First-principles calculation of topological invariants Z_2 within the FP-LAPW formalism

Wanxiang Feng,[1,2,3] Jun Wen,[4] Jinjian Zhou,[1] Di Xiao,[2] and Yugui Yao[1,*]

[1]*Beijing National Laboratory for Condensed Matter Physics and Institute of Physics,*

Chinese Academy of Sciences, Beijing 100190, China

[2]*Materials Science & Technology Division,*

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

[3]*Department of Physics and Astronomy,*

University of Tennessee, Knoxville, Tennessee 37996, USA

[4]*Department of Physics, University of Texas at Austin, Austin, Texas 78712, USA*

(Dated: July 15, 2011)

Abstract

In this paper, we report the implementation of first-principles calculations of topological invariants Z_2 within the full-potential linearized augmented plane-wave (FP-LAPW) formalism. In systems with both time-reversal and spatial inversion symmetry (centrosymmetric), one can use the parity analysis of Bloch functions at time-reversal invariant momenta to determine the Z_2 invariants. In systems without spatial inversion symmetry (noncentrosymmetric), however, a more complex and systematic method in terms of the Berry gauge potential and the Berry curvature is required to identify the band topology. We show in detail how both methods are implemented in FP-LAPW formalism and applied to several classes of materials including centrosymmetric compounds Bi_2Se_3 and Sb_2Se_3 and noncentrosymmetric compounds LuPtBi, $AuTlS_2$ and $CdSnAs_2$. Our work provides an accurate and effective implementation of first-principles calculations to speed up the search of new topological insulators.

PACS numbers: 71.15.-m, 71.20.-b, 71.70.-d, 73.20.At

I. INTRODUCTION

Recently, topological insulators (TIs) have attracted great attention in the fields of condensed matter physics and materials science. Based on the noninteracting band theory, TIs have gapped bulk gap and time-reversal symmetry protected metallic helical surface (edge) states where spin and momentum are locked together.[1,2] These novel physical properties hold great promise in applications of spintronics and quantum computing[3] and have stimulated both experimental and theoretical studies. Indeed, the field of TIs is expanding so rapidly and there have been several excellent review articles on it.[4–6] Although many TIs including alloy[7,8], binary compounds[9–14], ternary compounds[15–28], and quaternary compounds[29] have already been theoretically predicted and experimentally realized, real materials that can be used in practical engineering are still needed. Therefore searching for new TIs with a variety of excellent physical properties has become a central task in this filed. To achieve this goal, one has to develop an accurate and effective method to distinguish TIs from normal insulators.

There are several general methods to determine the band topology of an insulator:

(i) Based on the idea of bulk-edge correspondence of TIs,[3–6] one can calculate surface (edge) states for a given insulator and count the number of gapless modes across the Fermi level. An odd number of gapless modes implies a TI while an even number indicates a normal insulator. This is a straightforward but not efficient way because the surface state dispersion may depend on every detail of the surface, for example, grown directions, terminated chemical elements and surface reconstructions. In some materials, the topologically nontrivial and trivial surface states can coexist, which further complicates the identification of the bulk topological order. To make sure that the gapless modes are topologically protected, one has to vary surface crystal structures and see if gapless modes can survive. Furthermore, a huge amount of computational resources is required in first-principles surface calculations.

(ii) It is possible to use adiabatic continuity and so-called band inversion mechanism to identify TIs.[16–19,23,36] The adiabatic continuity can be realized by artificially changing some external parameter such as the spin-orbit coupling (SOC) strength or lattice constant. Suppose the unknown state is near some known topological trivial or nontrivial states in a parameter space. If one tunes the parameter and the band gap stays open until it reaches

the known state, then by the principle of adiabatic continuity, these two states share the same topological classification. Otherwise, the unknown state and known state may have different topological classifications if the band gap closes. Obviously, many intermediate calculations are required, making it a very tedious work. Band inversion at high-symmetry points within the Brillouin zone (BZ), as an empirical rule, can also be used to reveal the band topology. Although this empirical rule is adapted in some materials, such as half-Heusler[15–17], chalcogenide[18,19], and chalcopyrite[23] compounds, it is not an universal way for arbitrary systems.

(iii) The most general and direct approach is to calculate Z_2 topological invariants from the knowledge of Bloch band theory.[30–32] For materials with both time-reversal and spatial inversion symmetry (centrosymmetric systems), the simple parity criterion developed by Fu and Kane[11] have been applied in a number of works.[12,19,25,26,28] On the other hand, if the spatial inversion symmetry is absent (noncentrosymmetric systems), one must resort to a more complex method to evaluate Z_2 invariants.[33] Within a tight-binding framework, Fukui and Hatsugai[34] have developed an effective algorithm to compute Z_2 invariants in terms of the Berry gauge potential and the Berry curvature[35] associated with the Bloch functions (BFs). This method has already been implemented in our first-principles codes and successfully predicted three-dimensional (3D) TIs in ternary half-Heusler[15] and chalcopyrite[23] compounds and two-dimensional (2D) quantum spin hall effect (QSHE) in Silicene.[36] Recently there appears another method which is in the same spirit of Ref. 33 but employs the charge center of Wannier functions.[37,38]

In this work, we illustrate the detailed implementation of first-principles calculations of topological invariants Z_2 in both centrosymmetric and noncentrosymmetric systems within the full-potential linearized augmented plane-wave (FP-LAPW) formalism. Although the latter method for noncentrosymmetric systems can be applied to centrosymmetric systems, the parity criterion for centrosymmetric systems is a simpler and quicker way to determine the band topology. For this reason, we here introduce both of these methods. It should be emphasized that our methods are standard post-process after ground state wavefunctions are obtained in self-consistent calculation, so the calculation of Z_2 invariants becomes a routine task just like band structures and density of states. Additionally, we have already paralleled our first-principles codes to speed up the calculation. Our implementation of the calculation of Z_2 invariants is expected to be an efficient way for searching new TIs.

The paper is organized as follows. In Sec. II, we review the fundamental expression of BFs within FP-LAPW formalism and the construction of overlap matrix, and then give the detailed formalism for implementation of parity analysis in centrosymmetric systems and lattice calculation of Z_2 invariants in noncentrosymmetric systems. In Sec. III, we take centrosymmetric compounds Bi_2Se_3 and Sb_2Se_3 and noncentrosymmetric compounds LuPtBi, $AuTlS_2$ and $CdSnAs_2$ to illustrate the efficiency of our methods. Finally, we give a brief summary of our work in Sec. IV. In App. A, we provide details on the overlap matrix and its derivatives.

II. METHODS

In this section, we start by reviewing the formalism of BFs within FP-LAPW formalism and the construction of overlap matrix,[39–41] then illustrate the calculation of Z_2 invariants in both centrosymmetric and noncentrosymmetric systems. The key is to calculate the eigenvalues of parity operator according to parity criterion[11] (in the former case) or the overlap matrices related to time-reversal operator[34] (in the latter case).

A. Bloch functions and overlap matrix

In the case of SOC, we consider BFs with two components,

$$\Psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \begin{bmatrix} \psi_{n\boldsymbol{k}}^{\uparrow}(\boldsymbol{r}) \\ \psi_{n\boldsymbol{k}}^{\downarrow}(\boldsymbol{r}) \end{bmatrix}, \tag{1}$$

where $\uparrow$ and $\downarrow$ refer to the up and down component of spin. The periodic part of BFs is $u_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \begin{bmatrix} \psi_{n\boldsymbol{k}}^{\uparrow}(\boldsymbol{r}) & \psi_{n\boldsymbol{k}}^{\downarrow}(\boldsymbol{r}) \end{bmatrix}^{\mathrm{T}}$, where T is the transpose operator. The electrons in a solid environment have two different behaviors: those that are far from the nuclei and "free"-like can be described by plane waves, and those that are close to nuclei and unaffected by other nuclei can be described by atomic like functions. Within FP-LAPW formalism, the space is divided into two regions: a sphere with radius R_α around each atom, often called the muffin-tin region and the remaining space is interstitial region.[39–41] As a result, the BFs of electrons are always divided into two parts. Plane waves are used to construct the BFs in interstitial region

$$\psi_{nk}^{\sigma}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{j} z_{nk,j}^{\sigma} e^{i(\boldsymbol{k}+\boldsymbol{K}_j)\cdot\boldsymbol{r}}, \quad \boldsymbol{r} \in I, \tag{2}$$

where Ω is unit cell volume, $z_{nk,j}^{\sigma}$ is the expansion coefficient, σ and n stand for spin and band index, $\boldsymbol{k}$ for $\boldsymbol{k}$-points wave vector, $\boldsymbol{K}_j$ for the j-th reciprocal-lattice vector, j for the loop index of every expansion term and up to a largest value by the condition $|\boldsymbol{k}+\boldsymbol{K}_j| \leq \boldsymbol{K}_{max}$, and $\boldsymbol{K}_{max}$ for the cutoff vector. Within the muffin-tin region (suppose the α-th atom sphere with radius R_α), the BFs can be written as

$$\psi_{nk}^{\sigma,\alpha}(\boldsymbol{r}) = \sum_{lm} \left[A_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) u_{l,1}^{\sigma,\alpha} + B_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) \dot{u}_{l,1}^{\sigma,\alpha} + C_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) u_{l,2}^{\sigma,\alpha} + D_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) u_{l,1/2}^{\sigma,\alpha} \right] Y_{lm}(\hat{\boldsymbol{r}}^{\alpha}),$$

$$|\boldsymbol{r} - \boldsymbol{\tau}^{\alpha}| \in \boldsymbol{R}_{\alpha}, \quad (3)$$

