First Principles Evaluation of Topologically Protected Edge States in MoS$_2$ 1T' Nanoribbons with Realistic Terminations

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Abstract—Exploiting novel materials with advanced properties is necessary to improve device performance and continue with their scaling for high performance applications at reduced power. Among these materials, topological insulators (TIs) present an exciting opportunity where the highly conductive edge states, which are protected against back scattering, can lead to advances in electronic as well as spin controlled devices. Here, we present first principles results that evaluate topologically protected edge states in MoS$_2$ nanoribbons. We vary the width of the nanoribbons and show that they transition to trivial insulators below a critical width. Furthermore, the trivial insulator can be a direct or indirect band gap insulator depending on the width and the edge termination. Our results show that including realistic edge terminations can provide valuable insight, especially for narrow width TIs.

Index Terms—Density Functional Theory, Edge States, Topological Insulators, Nanoribbons

I. INTRODUCTION

Over the past decade, well-known two-dimensional transition metal dichalcogenides (TMDs) – such as MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ – have been shown to exist in topologically non-trivial phases known synonymously as either TIs or quantum spin hall insulators [1]–[5]. This behavior does not occur in their 2H polymorph, which is their ground state, but rather in other high energy polymorphs including the 1T’ phase. Their topological nature stems from the underlying symmetries that their Hamiltonians possess, which leads to their electronic structure being classified by a robust $Z_2$ invariant of 1, whereas that of a trivial insulator is 0 [6]. As a necessary consequence of their non-trivial topology, interfacing them with a trivial insulator results in chiral, zero gap edge states with outstanding properties including linear dispersion, spin-momentum locking, and resistance to back-scattering [6], [7]. Reliably understanding their behavior is expected to bring about exciting advances in electronic and spintronic devices.

Studies in the literature have used both ab initio and semi-empirical methods to describe the electronic structure of the different 1T’ TMDs. Various $k \cdot p$ and tight-binding model Hamiltonians whose parameters were fitted to the bulk dispersion relations have been used to predict the behavior of the topologically protected edge modes in nanoribbons [1], [3], [4], [8]. At small nanoribbon widths, due to an interaction of the topologically protected states from the opposite edges in a nanoribbon, a small gap in the otherwise gapless linear spectrum of the edge states is predicted to open [8]. This results in a decrease of the ballistic conductance compared to a semi-infinite sample. This gap increases when an electric field is applied perpendicular to the nanoribbon resulting in a further reduction of the conductance. At the same time the separation between the bulk bands decreases with the orthogonal field. The edge-localized modes transform into the bulk-like modes when their dispersion intersect, signifying a transition from a TI to a trivial insulator. As no edge modes protected from back-scattering exist at higher electric fields, the conductance decreases dramatically [9]. Studies using ab initio and tight-binding calculations also show that a gap opens in the edge states [4], [5], [10]. However, these studies additionally show that the electronic structure of these narrow nanoribbons are highly dependent on the reconstruction of the edges’ atomic.
Here, we use density functional theory (DFT) to model monolayer and realistic terminations of narrow nanoribbons of MoS$_2$ 1T$'$, We focus on nanoribbons cleaved in the y-direction, such as the terminations shown in Fig. 1, in contrast to previous studies in the literature which studied nanoribbons cleaved in the x-direction [5], [10]. We show that at small widths, the nanoribbons no longer have edge states in the band gap. This is in contrast to nanoribbons cleaved in the x-direction which possess gapless edge states even at relatively small widths. Furthermore, we show that depending on the termination, the electronic structure transitions to an indirect band gap.

**Fig. 1.** The MoS$_2$ 1T$'$ structure from the top and the side. The black and red dashed lines indicate the two possible, chemically equivalent, terminations along the y-direction and are made along the same plane for both top and side views. The red arrow in the bottom panel indicates the direction of the y-axis for both the top and side views. The pink spheres are the Mo atoms while the yellow spheres are S atoms.

**II. METHODS**

We use DFT as implemented in the Vienna Ab-Initio Simulation Package (VASP) to calculate both monolayer and nanoribbon systems of MoS$_2$ 1T$'$. Exchange and correlation were described using the generalized gradient Perdew-Burke-Ernzerhof (PBE) functional [11]. The projector augmented wave method and its associated pseudopotentials were used in all calculations. The electron density was expanded in a plane wave basis set whose cutoff was set to 280 eV. The system’s k-space was sampled on a Monkhorst pack grid of $8 \times 1 \times 1$ for geometry optimizations and $12 \times 1 \times 1$ for band structure calculations of the nanoribbons. For the bulk monolayer, this changes to $8 \times 8 \times 1$ for geometry optimizations and $12 \times 12 \times 1$ for band structure calculations. Electron densities were converged until the energy change was less than $10^{-4}$ eV. Geometries were optimized so that the energy changed by less than $10^{-3}$ eV. The topological edge states of TMDs depend on the band gap opening due to a spin-orbit interaction; therefore, all band structure calculations include the spin-orbit coupling [12].

