Schemes for realizing topological superconductivity in monolayer $\beta$-Bi$_2$Pd: A tight-binding model study

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In light of tight-binding model, we investigate the emergence of high-order Dirac point and quantum spin Hall state in monolayer $\beta$-Bi$_2$Pd without and with spin-orbital coupling. By introducing the Zeeman field, we show the clear quantum anomalous Hall state at the edge. Since the existence of intrinsic superconductivity, the system gets into a topological superconducting state via introducing the $\pi$-shifted superconductor (Zeeman field) that preserves (destroys) time reversal symmetry. Meanwhile, we observe the corresponding helical (chiral) Majorana zero modes at the boundary. The topological phase transition gives a workable approach to realize topological superconductivity in experiment.

I. INTRODUCTION

Majorana Fermions are their own antiparticle and obey non-Abelian braiding statistics [11] which possess potential application for quantum computation [2 3]. Topological superconductors (TS) are a natural platform for realizing topologically protected gapless boundary states which is essentially Andreev bound state hosting Majorana fermions at the vortex[4]. Theoretically, odd-parity superconductors such as p-wave superconductor Sr$_2$RuO$_4$ [5 6] are judged as intrinsic TS from the Fermi surface that encloses an odd number of time reversal invariant momenta (TRIM) in the Brillouin zone (BZ) [7 8]. In addition, Sato proposed a feasible project for supporting non-Abelian anyon excitations in s-wave superconductors that are realized in two dimensional (2D) Dirac Fermions [9]. Subsequently, Fu et al. [10] explicitly demonstrated that the Dirac-type surface state of a topological insulator couplings to a s-wave superconductor resembles a spinless p-wave superconductor which can realize Majorana zero modes (MZMs) at the certain limit. Also, a Chern insulator with quantum anomalous Hall states (QAHSs) [11] proximitized with a s-wave superconductor supports chiral MZMs at the vortex [12 14].

Recently, a strong topological superconductor candidate $\beta$-Bi$_2$Pd reported by both theory and experiment has attracted much attention on its topological surface states [15-17] and superconductivity [18 19]. Li et al. [20] proposed that $\beta$-Bi$_2$Pd is a unconventional superconductor with a spin-triplet pairing symmetry on account of the observation of half-quantum magnetic flux quantization. Furthermore, a signature of MZMs on $\beta$-Bi$_2$Pd thin films was observed via cryogenic scanning tunneling microscopy [21]. Besides bulk structure, 2D monolayer materials worth equal studying owing to their ability to fabricate stacked structures and manipulate properties.

In this letter, we focus on monolayer $\beta$-Bi$_2$Pd stripped from layered bulk structure. Based on the tight-binding model (TBM) constructed by p-orbital of Bi atoms, the high-order quadratic Dirac point (DP) appears at the M point when ignoring the effect of spin-orbital coupling (SOC), which is protected by $C_z$ and $\sigma_y$ symmetry. Considering SOC, we predict the nontrivial topological edge states (TESs) at the $\Gamma$ point by breaking periodic boundary condition along y direction. The QAHSs are also obtained at the boundary by introducing the Zeeman field which violates the TR symmetry. In addition, the intrinsic superconductivity of monolayer $\beta$-Bi$_2$Pd [22] helps us to realize the chiral MZMs. Alternatively, coupling to a $\pi$-shifted superconductor by proximity effect instead of magnetism is a feasible method as well to gain the helical MZMs. Which worth mentioning is that all first-principles results (FPRs) in the letter are implemented in the QUANTUM ESPRESSO package.

II. BASES

In order to get a physics picture of monolayer $\beta$-Bi$_2$Pd, we begin to choose suitable atomic orbitals of Bi and Pd as bases to construct TBM. The outmost shells for Bi and Pd are p-orbital and d-orbital, respectively. From the orbital-resolved band structure [22], we find that only the p-orbital of Bi atoms does the main contribution to the band structure around the Fermi level through the whole BZ, while the d-orbital of Pd atoms is dominant for the valence bands and can be negligible. The point group of $D_{4h}$ of monolayer $\beta$-Bi$_2$Pd shows us clearly the inversion symmetry which links two equivalent Bi atoms within a primitive cell. Thus, it is natural to set up bonding and anti-bonding states with definite parity [23] for Bi atoms as follow

$$|Bi_{x,y,z}^\pm > = |Bi_{1;x,y,z} > \mp |Bi_{2;x,y,z} >,$$  \hspace{1cm} (1)

where the superscript represents the parity. Since anti-bonding states always have higher energy than bonding states, it is reasonable to pick $|Bi_{x,y}^- >$ and $|Bi_{y,z}^- >$ these three bases (as shown in Fig. 1) to construct a three-band TBM of...
monolayer $\beta$-Bi$_2$Pd which can capture the main low-energy physics.