with

$$A_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) = \sum_{j} z_{nk,j}^{\sigma} \tilde{A}_{lm}^{\sigma,\alpha}(\boldsymbol{k}+\boldsymbol{K}_j) + \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{A}_{l_0 m_0}^{\sigma,\alpha}(\boldsymbol{k}+\boldsymbol{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0},$$

$$B_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) = \sum_{j} z_{nk,j}^{\sigma} \tilde{B}_{lm}^{\sigma,\alpha}(\boldsymbol{k}+\boldsymbol{K}_j) + \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{B}_{l_0 m_0}^{\sigma,\alpha}(\boldsymbol{k}+\boldsymbol{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0},$$

$$C_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) = \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{C}_{l_0 m_0}^{\sigma,\alpha}(\boldsymbol{k}+\boldsymbol{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0},$$

$$D_{lm}^{\sigma,\alpha}(n,\boldsymbol{k}) = \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{D}_{l_0 m_0}^{\sigma,\alpha}(\boldsymbol{k}+\boldsymbol{K}_{j_0}) \delta_{l,l_0} \delta_{m,m_0}. \tag{4}$$

where $\boldsymbol{r}^{\alpha} = \boldsymbol{r} - \boldsymbol{\tau}^{\alpha}$ and $\boldsymbol{\tau}^{\alpha}$ is the position of atom α; lm is the angular momentum index; Y_{lm} is spherical harmonics. In above formulas, $u_{l,1}^{\sigma,\alpha} \equiv u_l^{\sigma}(r^{\alpha}, E_{l,1}^{\alpha})$ and $\dot{u}_{l,1}^{\sigma,\alpha} \equiv \dot{u}_l^{\sigma}(r^{\alpha}, E_{l,1}^{\alpha})$ are the radial solutions of scalar-relativistic Schrï¿œedinger equation of atom α and their energy derivatives, both evaluated at energy $E_{l,1}^{\alpha}$. The local orbit radial functions $u_{l,2}^{\sigma,\alpha} \equiv u_l^{\sigma}(r^{\alpha}, E_{l,2}^{\alpha})$ are added to the $u_{l,1}^{\sigma,\alpha}$ and $\dot{u}_{l,1}^{\sigma,\alpha}$ for semi-core states (when $l = l_0$) and aimed to increase the variational freedom of standard basis functions. The last radial functions $u_{l,1/2}^{\sigma,\alpha} \equiv u_l^{\sigma}(r^{\alpha}, E_{l,1/2}^{\alpha})$, as the radial solution of full-relativistic Dirac equation, is also added to the u_l^{σ} and $\dot{u}_{l,1}^{\sigma,\alpha}$ but only for $5p_{1/2}$ or $6p_{1/2}$ orbits in heavy elements.[42] This extended full-relativistic local orbit can improve the accuracy of second-variational step when taking account of SOC. The $\tilde{A}_{lm}^{\sigma,\alpha}$ and $\tilde{B}_{lm}^{\sigma,\alpha}$ are the coefficients of LAPW basis set, and $\tilde{B}_{lm}^{\sigma,\alpha}$ is zero

when APW basis set is used. $\tilde{A}^{\sigma,\alpha}_{l_0 m_0}$, $\tilde{B}^{\sigma,\alpha}_{l_0 m_0}$, $\tilde{C}^{\sigma,\alpha}_{l_0 m_0}$, and $\tilde{D}^{\sigma,\alpha}_{l_0 m_0}$ are the coefficients of local orbit basis set. These coefficients can be determined by imposing various boundary conditions at the muffin-tin boundaries.[39–41]

Considering a lattice division within BZ, the overlap matrix between $\boldsymbol{k}$ point and its nearest-neighbor $\boldsymbol{k} + \boldsymbol{b}$ has the form

$$M^{(\boldsymbol{k},\boldsymbol{b})}_{mn} = \left\langle u^{\uparrow}_{m,\boldsymbol{k}} | u^{\uparrow}_{n,\boldsymbol{k}+\boldsymbol{b}} \right\rangle + \left\langle u^{\downarrow}_{m,\boldsymbol{k}} | u^{\downarrow}_{n,\boldsymbol{k}+\boldsymbol{b}} \right\rangle . \tag{5}$$

Overlap matrix $M^{(\boldsymbol{k},\boldsymbol{b})}_{mn}$ is a very useful quantity in many Berry-phase related calculations,[43,44] and the detailed formulas for its calculations are demonstrated in Appendix.

B. Parity criterion in centrosymmetric system

For systems with spatial inversion symmetry, Z_2 invariants can be obtained by parity analysis developed by Fu and Kane[11]. In 3D system there are eight time-reversal invariant momenta (TRIM) in BZ, $\boldsymbol{\Gamma}_{i=(n_1 n_2 n_3)} = \frac{1}{2}(n_1 \boldsymbol{G}_1 + n_2 \boldsymbol{G}_2 + n_3 \boldsymbol{G}_3)$, where $\boldsymbol{G}_j$ are primitive reciprocal-lattice vectors with $n_j = 0$, or 1. The Z_2 invariants are determined by the quantities

$$\delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i). \tag{6}$$

Here, $\xi_{2m}(\Gamma_i) = \pm 1$ is the parity eigenvalue of the *2m*-th occupied energy band at TRIMs Γ_i, i.e. $\langle \Psi_{2m,\Gamma_i} | P | \Psi_{2m,\Gamma_i} \rangle$, where P is parity operator. Because of the Kramers degeneracy at TRIMs, the *2m*-th and (*2m-1*)-th occupied bands have the same eigenvalues, i.e., $\xi_{2m} = \xi_{2m-1}$. In 3D system, there are four independent invariants $\nu_0; (\nu_1 \nu_2 \nu_3)$, given by[11]

$$(-1)^{\nu_0} = \prod_{i=1}^{8} \delta_i, \tag{7}$$

$$(-1)^{\nu_k} = \prod_{n_k=1, n_{j \neq k}=0,1} \delta_{i=(n_1 n_2 n_3)}, \tag{8}$$

where ν_0 is independent of the choice of primitive reciprocal-lattice vectors $\boldsymbol{G}_j$ while ν_1, ν_2, and ν_3 are not. A nonzero ν_0 indicates that the system is a strong topological insulator (STI). When $\nu_0 = 0$, the systems are further classified according to ν_1, ν_2, and ν_3. The

systems with $\nu_{1,2,\text{or }3} \neq 0$ are called weak topological insulators (WTI), while $0; (000)$ is normal insulator (NI).

To obtain Z_2 invariants, the basic job is to calculate the matrix elements of parity operator $\langle \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) |P| \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) \rangle$ with even band index n at eight TRIMs Γ_i. The parity operator P is defined as $\{I; \boldsymbol{t}\}$, where I is an inverse matrix making $\boldsymbol{r} \rightarrow -\boldsymbol{r}$ and $\boldsymbol{t}$ is a translational vector. Since parity operation will not change spin component of BFs, then,

$$\langle \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) |P| \Psi_{n\boldsymbol{k}}(\boldsymbol{r}) \rangle = \left\langle \psi_{n\boldsymbol{k}}^{\uparrow}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}^{\uparrow}(\boldsymbol{r}) \right\rangle + \left\langle \psi_{n\boldsymbol{k}}^{\downarrow}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}^{\downarrow}(\boldsymbol{r}) \right\rangle. \tag{9}$$

In the following, we take $\left\langle \psi_{n\boldsymbol{k}}^{\uparrow}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}^{\uparrow}(\boldsymbol{r}) \right\rangle$ as an example and suppress the spin index from here. Suppose that $\tilde{\psi}_{n\boldsymbol{k}}(\boldsymbol{r}) = P\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ and inversion center at $\frac{\boldsymbol{t}}{2}$, then $\tilde{\psi}_{n\boldsymbol{k}}\left(\frac{\boldsymbol{t}}{2} - \boldsymbol{r}\right) = \psi_{n\boldsymbol{k}}\left(\frac{\boldsymbol{t}}{2} + \boldsymbol{r}\right)$. It can be rewritten as $\tilde{\psi}_{n\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{t} - \boldsymbol{r})$, and finally we have $P\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{t} - \boldsymbol{r})$. The matrix elements of parity operator are divided into two parts

$$\langle \psi_{n\boldsymbol{k}}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}(\boldsymbol{r}) \rangle = \langle \psi_{n\boldsymbol{k}}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}(\boldsymbol{r}) \rangle_I + \sum_{\alpha} \langle \psi_{n\boldsymbol{k}}^{\alpha}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}^{\alpha}(\boldsymbol{r}) \rangle_{MT^{\alpha}}. \tag{10}$$

The contribution of interstitial region is

$$\langle \psi_{n\boldsymbol{k}}(\boldsymbol{r}) |P| \psi_{n\boldsymbol{k}}(\boldsymbol{r}) \rangle_I = \frac{1}{\Omega} \sum_{ij} z_{n\boldsymbol{k},i}^* z_{n\boldsymbol{k},j} \int_{cell} e^{-i(\boldsymbol{k}+\boldsymbol{K}_i)\cdot \mathbf{r}} e^{i(\boldsymbol{k}+\boldsymbol{K}_j)\cdot(\boldsymbol{t}-\boldsymbol{r})} \Delta(\boldsymbol{r}) d^3 r$$

$$= \frac{1}{\Omega} \sum_{ij} z_{n\boldsymbol{k},i}^* z_{n\boldsymbol{k},j} e^{i(\boldsymbol{k}+\boldsymbol{K}_j)\cdot \boldsymbol{t}} \Delta(2\boldsymbol{k} + \boldsymbol{K}_i + \boldsymbol{K}_j). \tag{11}$$

