Multi-band nodal links in triple-point materials

Patrick M. Lenggenhager,1,2,3, * Xiaoxiong Liu,3 Stepan S. Tsirkin,3 Titus Neupert,3 and Tomáš Bzdušek1,3

1 Condensed Matter Theory Group, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
2 Institute for Theoretical Physics, ETH Zurich, 8093 Zurich, Switzerland
3 Department of Physics, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

(Dated: August 10, 2020)

We study a class of topological materials which in their momentum-space band structure exhibit three-fold degeneracies known as triple points. Specifically, we investigate and classify triple points occurring along high-symmetry lines of $PT$-symmetric crystalline solids with negligible spin-orbit coupling. By employing the recently discovered non-Abelian band topology, we argue that a rotation-symmetry-breaking strain transforms a certain class of triple points into multi-band nodal links. Although multi-band nodal-line compositions were previously theoretically conceived, a practical condensed-matter platform for their manipulation and inspection has hitherto been missing. By reviewing the known triple-point materials in the considered symmetry class, and by performing first-principles calculations to predict new ones, we identify suitable candidates for the realization of multi-band nodal links. In particular, we find that Li$_3$Na$_2$N is an ideal compound to study this phenomenon, where the band nodes facilitate largely tunable density of states and optical conductivity with doping and strain, respectively. The multi-band linking is expected to equip the nodal rings with monopole charges, making such triple-point materials a versatile platform to probe the non-Abelian band topology.

Introduction.— The recent rapid developments in topological band theory of crystals [1–13] and engineered meta-materials [14–19] fuelled a fruitful research into topological band degeneracies. While two-fold degenerate Weyl [20–26] and four-fold degenerate Dirac [27–32] point nodes originally came into spotlight because of their relation to high-energy physics theories and chiral-anomaly-related phenomena [33–37], it has soon been realized that a much wider range of band nodes can be topologically stabilized in condensed-matter settings with crystalline symmetry [38–42]. Currently, nodal lines (NLs) [43–45] protected by quantized Zak-Berry phase [46–48] are arguably the most investigated type of band degeneracy, and were found to form intricate structures including chains, links and knots [49–52]. Furthermore, an intermediate step between Weyl and Dirac points is possible in the form of triple points (TPs) [53–59]. They are conventionally classified as type-A vs. B according to absence vs. presence of attached NL arcs [Fig. 2], and we call compounds exhibiting them in the band structure triple-point materials.

Curiously, the topological stability of both NLs and TPs is fully captured only if one partitions the energy bands via multiple energy gaps. On the one hand, NLs in spinless space-time-inversion ($PT$) symmetric systems exhibit Euler and Stiefel-Whitney monopole charges [60–63], which have been related to linking with NLs inside adjacent energy gaps [64, 65]. On the other hand, TPs formed by a crossing of a one-dimensional (1D) and a two-dimensional (2D) irreducible co-representation (ICR) along a rotation axis are end-points at which a NL is transferred between two adjacent energy gaps. Although TPs are often studied in the context of spin-orbit coupled (SOC) metals [53–56], here we inspect their realization in spinless systems with $PT$ symmetry [66–70], such as Bernal graphite [71]. Multi-band nodal structures in $PT$-symmetric spinless systems were recently characterized with non-Abelian quaternion invariants [72–76], which generalize the Zak-Berry-phase quantization. However, practical condensed-matter platforms to manipulate and probe the non-Abelian band topology have remained limited.

Here we report that multi-band nodal-line structures arise and could be observed in triple-point materials with applied strain. We reveal, using the non-Abelian quaternion charges, a previously overlooked relation between the NL and TP topology. In particular, we predict type-A TPs in spinless $PT$-symmetric models to evolve into multi-band nodal links [Fig. 1] under rotation-symmetry-breaking perturbations such as in-plane uniaxial strain. To identify suitable compounds to confirm our predictions, we develop a symmetry-based classification of TPs in spinless $PT$-symmetric systems. We review the known TP-materials belonging to this symmetry class and perform first-principles calculations to predict additional ones. We find that the recently reported triple-point metal Li$_3$Na$_2$N [68] produces an ideal multi-band nodal-link with a very sensitive dependence of the density of states and optical conductivity on doping and strain. A detailed discussion of the mathematical methods, the other material candidates, and linking-imposed monopole charges of the nodal rings appears in our companion manuscript [70]. Our results open a new avenue to investigate a wider range of phenomena related to non-Abelian band topology in crystalline matter.

Triple points and non-Abelian band topology.— TPs are symmetry-protected crossings of a 1D and a 2D ICR occurring along rotation-invariant lines in k-space [Fig. 1(a)] [53]. It is possible to recast the corresponding 2D ICR as a NL, in which case the TP marks a location where the NL is transferred from one energy gap (i.e. one pair of energy bands) to another one [Fig. 1(c)]. In this work we consider $PT$-symmetric systems with negligible SOC (i.e. spinless), such that $(PT)^2 = ± 1$ [77]. A mathematical theorem [74] then implies a basis in which the Bloch states are real (rather than complex) vectors. Under these circumstances, topological properties of multi-band nodal-line compositions are captured within the framework of non-Abelian band topology [72].

While the Zak-Berry phase $\varphi_{ZB}$ (quantized by $PT$ to 0 vs. $\pi$...
on closed paths) of a block of bands remains invariant provided that these bands are separated by an energy gap from other groups of bands, the non-Abelian invariant (called generalized quaternion charge by Ref. [72]) \( q \in \mathbb{Q}_N \) of an \( N \)-band system is susceptible to closing any of the \((N-1)\) energy gaps [labelled 1 to \((N-1)\) according to increasing energy] between consecutive bands. If \( \varphi_{2B}(\gamma) = \pi \) for some band \( j \) on path \( \gamma \), then the square \( q^2(\gamma) = -1 \in \mathbb{Q}_N \) is the unique non-trivial element that squares to identity \(+1\) in \( \mathbb{Q}_N \) [65]. For \( q(\gamma') = -1 \) all energy bands on \( \gamma' \) have a trivial Zak-Berry phase, nevertheless there is a topological obstruction corresponding to an overall \( 2\pi \) rotation of the \( N \)-frame (the eigenframe) spanned by the Bloch states [74].

Multi-band nodal links.— To understand the formation of multi-band nodal links from type-A TPs under strain, consider a loop \( \gamma_0 \) [green in Fig. 1(c)] that encircles the NL [blue in Fig. 1] extending to one side of a TP [yellow in Fig. 1]. To study the stability of the NL, one could compute the Zak-Berry phase \( \varphi_{2B}(\gamma_0) \) [Fig. 1(c)] assuming a gap between the two bands that meet at the NL. For a type-A TP it must hold that \( \varphi_{2B}(\gamma_0) = 0 \), because the loop can be slid to the other side of the TP, where it can be trivialized without closing the corresponding energy gap. However, from the perspective of the non-Abelian band invariant [72] the path \( \gamma_0 \) cannot be shrunk to a point on the other side of the TP due to the presence of the NL [red in Fig. 1] in the adjacent energy gap. This suggests a non-trivial value \( q(\gamma_0) \neq +1 \) characterizing the NL composition around the type-A TP.

The outlined characterization of the NLs is consistent with the 2D ICR being a double nodal line, i.e. one with a quadratic splitting of the two energy bands away from the high-symmetry line. In that case, the Zak-Berry phase on \( \gamma_0 \) would be trivial [78], but the quaternion charge would exhibit the non-trivial value \( q(\gamma_0) = -1 \) [72]. Crucially, the non-Abelian invariant remains well-defined even after the 2D ICR is split by a rotation-symmetry-breaking perturbation [Fig. 1(b)] when the TP is lost. While the Zak-Berry phase

\[
\varphi_{2B}(\gamma_0) = 0
\]

cannot be directly applied to predict the fate of the NL composition upon such a symmetry breaking, the value \( q(\gamma_0) = -1 \) implies that \( \gamma_0 \) must enclose a pair of NLS in some energy gap. It therefore follows that the symmetry breaking transforms the TP into a multi-band nodal link extending around the Brillouin zone torus [Fig. 1(d)]. The topological stability of the pair of NLS implies that they carry parallel orientation, which is consistent with the noncommutativity of the non-Abelian invariant [65].

