and $\lambda/k = 1.0$ (green dotted line). (b) Tunneling conductance as a function of the strength of the RSOI λ at zero voltage for $Z = 0$ (black solid line), $Z = 0.5$ (blue dashed line), and $Z = 1.0$ (green dotted line).

spin degeneracy of the Andreev level is lifted and the Andreev level is described by

$$\varepsilon = \pm\Delta \cos \frac{\phi}{2} \pm h, \quad (4.22)$$

where $\phi = \phi_R - \phi_L$ and $Z = 0$. The first term of the right hand of Eq. (4.22) is the Andreev level in the absence of the Zeeman field [223]. Namely, the effect of the Zeeman field is simply the energy shift of $\pm h$ as shown in Fig.4.5 (a). In this case, the Andreev level exists for $-\Delta - h < E < \Delta + h$. By changing the relative direction of the Zeeman field from the parallel configuration (vary θ_R), the magnitude of the band splitting decreases. When the Zeeman field in the right superconductor has a finite angle, the spin dependent Andreev reflection occurs at the right boundary, and a right-moving electron with up-spin is reflected as a left moving hole that has both spin up and down component. However, if the energy of the Andreev-reflected hole is less than $-\Delta + h$ (or the energy of the injected electron is more than $\Delta - h$), the spin-up component of the hole is not Andreev reflected at the left boundary because of the spin-splitting energy gap of the left superconductor. This means that the amplitude of the wave decays for every single scattering process and the Andreev bound state can not be formed for the energy region. Therefore, there are no lines for $\Delta - h < |E| < \Delta + h$ in Fig.4.5 (b). When Zeeman fields in the two superconductors are antiparallel

Figure 4.5: Andreev level ε as a function of the phase difference ϕ in the absence of the RSOI for (a) $\theta_R = 0$, (b) $\theta_R = \pi/2$, and (c) $\theta_R = \pi$, where the direction of the Zeeman field in the left superconductor is fixed to $\theta_L = 0$. When $\theta_L \neq 0$, the Andreev levels ε for $E - \Delta < |\varepsilon| < E + \Delta$ are absent, the regions of which are shown with blue shading.

the energy band is degenerate, as shown Fig. 4.5 (c). In this case, the Andreev level is described by the following expression:

$$\varepsilon = \pm \cot \frac{\phi}{2} \sqrt{\Delta^2(1 - \cos \phi) - 2h^2}. \quad (4.23)$$

It follows from Eq.(4.23) that the Andreev level exists for $\phi_c < \phi < 2\pi - \phi_c$ with $\phi_c = \cos^{-1}(1 - 2h/\Delta)$.

4.4.2 In the presence of Rashba spin-orbit interaction

We now turn to the case with finite RSOI, which has not been studied previously in the literature. In the presence of RSOI, a degenerate energy band of the normal region splits into two branches and the wave vectors have a different value from that in the superconducting region. This wave vector mismatch causes a natural barrier at the interface and leads to the energy gap at $\phi = \pi$. This gap opening effect at $\phi = \pi$ can be seen in the absence of the Zeeman field and does not depend on the relative direction of the Zeeman field and the RSOI. The analytical expression of the Andreev level in the absence of the Zeeman field is given by

$$\varepsilon = \pm \Delta \sqrt{\frac{1}{2} \left(1 + \frac{4k^2(k^2 + \lambda^2) \cos \phi + \lambda^4 \sin^2(\sqrt{k^2 + \lambda^2}l)}{4k^2(k^2 + \lambda^2) - \lambda^4 \sin^2(\sqrt{k^2 + \lambda^2}l)} \right)}, \quad (4.24)$$

and the energy gap at $\phi = \pi$ is

$$\varepsilon_0 = \Delta \sqrt{\frac{\lambda^4 \sin^2(\sqrt{k^2 + \lambda^2}l)}{4k^2(k^2 + \lambda^2) + \lambda^4 \sin^2(\sqrt{k^2 + \lambda^2}l)}}, \quad (4.25)$$

where we set $Z = 0$ for simplicity. As seen from the above equation, the magnitude of the energy gap depends on λ , k , and l . The energy gap is closed when the parameters satisfy $\sqrt{k^2 + \lambda^2}l = n\pi$ where n is an integer number. Figure 4.6 (a) shows the magnitude of the energy gap at $\phi = \pi$ as a function of λ for various l . The magnitude of the energy gap increases with increasing λ with oscillation and the energy gap is closed at

$$\lambda/k = \sqrt{(n\pi/kl)^2 - 1}. \quad (4.26)$$

Figure 4.6 (b) shows the magnitude of the energy gap as a function of l for various λ . The magnitude of the energy gap oscillates by changing l , but the maximum value of each interval does not change. The energy gap is closed at

$$kl = n\pi / \sqrt{1 + \lambda^2/k^2}, \quad (4.27)$$

and the period of the oscillation slightly decreases with increasing λ . Note that, in the presence of the Zeeman field, the energy bands in the superconducting region also split so that the wave vectors for up spin and down spin are different. However, the difference between the wave vectors for up spin and down spin caused by the Zeeman field are much smaller than that caused by the RSOI since here we restrict the Zeeman energy $h < \Delta$. Therefore, we ignore the effect of the wave-vector mismatch originating in the superconducting region.

