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

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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$_2$Se$_3$ and Sb$_2$Se$_3$ 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.

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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. These novel physical properties hold great promise in applications of spintronics and quantum computing 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. Although many TIs including alloy, binary compounds, ternary compounds, and quaternary compounds 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 field. 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, 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. 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\textsuperscript{15–17}, chalcogenide\textsuperscript{18,19}, and chalcopyrite\textsuperscript{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.\textsuperscript{30–32} For materials with both time-reversal and spatial inversion symmetry (centrosymmetric systems), the simple parity criterion developed by Fu and Kane\textsuperscript{11} have been applied in a number of works.\textsuperscript{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.\textsuperscript{33} Within a tight-binding framework, Fukui and Hatsugai\textsuperscript{34} have developed an effective algorithm to compute $Z_2$ invariants in terms of the Berry gauge potential and the Berry curvature\textsuperscript{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\textsuperscript{15} and chalcopyrite\textsuperscript{23} compounds and two-dimensional (2D) quantum spin hall effect (QSHE) in Silicene.\textsuperscript{36} Recently there appears another method which is in the same spirit of Ref. 33 but employs the charge center of Wannier functions.\textsuperscript{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$_2$Se$_3$ and Sb$_2$Se$_3$ 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, 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 (in the former case) or the overlap matrices related to time-reversal operator (in the latter case).

A. Bloch functions and overlap matrix

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

$$\Psi_{nk}(r) = \begin{bmatrix} \psi_{nk}^\uparrow (r) \\ \psi_{nk}^\downarrow (r) \end{bmatrix},$$

(1)

where $\uparrow$ and $\downarrow$ refer to the up and down component of spin. The periodic part of BFs is $u_{nk}(r) = e^{-ik\cdot r} \begin{bmatrix} \psi_{nk}^\uparrow (r) \\ \psi_{nk}^\downarrow (r) \end{bmatrix}^T$, 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 $R_\alpha$ around each atom, often called the muffin-tin region and the remaining space is interstitial region. As a result, the BFs of electrons are always divided into two parts. Plane waves are used to construct the BFs in interstitial region.
\[ \psi_{nk}^{\sigma}(r) = \frac{1}{\sqrt{\Omega}} \sum_{j} z_{nk,j}^{\sigma} e^{i(k+K_j)r}, \quad r \in I, \] (2)

where \( \Omega \) is unit cell volume, \( z_{nk,j}^{\sigma} \) is the expansion coefficient, \( \sigma \) and \( n \) stand for spin and band index, \( k \) for \( k \)-points wave vector, \( K_j \) 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 \( |k + K_j| \leq K_{max} \), and \( K_{max} \) for the cutoff vector. Within the muffin-tin region (suppose the \( \alpha \)-th atom sphere with radius \( R_\alpha \)), the BFs can be written as

\[
\psi_{nk}^{\sigma,\alpha}(r) = \sum_{lm} \left[ A_{lm}^{\sigma,\alpha}(n, k) u_{l,1}^{\sigma,\alpha}(r) + B_{lm}^{\sigma,\alpha}(n, k) u_{l,1}^{\sigma,\alpha}(r) + C_{lm}^{\sigma,\alpha}(n, k) u_{l,2}^{\sigma,\alpha}(r) + D_{lm}^{\sigma,\alpha}(n, k) u_{l,1/2}^{\sigma,\alpha}(r) \right] Y_{lm}(\hat{r}), \quad \quad |r - \tau^\alpha| \in R_\alpha, \quad (3)
\]

with

\[
A_{lm}^{\sigma,\alpha}(n, k) = \sum_{j} z_{nk,j}^{\sigma} \tilde{A}_{lm}^{\sigma,\alpha}(k + K_j) + \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{A}_{lm}^{\sigma,\alpha}(k + K_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \\
B_{lm}^{\sigma,\alpha}(n, k) = \sum_{j} z_{nk,j}^{\sigma} \tilde{B}_{lm}^{\sigma,\alpha}(k + K_j) + \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{B}_{lm}^{\sigma,\alpha}(k + K_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \\
C_{lm}^{\sigma,\alpha}(n, k) = \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{C}_{lm}^{\sigma,\alpha}(k + K_{j_0}) \delta_{l,l_0} \delta_{m,m_0}, \\
D_{lm}^{\sigma,\alpha}(n, k) = \sum_{j_0} z_{nk,j_0}^{\sigma} \tilde{D}_{lm}^{\sigma,\alpha}(k + K_{j_0}) \delta_{l,l_0} \delta_{m,m_0}. \quad (4)
\]

