Topological semi-metals with line nodes and drumhead surface states

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In an ordinary three-dimensional metal the Fermi surface forms a two-dimensional closed sheet separating the filled from the empty states. Topological semimetals, on the other hand, can exhibit protected one-dimensional Fermi lines or zero-dimensional Fermi points, which arise due to an intricate interplay between symmetry and topology of the electronic wavefunctions. Here, we study how reflection symmetry, time-reversal symmetry, SU(2) spin-rotation symmetry, and inversion symmetry lead to the topological protection of line nodes in three-dimensional semi-metals. We obtain the crystalline invariants that guarantee the stability of the line nodes in the bulk and show that a quantized Berry phase leads to the appearance of protected surfaces states with a nearly flat dispersion. By deriving a relation between the crystalline invariants and the Berry phase, we establish a direct connection between the stability of the line nodes and the topological surface states. As a representative example of a topological semimetal with line nodes, we consider Ca$_3$P$_2$ and discuss the topological properties of its Fermi line in terms of a low-energy effective theory and a tight-binding model, derived from ab initio DFT calculations. Due to the bulk-boundary correspondence, Ca$_3$P$_2$ displays nearly dispersionless surface states, which take the shape of a drumhead. These surface states could potentially give rise to novel topological response phenomena and provide an avenue for exotic correlation physics at the surface.

I. INTRODUCTION

The study of band structure topology of insulating and semi-metallic materials has become an increasingly important topic in modern condensed matter physics [1–5]. The discovery of spin-orbit induced topological insulators has revealed that a non-trivial momentum-space topology of the electronic bands can give rise to new states of matter with exotic surface states [6–11] and highly unusual magneto-transport properties [12–14]. Recently, due to the experimental detection of arc surface states in Weyl semi-metals [15], considerable attention has focused on the investigation of topological semi-metals [16–31]. While in ordinary three-dimensional metals filled and empty states are separated by two-dimensional Fermi sheets, topological semi-metals can exhibit zero-dimensional Fermi points or one-dimensional Fermi lines.

Classic examples of topological semi-metals are the Weyl and Dirac semi-metals which exhibit two-fold and four-fold degenerate Fermi points, respectively. Weyl points can occur in the absence of any symmetry besides translation, whereas Dirac points are topologically stable only in the presence of time-reversal symmetry together with a crystal lattice symmetry, such as rotation or reflection. For example in the Dirac materials Cd$_3$As$_2$ [32, 34, 57] and Na$_3$Bi [35, 44], the gapless property of the Dirac points is protected by a $C_4$ and $C_5$ crystal rotation symmetry, respectively. Correspondingly, the stability of Weyl points is guaranteed by a Chern number, while Dirac points are protected by a crystalline invariant, e.g., a mirror number [3]. Due to their topological characteristics these point-node semi-metals display a number of exotic transport phenomena, such as negative magneto-resistance and chiral magnetic effect [24, 43–46].

Probably even more interesting than semi-metals with point nodes are topological materials with line nodes, since they support weakly dispersing surface states that could provide an interesting platform for exotic correlation physics [47–49]. Moreover, these semi-metals are expected to exhibit long-range Coulomb interaction [50] and graphene-like Landau levels [51]. In nodal line semi-metals the valence and conduction bands cross along one-dimensional lines in momentum space forming a ring-shaped Fermi line. From the general classification of gapless topological materials [3] it follows, that line nodes in semi-metals are stable against gap opening only in the presence of a lattice symmetry, such as, e.g., reflection [18, 20]. That is, the two bands that cross at (or near) the Fermi level of a nodal line semi-metal have opposite crystal symmetry eigenvalues, which prevents hybridization. For example, in non-centrosymmetric PbTaSe$_2$ [52, 53] and TiTaSe$_2$ [54] the reflection about the Ta atomic planes protects the topological nodal lines. Similarly, the band crossings in Cu$_3$PdN [55], ZrSiS [56], and Ca$_3$P$_2$ [57] are protected by point group symmetries. Since the latter three systems are symmetric under both inversion and time reversal, their nodal rings are four-fold
A. Tight-binding model for Ca$_3$P$_2$

Recently, a new polymorph of Ca$_3$P$_2$ has been synthesized which crystallizes in a hexagonal lattice structure with space group $P6_3/mmc$ [57]. Figures 1(a) and 1(b) display the crystal structure of this polymorph of Ca$_3$P$_2$, which contains two layers with three Ca and three P atoms separated by four interstitial Ca atoms. X-ray diffraction measurements show that the Ca site is only partially occupied, yielding a Ca$_2^{+}$–P$_3^{-}$ charge-balanced compound.

To determine the electronic band structure we perform first principles calculations with the WIEN2k code [63] using as an input the experimental crystal structure of Ref. [57]. For the exchange-correlation functional we choose the generalized-gradient approximation of Perdew-Burke-Ernzerhof type [64]. The full Brillouin zone is sampled by $21 \times 21 \times 22$ $k$-points and the plane-wave cut-off is set to $R K_{\text{max}} = 7$. We treat the par-
Fig. 1. Crystal structure and electronic bands of Ca$_3$P$_2$.

(a) Crystal structure of Ca$_3$P$_2$, which contains two planes with three Ca atoms (blue) and three P atoms (red) that are separated by interstitial Ca atoms (black). The grey dashed lines indicate the unit cell. (b) Top and side view of the crystal structure. The P-p$_x$ and Ca-d$_{z^2}$ orbitals included in the tight-binding model are shown schematically. (c) Calculated electronic band structure of Ca$_3$P$_2$. The weights of the P-p$_x$ and Ca-d$_{z^2}$ orbitals that are located within the layers are indicated by the width of the corresponding band. The weight of the Ca-d$_{z^2}$ orbital is multiplied by two to make it more visible on the scale of the plot. (d) Fermi ring of Ca$_3$P$_2$ as obtained from the tight-binding model, Eq. (2.2). The bulk and surface Brillouin zones are outlined by the green and black lines, respectively.

The tight-binding model is defined in terms of a twelve-component Bloch spinor

$$|\psi_k^\alpha\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{s}_\alpha)} |\phi_\alpha^\beta\rangle,$$

where $\alpha$ is the orbital index, $\mathbf{R}$ denotes the lattice vectors, and $\mathbf{s}_\alpha$ represents the position vectors of the six Ca ($\alpha = 1, \ldots, 6$) and the six P sites ($\alpha = 7, \ldots, 12$) as specified in Figs. (a) and (b). For completeness, the numerical values of the position vectors $\mathbf{s}_\alpha$ are given in Table I of Appendix A. At this stage of the discussion, we ignore the spin degree of freedom of the Bloch spinor, since spin-orbit coupling is negligibly small for the light elements Ca and P. Using the spinor (2.1), we construct the matrix elements of the Bloch Hamiltonian as

$$H_{ij}^{\alpha\beta}(k) = \langle \psi_k^\alpha | H | \psi_k^\beta \rangle = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \mathbf{s}_\alpha - \mathbf{s}_\beta)} t_{ij}^{\alpha\beta},$$

where $t_{ij}^{\alpha\beta}$ is the hopping amplitude from orbital $\alpha$ in the unit cell at the origin to orbital $\beta$ in the unit cell at position $\mathbf{R}$. To simplify the form of the matrix elements (2.2) and have a single-valued Hamiltonian, we absorb a momentum dependent phase factor in the definition of the basis orbitals, i.e., we let $|\psi_k^\alpha\rangle \rightarrow e^{-ik \cdot \mathbf{s}_\alpha} |\psi_k^\alpha\rangle$. We observe that Hamiltonian (2.2) has a nested block structure

$$H(k) = \begin{pmatrix} H_{\text{CaCa}} & H_{\text{CaP}} \\ H_{\text{PP}} & H_{\text{PP}} \end{pmatrix}, \quad H_{ij} = \begin{pmatrix} h_{ij}^{\text{uu}} & h_{ij}^{\text{ul}} \\ h_{ij}^{\text{lu}} & h_{ij}^{\text{ll}} \end{pmatrix},$$

where the sub-blocks $h_{ij}^{mn}$ with fixed $i, j \in \{\text{Ca, P}\}$ and fixed $m, n \in \{1, u\}$ are $3 \times 3$ matrices. The outer blocks $H_{ij}$ represent hopping processes among and between the Ca and P orbitals, whereas the inner blocks $(h_{ij}^{uu}, h_{ij}^{ul})$ and $(h_{ij}^{lu}, h_{ij}^{ll})$ describe intralyer and interlayer hoppings, respectively. The detailed form of the matrix elements $h_{ij}^{mn}$ is specified in Appendix A1 where we also describe how the hopping parameter values are determined from a maximally localized Wannier function (MLWF) method.

In Fig. 1(d) we plot the energy isosurface of Hamiltonian (2.2) at $E = E_F \pm 20$ meV, which shows that the tight-binding model correctly captures the fourfold degenerate Dirac ring of Ca$_3$P$_2$. Comparing the first-principles band structure of Fig. 1(c) with the tight-binding bands displayed in Fig. 2 we find that the tight-binding model closely reproduces the bands with dominant Ca-d$_{z^2}$ and P-p$_x$ orbital character. In particular, the linear dispersion close to the Dirac ring agrees well with the first-principles results.