Next, we discuss the phenomena that can be seen only in the simultaneous presence of the Zeeman field and RSOI. We begin with the case where the Zeeman field in both superconductors are oriented in the $+z$ direction. In Fig.4.7 (first row), we show the numerical results of the Andreev level ε as a function of ϕ for various λ . Here, black solid (blue dotted) lines show the Andreev level for $Z = 0$ ($Z = 0.5$). As shown in the figure, the magnitude of the energy splitting changes depending on λ and l , with a period $2\pi/\lambda l$. Note that in the numerical calculation, we have set $\lambda \ll k$, which gives rise to a quite small gap at $\phi = \pi$ in the figure. At $\lambda = n\pi/l$, the magnitude of the band splitting has a maximum value for any ϕ . On the other hand, if $\lambda = (n + 1/2)\pi/l$, the magnitude of the band splitting is minimum; $\delta\varepsilon = 0$ for any

Figure 4.6: (a) The magnitude of the energy gap ε_0 at $\phi = \pi$ as a function of λ at $lk = 10$ (black solid), $lk = 20$ (blue dashed) and $lk = 30$ (green dotted). (b) The magnitude of the energy gap at $\phi = \pi$ as a function of l at $\lambda/k = 0.1$ (black solid), $\lambda/k = 0.2$ (blue dashed), and $\lambda/k = 0.3$ (green dotted).

ϕ . The black solid line in Fig. 4.8 shows the magnitude of the band splitting at $\phi = \pi$ as a function of the $\lambda l/2\pi$. This oscillation of the band splitting $\delta\varepsilon$ can be described by

$$\delta\varepsilon = h \cos(\lambda l). \quad (4.28)$$

Note that if the Zeeman field in the two superconductors is an antiparallel configuration, the Andreev level is degenerated in the absence of the RSOI. Then with increasing λ or l , the magnitude of the band splitting oscillates, as shown by the blue dotted line in Fig. 4.8. In the presence of the barrier potential, the gap $\phi = \pi$ is enhanced as shown in Fig. 4.7. On the other hand, the oscillation period of the magnitude of the band splitting is not affected by the barrier potential.

This oscillatory behavior can be understood physically by the spin precession that takes place in the Rashba wire. If an electron or hole traveling in the Rashba wire has a spin component perpendicular to the y direction, the spin precession occurs [215,216]. The precession angle is given by

$$\theta_P = (k_2 - k_1)l = 2\lambda l. \quad (4.29)$$

When $\theta_P = \pi$, a spin-up particle is converted to that with down-spin by traveling through the Rashba wire and vice versa. In this case, even if the Zeeman field in both

Figure 4.7: Andreev levels ε as a function of the phase difference ϕ for various λ values in the direction of the Zeeman fields in the right superconductor $\hat{n}_R \parallel z$ (upper low), $\hat{n}_R \parallel y$ (middle low) and $\hat{n}_R \parallel x$ (bottom low). Here, the direction of the Zeeman field in the left superconductor is fixed to $\hat{n}_L \parallel z$. From left to right, λ/k varies from 0 to π/kl by $\pi/4kl$. The black solid (blue dotted) lines show the Andreev levels in the case of $Z = 0$ ($Z = 0.5$).

superconductors is parallel (+z direction), the particles behave as if the Zeeman field in the superconductors is antiparallel (+z and -z direction). As a result, the magnitude of the Andreev level is the same as that in the case of an antiparallel Zeeman field without RSOI, which can be seen by comparing the third panel of the first row of Fig.4.7 and Fig.4.5(c). Not only for the parallel or antiparallel Zeeman case but also for the arbitrary θ_R with fixed $\zeta_R = \pi/2$, the magnitude of the energy splitting of the Andreev level is the same as that with $\theta_R = \theta_P$ for the non-RSOI case. Note that although the magnitudes of the band splitting are identical to each other, the shapes of the Andreev levels are not the same. This is because an energy gap appears at $\phi = \pi$ in the presence of RSOI. In addition, the spin precession is not affected by the barrier potential. Therefore the oscillation period of the band splitting is not changed even in the presence of the barrier potential.

We also find that the oscillatory behavior of the band splitting by the RSOI changes depending on the relative direction of the Zeeman field in the two superconductors. First, we change the direction of the Zeeman field in the right superconductor in the y - z plane, i.e., vary θ_R for $\zeta_R = \pi/2$. With increasing θ_R for fixed $\zeta_R = \pi/2$, the

Figure 4.8: Normalized magnitude of the energy shift $\delta\epsilon/h$ as a function of $\lambda l/2\pi$ for the parallel (black solid line) and antiparallel (blue dotted) Zeeman case.

amplitude of the band splitting becomes smaller. Then if the Zeeman field in the right superconductor is parallel to the y direction, the magnitude of the band splitting does not depend on λ and l , as shown in the middle row of Fig. 4.7. Note that as long as the Zeeman field in either left or right superconductor is parallel to the y direction, the magnitude of the band splitting does not depend on λ and l . This is because, the spin of a particle coming from the superconductor with a y -oriented Zeeman field does not precess.

Next, we change the direction of the Zeeman field in the right superconductor in the z - x plane. If the Zeeman field of the right superconductor has the x component, the ϵ - ϕ curve becomes asymmetric for ϕ , $\epsilon(\phi) \neq \epsilon(2\pi - \phi)$, as shown in the third row of Fig.4.7. In addition, the same as the parallel Zeeman case, the magnitude of the band splitting oscillates as a function of λ and l with a period $2\pi/\lambda l$. The asymmetric Andreev level and resulting anomalous Josephson effect are predicted to be realized in S/F/S junctions with spin active interfaces [224–226], S/F/S junctions with the RSOI in the normal region [227–230], S/N/S junctions with unconventional superconductors [183, 231] and many other systems, e.g., Refs. [232–234]. In most systems considered so far, to achieve the anomalous Josephson effect, it is necessary to manipulate the magnetic field, which is experimentally difficult. On the other

hand, in our system, the anomalous Josephson effect can be realized by changing the strength of the RSOI, which is experimentally feasible.

