Probing the wavefunction of the surface states in Bi$_2$Se$_3$ topological insulator: a realistic tight-binding approach

A Pertsova and C M Canali

Department of Physics and Electrical Engineering, Linnaeus University, Norra Vägen 49, SE-391 82 Kalmar, Sweden
E-mail: anna.pertsova@lnu.se

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Abstract
We present results of a microscopic tight-binding modeling of Bi$_2$Se$_3$, three-dimensional topological insulator using a $sp^3$ Slater–Koster Hamiltonian, with parameters calculated from density functional theory. Based on the calculated atomic- and orbital-projections of the wavefunctions associated with valence- and conduction-band states at the center of the Brillouin zone, we propose a real-space description of band inversion for both bulk and a slab of finite thickness. A systematic analysis of the key features of the surface states, in particular the spatial distribution and the spin-character of the surface states wavefunction, is carried out for slabs of different thickness, ranging from one to tens of quintuple layers. We obtain an estimate of the slab thickness at which the energy gap induced by interaction between the top and bottom surface states becomes negligible, based on the present available numerical precision. We anticipate that this finding will be relevant for all microscopic calculations addressing the effect of external perturbations on the surface states near the Dirac point. The modifications in the helical spin-texture of the Dirac-cone surface states, in the form of in-plane and out-of-plane spin projections, are calculated as a function of the slab thickness. These calculations are important for the interpretation of ongoing experiments, which probe the spin-polarization of the surface states in topological insulator thin films.
1. Introduction

Topological insulator [1, 2] (TI) materials host on their boundaries a novel type of topological states of quantum matter, which, unlike the quantum Hall state, exist without the breaking of time-reversal (TR) symmetry [3, 4]. Theoretical prediction and subsequent experimental demonstration of these topological states in both two- [5, 6] (2D) and three-dimensional [7–17] (3D) systems have given rise to what is now one of the most rapidly developing fields in condensed matter physics. Apart from providing a test platform for fundamental concepts, the study of TIs holds promise for novel applications in materials science and chemistry [18], spintronics [19] and quantum computation [20, 21]. However, to be able to fully explore the potential of TIs, it is essential to have detailed knowledge of the nature and properties of topological surface states in real TI materials [22], as well as a quantitative understanding of how they respond to external perturbations [23–25]. Experimentally, these questions are being addressed with advanced surface-sensitive experimental probes, such as spin- and angle-resolved photoemission spectroscopy [16] ((SR)-ARPES) and scanning tunneling microscopy [26, 27] (STM).

Along with experimental advances, there is a growing need for atomistic modeling of TIs that would enable quantitative predictions and direct comparison with experiment. Significant progress has been made in using \textit{ab initio} methods to calculate electronic [13, 28–31] and magnetic [32–35] properties of TIs. However, such methods suffer from severe computational limitations, particularly in the case of slab geometry as well as surface supercell calculations, which are employed in studies of impurity-doping effects. In addition, more accurate \textit{ab initio} methods often lack the conceptual transparency and flexibility of the model Hamiltonian approaches, which have been of fundamental importance for driving progress in this research field [3, 4]. Microscopic tight-binding (TB) models, which have already proved successful in quantitative description of electronic and magnetic properties of semiconductors [36, 37], may provide a convenient platform to address similar issues in TIs. Several studies have recently appeared in the literature, in which TB descriptions with different levels of complexity have been introduced, ranging from models built on a simplified lattice structure [38] or a restricted orbital basis set inferred from symmetry arguments [39, 40] to fully microscopic models, with parameters extracted from density functional theory (DFT) [28, 41–43]. To date, the latter class of models is still the least represented among the model Hamiltonian approaches to TIs.

In this work we employ a microscopic TB model to study the properties of surface states in Bi$_2$Se$_3$, a prototypical 3D TI which exhibits topologically protected conducting surface states with linear (Dirac) dispersion and helical spin-texture, traversing the bulk insulating gap [14–17]. Due to a relatively large band gap (0.3 eV for Bi$_2$Se$_3$) and rather simple surface states, consisting of a single Dirac cone [16], the Bi$_2$Se$_3$ family of 3D TIs is the most studied both experimentally and theoretically.

Recently, a lot of experimental work has been focused on 3D TI thin films [44], due to both their importance for exploring profound physical phenomena, such as the quantum anomalous Hall effect [2], and for applications in realistic devices. In order to contribute to the interpretation of ongoing experiments and to predict novel properties, it is crucial to have a
theoretical description of the key properties of 3D TIs, such as band dispersion, thickness-dependent gap originating from the interaction between the opposite surfaces, and detailed spin and orbital character of the surface states as a function of the thickness. Such description for a wide range of thicknesses is lacking in the literature. Although some important results for the thickness-dependent gap and spin-polarization of the surface states have been obtained using \textit{ab initio} techniques, thicknesses investigated in these works do not exceed a few (typically five or six) quintuple layers (QLs) \cite{30, 31}. Recent studies based on a TB Hamiltonian have dealt with much larger systems, however the published work has mainly focused on calculating the properties of the surface states for a fixed and relatively large thickness of the order of tens of QLs \cite{28}. One of the main objectives of this work is to provide a thorough and systematic description of the key features of the surface states in Bi$_2$Se$_3$ 3D TI for a wide range of thicknesses, starting from the ultra-thin-film regime to large thicknesses, where inter-surface interaction becomes weak.

Our treatment is based on the $sp^3$ Slater–Koster Hamiltonian \cite{45}. We use the parametrization developed by Kobayashi \cite{41}, by fitting to DFT calculations. We consider slabs with thicknesses ranging from 1 to 100 QLs, which corresponds to length scales in the range of 1–100 nm. We perform bandstructure calculations for each slab thickness, from which the surface character of Bloch states is determined using the procedure put forward in \cite{29}, i.e. based on the contribution of the real-space projected wavefunction onto the two surfaces of the slab.

