Electronic structure of 9 quintuple layers Bi$_2$Se$_3$ within Density Functional Theory

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Abstract. Bismuth Selenide (Bi$_2$Se$_3$) is a well-known 3D-type topological insulator. The interior part of this material is insulating, while its surface state is metallic which is protected by time-reversal symmetry. The experimental study of this material by varying its thickness reveals that the metallic surface state starts to appear at a minimum thickness of six Quintuple Layer (QL). This study was performed within the Density Functional Theory (DFT) in which a vacuum gap is added to the multilayer structure in order to capture the surface states of the material. While a previous study has explored the electronic structure of this material up to a thickness of 8 QL, a more detailed information of how the system evolves from this thickness to a fully bulk limit has not much been explored. With this motivation, we propose to calculate the electronic structure of this material with thickness of 9 QL. We perform the DFT calculation using Quantum Espresso (QE) package. Our results show that the band structure of this system reveals the surface metallic states with many additional bands as compared to those of thinner layer systems.

Keywords: Topological insulator, Bi$_2$Se$_3$, DFT, surface states, electronic structure

1. Introduction

A topological insulator is a material that has opposite electrical properties in the inside and the surface of the material. The inside part of the material is insulating, but there is a metallic state that occurs on the surface because of the topological invariance of the wave function of the system. This phenomenon occurs due to spin-orbit coupling that drives the electron inside the material. The first study of the topological insulator starts from a simple system called Quantum Hall Droplet. Later, physicists found that topological insulator material should necessarily be built from atoms of nearly-heavy elements and small-band gap semiconductor. The requirement of a nearly heavy element is based on the fact that spin-orbit coupling would become strong enough to modify the band structure of the material, while the small-band gap is needed as the large-band gap material is hard to be modified by spin-orbit coupling [1].

The search of topological insulator was peaked on the material bismuth selenide (Bi$_2$Se$_3$) and bismuth telluride (Bi$_2$Te$_3$), which have fulfilled the requirements above. Bismuth Selenide is determined to be three dimensional (3D) kind of topological insulator. The boundary of this material is a metallic state, and the bulk is an insulator. There are many experimental and theoretical studies of this material [1, 2].

One of the experimental studies of this material was performed by varying the thickness of the material [3]. The experiment took samples of 1-6 Quintuple Layer (QL) thickness, except 4 QL. The sample with thicknesses of 1-3 QL exhibits small gaps between the conduction band and the valence band. Here, the surface states still appear as a pair of lower and upper band with a small gap separating
them. These surface states have to do with rashba-type spin-orbit coupling. The gap at low thicknesses appear due to hybridization between two surface states of opposite surfaces of the material [3, 4]. As the system thickness increases from 2 QL to 3 QL, these opposite surfaces get farther apart resulting in the splitting of the surface states. This splitting continues and evolves to form a band crossing at 5 QL, similar to the Dirac cone in graphene bandstructure. At 6 QL the formation of a nearly linear band crossing at the $\Gamma$ point becomes more apparent. Thus, the system can be considered to become a well-defined topological insulator starting at 6 QL.

The experimental study of Ref. [3] has motivated a number of further theoretical studies, especially to calculate the electronic structure using DFT. DFT is a common method to study electronic structure of solids or molecules [5]. Of our particular interest is the DFT study of the thickness dependence of bismuth selenide ($\text{Bi}_2\text{Se}_3$) up to 8 QL and its influence on the electronic structure and optical properties of the material [4].

This study has simulated the material with thickness variation from 1 up to 8 QL and reveals the metallic surface states in the band structure starting at the thickness of 3 QL. In this present study we would like to extend their study by investigating the electronic structure of the material with the thickness of 9 QL.

2. Computational method

We implement the DFT calculation using Quantum Espresso (QE) package [6]. Within the QE package there are two important calculations: SCF (self-consistent field) and NSCF (non self-consistent field). The SCF calculation essentially produces the self-consistent electron density, while NSCF yields the eigenvectors and eigenvalues of the system Hamiltonian. When we run the SCF calculation, we only need small number of k-points (here we use $8 \times 8 \times 1$). While for the NSCF calculation we need larger number of k-points (which in this case we use $32 \times 32 \times 1$).

We use primitive hexagonal cells to model the thin film of $\text{Bi}_2\text{Se}_3$ with lattice parameter $a = b = 4.13$ Å and $c = 26.32$ Å [7]. As the algorithm has been designed essentially to handle three-dimensional system, for calculation of quasi two-dimensional system one has to add vacuum spaces on top and bottom of the corresponding supercell. The length of the vacuum space on each side of the supercell needs to be made large enough such that when such a unit is repeated along the direction where the vacuum spaces are inserted it would generate a system with many quasi two-dimensional system with a vacuum gap separating every two adjacent slabs. If each vacuum space is large enough the entire system forms as a collection of independent quasi two-dimensional systems. This way, we can safely consider each individual slab as a good representative of independent quasi two-dimensional system. In our model, we construct a vacuum space with a thickness of 10 times 3 QL on each side of our super cell such that every two adjacent slabs is separated by 20 times 3 QL long vacuum gap. In figure 1, we illustrate how we construct our supercell. Note, however, that the figure only shows a small part of the length of the vacuum space on each side just for the illustration.

