Effect of dipole corrections and spin orbit coupling on tungsten dichalcogenides monolayer: A *in silico* first principles study

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***Abstract*— The structural and electronic properties of tungsten dichalogenides compounds (WS_2, WSe_2, WTe_2) were investigated from first principles calculations. We found that the structural and electronic properties changed both as a function of the dipole corrections and spin-orbit coupling (SOC). Comparing the calculated results with experimental values, we found that introducing SOC by itself in these 2D materials grossly underestimates the electronic band gap. Adding the self-consistent dipole correction results in larger electronic band gap for these tungsten dichalogenide compounds. Thus, the influence of dipole corrections in these 2D WX_2 materials was found to be significant. The SOC are not relevant for these materials and care should be taken on application of these dipole corrections**

***Keywords*— tungsten dichalogenides, monolayer, dipole correction, spin orbit coupling**

INTRODUCTION

The field of 2D material has attracted significant attention due to (a) their potential novel and innovative applications in various areas such as photocatalysis, spintronic materials, advanced solid state devices, etc. and (b) interesting physics that arises from quantum and geometric confinement attributed to reduced dimensionality. [1–16] Amongst these studied 2D materials is the group of compounds referred to as the transition metal dichalcogenides (TMDCs). They exhibit electronic properties that can tailored to for desired technological applications. Tungsten-based dichalcogenides (WX_2 = WS_2, WSe_2 and WTe_2) is one such systems due to its possible applications in topological quantum electronics and advanced solid state materials [17,18] due to their larger band gap. Mechanically exfoliated atomically thin sheets of WS_2 and WSe_2 have been shown to exhibit high in-plane carrier mobility and electrostatic modulation of conductance similar to MoS_2. [19–21] Some characteristics of WX_2 and MoS_2 are similar such as the metal-metal bond length and band structure features. [22]

Several studies have been carried out on the WX_2 systems. [23–30]. However, to the best of our knowledge there has been no study on the effect of dipole corrections on the calculated structural and electronic properties. Dipole corrections can be essential in eliminating non-physical electrostatic interactions between periodic images and improving the accuracy of calculated adsorption energies for molecules on surfaces. [31] For 2D materials, eliminating periodic images is essential in the proper description of the systems. The self-consistent scheme based on the method suggested by Neugebauer and Scheffler, which recalculates the correction potential at each SCF step, is used in the current study. The non self-consistent scheme, which is based on the approach by Yeh and Berkowitz involves the addition of a dipole correction after the SCF has converged. This involves the correction of the total energy and its gradients but not the electrostatic potential. Thus, the non self-consistent scheme would not be suitable in work-function calculations. Also, the effect of spin orbit coupling is evaluated to understand its role on the electronic structure of 2D WX_2 monolayers.

In this study, we computationally show that the dipole interaction and spin-orbit coupling leads to significant changes in the electronic properties of the WX_2 monolayers. The introduction of self-consistent dipole corrections in the WX_2 compounds significantly increased the electronic band gap of the tungsten-based dichalogenides in comparison to systems without the dipole corrections. However the introduction of spin-orbit coupling significantly decreases the electronic band gap of the WX_2 monolayers.

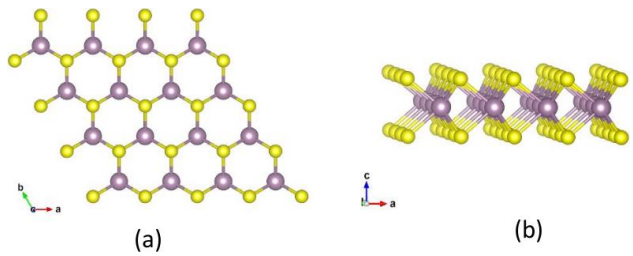

FIGURE 1: (Color online) Schematic model of pristine WS_2 monolayer structure (a) top view (b) side view. (magenta purple and yellow ball represents dopant, W and S atoms respectively).

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I. COMPUTATIONAL DETAILS

A spin polarized first-principles calculation [34, 35] as implemented in the CASTEP [31] module within the Materials Studio 2018 software package was used to evaluate the structural and electronic properties of WX_2 monolayers. The generalized gradient approximation (GGA) with norm-conversing pseudo-potentials [36, 37] in the form of Perdew-Burke-Ernzerhof [38] (PBE) was used.