Symmetry classification.— The discussed relation between TPs and multi-band nodal links relies on (i) the 2D ICR carrying a non-trivial quaternion charge \( q = -1 \) and (ii) the TP being type-A. We therefore classify symmetry-protected TPs in spinless \( P^T \)-symmetric systems according to those two aspects. We restrict our analysis to non-magnetic space groups (SGs), and to high-symmetry lines whose ICRs are not affected by a possible non-symmmorphicity of the SG [81].

Consider a rotation-invariant line in \( k \)-space (without loss of generality along \( k_z \)) of some SG and denote its little group by \( G \); then, under the above restrictions, \( G \) is a non-magnetic point group with a single rotation axis and without inver-

| \( G \) | Pairs of ICRs | \( |w_{2D}| \) | \( N_a \) | TP type | Material candidates |
|---|---|---|---|---|---|
| \( C_1 \) (any 2D+1D) | 1 | 3 | B | Na-O \[71\] |
| \( C_{iv} \) (any 2D+1D) | 1 | 3 | B | Bernal graphite [71] |
| \( C_4 \) (any 2D+1D) | 2 | 0 | A | - |
| \( C_{iv} \) (any 2D+1D) | 2 | 0 | A | ZrO [67], CaNaP \[7\] |
| \( C_6 \) (\( E_2, A \), \( E_1, B \)) | 2 | 0 | A | Li\(_2\)NaN [68], TiB\(_2\) [66] |
| \( C_6 \) (\( E_1, A \), \( E_2, B \)) | 2 | 0 | A | Na\(_2\)N [69], AlN \[7\] |

TABLE I: Classification of triple points (TPs) in spinless \( P^T \)-symmetric models (assumed non-magnetic and symmorphic). The TP species [characterized by the winding number \( w_{2D} \) of the 2D irreducible co-representation (ICR), and the number \( N_a \) of attached NL arcs per gap] depends on the little group \( G \). The TP is type-A if \( N_a = 0 \) (and type-B otherwise) [53]. For \( C_{iv} \), the result depends on the pair of intersecting ICRs, where \( i \in \{1, 2\} \) for \( C_{iv} \). TPs with \( |w_{2D}| = 2 \) carry quaternion charge \( q = -1 \), and when further \( N_a = 0 \) they transform to multi-band nodal links under strain. The TPs in compounds marked with \( \dagger \) are newly reported, and inspected in Ref. [70].
sion. By assumption the system is $\mathcal{PT}$-symmetric, such that the relevant symmetry group is enhanced to the non-unitary $\mathcal{M} = \mathcal{G} \cup (\mathcal{PT})\mathcal{G}$. The stability of a TP requires $\mathcal{M}$ to support both 1D and 2D ICRs, which is the case only for $\mathcal{G} \in \{C_{3v}, C_{4v}, C_{6v}\}$ [81]. To classify the possible TPs we construct minimal two-band (three-band) $\mathbf{k} \cdot \mathbf{p}$ models for all 2D ICRs (combinations of 1D+2D ICRs) of each $\mathcal{G}$ mentioned above. For that we obtain the necessary IRs from the Bilbao crystallographic server [82–85], then construct the corresponding ICRs [81] and finally obtain the models using the Python package kdotp-symmetry [86]. The constructed models are available in the Supplementary Data [87].

For two-band spinless $\mathcal{PT}$-symmetric models the Hamiltonian is of the form $\mathcal{H}(\mathbf{k}) = h_x(\mathbf{k})\sigma_x + h_y(\mathbf{k})\sigma_z$ [60], and we can define the winding number $w_{2D} \in \mathbb{Z}$ of the vector $\mathbf{h} = (h_x, h_y)$ [43] for a closed loop $\gamma_0$ [Fig. 1(c)] around the NL corresponding to the 2D ICR. While the winding number is unstable upon the inclusion of trivial bands, partial topological information is preserved in the quaternum charge [72]. In particular, there is a reduction $w_{2D}$ (mod 4) $= 2 \Rightarrow q(\gamma_0) = -1$ corresponding to the stability of a $2\pi$-rotation of the eigenframe [88]. The winding number can be analytically calculated for all the constructed two-band $\mathbf{k} \cdot \mathbf{p}$ models.

Finally, using methods detailed in the companion paper [70], we classify the TPs according to the number $N_e$ of additional attached NLs (which we call NL arcs) per band gap, such that $N_e = 0$ ($\neq 0$) corresponds to type-A (type-B) [53]. Thus, we analyze the NL compositions of the three-band models, which is fully determined by the real roots of the discriminant of the characteristic polynomial of the Hamiltonian [89–91]. For a given group $\mathcal{G}$ the possible combinations of ICRs fall into at most two topologically distinct equivalence classes.

The result of our analysis, presented in Table I, includes TPs with $N_e \in \{0, 3, 6\}$ with attached arcs scaling as $k_z = (k_x^2 + k_y^2)^{w_{2D}/2}$ near the TP [Fig. 2]. While the precise NL composition depends on the parameters of the $\mathbf{k} \cdot \mathbf{p}$ model, the characteristics $|w_{2D}|$ and $N_e$ (type) of a given TP class are universal. In particular, we find that $\mathcal{G} \in \{C_{4v}, C_{6v}\}$ enable type-A TPs with $q = -1$, which we predict to evolve into multi-band nodal links when subjected to strain. The table further lists previously reported TPs in spinless $\mathcal{PT}$-symmetric compounds [66–69, 71], as well as three newly predicted materials which we identified using first-principles calculations. We analyze those compounds in Ref. [70] and verify the agreement with our predictions.

**Case study: Li$_2$NaN.** — We study one of the materials listed in Table I more closely. The centrosymmetric Li$_2$NaN (ICSD #92308) was reported to be a ‘superior’ triple-point metal with negligible SOC [68]. In particular, there is a pair of type-A TPs at the Fermi level which we find to carry $q = -1$, and no other coexisting Fermi surfaces. The material has a centrosymmetric hexagonal crystal structure with SG $P6/mmm$ (No. 191) [Fig. 3(a)]. Additionally, the corresponding 2D ICR has a nearly flat dispersion [Fig. 3(b) path $\Gamma A$], which results in an approximately hundredfold change in the density of states within $40$ meV range around the Fermi level [70]. We therefore propose Li$_2$NaN as an ideal candidate to study the conversion of the TP into a multi-band nodal link as described.
above, and for experimental studies of the accompanying observable signatures which we discuss below.

We employ first-principles calculations and an effective tight-binding (TB) model to study Li$_2$NaN. The bands close to the Fermi level come mainly from nitrogen $p_{x,y,z}$ and sodium $s$ orbitals; thus we construct a corresponding four-band model that reproduces the low-energy theory of Li$_2$NaN [Fig. 3(b)] after being fitted to first-principles data (cf. Supplemental Material (SM) [80]). We find that the vertical NL at $k_z = 0$ (i.e. the 2D ICR) is well isolated from other NLs in the Brillouin zone (BZ), both in energy [Fig. 3(b)] and in momentum [Fig. 3(c)]. The little group along $\Gamma A$ is $C_{6v}$ and the involved ICRs are $(E_1, A_1)$, such that Table I predicts $N_p = 0$ and the formation of a multi-band nodal link after breaking the $C_{6v}$ symmetry down to $C_{3v}$. In the TB description we model this by adding an energy offset $\delta E = \pm \hbar \omega$ to nitrogen $p_{x,y,z}$ orbitals. In agreement with Fig. 1(c,d), we find that the central NL splits into linked NLs in adjacent band gaps [Fig. 3(c-f)].

We next examine the bulk-boundary correspondence, which has not yet been clarified for the quaternion charges. To analyze surface properties, we consider a finite slab with the surface termination indicated in Fig. 3(a). This corresponds to a projection of the BZ along reciprocal lattice vector $G_1$ [Fig. 3(c,d)] onto the surface Brillouin zone (SBZ). Each point in the SBZ corresponds to a projection of a closed path in the BZ, and thus carries a quaternion charge $q(k_z)$ [Fig. 3(g)].

