A Comparative Study of Electronic Properties of Bulk MoS$_2$ and Its Monolayer Using DFT Technique: Application of Mechanical Strain on MoS$_2$ Monolayer

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Abstract

Electronic structure calculation of bulk and monolayer MoS$_2$ has been performed using plane wave pseudopotential method based on density functional theory. The indirect band gap in the bulk MoS$_2$ was found to be 0.9 eV, whereas in the monolayer-MoS$_2$ the band gap of 1.57 eV was found to be direct one. The calculated physical parameters of monolayer MoS$_2$ are found to be very close to the bulk MoS$_2$ and compare well with available experimental and other theoretical results. The calculated density of states (DOS) may help explain this change in the nature of band gap in bulk and in monolayer MoS$_2$. A further variation in band gap has been observed in MoS$_2$ monolayer on applying biaxial strain.

Keywords

MoS$_2$, DFT, Electronic Properties, Monolayer, Strain

1. Introduction

Layered transition-metal di-chalcogenides (LTMDCs) have been extensively reviewed in the recent past [1]. MoS$_2$ is a typical example of LTMDC family of materials which attracts investigation because of its distinctive industrial applications, ranging from use as a lubricant [2] and a catalyst [3] as well as in photo-voltaics [4] and energy storage [5]. In its bulk form MoS$_2$ is a semiconductor with an indirect band gap of about 1.23 eV while

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its monolayer has a direct energy gap of 1.8 eV [6]. A special attention has been paid on single layer MoS2 in the recent years. Upon thinning from the bulk [7]-[9] the electronic structure of MoS2 undergoes an interesting transition. Recently, a monolayer MoS2-based field effect transistor (FET) with HfO2 as gate insulator has been successfully implemented [10]. These ideal properties make monolayer MoS2 a very promising candidate for next generation FET and as optoelectronic devices [11]. This has raised enormous interest in exploring the extraordinary properties of mono layers of MoS2.

Theoretically, there are various possibilities of energy gap manipulation in MoS2. By reducing the layer thickness from bulk to monolayer, the indirect band gap energies in the bulk are shifted relative to the direct band gap in the monolayer limit [12]. It undergoes a transition from an indirect to direct gap exhibiting strong photoluminescence when confined in a 2D monolayer [13]. It has been suggested a way to engineer 3D semiconducting MoS2 nanoparticles with direct band gaps as well as metallic di-chalcogenides nanowires with promising catalytic and thermoelectric properties [14]. Eellis et al. carried out a study using HSE screened hybrid functional and offered improvement over semi local density functional [13]. All electron calculations including spin orbit coupling were performed [15] and confirmed indirect to direct band gap transition. Electronic structure of transition metal di-chalcogenides has been studied using ab initio theory using Troullier-Martin norm conserving, relativistic pseudopotentials in fully separable Kleinman and Bylander form [16]. They used exchange and correlation energies within LDA.

The properties of transition metal di-chalcogenides (TMDs) not only can be tuned by varying number of layers, but also can be modified by application of external field or strain engineering. Studies [17] [18] have confirmed that applying strain is one of the best possible strategies to tune the band gap, since it neither attenuates the properties nor is inefficacious for single layers. It has been predicted that straining MoS2 modifies the band gap energy and the carrier effective mass. Moreover, at strains larger than 1% the lowest lying band gap changes from direct to indirect [19]-[22]. It has been suggested that strain engineering of the band structure of MoS2 could be used to increase carrier mobility of MoS2, to create tunable photonic devices and solar cells [23] and even to control the magnetic properties of MoS2 [19] [20]. While strain perturbs the band structure of all materials, two-dimensional materials such as MoS2 can sustain strains greater than 11% [24] allowing exceptional control of material properties by strain engineering. In a recent study [25] the conduction band valley structure of a few layer MX2 by close examination of temperature dependent indirect excitation emission peaks has been explored. A study on elastic constants and electronic structures of two-dimensional monolayer MoS2 under elastic strain using first principle calculations has been made [26]. It is shown that the band gap of monolayer MoS2 undergoes a descent trend with the increase in strain. They observed a direct to indirect transition at strain of 0.01 and semiconductor to metal transition at strain of 0.10.

With the goal of understanding the electronic properties of bulk and monolayer MoS2 and strain engineering, we carried out ab initio calculations of bulk and monolayer MoS2 using gradient corrected exchange-correlation functional in DFT framework and observed a transition from indirect to direct band gap. However if this band gap can be tuned such that a semiconductor with a lower band gap or a semiconductor to metal transition can be achieved with the application of strain, then a wide range of tunable nano device can be fabricated. In the present work, therefore we study the effects of mechanical strains on the electronic properties of monolayer of MoS2. Our results suggest a way of band gap engineering in MoS2.