**III. TIGHT-BINDING MODEL**

Under the bases mentioned before, we build the TBM upto next-nearest-neighbor hopping (NNNP) term. The matrix elements of the Hamiltonian is given by $H_{\mu\mu'}(k) = \sum_{R} e^{ik \cdot R} E_{\mu\mu'}^{ji}(R)$, in which

$$E_{\mu\mu'}^{ji}(R) = \left\langle Bi_{\mu}(r) | \hat{H} | Bi'_{\mu'}(r - R) \right\rangle$$

is the hopping integral between the atomic orbitals $| Bi_{\mu}\rangle$ at 0 and $| Bi'_{\mu'}\rangle$ at lattice vector $R$. The final Hamiltonian $H_0$ is given by

$$H_0 = \epsilon + T_{NN} + T_{NNN} = \begin{bmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \end{bmatrix},$$

where

$$h_{11} = \epsilon_1 + 2t_{11} [\cos(k_x a) + \cos(k_y a)]$$
$$h_{12} = 2it_{12} \sin(k_x a) + 4t_{12}' \cos(k_x a) \sin(k_y a)$$
$$h_{13} = 2it_{12} \sin(k_y a) + 4t_{12}' \cos(k_x a) \cos(k_y a)$$
$$h_{22} = c_2 + 2t_{22} \cos(k_x a)$$
$$2t_{33} \cos(k_y a) + 4t_{33}' \cos(k_x a) \cos(k_y a)$$
$$h_{23} = -4t'_{23} \sin(k_x a) \sin(k_y a)$$
$$h_{33} = c_2 + 2t_{33} \cos(k_x a)$$

and $a$ is the lattice constant, $\epsilon$ is the on-site energy, $T_{NN}$ and $T_{NNN}$ are the NNP and NNNP energy, respectively. The fitted parameters are listed in Table I.

**A. High-order Dirac point**

As shown in Fig. 1 (blue lines), the fitting bands show a distinct DP at the M point. It is protected by $C_4$ and $\sigma_v$ symmetry and robust against any perturbation unless destroying crystal symmetry. Here, $C_4$ is the 4-fold rotation symmetry and $\sigma_v$ is the reflection plane perpendicular to x-y plane. One can see that the DP disperses quadratic rather than linear indicating a high-order DP [24]. Comparing to FPRs, there is a band inversion along $\Gamma$-X path between $p_x$ and $p_{x-y}$ orbitals, which guarantees the existence of nontrivial topology and gives $Z_2$ index by 1. We will discuss later.

**B. Spin-orbital coupling**

Owing to the heavy halogen family Bi, SOC can’t be ignored. Under the bases, we obtain the SOC contribution to the Hamiltonian as follow

$$H_{SOC} = \lambda \hat{L} \cdot \hat{S} = \lambda L_z \sigma_z$$

where $\sigma$ is Pauli matrix for spin,

$$L_z = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{bmatrix}$$

is the matrix of z component of the orbital angular momentum, and $\lambda$ denotes the strength of the SOC. Note that, the matrix elements of $\hat{L}_x$ and $\hat{L}_y$ are all zeros. Then we get the full TB Hamiltonian with SOC as follows:

$$H_S(k) = I_2 \otimes H_0(k) + H'$$

$$= \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \end{bmatrix}$$

in which $I_2$ is the $2 \times 2$ identity matrix. The above Hamiltonian is block diagonal, which means that the spin $z$ component is not mixed by the SOC and hence is still a good quantum number. Since the coincidence of TR and inversion symmetry, the Kramer degeneracy ensures the double degeneracy of each bands. Therefore, it is no accident that SOC is nothing but splits the Dirac point and causes a full band gap. Here, we set $\lambda=0.2$ as an example in Fig. 1.