Explicit calculations of the atomic- and orbital-projections of the wavefunctions, associated with valence-band (VB) and conduction-band (CB) states at the center of the Brillouin zone in both bulk and slab geometry, allowed us to construct a real-space picture of band inversion. The latter effect is induced by spin–orbit (SO) interaction and is responsible for the occurrence of topological surface states across the bulk insulating gap \cite{13}. Furthermore, based on a similar analysis, we were able to track the changes in the spatial distribution and the spin character of the surface states wavefunctions at and in the vicinity of the Dirac point, for increasing slab thickness. Our results show that the gap induced by inter-surface interaction becomes of the order of the available numerical precision for relatively thick slabs containing tens of QLs (40 QLs in our calculations). At this point the surface states corresponding to top and bottom surfaces become completely decoupled, i.e. spatially separated, which can be clearly seen in the spatial distribution of the surface states wavefunction.

We also calculated the spin-orientation of the surface states in momentum space as a function of the slab thickness. The disturbances in the helical spin-texture, expressed through in-plane and out-of-plane tilting angles of the spin, are shown to be significant for thin slabs up to ten QLs and are manifestations of both inter-surface interaction and the proximity to bulk states. Some of our numerical results are in quantitative agreement with recent experimental observations, in particular the spin-polarization of the Dirac-cone states in the vicinity of the Dirac point in thick slabs \cite{46} and in ultra-thin films \cite{47}.

The rest of the paper is organized as follows. In section 2 we discuss the details of the TB model and some computational aspects. The results of the simulations are presented in section 3. We begin in section 3.1 by analyzing the effect of SO on the bulk bandstructure, where the bulk band inversion is interpreted as a characteristic change in the spatial distributions of the orbital-resolved projections of the wavefunctions of CB and VB states at the $\Gamma$ point. The results of surface bandstructure calculations are presented in section 3.2, in particular the spatial
character of the states emerging within the bulk gap and the opening of the gap at finite thicknesses are described quantitatively in section 3.2.1. We also discuss the procedure to identify the inverted character of CBs and VBs in the presence of SO for a slab geometry. In section 3.2.2, based on the analysis of the wavefunctions of the states at the Dirac point, we provide an estimate for a slab thickness, at which the interaction between the opposite surfaces becomes negligibly small with respect to numerical precision of the calculations. In addition, we comment on the orbital character of the wavefunctions at the Dirac point, especially on the non-negligible contribution of the in-plane $p$-orbitals. The spin-properties of the Dirac-cone states and deviations from the perfect spin-momentum locking due to inter-surface interaction and the presence of bulk states are calculated in section 3.2.3. Finally, section 4 contains our conclusions.

2. Methods

We begin with a brief description of the crystal structure and chemical bonding in Bi$_2$Se$_3$. Along with Bi$_2$Te$_3$ and Sb$_2$Te$_3$, Bi$_2$Se$_3$ belongs to the family of binary tetradymite semiconductors with layered structure [48]. Before their discovery as 3D TIs, these materials had been studied extensively due to their excellent thermoelectric properties [49–51]. Bi$_2$Se$_3$ has a rhombohedral crystal structure with crystallographic $R\bar{3}m$ [$D_{3d}^5$] space group, with five atoms in the unit cell (see figure 1(a)). The crystal is formed by stacking hexagonal monolayers of either Bi or Se in a close-packed fcc (ABC) fashion. The sequence of five atomic layers, i.e. Se1-Bi-Se2-Bi-Se1, forms a QL (see figure 1(b)), with Se1 and Se2 indicating two
non-equivalent positions of Se atom. Hence it is convenient to describe the crystal structure of bulk Bi$_2$Se$_3$ in terms of QLs stacked along the direction perpendicular to atomic planes (c-axis).

The chemical bonding between atoms in the atomic layers within a QL is of covalent–ionic type with dominant covalent character. Adjacent QLs are weakly bound through Se1–Se1 bonds by van der Waals forces [49], allowing easy cleavage of Bi$_2$Se$_3$ on the (111) Se surface plane. Based on the electronic configurations of Bi and Se, with the outermost orbitals being of $p$-character for both types of atoms, it is reasonable to expect that the bonding within QLs is mainly due to interactions between $p$-orbitals. In fact, a simple but useful physical picture of the chemical bonding present in QLs features $pp\sigma$-chains formed by strongly interacting $p$-orbitals of atoms in nearest-neighbor atomic layers. Evidence of this coupling can be indirectly inferred from STM topographies of Bi-antisite defects in Bi$_2$Se$_3$ [50]. In sections 3.1 and 3.2, we will comment on the orbital character of the VB and CB states in bulk Bi$_2$Se$_3$ and of surface states in Bi$_2$Se$_3$ slab, respectively.