2. Computational Details

The calculations were performed using self consistent plane wave pseudopotential total energy method based on density functional technique as implemented in Quantum Espresso code [27]. This method has been previously used to study the electronic properties of undoped and doped graphene [28] [29]. The exchange correlation potential was approximated by generalized gradient approximation using Perdew-Wang 91 functional (GGA-PW91) [30]. The atomic positions and cell parameters were fully relaxed until an energy convergence of 10^{-9} eV reached. We used wave function- and charge-density cut-offs of 70 Ryd and 300 Ryd, respectively. First, we obtained lattice constants \(a\) and \(c\) by the process of total energy minimization. Optimized structure (coordinates) was used to perform self consistent calculations with a Monkhorst-Pack [31] 8x8x8 k-mesh followed by the non-self consistent calculations for band structures, density of states and partial density of states of bulk MoS2. We used 80x80x80 k-points mesh along the path \(\Gamma-K-M-\Gamma\) in the irreducible Brillouin zone to obtain the band structure with a very fine mesh points. However, for monolayer we used 8x8x1 and 80x80x1 Monk-
horst-Pack of \( k \)-points respectively for sampling Brillouin zone for calculations of structural properties and electronic structure. In case of monolayer MoS\(_2\), we created 15 Å vacuum along \( Z \) axis to isolate it and to prevent any interaction between the layers. The cohesive energy per atom of bulk MoS\(_2\) was calculated as \( E_{\text{coh}} = E(\text{MoS}_2) - E(\text{Mo}) - 2E(\text{S}) \), where \( E(\text{MoS}_2) \) is the total energy of the unit cell of Molybdenum disulphide, \( E(\text{Mo}) \) is the energy of Mo atom and \( E(\text{S}) \) is the energy of S atom. The cohesive energies per atom of monolayer MoS\(_2\) was also calculated accordingly. A uniform tensile strain ranging from 0 to 10\% were applied on monolayer MoS\(_2\) to study the change in behavior of its band gap.

3. Results and Discussion

3.1. Structural Parameters

Molybdenum disulphide has a hexagonal structure consisting of S-Mo-S layers as shown in Figure 1. Bulk MoS\(_2\) has two such layers and Mo atoms of one layer are directly above the sulphur atoms of the other layer and vice versa while monolayer MoS\(_2\) has a single S-Mo-S layer. We have calculated the structural parameters of bulk and monolayer MoS\(_2\) using GGA as shown in Table 1. The results of bulk MoS\(_2\) have been compared with experimental data while the results of monolayer are compared with some other theoretical results. We find excellent agreements as can be seen in Table 1. Our calculated lattice parameters overestimate the experimental values which is an inherent feature of standard GGA functional. It is concluded that all the structural parameters calculated for monolayer MoS\(_2\) are nearly identical to the structural parameters calculated for bulk MoS\(_2\).

3.2. Electronic Band Structure and Density of States

The electronic band structure of bulk MoS\(_2\) and corresponding density of states are shown in Figure 2. The electronic band structure and density of states can be divided into three sets of bands and states respectively, separated by gaps. In the first set, bands in electronic band structure and states in density of states around \(-14\) eV are mainly due to \(3s\) orbital of S atom separated by large gap from second set below Fermi energy in which \(3p\) orbital of S and \(4d\) orbital of Mo are mainly contributing and show strong hybridization. Third set above the Fermi energy in which main contribution is due to \(4d\) orbital of Mo is separated by band gap from second group.
Figure 2. Calculated band structure (left panel) and orbital-projected density of states (PDOS) on Mo (middle panel) and S atoms (right panel) in bulk MoS₂.

Table 1. Calculated structural parameters of bulk MoS₂ and mono layer MoS₂ using GGA. The available results have also been given for the purpose of comparison.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bulk-MoS₂</th>
<th>Monolayer MoS₂</th>
</tr>
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<tbody>
<tr>
<td>Lattice constant (a)</td>
<td>3.19 (present calculation)</td>
<td>3.195</td>
</tr>
<tr>
<td>[angstrom]</td>
<td>3.16 (Ref [1])</td>
<td>3.20 (Ref [32])</td>
</tr>
<tr>
<td>c/a ratio</td>
<td>3.86 (present calculation)</td>
<td>3.89 (Ref [1])</td>
</tr>
<tr>
<td>Cohesive energy (eV/atom)</td>
<td>4.960</td>
<td>4.979</td>
</tr>
</tbody>
</table>

below Fermi energy. A comparative band structure of MoS₂ bulk and its monolayer and bilayer are shown in Figure 3. The bands on each side of the band gap are derived mainly from the 4d states of Mo and 3p states of S in bulk, bilayer and monolayer MoS₂. The bands around the band gap are relatively flat, as expected from the d-character of electron states at these energies.