**C. Zeeman field**

In order to realize QAHSs, we plus the Zeeman field along $z$ direction on each Bi atoms. The contribution reads

$$H_B = g_s \mu_B B \cdot S = g_s \mu_B B_3 \sigma_z = g_s \mu_B B I_3 \sigma_z,$$

where $\mu_B$ is the Bohr magneton, $g_s$ is the electron-spin g-factor, $I_3$ is a $3 \times 3$ identity matrix, and B is the strength of magnetic field. For simplicity, we set $g_s=\mu_B=1$. One can see that the SOC term we mentioned before preserves the TRI, while the Zeeman term violates it and results in different
TABLE I. Fitted parameters of the three-band TBM based on the FP band structures of monolayer $\beta$-Bi$_2$Pd. $\epsilon$s are the on-site energy and $t$s are hopping energy. All energy parameters are in units of eV.

| Fitted parameters | $\epsilon_1$ | $t_{11}$ | $t_{12}$ | $\epsilon_2$ | $t_{22}$ | $t_{33}$ | $t_{11}$ | $t_{12}$ | $t_{22}$ | $t_{23}$ |
|-------------------|--------------|----------|----------|--------------|----------|----------|----------|----------|----------|----------|
| Values            | 0.85         | -0.45    | -0.52    | 0.54         | 1.42     | -0.78    | -0.175   | 0.09     | 0.135    | 0.2      |

physics pictures. Here, we suggest two different ways to introduce Zeeman field. One is transforming the system into Ferromagnetism [24, 25] i.e. exerting the field toward the same direction on all Bi atoms. The other is exerting an alternate converse field on adjacent nanoribbons of Bi along y axis then make the system into antiferromagnetic phase [20]. We call them Plan I and Plan II, respectively. Experimentally, one can deposit monolayer $\beta$-Bi$_2$Pd on a magnetic material to realize QAHSs via proximity effect. Alternatively, doping magnetic atoms like Fe, Cr, or Ni may do the trick as well [27, 28].

IV. $Z_2$ INDEX

By the criterion of parity introduced by Fu et al. [29], the $Z_2$ index $v_0$ can be calculated by $(-1)^{v_0} = \prod_{i=1}^{4} \delta (\Gamma_i)$, where $\delta (\Gamma_i)$ is the product of parity eigenvalues of the occupied bands at the four TRIM $\Gamma_i$ in 2D. The TRIM are defined as $\Gamma_{n_1,n_2} = \frac{1}{2} (n_1 \mathbf{G}_1 + n_2 \mathbf{G}_2)$, where $n_{1,2} = 0$ or $1$ and $\mathbf{G}_{1,2}$ are the primitive reciprocal lattice vectors. We show the parity of each TRIM in Table II. Due to the band inversion exchanges the parity of $\Gamma$ and $K$ between valence and conduction bands, the nontrivial $Z_2$ index $v_0=1$ is obtained and guarantees the existence of nontrivial TES. This nontrivial topology is independent of SOC indicating an inevitable node in BZ which is the Dirac point when excluding SOC.

V. TOPOLOGICAL EDGE STATES

Considering an infinite nanoribbon of monolayer $\beta$-Bi$_2$Pd where y direction is limited, in the case, the momentum $k_y$ is not a good quantum number yet. We plot such band structures in Fig. 2.

A. Quantum spin Hall states

Due to the $Z_2$ number is nontrivial, the TES will exists in monolayer $\beta$-Bi$_2$Pd even without SOC [dashed line in Fig. 2(a)]. Once turning on SOC, the band structure will be divided then forms a full band gap in bulk. However, the TES closes the band gap at the $\Gamma$ point (solid lines). This TES corresponding to quantum spin Hall state (QSHS) that two electrons with opposite spin travel at the boundary along adverse directions. One can see this intriguing phenomenon by adding an external electric field [30].