where \( \tau^\alpha = r - \tau^\alpha \) and \( \tau^\alpha \) is the position of atom \( \alpha \); \( lm \) is the angular momentum index; \( Y_{lm} \) is spherical harmonics. In above formulas, \( u_{l,1}^{\sigma,\alpha} \equiv u_{l,1}^{\sigma}(r^\alpha, E_{l,1}^{\alpha}) \) and \( \dot{u}_{l,1}^{\sigma,\alpha} \equiv \dot{u}_{l,1}^{\sigma}(r^\alpha, E_{l,1}^{\alpha}) \) are the radial solutions of scalar-relativistic Schrödinger equation of atom \( \alpha \) and their energy derivatives, both evaluated at energy \( E_{l,1}^{\alpha} \). The local orbit radial functions \( u_{l,2}^{\sigma,\alpha} \equiv u_{l,2}^{\sigma}(r^\alpha, E_{l,2}^{\alpha}) \) 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 \( u_{l,1/2}^{\sigma,\alpha} \equiv u_{l,1/2}^{\sigma}(r^\alpha, E_{l,1/2}^{\alpha}) \), as the radial solution of full-relativistic Dirac equation, is also added to the \( u_{l}^{\sigma} \) and \( \dot{u}_{l,1}^{\sigma,\alpha} \) but only for \( 5p_{1/2} \) or \( 6p_{1/2} \) orbits in heavy elements. 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. $A_{l_{0},m_{0}}^{\sigma,\alpha}$, $B_{l_{0},m_{0}}^{\sigma,\alpha}$, $C_{l_{0},m_{0}}^{\sigma,\alpha}$, and $D_{l_{0},m_{0}}^{\sigma,\alpha}$ are the coefficients of local orbit basis set. These coefficients can be determined by imposing various boundary conditions at the muffin-tin boundaries.\textsuperscript{49,51}

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

$$
M_{mn}^{(k,b)} = \left\langle u_{m,k}^{\uparrow} u_{n,k+b}^{\uparrow} \right\rangle + \left\langle u_{m,k}^{\downarrow} u_{n,k+b}^{\downarrow} \right\rangle.
$$

Overlap matrix $M_{mn}^{(k,b)}$ is a very useful quantity in many Berry-phase related calculations,\textsuperscript{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\textsuperscript{11}. In 3D system there are eight time-reversal invariant momenta (TRIM) in BZ, $\Gamma_{i=(n_1,n_2,n_3)} = \frac{1}{2} (n_1 G_1 + n_2 G_2 + n_3 G_3)$, where $G_j$ are primitive reciprocal-lattice vectors with $n_j = 0, \text{ or } 1$. The $Z_2$ invariants are determined by the quantities

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

Here, $\xi_{2m} (\Gamma_i) = \pm 1$ is the parity eigenvalue of the $2m$-th occupied energy band at TRIMs $\Gamma_i$, i.e. $\left\langle \Psi_{2m,\Gamma_i} | P | \Psi_{2m,\Gamma_i} \right\rangle$, 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\textsuperscript{11}

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

$$
(-1)^{\nu_k} = \prod_{n_k=1,n_j\neq k=0,1} \delta_i=(n_1,n_2,n_3),
$$

where $\nu_0$ is independent of the choice of primitive reciprocal-lattice vectors $G_j$ while $\nu_1$, $\nu_2$, and $\nu_3$ are not. A nonzero $\nu_0$ indicates that the system is a strong topological insulator (STI). When $\nu_0 = 0$, the systems are further classified according to $\nu_1$, $\nu_2$, and $\nu_3$. The
systems with $\nu_{1,2,3} \neq 0$ 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
\[ \langle \Psi_{nk}(r) | P | \Psi_{nk}(r) \rangle \] with even band index $n$ at eight TRIMs $\Gamma_i$. The parity operator $P$ is defined as \( \{ I; t \} \), where $I$ is an inverse matrix making $r \rightarrow -r$ and $t$ is a translational vector. Since parity operation will not change spin component of BFs, then,

\[ \langle \Psi_{nk}(r) | P | \Psi_{nk}(r) \rangle = \left\langle \psi_{nk}^\dagger(r) | P | \psi_{nk}^\dagger(r) \right\rangle + \left\langle \psi_{nk}^\dagger(r) | P | \psi_{nk}^\dagger(r) \right\rangle. \quad (9) \]

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

\[ \langle \psi_{nk}(r) | P | \psi_{nk}(r) \rangle = \langle \psi_{nk}(r) | P | \psi_{nk}(r) \rangle_I + \sum_{\alpha} \left\langle \psi_{nk}^{\alpha}(r) | P | \psi_{nk}^{\alpha}(r) \right\rangle_{MT^\alpha}. \quad (10) \]

The contribution of interstitial region is

\[ \langle \psi_{nk}(r) | P | \psi_{nk}(r) \rangle_I = \frac{1}{\Omega} \sum_{ij} z_{nk,i}^* z_{nk,j} \int_{cell} e^{-i(k + K_i) \cdot r} e^{i(k + K_j - t) \cdot r} \Delta(r) \, d^3r \]

\[ = \frac{1}{\Omega} \sum_{ij} z_{nk,i}^* z_{nk,j} e^{i(k + K_j - t) \cdot \Delta(2k + K_i + K_j)}. \quad (11) \]