For modeling of the electronic structure of Bi$_2$Se$_3$ we employ the $sp^3$ TB model with Slater–Koster parameters obtained by Kobayashi [41] by fitting to bulk bandstructures calculated with DFT. Interactions between atoms in the same atomic layer and between atoms in first and second nearest-neighbor layers are included. SO interaction, which is the key element leading to a non-trivial bulk band structure and metallic surface states, is incorporated in the intra-atomic matrix elements [56]. Thus the Hamiltonian of the system reads

$$\hat{H}(\mathbf{k}) = \sum_{i',\alpha'} t_{ii'}^{\alpha\alpha'} e^{i\mathbf{k} \mathbf{r}_{i'}} \hat{c}_{i\alpha}^{\sigma} \hat{c}_{i'\alpha'}^{\sigma} + \sum_{i,\alpha',\alpha''} \lambda_i \langle i, \alpha, \sigma | \hat{L} \cdot \hat{S} | i, \alpha', \sigma' \rangle \hat{c}_{i\alpha}^{\sigma} \hat{c}_{i'\alpha'}^{\sigma'},$$

where $\mathbf{k}$ is the reciprocal-lattice vector that spans the Brillouin zone, $i (i')$ is the atomic index, $\alpha (\alpha')$ labels atomic orbitals $\{s, p_x, p_y, p_z\}$, and $\sigma (\sigma')$ denotes the spin. Here $i$ refers to the atomic positions in the unit cell, while $i' \neq i$ runs over all neighbors of atom $i$, including atoms in the adjacent cells, with $\mathbf{r}_{ii'}$ being the vector connecting the two atoms ($\mathbf{r}_{ii} = 0$ for $i = i'$). The coefficients $t_{ii'}^{\alpha\alpha'}$ are the Slater–Koster parameters (for $i = i'$ $t_{ii'}^{\alpha\alpha'} \equiv t_{ii}^{\alpha\alpha'}$ give the on-site energies) and $\hat{c}_{i\alpha}^{\sigma} (\hat{c}_{i\alpha}^{\sigma})$ is the creation (annihilation) operator for an electron with spin $\sigma$ at the atomic orbital $\alpha$ of site $i$. The second term in equation (1) represents the on-site SO, where $|i, \alpha, \sigma>$ are spin- and orbital-resolved atomic orbitals, $\hat{L}$ is the orbital angular momentum operator and $\hat{S}$ is the spin operator; $\lambda_i$ is the SO strength. We refer to [41] for the exact parametrization of $t_{ii'}^{\alpha\alpha'}$ and $\lambda_i$.

In bulk-bandstructure calculations we use the rhombohedral unit cell with five non-equivalent atoms, with the cell repeated periodically in $x$-, $y$- and $z$-directions. In calculations involving the Bi$_2$Se$_3$ (111) surface we consider a slab consisting of $N$ QLs, or, equivalently, of $5N$ atomic layers. Since each atomic layer is an equilateral triangular lattice, it is sufficient to assign one atom per layer, which gives a total of $5N$ atoms in the slab unit cell. The slab is finite along the $z$-direction (QL-stacking axis), with the unit cell repeated periodically in the $x$-$y$ plane. Using this TB model we were able to compute bandstructures of slabs with thicknesses up to 100 QLs with a reasonable computational cost. Finally, we note that since the (111) Bi$_2$Se$_3$ surface does not exhibit any substantial reconstruction or relaxation effects [29], we do not
perform any renormalization for the Slater–Koster parameters for the surface, and use the same set of parameters for both bulk and slab bandstructure calculations.

3. Results and discussion

3.1. Band inversion in bulk Bi₂Se₃

The presence of gapless edge or surface states, robust against TR-invariant perturbations, distinguishes a topological insulating phase from a trivial one. However, in order to elucidate the origin of the topological order in existing TIs and to facilitate the search for new TI materials, it is necessary to have a set of criteria that allow us to differentiate between topologically trivial and non-trivial insulators, based on the information about their bulk properties. The emergence of topological order can be understood using the concept of band inversion [8, 13, 58, 59]. Clearly, a necessary condition for a TI is the existence of a non-trivial bulk band gap. In 3D TIs, such as strained α-Sn and HgTe, Bi₁₋ₓSbx and Bi₂Se₃-like 3D TIs, a topological phase transition, or alternatively a change in the value of the $Z₂$ topological invariant [4, 7–9, 11, 57], which in turn implies the existence of gapless states on the boundary, is accompanied by a visible and well-defined change in the bandstructure. This change occurs precisely in the insulating gap and can be observed as a function of an external or an intrinsic parameter. In Bi₂Se₃, a non-trivial bulk band gap owns its existence to SO, with the parity of the VB and CB inverted at the Γ point [13]. Without SO the material would be a trivial insulator. However, in the presence of SO the change in the parity of one of the occupied bands leads to a change in the value of the $Z₂$ invariant, signaling a topological phase transition.

An intuitive way of describing band inversion theoretically is to look at charge density distributions of the inverted bands at the point of the Brillouin zone, where the inversion is expected to occur, as functions of a characteristic parameter [58]. Here we apply this procedure to bulk Bi₂Se₃. The calculated bandstructures without and with SO are shown in figures 2(a)
and (b), respectively. The effect of SO is clearly seen as an increase of the gap and a change in the curvature of the VB at the $\Gamma$ point.

To further quantify the effect of SO on the bandstructure, we calculate the atomic- and orbital-projections of the wavefunctions associated with the states in the VB (filled circles in figure 2) and in the CB (open circles in figure 2) at the $\Gamma$ point. The orbital-resolved projection of the wavefunction $\phi$, corresponding to an eigenvalue $\varepsilon_n$ of the TB Hamiltonian in equation (1), onto atomic orbital $|i, \alpha, \sigma\rangle$ is calculated as $|\phi_i^{\alpha\sigma}|^2 \equiv \sum_{\alpha\sigma} |\langle i, \alpha, \sigma | \phi \rangle|^2$. The total weight of the wavefunction at the atomic site $i$ is then given by $|\phi|^2 = \sum_\alpha |\phi_i^{\alpha\sigma}|^2$. The calculated spatial distribution and orbital character of the wavefunctions of VB and CB states at the $\Gamma$ point are plotted in figure 3 for all five atoms of the bulk unit cell.

The most noticeable feature of figure 3 is the inversion in the spatial distribution of the wavefunctions when SO is switched on. Without SO the CB wavefunction has a node at Se2, which is in fact the inversion center of the bulk crystal, with the maximum weight on the two Bi atoms. In contrast, the maximum weight of the VB wavefunction is distributed over Se2 and two Se1 atoms. With SO the situation is the opposite: now the VB wavefunction has a node at Se2 while the CB wavefunction is predominantly localized on Se atoms.