Equilibrium lattice constants for the WX_2 monolayers were obtained using a Monkhorst-Pack [39] grid of 8×8×1. Convergence criteria of 10^{-7} eV were enforced for the calculated total energies and the monolayers were relaxed until the forces acting on each atom were less than 10^{-4}eVÅ^{-1}. To prevent interactions between its periodic images in the out-of-plane direction, an optimized vacuum distance of 18 Å was found to be adequate. The electronic band structures, density of states and optical properties for the unit cell were calculated using a more refined Monkhorst-Pack grid of 8×8×1.

As mentioned in section 1, the dipole correction was applied to the various considered WX_2 monolayers. The form of dipole correction applied is the Self-consistent, which is the most accurate option. This is because it affects the electrostatic potential as well as the total energy and its gradients unlike the non self-consistent correction. This option is known to be suitable for evaluating the effect of dipole corrections on surface work functions of a given system. The WX_2 monolayers were also evaluated without dipole corrections and with spin-orbit coupling to understand the nature of interactions in these monolayers.

II. RESULTS AND DISCUSSION

In this section, the calculated structural and electronic properties were presented and discussed.

A. *Structural properties*

The investigated WX_2 mono-layers crystallize in the hexagonal (1H) structure with the P-6M2 (D3H-1) symmetry group similar to MoS_2 mono-layers as shown in figure 1. The theoretically optimized lattice parameters using the GGA approach with (without) dipole corrections for the WS2, WSe2 and WTe2 monolayers are 3.1858 Å (3.1857), 3.3264 Å (3.3268) and 3.5712 Å (3.5712). Using the LDA approach, the theoretically optimized lattice parameters with (without) dipole corrections for the WS_2, WSe_2 and WTe_2 unit cells are 3.1243 Å (3.1242), 3.2543 Å (3.2543) and 3.4850 Å (3.4853). Using the LDA exchange correlation functional is known to consistently underestimate the lattice parameter compared to the GGA exchange correlation functional. [40]This findings also applies to the current investigation. The experimental lattice constant for the WS_2 and WSe_2 monolayers are 3.153 Å and 3.282 Å[41] These experimental values are in reasonable agreement with our calculated theoretical values within the GGA and LDA approaches. For the WTe_2, other theoretical studies have reported lattice parameter of ~3.60Å. [17,18,42,43]

The calculated lattice parameters for the WX2 compounds with spin-orbit coupling (SOC) using the GGA and LDA functional is presented in Table 1. The calculated lattice parameters within the GGA + SOC (LDA + SOC) approach were 3.1776 Å (3.1002), 3.3204 Å (3.2351) and 3.5698 Å (3.4746). The SOC calculations lead to a significant reduction in the lattice parameters in comparison to the calculations with and without dipole correction self-consistent respectively.

TABLE 1: The calculated lattice parameter (a in Å) and band gap (in eV), without dipole correction (without), with dipole correction only (with) and spin-orbit coupling (SOC) only using the GGA and LDA approach were presented.

		GGA		LDA	
Compounds	Calc	a	Band gap	a	Band gap
WS_2	Without	3.1857	1.814	3.1242	1.992
	With	3.1858	2.318	3.1243	2.455
	SOC	3.1766	1.530	3.1002	1.671
WSe_2	Without	3.3268	1.545	3.2543	1.703
	With	3.3266	2.232	3.2543	2.372
	SOC	3.3204	1.226	3.2351	1.352
WTe_2	Without	3.5712	1.036	3.4853	1.212
	With	3.5798	0.673	3.4746	0.829
	SOC	3.5712	2.020	3.4850	1.978

B. *Electronic properties*

The calculated density of states for the pristine WX_2 structures were presented to understand the effect of dipole interactions on the electronic properties.

