Role of spin-orbit coupling in semimetallic bulk Bismuth

Soumyasree Jena¹, Sanjoy Datta²

¹Research Scholar, Department of Physics & Astronomy, Nit Rourkela, Rourkela, India
²Assistant Professor, Department of Physics & Astronomy, Nit Rourkela, Rourkela, India
E-mail: 515ph1013@nitrkl.ac.in, dattas@nitrkl.ac.in

Abstract. Ever since the prediction of nontrivial topological band structure in Bi₁ₓSbx and its subsequent experimental verification, semimetallic bismuth (Bi) has been used quite regularly in a large class of topologically nontrivial materials. On top of it, the recent unexpected discovery of superconductivity in the bulk Bismuth has made it an even more enigmatic material. Although, bulk bismuth has been studied quite extensively both theoretically and experimentally, the observation of superconducting ground state in bulk Bismuth at ambient pressure demands elaborate cross-examination of the electronic structure of Bi. Here, we have used density-functional-theory based first principle calculation to probe the system systematically and obtained qualitative agreement with the experimental result. Interestingly, we have observed the presence of electron pocket close to the symmetry point L and hole pocket near the symmetry point T albeit without the inclusion of spin-orbit coupling. Furthermore, when spin-orbit interaction is taken into account the hole pocket at T disappears and reappears close to Γ rather strongly. We demonstrated the importance of structural optimization and proper Brillouin zone sampling in reproducing the semimetallic behaviour of Bi.

1. Introduction

Theoretical understanding of the intricate connection between the topology of the band structure of a material and resultant nontrivial transport properties during the beginning of twenty first century has led to an intensive theoretical and experimental effort. These materials, now commonly known as topological insulators (TI), have insulating bulk electronic band structure along with the presence of conducting surface states inside this bulk band gap. In 2005, Kane and Mele [1] have proposed classification of these materials into two categories, weak and strong, based on Z₂ index. Fu and Kane [2] had predicted Bi₁ₓSbx as the first candidate for three-dimensional topological insulator. Soon after this prediction, it was verified experimentally by D. Hsieh et al.[3]. Within the next few years, Bi₁₋ₓTeₓ and Bi₁₋ₓSeₓ had been predicted and experimentally verified as topological insulators [4][5][6]. These discoveries motivated researchers to come up with theoretical proposal of new Bi based topological insulators, for instance, using first-principles calculations M. S. Barhamy et al.[7] have shown that under pressure non-centrosymmetric topological insulating phase appears in BiTeI. On the other hand, very recently it has been found [8] that at ambient pressure single crystalline semimetallic Bi becomes a superconductor below 0.53 mK. This was quite unexpected as the carrier density in bulk Bismuth is typically quite low at ambient pressure. Understanding these wide range of properties of materials involving Bi is a challenging task. However, first-principles based study of its electronic properties can improve our understanding. Earlier, Gonze et al.[9] have performed density-functional-theory (DFT) based first principle calculation with Perdew-Zunger [10] exchange-correlation and norm-conserving ionic pseudopotentials. For Bi, in presence of spin-orbit (SO) coupling, they have found the existence of free electrons at L and free holes at T. A similar conclusion was drawn [11] from a
tight-binding based first-principle calculations. They have constructed third neighbour tight binding model with the inclusion of the spin-orbit coupling parameter to justify the hole and electron pockets in the Fermi surface. Both of these first-principle based calculations emphasize the importance of SO coupling for the semimetallicity of Bi.

Here, we have used DFT-based first principle method [12], [13] supplemented by ionic pseudopotentials for the reassessment of the semi-metallic nature of Bi. The role of the structural details, nature of the pseudopotentials and SO coupling have been studied systematically in order to reproduce the experimental observation of Bi. We have calculated the band structure and density of states (DOS) in each case and analyzed it.

This article starts with a brief introduction of the structure and the structural details that has been used for our calculations. Next, we have presented our theoretical method. Finally, we have presented our results and discussed the similarities and dissimilarities compared to previously reported theoretical results.

2. Structural details

![Figure 1. (a) rhombohedral unit cell of Bi (left) and (b) the corresponding Brillouin zone (right).](image)

The crystal structure of Bi possesses rhombohedral symmetry with A7 structure as shown in Figure 1(a). This unit cell contains two Bi atoms indicated as dark circle and red circle. Lattice vectors are shown in solid black lines with arrows which are of equal length $a_0 = 4.7236$ Å. The angle between any pair of translational vectors is $\theta = 57.35$. Specifying the ratio $c_1/c_2$ completes the description of the rhombohedral unit cell. In case of Bi, $c_1/c_2 = 0.88$; The Brillouin zone (BZ) and the symmetry points along which the band structure has been calculated is shown in Fig. 1(b). These data have been obtained from reference [14].

