Effect of external electric field on spin-orbit splitting of the two-dimensional tungsten dichalcogenides $WX_2$ ($X = S, Se$)

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Abstract. Tungsten dichalcogenides $WX_2$ ($X = S, Se$) monolayer (ML) attracted much attention due to their large spin splitting, which is promising for spintronics applications. However, manipulation of the spin splitting using an external electric field plays a crucial role in the spintronic device operation, such as the spin-field effect transistor. By using first-principles calculations based on density functional theory (DFT), we investigate the impact of external electric field on the spin splitting properties of the $WX_2$ ML. We find that large spin-splitting up to 441 meV and 493 meV is observed on the $K$ point of the valence band maximum, for the case of the WS$_2$ and WSe$_2$ ML, respectively. Moreover, we also find that the large spin-orbit splitting is also identified in the conduction band minimum around $Q$ points with energy splitting of 285 meV and 270 meV, respectively. Our calculation also show that existence of the direct semiconducting $\rightarrow$ indirect semiconducting $\rightarrow$ metallic transition by applying the external electric field. Our study clarify that the electric field plays a significant role in spin-orbit interaction of the $WX_2$ ML, which has very important implications in designing future spintronic devices.

1. Introduction

Recent discovery of graphene as a pioneer of a two-dimensional material with an extraordinary electronic, optical and magnetic properties motivates researchers to find new materials of two-dimensional structures. Especially in spintronics applications, these new materials are including topological insulators, Dirac materials and majorana fermions [1–3]. In addition to these materials, the two-dimensional material of transition metal dichalcogenides (TMDs) has also attracted much attention recently due to its unique properties such as large spin-splitting, spin-valley coupling and the sensitivity of its electronic structure [4–6]. Bulk TMDs have a $MX_2$ stoichiometry with $M$ is a transition metal atoms and $X$ is a chalcogen atoms. In contrast to bulk TMDs which have an indirect band gap with valence band maximum (VBM) at the $\Gamma$ point and conduction band minimum (CBM) at the $Q$ point, monolayer (ML) TMDs has a direct band gap with VBM and CBM are centered at the $K$ point. This transition from indirect to direct band gap is due to missing of van der Waals interactions [4,7,8], which has important implications in photonics, optoelectronics, and sensing devices [7].

Another unique phenomenon in ML TMDs is emergence of spin-splitting in the VBM and CBM. Especially the WS$_2$ and WSe$_2$ ML which attracted much attention since their spin-splitting are predicted to be the largest among the ML families of TMDs [4]. In the $WX_2$ ($X = S, Se$) ML, the maximum spin-splitting is observed at $K$ point of the VBM, which varies from 426 to 463 meV [4,6]. This large spin-splitting is believed to be responsible for inducing some interesting phenomena such as spin Hall effect, spin-dependent selection rule for optical transition, and magnetoelectric effect in
TMDs [9]. It is also reported that the large spin-splitting is also observed at the $Q$ point of the CBM, which is from ranging 200 to 330 meV. This splitting is also plays important role in the properties of spintronics such as spin-conserving scattering [5]. However, the electronic structure of $WX_2$ ML is sensitive to some external treatments such as external electric field [10]. Therefore it is important to clarify the electric field effect on the spin-splitting properties of the $WX_2$ ML material, which is expected to be useful for designing spintronic devices.

In this paper, we report fully relativistic calculations within density functional theory on electronic properties of the WS$_2$ and WSe$_2$ ML. For all such systems, we clarified the emergence of spin splitting in the VBM and CBM. We have also examined the electronic structure and the spin-splitting properties of the $WX_2$ ML by applying electric field. Finally, the possibility of implementing such systems for spintronics will be discussed.

2. Computational Method

Crystal structure of the bulk $WX_2$ ($X = \text{S, Se}$) has a hexagonal structure (2H) with P63/mmc ($D_{6h}^3$) point group symmetry. It consists of several layers $X$-$W$-$X$ characterized by a weak van der Waals interaction. Each layer consists of W atom layer that is sandwiched by two $X$ atoms with a strong covalent bonding. Due to the weak van der Waals interaction, it is possible to create $WX_2$ ML by using micromechanical cleavage and liquid exfoliation [11].

In contrast to the bulk $WX_2$, inversion symmetry is broken in the $WX_2$ ML (figure 1. (a)), thus reduces its symmetry becomes P6m2 ($D_{3h}^2$). The $D_{3h}^2$ symmetry itself consists of $C_{3v}$ and mirror symmetry $M_{3y}$ (figure 1. (a)). The $k$ space in first Brillouin zone characterizing the crystal structures of the $WX_2$ ML is shown in figure 1. (b). Electronic structure calculations are carried-out using density functional theory within the generalized gradient approximation (GGA) [12] as implemented in the OpenMX code [13]. We use norm-conserving pseudo-potentials, and the wave functions are expanded by the linear combination of multiple pseudo-atomic orbitals (LCPAOs) generated using a confinement scheme [14,15]. The orbitals are specified by W7.0-$s^2p^2d^4$, S9.0-$s^1p^1d^1$ and Se9.0-$s^1p^1d^1$, which means that the cut off radii are 7.0, 9.0, and 9.0 bohr for the W, S and Se atoms, respectively. A $12 \times 12 \times 1$ $k$-point grid and energy cutoff 200 Ry are used. Spin orbit coupling (SOC) was also included in these fully relativistic calculations. The $WX_2$ ML are modelled as a periodic slab with a sufficiently large vacuum layer (24 Å) in order to avoid interaction between another layers. The structures are relaxed until the force acting on each atom was less than 0.5×10$^{-3}$ eV/Å. The external electric field are applied in the direction of the positive $z$ axis.