As expected, both VB and CB states are predominantly of $p$-character. The $s$-orbital contribution to the wavefunctions is approximately 10% for calculations with or without SO and the $s$-projections are not affected by the inversion. Note that in the presence of SO, the states at the $\Gamma$ point are mostly originating from $p_z$ orbitals, however the $p_{x(y)}$ (in-plane) contribution is not negligible (40% for VB and 20% for CB).
Figure 4. Bandstructures of a Bi$_2$Se$_3$ slab of varying thickness. Panels (a)–(e) correspond to 1–5 QLs, (f) 20 QLs and (g) 100 QLs. The inset of panel (a) shows the two-dimensional Brillouin zone of (111) surface of Bi$_2$Se$_3$. Symbols mark the surface states, identified according to the critical weight of the wavefunction projection onto the surfaces of the slab (see text for details).
In the next section, we will discuss the results of bandstructure calculations for Bi$_2$Se$_3$ slabs, namely the emergence of conducting states across the inverted bulk gap in the presence of SO. In particular, we will show that the band inversion, characteristic of the bulk gap, can also be identified in the surface bandstructures.

3.2. Wavefunction-based analysis of surface states in Bi$_2$Se$_3$ slab

3.2.1. Surface bandstructures and thickness-dependent gap. The bandstructures of Bi$_2$Se$_3$ slab of varying thickness, calculated using the TB model including SO, are shown in figure 4. A clear and sizable gap is found for 1 and 2 QLs. Starting from 3 QLs, two surface bands, resembling the Dirac states, extend in the range of (−0.1–0.4) eV, with valence and CBs beginning to form below and above this range. Already for 3 and 4 QLs the two bands appear to be almost touching at the $\bar{\Gamma}$ point, however the calculated gap is not negligible ($\Delta = 0.043$ eV for 3QLs and $\Delta = 0.007$ eV for 4 QLs). The presence of the gap due to finite thickness is a recently discovered feature of 3D TI thin films, which has been attributed to tunneling between surface states localized on the opposite surfaces of the film [53]. Such a gap-opening mechanism has been considered for possible applications in TI-based MOSFET devices [60].

The value of the gap for increasing slab thickness is plotted in figure 5. By fitting to an exponentially decaying function of the thickness, we find the exponential decay constant $\lambda \approx 0.66$ nm (see the inset of figure 5). This gives an estimate for the penetration depth of the surface states, which is determined by the spatial extent of the surface-state wavefunction into the bulk, which is found to be approximately 1 nm in other work [28]. The obtained estimate is also consistent with the typical spread of the wavefunctions, associated with the states near the Dirac point, which we calculate explicitly as a function of the distance from the surface (see section 3.2.2).

Interestingly, we find that the gap initially decreases and reaches the value of $1.7 \times 10^{-5}$ eV for 5 QLs but then increases up to $6.2 \times 10^{-4}$ eV for 6 QLs. After this sudden increase, the
gap continues to decrease exponentially and we find $\Delta = 2.6 \times 10^{-6}$ eV for 10 QLs. A similar non-monotonicity in the thickness-dependence of the gap was found in the range of 4–6 QLs in \textit{ab initio} calculations for Bi$_2$Se$_3$ and Bi$_2$Te$_3$ thin films [29, 52]. From the logarithmic plot of the energy gap as a function of the thickness, one can see that there is another local minimum at 11 QLs, however it is less pronounced and the gap is of the order of $10^{-6}$ eV. This result also resembles the oscillating behavior of the gap found in theoretical work based on effective models [39, 54, 55]. However, a direct comparison with these effective-model results is not straightforward since, in contrast to our atomistic model with slab thickness measured in terms of elementary building blocks of the real material (QLs), there the gap is calculated as a continuous function of the size along the z-direction.

We found no detailed explanation of the physical origin of such non-monotonic behavior in the literature, except for some indications that it might be material-dependent. Clearly, the magnitude of the hybridization gap is related to the way the wavefunctions of the surface states localized on the opposite surfaces overlap in real space. Therefore, we suggest that the occurrence of local extrema in the thickness-dependence of the gap can be linked to specific situations, in which the surface states wave functions overlap ‘in-phase’ or ‘anti-phase’, leading to a local maximum (anti-node) or a local minimum (node) for the resulting mixed state in the middle of the film. By looking at the spatial distribution of the wavefunctions associated with the states at the Dirac point, we find that for an odd number of QLs one of the wavefunctions has a node in the center of the slab, while this does not happen for an even number of QLs. Since the gap becomes very small above 7 QLs, it is reasonable to expect that this effect will be most pronounced in the range of 4–6 QLs, which might explain a small gap at 5 QLs.

Since the gap decreases exponentially, we do not display the results for thicknesses greater than 10 QLs. Note, however, that for 40 QLs the size of the gap becomes smaller than the numerical accuracy of our calculations. We conclude that for this thickness, the surface states localized on the opposite surfaces of the slab are effectively decoupled. For thicknesses larger than this value, we identify the crossing of the two branches of Dirac states with opposite group velocity as the Dirac point, which is found at 0.09 eV. In section 3.2.2 we will investigate in more detail the effect of the coupling between the two surfaces of the slab on the states at the Dirac point. In particular, we will look at the spatial character of the wavefunctions associated with these states and their dependence on the slab thickness.