Here, $\Delta(r)$ is a step function with zero value in muffin-tin sphere and unit value in interstitial region and $\Delta(K)$ 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,

\[ A_{lm}^{\alpha}(n, k) = \sum_j \eta_{n,lm}(k + K_j, R_\alpha) e^{i(k + K_j) \cdot \tau^\alpha}, \] where $\tau^\alpha$ is the position of $\alpha$-th atom and $\eta_{n,lm}(k + K_j, R_\alpha)$ is independent of $\tau^\alpha$. Therefore,

\[ PA_{lm}^{\alpha}(n, k) = \sum_j \eta_{n,lm}(k + K_j, R_\alpha) e^{i(k + K_j) \cdot (t - \tau^\alpha)}. \quad (12) \]

If atom $\alpha$ is operated by parity operator, it must overlap another equivalent atom $\beta$ by translated integer numbers of primitive real-lattice, i.e. $t - \tau^\alpha = R_h + \tau^\beta$ with $R_h =$
\[ h_1 \mathbf{a}_1 + h_2 \mathbf{a}_2 + h_3 \mathbf{a}_3, \text{ where } h_j \text{ is integer number and } \mathbf{a}_j \text{ is primitive real-lattice vector.} \] Then above equation can be rewritten as

\[
PA_{im}^\alpha (n, \mathbf{k}) = \sum_j \eta_{n,lm} (\mathbf{k} + \mathbf{K}_j, R_\beta) e^{i(k + \mathbf{K}_j \cdot \mathbf{R}_h)} e^{i\mathbf{k} \cdot \mathbf{R}_h},
\]

and there are similar operations for \( PB_{im}^\alpha (n, \mathbf{k}), PC_{im}^\alpha (n, \mathbf{k}), \text{ and } PD_{im}^\alpha (n, \mathbf{k}). \) The spherical harmonics operated by parity operator is, \( PY_{lm} \) \( \hat{r} \alpha \) = \( (-1)^l Y_{lm} \) \( \hat{r} \alpha \). Then we have

\[
P\psi_{nk}^\alpha (\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}_h} \sum_{lm} \left[ A_{im}^\beta (n, \mathbf{k}) u_{i,1}^\alpha + B_{im}^\beta (n, \mathbf{k}) \dot{u}_{i,1}^\alpha + C_{im}^\beta (n, \mathbf{k}) u_{i,2}^\alpha + D_{im}^\beta (n, \mathbf{k}) \dot{u}_{i,1/2}^\alpha \right] (1)^l Y_{lm} (\hat{r}^\alpha).
\]

Therefore, we can easily obtain \( P\psi_{nk}^\alpha (\mathbf{r}) \) by using radial coefficients of atom \( \beta, A_{im}^\beta (n, \mathbf{k}), B_{im}^\beta (n, \mathbf{k}), C_{im}^\beta (n, \mathbf{k}), \text{ and } D_{im}^\beta (n, \mathbf{k}), \) which have already been calculated. Finally, the calculation of \( \langle \psi_{nk}^\alpha (\mathbf{r}) | P | \psi_{nk}^\alpha (\mathbf{r}) \rangle \) is very similar to \( \langle \psi_{nk}^\alpha (\mathbf{r}) | \psi_{nk}^\alpha (\mathbf{r}) \rangle \), 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

\[
Z_2 = \frac{1}{2\pi} \left[ \oint_{B^+} d\mathbf{k} \cdot \mathbf{A} (\mathbf{k}) - \int_{B^+} d^2 k \mathcal{F} (\mathbf{k}) \right] \mod 2,
\]

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

\[
\mathbf{A} = i \sum_n \langle u_n (\mathbf{k}) | \nabla_k u_n (\mathbf{k}) \rangle
\]
Under the time-reversal constraint, only half of Brillouin zone $B^+$ is needed, which is denoted by shaded region. The thick lines indicate the boundary of $B^+$, i.e., $\partial B^+$, and the open arrows denote their directions. All $k$-points are divided into three classes: $B^+_s$, $B^-_s$, and $B^0_s$, which are represented by small (black) solid, small (black) open and large (blue) solid circles, respectively.