1. Symmetries

As we will see in the following sections, time-reversal, inversion, reflection, and SU(2) spin-rotation symmetry play a crucial role for the protection of the Dirac ring. Let us therefore discuss how these symmetries act on the tight-binding Hamiltonian.
First of all, since we did not include the spin degree of freedom in Eq. (2.2), the tight-binding model is fully SU(2) spin-rotation invariant. That is, our model is diagonal in spin space with Hamiltonian (2.2) representing the diagonal element. As a consequence, the time-reversal operator is simply given by the identity matrix times the complex conjugation operator $K$, i.e., $T = \mathbb{I}K$, which acts on the Hamiltonian as

$$T^{-1}H(-k)T = H(k).$$  \hfill (2.4)

Hence, Hamiltonian (2.2) belongs to symmetry class AI, since $T^2 = +1$. According to the classification of Ref. [1], Fermi rings in this symmetry class are unstable in the absence of lattice symmetries. However, as we will discuss below, reflection symmetry or a combination of inversion with time-reversal symmetry can produce a topological protection of the Dirac ring.

The two layers of the crystal structure of Ca$_3$P$_2$, indicated in green and brown in Fig. 1(a), are reflection planes. For brevity, we only discuss the lower reflection plane [colored in green in Fig. 1(a)], but the following analysis also holds, mutatis mutandis, for the upper plane. The invariance of the tight-binding Hamiltonian (2.2) under reflection about the lower plane implies

$$R^{-1}(k_z)H(k_x, k_y, -k_z)R(k_z) = H(k_x, k_y, k_z),$$  \hfill (2.5a)

with the $k_z$-dependent reflection operator

$$R(k_z) = \tau_2 \otimes e^{\frac{i}{2}(\rho_z - p_0)c} \otimes \mathbb{I}_{3 \times 3} = \tau_2 \otimes \begin{pmatrix} 1 & 0 \\ 0 & e^{ik_zc} \end{pmatrix} \otimes \mathbb{I}_{3 \times 3},$$  \hfill (2.5b)

where $c$ is the length of the lattice vector along the (001) direction. Here, the two sets of Pauli matrices $\tau_2$ and $\rho_z$ describe the orbital (Ca-$d_{z^2}$, P-$p_z$) and the layer (l, u) degrees of freedom, respectively. The form of the reflection operator $R(k_z)$ follows from the observations that (i) the $P-p_z$ orbitals are odd under reflection, while the Ca-$d_{z^2}$ orbitals are even; and (ii) the mirror symmetry maps the orbitals in the upper layer to the next unit cell, which gives rise to the phase factor $e^{ik_zc}$. Finally, we find that the tight-binding model is also inversion symmetric. That is, Hamiltonian (2.2) satisfies

$$I^{-1}H(-k)I = H(k),$$  \hfill (2.6)

with the spatial inversion operator $I = \gamma_0 \otimes \rho_x \otimes \mathbb{I}_{3 \times 3}$.

**B. Topological protection of the Fermi ring**

Let us now discuss how reflection symmetry (2.5) leads to the topological protection of the Dirac ring. First, we observe that for $k$ within the reflection plane $k_z = 0, \pi$ the mirror operator $R(k_z)$ commutes with Hamiltonian (2.2), i.e., $[R(k_z), H(k_x, k_y, k_z)] = 0$ for $k_z = 0, \pi$. Therefore, it is possible to block-diagonalize $H(k)$ within the mirror planes with respect to $R$. In this block-diagonal basis each eigenstate of $H(k)$ has either mirror eigenvalue $R = +1$ or $R = -1$. As we can see from Fig. 2(a), the two bands that cross at the Dirac point have opposite mirror eigenvalues, which prevent hybridization between them. In other words, any term that couples the two bands breaks reflection symmetry. The stability of the band crossing is guaranteed by a mirror invariant of type $MZ$ [18]. This mirror index is given by the difference of occupied states with eigenvalue $R = +1$ on either side of the Dirac ring, i.e.,

$$N_{MZ}^0 = n_{occ}(|k|| > k_0) - n_{occ}(|k|| < k_0),$$  \hfill (2.7)

where $|k|| = (k_x, k_y)$ is the in-plane momentum and

$$n_{occ}(|k||) = \begin{cases} 1, & |k|| < k_0 \text{ (inside the ring)} \\ 0, & |k|| > k_0 \text{ (outside the ring)} \end{cases}$$  \hfill (2.8)

denotes the number of occupied states at $(|k||, 0)$ in the mirror eigenspace $R = +1$.

In passing, we note that Hamiltonian (2.2) is a member of symmetry class AI with $R_+$ in the terminology of Ref. [18] since $T^2 = +1$ and $R$ commutes with $T$. However, nodal lines with codimension $p = 2$ in class AI with $R_+$ are unstable, since for this class there does not exist any zero-dimensional invariant defined at time-reversal invariant momenta within the mirror plane. Nevertheless, the Dirac band crossing is protected, since the Hamiltonian can also be viewed as a member of class A with $R$. The mirror invariant for the latter class [i.e., Eq. (2.8)], which is defined for any in-plane momentum $k_p$, can be non-zero even in the presence of time-reversal symmetry. Besides reflection symmetry, the product of inversion and time-reversal symmetry $IT$ also protects the Dirac line. This will be discussed at the end of Sec. IIIC and in Sec. III B 1 in terms of a low-energy continuum model.

![FIG. 2. Band structure of the tight-binding model. Panels (a) and (b) show the energy bands of Hamiltonian (2.2) along high-symmetry lines within the mirror planes $k_z = 0$ and $k_z = \pi/c$, respectively [cf. Fig. 1(d)] . The reflection eigenvalues of the bands are indicated by color, with blue and red corresponding to $R = +1$ and $R = -1$, respectively.](image)
C. Surface states and Berry phase

In this section, we present the surface spectrum of Ca₅P₂ as obtained from the tight-binding model (2.2) and show that, due to a non-zero Berry phase, there appear nearly flat ingap states at the surface. Figure 3(a) displays the surface band structure for the (001) surface in a three-dimensional slab geometry with 60 unit cells. The surface momentum is varied along a high-symmetry path, which is drawn in red in the surface Brillouin zone of Fig. 1(d). Using an iterative Green’s function method [63] we compute the momentum-resolved surface density of states for a semi-infinite (001) slab, which is shown in Fig. 3(b). As indicated by the green area in Fig. 3(d) and by the green and yellow lines in Figs. 3(a) and 3(b), respectively, the surface state is nearly dispersionless, taking the shape of a drumhead that is bounded by the projected Dirac ring. We note that nearly or completely flat surface states have recently also been studied in photonic crystals [69], in noncentrosymmetric superconductors [70–73], in bernal graphite [74], and in topological crystalline insulator heterostructures [75].

In contrast to crystalline topological insulators the surface states of the semimetal (2.2) are not directly related to the mirror invariant (2.7), but are connected to a non-zero Berry phase. To make this connection explicit, we decompose the (001) slab considered in Fig. 3 into a family of one-dimensional systems parametrized by the in-plane momentum \( k_\parallel = (k_x, k_y) \). For fixed \( k_\parallel \), the Berry phase is defined as

\[
\mathcal{P}(k_\parallel) = -i \sum_{E_i < E_F} \int_{-\pi}^{\pi} \langle u_j(k) | \partial_{k_\parallel} | u_j(k) \rangle dk_z, \tag{2.9}
\]

where the sum is over filled Bloch eigenstates \( |u_j(k)\rangle \) of Hamiltonian (2.2). As was shown by King-Smith and Vanderbilt [75], the Berry phase \( \mathcal{P}(k_\parallel) \) is related to the charge \( q_{\text{end}} \) at the end of the one-dimensional system with fixed in-plane momentum \( k_\parallel \), i.e.,

\[
q_{\text{end}} = \frac{e}{2\pi} \mathcal{P}(k_\parallel) \mod e. \tag{2.10}
\]

Hence, when \( \mathcal{P}(k_\parallel) \neq 0 \) an ingap state appears at \( k_\parallel \) in the surface Brillouin zone. For the tight-binding Hamiltonian (2.2) we find that there are two different symmetries which each quantize the Berry phase (2.9) to 0 or \( \pi \), namely, the reflection symmetry (2.5) and the product of time-reversal and inversion symmetry IT, see Appendix B. In Fig. 3(c) we numerically compute \( \mathcal{P}(k_\parallel) \) using the tight-binding wave functions of Hamiltonian (2.2). We obtain that the Berry phase equals \( \pi \) for \( k_\parallel \) inside the projected Dirac ring, while it is zero for \( k_\parallel \) outside the ring. This indicates that surface states occur within the projected Dirac ring, which is in agreement with the surface spectrum of Figs. 3(a) and 3(b).

The Berry phase is defined modulo \( 2\pi \), since large gauge transformations of the wave functions change it by \( 2\pi \). As a result, \( \mathcal{P} \) protects only single, but not multiple, surface states at a given \( k_\parallel \).

Remarkably due to the IT symmetry, the Berry phase \( \mathcal{P} \) along any closed loop in the three-dimensional Brillouin zone is quantized (see Appendix B). This allows us to interprete the Berry phase as a topological invariant which guarantees the stability of the Dirac line in the presence of the IT symmetry. That is, for a loop interlinking with the Dirac ring, we find that \( \mathcal{P} = \pm \pi \) which shows that the Dirac band crossing is protected by the product of inversion with time-reversal symmetry. The Berry phase represents a \( \mathbb{Z}_2 \)-type invariant, since it is defined only up to multiples of \( 2\pi \). In contrast, the mirror number (2.7) is a \( \mathbb{Z} \)-type invariant, which can take on any integer number. Therefore, only the mirror invariant \( N_{\text{M}} \) can give rise to the stability of multiple Dirac lines at the some location in the Brillouin zone.