Here, $\Delta(\boldsymbol{r})$ is a step function with zero value in muffin-tin sphere and unit value in interstitial region and $\Delta(\boldsymbol{K})$ is its Fourier transformation. While inside the muffin-tin region, the radial coefficients in Eq. (4) can be rewritten as a product of two parts, one of which depends on atomic positions and the other does not. For example, $A_{lm}^{\alpha}(n, \boldsymbol{k}) = \sum_j \eta_{n,lm}(\boldsymbol{k} + \boldsymbol{K}_j, R_\alpha) e^{i(\boldsymbol{k}+\boldsymbol{K}_j)\cdot \boldsymbol{\tau}^{\alpha}}$, where $\boldsymbol{\tau}^{\alpha}$ is the position of α-th atom and $\eta_{n,lm}(\mathbf{k} + \boldsymbol{K}_j, R_\alpha)$ is independent of $\boldsymbol{\tau}^{\alpha}$. Therefore,

$$PA_{lm}^{\alpha}(n, \boldsymbol{k}) = \sum_j \eta_{n,lm}(\boldsymbol{k} + \boldsymbol{K}_j, R_\alpha) e^{i(\boldsymbol{k}+\boldsymbol{K}_j)\cdot(\boldsymbol{t}-\boldsymbol{\tau}^{\alpha})}. \tag{12}$$

If atom α is operated by parity operator, it must overlap another equivalent atom β by translated integer numbers of primitive real-lattice, i.e. $\boldsymbol{t} - \boldsymbol{\tau}^{\alpha} = \boldsymbol{R}_h + \boldsymbol{\tau}^{\beta}$ with $\boldsymbol{R}_h = $

$h_1\mathbf{a}_1 + h_2\mathbf{a}_2 + h_3\mathbf{a}_3$, where h_j is integer number and $\mathbf{a}_j$ is primitive real-lattice vector. Then above equation can be rewritten as

$$PA^{\alpha}_{lm}(n, \boldsymbol{k}) = \sum_j \eta_{n,lm}(\boldsymbol{k} + \boldsymbol{K}_j, R_\beta) e^{i(\boldsymbol{k}+\boldsymbol{K}_j)\cdot\boldsymbol{\tau}^\beta} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_h}$$

$$= A^{\beta}_{lm}(n, \boldsymbol{k}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}_h}, \tag{13}$$

and there are similar operations for $PB^{\alpha}_{lm}(n, \boldsymbol{k})$, $PC^{\alpha}_{lm}(n, \boldsymbol{k})$, and $PD^{\alpha}_{lm}(n, \boldsymbol{k})$. The spherical harmonics operated by parity operator is, $PY_{lm}(\hat{\boldsymbol{r}}^\alpha) = (-1)^l Y_{lm}(\hat{\boldsymbol{r}}^\alpha)$. Then we have

$$P\psi^{\alpha}_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}_h} \sum_{lm}\left[A^{\beta}_{lm}(n,\boldsymbol{k})u^{\alpha}_{l,1} + B^{\beta}_{lm}(n,\boldsymbol{k})\dot{u}^{\alpha}_{l,1} + C^{\beta}_{lm}(n,\boldsymbol{k})u^{\alpha}_{l,2} + D^{\beta}_{lm}(n,\boldsymbol{k})u^{\alpha}_{l,1/2}\right](-1)^l Y_{lm}(\hat{\boldsymbol{r}}^\alpha).$$
$$\tag{14}$$

Therefore, we can easily obtain $P\psi^{\alpha}_{n\boldsymbol{k}}(\boldsymbol{r})$ by using radial coefficients of atom β, $A^{\beta}_{lm}(n, \boldsymbol{k})$, $B^{\beta}_{lm}(n, \boldsymbol{k})$, $C^{\beta}_{lm}(n, \boldsymbol{k})$, and $D^{\beta}_{lm}(n, \boldsymbol{k})$, which have already been calculated. Finally, the calculation of $\langle\psi^{\alpha}_{n\boldsymbol{k}}(\boldsymbol{r})|P|\psi^{\alpha}_{n\boldsymbol{k}}(\boldsymbol{r})\rangle$ is very similar to $\langle\psi^{\alpha}_{n\boldsymbol{k}}(\boldsymbol{r})|\psi^{\alpha}_{n\boldsymbol{k}}(\boldsymbol{r})\rangle$, which can be found in Appendix.

C. Lattice calculation of Z_2 invariants in noncentrosymmetric system

A nontrivial topological invariant Z_2 can be interpreted as an obstruction to make the BFs smoothly defined over BZ under time-reversal constrains.[30–32] Here, we present a lattice evaluation of the Z_2 invariants in terms of the Berry gauge potential and Berry curvature associated with the BFs.[34] This method has been recently applied to our first-principles studies of ternary half-Heusler[15] and chalcopyrite[23] TIs and QSHE in Silicene thinfilm.[36]

We first briefly describe the formalism for a 2D system. It was shown by Fu and Kane[33] that under the time-reversal constraint, the Z_2 invariants can be written as

$$Z_2 = \frac{1}{2\pi}\left[\oint_{\partial\mathcal{B}^+} d\boldsymbol{k}\cdot\boldsymbol{\mathcal{A}}(\boldsymbol{k}) - \int_{\mathcal{B}^+} d^2k\,\mathcal{F}(\boldsymbol{k})\right]\bmod 2, \tag{15}$$

where $\mathcal{B}^+$ and $\partial\mathcal{B}^+$ represent *half* of BZ and its boundary (Fig. 1). The central quantities are the Berry connection

$$\boldsymbol{\mathcal{A}} = i\sum_n \langle u_n(\boldsymbol{k})|\boldsymbol{\nabla}_{\boldsymbol{k}} u_n(\boldsymbol{k})\rangle \tag{16}$$

Figure 1: (Color online) Schematic drawing of lattice mesh in a two-dimensional Brillouin zone. Under the time-reversal constraint, only *half* of Brillouin zone $\mathcal{B}^+$ is needed, which is denoted by shaded region. The thick lines indicate the boundary of $\mathcal{B}^+$, i.e., $\partial\mathcal{B}^+$, and the open arrows denote their directions. All $\boldsymbol{k}$-points are divided into three classes: $\mathcal{B}_s^+$, $\mathcal{B}_s^-$, and $\mathcal{B}_s^0$, which are represented by small (black) solid, small (black) open and large (blue) solid circles, respectively.

and the Berry curvature

$$\mathcal{F}(\boldsymbol{k}) = \boldsymbol{\nabla}_{\boldsymbol{k}} \times \boldsymbol{\mathcal{A}}(\boldsymbol{k}) \mid_z, \tag{17}$$

where $|u_n(\boldsymbol{k})\rangle$ is the periodic part of BFs and the sum is over occupied bands. TIs are characterized by $Z_2 = 1$ while normal insulators have $Z_2 = 0$.

In the following, we introduce the calculation of $|u_n(\boldsymbol{k})\rangle$ in *half* of BZ referred to as $\mathcal{B}^+$ ($[-\boldsymbol{G}_1/2, \boldsymbol{G}_1/2] \otimes [-\boldsymbol{G}_2/2, 0]$) according to the time-reversal constraint. As shown in Fig. 1, the $\boldsymbol{k}$-points on a 2D BZ with $N \times N$ division are divided into three classes: $\mathcal{B}_s^+$, $\mathcal{B}_s^-$, and $\mathcal{B}_s^0$. Firstly, we obtain $|u_n(\boldsymbol{k})\rangle$ in $\mathcal{B}_s^+$ except for the points on the right edge. The points on the right edge ($\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G_1}$) are the periodic images of those on the left edge ($\boldsymbol{k}$), and can be calculated by using the periodic gauge[43,44]

$$|u_n(\boldsymbol{k} + \boldsymbol{G_1})\rangle = e^{-i\boldsymbol{G_1} \cdot \boldsymbol{r}} |u_n(\boldsymbol{k})\rangle. \tag{18}$$

Secondly, we consider the $\mathcal{B}_s^-$ points on the boundary $\partial\mathcal{B}^+$, i.e., the left part of the bottom

9

edge and the right part of top edge. These points $-\boldsymbol{k} \in \mathcal{B}_s^-$ are the Kramers doublets of $\boldsymbol{k} \in \mathcal{B}_s^+$ points, so they can be calculated by the time-reversal constraint,

$$|u_n\left(-\boldsymbol{k}\right)\rangle = \Theta\left|u_n\left(\boldsymbol{k}\right)\right\rangle, \text{ for } \boldsymbol{k} \in \mathcal{B}_s^+. \tag{19}$$

where $\Theta = -i\sigma_y K$ is the time-reversal operator with K the complex conjugation. Note that translational phase factors must be properly considered. For example, $\boldsymbol{k}' \in \mathcal{B}_s^-$ and $\boldsymbol{k} \in \mathcal{B}_s^+$ are two points which are centrosymmetric about the midpoint of the bottom edge, i.e., $\boldsymbol{k}' = -\boldsymbol{k} - \boldsymbol{G}_2$, then we have

$$\begin{aligned}
|u_n\left(\boldsymbol{k}'\right)\rangle &= |u_n\left(-\boldsymbol{k} - \boldsymbol{G_2}\right)\rangle \\
&= e^{i\boldsymbol{G_2}\cdot\boldsymbol{r}}\left|u_n\left(-\boldsymbol{k}\right)\right\rangle \\
&= e^{i\boldsymbol{G_2}\cdot\boldsymbol{r}}\Theta\left|u_n\left(\boldsymbol{k}\right)\right\rangle.
\end{aligned} \tag{20}$$