Recall [65] that any element of $Q_N$ is given (up to a sign) by an ordered product of some of the $(N-1)$ generators $g_j$, where $g_j$ represents the band inversion of energy gap $\beta$ (cf. legend to Fig. 3(g)). We observe in the surface spectrum along $k_z = 0$ two clear surface bands [Fig. 3(h)]. Additional surface bands that hybridize with the bulk states in the second gap are not discernible for small strain. A careful analysis (see SM [80]) reveals that the surface states appear exactly in the gaps with a band inversion according to the value of $q$, when including those that have hybridized with bulk states.

The NLs at the Fermi level and their splitting into multi-band nodal links suggests non-trivial signatures in transport. Using the Kubo-Greenwood formula [92, 93] which we have implemented in the Python package wannier-berry [79, 94], we compute the interband optical conductivity $\sigma_{o-o}(\omega)$ [Fig. 3(i)] with and without strain. We observe that the suppression of strain leads to a strong suppression of $\text{Re} \sigma_{xx}$ for $\hbar \omega \lesssim |s|$. This results from a suppression of optical transitions due to strain-induced mismatch between the chemical potential and the energy of the NLs [95]. We expect this depletion to be experimentally accessible in clean samples at low temperatures, when the Drude peak occurs at even lower frequencies. In contrast, $\text{Re} \sigma_{xx}$ vanishes at $\omega \to 0$ already without strain, while a finite value of strain leads to an enhancement for the intermediate range $\hbar \omega \lesssim 25 |s|$.

Conclusions and outlook.— Besides enriching the library of catalogued band-structure nodes, we predict the transition from type-A TPs to multi-band nodal links to result in a rapid and experimentally testable change in optical conductivity. We expect the non-trivial linking to furnish the NL-rings with monopole charges [60–65]. We report in the companion work [70] that the ‘red’ NL of Li$_2$NaN in Fig. 3(e,f) carries Euler class $\chi = 2$, and we identify the general conditions for the realization of non-trivial Euler or Stiefel-Whitney monopole charges in triple-point materials. Note that nodal rings with a non-trivial monopole charge were theoretically related to higher-order topology with hinge Fermi arcs [96–99], yet suitable material candidates have so far remained very scarce [63]. Our findings thus also suggest that higher-order topology might play a role in triple-point materials.

We anticipate analogous reasonings via the non-Abelian band topology to be applicable also to other species of band nodes, including nodal chains [72, 75] and to TPs with attached NL arcs. This strategy has very recently been exemplified by the Weyl-points-to-nodal-ring conversion in ZrTe [74, 100]. We also emphasize the generality of the discussed framework as the condition $(\mathcal{P}T)^2 = +\mathbb{I}$ extends to photonic, phononic and magnonic bands [61].

Acknowledgments.— We thank A. A. Soluyanov for valuable discussions and to Q.S. Wu for providing early data that facilitated our work on this project. We further acknowledge discussions and helpful comments on the manuscript from F. O. von Rohr, R.-J. Slager, L. Trifunovic, and N. A. Winter. P. M. L. and T. B. were supported by the Ambizione grant No. 185806 by the Swiss National Science Foundation. T. N. and S. S. T. acknowledge support from the European Research Council (ERC) under the European Unions Horizon 2020 research and innovation program (ERC-StG-Neupert-757867-PARATOP) and from the NCCR MARVEL funded by the Swiss National Science Foundation. S. S. T. is additionally supported by the grant No. PP00P2_176877 by the Swiss National Science Foundation. X. X. L was supported by the China Scholarship Council (CSC).
[73] J. Ahn, S. Park, and B.-J. Yang, Phys. Rev. X 9, 021013 (2019).
[74] A. Bouhon, Q. Wu, R.-J. Slager, H. Weng, O. V. Yazyev, and T. Bzdušek, Nat. Phys. (2020). 10.1038/s41567-020-0967-9.
[75] E. Yang, B. Yang, O. You, H.-C. Chan, P. Mao, Q. Guo, S. Ma, L. Xia, D. Fan, Y. Xiang, and S. Zhang, Phys. Rev. Lett. 125, 033901 (2020).
[76] J. Kang and O. Vafek, Phys. Rev. B 102, 035161 (2020).
[77] Y. X. Zhao and Y. Lu, Phys. Rev. Lett. 118, 056401 (2017).
[78] C.-H. Park and N. Marzari, Phys. Rev. B 84, 205440 (2011).
[79] X. Liu, M. A. Jimenez Herrera, I. Souza, S. S. Tsirkin, et al., in preparation (2020).
[80] The Supplemental Material, which cites additional Refs. [101–112], contains additional information about the construction of the tight-binding model of Li$_2$NaN and the study of its properties, in particular the surface states.
[81] C. J. Bradley and A. P. Cracknell, The mathematical theory of symmetry in solids: representation theory for point groups and space groups, 2011th ed. (Clarendon Press, Oxford, 1972).
[82] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Blügel, F. Freimuth, G. Géranton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, et al., J. Phys. Condens. Matter 32, 165902 (2020).
[83] M. G. Vergniory, L. Elcoro, Z. Wang, J. Cano, C. Felser, M. I. Aroyo, B. A. Bernevig, and B. Bradlyn, Phys. Rev. E 96 (2017), 10.1103/PhysRevE.96.023310.
[84] D. Varjas, T. Rosdahl, and A. R. Akhmerov, New J. Phys. 20 (2018), 10.1088/1367-2630/aa8567.
[85] N. D. Mermin, Rev. Mod. Phys. 51, 591 (1979).
Supplemental Material to:
Multi-band nodal links in triple-point materials

Patrick M. Lenggenhager,1,2,3, * Xiaoxiong Liu,3 Stepan S. Tsirkin,3 Titus Neupert,3 and Tomáš Bzdušek1,3

1Condensed Matter Theory Group, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland
2Institute for Theoretical Physics, ETH Zurich, 8093 Zurich, Switzerland
3Department of Physics, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

(Dated: August 10, 2020)

CONTENTS

I. Construction of a tight-binding model for Li$_2$NaN 1
   A. First-principles calculations 2
   B. Effective low-energy tight-binding model 2

II. Finding nodal lines based on a tight-binding model 5

III. Bulk-boundary correspondence for quaternion charges in Li$_2$NaN without and with strain 6
   A. Review of the generalized quaternion charge 6
   B. Surface Spectrum Li$_2$NaN without and with strain 8

IV. Density of states and optical conductivity of Li$_2$NaN 11
   A. Density of states 11
   B. Optical conductivity 12

V. Triple-point materials 12

OVERVIEW

In this Supplemental Material we provide supporting information related to our numerical methods, and concerning the triple points (TPs) and the multi-band nodal-line (NL) links of Li$_2$NaN without and with strain, respectively. The information is organized into four parts. We begin in Sec. I with our construction of a four-band tight-binding (TB) model of the compound fitted to first-principles calculations. Here, we first summarize in Sec. I A the methods employed in the first-principles modelling of Li$_2$NaN, and then in Sec. I B we present a symmetry-based detachment scheme that allows us to separate the four most relevant bands from the rest of the spectrum. The fitted TB model has been made available as part of the Supplementary Data [87].

We continue in Sec. II with presenting the algorithm used to find the nodal lines in the full Brillouin zone (BZ) [cf. Fig. 3(c–f) of the main text] for the fitted TB model. Next, in Sec. I we carefully analyze the surface states of Li$_2$NaN without and with strain [cf. Fig. 3(h) of the main text]. We compare them against the bulk quaternion charges [cf. Fig. 3(g) of the main text] and observe a consistency with a bulk-boundary correspondence conjectured by Ref. [72] after also including the surface states that hybridize with the bulk states. In Sec. IV we present additional data showing the imprint of the strain-induced nodal conversion in Li$_2$NaN on its bulk density of states and optical conductivity. Finally, in Sec. V, we present the first-principles data showing the TPs in the newly proposed material candidates in Table I and justifying their placement in that table.

I. CONSTRUCTION OF A TIGHT-BINDING MODEL FOR Li$_2$NaN

In the main text we discuss the triple-point metal Li$_2$NaN as a model material which we predict to exhibit the conversion of TPs to multi-band nodal links, and we study certain associated material properties. The results discussed there are obtained from a TB model, whose construction we describe in this section. We first summarize the methods used in the first-principles modelling of Li$_2$NaN in Sec. I A, before presenting a symmetry-consistent scheme for detaching the four most relevant bands near the Fermi level as well as our method of fitting the free parameters of the constructed TB model in Sec. I B.