D. Relation between Berry phase and mirror invariant

The analysis of the previous section suggests that the topological stability of the Dirac ring is closely related to the appearance of surface states. In order to put this connection on a firmer footing, we present here a relation...
between the mirror invariant and the Berry phase $\mathcal{P}(k_\parallel)$. Namely, we find that

$$(-1)^{n_{\text{occ}}^+\pi(k_\parallel)} e^{i\partial R} = e^{i\mathcal{P}(k_\parallel)} \quad (2.11a)$$

for all in-plane momenta $k_\parallel = (k_x, k_y)$, where

$$\partial R = i \sum_{E_j < E_0} \int_0^\pi \langle u_j(k) | R^\dagger(k_z) [\partial k_z R(k_z)] | u_j(k) \rangle dk_z \quad (2.11b)$$

denotes the change in phase of the reflection operator $R(k_z)$ along the reflection direction $k_z$. The invariants $n_{\text{occ}}^{+,0}(k_\parallel)$ and $n_{\text{occ}}^{+,\pi}(k_\parallel)$ correspond to the number of occupied states at $(k_\parallel, 0)$ and $(k_\parallel, \pi)$, respectively, with mirror eigenvalue $R = +1$. Formula (2.11), whose proof is derived in Appendix [3], is one of the main results of this paper. For concreteness we have assumed in (2.11) that reflection symmetry $R(k_z)$ maps $z$ to $-z$. But relation (2.11) is valid more generally, i.e., for any reflection symmetric semimetal, in particular also for line-node materials with strong spin-orbit coupling, such as PbTaSe$_2$ [52, 53].

We observe that in general the reflection operator only depends on the momentum along the reflection direction [i.e., on $k_z$ in the case of Eq. (2.5)], but is independent of the in-plane momenta $k_\parallel$. Hence, we infer from Eq. (2.11) that when the mirror invariant $n_{\text{occ}}^{+,0}(k_\parallel)$ [or $n_{\text{occ}}^{+,\pi}(k_\parallel)$] changes by one as the in-plane momentum $k_\parallel$ is moved across the topological Dirac line, the Berry phase increases by $\pi$, since $\partial R$ does not depend on $k_\parallel$. As a consequence, a drumhead surface state appears either inside or outside the projected Dirac ring. This proofs the direct connection between the stability of the Dirac ring and the existence of drumhead surface states. For the tight-binding model of Ca$_3$P$_2$, Eq. (2.2), we find that the phase change $\partial R$ of the reflection operator (2.5) evaluates to $3\pi$ independent of $k_\parallel$. Figure 2(b) shows that the number of occupied states with momentum $(k_\parallel, \pi)$ and mirror eigenvalue $R = +1$ is $n_{\text{occ}}^{+,\pi}(k_\parallel) = 3$ for all $k_\parallel$.

Using relation (2.11) together with Eq. (2.8), it follows that the Berry phase $\mathcal{P}$ equals $\pi$ inside and $0$ outside the Dirac ring, which agrees with the explicit calculation of $\mathcal{P}$, see Fig. 3(c).

In closing this section, we note that for certain highly symmetric lattice models [60, 79] the reflection operator $R$ is completely momentum independent, in which case formula (2.11) simplifies to

$$[n_{\text{occ}}^{+,0}(k_\parallel) + n_{\text{occ}}^{+,\pi}(k_\parallel)] \pi = \mathcal{P}(k_\parallel) \quad (2.12)$$

for all $k_\parallel$ [77]. Hence, in this case the Berry phase, and therefore the location of the surface states, is fully determined by the mirror invariant (2.8). This is useful, since the mirror number (2.8) is easier to compute than the Berry phase, for which one needs to determine the momentum dependence of the tight-binding wave functions.

E. Symmetry-breaking perturbations

We have seen that the stability of the Dirac ring of Ca$_3$P$_2$ is protected by SU(2) spin-rotation symmetry, reflection symmetry, and the product of inversion and time-reversal symmetry $IT$. In this section, we study how the breaking of these symmetries modifies the bulk and surface spectrum of Ca$_3$P$_2$.

1. Reflection and time-reversal symmetry breaking

First, we consider a reflection and time-reversal breaking perturbation with the following nonzero matrix elements

$$\langle \psi_k^1 | H | \psi_k^0 \rangle = +0.2 \sin(k \cdot r_0) \quad (2.13a)$$

and

$$\langle \psi_k^4 | H | \psi_k^2 \rangle = -0.2 \sin(k \cdot r_0), \quad (2.13b)$$

where $r_0 = (0.5, 0.5, 0)$ is a vector within the reflection plane along the diagonal direction. This term is odd in momentum $k$ and couples the $d_{z^2}$ orbitals at the Ca1 and Ca4 sites with the $p_x$ orbitals at the P3 and P6 sites [{cf. Figs. 1(a) and 1(b)]}. It follows from Eqs. (2.5) and (2.6) that perturbation (2.13) breaks reflection and time-reversal symmetry, but respects inversion symmetry. Therefore, Eq. (2.13) gaps out the Dirac ring except for two points along the diagonal direction $(1, 0, 0)$, where it vanishes [see Fig. 4(b)]. These two gap closing points are Dirac nodes (or Weyl nodes, if one disregards the spin degree of freedom), whose stability is guaranteed by the spin Chern number [78].

$$C_s(k_\parallel) = \frac{1}{2\pi i} \sum_{E_j < E_0} \int_{T^2} [\partial_{k_x} A_z^{(j)} - \partial_{k_z} A_x^{(j)}] dk_x dk_y \quad (2.14)$$

FIG. 4. Arc surface state and spin Chern number. (a) $k_\parallel$ dependence of the spin Chern number $C_s$ of Hamiltonian (2.2) in the presence of the mirror and time-reversal symmetry breaking perturbation (2.13). (b) Surface and bulk spectra of the low-energy model (3.1) perturbed by the mass term (3.2) with $d = 0.9$ eV and $\theta_0 = -\pi/4$, which breaks reflection and time-reversal symmetry. The bulk states and the arc state at the (001) surface are indicated in gray and green, respectively.
where \( A^{(j)}_\alpha = \langle u_j | \partial_{k_\alpha} | u_i \rangle \) is the Berry connection. We find that \( C_\alpha(k_{\alpha}) \) evaluates to +1 for \( k_xk_z \) planes between the two Dirac points, while it is zero otherwise [Fig. 3(a)]. By the bulk-boundary correspondence, the nonzero spin Chern number (2.13) implies the appearance of an arc state in the surface Brillouin zone connecting the projections of the two Dirac nodes [green area in Fig. 4(b)]. As perturbation (2.13) is turned to zero, the arc state transforms into the drumhead surface state of Fig. 3.

### 2. Spin-rotation symmetry breaking

Second, we study the effects of SU(2) spin-rotation symmetry breaking induced, for example, by spin-orbit coupling. For CaAsP$_2$ the spin-orbit interactions are negligible due to the small atomic number of Ca and P. However, there are a number of topological semimetals with heavy elements, such as PbTaSe$_2$ and TiTaSe$_2$, for which spin-orbit coupling is strong. Spin-orbit interactions can modify the energy spectrum of nodal line semimetals in two different ways: either they open up a full gap in the spectrum, or they split the Dirac ring into two Weyl rings. Here, we study the latter possibility. In order to do so, we need to explicitly include the spin degree of freedom in Hamiltonian (2.3), i.e., we consider

\[
\hat{H}(k) = H(k) \otimes \sigma_0 + \hat{H}_{sb}(k), \quad (2.15)
\]

where \( \sigma_0 \) operates in spin space and \( \hat{H}_{sb} \) represents a spin-rotation symmetry breaking term, which we specify below. Time-reversal symmetry acts on \( H \) according to Eq. (2.4), but with the modified time-reversal operator \( \hat{T} = T \otimes \sigma_y \). Similarly, the reflection operator and the spatial inversion operator are changed to \( \hat{R} = R \otimes \sigma_z \) and \( \hat{I} = I \otimes \sigma_0 \), respectively. To split the four-fold degenerate Dirac ring of Eq. (2.15) into two two-fold degenerate Weyl rings, it is necessary to also break time-reversal or inversion symmetry, besides spin-rotation symmetry.

#### a. Time-reversal breaking perturbation

The staggered Zeeman field

\[
\hat{H}_{sb}(k) = h_z \tau_z \otimes \rho_0 \otimes I_{3,3} \otimes \sigma_x \quad (2.16)
\]

breaks both time-reversal and spin-rotation symmetry, but satisfies inversion and reflection symmetry. It describes an external staggered magnetic field with opposite signs on the Ca and P sites. According to the terminology of Ref. 12, Hamiltonian (2.15) perturbed by Eq. (2.16) is a member of class A with \( R \), which exhibits an integer number of equivalence classes distinguished by a mirror invariant. In Figs. 5(a) and 5(c) we present the bulk energy bands of Hamiltonian (2.15) with an applied staggered Zeeman field of strength \( h_z = 0.1 \) eV. The bulk spectrum displays two Weyl rings, whose stability is guaranteed by the mirror number (2.7). Figures 5(b) and 5(d) show the surface energy spectrum at the (001) face. We find that there are two drumhead surface states which are bounded by the projections of the two Weyl rings. In accordance with the discussion of Secs. II C and II D [cf. Eq. (2.11)] the single surface state that appears between the projections of the outer and inner Weyl rings is protected by the Berry phase (2.9), which takes on the nonzero quantized value \( P = \pm \pi \). The two surface states that exist inside the projection of the inner Weyl ring, on the other hand, are topologically unstable.