Finally, we calculate $|u_n\left(\boldsymbol{k}\right)\rangle$ on TRIMs, i.e., $\mathcal{B}_s^0$, satisfied by $\Theta H(\boldsymbol{k})\Theta^{-1} = H(\boldsymbol{k})$. The eigenvalues are $\ldots\varepsilon_{2n-1}\left(\boldsymbol{k}\right) = \varepsilon_{2n}\left(\boldsymbol{k}\right) \leq \varepsilon_{2n+1}\left(\boldsymbol{k}\right) = \varepsilon_{2n+2}\left(\boldsymbol{k}\right)\ldots$ because of the Kramers degeneracy. In this situation, the time-reversal constraint is given by

$$|u_{2n}\left(-\boldsymbol{k}\right)\rangle = \Theta\left|u_{2n-1}\left(\boldsymbol{k}\right)\right\rangle, \ -\boldsymbol{k} \text{ and } \boldsymbol{k} \in \mathcal{B}_s^0. \tag{21}$$

There are six TRIMs in *half* of BZ $\mathcal{B}^+$, $-\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2$, $-\boldsymbol{G}_1/2$, $-\boldsymbol{G}_2/2$, $\boldsymbol{0}$, $\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2$, and $\boldsymbol{G}_1/2$. For the former four points, the $2n$-th eigenstates can be obtained from $(2n-1)$-th eigenstates by using above constraint. Here, one should also consider the translational phase factor, for example,

$$\begin{aligned}
|u_{2n}\left(-\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2\right)\rangle &= e^{i(\boldsymbol{G}_1+\boldsymbol{G}_2)\cdot\boldsymbol{r}}\left|u_{2n}\left(\boldsymbol{G}_1/2 + \boldsymbol{G}_2/2\right)\right\rangle \\
&= e^{i(\boldsymbol{G}_1+\boldsymbol{G}_2)\cdot\boldsymbol{r}}\Theta\left|u_{2n-1}\left(-\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2\right)\right\rangle.
\end{aligned} \tag{22}$$

The other two points, $\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2$, and $\boldsymbol{G}_1/2$, can be obtained by their periodic image points, i.e. $|u_n\left(\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2\right)\rangle = e^{-i\boldsymbol{G}_1\cdot\boldsymbol{r}}\left|u_n\left(-\boldsymbol{G}_1/2 - \boldsymbol{G}_2/2\right)\right\rangle$, $|u_n\left(\boldsymbol{G}_1/2\right)\rangle = e^{-i\boldsymbol{G}_1\cdot\boldsymbol{r}}\left|u_n\left(-\boldsymbol{G}_1/2\right)\right\rangle$.

After applying the time-reversal constrain Eq. (19) and Eq. (21) and periodic gauge Eq. (18), we have obtained a new set of basis functions $|\tilde{u}_n\left(\boldsymbol{k}\right)\rangle$. Next, we introduce the link variable that is central to many Berry-phase related calculations,[43,44] given by

$$U_{\boldsymbol{\mu}}(\boldsymbol{k}_j) = N_{\boldsymbol{\mu}}^{-1}(\boldsymbol{k}_j) \det \langle \tilde{u}_m(\boldsymbol{k}_j) \mid \tilde{u}_n(\boldsymbol{k}_j + \boldsymbol{\mu}) \rangle, \tag{23}$$

where $N_{\boldsymbol{\mu}}^{-1}(\boldsymbol{k}_j) = |\det \langle \tilde{u}_m(\boldsymbol{k}_j) \mid \tilde{u}_n(\boldsymbol{k}_j + \boldsymbol{\mu}) \rangle|$ is the normalizing factor and $\boldsymbol{\mu}$ is the unit vector on the $\boldsymbol{k}$-mesh. In practice, $\langle \tilde{u}_m(\boldsymbol{k}_j) \mid \tilde{u}_n(\boldsymbol{k}_j + \boldsymbol{\mu}) \rangle$ is the overlap matrix $\langle u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k}+\boldsymbol{\mu}} \rangle$ or its derivatives with the time-reversal operator Θ including $\langle u_{m,\boldsymbol{k}}|\Theta u_{n,\boldsymbol{k}+\boldsymbol{\mu}} \rangle$, $\langle \Theta u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k}+\boldsymbol{\mu}} \rangle$, and $\langle \Theta u_{m,\boldsymbol{k}}|\Theta u_{n,\boldsymbol{k}+\boldsymbol{\mu}} \rangle$. The calculation of $\langle \tilde{u}_m(\boldsymbol{k}_j) \mid \tilde{u}_n(\boldsymbol{k}_j + \boldsymbol{\mu}) \rangle$ is demonstrated in Appendix.

The finite element expressions for Berry connection $\boldsymbol{\mathcal{A}}$ and Berry curvature $\mathcal{F}$ are

$$\boldsymbol{\mathcal{A}}_{\boldsymbol{\mu}}(\boldsymbol{k}_j) = \operatorname{Im} \log U_{\boldsymbol{\mu}}(\boldsymbol{k}_j), \tag{24}$$

and

$$\mathcal{F}(\boldsymbol{k}_j) = \operatorname{Im} \log U_{\boldsymbol{\mu}}(\boldsymbol{k}_j) U_{\boldsymbol{\nu}}(\boldsymbol{k}_j + \boldsymbol{\mu}) U_{\boldsymbol{\mu}}^{-1}(\boldsymbol{k}_j + \boldsymbol{\nu}) U_{\boldsymbol{\nu}}^{-1}(\boldsymbol{k}_j), \tag{25}$$

where the return value of the complex logarithm function is confined to its principal branch $(-\pi, \pi]$. We can then insert these expressions into Eq. (15) to calculate the Z_2 invariants.

To visualize the above procedure, an integer field $n(\boldsymbol{k}_j)$ can be defined for each torus:

$$n(\boldsymbol{k}_j) = \frac{1}{2\pi} \left\{ [\Delta_{\boldsymbol{\nu}} \boldsymbol{\mathcal{A}}_{\boldsymbol{\mu}}(\boldsymbol{k}_j) - \Delta_{\boldsymbol{\mu}} \boldsymbol{\mathcal{A}}_{\boldsymbol{\nu}}(\boldsymbol{k}_j)] - \mathcal{F}(\boldsymbol{k}_j) \right\}, \tag{26}$$

where $\Delta_{\boldsymbol{\mu}}$ is the forward difference operator. The Z_2 invariants are given by the sum of the n-field in *half* of the BZ, i.e., $Z_2 = \sum_{\boldsymbol{k}_j \in \mathcal{B}^+} n(\boldsymbol{k}_j) \bmod 2$. The sum of n-field configuration over the entire BZ gives a vanished Chern number for time-reversal invariant systems. It must be emphasized that the n-field summed over *half* of BZ is gauge-invariant module 2 even though itself depends on a specific gauge choice.

In 3D system, there are six possible 2D tori. These 2D tori are defined as follows: for example, the torus $T(X_0)$ is spanned by G_2 and G_3 with the first component fixed at 0, and $T(X_1)$ is obtained by fixing the first component at $-G_1/2$. The other four tori $T(Y_0)$, $T(Y_1)$, $T(Z_0)$, and $T(Z_1)$ are defined similarly. For each torus, one can calculate the corresponding Z_2 invariants, x_0, x_1, y_0, y_1, z_0, and z_1, by using the steps outlined above for 2D BZ. Out of the six possible Z_2 invariant only four of them are independent due to the constraint $x_0 + x_1 = y_0 + y_1 = z_0 + z_1 \pmod 2$. Following Refs. 30–32, we denote four independent

11

Figure 2: Schematic drawing of four independent tori in a three-dimensional Brillouin zone. The four independent tori $T(Z_0)$, $T(Z_1)$, $T(X_0)$ and $T(Y_0)$ are located at $k_3 = 0$, $k_3 = -G_3/2$, $k_1 = 0$, and $k_2 = 0$, respectively.

Z_2 invariants by $\nu_0; (\nu_1\nu_2\nu_3)$, with $\nu_0 = (z_0 + z_1) \bmod 2$, $\nu_1 = x_1$, $\nu_2 = y_1$ and $\nu_3 = z_1$. The corresponding four independent tori $T(Z_0)$, $T(Z_1)$, $T(X_0)$ and $T(Y_0)$ are shown in Fig. 2.

III. RESULTS

In this section, we apply our methods to both centrosymmetric and noncentrosymmetric systems. In the case of centrosymmetric compounds Bi_2Se_3 and Sb_2Se_3, our parity analysis shows that Bi_2Se_3 is a STI while Sb_2Se_3 is a NI. The lattice calculation of Z_2 invariants has also been used as a double check and the results are consistent with the parity analysis. We then turn to noncentrosymmetric compounds LuPtBi, $AuTlS_2$ and $CdSnAs_2$. By turning lattice constant, we studied three different topological phases of LuPtBi, i.e., STI, topological metal (TM), and NI. Furthermore, the Z_2 invariants show that chalcopyrite compounds $AuTlS_2$ and $CdSnAs_2$ are STI and NI, respectively, in their native states without any strain.

The calculations of band structures and Z_2 invariants in this work were performed using FP-LAPW method,[39,40] implemented in the package WIEN2K.[41] We used two types of exchange-correlation potentials. The generalized gradient approximation (GGA)[45] was used for Bi_2Se_3 and Sb_2Se_3, while the modified Becke-Johnson exchange potential together

with local-density approximation for the correlation potential (MBJLDA)[46] was used for LuPtBi, AuTlS$_2$, and CdSnAs$_2$ because the resulting band topology is sensitive to the choice of exchange-correlation potentials in these systems.[47] The converged ground state was obtained using $K_{max}R_{MT} = 9.0$ for each system, where K_{max} is the maximum size of reciprocal-lattice vector and R_{MT} represents the smallest muffin-tin radius. The $\boldsymbol{k}$-points sampling in BZ was also carefully checked such that self-consistent field calculations were well converged. Spin-orbit coupling was included by a second-variational procedure,[39] where states up to 9 Ry above Fermi level were included in the basis expansion, and the relativistic $p_{1/2}$ corrections[42] were also considered for $5p$ and $6p$ orbit in order to improve the accuracy for systems including heavy elements.