and the Berry curvature

$$\mathcal{F}(k) = \nabla_k \times \mathbf{A}(k) \bigg|_z,$$

where $|u_n(k)\rangle$ 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 $|u_n(k)\rangle$ in half of BZ referred to as $B^+$ ($[-G_1/2, G_1/2] \otimes [-G_2/2, 0]$) according to the time-reversal constraint. As shown in Fig. 1 the $k$-points on a 2D BZ with $N \times N$ division are divided into three classes: $B^+_s$, $B^-_s$, and $B^0_s$. Firstly, we obtain $|u_n(k)\rangle$ in $B^+_s$ except for the points on the right edge. The points on the right edge ($k' = k + G_1$) are the periodic images of those on the left edge ($k$), and can be calculated by using the periodic gauge:

$$|u_n(k + G_1)\rangle = e^{-iG_1 \cdot r} |u_n(k)\rangle.$$

Secondly, we consider the $B^-_s$ points on the boundary $\partial B^+$, i.e., the left part of the bottom
edge and the right part of top edge. These points \(-\mathbf{k} \in \mathcal{B}_s^-\) are the Kramers doublets of \(\mathbf{k} \in \mathcal{B}_s^+\) points, so they can be calculated by the time-reversal constraint,

\[
|u_n(-\mathbf{k})\rangle = \Theta |u_n(\mathbf{k})\rangle, \quad \text{for } \mathbf{k} \in \mathcal{B}_s^+.
\]  

(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, \(\mathbf{k}' \in \mathcal{B}_s^-\) and \(\mathbf{k} \in \mathcal{B}_s^+\) are two points which are centrosymmetric about the midpoint of the bottom edge, i.e., \(\mathbf{k}' = -\mathbf{k} - \mathbf{G}_2\), then we have

\[
|u_n(\mathbf{k}')\rangle = \Theta |u_n(-\mathbf{k} - \mathbf{G}_2)\rangle
\]

(20)

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

\[
|u_{2n-1}(-\mathbf{k})\rangle = \Theta |u_{2n-1}(\mathbf{k})\rangle, \quad -\mathbf{k} \text{ and } \mathbf{k} \in \mathcal{B}_s^0.
\]  

(21)

There are six TRIMs in half of BZ \(\mathcal{B}_s^+\), \(-\mathbf{G}_1/2 - \mathbf{G}_2/2, -\mathbf{G}_1/2, -\mathbf{G}_2/2, 0, \mathbf{G}_1/2 - \mathbf{G}_2/2, \) and \(\mathbf{G}_1/2\). 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,

\[
|u_{2n}(-\mathbf{G}_1/2 - \mathbf{G}_2/2)\rangle = e^{i(G_1+G_2) \cdot r} |u_{2n}((\mathbf{G}_1/2 + \mathbf{G}_2/2))\rangle
\]

(22)

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

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 \(|\tilde{u}_n(\mathbf{k})\rangle\). Next, we introduce the link variable that is central to many Berry-phase related calculations, given by
\[ U_\mu(k_j) = N_\mu^{-1}(k_j) \det \langle \tilde{u}_m(k_j) | \tilde{u}_n(k_j + \mu) \rangle, \quad (23) \]

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

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

\[ \mathcal{A}_\mu(k_j) = \text{Im} \log U_\mu(k_j), \quad (24) \]

and

\[ \mathcal{F}(k_j) = \text{Im} \log U_\mu(k_j) U_\nu(k_j + \mu) U_\mu^{-1}(k_j + \nu) U_\nu^{-1}(k_j), \quad (25) \]

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 \( n(k_j) \) can be defined for each torus:

\[ n(k_j) = \frac{1}{2\pi} \{ [\Delta_\nu \mathcal{A}_\mu(k_j) - \Delta_\mu \mathcal{A}_\nu(k_j)] - \mathcal{F}(k_j) \}, \quad (26) \]

where \( \Delta_\mu \) 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., \( Z_2 = \sum_{k_j \in B^+} n(k_j) \mod 2 \). 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 modulo 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 \( x_0 + x_1 = y_0 + y_1 = z_0 + z_1 \mod 2 \). Following Refs. \[30,32\], we denote four independent
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 $\nu_0 = (z_0 + z_1) \mod 2$, $\nu_1 = x_1$, $\nu_2 = y_1$ 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$_2$Se$_3$ and Sb$_2$Se$_3$, our parity analysis shows that Bi$_2$Se$_3$ is a STI while Sb$_2$Se$_3$ 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 implemented in the package WIEN2K. We used two types of exchange-correlation potentials. The generalized gradient approximation (GGA) was used for Bi$_2$Se$_3$ and Sb$_2$Se$_3$, while the modified Becke-Johnson exchange potential together
with local-density approximation for the correlation potential (MBJLDA) was used for LuPtBi, AuTlS₂, and CdSnAs₂ because the resulting band topology is sensitive to the choice of exchange-correlation potentials in these systems. The converged ground state was obtained using \( K_{\text{max}} R_{MT} = 9.0 \) for each system, where \( K_{\text{max}} \) is the maximum size of reciprocal-lattice vector and \( R_{MT} \) represents the smallest muffin-tin radius. The \( \mathbf{k} \)-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, where states up to 9 Ry above Fermi level were included in the basis expansion, and the relativistic \( p_{1/2} \) corrections 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 \( 10 \times 10 \) 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), \( 50 \times 50 \) 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 Bi₂Se₃, Sb₂Se₃, LuPtBi, AuTlS₂ and CdSnAs₂, respectively.