#### b. Inversion breaking perturbation

To break inversion and spin-rotation symmetry we consider a perturbation with the following nonzero matrix elements

\[
\langle \psi_{k\alpha}^4 | \hat{H} | \psi_{k\alpha}^5 \rangle = +0.6i \mathrm{sgn}(\sigma) e^{i k \cdot (s_6 - s_1)} \left[ 1 + e^{i k \cdot \mathbf{e}_3} \right] \quad (2.17a)
\]

and

\[
\langle \psi_{k\alpha}^7 | \hat{H} | \psi_{k\alpha}^{12} \rangle = -0.3i \mathrm{sgn}(\sigma) e^{i k \cdot (s_{12} - s_7 + R_{13})} \left[ 1 + e^{i k \cdot \mathbf{e}_3} \right] \quad (2.17b)
\]

where \( \psi_{k\alpha}^\beta \) denotes the Bloch spinor with orbital index \( \alpha \) and spin index \( \sigma = \pm \). The vectors \( s_\alpha \) are the position vectors of the atoms in the unit cell and are given in Table 3 of Appendix A. Perturbation (2.17) couples the orbitals at the Ca1 and P1 sites with the orbitals at the Ca6 and P6 sites, respectively. Using Eqs. (2.3), (2.5),
and (2.6) one can check that the term (2.17) satisfies reflection and time-reversal symmetry, but breaks inversion symmetry. Since $\{T, R\} = 0$, Hamiltonian (2.15) perturbed by Eq. (2.17) is a member of class AII with $R_z$ of Ref. [18], for which a mirror invariant can be defined. The bulk bands at $k_z = 0$ of Hamiltonian (2.15) in the presence of the inversion-breaking term (2.17) are presented in Figs. 6(a) and 6(b). We observe that the Dirac ring is split into two Weyl rings, which intersect on the $(\sqrt{3}, -1, 0)$ axis. As in the previous cases, the Weyl nodal lines are protected by the nonzero mirror number (2.7). Figures 6(b) and 6(d) show the surface spectrum at the $(001)$ surface, which exhibits two drumhead surface states. As before, we find that only the single surface state which occurs between the projections of the inner and outer rings is protected by the Berry phase (2.9).

III. LOW-ENERGY CONTINUUM THEORY OF NODAL LINE SEMIMETALS

In this section we present a low-energy effective theory for a general topological nodal line semimetal with time-reversal, reflection, and inversion symmetry. The form of this low-energy description is universal, since it is entirely dictated by symmetry. We start by discussing Dirac rings, which arise in semimetals with conserved SU(2) spin-rotation symmetry. Spin rotation breaking semimetals with Weyl nodal lines will be discussed in Sec. III B 2.

Consider the following low-energy Hamiltonian with spin-rotation symmetry

$$H_{\text{eff}}(k) = \nu_\parallel (k_\parallel^2 - k_0^2) \tau_z + \nu_\perp k_z \tau_y + f(k) \tau_0,$$  (3.1)

which describes a Dirac ring within the $k_z = 0$ plane, located at $k_0^2 := k_x^2 + k_y^2 = k_0^2$. In Eq. (3.1) we suppress the spin degree of freedom, since any spin-dependent terms are forbidden by symmetry. The Pauli matrices $\tau_i$ operate in orbital space and the function $f(k)$ is restricted by symmetry to be even in $k$. We assume that $f(k) = \nu_0 (k_0^2 - k_0^2) + V_0$, neglecting any terms of higher order in $k$. To make a connection with the previous section, we fit the parameters $\nu_0$, $\nu_\parallel$, $\nu_\perp$, $k_0$, and $V_0$ to the low-energy band structure of the DFT calculations of Sec. II A [see Fig. 3(c)]. We find that the momentum parameter $k_0$ equals $k_0 = 0.206 \text{ Å}^{-1}$, the chemical potential is $\nu_0 = 0.095 \text{ eV}$, and the velocities are given by $\nu_\parallel = -0.993 \text{ eVÅ}^2$, $\nu_\perp = 4.34 \text{ eVÅ}^2$, and $\nu_z = 2.50 \text{ eVÅ}$. Employing Eqs. (2.4), (2.5), and (2.6), one can show that the low-energy Hamiltonian $H_{\text{eff}}$ satisfies time-reversal, reflection, and inversion symmetry, with the symmetry operators $T_{\text{eff}} = \tau_0 K$, $R_{\text{eff}} = \tau_z$, and $I_{\text{eff}} = \tau_z$, respectively. Before we discuss in the next section the topological stability of the Dirac line (3.1), let us remark that $H_{\text{eff}}(k)$ can be converted in a straightforward manner to a lattice model, see Appendix C. In Figs. 3(d), 4(b), 5(d), and 6(d) we use the lattice version of Eq. (3.1) to plot the surface states. Observe that there are some minor differences in the shape of the surface states between the tight-binding model (2.2) and the effective theory (3.1) [compare Fig. 3(b) with Fig. 3(d)]. We attribute this difference to the omission of longer range hopping terms in Eq. (3.1).

A. Topological protection of the Fermi ring

As mentioned in Sec. III B, Dirac nodal lines are protected by either reflection symmetry $R$ or the product of inversion with time-reversal symmetry $IT$. Let us now discuss this in terms of the low-energy theory (3.1).

a. $\mathbb{Z}$ classification due to reflection symmetry

Considering only reflection symmetry and disregarding the spin degree of freedom, Hamiltonian (3.1) belongs to class A with $R$. Since the codimension of the Dirac ring is $p = 2$, it is classified by an $\mathbb{M}$ invariant (see Table II of Ref. [18]), i.e., by the mirror number (2.7), which measures the difference of occupied states with mirror eigenvalue $R_{\text{eff}} = +1$ on either side of the Dirac ring. The two bands that cross at the nodal line have opposite reflection eigenvalues, which prohibits hybridization between them. Indeed, we find that the hybridization term $\tau_x$
breaks reflection symmetry $R_{\text{eff}}$. We note that the mirror invariant (2.7) is of $\mathbb{Z}$ type and can therefore protect multiple Dirac crossings in the Brillouin zone. To verify this for the low-energy model (3.1), we enlarge the matrix dimension of Hamiltonian $H_{\text{eff}}$ by considering $H_{\text{eff}} \otimes I_{n \times n}$, which respects reflection symmetry with the enlarged reflection operator $R'_{\text{eff}} = R_{\text{eff}} \otimes I_{n \times n}$. Hybridization terms for the enlarged Hamiltonian are of the form $\tau_\alpha \otimes A$, with $A$ an arbitrary $n \times n$ Hermitian matrix. However, since $(R'_{\text{eff}})^{-1} (\tau_\alpha \otimes A) R'_{\text{eff}} = -\tau_\alpha \otimes A$, all of these terms break reflection symmetry $R'_{\text{eff}}$.

b. $\mathbb{Z}_2$ classification due to IT symmetry Besides reflection, also the product of inversion with time-reversal symmetry $I_{\text{eff}} T_{\text{eff}}$ prohibits hybridization between the two bands, since the hybridization term $\tau_x$ is not invariant under $I_{\text{eff}} T_{\text{eff}} = \tau_x K$. But in the presence of $I_{\text{eff}} T_{\text{eff}}$, Dirac nodal lines are classified as $\mathbb{Z}_2$ instead of $\mathbb{Z}/2$. To see this, consider two copies of Hamiltonian $H_{\text{eff}}$, i.e., $H_{\text{eff}} \otimes \mu_0$, which satisfies IT symmetry with the doubled operator $I_{\text{eff}} T_{\text{eff}} \otimes \mu_0$. Here, $\mu_0$ denotes an additional set of Pauli matrices. The Dirac rings of this doubled Hamiltonian are topologically unstable, since the symmetry-preserving term $\tau_x \otimes \mu_y$ gaps out the nodal lines. As discussed at the end of Sec. II C, the product of inversion with time-reversal symmetry IT quantizes the Berry phase $\mathcal{P}$ to 0 or $\pi$ [19, 79]. Hence, $\mathcal{P}$ can be interpreted as a $\mathbb{Z}_2$ topological invariant that guarantees the stability of the nodal ring. In contrast to the mirror invariant, the integration path that enters in the definition of this $\mathbb{Z}_2$ number [cf. Eq. (2.9)], is not confined to the mirror plane. For any integration path that interlinks with the nodal line, $\mathcal{P} = \pm \pi$ signals the stability of the Dirac ring.

In closing we note that, while the low-energy theory (3.1) accurately captures the topological stability of the nodal ring of a given semi-metal, it does not necessarily correctly reproduce the location of the drumhead surface state. That is, in order to determine whether the drumhead surface state is located inside or outside the projected Dirac ring, it is necessary to compute the Berry phase of all the occupied states. This information is not contained in the low-energy model (3.1), cf. Appendix C.

B. Symmetry-breaking perturbations

In analogy to the discussion of Sec. II C, we now study how different symmetry breaking perturbations transform the Dirac ring (3.1) into Dirac points or Weyl rings.