There is another feature originating from the RSOI: the disappearance of the Andreev level for $\Delta - h < |E| < \Delta + h$. Even if one introduces a small magnitude of the RSOI and the Zeeman field is parallel, the Andreev level of the energy region suddenly disappears. This is because in the presence of RSOI, there is the spin-dependent scattering at the interface. This spin-dependent scattering prohibits the formation of the bound state, as is discussed for the case of without RSOI in Sec.4.4.1.

The main effects of the RSOI on the shape of the Andreev levels are (i) band shift, which is represented by Eq. (4.28), and (ii) gap opening effect at $\phi = \pi$, which is captured by Eq. (4.24). In the presence of both RSOI and Zeeman field, the analytical formula of the Andreev level is quite complicated. However, by combining the above effects represented by Eqs. (4.24) and (4.28), we derive the following approximate solution for the parallel Zeeman case (z direction):

$$\varepsilon = \pm \Delta \sqrt{\frac{1}{2} \left(1 + \frac{4k^2(k^2 + \lambda^2) \cos \phi + \lambda^4 \sin^2(\sqrt{k^2 + \lambda^2}l)}{4k^2(k^2 + \lambda^2) - \lambda^4 \sin^2(\sqrt{k^2 + \lambda^2}l)} \right)} \pm h \cos \lambda l. \quad (4.30)$$

This solution reproduces the numerical results quite well especially near $\phi = \pi$.

Finally, we briefly comment on the difference between the Andreev levels in the present system and those in the S/F/S junctions. The periodic change of the Andreev level is also known for the S/F/S junction [235–237]. In the S/F/S junction, the Andreev level is given by

$$\varepsilon = \pm \Delta \cos \frac{\phi \pm lk\rho}{2}, \quad (4.31)$$

where ρ is the magnitude of the exchange field normalized by the Fermi energy and is considered as $\rho \ll 1$. In this case, with increasing the strength of the exchange field, the degenerate branches shift to the $\pm\phi$ direction (horizontal direction in ε - ϕ plot), which causes the π transition. On the other hand, in the present system, the energy band shifts to a vertical direction by changing the strength of the RSOI, which does not cause a π transition.

4.5 Summary

In summary, we have theoretically studied how the Rashba spin-orbit interaction in the normal region and the Zeeman field in the superconducting region affect the formation of Andreev levels in a Josephson junction. We have found that the total tunneling conductance remains invariant, whereas the Andreev reflection processes and the resulting Andreev levels are sensitive to the relative orientation of the spin-orbit field and the Zeeman field.

We have shown that the Andreev level is systematically changed by tuning the strength of the Rashba spin-orbit interaction λ or length of the Rashba wire l . In particular, the magnitude of the band splitting $\delta\varepsilon$ oscillates as a function of λ and l , and we have clarified that this behavior is interpreted physically by the spin precession in the Rashba wire. It has been also found that the ε - ϕ curve changes depending on the relative angle of the three independent vectors, i.e., the orientation of Zeeman fields in the left superconductor, that in the right superconductor, and the vector characterizing the spin-orbit interaction. In particular, the ε - ϕ curve becomes asymmetric with respect to the phase difference ϕ when either the left or right Zeeman field has a component parallel to the junction (x component). An interesting future direction is the possibility to control the Josephson current in the considered system by the change of the Andreev levels, which will be a subject of future study. Moreover, it would be also interesting to study the finite frequency response of this system as discussed in other systems [238,239].

4.6 Appendix: Andreev reflection coefficients

In this Appendix, we show the analytical formulas for the normal and Andreev reflection coefficients of the RM/ZS junction. The reflection coefficients in the case of $\hat{n}_R \parallel z$ are given by

$$b_1^{(1)} = [2kk_\lambda \lambda^2 (u_2 v_1 - u_1 v_2)(u_2 v_1 + u_1 v_2)] / \Gamma, \quad (4.32)$$

$$b_2^{(1)} = \lambda^2 [(k^2 + k_\lambda^2)(u_1^2 - v_1^2)(u_2^2 - v_2^2) + 2kk_\lambda(u_1^2 u_2^2 - v_1^2 v_2^2)] / \Gamma, \quad (4.33)$$

$$d_1^{(1)} = 2ikk_\lambda(u_2 v_1 + u_1 v_2)[(k^2 + k_\lambda^2)(u_1 u_2 - v_1 v_2) + 2kk_\lambda(u_1 u_2 + v_1 v_2)] / \Gamma, \quad (4.34)$$

$$d_2^{(1)} = 2ikk_\lambda(u_2 v_1 - u_1 v_2)[(k^2 + k_\lambda^2)(u_1 u_2 + v_1 v_2) + 2kk_\lambda(u_1 u_2 - v_1 v_2)] / \Gamma, \quad (4.35)$$

$$b_1^{(2)} = b_2^{(1)}, b_2^{(2)} = b_1^{(1)}, d_1^{(2)} = d_2^{(1)}, d_2^{(2)} = d_1^{(1)}, \quad (4.36)$$

with

$$k_\lambda = \sqrt{k^2 + \lambda^2}, \quad (4.37)$$

$$\Gamma = [(k^2 + k_\lambda^2)(u_1^2 - v_1^2) + 2kk_\lambda(u_1^2 + v_1^2)][(k^2 + k_\lambda^2)(u_2^2 - v_2^2) + 2kk_\lambda(u_2^2 + v_2^2)]. \quad (4.38)$$