A. Centrosymmetric systems

To demonstrate the quality of our methods, we first test the centrosymmetric systems Bi₂Se₃ and Sb₂Se₃. Recently, Bi₂Se₃ family of compounds have been both theoretically and experimentally observed to be TIs with an exception of Sb₂Se₃. Tetradymite semiconductor Bi₂Se₃ 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 Bi₂Se₃ and Sb₂Se₃ are presented in Fig. 3 with the lattice constants taken from previous studies. The 18 occupied bands (−6 ~ 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 $\delta_i$ at eight TRIMs for $\text{Bi}_2\text{Se}_3$ and $\text{Sb}_2\text{Se}_3$. 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 $\text{Bi}_2\text{Se}_3$ and 0;$(000)$ for $\text{Sb}_2\text{Se}_3$, which indicate a STI and a NI respectively.

|       | $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ | $\delta_6$ | $\delta_7$ | $\delta_8$ | $\nu_0; (\nu_1\nu_2\nu_3)$ |
|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------------|
| $\text{Bi}_2\text{Se}_3$ | -1         | +1         | +1         | +1         | +1         | +1         | +1         | +1         | 1;$(000)$         |
| $\text{Sb}_2\text{Se}_3$ | +1         | +1         | +1         | +1         | +1         | +1         | +1         | +1         | 0;$(000)$         |

Because the existence of spatial inversion symmetry, the parity criterion\textsuperscript{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 $\nu_0$ is obtained by multiplying over the parities of all TRIMs according to Eq. (7), while $\nu_k$ by multiplying over the parities of TRIMs resided in the same plane according to Eq. (8). The $\delta_i$ and $Z_2$ invariants are listed in Table I. The $Z_2$ invariants are 1;$(000)$ for $\text{Bi}_2\text{Se}_3$ and 0;$(000)$ for $\text{Sb}_2\text{Se}_3$, indicating a STI and a NI respectively. One can see that the main difference lies at $\Gamma$ point, i.e., $\delta_1$ is $-1$ for $\text{Bi}_2\text{Se}_3$ and $+1$ for $\text{Sb}_2\text{Se}_3$, while the other TRIMs share the same parities. We also give the parity eigenvalues of these 9 bands at $\Gamma$ 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 $\text{Bi}_2\text{Se}_3$. 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 $\text{Bi}_2\text{Se}_3$ is a STI. On the other hand, Figure 5 shows the $n$-field configuration for $\text{Sb}_2\text{Se}_3$ 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 $\text{Sb}_2\text{Se}_3$ 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.\textsuperscript{12}
Figure 3: Band structures of strong topological insulator Bi$_2$Se$_3$ with $Z_2$ invariants 1; (000) and normal insulator Sb$_2$Se$_3$ 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$_2$Se$_3$ and Sb$_2$Se$_3$ at $\Gamma$ point for 9 occupied bands. The corresponding band energy increases from left to right. The parity of $\Gamma$ point, $\delta_1$, is $-1$ for Bi$_2$Se$_3$ and $+1$ for Sb$_2$Se$_3$ respectively.

|        | $\delta_1$ |
|--------|-------------|
| Bi$_2$Se$_3$ | -1  +1  +1  -1  -1  +1  -1  -1  +1  (-1) |
| Sb$_2$Se$_3$ | -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.\textsuperscript{15,17,47,48} The crystal structure of LuPtBi is described by space group $F\overline{4}3m$ (No. 216) with three nonequivalent atoms in a primitive cell. The calculations were performed using the experimental lattice constant of 6.574 Å.\textsuperscript{49} As shown in Fig. 6(a), LuPtBi is a semi-metal with small electron and hole pockets around Fermi level at $\Gamma$ point. The band gap around $\Gamma$ 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$_2$Se$_3$ 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, 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 $\Gamma$ 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 $\Gamma$ 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\(_2\)Se\(_3\). 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 \( \delta u = 0.26 \)\(^{50} \) are used for CdSnAs\(_2\), where \( \eta = c/2a \) is the tetragonal distortion ratio and \( \delta u \) 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.

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

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

Firstly, we consider the overlap matrix $\langle u_m, k | u_n, k+b \rangle$ according to Eq. (5),

$$
\langle u_m, k | u_n, k+b \rangle = \langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle + \langle u^\downarrow_m, k | u^\downarrow_n, k+b \rangle.
$$

(A1)

Here we only discuss $\langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle$ because that $\langle u^\downarrow_m, k | u^\downarrow_n, k+b \rangle$ has the similar formulas. Like the BFs, the overlap matrix can also be divided into two parts: interstitial region and muffin-tin region,

$$
\langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle = \langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle_I + \sum_{\alpha} \langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle_{MT\alpha}.
$$

(A2)