For a given system, the time taken by calculating of Z_2 invariants depends on numbers of lattice divisions on four independent tori in 3D BZ and numbers of occupied bands considered below the Fermi level. For most of systems, a 10×10 lattice division on each torus is enough for obtaining a converged result just as mentioned in Ref. 34. However, one must be very careful with the cases of small local band gaps, for example the system shown in Fig. 6(c), 50×50 lattice division is need to reach the convergence. The included number of occupied bands should always been explicitly separated with other low-lying bands with an obvious global energy gap. The principle is that these low-lying bands are usually closed shell with much lower energy and should have trivial band topology. In the following, we chose 18, 18, 30, 40 and 20 occupied bands for Bi$_2$Se$_3$, Sb$_2$Se$_3$, LuPtBi, AuTlS$_2$ and CdSnAs$_2$, respectively.

A. Centrosymmetric systems

To demonstrate the quality of our methods, we first test the centrosymmetric systems Bi$_2$Se$_3$ and Sb$_2$Se$_3$. Recently, Bi$_2$Se$_3$ family of compounds have been both theoretically and experimentally observed to be TIs with an exception of Sb$_2$Se$_3$.[12–14] Tetradymite semiconductor Bi$_2$Se$_3$ family has a rhombohedral crystal structure with space group $R\bar{3}m$ (No. 166) and three nonequivalent atoms in a primitive cell. The calculated band structures of Bi$_2$Se$_3$ and Sb$_2$Se$_3$ are presented in Fig. 3 with the lattice constants taken from previous studies.[12] The 18 occupied bands ($-6 \sim 0$ eV) are isolated from other low-lying bands and fully determine the topological nature of the systems, so we consider them as a bands group in the following calculation of Z_2 invariants.

Table I: Parities δ_i at eight TRIMs for Bi_2Se_3 and Sb_2Se_3. The relative coordinates in primitive reciprocal-lattice of eight TRIMs are (0, 0, 0), (0, 0, 0.5), (0, 0.5, 0), (0, 0.5, 0.5), (0.5, 0, 0), (0.5, 0, 0.5), (0.5, 0.5, 0), (0.5, 0.5, 0.5). The Z_2 invariants are 1; (000) for Bi_2Se_3 and 0; (000) for Sb_2Se_3, which indicate a STI and a NI respectively.

	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	$\nu_0; (\nu_1\nu_2\nu_3)$
Bi_2Se_3	-1	+1	+1	+1	+1	+1	+1	+1	1;(000)
Sb_2Se_3	+1	+1	+1	+1	+1	+1	+1	+1	0;(000)

Because the existence of spatial inversion symmetry, the parity criterion[11] is applicable here. As a first step, we choose eight TRIMs in 3D BZ with relative coordinates (0, 0, 0), (0, 0, 0.5), (0, 0.5, 0), (0, 0.5, 0.5), (0.5, 0, 0), (0.5, 0, 0.5), (0.5, 0.5, 0), (0.5, 0.5, 0.5) in a primitive reciprocal-lattice. Then, we calculate the parity eigenvalues of 9 occupied bands with even band index (sorted by energy) out of 18 occupied bands at every TRIM. The parity of each TRIM, $\delta_{i=1,2,...8}$ in Eq. (6), are obtained by multiplying over the parity eigenvalues of these 9 bands. The Z_2 invariant ν_0 is obtained by multiplying over the parities of all TRIMs according to Eq. (7), while $\nu_{k=1,2,3}$ by multiplying over the parities of TRIMs resided in the same plane according to Eq. (8). The δ_i and Z_2 invariants are listed in Table I. The Z_2 invariants are 1; (000) for Bi_2Se_3 and 0; (000) for Sb_2Se_3, indicating a STI and a NI respectively. One can see that the main difference lies at Γ point, i.e., δ_1 is -1 for Bi_2Se_3 and $+1$ for Sb_2Se_3, while the other TRIMs share the same parities. We also give the parity eigenvalues of these 9 bands at Γ point, as listed in Table II.

We have also used the lattice calculation of Z_2 invariants as a double check. Figure 4 shows the n-field configuration for Bi_2Se_3. The Z_2 invariants on each torus are $z_0 = 1$, $z_1 = 0$, $x_0 = 1$, and $y_0 = 1$ by the sum of the n-field in *half* of 2D BZ and then moduling 2. Total Z_2 invariants 1;(000) indicate that Bi_2Se_3 is a STI. On the other hand, Figure 5 shows the n-field configuration for Sb_2Se_3 with $z_0 = 0$, $z_1 = 0$, $x_0 = 0$, and $y_0 = 0$ on each torus. Total Z_2 invariants 0;(000) indicate that Sb_2Se_3 is a NI. As expected, our lattice calculation of Z_2 invariants are the same as parity analysis, and all of these two methods are consistent with the previous work.[12]

Figure 3: Band structures of strong topological insulator Bi_2Se_3 with Z_2 invariants $1;(000)$ and normal insulator Sb_2Se_3 with Z_2 invariants $0;(000)$. The eighteen occupied bands (every two of them are twofold degenerate) from -6 to 0 eV are used to calculate Z_2 invariants. The high-symmetry points in Brillouin zone are the same as Ref. 12.

Table II: Parity eigenvalues of Bi_2Se_3 and Sb_2Se_3 at Γ point for 9 occupied bands. The corresponding band energy increases from left to right. The parity of Γ point, δ_1, is -1 for Bi_2Se_3 and $+1$ for Sb_2Se_3 respectively.

										δ_1
Bi_2Se_3	-1	+1	+1	-1	-1	+1	-1	-1	+1	(-1)
Sb_2Se_3	-1	-1	+1	-1	+1	+1	-1	-1	-1	(+1)

B.   Noncentrosymmetric systems

Having established the effectiveness of our methods in centrosymmetric systems, we now turn to noncentrosymmetric systems by taking LuPtBi as the first example. It has been predicted that LuPtBi, as a member of ternary half-Heusler family, can realize a topological nontrivial state under uniaxial strain.[15–17,47,48] The crystal structure of LuPtBi is described by space group $F\bar{4}3m$ (No. 216) with three nonequivalent atoms in a primitive cell. The calculations were performed using the experimental lattice constant of 6.574 Å.[49] As shown in Fig. 6(a), LuPtBi is a semi-metal with small electron and hole pockets around Fermi level at Γ point. The band gap around Γ point can be obtained by applying an uniaxial strain, then 30 occupied bands (from -8 to about 0 eV) were used to calculate Z_2 invariants.

Figure 4: The n-field configuration for Bi_2Se_3 computed under the time-reversal constraints. The four tori are $T(Z_0)$, $T(Z_1)$, $T(X_0)$ and $T(Y_0)$ with the shaded area indicating *half* of the 2D BZ. The white and black circles denote n = 1 and −1, respectively, while the blank denotes 0. The Z_2 invariants for each individual torus is obtained by summing the n-field over *half* of the torus and then moduling 2. These read $z_0 = 1$, $z_1 = 0$, $x_0 = 1$, and $y_0 = 1$. The Z_2 invariants of the system are 1;(000).

As mentioned in our previous works,[15,47] topological phases of half-Heusler family are very sensitive to the change of lattice constants. Generally speaking, hydrostatic expansion leads to topological nontrivial phases while hydrostatic compression leads to topological trivial phases. Additionally, one must apply an uniaxial strain based on hydrostatic strain, i.e., a non-hydrostatic strain, to realize true topological insulating state because the states around Fermi level at Γ point are fourfold degenerate and protected by cubic symmetry. Therefore it is necessary to fully understand how the strain (hydrostatic and non-hydrostatic) acts on the topological phase in half-Heusler family.

By turning lattice constants $a(= b)$ and c, we found three different topological phases of LuPtBi including STI, TM, and NI, as shown in Fig. 6(b), 6(c), and 6(d), respectively. The non-hydrostatic strains can separate the fourfold degenerate states of valence and conduction bands around Γ point. In the case of Fig. 6(b), the global band gap together with Z_2 invariants 1; (000) indicate that this is a STI. While in the case of Fig. 6(c), it is essentially

Figure 5: The n-field configuration of Sb_2Se_3. The labels are the same as Fig. 4. The Z_2 invariants for each individual torus read $z_0 = 0$, $z_1 = 0$, $x_0 = 0$, and $y_0 = 0$. The Z_2 invariants of the system are $0;(000)$.

a metallic state but has local band gap everywhere in the BZ. The Z_2 invariants $1;(000)$ show a nontrivial state which is usually called TM. On the other hand, hydrostatic strain (large enough compression) can also create a band gap, just like Fig. 6(d), but this is a NI because the Z_2 invariants are $0;(000)$.