* corresponding author: lenpatri@ethz.ch
A. First-principles calculations

The tight-binding model is set up as an effective low-energy theory of the results of first-principles calculations. Therefore, density functional theory (DFT) calculations are performed with the projected augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP) [101, 102] with generalized gradient approximation (GGA) and PBE approximation [103]. We use a Γ-centered $10 \times 10 \times 8$ $k$-mesh. Using plane-wave-based wave functions and space group operators generated by VASP, we calculate the traces of matrix representations to get the irreducible representations of the energy bands at high-symmetry points in the first Brillouin zone [cf. Fig. S1(a)] with the help of irvsp [104]. Using compatibility relations [85] we then deduce that the irreducible representations of the lines of symmetry. The contributions to energy bands from orbitals [cf. Fig. S1(b)] are obtained by projecting wavefunctions to ion-centered spherical harmonic functions with different quantum numbers. In the following we will number the bands starting from the yellow band in Fig. S1(a), which we will refer to as the ‘first’ band, even though the first-principles results contain an additional band at even lower energy (approximately $-10$ eV).

Furthermore, we rebuild the crystal structures for compressive and tensile strain by reducing and enlarging the $y$-component of each lattice vector. Surface states are then calculated using the WannierTools package [105] which is based on the maximally localized Wannier-function tight-binding model [106–108] constructed by the Wannier90 package [109]. We use the sodium $s$-orbital, and nitrogen $p$-orbitals as initial wave functions for the localization.

B. Effective low-energy tight-binding model

To construct an effective low-energy TB model for Li$_2$NaN, we need to choose a minimal set of orbitals. From the first-principles data [Fig. S1(b)] we deduce that the band structure close to the Fermi level is dominated by four orbitals, namely sodium (Na) $s$, and nitrogen (N) $p_{x,y,z}$ [Table S1]. The compound contains one of each per the primitive unit cell, suggesting it is possible to construct a four-band model that reproduces the low-energy properties of Li$_2$NaN. Note, however, that in the first-principles data the fourth band intersects with the fifth band multiple times, in particular leading to two-dimensional (2D) irreducible representations (IRs) at $K$ and $H$ [Fig. S1(a)]. Furthermore, other orbitals become dominant at these locations, notably the lithium (Li) $p_z$ along $LH$ and $HA$ [Fig. S1(b)]. Thus, we need to artificially detach the fourth and fifth band, which prevents the resulting TB model from reproducing the band structure near those crossings. Nevertheless, as these degeneracies lie at energies far from the Fermi level (3 to 4 eV), this mismatch is not relevant for the low-energy properties.

We verify that such a detachment of bands is consistent with symmetries using the machinery of topological quantum chemistry (TQC) [7–9]. Using the WYCKPOS and POINT applications [84] on the Bilbao crystallographic server (BCS) [82–84] we
determine the Wyckoff letters and irreducible representations (IRs) of the four orbitals in the model [Table S1]. These serve as an input for the BANDREP application [9, 85, 110] on the BCS which calculates the elementary band representations (EBRs) induced from the IRs of the site-symmetry group of the Wyckoff positions [Table S2]. Matching them to the IRs in Fig. S1(a), we notice that not only the ones at the Dirac points at $K$ and $H$ need to be replaced, but also the one at $L$, namely

$$K_5 \rightarrow K_1, \quad H_6 \rightarrow H_3, \quad L_5 \rightarrow L_7.$$  (S1)

Due to band inversions, these IRs appear in the band structure at somewhat higher energies ($K_1$ is the eighth band at $E \approx 6.5$ eV, $H_3$ is the ninth band at $E \approx 8.7$ eV, and $L_7$ is the fifth band at $E \approx 5.0$ eV). Finally, we need to check the compatibility relations for the modified IRs of the detached fourth band to ensure that the observed band connectivity is compatible with the IRs. Using the COMPATIBILITY RELATIONS application [85] on the BCS we find that both $M_1^+ \rightarrow T_1 \rightarrow K_1$ and $A_2^- \rightarrow R_3 \rightarrow L_2^- \rightarrow S_3 \rightarrow H_3 \rightarrow Q_3 \rightarrow A_2^-$ are compatible.

Having identified the relevant orbitals and the parts of the band-structure to be reproduced, we construct a symmetry-consistent TB model. Given the orbitals and the isogonal point group $D_{6h}$ we determine the symmetry-restricted family of Bloch Hamiltonians using the qsymm Python package [111]. We choose primitive lattice vectors

$$t_1 = \begin{pmatrix} 0 \\ -a \\ 0 \end{pmatrix}, \quad t_2 = \begin{pmatrix} \sqrt{3}/2 \\ a/2 \\ 0 \end{pmatrix}, \quad t_3 = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix}.$$  (S2)

with $a$ and $c$ being the in-plane and out-of-plane lattice constants, respectively. We further fix the Hilbert-space basis ($Np_x, Np_y, Np_z, Nas$), i.e. in terms of the IRs ($E_{1u}(2), A_{2u}(1), A_{1g}(1)$).

As the input to the qsymm package, we provide (i) the set of generators of $D_{6h}$, including the matrix co-representations which are determined by the IRs of the orbitals [listed in Table S3(left)], and (ii) the considered hopping vectors [listed in Table S3(right)] between nearby atoms. We only consider hoppings up to nearest neighbors in terms of unit cells, which results in six independent terms (all symmetry-related hopping terms are taken into account implicitly). The relevant Python script as well as its output can be found in the Supplementary Data [87]. We note that the resulting family of Bloch Hamiltonians does not consist of real matrices. However, because we need the Hamiltonian to be real when computing the quaternion invariant, we rotate the basis such that $PT = \bar{V}K$ using the unitary transformation $U = \text{diag}(1, 1, 1, i)$.

We arrive at a 13-parameter family of Bloch Hamiltonians, which we now fit to the first-principles band structure along the lines of symmetry. We cannot expect the model to fit well everywhere, because it contains a reduced number of orbitals, and because of the symmetry-consistent replacement of IRs at points $K, H$ and $L$, as argued above. In order to capture the relevant features, i.e. the energies close to the Fermi level and the band connectivity, we proceed as follows: First, we set the energy of the 2D IR along $\Gamma K$ exactly to zero, which is almost exact according to the first-principles data. Then, we determine initial values for ten out of the remaining eleven parameters by diagonalizing the eleven-parameter family of Hamiltonians on lines of symmetry and using the dimension of the IRs to match the resulting expressions for eigenvalues to the numerically obtained band structure. Finally, we fix the eleven parameters not fixed in the first step using a weighted least-square algorithm with the weight function

$$w(E) = \frac{w_0 + \frac{1}{2} \coth \left( \frac{\Delta E}{2} + E \right) \left[ \tanh \left( \frac{\Delta E}{2} + E \right) + \tanh \left( \frac{\Delta E}{2} - E \right) \right]}{1 + w_0},$$  (S3)

where $\lambda = 4 \text{ eV}^{-1}$, $\Delta E = 2 \text{ eV}$, $w_0 = 0.01$ and $E$ is the band energy according to the first-principles calculations. The choice of weight function in Eq. (S3), illustrated in Fig. S2(b), ensures that the fitted model reproduces features within an approximately $\Delta E/2 = 1 \text{ eV}$ wide energy window around the Fermi level more faithfully than those farther away. We provide an implementation of the fitting procedure in Mathematica as well as our results in the Supplementary Data [87].

| Wyckoff pos. | Band rep. | $1a (6/mmm)$ | $1a (6/mmm)$ | $1b (6/mmm)$ |
|-------------|-----------|--------------|--------------|--------------|
| $\Gamma$    | $\Gamma_3(2)$ | $\Gamma_3(1)$ | $\Gamma_3(1)$ |
| $M$         | $M_1(1) \oplus M_1(3)$ | $M_1(1)$ | $M_1(3)$ |
| $K$         | $K_2(2)$ | $K_2(1)$ | $K_2(1)$ |
| $A$         | $A_4(2)$ | $A_4(1)$ | $A_4(1)$ |
| $L$         | $L_3(1) \oplus L_3(1)$ | $L_3(1)$ | $L_3(1)$ |
| $H$         | $H_6(2)$ | $H_6(1)$ | $H_6(1)$ |