Here, b_1^i, b_2^i, d_1^i , and d_2^i with $i = 1 (i = 2)$ are the reflection coefficients b_1, b_2, d_1 , and d_2 in Eq.(4.13) when an electron with k_1 (k_2) is injected. On the other hand, the reflection coefficients in the case of $\hat{n}_R \parallel y$ are given by

$$b_1^{(1)} = 0, \quad (4.39)$$

$$b_2^{(1)} = \frac{\lambda^2(u_1^2 - v_1^2)}{(k^2 + k_\lambda^2)(u_1^2 - v_1^2) + 2kk_\lambda(u_1^2 + v_1^2)}, \quad (4.40)$$

$$d_1^{(1)} = \frac{4ikk_\lambda u_1 v_1}{(k^2 + k_\lambda^2)(u_1^2 - v_1^2) + 2kk_\lambda(u_1^2 + v_1^2)}, \quad (4.41)$$

$$d_2^{(1)} = 0, \quad (4.42)$$

$$b_1^{(2)} = \frac{\lambda^2(u_2^2 - v_2^2)}{(k^2 + k_\lambda^2)(u_2^2 - v_2^2) + 2kk_\lambda(u_2^2 + v_2^2)}, \quad (4.43)$$

$$b_2^{(2)} = 0, \quad (4.44)$$

$$d_1^{(2)} = 0, \quad (4.45)$$

$$d_2^{(2)} = \frac{4ikk_\lambda u_2 v_2}{(k^2 + k_\lambda^2)(u_2^2 - v_2^2) + 2kk_\lambda(u_2^2 + v_2^2)}. \quad (4.46)$$

Chapter 5

Proximity induced superconductivity in topological insulator surface in the presence of hexagonal warping effect

We systematically study proximity induced superconductivity in topological insulator surface in the presence of hexagonal warping effect. Since the spin structure of a chiral p -wave state does not coincide with that of the helical surface state in the topological insulator, the chiral p -wave superconductivity can not create a gap in the energy spectrum. However, we find that in the presence of hexagonal warping effect, chiral p -wave superconductivity can be induced and the resulting induced chiral p -wave pairing gives rise to effective f -wave superconductivity in the topological insulator surface.

5.1 Introduction

Proximity induced superconductivity in topological insulator surface is currently attracting a great research interest. L. Fu and C. L. Kane have first studied this system and found that induced s -wave superconductivity can be effectively considered as a spinless chiral p -wave state [49]. More importantly, Fu and Kane have predicted that the spin momentum locking of topological insulator surface leads to the Majorana zero mode in a SNS junction on a topological insulator [49]. Not only the theoretical prediction, but also the device fabrication has been already done by several groups [240–243], and a signature originating from the Majorana fermion has been observed [244].

In Bi_2Te_3 , ARPES measurements have shown that the surface electronic states in momentum space for fixed energy has snowflake shape as shown in Fig. 5.1. By considering the lattice symmetry of Bi_2Te_3 , L. Fu has revealed that an unconventional hexagonal warping term, which is the higher order spin-orbit interaction term, leads to the snowflake shape [245]. The surface induced superconductivity has been systematically studied by A. M. Black Schaffer and A. V. Balatsky [246]. However, the effect of hexagonal warping term on proximity induced superconductivity has not yet clarified though the hexagonal warping term also changes the spin structure on the Fermi surface, changing the spin state of a Cooper pair.

In this chapter, we theoretically study the induced superconductivity in the topological insulator surface with strong hexagonal warping effect. We systematically study the superconductivity in the topological insulator surface by considering the point group symmetry of the surface state (C_{3v}). We find that the chiral p -wave state can be induced and gives rise to a superconducting gap only when the hexagonal warping term is present. Once the superconductivity is induced, it gives rise to the spinless f -wave gap structure, where the gap function is proportional to the warping term.

This chapter is organized as follows; first of all, we briefly see how the Fermi surface and the spin structure on the Fermi surface changes by introducing the hexagonal warping term in Sec.5.2. In Sec.5.3, we discuss the possible pair potentials in this system and reveal the effective superconducting state on the TI surface by obtaining the single band description of each pair potential. Finally, we make a short summary and discuss future directions in Sec.5.4.