1. Reflection and time-reversal symmetry breaking

The Dirac line node of $H_{\text{eff}}$ can be deformed into two Dirac points by the perturbation

$$d \sin(\theta_\parallel - \theta_0) k_\parallel \tau_x,$$

which breaks reflection and time-reversal symmetry, but respects inversion symmetry. Here, $\theta_\parallel = \tan^{-1}(k_y/k_z)$ and $k_\parallel = \sqrt{k_y^2 + k_z^2}$ denote polar angle and absolute value of the in-plane momentum $k_\parallel$, respectively. The term (3.2) gaps the Dirac ring except at $k = \pm k_0(\cos \theta_0, \sin \theta_0, 0)$. These two gap closing points are Dirac nodes with opposite chiralities, which are protected by the spin Chern number (2.14). Due to the bulk-boundary correspondence an arc state appears at the surface, connecting the projected Dirac points in the surface Brillouin zone. This is illustrated in Fig. 4(b), where we set $\theta_0 = -\pi/4$ and $d = 0.9$ eVÅ, which mimics the effects of perturbation (2.13) for the tight-binding Hamiltonian (2.2).

From the arc surface state of the above Dirac semimetal one can infer the existence of the drumhead surface state of $H_{\text{eff}}$, since the two transform into each other by letting $d$ tend to zero in Eq. (3.2). Moreover, the one-dimensional set of Dirac nodes, induced by Eq. (3.2) and parametrized by $\theta_0$, can be interpreted as the Dirac ring of $H_{\text{eff}}$. That is, as we let $\theta_0$ in Eq. (3.2) run from 0 to $\pi$ a nodal ring is created. For each fixed $\theta_0$ there is an arc surface state connecting the two points $k_\parallel = \pm k_0(\cos \theta_0, \sin \theta_0)$ in the surface Brillouin zone. Hence, a drumhead surface state is generated when $\theta_0$ is varied from 0 to $\pi$. From this argument one infers that drumhead states also appear at surfaces for which the Berry phase (2.9) is not quantized (cf. Sec. II C), since the appearance of arc states does not depend on any crystal symmetries.

2. Spin-rotation symmetry breaking

In the absence of SU(2) spin-rotation symmetry, the Dirac ring of $H_{\text{eff}}$ is topologically unstable. To discuss this, we consider as in Sec. II C 2 a spinful version of Hamiltonian (3.1)

$$H_{\text{eff}}(k) = H_{\text{eff}}(k) \otimes \sigma_0 + H_{\text{eff}}^s(k),$$

where the Pauli matrices $\sigma_\alpha$ describe the spin degree of freedom and $H_{\text{eff}}^s$ denotes a spin-rotation symmetry breaking term. $H_{\text{eff}}$ is invariant under the same symmetries as the spinful tight-binding Hamiltonian (2.15). That is, it satisfies time-reversal, reflection, and inversion symmetry with the operators $T = \tau_0 \otimes \sigma_y K$, $R = \tau_z \otimes \sigma_x$, and $I = \tau_\alpha \otimes \sigma_0$, respectively. We find that, the Dirac nodal lines of $H_{\text{eff}}$ can be gapped out by the spin-rotation symmetry breaking mass terms $\tau_\alpha \otimes \sigma_x$ and $\tau_\alpha \otimes \sigma_y$, which preserve reflection symmetry $R$ as well as $IT$ symmetry. These perturbations turn Hamiltonian (3.3) into a trivial insulator. However, there exist also other spin-rotation symmetry breaking terms that deform the Dirac ring into two Weyl rings. These perturbation terms break either time-reversal symmetry or inversion symmetry.

a. Time-reversal breaking perturbation First, we add a spin-rotation and time-reversal breaking term to
the Hamiltonian $\hat{H}_\text{eff}$, which takes the form of a staggered Zeeman field

$$\hat{H}_\text{eff}^{zh}(\mathbf{k}) = \nu h_\text{eff}^z \tau_z \otimes \sigma_z.$$  \hfill (3.4)

This perturbation respects reflection and inversion symmetry. It splits the Dirac ring into two Weyl rings that are located within the mirror plane $k_z = 0$ at $k_\parallel = \sqrt{k_0^2 \pm h_\text{eff}^z}$. The stability of these Weyl nodal lines is guaranteed by the mirror invariant \([2.7]\), which evaluates to

$$n_{\text{occ}}^{+,0}(k_\parallel) = \begin{cases} 
1, & k_\parallel < \sqrt{k_0^2 - h_\text{eff}^z} \\
0, & \sqrt{k_0^2 - h_\text{eff}^z} < k_\parallel < \sqrt{k_0^2 + h_\text{eff}^z} \\
1, & \sqrt{k_0^2 + h_\text{eff}^z} < k_\parallel 
\end{cases}. \hfill (3.5)$$

In Fig. 6(d) we plot the surface spectrum of $H_{\text{eff}}$ in the presence of the staggered Zeeman term with $\nu h_\text{eff}^z = 0.07$ eV. There appear two drumhead surface states which are bounded by the two projected Weyl rings.

b. Inversion breaking perturbation

Alternatively, the Dirac ring can be split into Weyl rings by an inversion breaking perturbation. To show this, we consider

$$\hat{H}_\text{eff}^{zh}(\mathbf{k}) = \delta(x_3 + \sqrt{3} k_y) \tau_z \otimes \sigma_z,$$  \hfill (3.6)

which respects reflection and time-reversal symmetry. In the presence of this term Hamiltonian \([3.3]\) exhibits two Weyl rings within the mirror plane $k_z = 0$ with in-plane momenta given by the equation $(k_x \pm \delta/2)^2 + (k_y \pm \sqrt{3}/2)^2 = k_0^2 + \delta^2$. These two Weyl rings intersect on the $(3, -1, 0)$ axis, where the gap term \((3.6)\) vanishes [cf. Fig. 6(c)]. We find again that these Weyl rings are protected by the mirror number \([2.7]\), with

$$n_{\text{occ}}^{+,0}(k_\parallel) = \begin{cases} 
1, & (k_x \pm \frac{\delta}{2})^2 + (k_y \pm \frac{\sqrt{3}}{2})^2 > k_0^2 + \delta^2 \& (k_x \pm \frac{\delta}{2})^2 + (k_y \pm \frac{\sqrt{3}}{2})^2 < k_0^2 + \delta^2 \\
0, & \text{otherwise} 
\end{cases}. \hfill (3.7)$$

Fig. 6(d) shows the surface spectrum of $H_{\text{eff}}$ perturbed by Eq. \((3.6)\). As for the tight-binding model with the inversion-breaking term \((2.17)\), there appear two drumhead surface states. We note that PbTaSe$_2$ \([52, 53]\) and TlTaSe$_2$ \([54]\) are examples of inversion breaking semimetals with Weyl nodal lines. The low-energy physics of these materials can be described by the effective theory \([3.3]\) perturbed by a term of the form \((3.6)\).

IV. SUMMARY AND DISCUSSION

In this paper we have studied the topological stability of Dirac and Weyl line nodes of three-dimensional semimetals in the presence of reflection symmetry, time-reversal symmetry, inversion symmetry, and SU(2) spin-rotation symmetry. We have shown that when spin-rotation symmetry is preserved, the Dirac line is protected by either reflection symmetry or the product of inversion with time-reversal symmetry $IT$. In the former case, the nodal lines are classified by an $M\mathbb{Z}$ invariant \([18]\), which takes the form of a mirror number, see Eq. \((2.7)\). In the latter case the stability of the Dirac line is guaranteed by a quantized nonzero Berry phase, which leads to a $\mathbb{Z}_2$ classification, see Eq. \((2.9)\). As a representative example of a line node semimetal, we have considered Ca$_3$P$_2$ \([55]\), which exhibits a topologically stable Dirac ring at the Fermi energy. By means of a tight-binding model derived from ab initio DFT calculations, we have computed the mirror number and the quantized Berry phase for this material (Fig. 5) and shown that the Dirac band crossing is protected by reflection or $IT$ symmetry. The band topology of this Dirac line semimetal was also discussed in terms of a low-energy effective theory, see Eq. \((3.1)\).

Even though the mirror invariant \((2.7)\) does not directly give rise to topological surface states, Dirac line semimetals generically exhibit drumhead surface states which are due to a quantized Berry phase. By deriving a relation between the mirror number \((2.7)\) and the Berry phase \((2.9)\), we have established a direct connection between the existence of drumhead surface states and the topological stability of Dirac nodal lines in the bulk, see Eq. \((2.11)\). Using the ab initio derived tight-binding model, we have computed the surface spectrum of Ca$_3$P$_2$, showing that its drumhead surface state is weakly dispersing with an effective mass $m^* \approx 4m_e$ [Fig. 3(b) and 3(d)].

In Ca$_3$P$_2$ spin-rotation symmetry is conserved to a very good approximation, since spin orbit coupling for the light elements Ca and P is very small. However, there are nodal line semimetals with heavy atoms, such as PbTaSe$_2$ and TlTaSe$_2$, in which spin-rotation symmetry is broken, due to the non-negligible spin-orbit interactions. In these systems the four-fold degenerate Dirac rings are unstable. Two-fold degenerate Weyl rings, on the other hand, can be protected against gap opening by reflection symmetry, provided either time-reversal or reflection symmetry is broken. We have shown that the stability of these Weyl rings is guaranteed by the mirror invariant \((2.7)\). Similar to the Dirac nodal line semimetals, Weyl ring semimetals support drumhead surface states (Figs. 3 and 6). The region in the surface Brillouin zone where these drumhead states appear are bounded by the projected Weyl rings.