For bulk MoS₂ the valence band maximum is at high-symmetric Γ-point and conduction band minima is in between Γ- and K-points, revealing indirect band semiconductor as can be seen in Figure 3. If we compare the band structure of bulk and monolayer MoS₂, we observe that the band edge near Γ point has been shifted up by around 0.7 eV. In case of monolayer, at Λ and Σ point the band edge shifted up in such a way that the conduction band minima occurs at K-point. For monolayer the valence band maxima and conduction band minima are both at high-symmetric K-point revealing direct band gap semiconductor as can be seen in Figure 3. Thus there is a transition from indirect band gap to direct band gap as we go from bulk MoS₂ to its monolayer. A PDOS comparison of bulk and mono layer MoS₂ (as shown in the Figure 4) reflects that the states are essentially due to dₓ²₋ᵧ² and degenerate states dₓᵧ and dₓ₋₂ᵧ₂. The states dₓ₋₂ᵧ₂ and dₓᵧ are degenerate in case of bulk while little bit separating in monolayer. The calculated and measured band gap for mono layer MoS₂ and bulk are shown in Table 2. Our calculated band gaps are in good agreements with other theoretical values.

3.3. Tuning Electronic Properties by Biaxial Strain

To study the effect of strain on the electronic properties of monolayer MoS₂, we first relaxed the atomic position and obtained the optimized geometry. We apply the uniform strain (ε) to the monolayer MoS₂ in the range 0.0 - 0.10. The strained atomic structure is achieved by enlarging the hexagonal lattice a₀ with an increment of εa₀. Similarly the atomic structure is fully optimized and the band structure is calculated. As for strained structure of MoS₂, the band gap versus strain is shown in the Figure 5. The band gap is monotonic as the strain increases.
Figure 3. Calculated band structure of bulk (left), bilayer (middle) and monolayer (right) of MoS$_2$ at high-symmetric points in the irreducible Brillouin zone. The position of valence band maxima, conduction band minima and the band gap ($E_g$) are indicated. For monolayer MoS$_2$ the direct band gap occurs at K-point, unlike in other cases.

Figure 4. Calculated projected density of states (PDOS) of bulk and monolayer of MoS$_2$ are shown for Mo(4$d$) and S(3$p$) states. The legends for the $p$- and $d$-orbitals are similar for the monolayer and bulk.
Figure 5. The variation of band gap energy with strain of monolayer MoS$_2$.

Table 2. Energy gaps (eV) for bulk MoS$_2$ and monolayer MoS$_2$.

<table>
<thead>
<tr>
<th></th>
<th>Bulk MoS$_2$</th>
<th>Monolayer MoS$_2$</th>
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<tr>
<td>Present calculation</td>
<td>0.89</td>
<td>1.57</td>
</tr>
<tr>
<td>Experimental value</td>
<td>1.23 (Ref [6])</td>
<td>1.80 (Ref [6])</td>
</tr>
<tr>
<td></td>
<td>1.29 (Ref [35])</td>
<td></td>
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<tr>
<td>Theoretical results</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.7 (Ref [36])</td>
<td>1.55 (Ref [16])</td>
</tr>
<tr>
<td></td>
<td>1.05 (Ref [16])</td>
<td>1.70 (Ref [33])</td>
</tr>
<tr>
<td></td>
<td>1.15 (Ref [37])</td>
<td>1.78 (Ref [34])</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9 (Ref [38])</td>
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</table>

While the strain reaches 0.06, the indirect band gap vanishes. We observe a cross over in the figure. Upon $\varepsilon = 0.0$, the monolayer MoS$_2$ shows a behavior of semiconductor with direct gap, at $\varepsilon = 0.005$ it has direct (at K) and indirect (Γ-K) band gap of almost equal amount. These results are interesting. Not only the band gap of monolayer MoS$_2$ can be tuned by uniform strain, but also direct to indirect and semiconductor to metal transitions are controlled.

Very recently, in a paper by Das et al. [39] the strain driven direct to indirect transition in the band gap of MoS$_2$ and ZnO has been theoretically studied. They have found such transition in MoS$_2$ to occur at strain 0.83%, close to our calculated value of 0.5%.

4. Conclusion

In summary, we studied the structural and electronic properties of MoS$_2$ using plane wave pseudopotential method under GGA scheme based DFT calculations. Electronic band structure and density of states calculation show many similarities between monolayer-MoS$_2$ and bulk-MoS$_2$ except the nature of the band gap which is found direct for monolayer-MoS$_2$ as compared to indirect for bulk-MoS$_2$. This observation is consistent with the theoretical prediction of indirect to direct band gap transition in going from bulk to monolayer. Such behavior, arising from d-orbital related interaction in MoS$_2$, may also arise in other layered transition metal di-chalcogenides. A further variation in band gap has been observed in MoS$_2$ monolayer on applying strain. It points out a new direction of band engineering, hence such capability can lead to engineering novel behaviors and holds promise for new applications.
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References


Transitions in Few Layer MoS2, WS2 and WSe2.


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