Finally, we note that for ultra-thin films with thicknesses below 3 QLs, the values of the energy gap obtained in our calculations are in quantitative agreement with ARPES data for Bi$_2$Se$_3$ [53]. However, in the range of 3–5 QLs, the calculated gap is approximately ten times smaller than the experimental estimate (except for the special thickness of 5 QLs, for which we find a very small energy gap of the order of 0.02 meV). Similar deviations from experimental result are found in DFT calculations for the same range of thicknesses [52]. Among many factors that distinguish the experimental set-up from an idealized calculation is the presence of the substrate. While in our model, as well as in many DFT calculations, we consider a free-standing slab with two identical surfaces, in experiment one of the surfaces of the film is in contact with the substrate. This represents a strong perturbation to the surface, which can lead to an enhancement of the small ($\lesssim$1 meV) gap arising purely from the interaction between the opposite surfaces. Other imperfections present in 3D TI thin films might also enhance the size of the gap at crossover thicknesses (~5 QLs) where
the gap starts to become small but topologically protected surface states are not yet fully developed.

We will now comment on the procedure used to identify the surface states in the bandstructure calculations (figure 4). The character of each Bloch state \( \varepsilon_n(k) \), where \( n \) is the band index and \( k \) is momentum, is determined by the spatial distribution of the corresponding wavefunction \([29]\): if the relative weight of the atom-projected wavefunction \( \sum_i |\varphi_i|^2 \) on the top and bottom QLs exceeds a critical value (critical percentage) \( \gamma \), \( \varepsilon_n(k) \) is identified as a surface state. Such a criterion is reasonable for slabs with thickness greater than 3 QLs, since the typical penetration depth of the surface states in \( \text{Bi}_2\text{Se}_3 \) is of the order of 1 QL, or 1 nm. For ultra-thin slabs with thickness below 3QLS, the criterion has to be modified, namely we calculate the wavefunction projections onto top two and bottom two atomic layers. The value of the critical percentage is found empirically. Starting from a rough estimate of \( \gamma \) based on the ratio between the penetration depth and the slab thickness, the value should then be optimized in such a way that a small change around this value does not significantly modify the resulting distribution of the surface states.

We find, however, that for 1–3 QLs the identification of such an optimized value of \( \gamma \) is problematic. To illustrate this point, we present the results of calculations for two different values of \( \gamma \). In the case of 1 QL and \( \gamma = 65\% \), for instance, all states in the range of energies considered can be identified as surface states. Hence, for such a thin slab it is reasonable to use a stronger criterion. As one can see from figure 4(a), for \( \gamma = 90\% \) only the upper band preserves the surface character while the lower band does not satisfy the criterion (we use terms ‘lower’ and ‘upper’ for the two bands defining the gap). This observation is consistent with scanning tunneling spectroscopy measurements on \( \text{Sb}_2\text{Te}_3 \) ultra-thin films \([61]\). For slabs with thicknesses greater than 3 QLs, the search for an optimized value of \( \gamma \) is significantly simplified (already for 4 QLs, changing \( \gamma \) from 50\% to 60\% does not produce any significant difference). For a very thick slab of 100 QLs, we focus particularly on the states in the vicinity of the Dirac point, e.g. in the range 0.0–0.3 eV, and do not apply the procedure for the near-continuum of bulk states appearing above and below this range. In figure 4(g) we present the result for 100 QLs with \( \gamma = 40\% \), where the surface character of the Dirac states is clearly confirmed.

Before concluding this section we repeat the procedure that was used in section 3.1 to illustrate the mechanism of band inversion in bulk \( \text{Bi}_2\text{Se}_3 \). The atomic-layer projected wavefunctions of VB and CB states at the \( \Gamma \) point for a 20 QLs-thick slab without and with SO are shown in figures 6(a) and (b), respectively. One immediately notices that the spatial character of VB and CB is inverted when SO is switched on: similarly to the bulk case, with (without) SO the VB (CB) wavefunction has nodes on Se2 atoms. The effect becomes even more appreciable, if we sum the wavefunction projections on Se1, Se2 and Bi atoms over the entire slab (figure 6(c)). The result is clearly similar to what we found in the bulk case, indicating that the inverted character of the valence and CBs in the presence of SO is also an intrinsic property of the surface, with the difference that in the surface bandstructures one finds the topological surface states, dispersing linearly across the inverted band gap.

### 3.2.2. Probing the wavefunction at the Dirac point: effect of finite thickness.

We will now consider the surface states and their corresponding wavefunctions, found at the \( \Gamma \) point in our
surface bandstructure calculations. In a hypothetical situation, when the slab is thick enough so that the two surfaces do not interact with each other, one expects to find four degenerate states at the \( \bar{\Gamma} \) point, namely one Kramers degenerate pair for each of the two surfaces. Away from the \( \bar{\Gamma} \) point, the four-fold degeneracy is lifted and one expects a doubly degenerate state at each momentum \( k \), with degeneracy guaranteed by inversion symmetry. In addition, for each state at \( k \), there is an identical state with opposite spin at \( -k \) due to TR symmetry.