Determining the stability of the drumhead surface states against disorder and interactions needs a careful analysis of different types of scattering and interaction processes, involving both states near the bulk line nodes and surface states. The drumhead surface state of Ca$_3$P$_2$ has a relatively weak dispersion (Fig. 3), which gives rise to a large density of states thereby enhancing interaction effects. Therefore, even small interactions may lead to unusual symmetry-broken states at the surface, such as surface superconductivity \([47, 48]\) or surface magnetism \([49]\). Disorder scattering, on the other hand, breaks the crystalline symmetries that protect the surface states. Moreover, it mixes bulk and surface states, since there is no full gap in the bulk energy spectrum. For the case of crystalline topological insulators it has been
shown that the surface states are robust against disorder when the disorder respects the crystal symmetries on average [81]. In appendix [D] we study this question in terms of a one-dimensional reflection symmetric toy model with a quantized Berry phase. In order to infer how impurity scattering affects the topological properties, we determine the charge that is accumulated at the two ends of this one-dimensional system [79]. We find that even in the presence of disorder that respects reflection symmetry on average, the end charges remain to a good approximation quantized to ±e/2. Due to Eq. (2.10), which relates the end charges to the Berry phase, this indicates that the bulk topological properties remain unaffected by this type of disorder. This finding suggests that the drumhead surface states of nodal line semimetals are not destroyed by impurities, as long as the disorder respects reflection symmetry on average and its strength is smaller than the energy gap between the conduction and valence bands.

In conclusion, Dirac ring and Weyl ring semimetals are a new type of topological material which is characterized by a non-zero mirror invariant and a quantized Berry phase. The nontrivial band topology of these systems manifests itself at the surface in terms of protected Berry phase, this indicates that the bulk topological properties remain unaffected by this type of disorder. This finding suggests that the drumhead surface states of nodal line semimetals are not destroyed by impurities, as long as the disorder respects reflection symmetry on average and its strength is smaller than the energy gap between the conduction and valence bands.

Note added. — Upon completion of this work, we became aware of a study by Yamakage et al. [81], which discusses the topology of line node semi-metals in terms of a one-dimensional reflection symmetric toy model with a quantized Berry phase. Another promising direction for future work is the study of novel topological response phenomena in these systems.

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Appendix A: Details of the tight-binding model

In this Appendix we give a detailed description of the tight-binding Hamiltonian of Sec. II.

Table I. Position vectors $\mathbf{s}_\alpha$ of each orbital. All vectors are given in the crystal coordinate system, which is indicated by the red/green arrows in Fig. 7. The lattice vectors are $\mathbf{a} = [7.150, -4.218, 0.000]$, $\mathbf{b} = [0.000, 8.256, 0.000]$, and $\mathbf{c} = [0.000, 0.000, 6.836]$ in the unit of Å.

| $\alpha$ | Orbital | $\mathbf{s}_\alpha$ |
|----------|---------|---------------------|
| 1        | Ca1     | (0.2029, 0.0, 0.25) |
| 2        | Ca2     | (-0.2029, -0.2029, 0.25) |
| 3        | Ca3     | (0.0, 0.2029, 0.25) |
| 4        | Ca4     | (-0.2029, 0.0, -0.25) |
| 5        | Ca5     | (0.2029, 0.2029, -0.25) |
| 6        | Ca6     | (0.0, -0.2029, -0.25) |
| 7        | P1      | (0.6215, 0.0, 0.25) |
| 8        | P2      | (-0.6215, -0.6215, 0.25) |
| 9        | P3      | (0.0, 0.6215, 0.25) |
| 10       | P4      | (-0.6215, 0.0, -0.25) |
| 11       | P5      | (0.6215, 0.6215, -0.25) |
| 12       | P6      | (0.0, -0.6215, -0.25) |

1. Matrix elements

The matrix elements given below closely follows Eq. (2.2). The position vectors $\mathbf{s}_\alpha$ of each orbital are listed in Table I. We illustrate each hopping term in Fig. 7.

a. Ca-Ca matrix elements

In the $H_{Ca}$ block, we can further divide orbitals in each atomic species into those belong to the lower layer and the upper layer,

$$H_{Ca} = \begin{pmatrix} H_{Ca}^{ll} & H_{Ca}^{lu} \\ H_{Ca}^{ul} & H_{Ca}^{uu} \end{pmatrix} ,$$

where sub-blocks $H_{Ca}^{ll}$, $H_{Ca}^{uu}$, and $H_{Ca}^{lu}$ are $3 \times 3$ matrices. The Hamiltonian matrix $H_{Ca}^{ll}$ and $H_{Ca}^{uu}$ have 3 independent intra-layer hopping terms, the nearest-neighbor, second nearest-neighbor, and third nearest neighbor hoppings, $td_2$, $td_4$, and $td_5$ as shown in Fig. 7.

$$H_{Ca}^{ll} = \begin{pmatrix} h_{11}^{c,ll} & h_{12}^{c,ll} & h_{13}^{c,ll} \\ h_{21}^{c,ll} & h_{22}^{c,ll} & h_{23}^{c,ll} \\ h_{31}^{c,ll} & h_{32}^{c,ll} & h_{33}^{c,ll} \end{pmatrix} ,$$

where

$$h_{12}^{c,ll} = e^{ik_{12}^s} (td_2 + td_4 c_{12}^d + td_5 c_{12}^5) \quad (A3)$$
$$h_{13}^{c,ll} = e^{ik_{13}^s} (td_2 + td_4 c_{13}^d + td_5 c_{13}^5) \quad (A4)$$
$$h_{23}^{c,ll} = e^{ik_{23}^s} (td_2 + td_4 c_{23}^d + td_5 c_{23}^5) \quad (A5)$$
and $h_{11}^{c,ll} = h_{22}^{c,ll} = h_{33}^{c,ll} = \mu_d$. We define phase factors
where $\epsilon_{\alpha,\beta}^{i}$ for hopping integral $td_{i}$ with matrix indices $\alpha$ and $\beta$

\begin{align}
\epsilon_{12}^{4} &= e^{i k \cdot R} + e^{i k \cdot R_{10}^{10}} \\
\epsilon_{13}^{4} &= e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{10}^{10}} \\
\epsilon_{23}^{4} &= e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{10}^{10}} \\
\epsilon_{12}^{5} &= e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{10}^{10}} \\
\epsilon_{13}^{5} &= e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{10}^{10}} \\
\epsilon_{23}^{5} &= e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{10}^{10}} \\
\end{align}

where $R_{ijkl}$ is the lattice vector connecting the unit cell in the $(i, j, k)$ direction and $s_{ij} = s_{m} - s_{i}$, $H_{Ca}^{iu}$ is defined similarly.

$H_{Ca}^{iu}$ contains 2 independent inter-plane hopping integrals $td_{1}$ and $td_{3}$,

$$H_{Ca}^{iu} = c_{0} \begin{pmatrix}
    td_{1} e^{i k \cdot s_{1,4}} & td_{1} e^{i k \cdot s_{1,5}} & td_{1} e^{i k \cdot s_{1,6}} \\
    td_{2} e^{i k \cdot s_{2,4}} & td_{2} e^{i k \cdot s_{2,5}} & td_{2} e^{i k \cdot s_{2,6}} \\
    td_{3} e^{i k \cdot s_{3,4}} & td_{3} e^{i k \cdot s_{3,5}} & td_{3} e^{i k \cdot s_{3,6}}
\end{pmatrix}$$

where $c_{0} = (1 + e^{i k \cdot R_{101}})$.

(b) $P-P$ matrix elements

We apply similar division of layer indices for $H_{P}$ matrix.

$$H_{P} = \begin{pmatrix}
    H_{P}^{ll} & H_{P}^{lu} \\
    H_{P}^{ul} & H_{P}^{uu}
\end{pmatrix}.$$  

The Hamiltonian matrix $H_{P}^{ll}$ and $H_{P}^{uu}$ have 2 independent hopping integrals $tp_{1}$ and $tp_{5}$ coupling orbitals in the same layer.

$$H_{P}^{ll} = \begin{pmatrix}
    h_{12}^{p,l} & h_{12}^{p,l} & h_{12}^{p,l} \\
    h_{21}^{p,l} & h_{21}^{p,l} & h_{21}^{p,l} \\
    h_{31}^{p,l} & h_{31}^{p,l} & h_{31}^{p,l}
\end{pmatrix},$$

where

$$h_{12}^{p,l} = e^{i k \cdot s_{1,10}} (tp_{5} + tp_{1} a_{12}^{1})$$

$$h_{12}^{p,l} = e^{i k \cdot s_{1,10}} (tp_{5} + tp_{1} a_{13}^{1})$$

$$h_{12}^{p,l} = e^{i k \cdot s_{1,10}} (tp_{5} + tp_{1} a_{23}^{1})$$

and $h_{11}^{p,l} = h_{22}^{p,l} = h_{33}^{p,l} = \mu \rho \alpha_{\alpha,\beta}$ are phase factors from hopping $tp_{i}$ with matrix index $\alpha$ and $\beta$,

$$a_{12} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

$$a_{13} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

$$a_{23} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

$H_{P}^{ul}$ can be defined similarly.