B. Quantum anomalous Hall states

For Plan I, since the magnetic field lifts the Kramers degeneracy, each two-fold degenerate edge band splits and cause a QAHS at the $\Gamma$-$X$ path including SOC in Fig. 2 (b). Through tuning $\lambda$ and $B$, the system gets into QAHS from Dirac phase only when $|\lambda| > |B|$. When the system enters the antiferromagnetic phase and number of nanoribbons is odd, this is quite similar to Plan I. However, if number of nanoribbons is even, edge bands remain two-fold degeneracy and give a four-fold degenerate point alone $\bar{\Gamma}$-$\bar{X}$ (c) once SOC is nonzero. Interestingly, there is no reflection symmetry with regard to $\Gamma$ point, because adjacent Bi nanoribbons have opposite magnetism that destroys the according crystal symmetry.

VI. MAJORANA ZERO MODES

In this section, we introduce a s-wave superconducting gap $\Delta$ as follow

$$H_{\Delta} = \sum_{\alpha = x,y,z} \Delta C_{k,\alpha,\uparrow} C_{-k,\alpha,\downarrow}^\dagger + h.c.$$
FIG. 3. The MZMs realized by coupling to a \( \pi \)-shifted superconductor (a), introducing the Zeeman field toward the same direction on all Bi atoms, and introducing the Zeeman field toward the converse direction on adjacent Bi layer along y direction. Here, SOC is zero (a) and B=0.15 eV (b) and (c).

where \( \alpha \) is p-orbital. In Nambu space \([C_{k,\alpha,\uparrow}, C_{k,\alpha,\downarrow}^\dagger, C_{-k,\alpha,\downarrow}, C_{-k,\alpha,\uparrow}]\), the Bogoliubovde Gennes (BdG) Hamiltonian is given by

\[
H_{BdG} = H + \Delta = H_0 + H_{SOC} + H_B + \Delta
\]

where

\[
\Delta_0 = \Delta \sigma_y I_3.
\]

Below the superconducting transition temperature \( T = 1.95 \) K \([22]\), the system enter the superconducting phase and the entire edge will become gapped. To realize MZMs, we offer three different schemes: Plan 0, I, and II. We set \( \Delta = 0.1 \) eV for all situations. For Plan 0, we cover the half of monolayer \( \beta \)-Bi\(_2\)Pd with a \( \pi \)-shifted s-wave superconductor on the surface, then the system becomes a helical TS when SOC is negligible. The MZM appears at the \( \Gamma \)-X path as shown in Fig. 3 (a). On the edge, there will be a chiral Majorana fermion and an anti-Chiral Majorana fermion with the opposite spin traveling along opposite directions. Plan I and Plan II are mentioned before. When the strength of Zeeman field is comparable to superconducting gap at least, there will be chiral MZMs at the edge [(b) and (c)]. If SOC is large enough (nearly twice as much as B), band structure will be gapped at the edge for antiferromagnetic phase.

VII. CONCLUSION

In summary, we construct a three-band TBM for monolayer \( \beta \)-Bi\(_2\)Pd to analyze topological and superconducting properties. Without SOC, there is the high-order quadratic Dirac point at the M point protected by \( C_3 \) and \( \sigma_y \) symmetry. When turning on SOC, the band structure of bulk is gapped but the nontrivial TES closes the band at the edge. Since it itself is a superconductor, Majorana fermions will appear on the vortex by covering half surface of monolayer \( \beta \)-Bi\(_2\)Pd with a \( \pi \)-shifted superconductor. When monolayer \( \beta \)-Bi\(_2\)Pd gets into ferromagnetic and antiferromagnetic phase by magnetic proximity effect or doping magnetic atoms in experiment, QAHSs and chiral MZMs will be possibly observed as well.

