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First Principles Study of Molybdenum Disulfide Electronic Structure

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First Principles Study of Molybdenum Disulfide Electronic Structure

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Abstract. The study of two dimensional material has gain interest due to unique properties which are different from the bulk precursors. Mono- and few-layered of Transition metal dichalcogenides (TMDCs) has band gap properties between 1-2 eV that suitable of FET devices or any optoelectronic devices. Among TMDCs, Molybdenum Disulfide (MoS2) has gain interest due to its promising band gap-tuning and transition between direct to indirect band gap properties depends on its thickness. First principles calculation by Density Functional Theory has been performed to study the characteristic of MoS2 electronic structure. Indirect band gap of MoS2 lies between point Γ to Γ-K in first brillouine zone, while the direct bandgap lies in point-K. The indirect band gap became larger while the number of layer decreased due to quantum confinement effect in c axis direction. In monolayer MoS2, the indirect band gap become larger than direct one, band gap properties transitioned from indirect to direct. The unique bandgap properties of MoS2 can lead into better application in energy devices such as solar cell [11], FET [10], and photoluminescence device.

1. Introduction

The study of two dimensional material has gain interest due to unique properties which are different from the bulk precursors either in its electrical properties also in its optoelectronical properties.This kind of thin material also allowed to make very thin devices since its already two dimensional.

Most viral two dimensional material is graphene that has outstanding electrical properties [9]. Graphene is semi-metal material that has zero band gap. It good electrical properties allow graphene be a suitable material for any conductor application. But since graphene has zero bandgap, it can not be applied as semiconductor devices. Whereas a lot of technology developed based on semiconductor properties of material included energy devices such as photoluminescence device, Solar Cell, etc.

TMDSc (Transition Metal Dichalcogenide) group of material can be suitable candidate as two dimensional material that has band gap, since its band gap in range 1 to 2 eV [12]. Among TMDCs, MoS_2 (Molybdenum Disulfide) is the most interesting for its fine electrical and optoelectronic properties in two dimensional state. In bulk, MoS_2 known has 1.29 eV [2] band gap with indirect one yet shifted into 1.8-1.9 eV [7] with direct band gap in two dimensional single layer. This value of band gap allow MoS_2 to be applied in semiconductor based devices, including any energy devices. Several study show MoS_2 application in solar cell [11], FET [10], and photoluminescence devices.

Since its wide use of MoS_2, in this work will be focused in basic properties of MoS_2. This work will show how electronic structure of MoS_2 shifted by its structure and number of layer. This preliminary study using Density Functional Theory (DFT) for identifying theoretical electronic structure shift along it structure change.

2. Method

Structure electronic of material defined by interaction of its all of electron and nuclei. Density Functional Theory calculate these interaction with simplified quantum calculation. In DFT, Kohn Sham Equation used instead of classic Schrdinger equation [3]. K-S Equation shown,

$$\left(-\frac{1}{2}\nabla + \int \frac{n(r')}{|r-r'|}\, d^3r' + \frac{\partial}{\partial n(r)} E_{xc} + v_{ext}\right)\phi_i = \lambda_i \phi_i \tag{1}$$

Since input of K-S Equation is electron density $(n(r))$ yet $n(r)$ it self is a square of solution wave function ϕ_i, this equation can be solved using Self Consistent Field algorithm. In this

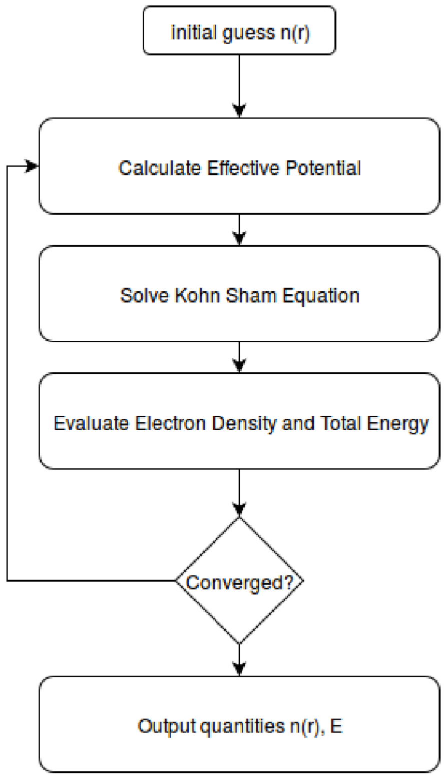

Figure 1. Self Consistent Field Flow Chart. First make initial guest in n(r), then calculate effective potential and solve Kohn Sham Equation. Final step in iteration is to evaluate total energy which are converged or not, if not, make output of electron density as new n(r) and do iteration again.