$H_{P}^{ul}$ contains 3 independent inter-plane hopping integrals $tp_{2}$, $tp_{3}$, and $tp_{4}$.

$$H_{P}^{ul} = \begin{pmatrix}
    h_{11}^{p,u} & h_{12}^{p,u} & h_{13}^{p,u} \\
    h_{21}^{p,u} & h_{22}^{p,u} & h_{23}^{p,u} \\
    h_{31}^{p,u} & h_{32}^{p,u} & h_{33}^{p,u}
\end{pmatrix},$$

where

$$h_{11}^{p,u} = tp_{2} e^{i k \cdot s_{1,10}} (e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}})$$

$$h_{22}^{p,u} = tp_{2} e^{i k \cdot s_{1,10}} (e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}})$$

$$h_{33}^{p,u} = tp_{2} e^{i k \cdot s_{1,10}} (e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}})$$

and

$$h_{12}^{p,u} = e^{i k \cdot s_{1,10}} (tp_{3} c_{0} + tp_{4} a_{12}^{4})$$

$$h_{13}^{p,u} = e^{i k \cdot s_{1,10}} (tp_{3} c_{0} + tp_{4} a_{13}^{4})$$

$$h_{23}^{p,u} = e^{i k \cdot s_{1,10}} (tp_{3} c_{0} + tp_{4} a_{23}^{4})$$

$$h_{32}^{p,u} = e^{i k \cdot s_{1,10}} (tp_{3} c_{0} + tp_{4} a_{32}^{4})$$

The corresponding phase factors are,

$$c_{0} = 1 + e^{i k \cdot R_{101}}$$

$$a_{12}^{4} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

$$a_{13}^{4} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

$$a_{23}^{4} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

$$a_{32}^{4} = e^{i k \cdot R_{10}^{10}} + e^{i k \cdot R_{11}^{11}}$$

(c) $Ca-P$ matrix elements

Finally, the inter-orbital hopping matrix $V$ describes the hybridization between Ca and P orbitals. We again divide $V$ into four $3 \times 3$ matrices according to their layer indices,

$$V = \begin{pmatrix}
    V_{ll} & V_{lu} \\
    V_{ul} & V_{uu}
\end{pmatrix},$$
The phase factors are, which can be written down with the hopping integrals \( tdp_4 \),

\[
V^{ll} = b_1 tdp_4 \begin{pmatrix}
  e^{i \mathbf{k} \cdot s_{1,7}} & 0 & 0 \\
  0 & e^{i \mathbf{k} \cdot s_{2,8}} & 0 \\
  0 & 0 & e^{i \mathbf{k} \cdot s_{3,9}}
\end{pmatrix}
\]

(A39)

and

\[
V^{uu} = -b_1 tdp_4 \begin{pmatrix}
  e^{i \mathbf{k} \cdot s_{4,10}} & 0 & 0 \\
  0 & e^{i \mathbf{k} \cdot s_{5,11}} & 0 \\
  0 & 0 & e^{i \mathbf{k} \cdot s_{6,12}}
\end{pmatrix}
\]

(A40)

where the phase factor \( b_1 = (e^{i \mathbf{k} \cdot R_{001}} - e^{i \mathbf{k} \cdot R_{001}}) \). We note that the minus sign in \( V^{uu} \) is due to the opposite orientation of \( p_x \) orbitals in the different layer. Also due to the opposite inversion symmetry eigenvalue of the \( p_x \) and the \( d_{z^2} \) orbital, hopping integrals vanish if both of them lie in the same plane. Hence, only hopping integrals from different unit cell contribute to diagonal elements.

Inter-layer coupling \( tdp_1, tdp_2 \), and \( tdp_3 \) contributes to \( V^{lu} \) and \( V^{ul} \) matrices,

\[
V^{lu} = \begin{pmatrix}
  V^{lu}_{11} & V^{lu}_{12} & V^{lu}_{13} \\
  V^{lu}_{21} & V^{lu}_{22} & V^{lu}_{23} \\
  V^{lu}_{31} & V^{lu}_{32} & V^{lu}_{33}
\end{pmatrix}
\]

(A41)

where

\[
V^{lu}_{11} = -tdp_1 e^{i \mathbf{k} \cdot s_{110}} (e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}}) \\
V^{lu}_{22} = -tdp_1 e^{i \mathbf{k} \cdot s_{211}} (e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}}) \\
V^{lu}_{33} = -tdp_1 e^{i \mathbf{k} \cdot s_{311}} (e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}})
\]

(A42)

(A43)

(A44)

and off-diagonal elements

\[
V^{lu}_{12} = e^{i \mathbf{k} \cdot s_{110}} (tdp_2 b_2 + tdp_3 b_3^{3_{12}}) \\
V^{lu}_{13} = e^{i \mathbf{k} \cdot s_{110}} (tdp_2 b_2 + tdp_3 b_3^{3_{13}}) \\
V^{lu}_{21} = e^{i \mathbf{k} \cdot s_{210}} (tdp_2 b_2 + tdp_3 b_3^{3_{21}}) \\
V^{lu}_{23} = e^{i \mathbf{k} \cdot s_{210}} (tdp_2 b_2 + tdp_3 b_3^{3_{23}}) \\
V^{lu}_{31} = e^{i \mathbf{k} \cdot s_{310}} (tdp_2 b_2 + tdp_3 b_3^{3_{31}}) \\
V^{lu}_{32} = e^{i \mathbf{k} \cdot s_{310}} (tdp_2 b_2 + tdp_3 b_3^{3_{32}})
\]

(A45)

(A46)

(A47)

(A48)

(A49)

(A50)

The phase factors are,

\[
b_2 = -(e^{i \mathbf{k} \cdot R_{001}} - e^{i \mathbf{k} \cdot R_{001}}) \\
b_{12} = -(e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}}) \\
b_{13} = -(e^{i \mathbf{k} \cdot R_{111}} - e^{i \mathbf{k} \cdot R_{111}}) \\
b_{21} = -(e^{i \mathbf{k} \cdot R_{001}} - e^{i \mathbf{k} \cdot R_{001}}) \\
b_{23} = -(e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}}) \\
b_{31} = -(e^{i \mathbf{k} \cdot R_{111}} - e^{i \mathbf{k} \cdot R_{111}}) \\
b_{32} = -(e^{i \mathbf{k} \cdot R_{111}} - e^{i \mathbf{k} \cdot R_{111}})
\]

(A51)

(A52)

(A53)

(A54)

(A55)

(A56)

(A57)

where \( b_{\alpha \beta} \) belongs to hopping \( tdp_i \) between index \( \alpha \) and \( \beta \).

Similarly, we have

\[
V^{ul} = \begin{pmatrix}
  V^{ul}_{11} & V^{ul}_{12} & V^{ul}_{13} \\
  V^{ul}_{21} & V^{ul}_{22} & V^{ul}_{23} \\
  V^{ul}_{31} & V^{ul}_{32} & V^{ul}_{33}
\end{pmatrix}
\]

(A58)

where

\[
V^{ul}_{11} = -tdp_1 e^{i \mathbf{k} \cdot s_{410}} (e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}}) \\
V^{ul}_{22} = -tdp_1 e^{i \mathbf{k} \cdot s_{410}} (e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}}) \\
V^{ul}_{33} = -tdp_1 e^{i \mathbf{k} \cdot s_{410}} (e^{i \mathbf{k} \cdot R_{011}} - e^{i \mathbf{k} \cdot R_{011}})
\]

(A59)

(A60)

(A61)

and off-diagonal elements

\[
V^{ul}_{12} = e^{i \mathbf{k} \cdot s_{410}} (tdp_2 b_2 + tdp_3 b_3^{3_{12}}) \\
V^{ul}_{13} = e^{i \mathbf{k} \cdot s_{410}} (tdp_2 b_2 + tdp_3 b_3^{3_{13}}) \\
V^{ul}_{21} = e^{i \mathbf{k} \cdot s_{410}} (tdp_2 b_2 + tdp_3 b_3^{3_{21}}) \\
V^{ul}_{23} = e^{i \mathbf{k} \cdot s_{410}} (tdp_2 b_2 + tdp_3 b_3^{3_{23}}) \\
V^{ul}_{31} = e^{i \mathbf{k} \cdot s_{410}} (tdp_2 b_2 + tdp_3 b_3^{3_{31}}) \\
V^{ul}_{32} = e^{i \mathbf{k} \cdot s_{410}} (tdp_2 b_2 + tdp_3 b_3^{3_{32}})
\]

(A62)

(A63)

(A64)

(A65)

(A66)

(A67)

where * denotes the complex conjugate.

### 2. Tight-binding parameters

We list parameters of the tight-binding model in the unit of eV below. The hopping integrals between two Ca orbitals are \( t_{d1} = -0.2031 \), \( t_{d2} = -0.6388 \), \( t_{d3} = -0.0786 \), \( t_{d4} = -0.216 \), and \( t_{d5} = 0.0516 \). Those between two P orbitals are \( t_{fp} = -0.011 \), \( t_{fp} = -0.077 \), \( t_{fp} = -0.0479 \), \( t_{fp} = -0.1067 \), and \( t_{fp} = 0.0548 \). Finally, the hopping amplitudes between Ca and P orbitals are \( t_{dp} = 0.1415 \), \( t_{dp} = 0.0379 \), \( t_{dp} = 0.0443 \) and \( t_{dp} = 0.0376 \). The chemical potentials are \( \mu_d = 2.6808 \) and \( \mu_p = -1.2186 \) for Ca and P respectively.