The unavailability of the detailed information of atomic positions of the system leads us to determine the atomic positions solely based on the general information of the crystal structure [7]. After doing so we obtain the crystal structure, where we illustrate only for 3 QL thickness as shown in figure 2a. For 3 QL thickness, there are effectively 15 atoms contained in the supercell. The bismuth selenide structure is arranged in one quintuple layer composed of 5 atoms consisting of two Bi atoms and three Se atoms arranged alternately. As the standard procedure in DFT to ensure that we obtain the correct, i.e. stable, atomic positions we need to do structural optimization by relax calculation. After the relax calculation, we obtain the optimal structure as shown in figure 2b.

The resulting atomic positions after structural optimization are presented in table 1. In this study we aim to calculate the $\text{Bi}_2\text{Se}_3$ system with a thickness of 9 QL. In our calculations we use the cutoff energy of wave function about 40 Ry. We set this value after the convergence test of the cutoff energy ($\text{ecutwfc}$) on the system with 3 QL thickness, as shown in figure 3. We accommodate possible Van der Waals interaction between adjacent QL layers in a unit cell by setting the DFT-D3 correction on the input of
Figure 1. Unit supercell with thickness of 3 QL and vacuum gaps on top and bottom.

Figure 2. Crystal structure (a) before and (b) after relax calculation.

Table 1. Atomic positions after relax calculation.

| Atom | x(Å)     | y(Å)     | z(Å)     |
|------|----------|----------|----------|
| Bi   | 0.000000000 | 2.389013277 | 26.381185952 |
| Se   | 2.069000000 | 1.194459769 | 24.786420167 |
| Se   | 0.000000000 | -0.000006300 | 22.413978240 |
| Bi   | 0.000000000 | 2.389084152 | 20.819254311 |
| Se   | 2.069000000 | 1.194527324 | 18.880458959 |
| Bi   | 0.000000000 | -0.000011495 | 16.941658632 |
| Se   | 0.000000000 | 2.389061005 | 15.346917468 |
| Se   | 0.000000000 | 2.389034286 | 12.973383870 |
| Bi   | 0.000000000 | 0.000003074 | 11.378522723 |
| Se   | 0.000000000 | 2.389070870 | 9.439411840 |
| Bi   | 2.069000000 | 1.194546022 | 7.500293317 |
| Se   | 0.000000000 | -0.000011495 | 5.905492677 |
| Se   | 0.000000000 | 2.388992782 | 3.533618949 |
| Bi   | 2.069000000 | 1.194469511 | 1.938900504 |
| Se   | 0.000000000 | -0.000237370 | 0.000102391 |

QE. We use the norm-conserving pseudopotential [8]. The spin-orbit coupling is included by setting-up the non-collinear calculation and using the relativistic pseudopotential. Band structure calculation is started by SCF calculation using automatic mode k-points generation, where in our case we use $8 \times 8 \times 1$ k-poins. We then continue with NSCF calculation using k-points in crystal_b mode for $\Gamma$, K, and M high symmetry points that are listed in table 2. This high symmetry points of the hexagonal Brillouine
3. Results and discussion

After running SCF, NSCF, and bands calculation, we obtain the band structure of 9 QL bismuth selenide as shown in figure 5. There are 518 bands calculated through quantum espresso package, and we include all bands to be plotted. The Fermi energy of this system is found to be 5.7934 eV. This Fermi energy line crosses a band, namely it does not lie inside a gap, which indicates that the states represented by this band of the system is metallic. However, it is important to note that the band in which the Fermi energy is located only comes from the surface states, whereas all the bands corresponding to the bulk states form groups of lower and upper bands that are very well separated by a gap, indicating that the bulk part of the system is insulating. The surface band exhibits a crossing at the Γ point similar to that of the Dirac cone in graphene band structure. This Dirac cone-like structure confirms the topological insulator behavior of the system, as explained before. Other features of this band structure are inverted bands near the Γ point. These inverted bands occur as a consequence of the presence of spin-orbit coupling included in the calculation consistent with that explained explained in Ref. [2]. The result of this study confirms that the thin film with 9 QL thickness exhibits metallic surface states with the bulk states having well defined energy gap, characterizing the topological insulator. Of course we obtain more bands as compared to the systems with less number of QL layers.
4. Conclusion
We have presented our DFT study for a 9 QL thickness Bi$_2$Se$_3$. From our calculation results, it is clear that the system we study exhibits metallic states on the surface of the system while maintaining the bulk part of the band structure with a well-defined energy gap. In addition, we obtain all the expected features of the topological insulating characteristics of Bi$_2$Se$_3$, such as the Dirac cone-like structure and the inverted bands. Our overall results confirm the properness of the computational method we implement with the Quantum Espresso package.
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