work PHASE0 package software used to calculate structure electronic of MoS_2. Structural optimization calculated with c/a optimization first then volume optimization. 10^{-9} Hartree used as converged energy criteria in SCF. K-poin sampling used is 8x8x8 for bulk and 8x8x1 for two dimensional, with 50 Rydberg Wave Function cutoff.

MoS_2 bulk model used as in figure 2. 2H structure is known most stable structure for MoS_2, since 3R structure can be reformed into 2H trough heating [14]. For two dimensional model, single layer and double layer calculated with 15 $\dot{A}$ vacuum gap to make sure no interaction between layer. Model shown in figure 3.

3. Result and Discussion

Lattice constant of MoS_2 calculated shown in table 1. It shown also total energy per MoS_2 in 2H structure has lower than in 3R. This show that 2H has more stable structure rather

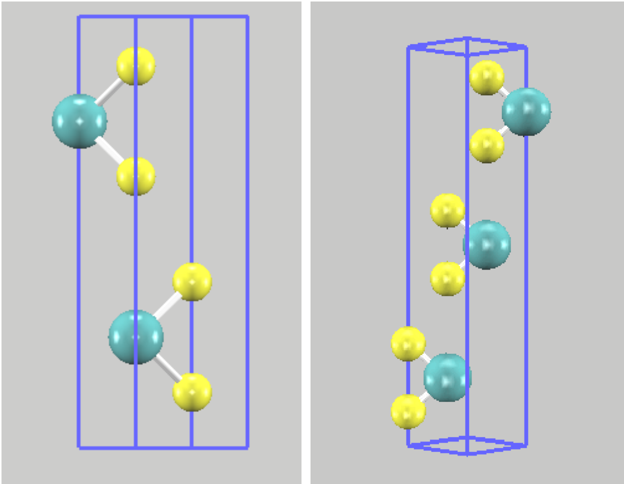

Figure 2. Bulk structure model of MoS_2 with 2H (left) and 3R (right). 2H has 2 molecule of MoS_2 in each cell while 3R has 3 molecule of MoS_2 in each cell.

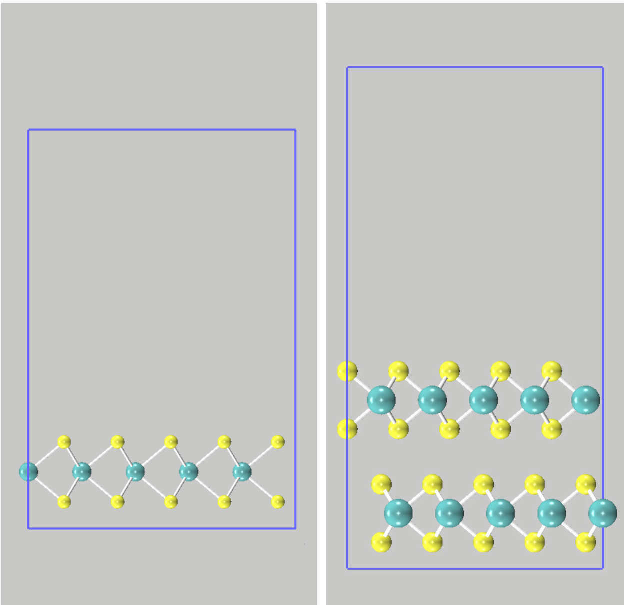

Figure 3. Model for monolayer (left) and dual layer (right) of MoS_2. 15 $\dot{A}$ used as vacuum layer for each model.

than 3R. Also provided the comparison table between this work and some reference in table 2. Optimization of lattice constant show very close result for each reference and this work. This show optimization work well enough and can be used to calculate electronic structure of each model.