The contribution of interstitial region is

$$
\langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle_I = \sum_j \sum_{j'} z^*_{m, k, j} z^\uparrow_{n, k+b, j'} \frac{1}{\Omega} \int_{cell} e^{[i(K_j - K_{j'}) \cdot r]} \Delta(r) d^3r
$$

$$
= \sum_j \sum_{j'} z^*_{m, k, j} z^\uparrow_{n, k+b, j'} \Delta(K_j - K_{j'}). \quad \text{(A3)}
$$

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

$$
\Delta(K) = \delta_{K, 0} - \sum_{\alpha} e^{-iK \cdot R_{\alpha}} \frac{4\pi}{\Omega} \frac{R_{\alpha}^2}{R_{\alpha}} j_1(KR_{\alpha}).
$$

The contribution of $\alpha$-th muffin-tin sphere is

$$
\langle u^\uparrow_m, k | u^\uparrow_n, k+b \rangle_{MT\alpha} = \int_{MT\alpha} e^{iK \cdot (r^\alpha + r^\alpha)} \left[ \psi_{m, k}^{\uparrow\alpha}(r) \right]^* e^{-i(k + b) \cdot (r^\alpha + r^\alpha)} \psi_{n, k+b}^{\uparrow\alpha}(r) d^3r
$$

$$
= e^{-ib \cdot r^\alpha} \int_{MT\alpha} \left[ \psi_{m, k}^{\uparrow\alpha}(r) \right]^* \psi_{n, k+b}^{\uparrow\alpha}(r) e^{-ib \cdot r^\alpha} d^3r. \quad \text{(A4)}
$$

Using the Rayleigh plane-wave expansion
\[ e^{-ib\mathbf{r}^{\alpha}} = 4\pi \sum_{l''m''} (-i)^{l''} Y_{l''m''}^* (\mathbf{b}) Y_{l''m''} (\mathbf{r}^{\alpha}) j_{l''}(br^{\alpha}), \quad (A5) \]

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

\[
\left\langle u_{m,k}^\uparrow | u_{n,k+b}^\uparrow \right\rangle _{MT^{\alpha}} = 4\pi e^{-ib\mathbf{r}^{\alpha}} \sum_{l''m''} (-i)^{l''} Y_{l''m''}^* (\mathbf{b}) \]

\[
\times \sum_{lm} \sum_{l'm'} \left\{ A_{lm}^{\alpha} (m, k) A_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \right. \\
+ [A_{lm}^{\alpha} (m, k)] B_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [A_{lm}^{\alpha} (m, k)] C_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [A_{lm}^{\alpha} (m, k)] D_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [B_{lm}^{\alpha} (m, k)] A_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [B_{lm}^{\alpha} (m, k)] B_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [B_{lm}^{\alpha} (m, k)] C_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [B_{lm}^{\alpha} (m, k)] D_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [C_{lm}^{\alpha} (m, k)] A_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [C_{lm}^{\alpha} (m, k)] B_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [C_{lm}^{\alpha} (m, k)] C_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [C_{lm}^{\alpha} (m, k)] D_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [D_{lm}^{\alpha} (m, k)] A_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [D_{lm}^{\alpha} (m, k)] B_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [D_{lm}^{\alpha} (m, k)] C_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \\
+ [D_{lm}^{\alpha} (m, k)] D_{l'm'}^{\alpha} (n, k + b) \left[ u_{l',1}^{\alpha} u_{l''1}^{\alpha} j_{l''}(b) \right] \left\} G_{ll''l''m''}^{mm'm''}. \quad (A6) \right. \]

Therefore, the matrix elements \( \left\langle u_{m,k}^\uparrow | u_{n,k+b}^\uparrow \right\rangle _{MT^{\alpha}} \) are constructed by two parts: radial in-
The radial integrals are

\[
\left[ u_{l_1}^{\alpha, \hat{r}, \alpha} u_{l_2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^\alpha \right) u_i^\alpha \left( r^\alpha, E_{l_2}^\alpha \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^\alpha \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^\alpha \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} u_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^\alpha \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 1} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2,1}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^\alpha \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 1} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} u_{l_2,1}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^\alpha \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2,1}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^\alpha \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,2}^{\alpha, \hat{r}, \alpha} u_{l_2,1}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 2} \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 1} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,2}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 2} \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,2}^{\alpha, \hat{r}, \alpha} u_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 2} \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,2}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2,1}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 2} \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} u_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 1} \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,2}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 1} \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} u_{l_2,1}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 1} \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} \hat{u}_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 1} \right) \hat{u}_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

\[
\left[ u_{l_1,1}^{\alpha, \hat{r}, \alpha} u_{l_2,2}^{\alpha, \hat{r}, \alpha} j_{l_3}^{\hat{r}, \alpha} \right] = \int_0^R r^2 u_i^\alpha \left( r^\alpha, E_{l_1}^{\alpha, 1} \right) u_i^\alpha \left( r^\alpha, E_{l_2}^{\alpha, 2} \right) j_{l_3}^\hat{r} \left( br^\alpha \right) dr,
\]

and the angular integrals is the Gaunt coefficients

\[
G_{l_1 l_2 l_3}^{m_1 m_2 m_3} = \int Y_{l_1 m_1}^* (\hat{r}) Y_{l_2 m_2} (\hat{r}) Y_{l_3 m_3} (\hat{r}) d\Omega.
\]