Ternary chalcopyrite compounds of composition I-III-VI$_2$ or II-IV-V$_2$ are another important class of noncentrosymmetric TIs. In our previous work,[23] we have shown that a large number of ternary chalcopyrite compounds can realize the topological insulating phase in their native states. Here we take $AuTlS_2$ and $CdSnAs_2$ as noncentrosymmetric examples to show our methods for Z_2 invariants calculation. The crystal structure of chalcopyrite is described by the space group $I\bar{4}2d$ (No. 122) with three nonequivalent atoms in a primitive cell, which can be regarded as a superlattice of the zinc-blende structure with small structural distortions. The crystal structure parameters of $AuTlS_2$ $\eta = 1.016$ and $\delta u = -0.018$ are obtained by first-principles total energy minimization, and the experimental data $\eta = 0.980$ and $\delta u = 0.261$[50] are used for $CdSnAs_2$, where $\eta = c/2a$ is the tetragonal distortion ratio and δu is the internal displacement of anion.[23] $AuTlS_2$ and $CdSnAs_2$ are all semiconductors with band gap of 0.14 eV and 0.13 eV, as shown in Fig. 7(a) and 7(b) respectively. Totally

Figure 6: Band structures of LuPtBi with the static lattice constant (a) $[a_0 = b_0 = c_0 = 6.574\text{Å}]$, non-hydrostatic strains (b) $[a_0 - 4\%a_0, c_0 - 6\%c_0]$ and (c) $[a_0 + 6\%a_0, c_0 - 2\%c_0]$, and hydrostatic strain (d) $[a_0 - 8\%a_0, c_0 - 8\%c_0]$. The topological phases in (a), (b), and (c) are topological insulator, topological metal, and normal insulator, respectively. The 30 occupied bands (from -8 to about 0 eV) are used to calculate Z_2 invariants.

40 and 20 occupied bands ($-6 \sim 0$ eV) are used to calculate Z_2 invariants for $AuTlS_2$ and $CdSnAs_2$, respectively. We find that $AuTlS_2$ is a STI with the Z_2 invariants 1;(000) while $CdSnAs_2$ is a NI with the Z_2 invariants 0;(000).

IV. SUMMARY

In summary, we have presented the implementation of first-principles calculations of topological invariants Z_2 in both centrosymmetric and noncentrosymmetric systems within FP-LAPW formalism. Generally, one can use a lattice version of Z_2 invariants to identify the band topology, though in centrosymmetric systems, a simple parity criterion is possible.

Figure 7: Band structures of strong topological insulator $AuTlS_2$ with Z_2 invariants $1;(000)$ and normal insulator $CdSnAs_2$ with Z_2 invariants $0;(000)$. The occupied bands which range from $-6 \sim 0$ eV are included for calculating Z_2 invariants, i.e. 40 bands for $AuTlS_2$ and 20 bands for $CdSnAs_2$ respectively. The high-symmetry points in Brillouin zone are the same as Ref. 51.

The n-field configuration depends on a specific gauge, but the resulting Z_2 invariants are gauge-invariant. Our method has two merits: (i) the algorithm implemented in our FP-LAPW framework is not expensive and the first-principles code can be easily paralleled; (ii) it is designed as a standard post-process of first-principles calculations, so the identification of topological nature for a given material becomes a routine task. Therefore, our method is able to identify TIs in relatively short time and we anticipate it will speed up the discovery of new topological insulators in future.

Acknowledgments

Appendix A: Overlap matrix and its derivatives with the time-reversal operator

In this appendix, we give the overlap matrix $\langle u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k}+\boldsymbol{b}}\rangle$ and its derivatives with the time-reversal operator Θ, including $\langle u_{m,\boldsymbol{k}}|\Theta u_{n,\boldsymbol{k}+\boldsymbol{b}}\rangle$, $\langle \Theta u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k}+\boldsymbol{b}}\rangle$, and $\langle \Theta u_{m,\boldsymbol{k}}|\Theta u_{n,\boldsymbol{k}+\boldsymbol{b}}\rangle$, where m and n stand for band indexes, and $\boldsymbol{b}$ stands for unit vector $\boldsymbol{\mu}$ or $\boldsymbol{\nu}$ on $\boldsymbol{k}$-mesh (see Fig. 1).

Firstly, we consider the overlap matrix $\langle u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k}+\boldsymbol{b}}\rangle$ according to Eq. (5),

$$\langle u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k}+\boldsymbol{b}}\rangle = \left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle + \left\langle u_{m,\boldsymbol{k}}^{\downarrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow}\right\rangle. \tag{A1}$$

Here we only discuss $\left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle$ because that $\left\langle u_{m,\boldsymbol{k}}^{\downarrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow}\right\rangle$ has the similar formulas. Like the BFs, the overlap matrix can also be divided into two parts: interstitial region and muffin-tin region,

$$\left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle = \left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle_{I} + \sum_{\alpha}\left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle_{MT^{\alpha}}. \tag{A2}$$

The contribution of interstitial region is

$$\begin{aligned}\left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle_{I} &= \sum_{j}\sum_{j'} z_{m,\boldsymbol{k},j}^{\uparrow*} z_{n,\boldsymbol{k}+\boldsymbol{b},j'}^{\uparrow} \frac{1}{\Omega}\int_{cell} e^{\left[-i(\boldsymbol{K}_{j}-\boldsymbol{K}_{j'})\cdot\boldsymbol{r}\right]}\Delta\left(\boldsymbol{r}\right) d^{3}r \\ &= \sum_{j}\sum_{j'} z_{m,\boldsymbol{k},j}^{\uparrow*} z_{n,\boldsymbol{k}+\boldsymbol{b},j'}^{\uparrow} \Delta\left(\boldsymbol{K}_{j}-\boldsymbol{K}_{j'}\right). \end{aligned} \tag{A3}$$

Here, $\Delta(\boldsymbol{r})$ is a step function, it have zero value in muffin-tin sphere and unit value in interstitial region, and it's Fourier transform is

$$\Delta\left(\boldsymbol{K}\right) = \delta_{\boldsymbol{K},\boldsymbol{0}} - \sum_{\alpha} e^{-i\boldsymbol{K}\cdot\boldsymbol{\tau}^{\alpha}}\frac{4\pi R_{\alpha}^{3}}{\Omega}\frac{j_{1}\left(KR_{\alpha}\right)}{KR_{\alpha}}.$$

The contribution of α-th muffin-tin sphere is

$$\begin{aligned}\left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow}\right\rangle_{MT^{\alpha}} &= \int_{MT^{\alpha}} e^{i\boldsymbol{k}\cdot(\boldsymbol{\tau}^{\alpha}+\boldsymbol{r}^{\alpha})}\left[\psi_{m,\boldsymbol{k}}^{\uparrow\alpha}(\boldsymbol{r})\right]^{*} e^{-i(\boldsymbol{k}+\boldsymbol{b})\cdot(\boldsymbol{\tau}^{\alpha}+\boldsymbol{r}^{\alpha})}\psi_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow\alpha}(\boldsymbol{r})d^{3}r \\ &= e^{-i\boldsymbol{b}\cdot\boldsymbol{\tau}^{\alpha}}\int_{MT^{\alpha}}\left[\psi_{m,\boldsymbol{k}}^{\uparrow\alpha}(\boldsymbol{r})\right]^{*}\psi_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow\alpha}(\boldsymbol{r})e^{-i\boldsymbol{b}\cdot\boldsymbol{r}^{\alpha}}d^{3}r. \end{aligned} \tag{A4}$$

Using the Rayleigh plane-wave expansion

$$e^{-i\boldsymbol{b}\cdot\boldsymbol{r}^\alpha} = 4\pi \sum_{l''m''} (-i)^{l''} Y_{l''m''}^* \left(\hat{\boldsymbol{b}}\right) Y_{l''m''} \left(\hat{\boldsymbol{r}}^\alpha\right) j_{l''} \left(br^\alpha\right), \tag{A5}$$

where $r^\alpha = |\boldsymbol{r}^\alpha|$, $b = |\boldsymbol{b}|$, and $j_{l''}\left(br^\alpha\right)$ is the spherical bessel function. Then,

$$
\begin{aligned}
\left\langle u_{m,\boldsymbol{k}}^\uparrow | u_{n,\boldsymbol{k}+\boldsymbol{b}}^\uparrow \right\rangle_{MT^\alpha} &= 4\pi e^{-i\boldsymbol{b}\cdot\boldsymbol{\tau}^\alpha} \sum_{l''m''} (-i)^{l''} Y_{l''m''}^* \left(\hat{\boldsymbol{b}}\right) \\
&\times \sum_{lm}\sum_{l'm'} \Bigg\{ \left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[\dot{u}_{l,1}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[\dot{u}_{l,1}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[\dot{u}_{l,1}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[\dot{u}_{l,1}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,2}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,2}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,2}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,2}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1/2}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1/2}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1/2}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] \\
&+ \left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^* D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k}+\boldsymbol{b}) \left[u_{l,1/2}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] \Bigg\} G_{ll'l''}^{mm'm''}. \tag{A6}
\end{aligned}
$$

Therefore, the matrix elements $\left\langle u_{m,\boldsymbol{k}}^\uparrow | u_{n,\boldsymbol{k}+\boldsymbol{b}}^\uparrow \right\rangle_{MT^\alpha}$ are constructed by two parts: radial in-

tegrals and angular integrals. The radial integrals are

$$\left[u_{l,1}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) \dot{u}_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1/2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[\dot{u}_{l,1}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 \dot{u}_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[\dot{u}_{l,1}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 \dot{u}_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) \dot{u}_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[\dot{u}_{l,1}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 \dot{u}_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[\dot{u}_{l,1}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 \dot{u}_l^\uparrow \left(r^\alpha, E_{l,1}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1/2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,2}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,2}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,2}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,2}^\alpha\right) \dot{u}_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,2}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,2}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,2}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,2}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1/2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1/2}^{\uparrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1/2}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1/2}^{\uparrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1/2}^\alpha\right) \dot{u}_{l'}^\uparrow \left(r^\alpha, E_{l',1}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1/2}^{\uparrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1/2}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr,$$

$$\left[u_{l,1/2}^{\uparrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',b}\right] = \int_0^{R^\alpha} r^2 u_l^\uparrow \left(r^\alpha, E_{l,1/2}^\alpha\right) u_{l'}^\uparrow \left(r^\alpha, E_{l',1/2}^\alpha\right) j_{l''} \left(br^\alpha\right) dr, \tag{A7}$$

and the angular integrals is the Gaunt coefficients

$$G_{ll'l''}^{mm'm''} = \int Y_{lm}^* \left(\hat{r}\right) Y_{l'm'} \left(\hat{r}\right) Y_{l''m''} \left(\hat{r}\right) d\Omega. \tag{A8}$$