Table 1. Calculated lattice constant and total energy

	2H	**3R**
a ($\dot{A}$)	3.22	3.24
c ($\dot{A}$)	13.26	18.92
E (Hartree)	68.021	68.017

Calculated electronic structure represented in band structure and density of states for each structure shown in figure 4, 5, 6, and 7. Comparison of band gap calculation result with some reference shown in table 3. Some of theoretical result lies very close with result of this work,

Table 2. Lattice constant on 2H-Bulk and MoS_2 single layer comparison with some reference

	MoS_2 Bulk		**MoS_2 *Monolayer***	
	Result ($\dot{A}$)	Reference ($\dot{A}$)	Result ($\dot{A}$)	Referensi ($\dot{A}$)
Lattice Constant (a)	3.22	3.19 [1], 3.16 [13]	3.24	3.195 [1], 3.23 [6]
c/a ratio	3.84	3.86 [1], 3.89 [13]		

Table 3. Calculated band gap comparison with some reference

	MoS_2 Bulk		**MoS_2 Monolayer**	
	Result (eV)	Reference (eV)	Result (eV)	Reference (eV)
Bandgap	0.9	Theoritical Study 0.89 [1], 0.7 [4], 1.15 [8] Eksperimen 1.23 [7], 1.29 [2]	1.6	Theoritical Study 1.57 [1], 1.9 [5] Eksperimen 1.80 [7]

while other result seems pretty much different. But it show that experimental result show significant shift from theoretical result. Theoretical result gives lower magnitude of band gap than experiment. This shows that DFT can not really be a good estimation in calculation of exact band gap, yet still can be used as preliminary study of band gap and knows the shift trends of band gap while structure of material modified.

From electronic structure shown that 3R structure have larger band gap compared to 2H one. While in 2 dimensional state, band gap of MoS_2 become larger from the bulk one, since in dual layer has 1.26 eV band gap meanwhile it has 1.6 eV in monolayer state. This indicated that band gap of MoS_2 become shifted up while there is few layer only because of quantum confinement effect in c-axis direction. Interesting case in monolayer MoS_2, since the characteristic of indirect band gap that naturally occur in MoS_2 change to direct one in point K. This characteristic make MoS_2 more applicable in wide kind of devices. This also shows that band gap of MoS_2 can be tunable with variety of its number of layer. Resume of MoS_2 band gap properties show in table 4.

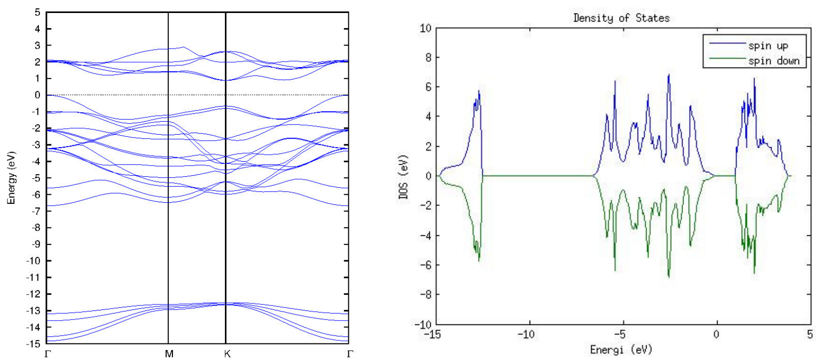

Figure 4. Electronic structure of 2H Bulk MoS_2 represented as band diagram (left) and density of states (right), this shown that 2H structure has 0.9 eV band gap lies between point Γ to $\Gamma - K$. Spin density shown to be very simmetry for spin up and spin down.