3. Theory and computational method

We have performed our DFT based first-principle calculations with plane-wave basis set and ionic pseudopotentials as implemented in the QUANTUM ESPRESSO (QE) package [15]. In this article, we have systematically calculated the band structure for non-relativistic, scalar-relativistic and full-relativistic pseudopotentials. For the non-relativistic case, we have used a norm-conserving pseudopotential with Perdew-Zunger(PZ) exchange-correlation functional. The scalar-relativistic pseudopotential has been used with Perdew-Burke-Ernzerhof(PBE) exchange-correlation functional [16], [17]. These two type pseudopotentials do not take into account of the SO coupling and has been used as a hypothetical scenario. But surprisingly these pseudopotentials reproduce the semimetallic behaviour of Bi. Finally, we have used the full-relativistic pseudopotential with PZ exchange-
correlation functional. This pseudopotential explicitly takes into account of the SO coupling. Before performing further calculation with any pseudopotential, we have tested the convergence of the total energy and the minimization of force on the structure with respect to cut-off energy of the plane-wave basis set, the BZ sampling, i.e. choice of k grid and structural parameters. The choice of k-grid plays an important role for correct sampling of the BZ. We have used two types of k-grids for the self-consistent field (scf) solution of the Kohn-Sham equations. First we have chosen our BZ sampling based on Monkhorst and Pack (MP) [18] and for the second type, we have used a set of 30 k-points taken along the path Γ-L-T-Γ. The weight factor of these 30 k-points have been calculated by following the prescription of Chadi-Cohen [19]. For the calculation of the band structure, we always use the second type of k-input. The MP grid can be centered at Γ or can be shifted from it. Also, the choice of MP grid is very sensitive on the choice of pseudopotential. For example, for the non-relativistic pseudopotential we have used a shifted MP grid of size 14*14*14 while a shifted k-grid of size 4*4*4 has been used for the scalar-relativistic pseudopotential. For full-relativistic pseudopotential the optimum MP k-grid turns out to be 7*7*7 centered at Γ. In the results section, we have compared our results for these two types of BZ sampling and have discussed in detail what is the best for a given pseudopotential.

4. Results

Before calculating the band structure and the DOS, it is utmost important to ensure our structural parameters. We have found that irrespective of the nature of the pseudopotential and choice of k-grid, the force on the structure is always significant when the experimental structural data mentioned in Sec. 2 is used. Hence, at first we have allowed the structure to relax by making the force on it to be zero. This criterion helped us to choose the optimum set of k points for the BZ sampling. In the following, we presented systematic analysis of the force on the structure for each type of pseudopotential. After optimizing the force, we performed our band structure and DOS calculations. Subsequently, we analyzed our data and pointed out the similarities and dissimilarities compared to previously published results.

4.1. Non-relativistic pseudopotential

In reference [9], Bi band structure without SO coupling has been calculated. We revisited this hypothetical situation and found surprising but interesting differences in the band structure as compared to previously reported results. For our purpose, we have used a non-relativistic pseudopotential with PZ type exchange-correlation functional.

In Table 1, we have shown the comparison between the force on the structure with the structural data of Sec. 2 and fully relaxed structure. As it is evident from the data, that the force on the structure reduces significantly, once it is allowed to relax. However, it is not immediately clear what should be the choice of k-input type. In Fig. 2 we have shown the band structure of unrelaxed and relaxed Bi structure for our BZ sampling. It is evident that the structural data of Sec. 2 is not suitable to reproduce the observed semimetallic behaviour of Bi within our chosen computational method. When the relaxed structure of Bi is used in our calculations, it shows vast improvement in the band structure calculations.

| k-Grid Type | Force without relax | Force with relax |
|-------------|---------------------|-----------------|
| 30 k-points | 0.017527            | 0.000003        |
| MP (14 × 14 × 14 1 1 1) | 0.001343 | 0.000004 |
Figure 2. Band structure of Bi for 30 input k values and without SO coupling for (a) unrelaxed and (b) relaxed structure. (c) Magnified view of the relaxed band structure around the Fermi level.