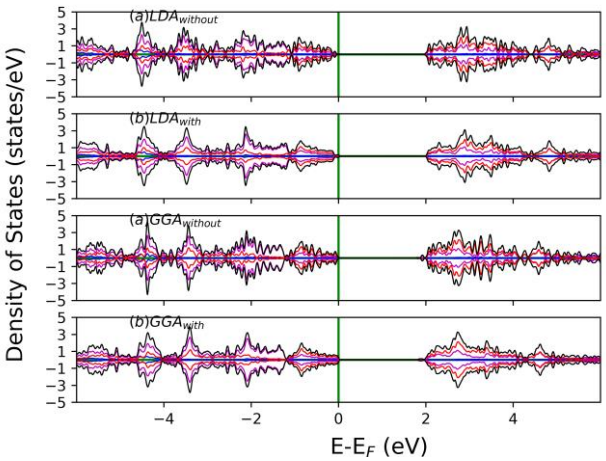

Figure 2: (Color online) The calculated spin-polarized projected density of states (PDOS) of the pristine WS_2 monolayer, where (a) LDA without dipole correction, (b) LDA with dipole correction, (c) GGA without dipole correction and (d) GGA with dipole correction . The blue, magenta and red lines represent the s-, p- and d- orbitals, while the sum of the s-, p and d- orbital is given as the black line. The energy levels are adjusted with respect to the Fermi energy.

Figure 2 shows the calculated total and partial density of states for the pristine WS_2 monolayer using the GGA and LDA functionals with and without dipole corrections. The electronic band gap for the WS_2 monolayer is 1.814 (2.318) and 1.992

(2.455) with the GGA (with dipole corrections) and LDA (with dipole corrections) respectively. The introduction of dipole interaction resulted in significant increase of the band gap by ~ 28% (23%) for the GGA(LDA) approach, however, the introduction of only the SOC correction to the GGA(LDA) approach resulted in significant reduction of the electronic band gap by ~ 15% (16%) (see Table 1).

The density of states profile for these structures with SOC are not presented. We observed that there is a strong hybridization of the p- and d- states of the S and W atoms at the valence band maximum and conduction band minimum. The valence band states between 0 eV to -1 eV are dominated by the d states and between -1 eV to -5 eV is dominated by the p states, while the conduction band states between 2 eV and 4 eV are dominated by the d states. This observation is consistent irrespective of the functional used or correction applied to the system. The spin up and down channel of WS_2 monolayer are symmetric. This led to a non-magnetic semiconducting ground state.

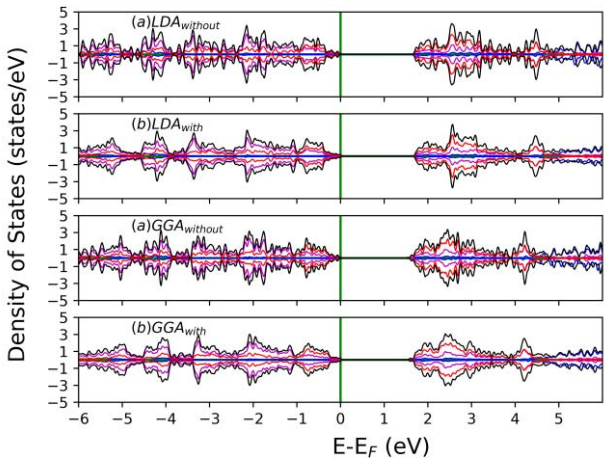

Figure 3: (Color online) The calculated spin-polarized projected density of states (PDOS) of the pristine WSe_2 monolayer, where (a) LDA without dipole correction, (b) LDA with dipole correction, (c) GGA without dipole correction and (d) GGA with dipole correction. The blue, magenta and red lines represent the s-, p- and d- orbitals, while the sum of the s-, p and d- orbital is given as the black line. The energy levels are adjusted with respect to the Fermi energy.

Figure 3 shows the calculated total and partial density of states for the pristine WSe_2 monolayer using the GGA and LDA functionals with and without self-dipole interactions. The electronic band gap for the WSe_2 monolayer is 1.545 (2.232) and 1.703 (2.372) with the GGA (with self-dipole interactions) and LDA (with self-dipole interactions) respectively. The introduction of dipole interaction resulted in significant increase of the band gap by ~44% (39%) for the GGA(LDA) approach, however, the introduction of only the SOC correction to the GGA(LDA) approach resulted in significant reduction of the electronic band gap by ~20% (20%) (see Table 1). The density of states profile for these structures with SOC are not presented. We observed that there is a strong hybridization of the p- and d- states of the Se and W atoms at the valence band maximum and conduction band minimum. The valence band states between 0 eV to -1 eV are dominated by the d states and between -1 eV to -5 eV are dominated by the p states, while the conduction band states between 1.8 eV and 3 eV are dominated by the d states. The observation is consistent irrespective of the functional used or correction applied to the system. The spin up and down channel of WSe_2 monolayer are symmetric. This led to a non-magnetic semiconducting ground state.