Secondly, we consider the matrix element $\langle u_{m,\boldsymbol{k}} | \Theta u_{n,\boldsymbol{k+b}} \rangle$,

$$\langle u_{m,\mathbf{k}}|\Theta u_{n,\mathbf{k}+\mathbf{b}}\rangle = -\left\langle u_{m,\mathbf{k}}^{\uparrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\downarrow *}\right\rangle + \left\langle u_{m,\mathbf{k}}^{\downarrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\uparrow *}\right\rangle, \tag{A9}$$

and take $\left\langle u_{m,\mathbf{k}}^{\uparrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\downarrow *}\right\rangle$ as example, it can be divided into two parts:

$$\left\langle u_{m,\mathbf{k}}^{\uparrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\downarrow *}\right\rangle = \left\langle u_{m,\mathbf{k}}^{\uparrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\downarrow *}\right\rangle_{I} + \sum_{\alpha}\left\langle u_{m,\mathbf{k}}^{\uparrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\downarrow *}\right\rangle_{MT^{\alpha}}. \tag{A10}$$

Within the interstitial region,

$$
\begin{aligned}
\left\langle u_{m,\mathbf{k}}^{\uparrow}|u_{n,\mathbf{k}+\mathbf{b}}^{\downarrow *}\right\rangle_{I} &= \sum_{j}\sum_{j'} z_{m\mathbf{k},j}^{\uparrow *} z_{n\mathbf{k}+\mathbf{b},j'}^{\downarrow *} \frac{1}{\Omega}\int_{cell} e^{\left[-i\left(\mathbf{K}_{j}+\mathbf{K}_{j'}\right)\cdot\mathbf{r}\right]}\Theta\left(\mathbf{r}\right)d^{3}r \\
&= \sum_{j}\sum_{j'} z_{m\mathbf{k},j}^{\uparrow *} z_{n\mathbf{k}+\mathbf{b},j'}^{\downarrow *}\Theta\left(\mathbf{K}_{j}+\mathbf{K}_{j'}\right), \tag{A11}
\end{aligned}
$$

while inside the muffin-tin region (α-th atom sphere),

23

$$\left\langle u_{m,\boldsymbol{k}}^{\uparrow}|u_{n,\boldsymbol{k+b}}^{\downarrow *}\right\rangle_{MT^{\alpha}} = 4\pi e^{i(2\boldsymbol{k+b})\cdot\boldsymbol{\tau}^{\alpha}}\sum_{l''m''}i^{l''}Y_{l''m''}^{*}\left(\widehat{2\boldsymbol{k+b}}\right)$$

$$\times\sum_{lm}\sum_{l'm'}\left\{\left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[A_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1}^{\uparrow,\alpha}u_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]\right.$$

$$+\left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[B_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1}^{\uparrow,\alpha}\dot{u}_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[C_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1}^{\uparrow,\alpha}u_{l',2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[A_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[D_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1}^{\uparrow,\alpha}u_{l',1/2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[A_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[\dot{u}_{l,1}^{\uparrow,\alpha}u_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[B_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[\dot{u}_{l,1}^{\uparrow,\alpha}\dot{u}_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[C_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[\dot{u}_{l,1}^{\uparrow,\alpha}u_{l',2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[B_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[D_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[\dot{u}_{l,1}^{\uparrow,\alpha}u_{l',1/2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[A_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,2}^{\uparrow,\alpha}u_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[B_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,2}^{\uparrow,\alpha}\dot{u}_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[C_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,2}^{\uparrow,\alpha}u_{l',2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[C_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[D_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,2}^{\uparrow,\alpha}u_{l',1/2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[A_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1/2}^{\uparrow,\alpha}u_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[B_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1/2}^{\uparrow,\alpha}\dot{u}_{l',1}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$+\left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[C_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1/2}^{\uparrow,\alpha}u_{l',2}^{\downarrow,\alpha}j_{l'',2k+b}\right]$$

$$\left.+\left[D_{lm}^{\uparrow\alpha}(m,\boldsymbol{k})\right]^{*}\left[D_{l'm'}^{\downarrow\alpha}(n,\boldsymbol{k+b})\right]^{*}\left[u_{l,1/2}^{\uparrow,\alpha}u_{l',1/2}^{\downarrow,\alpha}j_{l'',2k+b}\right]\right\}(-1)^{m'}G_{ll'l''}^{m-m'm''}.$$

$$\tag{A12}$$

Thirdly, we consider the matrix element $\langle\Theta u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k+b}}\rangle$,

$$\langle\Theta u_{m,\boldsymbol{k}}|u_{n,\boldsymbol{k+b}}\rangle = -\left\langle u_{m,\boldsymbol{k}}^{\downarrow *}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle + \left\langle u_{m,\boldsymbol{k}}^{\uparrow *}|u_{n,\boldsymbol{k+b}}^{\downarrow}\right\rangle, \tag{A13}$$

and take $\left\langle u_{m,\boldsymbol{k}}^{\downarrow *}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle$ as example, it can be divided into two parts

$$\left\langle u_{m,\boldsymbol{k}}^{\downarrow *}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle = \left\langle u_{m,\boldsymbol{k}}^{\downarrow *}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle_{I} + \sum_{\alpha}\left\langle u_{m,\boldsymbol{k}}^{\downarrow *}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle_{MT^{\alpha}}. \tag{A14}$$

Within the interstitial region,

$$\left\langle u_{m,\boldsymbol{k}}^{\downarrow*}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle_I = \sum_j \sum_{j'} z_{m\boldsymbol{k},j}^{\downarrow} z_{n\boldsymbol{k+b},j'}^{\uparrow} \frac{1}{\Omega} \int_{cell} e^{\left[i\left(\boldsymbol{K}_j+\boldsymbol{K}_{j'}\right)\cdot\boldsymbol{r}\right]} \Theta\left(\boldsymbol{r}\right) d^3 r$$

$$= \sum_j \sum_{j'} z_{m\boldsymbol{k},j}^{\downarrow} z_{n\boldsymbol{k+b},j'}^{\uparrow} \Theta\left[-\left(\boldsymbol{K}_j+\boldsymbol{K}_{j'}\right)\right], \tag{A15}$$

while inside the muffin-tin region (α-th atom sphere),

$$\left\langle u_{m,\boldsymbol{k}}^{\downarrow*}|u_{n,\boldsymbol{k+b}}^{\uparrow}\right\rangle_{MT^\alpha} = 4\pi e^{-i(2\boldsymbol{k+b})\cdot\boldsymbol{\tau}^\alpha} \sum_{l''m''} (-i)^{l''} Y_{l''m''}^* \left(\widehat{2\boldsymbol{k+b}}\right)$$

$$\times \sum_{lm} \sum_{l'm'} \Bigg\{ A_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1}^{\downarrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ A_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1}^{\downarrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ A_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1}^{\downarrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ A_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1}^{\downarrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ B_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[\dot{u}_{l,1}^{\downarrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ B_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[\dot{u}_{l,1}^{\downarrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ B_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[\dot{u}_{l,1}^{\downarrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ B_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[\dot{u}_{l,1}^{\downarrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ C_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,2}^{\downarrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ C_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,2}^{\downarrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ C_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,2}^{\downarrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ C_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,2}^{\downarrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ D_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) A_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1/2}^{\downarrow,\alpha} u_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ D_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) B_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1/2}^{\downarrow,\alpha} \dot{u}_{l',1}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ D_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) C_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1/2}^{\downarrow,\alpha} u_{l',2}^{\uparrow,\alpha} j_{l'',2k+b}\right]$$

$$+ D_{lm}^{\downarrow\alpha}(m,\boldsymbol{k}) D_{l'm'}^{\uparrow\alpha}(n,\boldsymbol{k+b}) \left[u_{l,1/2}^{\downarrow,\alpha} u_{l',1/2}^{\uparrow,\alpha} j_{l'',2k+b}\right] \Bigg\} (-1)^m G_{ll'l''}^{-mm'm''}. \tag{A16}$$

Finally, we consider the matrix element $\langle \Theta u_{m,\boldsymbol{k}} | \Theta u_{n,\boldsymbol{k}+\boldsymbol{b}} \rangle$,

$$\langle \Theta u_{m,\boldsymbol{k}} | \Theta u_{n,\boldsymbol{k}+\boldsymbol{b}} \rangle = \left\langle u_{m,\boldsymbol{k}}^{\downarrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow *} \right\rangle + \left\langle u_{m,\boldsymbol{k}}^{\uparrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\uparrow *} \right\rangle, \tag{A17}$$

and take $\left\langle u_{m,\boldsymbol{k}}^{\downarrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow *} \right\rangle$ as example, it also can be divided into two parts

$$\left\langle u_{m,\boldsymbol{k}}^{\downarrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow *} \right\rangle = \left\langle u_{m,\boldsymbol{k}}^{\downarrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow *} \right\rangle_I + \sum_\alpha \left\langle u_{m,\boldsymbol{k}}^{\downarrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow *} \right\rangle_{MT^\alpha}. \tag{A18}$$