TABLE S2. Elementary band representations (EBRs) induced from the irreducible representations of the site-symmetry group of the Wyckoff positions for the orbitals given in Table S1.
Generator | Action on position | Matrix co-representation
---|---|---
$C_6$ | $\left(\begin{array}{ccc} \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & 0 \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & 1 \end{array}\right)$ | $\left(\begin{array}{ccc} \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & 0 \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & 1 \end{array}\right)$
$C_{2v}$ | $\left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array}\right)$ | $\left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array}\right)$
$T$ | $\left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right)$ | $\left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right)$
$P$ | $\left(\begin{array}{ccc} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{array}\right)$ | $\left(\begin{array}{ccc} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{array}\right)$

Atom 1 | Atom 2 | Hopping vector
---|---|---
N | N | $t_1$
N | N | $t_3$
Na | Na | $t_1$
Na | Na | $t_3$
N | Na | $\frac{1}{2}t_3$
N | Na | $t_1 + \frac{1}{2}t_3$

TABLE S3. (left) Generators of the isogonal point group $D_{6h}$ including their action on position and the matrix co-representation in the Hilbert space spanned by the orbital basis ($Np_x, Np_y, Np_z, Na_s$) [Table S1]. (right) Hopping terms between the atoms listed in Table S1.

FIG. S2. Band structure of Li$_2$NaN (a) along the lines of symmetry and (c) near the triple point. First-principles data (only a fraction of all the points is shown for better visibility) is indicated by points and the fitted tight-binding model by solid lines. (b) The fitting weight function given in Eq. (S3). For the description of the $Q'PQ$ path in panel (c) see the paragraph preceding Eq. (S4). The coloring of the energy bands follows their labelling according to increasing energy.

The band structure of the resulting TB model along the lines of symmetry is compared to the first-principles data in Fig. S2(a). We observe that the fit is good close to the Fermi level but diminishes for energies farther away. Except for the fourth band, the band connectivity and overall behaviour of the bands is reproduced, as expected. Figure S2(c) shows the band structure along the line $Q'PQ$ with $P$ being the position of the triple point and $Q$ a point on the BZ boundary directly above $K$ at the same $k_z$ as $P$. We thus expect the TB model to reproduce the band structure in the energy window $[-2, 2]$ eV very well even outside the lines of symmetry and in particular near the triple point.

To convert the TPs into multi-band nodal links, the $C_{6v}$ symmetry needs to be broken. In the TB model this is modelled by adding the leading $C_{6v}$-breaking term,

$$\mathcal{H}_{\text{strain}}(k) = s \begin{pmatrix} 1 & -1 \\ -1 & 0 \end{pmatrix},$$  \hspace{1cm} (S4)

which lifts the degeneracy along the $\Gamma A$ line. This term still satisfies the $C_{2v}$ symmetry and thus corresponds to the application of uniaxial strain.

In the first-principles calculations, we model uniaxial strain by deforming the lattice constants, such that a $C_{2v}$ symmetry remains, see Sec. 1A for more details on the numerics. In particular, we multiply the $y$-component of all lattice vectors by a factor of $1 + \varepsilon_y$ with experimentally reasonable values of $\varepsilon_y$ in the range from $-3.5\%$ to $3.5\%$. The dominant effect is the splitting
FIG. S3. First-principles data showing the effect of uniaxial strain $\varepsilon_y$. (a) Band structure and contribution of the N orbitals (colored overlays) for compression and expansion in the $y$-direction. The energy of the band dominated by $p_x$ decreases for $\varepsilon_y > 0$ and increases for $\varepsilon_y < 0$. (b) The extracted dependence of the energy splitting parameter $s$ on the strain $\varepsilon_y$.

II. FINDING NODAL LINES BASED ON A TIGHT-BINDING MODEL

Based on the ideas described in our companion paper [70], we have developed a simple partially adaptive numerical algorithm for finding nodal lines given a TB model. It is based on the fact that the discriminant $\Delta(k)$ of the characteristic polynomial of the Hamiltonian $H(k)$ vanishes if and only if there is a node at $k$ (corresponding to a multiple root of the characteristic polynomial). Because the Hamiltonian is Hermitian, the roots of the characteristic polynomial are always real, which implies that $\Delta \geq 0$. Thus, the roots of $\Delta$ are simultaneously local minima. It is convenient to go to cylindrical coordinates

$$k = \begin{pmatrix} k \cos(\theta) \\ k \sin(\theta) \\ k_z \end{pmatrix}$$

and consider $k = 0$ and $k \neq 0$ separately. The first case can be checked explicitly for roots, while we handle the second case using a grid of $(\theta, k_z)$ points. For each $(\theta, k_z)$ we sample $k$, detect minima and perform root finding around those. At the end, roots are selected according to a specified tolerance, duplicates are removed and the energy gap is determined by computing the eigenenergies. The most important parts of the algorithm are summarized in Fig. S4 in pseudocode and our implementation in Mathematica and the results can be accessed in the Supplementary Data [87].

The algorithm has one limitation: NLs confined to planes with constant $\theta$ and/or $k_z$ are not detected if the corresponding values of $\theta$ and $k_z$ are not in the initial grid. For mirror-symmetry protected NLs this can be easily alleviated by making sure that all of the 2D IR along $\Gamma A$, which can be related to the strain parameter $s$ from Eq. (S4) by

$$2s \equiv E_{Np_y}(\Gamma A) - E_{Np_y}(\Gamma A).$$

Extraction of the value of $s$ for different $\varepsilon_y$ we find that $\varepsilon_y > 0$ corresponds to $s < 0$ [Fig. S3(a)] and can establish the relationship $s(\varepsilon_y)$ [Fig. S3(b)]. For example, $s = -0.03$ eV corresponds to roughly 3% tensile strain in the $y$-direction.
candidate planes (according to the symmetries) are included in the \((\theta, k_z)\) grid, while other NLs do not generally lie inside such a plane, such that they will be detected for some values of \(k_z\) at least. Alternatively, one could add additional adaptive loops to take care of that. We have chosen the former way to deal with that limitation and found it sufficient for our purposes.

### III. BULK-BOUNDARY CORRESPONDENCE FOR QUATERNION CHARGES IN Li\(_2\)NaN WITHOUT AND WITH STRAIN

In this section we test the bulk-boundary correspondence for the generalized quaternion charge as proposed by Ref. [72]. To do so, we first review in Sec. III A the main concepts relevant for understanding and computing the generalized quaternion charge, following closely the discussion in Ref. [72]. Based on that discussion, we present in Fig. S5 an algorithm for the computation of the quaternion charge. In Sec. III B we then discuss the surface spectrum of Li\(_2\)NaN without and with strain, and relate it to the bulk quaternion charges. We observe an agreement with the anticipated bulk-boundary correspondence after the surface states that hybridize with the bulk states are explicitly included.

#### A. Review of the generalized quaternion charge

Consider an \(N \times N\) real Bloch Hamiltonian in one dimension for generic \(N \geq 2\). By the spectral theorem, it can be written as

\[
\mathcal{H}(k) = u(k)E(k)u(k)^T,
\]

where \(u(k)\) is the matrix with columns being the (ordered, real, orthonormal) eigenstates \(u_j(k)\) and \(E(k)\) the diagonal matrix of (ascending) eigenenergies of \(\mathcal{H}(k)\). The matrix \(u(k)\) is an orthogonal real matrix and thus defines an \(N\)-frame, the *eigenframe*. Note that the band energies \(E_j(k)\) can be continuously adjusted (as long as we do not produce a degeneracy) without affecting the band topology. Thus, as long as there are no degeneracies, the band topology of the Hamiltonian can be completely captured by the eigenframe \(u(k)\). Crucially, the frame has a remaining gauge freedom that manifests as the flipping of the sign of some of the vectors \(u_j\) of the frame. This is given by the \(N\)-dimensional point group \(P_{Nh} = O(1)^N = \mathbb{Z}_2^N\) generated by \(N\) mutually perpendicular mirror symmetries. We can fix the handedness of the frame by choosing a gauge where \(u(k) \in SO(N)\), which then reduces \(P_{Nh}\) to its special component \(P_N\). Consequently, the space of (spectrally normalized) Hamiltonians that we should consider [72] is

\[
M_N = O(N)/P_{Nh} = SO(N)/P_N = Spin(N)/\overline{P}_N,
\]

where we first restricted to the special components and then lifted each group to its respective double cover. We explain further below that the fundamentamental group of \(M_N\), which coincides with the discrete group \(\overline{P}_N\), captures the topology of NLs in spinless \(PT\)-symmetric models.