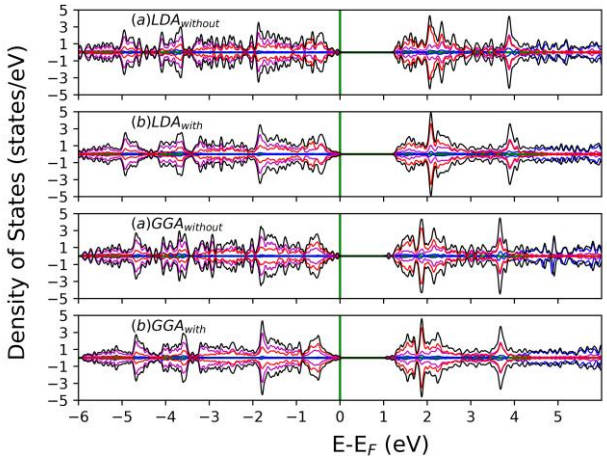

Figure 4: (Color online) The calculated spin-polarized projected density of states (PDOS) of the pristine WTe_2 monolayer, where (a) LDA without dipole correction, (b) LDA with dipole correction, (c) GGA without dipole correction and (d) GGA with dipole correction. The blue, magenta and red lines represent the s-, p- and d- orbitals, while the sum of the s-, p and d- orbital is given as the black line. The energy levels are adjusted with respect to the Fermi energy.

Figure 4 shows the calculated total and partial density of states for the pristine WTe_2 monolayer using the GGA and LDA functionals with and without self-dipole interactions. The electronic band gap for the WTe_2 monolayer is 1.036 (2.020) and 1.212 (1.978) with the GGA (with dipole correction) and LDA (with dipole correction) respectively. The introduction of dipole correction resulted in significant increase of the band gap by ~ 95% (63%) for the GGA(LDA) approach. However, the introduction of only the SOC correction to the GGA(LDA) approach resulted in significant reduction of the electronic band gap by ~ 56% (32%) (see Table 1). The density of states profile for these structures with SOC are not presented. We found that there is a strong hybridization of the p- and d- states of the Te and W atoms at the valence band maximum and conduction band minimum. The valence band states between 0 eV to -1 eV are dominated by the d states and between -1 eV to -5 eV are dominated by the p states, while the conduction band states between 1 eV and 3 eV are dominated by the d states. This observation is consistent irrespective of the functional or correction applied to the system. The spin up and down channel of WTe_2 monolayer are symmetric. This leads to a non-magnetic semiconducting ground state.

From the calculated projected density of states for the WX_2 monolayers as shown in figs. 2 to 4, we observe that both the spin up and spin down states are equivalent and symmetric resulting in a net zero magnetic moment. This implies that the

ground state of the WX_2 monolayers are non-magnetic in agreement with available literature. The effect of the dipole correction and SOC increases going from WS_2 to WTe_2. The SOC is known to be important for heavy atomic systems due to the presence of relativistic effects, however, we found that its inclusion in the WX_2 monolayers leads to underestimation of the electronic energy gap.

Conclusions

Density functional theory was used to investigate the influence of dipole correction and spin-orbit coupling on the structural and electronic properties WX_2 monolayers. The calculated lattice parameters were marginally changed in the presence of dipole interactions and spin-orbit coupling. However, we found that the presence of dipole correction and spin orbit coupling leads to significant changes in the electronic properties of the various WX_2 monolayers considered. The presence of SOC led to the reduction of the electronic band gap by about ~40% to 80% compared to the WX_2 monolayers calculation without dipole corrections. Including dipole correction self-consistently, the electronic band gap increased by ~40% to 80% compared to the WX_2 monolayers without dipole corrections. Furthermore, the SOC is known to be important for heavy atomic systems due to the presence of relativistic effects, therefore its inclusion in the further consideration of WX_2 monolayers is not important. This pedagogical study showed that for the WX_2 monolayers calculation without dipole correction and SOC corrections gave a more appropriate description of the structural and electronic properties. Thus, care should be taken applying the dipole corrections in the evaluation of work functions and other related properties of 2D WX_2 compounds.

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