5.2 Formulation

Here, we consider the surface state of the three fold rotational symmetric topological insulator like Bi_2Te_3 (C_{3v} point group). The effective Hamiltonian around the Γ point is given by

$$H_n(\mathbf{k}) = -\mu + \lambda(k_x\sigma_y - k_y\sigma_x) + c(\mathbf{k}), \quad (5.1)$$

where $\sigma_i (i = 0, x, y, z)$ are Pauli matrices for spin space, μ is the chemical potential, the second term of the right hand side is the helical spin-orbital interaction term and the third term is the hexagonal warping term. For this C_3 invariant system, L. Fu has obtained the possible warping term as [245]

$$c(\mathbf{k}) = \lambda_w(k_x^3 - 3k_xk_y^2) \quad (5.2)$$

This system has time-reversal symmetry, mirror symmetry on the k_y axis and three fold rotational symmetry, whereas, there is no inversion symmetry. By diagonalizing Eq.(5.1) with a unitary matrix

$$U = \begin{pmatrix} u & v \\ -ive^{i\theta} & iue^{i\theta} \end{pmatrix}, \quad (5.3)$$

where $e^{i\theta} = (k_x + ik_y) / \sqrt{k_x^2 + k_y^2}$, $u = \sqrt{[1 + c(k)/\eta] / 2}$, $v = \sqrt{[1 - c(k)/\eta] / 2}$ and $\eta = \sqrt{\lambda^2(k_x^2 + k_y^2) + c^2(\mathbf{k})}$, one can obtain eigenvalues as

$$U^\dagger H_n(\mathbf{k}) U = \text{diag}[E, -E], \quad (5.4)$$

$$E = -\mu + \eta. \quad (5.5)$$

In Fig.5.1, Fermi surfaces are shown for various λ_w . With increasing λ_w , the shape of the Fermi surface changes from circle to hexagon-like shape and, eventually, to a snow flake as shown in Fig.5.1. With increasing the warping effect, the spin structure on the Fermi surface is changed. The spin expectation value can be calculated with the wave function $|\psi\rangle = (u, -ive^{i\theta})^T$ as

$$\langle \hat{S}_e \rangle \equiv (\langle \psi | \sigma_x | \psi \rangle, \langle \psi | \sigma_y | \psi \rangle, \langle \psi | \sigma_z | \psi \rangle) \quad (5.6)$$

$$= (-\lambda k_{\parallel} \sin \theta / \eta, \lambda k_{\parallel} \cos \theta / \eta, c(k) / \eta). \quad (5.7)$$

Figure 5.1: Fermi surface and spin structure for various strengths of the warping term λ_w . With increasing λ_w , the Fermi surface become hexagonal shape and finally evolve into a snow flake shape. z component of spin is also induced with increasing λ_w except on the mirror symmetric line.

In this system, spin rotational symmetry is broken and spin and momentum are locked as shown in Fig.5.1. In the absence of the hexagonal warping term, the spin is fully polarized in the x - y plane. With increasing λ_w , a z component of spin is induced except on the mirror symmetric line. In general, Cooper pairs form between electrons with opposite momenta, k and $-k$. Because of the spin-momentum locking, to give rise to a superconducting gap, the spin configuration of the Cooper pair should be anti-parallel in this system, the details of which are discussed in the following section.

5.3 Possible superconducting state

In this section, we discuss the possible pair potentials in the topological surface state with C_{3v} point group symmetry. We also clarify the effective gap structure on the topological insulator surface by obtaining the single band description.

In the mean field regime, the BdG Hamiltonian is given by

$$H_{\text{BdG}} = \begin{pmatrix} H_n(k) & \Delta(k) \\ \Delta^\dagger(k) & -H_n^*(-k) \end{pmatrix} \quad (5.8)$$

where the basis is $(c_\uparrow, c_\downarrow, c_\uparrow^\dagger, c_\downarrow^\dagger)$. Here $\Delta(k)$ is the pairing potential given by

$$\Delta(k) = \Delta_0 \begin{pmatrix} -d_x + id_y & \psi + d_z \\ -\psi + d_z & d_x + id_y \end{pmatrix} \quad (5.9)$$

pairing	Rep.	$\psi, \mathbf{d}$	$\mathcal{T}$	$\mathcal{M}_+$	$\mathcal{C}_3$	$\Delta_{11}(k)$	effective paring
s-wave	A_1	$\psi = 1$	+	+	+	$\Delta_0 e^{i\theta}$	iso. chiral p -wave
helical p -wave	A_1	$\mathbf{d} = (-k_y, k_x, 0)$	+	+	+	$\Delta_0 \lambda k_{\parallel} e^{i\theta} / \eta$	aniso. chiral p -wave
Dirac p -wave	A_2	$\mathbf{d} = (k_x, k_y, 0)$	+	-	+	0	non-gap
chiral p -wave	E	$\mathbf{d} = (0, 0, k_x - ik_y)$	None	-	-	$i\Delta_0 c(k) / \eta$	f -wave

Table 5.1: Symmetry allowed pair potentials in topological insulator surface with C_{3v} point group. $\mathcal{T}$, $\mathcal{M}_y$ and $\mathcal{C}_3$ are time-reversal operator, mirror operator for the y axis, three-fold rotational operator along z axis, respectively. The last two columns show the effective pairing potential on the topological surface. $\Delta_{11}(k)$ is defined in Eq.5.11.

where ψ is the spin-singlet component and $d_i (i = x, y, z)$ is the spin-triplet component represented with the $\mathbf{d}$ -vector notation ($\mathbf{d} = d_x \sigma_x + d_y \sigma_y + d_z \sigma_z$). Note that the details of the $\mathbf{d}$ vector are discussed in Chap.1. In this thesis, we focus on the k independent pair potential and k -linear pairings, and ignore the higher order pairings. For the C_{3v} system, there are one k -independent pairing Δ_0 and three k -linear pairings, $\Delta_0(k_x \sigma_y - k_y \sigma_x)$, $\Delta_0(k_x \sigma_x + k_y \sigma_y)$ and $\Delta_0(k_x - ik_y) \sigma_z$. Here, we name the pairings as s -wave, helical p -wave, Dirac p -wave and chiral p -wave in the order. Because of the absence of inversion symmetry, s -wave and the helical p -wave states can be mixed and both belong to A_1 representation. On the other hand, Dirac p -wave and chiral p -wave states belong to A_2 and E representation, respectively. To satisfy the Pauli principle, the spin configuration of k -independent pairing is spin singlet and that of k -linear pairings is spin triplet. In Table 5.1, we summarize the pair potentials, classified into the irreducible representation of the C_{3v} point group.