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[1] E. Majorana and L. Maiani, in Ettore Majorana Scientific Papers (Springer Berlin Heidelberg) pp. 201–233.
[2] F. Wilczek, Nature Physics 5, 614 (2009).
[3] C. Beenakker, Annual Review of Condensed Matter Physics 4, 113 (2013).
[4] X.-L. Qi and S.-C. Zhang, Rev. Mod. Phys. 83, 1057 (2011).
[5] T. M. Rice and M. Sigrist, Journal of Physics: Condensed Matter 7, L643 (1995).
[6] K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z. Q. Mao, Y. Mori, and Y. Maeno, Nature 396, pgs. 658 (1998).
[7] M. Sato, Phys. Rev. B 79, 214526 (2009).
[8] M. Sato, Phys. Rev. B 81, 220504 (2010).
[9] M. Sato, Phys. Letters B 575, 126 (2003).
[10] L. Fu and C. L. Kane, Phys. Rev. Lett. 100, 096407 (2008).
[11] Z. Sun, Z. Cao, J. Cui, C. Zhu, D. Ma, H. Wang, W. Zhuo, Z. Cheng, Z. Wang, X. Wan, and X. Chen, npj Quantum Materials 5 (2020), 10.1038/s41535-020-0239-z.
[12] J. Zhang, B. Zhao, Y. Yao, and Z. Yang, Sci Rep 5, 10629 (2015).
[13] Z. Qiao, W. Ren, H. Chen, L. Bellaiche, Z. Zhang, A. H. MacDonald, and Q. Niu, Phys. Rev. Lett. 112, 116404 (2014).
[14] J. Zou, Q. Xie, G. Xu, and Z. Song, National Science Review (2020), 10.1093/nsr/nwaa169, https://academic.oup.com/nsw/advance-article-pdf/doi/10.1093/nsr/nwaa169;133528562/nwaa169.pdf.
[15] M. Sakano, K. Okawa, M. Kanou, H. Sanjo, T. Okuda, T. Sasagawa, and K. Ishizaka, Nature Communications 6 (2015), 10.1038/ncomms9595.
[16] T. Xu, B.-T. Wang, M. Wang, Q. Jiang, X.-P. Shen, B. Gao, M. Ye, and S. Qiao, Phys. Rev. B 100, 161109 (2019).
[17] B.-T. Wang and E. R. Margine, Journal of Physics: Condensed Matter 29, 325501 (2017).
[18] J.-J. Zheng and E. R. Margine, Phys. Rev. B 95, 014512 (2017).
[19] P. K. Biswas, D. G. Mazzone, R. Sibille, E. Pomjakushina, K. Conder, H. Luetkens, C. Baines, J. L. Gavilano, M. Kenzelmann, A. Amato, and E. Morenzoni, Physical Review B 93 (2016), 10.1103/physrevb.93.220504.
[20] Y.-F. Li, X.-Y. Xu, M.-H. Lee, M.-W. Chu, and C.-L. Chien, Science 366, 238 (2019).
[21] Y.-F. Lv, W.-L. Wang, Y.-M. Zhang, H. Ding, W. Li, L. Wang, K. He, C.-L. Song, X.-C. Ma, and Q.-K. Xue, Science Bulletin 62, 852 (2017).
[22] P.-F. Liu, J. Li, H. Yin, X.-H. Tu, B. Sa, J. Zhang, D. J. Singh, and B.-T. Wang, “Single-layer $\beta$-bi$_2$pd: a phonon-mediated 2d topological superconductor,” (2020), arXiv:2006.10947.
[23] C.-X. Liu, X.-L. Qi, H. Zhang, X. Dai, Z. Fang, and S.-C. Zhang, Physical Review B 82 (2010), 10.1103/physrevb.82.045122.
[24] W. Wu, Z.-M. Yu, X. Zhou, Y. X. Zhao, and S. A. Yang, Phys. Rev. B 101, 205134 (2020).
[25] H. Wu, D.-S. Ma, B. Fu, W. Guo, and Y. Yao, The Journal of Physical Chemistry Letters 10, 2508 (2019).
[26] D. Wang, F. Tang, H. C. Po, A. Vishwanath, and X. Wan, Phys. Rev. B 101, 115122 (2020).
[27] C.-Z. Chang, J. Zhang, X. Feng, J. Shen, Z. Zhang, M. Guo, K. Li, Y. Ou, P. Wei, L.-L. Wang, Z.-Q. Ji, Y. Feng, S. Ji, X. Chen, J. Jia, X. Dai, Z. Fang, S.-C. Zhang, K. He, Y. Wang, L. Lu, X.-C. Ma, and Q.-K. Xue, Science 340, 167 (2013).
[28] C.-X. Liu, S.-C. Zhang, and X.-L. Qi, Annual Review of Condensed Matter Physics 7, 301 (2016).
[29] L. Fu and C. L. Kane, Phys. Rev. B 76, 045302 (2007).
[30] M. Ezawa, Journal of the Physical Society of Japan 84, 121003 (2015).