In this paper, we focus on the 1T$'$ structure of MoS$_2$. To model the bulk monolayer, a vacuum gap of 2 nm was included in the z-direction and the cell and its atomic coordinates were optimized. The nanoribbon structures were then created by introducing another vacuum gap of 2 nm in the y-direction. Thus, the only remaining periodic dimension is the x-direction. After introduction of the vacuum gap, the atomic structure of the nanoribbons were optimized once more, resulting in significant reorganization of the edges which we refer to as realistic terminations.

**III. RESULTS**

We start by calculating the band structure of a monolayer of MoS$_2$ 1T$'$. Using a single unit cell containing six atoms, the cell and its atomic coordinates were optimized and the electronic structure was calculated. Fig. 1 shows the optimized atomic structure which is replicated for ease of visualization. The optimized 1T$'$ structure has Mo–S bond lengths of 2.39, 2.48, and 2.51 Å. The band structure of the system can be seen in Fig. 2 and has been projected onto the Mo ‘d’ and S ‘p’ orbitals. Around the Fermi level, which is at 0 eV, a
The electronic structure of the nanoribbons was calculated and varies with the width of the nanoribbon. The first thing to note is the appearance of a gap in the topologically protected edge states. This can be seen in Fig. 4, which shows the highest occupied and lowest unoccupied bands of two nanoribbons of different widths. The wider nanoribbon, 7.9 nm, shows linear dispersion of gapless states around the Fermi level at 0 eV, typically associated with the topologically protected edge states. As the width is reduced to 3.8 nm, the states are no longer linearly dispersed and appear to become more parabolic. This behavior was the same regardless whether the edge was symmetrically or asymmetrically terminated. In addition, a band gap of 0.1 eV appears between these edge states. Similar effects have also been seen in MoS$_2$ 1T′ nanoribbons that were cleaved in the x-direction [5], [10]. However, in that case, the gap only appeared at widths less than 2 nm and their magnitude was typically much smaller than the gap shown here for nanoribbons cleaved along the y-direction. In addition, ab initio calculations showed that of the six possible terminations, only two supported edge states without any other surface states [10]. However, on the y-axis edge, the topological edge states can be seen regardless of the
For narrow nanoribbons, the qualitative behavior changes depending on the termination. Fig. 5 shows the highest occupied and lowest unoccupied bands of a 1.2 nm wide nanoribbon terminated either symmetrically or asymmetrically as depicted in Fig. 1. Due to the narrow width of the nanoribbon and the interaction between the edge states, a large band gap opens up for both terminations. For the symmetric termination, the band gap is 0.3 eV, while it is 0.1 eV for the asymmetric termination. Curiously, for both terminations the qualitative nature of the edge state band gap changes from direct to indirect. For the symmetric nanoribbon, this is a slight shift, so that two minima appear in the conduction band which are shifted by 0.1 Å⁻¹ from the valence band maximum. However, for the asymmetric termination, the lowest conduction band minimum is located at the Γ point while the valence band maximum is at the Brillouin zone edge, indicating that band to band transitions in the asymmetric narrow nanoribbons could be suppressed due to the large change in crystal momentum required.

**DISCUSSION AND CONCLUSIONS**

The highly conductive topologically protected edge states of TIs can have a high impact on electronic devices. However, many fundamental models and theories are based on the properties of the bulk Hamiltonian and ignore the potential changes in the Hamiltonian for downsized systems as well as the effect of edge reorganization. Here, we have calculated the electronic structure of nanoribbons of topologically insulating MoS₂ 1T′ where the width of the nanoribbon was less than 8 nm. One can see that the edge states begin to interact with each other below 4 nm to open a band gap. This could indicate that some of the fundamental symmetries required for a topologically protected zero energy state have been broken. This effect, although still disputed, occurs for nanoribbons of MoS₂ 1T′ cleaved in the x-direction, where the introduction of certain edges introduce a magnetic moment which would break time-reversal symmetry, an essential component of the non-trivial Z₂ invariant [5, 14]. However, our calculations show that edges along the y-direction do not possess a magnetic moment. Furthermore, our results show that the edge termination can have a strong quantitative and qualitative effect on very narrow nanoribbons of MoS₂ 1T′.

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