Even if the matrix form of the pair potential is the same, the resulting superconducting gap structure can be different depending on the band structure of the normal state. For instance, it has been well known that the A_1 s -wave pair Δ_0 gives rise to an effective chiral p -wave gap structure $\Delta_0 e^{i\theta}$ for the non-degenerated TI surface band [49] though it leads to the momentum independent s -wave superconductivity Δ for the usual degenerate parabolic band: $E = -\mu + \frac{\hbar^2 k^2}{2m}$. Here, we derive the effective gap structure on the TI surface with hexagonal warping effect by changing the basis of the BdG Hamiltonian from the spin basis to band basis.

The BdG Hamiltonian can be transformed to the band basis by a 4×4 unitary matrix, $U_s = [U, U^*]$, as

$$H'_{\text{BdG}}(k) \equiv U_s^\dagger H_{\text{BdG}}(k) U_s \quad (5.10)$$

$$= \begin{pmatrix} -\mu + \eta & 0 & \Delta_{12}(k) & \Delta_{11}(k) \\ 0 & -\mu - \eta & \Delta_{22}(k) & \Delta_{21}(k) \\ \Delta_{12}^\dagger(k) & \Delta_{22}^\dagger(k) & \mu + \eta & 0 \\ \Delta_{11}^\dagger(k) & \Delta_{21}^\dagger(k) & 0 & \mu - \eta \end{pmatrix} \quad (5.11)$$

Here, the new basis is $(c_1, c_2, c_2^\dagger, c_1^\dagger)$ where 1 and 2 represent the conduction and valence band component, respectively. If the chemical potential is large enough compared with the magnitude of the pair potential ($\mu \gg \Delta_0$), we can effectively ignore the interband and valence band components and the BdG Hamiltonian is reduced to a 2×2 matrix as

$$H_{\text{BdG}}^s(k) = \begin{pmatrix} -\mu + \eta & \Delta_{11}(k) \\ \Delta_{11}^\dagger(k) & \mu - \eta \end{pmatrix} \quad (5.12)$$

The single band representation of the possible pairings in the C_{3v} point group is summarized in Table 5.1. In Fig.5.2, we show the superconducting gap structure on the Fermi surface. The black lines show the Fermi surface and the blue lines show the superconducting gap structure at each Fermi momentum. In the single band description, the A_1 state is effectively considered as a spinless chiral p -wave state. However, different from the case without the hexagonal warping effect, the effective superconducting gap structure become anisotropic for the helical p -wave case. The A_2 state does not give rise to the superconducting gap regardless of the existence of the hexagonal warping effect. The single band representation of the chiral p -wave state (E) is proportional to the hexagonal warping term. In other words, the chiral p -wave state does not lead to a superconducting gap in the absence of the hexagonal warping term λ_w . However, in the presence of the hexagonal warping term, the chiral p -wave state gives rise to the effective f -wave state.

The effective gap structure of each pair potentials can also be interpreted by looking at the spin structure of the Cooper pair in the spin basis. In general, the spin configuration of a spin-singlet Cooper pair is always antiparallel regardless of the orientation of the spin axis. On the other hand, for spin triplet pairings, the spin con-

Figure 5.2: Superconducting gap structure for the possible pair potentials. Black line show the Fermi surface and blue line show the magnitude of the superconducting gap as a function of θ . For the A_2 case, the superconducting gap can not open.

figuration of a Cooper pair changes depending on the direction of the spin axis. If we see a Cooper pair with a spin axis parallel (normal) to the d -vector, the spin configuration of the Cooper pair is antiparallel (parallel). As mentioned in the previous section, the spin configuration of a Cooper pair should be always antiparallel because of the presence of the time reversal symmetry and the absence of the inversion symmetry, and the z component of the spin is induced only in the presence of the warping effect. The s -wave pairing is a spin singlet one. Therefore, the spin configuration of this pairing is always consistent with the spin structure on the TI surface regardless of the presence or absence of the warping term. On the other hand, for the helical p -wave case, the Cooper pairs have an antiparallel spin configuration in x and y direction, and a parallel spin configuration along the z axis. Therefore, once the hexagonal warping effect is turned on, i.e., a z component is induced, the superconducting gap is suppressed because the spin configuration of the Cooper pair and the spin structure of the TI surface is inconsistent in the z direction. The superconducting gap at $\theta = \pi/3$

is not changed because there is no warping effect at $\theta = \pi/3$. In the case of the Dirac p -wave state, induced z -spin is also inconsistent with the spin structure of the pairing for entire Fermi surface, remaining the gapless state. The d -vector of the chiral p -wave state is pointing to the z direction. In other words, the spin configuration of a Cooper pair is parallel (anti-parallel) to the x - y plane (z direction). This implies that the superconducting gap of the chiral p -wave case is only supported by the hexagonal warping term. Therefore, as can be seen from Fig.5.2, point nodes appear on the superconducting gap along the mirror symmetric lines where the hexagonal warping term is absent as can be seen from Fig.5.2.