Secondly, we consider the matrix element \( \langle u_{m,k} | \Theta u_{n,k+b} \rangle \).
\[
\langle u_{m,k} | \Theta u_{n,k+b} \rangle = -\langle u_{m,k}^{\uparrow} | u_{n,k+b}^{\downarrow} \rangle + \langle u_{m,k}^{\downarrow} | u_{n,k+b}^{\uparrow} \rangle ,
\]
(A9)

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

\[
\langle u_{m,k}^{\uparrow} | u_{n,k+b}^{\downarrow} \rangle = \langle u_{m,k}^{\uparrow} | u_{n,k+b}^{\downarrow} \rangle_I + \sum_{\alpha} \langle u_{m,k}^{\uparrow} | u_{n,k+b}^{\downarrow} \rangle_{MT}^{\alpha} .
\]
(A10)

Within the interstitial region,

\[
\langle u_{m,k}^{\uparrow} | u_{n,k+b}^{\downarrow} \rangle_I = \sum_{j} \sum_{j'} z_{mkj}^{\uparrow} z_{nk+b,j'}^{\downarrow} \frac{1}{\Omega} \int_{cell} e^{-i(K_j + K_{j'}) \cdot r} \Theta(r) d^3r
\]
\[
= \sum_{j} \sum_{j'} z_{mkj}^{\uparrow} z_{nk+b,j'}^{\downarrow} \Theta(K_j + K_{j'}) ,
\]
(A11)

while inside the muffin-tin region (\( \alpha \)-th atom sphere),
\[\langle u_{m,k}^\downarrow | u_{n,k+b}^{\downarrow*} \rangle_{MT^\nu} = 4\pi e^{i(2k+b)\cdot \tau^\nu} \sum_{l,m'} i^{m'} Y_{l,m'}^{*} (2k + b) \]
\[
\times \sum_{lm} \sum_{l'm'} \left\{ \left[ A_{lm}^{\alpha} (m, k) \right]^* \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \right. \\
+ \left[ A_{lm}^{\alpha} (m, k) \right] \left[ B_{l'm'}^{\alpha} (n, k + b) \right]^* \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ A_{lm}^{\alpha} (m, k) \right] \left[ C_{l'm'}^{\alpha} (n, k + b) \right]^* \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ A_{lm}^{\alpha} (m, k) \right] \left[ D_{l'm'}^{\alpha} (n, k + b) \right]^* \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ B_{lm}^{\alpha} (m, k) \right]^* \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ B_{lm}^{\alpha} (m, k) \right]^* \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ B_{lm}^{\alpha} (m, k) \right]^* \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ B_{lm}^{\alpha} (m, k) \right]^* \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\alpha} u_{l',1}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ C_{lm}^{\alpha} (m, k) \right]^* \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,2}^{\alpha} u_{l',2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ C_{lm}^{\alpha} (m, k) \right]^* \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,2}^{\alpha} u_{l',2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ C_{lm}^{\alpha} (m, k) \right]^* \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,2}^{\alpha} u_{l',2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ C_{lm}^{\alpha} (m, k) \right]^* \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,2}^{\alpha} u_{l',2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ D_{lm}^{\alpha} (m, k) \right]^* \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1/2}^{\alpha} u_{l',1/2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ D_{lm}^{\alpha} (m, k) \right]^* \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1/2}^{\alpha} u_{l',1/2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ D_{lm}^{\alpha} (m, k) \right]^* \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1/2}^{\alpha} u_{l',1/2}^{\alpha} j_{l'i',2k+b} \right] \\
+ \left[ D_{lm}^{\alpha} (m, k) \right]^* \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1/2}^{\alpha} u_{l',1/2}^{\alpha} j_{l'i',2k+b} \right] \right\} (-1)^{m'} G_{l'l''}^{m-m'}.
\]

Thirdly, we consider the matrix element \(\Theta u_{m,k} | u_{n,k+b}^\downarrow\),

\[
\langle \Theta u_{m,k} | u_{n,k+b}^\downarrow \rangle = -\langle u_{m,k}^{\downarrow*} | u_{n,k+b}^\downarrow \rangle + \langle u_{m,k}^{\downarrow*} | u_{n,k+b}^\downarrow \rangle,
\]

and take \(\langle u_{m,k}^{\downarrow*} | u_{n,k+b}^\downarrow \rangle\) as example, it can be divided into two parts

\[
\langle u_{m,k}^{\downarrow*} | u_{n,k+b}^\downarrow \rangle = \langle u_{m,k}^{\downarrow*} | u_{n,k+b}^\downarrow \rangle_I + \sum_\alpha \langle u_{m,k}^{\downarrow*} | u_{n,k+b}^\downarrow \rangle_{MT^\nu}.
\]