Electron carriers are found close to the L and Γ symmetry point even without inclusion of SO coupling. This differs from the previous results [9], [11] as they have found the electron pocket exactly at L. However, the hole carriers are found exactly at T. Surprisingly the valence band and the conduction band create a Double-Dirac cone like structure at the Fermi level. We have compared our results by taking a MP grid for the SCF calculations, for which the force on the structure is negligible.

Figure 3. (a)complete and (b) Magnified view of the band structure of relax structure of Bi calculated with MP k-grids and without SO coupling. (c) DOS corresponding to Fig.2 (b).

The results are presented in Fig.3. Here also the unrelaxed Bi structure does not show signature of semimetallicity. This result is not included here. In case of the relaxed structure, we have found similar type of electron carriers close to L and Γ. However, there are no holes at the T symmetry point rather it contributes electrons to the system.

4.2. Scalar Relativistic Pseudopotential

Next, we turned our focus on to scalar-relativistic pseudopotential. We have found that when this pseudopotential is used with PBE type exchange-correlation functional, it gives reasonable agreement with experimental observations. In Table 2, we present the complete structural optimization data. Once again the importance of structural optimization is quite evident from the data. Without the SO coupling the force is lower in case of uniform BZ sampling using MP k-grid.

| k-Grid Type         | Force without relax | Force with relax |
|---------------------|---------------------|------------------|
| 30 k-points         | 0.043892            | 0.000046         |
| MP(4 × 4 × 4 1 1 1) | 0.002311            | 0.000039         |
In Fig. 4 and Fig. 5 we have presented the band structure and the DOS results without SO coupling for our input k set and MP k-grid respectively. It is clear that MP type BZ sampling fails to capture the electron carriers close to the L symmetry point but shows evidence of electrons close to Γ. Our k-input set does a better job as it shows evidence of electrons near to L and Γ while holes emerge clearly at T.

**Figure 4.** (a) Band structure of relaxed structure of Bi for scalar relativistic pseudopotential with 30 k-points and without SO coupling and (b) Magnified view of the band structure.

**Figure 5.** Scalar relativistic pseudopotential with MP k-grids and without SO coupling (a) relaxed band structure (b) Magnified view of band structure and the (c) density of states.

4.3. **Full relativistic pseudopotential**

| Grid Type                | Force without relax | Force with relax |
|--------------------------|---------------------|------------------|
| 30 k-points              | 0.025481            | 0.000022         |
| Mp grids(7 × 7 × 0 0 0)  | 0.002342            | 0.000035         |

Finally, we turned our attention to the full relativistic type pseudopotential which takes into account the SO coupling explicitly. In Table 3, we have compared the forces acting on the Bi structure and found that our way of doing the BZ sampling produces the structure closest to the equilibrium. We have used the PZ type of exchange-correlation functional in order to have direct comparison with the results of Gonze et al.[9]. In Fig. 6 the band structure is shown for our input k sample. There is clear signature of electrons close to L point and enhanced amount of holes close to Γ. However, the most striking difference compared to previously reported results appears at T symmetry point. In our calculations, a large gap appears between the conduction band and the valence band at T. As one case see from Fig. 7, a similar kind of gap opened up at the T symmetry point when MP type BZ sampling is used. In this case, also we have found the enhanced amount of holes close to Γ. However, the electron carriers appear barely close to the L symmetry point. The semimetallic nature of Bi is well captured in the DOS calculation.
4.4. Discussions and Conclusions

We have performed a systematic analysis of effect of the nature of pseudopotentials, BZ sampling and SO coupling on the band structure of bulk Bi using DFT based first-principle calculation as implemented in QE. We have found that the direct use of the experimental structural parameters does not reproduce the semimetallic property of Bi. This is because the structure is stressed. However, when the band structure is calculated after allowing the structure to relax, we managed to capture the semimetallicity qualitatively. Furthermore, by using this relaxed structure along with a non-relativistic and scalar-relativistic pseudopotential, we have demonstrated that it is possible to capture the semimetallic nature of Bi even without SO coupling. However, contrary to the previous theoretical claim, electrons appeared slightly away from the L symmetry point and also near to the Γ point. We have agreement about the hole carriers at the symmetry point T. When we use a full-relativistic pseudopotential which takes into account of the SO coupling explicitly, we found some surprising differences compared to previously reported result.

When SO coupling is considered explicitly, the amount of hole carriers increases significantly compared to non-SO pseudopotentials, but only close to Γ point and not at T. In fact, at T a relatively large gap opened up between the valence and conduction band.

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