5.4 Summary

In this section, we have studied the proximity induced superconductivity in a topological insulator surface with strong hexagonal warping effect. We have systematically studied the superconductivity in the topological insulator surface by considering the point group symmetry of the surface state (C_{3v}). We have interpreted the superconducting gap structure of each pair potential by comparing the spin structure of the Cooper pairs and that on the topological helical surface state. We have also found that the chiral p -wave state can be induced and it gives rise to a superconducting gap only when the hexagonal warping term is present. Once the superconductivity is induced, it gives rise to the spinless f -wave gap structure, where the gap function is proportional to the warping term.

As a future direction, it is interesting to investigate transport properties of S/N and S/N/S junctions in the presence of the hexagonal warping effect. This is because transport properties can be changed by the direction of the junction. Moreover, the magnitude of the hexagonal warping term is extracted from the size of the Fermi surface, meaning that the magnitude of the hexagonal warping effect can be tuned by gate voltage. Therefore, we can expect the gate tunable transport properties in this system. Moreover, clarifying whether Majorana state in S/N/S junctions can remain gapless or not even in the presence of the hexagonal warping effect is also important topic for future application of the Majorana zero energy state.

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Summary

This thesis studies superconductivity and its transport properties in the presence of spin-orbit interaction. Topological materials are now considered as a promising platform to realize unconventional superconductivity since spin-orbit interaction in some topological materials can support spin-triplet pairing state. In this thesis, we have found that exotic spin-orbit interaction in topological Dirac semimetals enhances the nodal spin-triplet state that hosts an exotic Andreev bound state. We have also studied the Josephson effect in Zeeman-split superconductor/ Rashba wire/ Zeeman-split superconductor trilayer junctions. Our calculations have shown that it is possible to manipulate Andreev levels in the Josephson junctions by tuning the strength of the spin-orbit interaction.

Chapter 1 introduces basic properties and historical progress of superconductivity and topological materials. In particular, we have shown why the unconventional superconductivity can be realized in topological materials using a Weyl semimetal as an example. We have also made a list of topological materials that have exhibited the superconductivity. We hope that the list provides a hint to find other superconducting topological materials.

In Chapter 2 we have theoretically studied intrinsic superconductivity in doped Dirac semimetals. Dirac semimetals host bulk Dirac points which are formed by doubly degenerate bands, so the Hamiltonian is described by 4×4 matrix and six types of k -independent pair potential are allowed by the Fermi-Dirac statistics. We have shown that the unique spin-orbit coupling leads to characteristic superconducting gap structures and d -vectors on the Fermi surface and the electron-electron interaction between intra and inter orbitals gives the novel phase diagram of superconductivity. We have found that when the inter-orbital attraction is dominant, the unconventional superconducting state with point nodes appears

Chapter 3 studies bulk and surface physical properties of intrinsic superconductivity in doped Dirac semimetals to verify the experimental signature of possible superconducting states. Here, we have calculated the temperature dependence of bulk physical properties such as electronic specific heat and spin susceptibility and surface state. In the unconventional superconducting phase, either dispersive or flat Andreev bound states appear between point nodes, which lead to double peaks or single peak in the surface density of state, respectively. As a result, it has been found that possible superconducting states can be distinguished by combining bulk and surface measurements

In Chapter 4, we have shown that the Andreev level is systematically changed by tuning the strength of the Rashba spin-orbit interaction λ or length of the Rashba wire l . In particular, the magnitude of the band splitting $\delta\varepsilon$ oscillates as a function of λ and l , and we have clarified that this behavior is interpreted physically by the spin precession in the Rashba wire. It has been also found that the ε - ϕ curve changes depending on the relative angle of the three independent vectors, i.e., the orientations of Zeeman fields in the left and right superconductor and the vector characterizing the spin-orbit interaction. In particular, the ε - ϕ curve becomes asymmetric with respect to the phase difference ϕ when either the left or right Zeeman field has a component parallel to the junction (x component).

Chapter 5 studies the proximity induced superconductivity in a topological insulator with strong hexagonal warping effect. We have systematically studied the superconductivity in the topological insulator surface by considering the point group symmetry of the surface state (C_{3v}). We have found that the chiral p -wave state can be induced and gives rise to a superconducting gap only when the hexagonal warping term is present. Once the superconductivity is induced, it gives rise to the spinless f -wave gap structure, where the gap function is proportional to the warping term.

Samenvatting

(Summary in Dutch)

Dit proefschrift beschrijft supergeleiding en bijbehorende transport eigenschappen in de aanwezigheid van spin-baankoppeling. Topologische materialen worden gezien als een veelbelovend platform voor het realiseren van onconventionele supergeleiding aangezien de spin-baankoppeling in sommige topologische materialen een spin-triplet gepaarde toestand kan ondersteunen. Uit dit proefschrift is gebleken dat de exotische spin-baaninteractie in topologische Dirac semimetalen de nodale spin-triplet toestand, die de gebonden Andreev toestand bevat, versterkt. We hebben ook het Josephson effect bestudeerd in Zeeman gesplitste supergeleider / Rashba nanodraad / Zeeman gesplitste supergeleider drielaagse juncties. Onze berekeningen hebben aangetoond dat het mogelijk is de Andreev niveaus in Josephson juncties te manipuleren door middel van het afstemmen van de sterkte van de spin-baaninteractie.