Within the interstitial region,

$$
\begin{aligned}
\left\langle u_{m,\boldsymbol{k}}^{\downarrow *} | u_{n,\boldsymbol{k}+\boldsymbol{b}}^{\downarrow *} \right\rangle_I &= \sum_j \sum_{j'} z_{m\boldsymbol{k},j}^{\downarrow} z_{n\boldsymbol{k}+\boldsymbol{b},j'}^{\downarrow *} \frac{1}{\Omega} \int_{cell} e^{\left[i \left(\boldsymbol{K}_j - \boldsymbol{K}_{j'} \right) \cdot \boldsymbol{r} \right]} \Theta\left(\boldsymbol{r} \right) d^3 r \\
&= \sum_j \sum_{j'} z_{m\boldsymbol{k},j}^{\downarrow} z_{n\boldsymbol{k}+\boldsymbol{b},j'}^{\downarrow *} \Theta\left[-\left(\boldsymbol{K}_j - \boldsymbol{K}_{j'} \right) \right],
\end{aligned}
\tag{A19}
$$

while inside the muffin-tin region (α-th atom sphere),

$$\left\langle u^{\downarrow *}_{m,\boldsymbol{k}}\big|u^{\downarrow *}_{n,\boldsymbol{k}+\boldsymbol{b}}\right\rangle_{MT^\alpha} = 4\pi e^{i\boldsymbol{b}\cdot\boldsymbol{\tau}^\alpha}\sum_{l''m''} i^{l''} Y^*_{l''m''}\left(\widehat{\boldsymbol{b}}\right)$$

$$\times \sum_{lm}\sum_{l'm'}\Big\{ A^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[A^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1}u^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ A^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[B^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1}\dot{u}^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ A^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[C^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1}u^{\downarrow,\alpha}_{l',2}j_{l'',b}\right]$$

$$+ A^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[D^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1}u^{\downarrow,\alpha}_{l',1/2}j_{l'',b}\right]$$

$$+ B^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[A^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[\dot{u}^{\downarrow,\alpha}_{l,1}u^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ B^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[B^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[\dot{u}^{\downarrow,\alpha}_{l,1}\dot{u}^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ B^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[C^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[\dot{u}^{\downarrow,\alpha}_{l,1}u^{\downarrow,\alpha}_{l',2}j_{l'',b}\right]$$

$$+ B^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[D^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[\dot{u}^{\downarrow,\alpha}_{l,1}u^{\downarrow,\alpha}_{l',1/2}j_{l'',b}\right]$$

$$+ C^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[A^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,2}u^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ C^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[B^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,2}\dot{u}^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ C^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[C^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,2}u^{\downarrow,\alpha}_{l',2}j_{l'',b}\right]$$

$$+ C^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[D^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,2}u^{\downarrow,\alpha}_{l',1/2}j_{l'',b}\right]$$

$$+ D^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[A^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1/2}u^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ D^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[B^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1/2}\dot{u}^{\downarrow,\alpha}_{l',1}j_{l'',b}\right]$$

$$+ D^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[C^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1/2}u^{\downarrow,\alpha}_{l',2}j_{l'',b}\right]$$

$$+ D^{\downarrow\alpha}_{lm}(m,\boldsymbol{k})\left[D^{\downarrow\alpha}_{l'm'}(n,\boldsymbol{k}+\boldsymbol{b})\right]^* \left[u^{\downarrow,\alpha}_{l,1/2}u^{\downarrow,\alpha}_{l',1/2}j_{l'',b}\right]\Big\} (-1)^{m+m'}\, G^{-m-m'm''}_{ll'l''}.$$

$$\text{(A20)}$$

[*] Electronic address: ygyao@iphy.ac.cn

[1] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **95**, 146802 (2005).

[2] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **95**, 226801(2005).

[3] J. E. Moore, Nature (London) **464**, 194 (2010).

[4] X.-L. Qi and S.-C. Zhang, Physics Today **63**, 33 (2010).

[5] X.-L. Qi and S.-C. Zhang arXiv:1008.2026.

[6] M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).

[7] J. C. Y. Teo, Liang Fu, and C. L. Kane, Phys. Rev. B **78**, 045426 (2008).

[8] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature (London) **452**, 970 (2008).

[9] B. A. Bernevig, T. L. Hughes, and S.-C. Zhang, Science **314**, 1757 (2006).

[10] M. König, S. Wiedmann, C. Brüne, A. Roth, H. Buhmann, L. W. Molenkamp, X.-L. Qi, and S.-C. Zhang, Science **318**, 766 (2007).

[11] L. Fu and C. L. Kane, Phys. Rev. B **76**, 045302 (2007).

[12] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Phys. **5**, 438 (2009).

[13] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Phys. **5**, 398 (2009).

[14] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z.-X. Shen, Science **325**, 178(2009).

[15] D. Xiao, Y. Yao, W. Feng, J. Wen, W. Zhu, X.-Q. Chen, G. M. Stocks, and Z. Zhang, Phys. Rev. Lett. **105**, 096404 (2010).

[16] S. Chadov, X. Qi, J. Kübler, G. H. Fecher, C. Felser, and S. C. Zhang, Nature Mater. **9**, 541 (2010).

[17] H. Lin, L. A. Wray, Y. Xia, S. Xu, S. Jia, R. J. Cava, A. Bansil, and M. Z. Hasan, Nature Mater. **9**, 546 (2010).

[18] H. Lin, R. S. Markiewicz, L. A. Wray, L. Fu, M. Z. Hasan, and A. Bansil, Phys. Rev. Lett. **105**, 036404 (2010).

[19] B. Yan, C.-X. Liu, H.-J. Zhang, C.-Y. Yam, X.-L. Qi, T. Frauenheim, and S.-C. Zhang, Europhys. Lett. **90**, 37002 (2010).

[20] Y. L. Chen, Z. K. Liu, J. G. Analytis, J.-H. Chu, H. J. Zhang, B. H. Yan, S.-K. Mo, R. G. Moore, D. H. Lu, I. R. Fisher, S. C. Zhang, Z. Hussain, and Z.-X. Shen, Phys. Rev. Lett. **105**, 266401 (2010).

[21] T. Sato, K. Segawa, H. Guo, K. Sugawara, S. Souma, T. Takahashi, and Y. Ando, Phys. Rev. Lett. **105**, 136802 (2010).

[22] K. Kuroda, M. Ye, A. Kimura, S. V. Eremeev, E. E. Krasovskii, E. V. Chulkov, Y. Ueda, K. Miyamoto, T. Okuda, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. Lett. **105**, 146801 (2010).

[23] W. Feng, D. Xiao, J. Ding, and Y. Yao, Phys. Rev. Lett. **106**, 016402 (2011).

[24] Y. Sun, X.-Q. Chen, S. Yunoki, D. Li, and Y. Li, Phys. Rev. Lett. **105**, 216406 (2010).

[25] B. Yan, H.-J. Zhang, C.-X. Liu, X.-L. Qi, T. Frauenheim, and S.-C. Zhang, Phys. Rev. B **82**, 161108 (2010).

[26] J. Kim, J. Kim, and S.-H. Jhi, Phys. Rev. B **82**, 201312 (2010).

[27] H. Jin, J.-H. Song, A. J. Freeman, M. G. Kanatzidis, Phys. Rev. B **83**, 041202 (2011).

[28] H.-J. Zhang, S. Chadov, L. Müchler, B. Yan, X.-L. Qi, J. Kübler, S.-C. Zhang, and C. Felser, Phys. Rev. Lett. **106**, 156402 (2011).

[29] S. Chen, X. G. Gong, C.-G. Duan, Z.-Q. Zhu, J.-H. Chu, A. Walsh, Y.-G. Yao, J. Ma, and S.-H. Wei, Phys. Rev. B **83**, 245202 (2011).

[30] L. Fu, C. L. Kane and E. J. Mele, Phys. Rev. Lett. **98**, 106803 (2007).

[31] J. E. Moore and L. Balents, Phys. Rev. B **75**, 121306 (2007).

[32] R. Roy, Phys. Rev. B **79**, 195322 (2009).

[33] L. Fu and C. L. Kane, Phys. Rev. B **74**, 195312 (2006).

[34] T. Fukui and Y. Hatsugai, J. Phys. Soc. Jpn. **76**, 053702 (2007).

[35] D. Xiao, M.-C. Chang, and Q. Niu, Rev. Mod. Phys. **82**, 1959 (2010).

[36] C.-C. Liu, W. Feng, and Y. Yao, arXiv:1104.1290, Phys. Rev. Lett. (in press).

[37] A. A. Soluyanov and D. Vanderbilt, Phys. Rev. B **83**, 235401 (2011).

[38] R. Yu, X.-L. Qi, A. Bernevig, Z. Fang, and X. Dai, arXiv:1101.2011.

[39] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994).

[40] S. Blügel and G. Bihlmayer, John von Neumann Institute for Computing, NIC Series **31**, 85 (2006).

[41] P. Blaha, K. Schwarz, G. Madsen, D. Kvaniscka, and J. Luitz, *Wien2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, Vienna, Austria, 2001).

[42] J. Kuneš, P. Novák, R. Schmid, P. Blaha, and K. Schwarz, Phys. Rev. B **64**, 153102 (2001).

[43] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).

[44] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).

[45] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[46] F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009).

[47] W. Feng, D. Xiao, Y. Zhang, and Y. Yao, Phys. Rev. B **82**, 235121 (2010).

[48] W. Al-Sawai, H. Lin, R. S. Markiewicz, L. A. Wray, Y. Xia, S.-Y. Xu, M. Z. Hasan, and A. Bansil, Phys. Rev. B **82**, 125208 (2010).

[49] M. G. Haase, T. Schmidt, C. G. Richter, H. Block and W. Jeitschko, J. Solid State Chem. **168**, 18 (2002).

[50] B. R. Pamplin, T. Kiyosawa, and K. Masumoto, Prog. Cryst. Growth Charact. **1**, 331 (1979).

[51] S. Limpijumnong, and W. R. L. Lambrecht, Phys. Rev. B **65**, 165204 (2002).