The analysis of the thickness-dependent gap, carried out in the previous section, shows that the limit of an infinitely thick slab with zero interaction between the two surfaces is most likely realized for 40 QLs in our system, a value determined by the available numerical precision. Although the size of the gap already for 6 QLs is considerably smaller than the value found in ultra-thin slabs, for 40 QLs the gap becomes identically zero within the numerical error of our calculations (note that we employ exact diagonalization to calculate the eigen-spectrum of the Hamiltonian at each \( k \)). By looking closely at the \( \bar{\Gamma} \) point, we indeed find four degenerate states \( \epsilon_i (i = 1, \ldots, 4) \) in the case of 40 QLs, as shown in figure 7(c). Within each pair of degenerate states, \( \epsilon_{1,3} \) and \( \epsilon_{2,4} \), the states have opposite spins and each pair is localized on either top or bottom surface. Note that the \( a \)th Cartesian component of the spin of each Bloch state is calculated as \( s^a_i(k) = \text{Tr} \left[ \rho_{nn} \sigma^a \right] \), where \( \sigma = \{ \sigma^a \} \) is the set of Pauli matrices and \( \rho_{nn} \) is the \( n \)th diagonal element of the density matrix constructed from the eigenfunctions of the Hamiltonian at each \( k \). By looking closely at the \( \bar{\Gamma} \) point, we indeed find four degenerate states \( \epsilon_i (i = 1, \ldots, 4) \) in the case of 40 QLs, as shown in figure 7(c). Within each pair of degenerate states, \( \epsilon_{1,3} \) and \( \epsilon_{2,4} \), the states have opposite spins and each pair is localized on either top or bottom surface. Note that the \( a \)th Cartesian component of the spin of each Bloch state is calculated as \( s^a_i(k) = \text{Tr} \left[ \rho_{nn} \sigma^a \right] \), where \( \sigma = \{ \sigma^a \} \) is the set of Pauli matrices and \( \rho_{nn} \) is the \( n \)th diagonal element of the density matrix constructed from the eigenfunctions of the Hamiltonian at each \( k \). From figure 7(c) we can also estimate the decay length of the surface states to be approximately 10 atomic layers, or, equivalently, 2 QLs in agreement with previous reports [28, 29].

For slabs with thicknesses below 40 QLs, we also find four states at the \( \bar{\Gamma} \) point, however there is a finite gap between degenerate states \( \epsilon_{1,2} \) and \( \epsilon_{3,4} \) (see the inset in figure 7(b)). Within
each pair of states, the Bloch states with identical energy have opposite spins but, in contrast to
the 40 QLs case, their wavefunctions are distributed over both top and bottom sides of the slab,
signaling a non-negligible interaction between the two surfaces. For 20 QLs, since the
difference in energy between $\epsilon_{1,2}$ and $\epsilon_{3,4}$ is finite but small (less than $-10^{-6}$ eV), the spatial
distributions of the corresponding wavefunctions are nearly identical and are therefore
indistinguishable on the scale of the graph (figure 7(b)). In the case of 5 QLs, when the gap at
the $\Gamma$ point is more appreciable, there is a clear difference between the spatial profiles of the
wavefunctions associated with the two degenerate states (figure 7(a)). The difference is the
largest in the middle of the slab, where the tails of the wavefunctions of the surface states
residing on the opposite sides overlap, creating a mixed state.

**Figure 7.** Atomic-layer projections of the wavefunctions, corresponding to four quasi-degenerate states exactly at the $\Gamma$ point for (a) 5 QLs, (b) 20 QLs and (c) 40 QLs of Bi$_2$Se$_3$. The inset of panel (b) shows schematically the two pairs of degenerate states at $\Gamma$, separated by an energy gap $\Delta$. The inset of panel (c) displays the crystal structure of a 40 QLs-thick slab of Bi$_2$Se$_3$ with top and bottom surfaces.

**Figure 8.** Orbital-resolved atomic-layer projection of the wavefunction, corresponding to one of the four degenerate states exactly at the $\Gamma$ point for a 20 QLs-thick slab of Bi$_2$Se$_3$. Since the wavefunction is symmetric with respect to the center of the slab (see figure 7(b)), only atomic layers belonging to the bottom surface are displayed.
Finally, we comment on the orbital character of surface states at the Dirac point. The orbital-resolved atomic-layer projections of the wavefunctions associated with one of the four quasi-degenerate states ($\varepsilon_1$) at the $\Gamma$ point in a 20 QLs-thick slab are plotted in figure 8. Similarly to VB and CB states at the $\Gamma$ point of the bulk bandstructure with SO (figure 2(b)), this state is predominantly of $p$-character with $s$-orbital contribution less than 10%. Although the contribution of $p_z$-orbitals is the largest, the relative weight of in-plane ($p_{x(y)}$) orbitals to the orbital-resolved wavefunction is non-negligible and is of the order of 40%. The importance of the SO-induced in-plane orbital contribution to the wavefunction of the Dirac states in Bi$_2$Se$_3$ has been recently demonstrated using orbital-selective SR-ARPES measurements [22].

### 3.2.3. Spin-resolved surface states on the Dirac cone.

In this section we analyze the surface states away from the $\Gamma$ point. We describe the spatial distribution and the spin-properties of the wavefunctions, associated with energy states found inside the inverted band gap at non-zero values of momentum $\mathbf{k}$. In particular, we quantify the effect of the finite slab thickness on the helical spin-character of the Dirac cone states.

Figure 9(a) shows an equi-energy contour located slightly above the Dirac point, within the energy range $-0.05$–$0.25$ eV. An equi-energy contour above the Dirac point (at approximately 0.13 eV) is shown with a dashed line. Red circles indicate a doubly degenerate state $\epsilon_1,2$ occurring at $\mathbf{k}$ and its TR partner at $-\mathbf{k}$. (b) Schematic of the two-dimensional Brillouin zone with the projection of the equi-energy contour and two doubly degenerate states at $\pm \mathbf{k} = \{0, \pm \mathbf{k}_y\}$. (c) Atomic-layer projections of the wavefunctions associated with four states $\epsilon_{1,2}(\pm \mathbf{k})$.

![Figure 9](image_url)
top or bottom surface. We will refer to the state whose wavefunction is localized predominantly on the top (bottom) surface as a top (bottom) state.