We first briefly characterize the groups and lifts appearing in Eq. (S8). The lift of an element of \(SO(N)\) close to the identity to \(Spin(N)\) is performed by working in the corresponding algebras \(so(N)\) and \(spin(N)\), where the lift can be simply performed on the level of the basis elements:

\[
\sum_{i<j} \alpha_{ij}L_{ij} \mapsto \sum_{i<j} \alpha_{ij}t_{ij}.
\]

(S9)

Here, \(\{L_{ij}\}_{i<j}\) and \(\{t_{ij}\}_{i<j}\) are bases of \(so(N)\) and \(spin(N)\), respectively, and we choose

\[
(L_{ij})_{ab} = -\delta_{ia}\delta_{jb} + \delta_{ib}\delta_{ja},
\]

\[
t_{ij} = -\frac{1}{4}[\Gamma_i, \Gamma_j],
\]

(S10)\hspace{1cm}(S11)

where the \(\{\Gamma_i\}\) are Gamma matrices in \(N\) dimensions. Furthermore, \(P_N\) is a subgroup of \(O(N)\), and we can obtain the generators \(\{e_1, e_2, \ldots, e_{N-1}\}\) of \(\overline{P}_N\) from the generators \(\{e^\rho_{L_{ij}}\}_{i<j=1}^N\) of \(P_N\):

\[
e_{j-1} = e^{\pi t_{ij}} = \frac{1}{2}[\Gamma_j, \Gamma_1] = 2t_{ij}
\]

(S12)

for \(2 \leq j \leq N - 1\). From its definition we can read off that \(e_{j-1}\) encodes a \(\pi\)-rotation in the \((1, j)\)-plane (i.e. a \(\pi\)-twist of the first and \(j\)th band). An alternative set of generators is provided by

\[
g_j = \begin{cases} e_1, & j = 1 \\ e_{j-1}e_j, & j \geq 2 \end{cases}
\]

(S13)
there is a band degeneracy along the path if
else
Input: $N$-band Hamiltonian along a closed path $\gamma: t \in [0, 1] \mapsto H(\gamma(t))$, stepsize $\Delta t$.
Output: Generalized quaternion charge $a(\gamma) \in Q_N$.
if there is a band degeneracy along the path then
  return NULL;
else
  initialize $V = \mathbb{1}_{2^{N(N+1)/2}}$;
  diagonalize $H(\gamma(0)) \mapsto u_0 \in O(3)$;
  select special component: $u_0 \text{diag}(1, 1, \ldots, 1, \det(u_0)) \mapsto u_0 \in SO(3)$;
  for $n = 1$ to $N/2$ do
    diagonalize $H(\gamma(n\Delta t)) \mapsto u_n \in O(3)$;
    select special component: $u_n \text{diag}(1, 1, \ldots, 1, \det(u_n)) \mapsto u_n \in SO(3)$;
    compute $u_n^T u_n \mapsto \Delta R_n$;
    fix gauge: $u_n \text{sign} (\text{diag}(\Delta R_n)) \mapsto u_n \in SO(3)$;
    update $u_{n+1}^T u_n \mapsto \Delta R_n$;
    decompose $\log(\Delta R_n)$ into so($N$) basis $\mapsto \{a_{ij}\}$;
    compute lift of $\Delta R_n$ to Spin($N$): $e^{\Delta R_n} \mapsto \Delta V$;
    update $V \mapsto V e^{\Delta R_n}$;
  end
  decompose $V$ into basis of generalized quaternions
  $\frac{1}{\sqrt{2}} \text{tr}(V) 1 + \sum_{i=1}^{2^{N-1}-1} \frac{1}{2^{N-1}} \text{tr}(q_i V) q_i \in Q_N \mapsto a(\gamma)$;
return $a(\gamma)$;
end

FIG. S5. Computation of the generalized quaternion charge $a(\gamma) \in Q_N$ for an $N$-band Hamiltonian $H(\mathbf{k})$ along a closed path $\mathbf{k} = \gamma(t)$, based on the discussion in Ref. [72]. A frame is defined to be the matrix with columns being the ordered real orthonormal eigenstates in order of ascending eigenenergies and sign(diag($\Delta R_n$)) is the diagonal matrix consisting of the signs the diagonal entries of $\Delta R_n$.

which corresponds to a $\pi$-rotation in the $(j, j+1)$-plane [i.e. the band inversion of the $j$th and $(j+1)$th band]. The elements of $\overline{P}_N$ are then given by all possible products of elements of either set of generators together with the identity. We call this group the generalized quaternion group $Q_N$ and denote its $2^N$ elements by

\[ \pm 1, \pm q_1, \pm q_2, \ldots, \pm q_{2^{N-1}-1}, \quad (S14) \]

where the corresponding matrix representations $q_i$ of the elements $q_i$ are the products of generators:

\[ q_1 = g_1, \quad q_2 = g_2, \quad \ldots, \quad q_{N-1} = g_{N-1}, \quad q_N = g_1 g_2, \quad q_{N+1} = g_1 g_3, \quad \ldots, \quad q_{2^{N-1}-1} = g_1 g_2 \cdots g_{N-1}. \quad (S15) \]

We now turn attention to the topological invariants in the momentum space. Closed paths $\gamma$ in momentum space with non-degenerate spectrum at each point $k \in \gamma$ are characterized by the first homotopy group $\pi_1(M_N)$, which is found to be $[72, 112]$

\[ \pi_1(M_N) = \overline{P}_N. \quad (S16) \]

This implies the existence of an invariant $a(\gamma) \in \overline{P}_N$, called generalized quaternion charge by Ref. [72]. Its numerical computation is based on tracking the rotation of the eigenframe lifted to Spin($N$) along the closed path $\gamma$. The total spin-rotation along $\gamma$ can be decomposed into a linear combination of the matrices in Eq. (S15), and if there are no band degeneracies along $\gamma$, the total rotation itself is (within numerical precision) equal to one of these matrices, i.e. it is an element of $Q_N$. Figure S5 shows this algorithm in pseudocode. We make our implementation in Mathematica available in the Supplementary Data [87].

Due to its non-Abelian character, the quaternion charge is only well-defined up to conjugation by elements in $Q_N$, such that the topology is classified by the equivalences classes of $Q_N$. They are $[72]$

- $\{ \pm g_1^{n_1} g_2^{n_2} \cdots g_{N-1}^{n_{N-1}} \}$, $n_i \in \{0, 1\}$ with the exceptions
- $\{+1, -1\}$ and
- if $N$ is even also $\{+g_1 g_3 \cdots g_{N-1}, -g_1 g_3 \cdots g_{N-1}\}$.

which follow from the commutation relations between the generators. The fact that $\pm 1$ are in distinct conjugacy classes for any $N$ results in the paths that are classified by these charges to be stably topologically inequivalent, while $\pm g_1 g_3 \cdots g_{N-1}$ result in an unstable topological inequivalence (since adding an additional band brings them into a single conjugacy class).
The set of generators given in Eq. (S13) provides a useful interpretation of the quaternion charge in terms of its factors $g_j$. Since $g_j$ corresponds to a $\pi$-rotation in the $(j, j+1)$-plane, it suggests a band inversion between bands $(j, j+1)$ [65, 72] with associated $\pi$ Berry phases on those two bands. Consequently, if the quaternion charge is computed on a closed loop in $k$-space that does not wind around the BZ torus, then each factor $g_j$ indicates that a band node (in 2D) or NL (in 3D) between bands $(j, j+1)$ is enclosed [72]. Equivalently, we consider the Hamiltonian along the closed loop as a 1D system. Then, deforming it to a constant Hamiltonian requires a closing of the gap between bands $(j, j+1)$ for each factor $g_j$. We make use of this interpretation in the following study of the bulk-boundary correspondence.