(A12)
Within the interstitial region,

\[
\langle u_{m,k}^{\downarrow} | u_{n,k+b}^{\downarrow} \rangle_I = \sum_j \sum_{j'} z_{mk,j}^\dagger z_{nk+b,j'}^\dagger \frac{1}{\Omega} \int_{\text{cell}} e^{i(\mathbf{K}_j + \mathbf{K}_{j'}) \cdot \mathbf{r}} \Theta(\mathbf{r}) \, d^3 r
\]

\[
= \sum_j \sum_{j'} z_{mk,j}^\dagger z_{nk+b,j'}^\dagger \Theta[-(\mathbf{K}_j + \mathbf{K}_{j'})],
\]

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

\[
\langle u_{m,k}^{\downarrow} | u_{n,k+b}^{\downarrow} \rangle_{\text{MT}^\alpha} = 4\pi e^{-i(2k+b) \cdot \mathbf{r}_0} \sum_{l^\prime m^\prime} \left( -i \right)^{m^\prime} Y^\dagger_{l^\prime m^\prime} \left( 2\mathbf{k} + \mathbf{b} \right)
\]

\[
\times \sum_{lm} \sum_{l^\prime m^\prime} \left\{ A_{lm}^{\alpha} (m, k) A_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + A_{lm}^{\alpha} (m, k) B_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + A_{lm}^{\alpha} (m, k) C_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + B_{lm}^{\alpha} (m, k) A_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + B_{lm}^{\alpha} (m, k) B_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + B_{lm}^{\alpha} (m, k) C_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + B_{lm}^{\alpha} (m, k) D_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + C_{lm}^{\alpha} (m, k) A_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + C_{lm}^{\alpha} (m, k) B_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + C_{lm}^{\alpha} (m, k) C_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + C_{lm}^{\alpha} (m, k) D_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + D_{lm}^{\alpha} (m, k) A_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + D_{lm}^{\alpha} (m, k) B_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + D_{lm}^{\alpha} (m, k) C_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] + D_{lm}^{\alpha} (m, k) D_{l^\prime m^\prime}^{\alpha} (n, k + b) \left[ u_{l^\prime l,1}^\dagger u_{l^\prime 1,2}^\dagger j_{l^\prime 2,l^\prime 2} j_{l^\prime 2,l^\prime 2} \right] \right\} (-1)^m G_{l^\prime m^\prime m''}.
\]
Finally, we consider the matrix element $\langle \Theta u_{m,k} | \Theta u_{n,k+b} \rangle$,

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

(A17)

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

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

(A18)

Within the interstitial region,

$$
\langle u_{m,k}^{\downarrow*} | u_{n,k+b}^{\downarrow*} \rangle_I = \sum_{j} \sum_{j'} \sum_{z_{m,k,j}^{\downarrow*} z_{n,k+b,j'}^{\downarrow*}}^{1} \int \frac{1}{\Omega} \int e^{i(K_j - K_j') \cdot r} \Theta (r) d^3r ,
$$

(A19)

while inside the muffin-tin region ($\alpha$-th atom sphere),
\[
\left\langle u_{m,k}^\dagger | u_{n,k+b}^\dagger \right\rangle_{MT} = 4\pi e^{ib\tau} \sum_{l'm'n'} \tilde{Y}_{l'm'n'}^{*} (b)
\]
\[
\times \sum_{lm} \sum_{l'm'} \left\{ A_{lm}^{\dagger \alpha} (m, k) \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + A_{lm}^{\dagger \alpha} (m, k) \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + A_{lm}^{\dagger \alpha} (m, k) \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + B_{lm}^{\dagger \alpha} (m, k) \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + B_{lm}^{\dagger \alpha} (m, k) \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + B_{lm}^{\dagger \alpha} (m, k) \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + B_{lm}^{\dagger \alpha} (m, k) \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + C_{lm}^{\dagger \alpha} (m, k) \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + C_{lm}^{\dagger \alpha} (m, k) \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + C_{lm}^{\dagger \alpha} (m, k) \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + C_{lm}^{\dagger \alpha} (m, k) \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + D_{lm}^{\dagger \alpha} (m, k) \left[ A_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + D_{lm}^{\dagger \alpha} (m, k) \left[ B_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] + D_{lm}^{\dagger \alpha} (m, k) \left[ C_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{* \alpha} u_{l',1}^{\dagger \alpha} j_{l',b} \right] + D_{lm}^{\dagger \alpha} (m, k) \left[ D_{l'm'}^{\alpha} (n, k + b) \right] \left[ u_{l,1}^{\dagger \alpha} u_{l',1}^{* \alpha} j_{l',b} \right] \right\} (-1)^{m+m'} C_{l'm'n''}^{\dagger \alpha \gamma}.
\]

(A20)

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