Table 4. Band gap of 2H, 3R, monolayer and dual layer MoS_2

	2H	**3R**	**monolayer**	**dual layer**
Band Gap (eV)	0.9	1.1	1.6	1.26
Band Gap Characteristic	indirect	indirect	direct	indirect

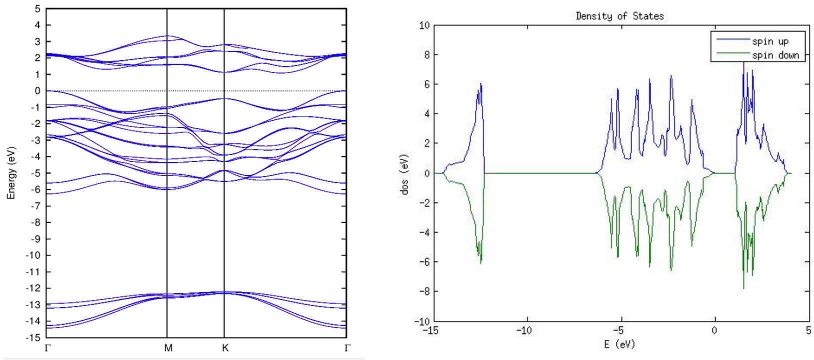

Figure 5. Electronic structure of 3R Bulk MoS_2 represented as band diagram (left) and density of states (right), this shown that 2H structure has 1.1 eV band gap lies between point Γ to $\Gamma - K$. Spin density shown to be very simmetry for spin up and spin down. This characteristic very similar with 2H, but with shifted up band gap.

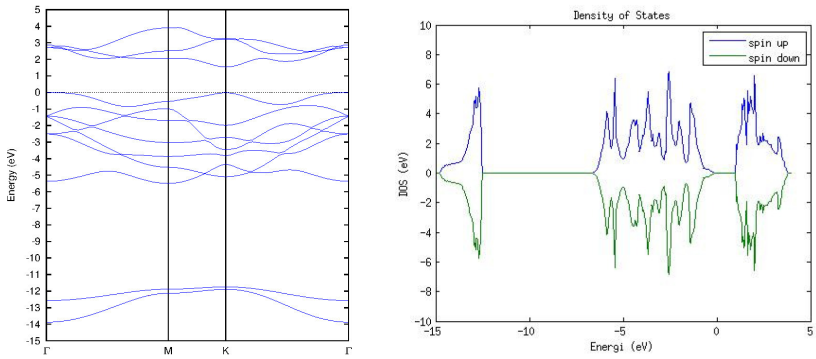

Figure 6. Electronic structure of monolayer MoS_2 represented as band diagram (left) and density of states (right), this shown that 2H structure has 1.6 eV band gap lies between point K to K. Spin density shown to be very simmetry for spin up and spin down. Interesting case within MoS_2 since in bulk phase, it has indirect band gap and yet shifted into direct one that lies in K point brillouin zone.

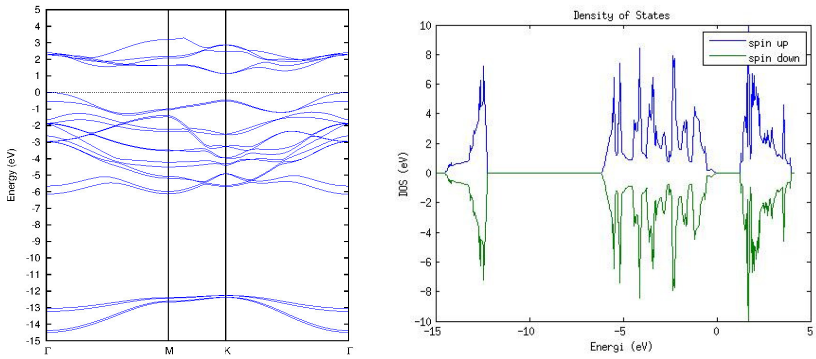

Figure 7. Electronic structure of dual MoS_2 represented as band diagram (left) and density of states (right), this shown that 2H structure has 1.26 eV band gap lies between point Γ to $\Gamma - K$. Spin density shown to be very simmetry for spin up and spin down.

From table 4, it shown that band gap of MoS_2 is varying around 0.9 eV to 1.6 eV. Also it properties is shifted from indirect band gap (bulk) into direct bandgap (monolayer). This unique properties of MoS_2 gives possibility on MoS_2 implementation on energy devices. Band gap with range 1-2 eV is suitable for application on semiconductor energy devices such as solar cell [11] and FET [10]. Also monolayer direct bandgap properties can lead into photoluminescence devices. This also shows that by shifting number of layer, also structure of MoS_2, can be tuned to suit more on energy devices design, which is, still open on future development.

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