Furthermore, we calculate the spins of top and bottom states at several momenta on the equi-energy contour. Figures 10(a) and (b) show the projection of the spin on the $x$–$y$ plane in momentum space for top and bottom states, respectively. The direction of the spin at each $k$ appears to be tangential to the equi-energy contour, which is a manifestation of the spin-momentum locking intrinsic to 3D TIs [16]. The direction of the spin is exactly opposite for the states $\varepsilon_1(k)$ and $\varepsilon_2(k)$, hence the top and bottom surface states have opposite helicities. These observations indicate that despite the opening of the gap at the $\Gamma$ point due to interaction between the two surfaces for a 5QLs-thick slab, the states appearing across the bulk band gap at this thickness are of topological character.

In order to investigate the effect of the slab thickness on the helical spin-texture of the surface states, we determine the orientation of the spin $s$ of the Bloch states $\varepsilon_{1,2}(k)$ for thicknesses in the range of 5–20 QLs. The orientation of vector $s$ in momentum space at each $k$ can be described by two angles: $\theta$, or in-plane tilting angle, which is the angle between $s$ and the normal to the contour at point $k$, and $\psi$, or out-of-plane tilting angle, which is the angle between $s$ and the direction perpendicular to the plane (see figure 11(c)). For a perfect spin-momentum locking $\theta = \psi = 90^\circ$. Note that the angles $\theta$ and $\psi$ oscillate as functions of $k$ along the equi-energy contour due to the three-fold rotational symmetry of the slab crystal structure [30]. In addition, at each value of momentum the in-plane and out-of-plane tilting angles of the top and bottom states are equal in magnitude and have opposite signs. Hence we compute the deviations of $\theta$ and $\psi$ from $90^\circ$ only for the top state. The resulting absolute-value deviations, averaged over $k$ on the equi-energy contour, $\langle \Delta \theta \rangle$ and $\langle \Delta \psi \rangle$, are plotted as functions of the thickness in figures 11(a) and (b), respectively.

Both in-plane and out-of-plane deviations decrease with increasing slab thickness. The dependence of $\langle \Delta \theta \rangle$ shows a kink at 6 QLs, consistent with the increase of the gap at the $\bar{\Gamma}$ point (see figure 5), while $\langle \Delta \psi \rangle$ decreases monotonically. Importantly, both $\langle \Delta \theta \rangle$ and $\langle \Delta \psi \rangle$ do not
decrease to zero with increasing thickness but instead saturate to a constant value. The saturation value is small for $\Delta \theta (\times 10^{-4})$ and relatively large for $\Delta \psi (0.03^\circ)$. The saturation starts at approximately 10 QLs for $\Delta \theta$ and at 7 QLs for $\Delta \psi$. The non-zero residual deviation from the perfect helical spin-texture at large thicknesses is a measure of the proximity of the equi-energy contour to bulk states. The further the contour is from the Dirac point, the stronger is the effect of the bulk continuum, with hexagonal wrapping in momentum space due to crystal symmetry, on the surface states located on the contour. For an equi-energy contour located at a higher energy (0.26 eV) we find considerably larger saturation values, namely $0.5^\circ$ for $\Delta \psi$ and $0.1^\circ$ for $\Delta \theta$. To summarize, both in-plane and out-of-plane deviations decrease with increasing slab thickness and with moving the equi-energy contour closer to the Dirac point. However, in the vicinity of the Dirac point the in-plane tilting angle appears to be more affected by the finite thickness while the out-of-plane tilting angle is more sensitive to the presence of bulk states.

The spin-polarization of the surface states at different energies and points in the 2D Brillouin zone is a quantity that can be probed experimentally [46, 47]. Based on the results of recent SR-ARPES measurements, we can make an assessment of some of the quantitative predictions of our calculations. We define the in-plane spin-polarization $P_\parallel$ of the Dirac-cone surface states as an averaged expectation value of the in-plane ($x$ or $y$) component of the spin on the equi-energy contour, located in the vicinity of the Dirac point (see figure 9(b)). For slabs with thicknesses above 5 QLs, we find $P_\parallel \approx 45-50\%$ (with 100% corresponding to the maximum value of the spin-projection, i.e. $\hbar/2$). This is in quantitative agreement with the

Figure 11. Deviation of the spin ($s$), associated with one of the states $\epsilon_{i,2}$ on the equi-energy contour, (a) from direction perpendicular to $k$ and (b) from in-plane orientation. (c) Orientation of $s$ in momentum space: $\theta$ is the angle between $s$ and the normal $n$ to the equi-energy contour, $\psi$ is the angle between $s$ and the direction perpendicular to the plane. We define $\Delta \theta (\Delta \psi) = |90^\circ - \theta (\psi)|$; $\langle \Delta \theta (\Delta \psi) \rangle$ is the average of $\Delta \theta (\Delta \psi)$ over $k$ on the equi-energy contour.
experimental result for $\text{Bi}_2\text{Se}_3$ family of 3D TIs [46]. The reduced spin-polarization of the surface states has been attributed to the effect of SO interaction [31].

Recent experimental work by Xu et al [47] investigated the effects of spin re-arrangements in the helical spin-texture of the surface states in both pristine ultra-thin films of $\text{Bi}_2\text{Se}_3$ and in magnetically doped samples. The authors demonstrated that deviations from the spin-momentum locking in ultra-thin films, where the inter-surface interaction is strong, respects TR symmetry, as clearly seen in our calculations. It was also shown that the coupling between the top and bottom surface states in ultra-thin films (3 QLs) leads to suppression of the in-plane spin-polarization at the $\Gamma$ point. Our calculations for a 3 QL-thick slab of $\text{Bi}_2\text{Se}_3$ are consistent with this observation. We found that the absolute value of the in-plane spin-component of the surface states at the $\Gamma$ point is less than 0.5% (for the upper branch of the surface states), while it increases to approximately 38% for large values of momenta away from the $\Gamma$ point (at $k_x = k_y = 0.1 \, \text{Å}^{-1}$), which is in quantitative agreement with experiment. Finally, we note that the important result of the work by Xu et al [47] is the observation of large out-of-plane spin-polarization near the Dirac point, which appears as a result of magnetic (Mn) doping and breaks TR symmetry. We anticipate that our calculations of the surface states spin-texture as a function of the thickness will be useful to study this effect in 3D TI thin films doped with magnetic impurities.