### B. Surface Spectrum Li$_2$NaN without and with strain

To analyze the surface properties we consider a slab geometry of the TB model $\mathcal{H}(k)$ [87] with termination at the surface indicated in Fig. 3(a) of the main text. In that illustration, the atoms intersected by the red layer are included in the slab, and the purple arrow indicates the surface normal pointing outside from the sample. Thus, we assume a finite-size system with open boundary conditions in the $t_1$ direction and an infinite size in the $t_2, t_3$ directions. The Bloch Hamiltonian for $N$ layers is

$$
\mathcal{H}(k_2, k_3)_{n' n} = \int_{-1/2}^{1/2} dk_1 \mathcal{H}\left(\sum_{j=1}^{3} k_j G_j\right) e^{2\pi i(n-n')k_1},
$$

where $n \in \{1, 2, \ldots, N\}$ is the layer index. By diagonalizing $\mathcal{H}(k_2, k_3)$ at each point $(k_2, k_3)$ in the surface Brillouin zone (SBZ),

$$
\mathcal{H}(k_2, k_3)|i\rangle = E_i|i\rangle,
$$

we obtain $4N$ eigenstates, and compute the surface spectral function

$$
A_S(E, k_2, k_3) = \sum_i \delta(E_i - E)(i|P_{\text{surface}}|i),
$$

where $P_{\text{surface}}$ is the projector onto the outermost surface layer $n = N$. For our calculations we use $N = 100$ and we replace the Dirac delta function by a Lorentzian with a half-width of 0.021 eV. The results of the calculation for the TB model without and with strain are shown in Figs. S6(a) and S6(c), respectively.

We compare the surface spectral function obtained from the TB model to the predictions from the first-principles modelling [cf. Sec. 1A]. While the constructed TB model does not include the lithium atoms, thus leading to a unique surface termination along the considered direction, the explicit presence of the lithium orbitals in the first-principles calculations enables terminations at various inequivalent layers. By comparing the data, we find that the TB model reproduces the first-principles calculations [Fig. S6(b,d)] for the termination at the layer shown in Fig. 3(a) of the main text with the specifications detailed above Eq. (S17). For this termination, the outermost layer of nitrogen atoms is enclosed in a complete hexagonal cage of lithium atoms, just like the bulk nitrogen atoms.

The observed correspondence suggests that the basis orbitals of the constructed TB model effectively correspond to a mixture of the nitrogen $p_{x,y}$ orbitals hybridized with the lithium $p_{x,y}$ orbitals of the enclosing hexagonal cage [as is indeed visible in

![FIG. S6. Surface spectral function of Li$_2$NaN (a,b) without strain and (c,d) with 3\% tensile strain (corresponding to $s \approx -0.03$ eV), which was obtained from (a,c) the tight-binding model with $N = 100$ layers [cf. Sec. 1B] and (b,d) first-principles calculations [cf. Sec. 1A]. Different relative color scales are used in the comparisons. Note that the surface band at energy $E > 1$ eV visible in the first-principles data (b,d) is not reproduced in our TB model (a,c). This difference arises due to the enforced detachment of the fourth band from the higher-energy ones.](https://example.com/figure.png)
FIG. S7. Band structure of the slab Hamiltonian of Li$_2$NaN defined in Eq. (S17) for $N = 200$ layers and $k_2 = 0$, plotted for increasing strain given by the parameter $s$ defined in Eq. (S4). The color scale indicates the inverse participation ratio (IPR), Eq. (S20), according to the legend on the right. In panel (a) the IPR reveals two surface bands, one in gap 1−2 and one in gap 2−3. In the strained case [panels (b–d)], not all surface bands are well visible, due to hybridization with the bulk states, whose degree depends on $s$. However, looking at panels (b–d) we can deduce that there are four surface bands [indicated by black arrows in panel (c)], even if they are not always visible [e.g. the upper surface state in gap 2−3 is best visible in panel (b) and the lower one in panel (d)].

Since the TB model implicitly assumes the same orbitals also at the boundary, the surface termination reproduced by the TB model must correspond to the case when the outermost nitrogen atoms are surrounded by unbroken hexagonal cages of lithium atoms, consistent with our findings. One obvious difference between the predictions of the TB model [Fig. S6(a,c)] as compared to the first-principles data [Fig. S6(b,d)] is the absence of a surface band in energy range of 1 to 2 eV, i.e. relatively far from the Fermi level. We expect this surface band to originate from a band inversion between the fourth and higher-energy bands, and that it is absent in the TB modelling due to the enforced detachment of those bands [cf. Sec. 1B].

To better visualize the surface states, we now consider the full slab band structure for $N = 200$ layers instead of just the surface spectral function, and we compute the inverse participation ratio (IPR) of each state. The IPR of a (normalized) state vector $\psi$ is defined as

$$\text{IPR}(\psi) = \sum_{n=1}^{N} p_n(\psi)^2,$$

where the sum is over the layer index $n$, and $p_n(\psi)$ is the probability of an electron in state $\psi$ to be found in layer $n$ (in any of

FIG. S8. (a) Quaternion charge in the full surface Brillouin zone and the projection of bulk nodal lines for $s = 0$. As indicated in the legend, we assign colors to the equivalence classes of the quaternion charge according to the representation in terms of the generators $g_1, g_2, g_3$, such that e.g. the overlap of red and green (yellow) corresponds to $\pm g_1 g_2$. For illustration purposes we do not distinguish between elements of different signs even in the cases where they are in different equivalence classes ($\pm 1$ and $\pm g_1 g_2$). This does not impair the presentation of results, because the gray region coincidentally is always $+1$, while the distinction of $\pm g_1 g_2$ is fragile under the addition of additional trivial bands. (b–d) Band structure of the unstrained slab Hamiltonian of Li$_2$NaN defined in Eq. (S17) for $N = 200$ layers and different values of $k_2$, corresponding to three cuts through the surface Brillouin zone. The color scale indicates the inverse participation ratio (IPR), Eq. (S20), according to the legend on the right. The cuts at $k_2 \neq 0$ clearly reveal that the two surface bands lie in gaps 1−2 and 2−3.
FIG. S9. Quaternion charge and the projection of bulk nodal lines for $s = -0.05 \text{ eV}$. See caption to Fig. S8(a) for a description of the legend. The panel on the left shows the full surface Brillouin zone (SBZ), the panel on the right a close-up on $|k_2| < 0.15$, with the inset showing the details of the multi-band nodal link. The four vertical gray lines in the right panel indicate the cuts for which the slab band structure and IPR are plotted in Fig. S10.

FIG. S10. Band structure of the slab Hamiltonian of Li$_2$NaN defined in Eq. (S17) for $N = 200$ layers and $s = -0.05 \text{ eV}$, plotted for different values of $k_2$ corresponding to the four cuts through the SBZ shown in the right panel of Fig. S9. The color scale indicates the inverse participation ratio (IPR), Eq. (S20), according to the legend on the right. Below panels (a--c) the extent of each surface band is indicated by a colored horizontal bar, where the color indicates the gap in which the surface band occurs. The color scheme matches the one of Fig. S9, which is indicated by the corresponding generators $g_j$. Multiplying the generators $g_j$ that are present at a given $k_3$ results in the quaternion charge, as shown in the bottom-most bar. The colors of this latter bar match Fig. S9 along the corresponding cut. We omit this discussion in panel (d) due to the difficulty to recognize the hybridized surface bands at this combination of $s$ and $k_2$. See main text for more details.

the four basis orbitals). The IPR is a measure of localization: a state $\psi$ perfectly and uniformly localized on $m$ layers satisfies $\text{IPR}(\psi) = 1/m$, which for a completely delocalized state becomes $1/N$.