Hoofdstuk 1 introduceert de basiseigenschappen en het historische verloop van supergeleiding en topologische materialen. In het bijzonder hebben we aangetoond waarom onconventionele supergeleiding in principe gerealiseerd kan worden in topologische materialen. We geven het gebruik van een Weyl semimetaal als voorbeeld. Ook hebben we een lijst samengesteld van topologische materialen die supergeleiding vertonen. We hopen dat deze lijst een aanwijzing geeft voor het vinden van andere supergeleidende topologische materialen.

In hoofdstuk 2 hebben we de intrinsieke supergeleiding in gedoteerde Dirac semimetalen theoretisch bestudeerd. Dirac semimetalen bevatten bulk Dirac punten die gevormd worden door dubbel ontaarde banden, zodat de Hamiltoniaan beschreven wordt door een 4×4 matrix. Zes typen k -onafhankelijke paringspotentialen zijn toegestaan door de Fermi-Dirac statistieken. We hebben aangetoond dat de unieke spin-baan koppeling leidt tot karakteristieke supergeleidende bandkloof structuren op d -vectoren op het Fermi oppervlak en de elektron-elektroninteracties binnen en tussen orbitalen resulteren in een nieuw fasediagram van supergeleiding. We hebben geconstateerd dat, wanneer de aantrekking tussen orbitalen dominant is, de onconventionele supergeleidende toestand met nulpunten in bepaalde richtingen optreedt.

Hoofdstuk 3 bestudeert de fysische eigenschappen van intrinsieke supergeleiding in gedoteerde Dirac semimetalen in de bulk en aan het oppervlak, met als doel het experimentele karakter van mogelijk supergeleidende toestanden te verifiëren. Hier berekenen we de temperatuur afhankelijkheid van de bulk fysische eigenschappen zoals de elektronische soortelijke warmte en spin susceptibiliteit en oppervlaktetoestanden. In de onconventionele supergeleidende fase, hetzij dispersieve of dis-

persiëloze Andreev gebonden toestanden treden op tussen de knooppunten. Deze leiden respectievelijk tot dubbele pieken of een enkele piek in de oppervlakte toestandsdichtheid. Hieruit volgt dat supergeleidende toestanden onderscheiden kunnen worden door het combineren van bulk- en oppervlaktemetingen.

In hoofdstuk 4 hebben we laten zien dat het Andreev niveau systematisch verandert door het aanpassen van de Rashba spin-baankoppeling sterkte λ of de lengte van de Rashba nanodraad l . De grootte van de band splitsing $\delta\varepsilon$ oscilleert als functie van λ en l . Daarmee hebben we opgehelderd dat dit gedrag fysisch geïnterpreteerd kan worden als de spinprecessie in de Rashba nanodraad. Ook is gebleken dat de ε - ϕ curve verandert afhankelijk van de relatieve hoek van drie onafhankelijke vectoren, namelijk de oriëntaties van de Zeemanvelden in de linker en rechter supergeleider en de vector die de spin-baan interactie karakteriseert. In het bijzonder, de ε - ϕ curve wordt asymmetrisch met betrekking tot het fase verschil ϕ wanneer ofwel het linker of het rechter Zeemanveld een component parallel aan de junctie (x component) heeft.

Hoofdstuk 5 beschrijft de door nabijheid geïnduceerde supergeleiding in een topologische isolator met een sterk hexagonaal vervormend effect. We hebben de supergeleiding in het topologische isolator oppervlak systematisch bestudeerd door het beschouwen van punt groep symmetrie van de oppervlakte toestand (C_{3v}). Het is gebleken dat de chirale p -golf symmetrie kan worden geïnduceerd en dat deze alleen een supergeleidende bandkloof veroorzaakt in de aanwezigheid van de hexagonale term. Wanneer de supergeleiding eenmaal geïnduceerd is, veroorzaakt deze een spinloze f -golf symmetrie daar waar de supergeleidende bandkloof functie proportioneel is aan de vervormende term.

translated by Linde A. B. Olde Olthof

List of publications

- **Publications related to this thesis**

1. Tatsuki Hashimoto, Shingo Kobayashi, Masatoshi Sato, and Yukio Tanaka, "Superconductivity in doped Dirac semimetals", *Physical Review B* **94**, 014510 (2016)
2. Tatsuki Hashimoto, Alexander A. Golubov, Yukio Tanaka, and Jacob Linder, "Tunability of Andreev levels via spin-orbit coupling in Zeeman-split Josephson junctions", *Physical Review B* **96**, 134508 (2017)
3. Tatsuki Hashimoto, Pablo Burset, Yukio Tanaka, and Alexander A. Golubov "Superconductivity on topological insulator surface and its transport properties in the presence of hexagonal warping effect" in preparation

- **Other publications**

1. Tatsuki Hashimoto, Keiji Yada, Ai Yamakage, Masatoshi Sato, and Yukio Tanaka, "Bulk Electronic State of Superconducting Topological Insulator", *Journal of the Physical Society of Japan* **82**, 044704 (2013)
2. Tatsuki Hashimoto, Keiji Yada, Ai Yamakage, Masatoshi Sato, and Yukio Tanaka, "Effect of Fermi surface evolution on superconducting gap in superconducting topological insulator", *Superconducting science and technology* **27**, 104002 (2014).
3. Tatsuki Hashimoto, Keiji Yada, Masatoshi Sato, and Yukio Tanaka, "Surface electronic state of superconducting topological crystalline insulator", *Physical Review B* **92**, 174527 (2015)

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