4. Conclusions

We have employed the $sp^3$ TB model, with parameters extracted from $ab\ initio$ calculations, to model the electronic structure of bulk and (111) surface of $\text{Bi}_2\text{Se}_3$ 3D TI. We presented a quantitative description of the band inversion mechanism for both bulk and slab geometry, which involves a detectable change in the spatial distribution of $p$-orbital projections of the wavefunctions of conduction band and valence band induced by spin–orbit interaction. The surface bandstructures, with the spatial character of Bloch states determined by quantitative criteria, were calculated for slabs with thicknesses up to 100 QLs. This thickness is well beyond what is accessible by $ab\ initio$ approaches.

Based on the calculated thickness-dependent gap due to inter-surface interaction and the atomic-projections of the wavefunctions for states at the $\Gamma$ point, we provided an estimate of the thickness ($\approx 40$ QLs) at which the energy gap is smaller than the numerical precision of our calculations and therefore the top and bottom surface states become completely decoupled.

Our calculations show that the TR invariant disturbances in the helical spin-texture of the Dirac-cone states, caused by the finite slab thickness and the proximity to bulk states, persist for thicknesses up to 10 QLs even in the vicinity of the Dirac point. The calculated in-plane spin-polarization of the surface states for thick slabs and the characteristic momentum-dependent spin-polarization of ultra-thin films are in agreement with recent experimental reports [46, 47]. These results indicate that our numerical approach is quite suitable to elucidate and predict the results of experimental studies addressing the effect of spin re-arrangement in 3D TI thin films, both in pristine materials and in the presence of magnetic dopants [47].

We would like to comment on our numerical observation that the top and bottom surface states become completely decoupled only for thick slabs containing tens of QLs. This numerical
estimate was obtained within the commonly available numerical precision and is therefore
relevant for any calculations similar to ours. For this thickness the estimated energy gap found
in our calculations is less than $10^{-3}$ meV, which is considerably smaller than the present
experimental resolution (few meV for typical ARPES experiments [14]). Our result implies that
systems above this thickness can be safely assumed to have decoupled surface states. However,
for the wide cross-over region between $10^{-3}$–$30$ QLs the assumption of decoupled surface states
must be taken with caution, both experimentally and computationally. Importantly, we showed
that the transition between the two different regimes (coupled or decoupled surface states) is
characterized by detectable changes in the real-space projection of the surface states
wavefunction. The ability to detect experimentally such subtle inter-surface coupling is
constantly improving.

We expect that the presence of a weak but finite interaction between the opposite surfaces
is going to be crucial for the analysis of subtle effects, caused by external perturbations, in the
vicinity of the Dirac point. Preliminary calculations have shown that even a weak perturbation
in the form of a local modification of the on-site potential for an atom on the surface, can open a
sizable gap for thicknesses as large as $20$ QLs [62]. We attribute this gap to the combined effect
of the hybridization between the opposite surfaces that is still non-negligible for this thickness,
and to finite-size effects related to the limited size of the slab supercell in the other two spatial
dimensions (perpendicular to QL stacking direction). This may further hinder the identification
of the gap induced purely by the presence of TR-breaking perturbations, such as magnetic
impurities.

Recent experimental work carried out by Kim et al [65], which investigated phase coherent
transport in Bi$_2$Se$_3$ thin films, supports our point of view on the importance of inter-surface
coupling and resulting small (sub-meV) hybridization gaps even for relatively thick slabs with
thicknesses greater than $10$ QLs. In [65] it was shown that the the magnitude of weak
antilocalization, which is expected for true 2D topological surface states, is extremely sensitive
to the inter-surface coupling and signals a hybridization gap of $0.3$ meV for a $12$ QL-thick slab.
Our estimated gap for this thickness ($10^{-3}$ meV) would imply that in these samples the phase
coherece time is of the order of $1$–$10$ ns.

Effects due to finite thickness can also be expected in Landau level spectroscopy of 3D TI
thin films [63]. On one hand, it has been shown experimentally that in Bi$_2$Se$_3$-like materials the
characteristic field-independent (zeroth) Landau level is absent for slabs with thicknesses
smaller than $3$ QLs but emerges already for $4$ QLs [61]. On the other hand, a recent theoretical
study suggests a splitting of the zeroth Landau level due to hybridization between top and
bottom surface states [64]. Based on these considerations, one might expect that a non-
negligible inter-surface interaction can lead to more subtle internal structure of the zeroth
Landau level, persisting even for relatively large thicknesses.

We anticipate that microscopic TB models, combined with input from ab initio
calculations, will play an increasingly important role in practical calculations of various
properties of TI materials. These include the detailed character of the surfaces states
wavefunction, which to some extent can already be probed experimentally [22], and the
interplay between the surface states and external perturbations [24]. In fact, a finite-cluster TB
approach, based on the model used in the present work, has already been employed in the study
of native defects in Bi$_2$Se$_3$, showing good agreement between the calculated local densities of
states around the defects and experimental STM topographies [66]. In connection to this last
point, we would like to mention that despite extensive studies of the effect of magnetic doping in 3D TIs, a consistent microscopic description of a single magnetic impurity in a TI environment appears to be incomplete, especially when compared to the progress that has been made in investigating similar questions in semiconductors, both theoretically [36, 37] and experimentally [67, 68]. A realistic TB approach could be indispensable in providing such a microscopic description for single impurities in 3D TIs.

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