In general, surface states can hybridize with bulk states that project to the same point in the SBZ and lie at the same energy. However, as long as the hybridization is not too strong, they are still localized and are thus visible via the IPR. To uncover all surface states, we look at the evolution of the band structure (and IPR) when increasing the strain parameter $s$ from 0 to $-0.2$ [Fig. S7] for $k_2 = 0$. In the strained case [panels (b–d)] we identify a total of four surface bands: one formed by bands $1-2$, two by $2-3$ and one by $3-4$. For large enough $s$, the first and last surface band are located in bulk energy gaps, while the other two clearly hybridize with bulk states. In the unstrained case [panel (a)], only two surface bands are visible, one between bands $1-2$, and one between bands $2-3$.

We now discuss the correspondence between the bulk quaternion charges and the surface states. The naively expected bulk-boundary correspondence [72] suggests that surface states appear between bands $j$ and $j+1$ if the quaternion charge contains the generator $g_j$ as a factor (which corresponds to an inversion of those two bands). Similar to Fig. 3(g) in the main text, we show the bulk quaternion charge for the closed paths projecting onto points in the SBZ in the absence of strain [Fig. S8(a)] and
with a large tensile strain [Fig. S9].

To start our comparison, we first consider the unstrained case, when the quaternion charge near $k_2 = k_3 = 0$ is $\pm g_1 g_2$ [Fig. S8(a)]. Note that the quaternion charge is not well-defined at the line $k_2 = 0$, because red NLs project onto the SBZ there. In accordance with the anticipated bulk-boundary correspondence, we find one surface band in both the first and the second energy gap [cf. Fig. S8(b,d)]. For another comparison, we consider a large strain value $s = -0.05 \text{ eV}$. The quaternion charges over the whole SBZ are displayed in Fig. S9, and we compare them to the surface states for various $k_2$ and $k_3$ [Fig. S10]. We again find a correspondence with the anticipated bulk-boundary correspondence [72], however, one has to be careful with the counting and with the inclusion of the surface bands that hybridize with the bulk states, therefore we expound a few cases in more detail.

Referring to Fig. S10 for surface bands and to the right panel of Fig. S9 for the quaternion charge, we make the following observations. In panels (a–c) there are four surface states states: one between bands 1–2, two of different extent along $k_3$ between bands 2–3 and one between 3–4. First, for all four cuts the quaternion charge contains a factor $g_1$, which is consistent with the surface band in the gap 1–2 extending over all $k_3$ values. Furthermore, the surface band in the gap 3–4 corresponds to a factor $g_3$ which appears inside the blue nodal ring in Fig. S9, and thus the corresponding range of $k_3$ shrinks for increasing $k_2$ [panels (a–c)] until it vanishes completely [panel (d)]. Finally, for the surface bands in the 2–3 gap, the discussion becomes a bit more involved due to the missing bulk gap, which leads to hybridization of the possible surface states with the bulk states. Nevertheless, we are able to identify two surface bands between these two bands, which are barely visible in panels (a–c), but not visible anymore in panel (d). For values of $k_3$ where both of these surface bands are present, we expect a trivialization ($\pm g_2^2 \sim \pm 1$) and thus correspondence to no factor $g_2$ in the quaternion charge, while $g_2$ should be present if there is only one of these two surface bands. Note that in panels (a,b) the 2–3 surface band higher in energy has an extent in $k_3$ which is slightly smaller than the one of the 3–4 surface band, such that a (small) region with surface bands in all three gaps results. This is consistent with the small white overlap shown in the inset of the right panel of Fig. S9. The white region has vanished in the third cut [panel (c)], which is reflected in the upper 2–3 surface band now having a larger extent in $k_3$ than the 3–4 surface band.

**IV. DENSITY OF STATES AND OPTICAL CONDUCTIVITY OF Li$_2$NaN**

In this section we elaborate on the calculations and results for the density of states and the optical conductivity of Li$_2$NaN, which have only been briefly discussed in the main text. In preparation for these calculations, we compute the cumulative density of states for the TB model for various values of the strain parameter using the Python package wannier-berri [79, 94]. We use an initial $k$-space grid of 400$^3$ points and perform 40 iterations of adaptive refinement, cf. [87] for the full Python script and the explicit results. By imposing charge neutrality, we can deduce the Fermi level $E_F$ for each case.

**A. Density of states**

We verify the observation of a large jump in the density of states (DOS) near the Fermi level by computing it for the TB model using the Python package wannier-berri [79, 94]. Starting with an initial $k$-space grid of 400$^3$ points we perform 2600

![FIG. S11. Density of states (DOS) of Li$_2$NaN for chemical potential $\mu$ near the Fermi level $E_F$ obtained from the tight-binding model without and with strain. The inset shows a close-up of the jump at $\mu = E_F$. The data is smoothed by a moving average over ten points.](image-url)
FIG. S12. The real and the imaginary part of the interband optical conductivity in S/cm for different values of the strain parameter $s$ (cf. inset legend on the top left).

iterations of adaptive refinement [cf. [87] for the full Python script]. The results of this calculation for $s \in \{0, -0.01, -0.03\}$ eV are presented in Fig. S11. Note that in reality the jumps would be smeared over a region of approximately 40 meV due to the dispersion along $\Gamma A$ which is assumed to be completely flat in the TB model.

The single large jump from approximately 0.5 eV$^{-1}$ to $7 \times 10^{-3}$ eV at the Fermi level for the unstrained case is split into two consecutive jumps at approximately $-2s$ and slightly above the Fermi level for the strained case. Just as the single jump is explained by the flat dispersion of the two degenerate bands of the 2D IR along $\Gamma A$, the double jump follows from the same two bands after being split by the symmetry-breaking strain. This is consistent with the distance between the two jumps being $2s$ and thus equal to the energy splitting of the nitrogen $p_{x,y}$ orbitals.

B. Optical conductivity

For the calculation of the optical (interband) conductivity of $\text{Li}_2\text{NaN}$ based on our TB model using the Python package wannier-berri [79, 94] we chose an initial grid of 625$^3$ points in $k$-space and ten iterations of adaptive refinement. Furthermore, the Kubo formula requires us to choose a smearing parameter for approximating the delta function [79] and we set that to $\eta = 0.01$ eV. The full Python script used to obtain the data is given in Ref. [87].

Here we present additional results for the optical conductivity that are not shown in the main text. We show both the real and the imaginary part of all non-vanishing components of $\sigma_{\alpha\beta}$. Note that in the absence of strain $\sigma_{xx} = \sigma_{yy}$ due to the symmetries. Similar to Re $\sigma_{xx}$, which we discussed in the main text, Re $\sigma_{yy}$ is strongly suppressed for small $\hbar \omega$ when increasing the strain parameter $s$. However, while the peak of Re $\sigma_{xx}$ near $\hbar \omega \approx 0.32$ eV is decreased when applying strain, it becomes more pronounced (and is shifted towards larger frequencies) for Re $\sigma_{yy}$. While the imaginary part can be obtained from the real part using the Kramers-Kronig relation, it highlights the differences of $\sigma_{xx}$ and $\sigma_{yy}$ under strain. In both cases there is a large drop and thus a local minimum for finite but small frequencies, but in Im $\sigma_{yy}$ this is accompanied by the formation of a sharp peak at higher frequencies. This peak is located roughly at $\hbar \omega \approx 2 |s|$ and becomes very pronounced for large $s$.

V. TRIPLE-POINT MATERIALS

In the main text we present three materials exhibiting TPs that have not been reported previously [cf. compounds in Table I marked with †]. We identified these materials based on the symmetry criteria given by our classification and first-principles calculations [cf. Sec. I A]. Figure S13 shows the band structure near one of the TPs along the relevant rotation-invariant line in each of those compounds as well as the irreducible co-representations of the involved bands. This justifies the placement of those material candidates in Table I of the main text. We study the TPs of these materials and their associated attached nodal-line arcs in detail in our companion paper [70], where we explicitly verify the agreement with the presented classification of the TPs.
FIG. S13. Band structure near the triple point (TP) and irreducible co-representations of the corresponding bands along the relevant rotation-invariant line for (a) AlN, (b) CaNaP, and (c) Na$_2$O. The relevant TP is marked by a yellow dot and arrow. Note that in some of the materials there are additional TPs present, some of them may be of a different type than the one marked. A detailed study of these materials appears in our companion work [70].