### Appendix B: Topological number and Berry phase

To show that the Berry phase in the \( k_z \) direction is quantized and is related to \( n_{\text{occ}}^+ \) in Eq. (2.11), we recall some basic facts of inversion symmetry. We assume no degeneracies so the inversion symmetry acts the wavefunctions \( |u_{k,j} \rangle \) in the unique expression \( (k \equiv k_z) \)

\[
|u_{-k,j} \rangle = -i e^{-i \alpha \cdot k} R_k |u_{k,j} \rangle
\]

(B1)

The reflection operator obeys \( R_{-k} R_k = \pm 1 \) for spinless/spin-1/2 systems respectively. For spin-1/2, we redefine \( R_k \to -i R_k \) so that \( R_{-k} R_k = 1 \). Also, \( R_k^2 = 1 \). Let us rewrite the Berry phase

\[
\mathcal{P} = -i \left( \int_0^{\pi} + \int_{-\pi}^0 \right) \sum_{j < E_F} \langle u_{k,j} | \partial_k | u_{k,j} \rangle dk
\]

(B2)
The reflection symmetry operator has a generic block-diagonalized form:

\[ R_k = U_{1,j_1} e^{i\alpha_{1,k}} \oplus U_{2,j_2} e^{i\alpha_{2,k}} \oplus \ldots \oplus U_{N,j_N} e^{i\alpha_{N,k}} \]  

where \( U_{i,j_i} \) is a unitary matrix and we use the lattice constant \( a = 1 \).

\[ R_k^\dagger \partial_k R_k = i n_1 \delta_{i1,j_1} \oplus i n_2 \delta_{i2,j_2} \oplus \ldots \oplus i n_N \delta_{IN,j_N}. \]  

Hence, \( \partial R \) is just \( m\pi \), where \( m \) is an integer

\[
i \int_0^\pi \sum_{E_j < E_F} \langle u_{k,j} | R_k^\dagger \partial_k R_k | u_{k,j} \rangle dk = - \sum_{l=1}^{n_l} m_l \pi, \tag{B5} \]

where \( m_l \) is the number of the occupied states in \( U_{i,j_i} \) block. Consider left hand side of Eq. (2.11)

\[
n_{\text{occ}}^{+,\pi} - n_{\text{occ}}^{+,0} = \frac{1}{2} \sum_{E_j < 0} \left( \langle u_{\pi,j} | R_k | u_{\pi,j} \rangle - \langle u_{0,j} | R_0 | u_{0,j} \rangle \right) \]

\[
= \frac{1}{2} \sum_{E_j < 0} (e^{i\alpha_{\pi,j}} - e^{-i\alpha_{\pi,j}}), \tag{B6} \]

Since \( R_k^\dagger = R_k \), where \( k_0 = -k_0 \), such as 0, \( \pi \) so \( e^{i\alpha_{j_0}} = \pm 1 \) and then

\[
n_{\text{occ}}^{+,\pi} - n_{\text{occ}}^{+,0} = \frac{1}{\pi} \sum_{E_j < E_F} (\alpha_{\pi,j} - \alpha_{0,j}) \, (\text{mod} \, 2). \tag{B7} \]

Thus, \((-1)^{n_{\text{occ}}^{+,\pi} - n_{\text{occ}}^{+,0}} = e^{i \sum_{E_j < E_F} (\alpha_{\pi,j} - \alpha_{0,j})}. \) By using Eq. (B2), (B7), we obtain the relation in Eq. (2.11) between the topological invariants and the Berry phase \( \mathcal{P} \) is either 0 or \( \pi \) (mod 2\pi) since \( 2\pi \) phase can be cancelled by a large \( U(1) \) gauge transformation.

****

Similarly, \( IT \) symmetry, the composite symmetry of time-reversal and inversion, also quantizes the Berry phase when \( dk \) is integrated along any closed loop. Since time-reversal and inversion operators both flip \( k \), the composite symmetry operators keep the same \( k \). The integration path can be arbitrarily chose to preserve \( IT \) symmetry. Unlike the Berry phase under reflection symmetry, the integration path should be strictly in the \( k_z \) direction to preserve reflection symmetry.

\( IT \) symmetry operator is the combination of a unitary matrix and complex conjugation \( T \mathcal{L} = U \mathcal{K} \); the unitary matrix \( U \) might be \( k \)-dependent. To simplify the problem, we assume \( U \) is \( k \)-independent, which is the case of \( \text{Ca}_3\text{P}_2 \) tight-binding model. The relation of wavefunctions under \( IT \) symmetry is given by

\[ |u_{k,j}\rangle = e^{i\beta_k} |u_{k,j}\rangle \tag{B8} \]

We note that \( |u_{k,j}\rangle \) and \( |u_{k,l}\rangle \) in the same energy level might be orthogonal or identical. Let us show the Berry phase is quantized

\[
\mathcal{P} = -i \int_{E_j < E_F} \sum_{E_j < E_F} \langle u_{k,j} | \partial_k | u_{k,j} \rangle dk 
= -i \int_{E_j < E_F} \sum_{E_j < E_F} \langle u_{k,j}^* | U^\dagger e^{-i\beta_k} \partial_k e^{i\beta_k} U | u_{k,j}^* \rangle dk 
= \sum_{E_j < E_F} (\beta^j_+ - \beta^j_-) - i \int_{E_j < E_F} \sum_{E_j < E_F} \langle u_{k,j}^* | \partial_k | u_{k,j}^* \rangle dk, \tag{B9} \]

where \( \beta^j_\pm \) represent the phases at the beginning and end of the integration path respectively. The first summation is \( 2\pi \) since the \( j \)-th and the \( l \)-th states share the same energy and each state in the second summation should be orthogonal, we safely change the index \( j \) to \( j \) in the summation. We use the identity

\[
\langle u_{k,j}^* | \partial_k | u_{k,j}^* \rangle = \langle \partial_k u_{k,j} | u_{k,j}^* \rangle = -\langle u_{k,j} | \partial_k | u_{k,j} \rangle \tag{B10} \]

The Berry phase is quantized

\[
\mathcal{P} = \sum_{E_j < E_F} (\beta^j_+ - \beta^j_-) = n\pi \tag{B11} \]

Appendix C: Toy model of topological nodal lines

The tight-binding model of \( \text{Ca}_3\text{P}_2 \) provides the way to investigate topological nodal lines in a realistic model. However, to capture the physical features of the nodal lines only the low energy theory is needed. We extend the low energy theory to a simple lattice model in order to provide an economic way to investigate topological nodal lines. Although the space group of \( \text{Ca}_3\text{P}_2 \) is \( P6_3/mmc \), we consider square lattice and extend and transfer the low energy equation (3.1) with spins to the lattice form

\[
H_{\text{spinful}}^\text{lattice}(k) = \frac{\nu'_{0}}{a^2} g(k_\parallel) \tau_z \sigma_0 + \frac{\nu_0}{c} \sin ck_z \tau_y \sigma_0 
+ (\frac{\nu'_0}{a^2} g(k_\parallel)) + V_0 \tau_0 \sigma_0 + H_{\cos k_z} \tag{C1} \]

where \( g(k_\parallel) = 1 + \cos ak_0 - \cos ak_x - \cos ak_y \), the lattice constants \( a = 8.26 \) Aand \( c = 6.84 \) A, \( \nu'_0 = \frac{2nu_0ak_0}{\sin ak_0} \), and \( \nu'_0 = \frac{2nu_0ak_0}{\sin ak_0} \). Furthermore, we define

\[
H_{\cos k_z} = (1 - \cos ck_z)(Z_\tau \tau_z \sigma_0 + Z_0 \tau_0 \sigma_0) \tag{C2} \]

in the simplest form so that the Berry phase inside the nodal ring is nonzero when the spin degree of freedom is neglected. By fitting the energy spectrum from the DFT calculation as \( k_z = 0, \pi \), we have \( Z_\tau = 0.287 \) eV and \( Z_0 = -0.156 \) eV.
APPENDIX D: Quantized end charge under disorders

To understand the robustness of the topology under disorder we consider the toy model of a 1d inversion-symmetric topological insulator. We note that in a 1d system inversion symmetry is equivalent to reflection symmetry; reflection symmetric nodal lines with fixed $k_x,k_y$ is equivalent to the 1d inversion symmetric topological insulator; the Berry phase, which is the integration along the 1d BZ, is quantized. The toy model in momentum space can be simply written as

$$H(p) = (\mu + \cos p)\sigma_x + \sin p \sigma_y + \delta \cos p \mathbf{1}, \quad (D1)$$

which preserves inversion symmetry by satisfying Eq. (2.6) with inversion symmetry operator $I = \sigma_x$. Broken chiral symmetry caused by $\delta \cos p \mathbf{1}$ destroys the definition of winding number so the Berry phase is the only valid topological invariant. Furthermore, by Eq. (2.4) time-reversal symmetry is preserved with time-reversal operator $T = K$. $IT$ symmetry also guarantees the quantized Berry phase. By choosing $\mu = 0.5$ and $\delta = 0.1$, the Berry phase $\mathcal{P} = \pi$ leads to the presence of charge $\pm e/2$ at each end, which is one of the topological features of this inversion symmetric insulator. The sign of the charge depends on the occupation of the end mode. Hence, we can numerically compute the charge on one of the ends. If the charge is no longer $\pm e/2$ under disorder, the topology is destroyed by disorders.

We add inversion symmetry breaking disorder $r_j c_j^\dagger \sigma_x c_j$ to the Hamiltonian in real space

$$\hat{H} = \sum_j \left( \frac{i}{2} c_j^\dagger \sigma_x c_j + c_{j+1}^\dagger \sigma_x + \delta \mathbf{1} + i \sigma_y c_j + \text{h.c.} \right), \quad (D2)$$

where $r_j$ is a random number from $-\Delta + m$ to $\Delta + m$. When $m = 0$, the average $\langle r_j \rangle = 0$ indicates the average disorder preserves inversion symmetry. As shown in Eq. (8) (a) when $m = 0$, the charge on one end is $\pm e/2$ on average. When inversion symmetry is broken on average, the charge is no longer quantized and then the topological phase is destroyed. Fig. 8(b) the standard deviation of the disorder is proportional to the deviation of the end disorder. Thus, the quantized end charge survive when disorder on average is zero and the fluctuation is small enough.

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