3. Result and discussion

3.1. Electronics structures of the $WX_2$ ($X = \text{S, Se}$) ML

First, we optimize lattice parameter, with the result shown in table 1. Consistent with previous calculation results [4], we find that optimized in-plane lattice constants are 3.194 Å and 3.4 Å for the case of WS$_2$ and WSe$_2$ ML, respectively. However, these values are slightly larger than that of the experiment [16,17].

| System | Calculated Lattice constant (Å) | Experiment Lattice constant (Å) | Previous Calculation (Å) |
|--------|--------------------------------|--------------------------------|--------------------------|
| WS$_2$ ML | 3.194 | 3.154$^a$ | 3.197$^c$ |
| WSe$_2$ ML | 3.401 | 3.280$^b$ | 3.310$^c$ |

$^a$ Experimental value for WS$_2$ ML [16]
$^b$ Experimental value for WSe$_2$ ML [17]
$^c$ Previous calculation result [4]
Next, we investigate the electronic properties of W\textsubscript{X} \textsubscript{2} ML. As shown in figure 2, both WS\textsubscript{2} and WSe\textsubscript{2} ML show a direct-gap where the VBM and CBM are centered at the K point. We find that the energy gap obtained from our calculations are 1.53 eV and 1.00 eV for WS\textsubscript{2} and WSe\textsubscript{2} ML, respectively. Our partial density of state (PDOS) analysis show that at the K point of the VBM is dominated by W\textsubscript{d}_{x^2-y^2}\textsubscript{+d}_{xy} orbitals, while at the K point of CBM mainly originated from W\textsubscript{d}_{3z^2-r^2} orbitals (figure 1. (c) and (d)).

By concerning to the spin-splitting, we find that a substantial spin-splitting is visible along M-K-\Gamma as show in figure 2. The energy of spin-splitting at VBM (K point) are identified to be 441 meV and 492 meV for WS\textsubscript{2} and WSe\textsubscript{2} ML, respectively (figure 2 (a) and (c)). These results are in a good agreement with previous experimental result [18,19]. In addition, the spin-splitting is also observed at Q point in the CBM for both WS\textsubscript{2} and WSe\textsubscript{2} ML, which is found to be 285 meV and 270 meV, respectively (figure 2 (b) and (d)). The origin of the spin-splitting is due to the presence of the broken inversion symmetry. In bulk W\textsubscript{X} \textsubscript{2} Kramer’s degeneracy \[E^\dagger(\tilde{k}) = E^\dagger(-\tilde{k})\] is suppressed by the existence of the time reversal symmetry \[E^\dagger(\tilde{k}) = E^\dagger(-\tilde{k})\] and inversion symmetry \[E^\dagger(\tilde{k}) = E^\dagger(-\tilde{k})\].
However, the inversion symmetry is broken in the monolayer, thus spin degeneracy is lifted, inducing the spin-splitting. Because the monolayer has in-plane dipole moment, the spin-splitting is established on the band except for the $\Gamma$-$M$ direction (figure 2(a) and (b)). Moreover, at $\Gamma$ point, the spin degeneracy is due to time reversal symmetry alone, whereas at the $M$ point, the spin degeneracy suppressed by the combination of time reversal symmetry and translation symmetry [4].

3.2. The electric field effect on the electronic structure of the $WX_2$ ML

Next, we study the effect of the electric field on the electronic properties of the $WX_2$ ML. We introduce the electric field ranging from 0.2 to 0.6 V/Å. As show in figure 3, we find direct semiconducting - indirect semiconducting - metallic transition, when the electric field increases. Consequently, the shifting of the VBM and CBM appears, which effects to the spin-splitting energy.
Interestingly, we find new spin-splitting along $\Gamma$–$M$ direction, which is not found in the system without the electric field. As a result, the Rashba-type spin-splitting is induced around the $\Gamma$ point as show in figure 4.

4. Conclusion

In summary, we report fully relativistic calculations within density functional theory to study the spin-splitting band in VBM and CBM of WS$_2$ and WSe$_2$ ML. We found that substantial spin-splitting bands are identified in VBM and CBM of WS$_2$ and WSe$_2$ ML. In VBM around $K$ point, we obtained the energy of spin-splitting are 441 meV and 492 meV for WS$_2$ and WSe$_2$ ML. Meanwhile, in CBM around $Q$ point, we found the large spin-splitting energy are 285 meV and 270 meV for WS$_2$ and WSe$_2$ ML, respectively. The spin-splitting bands is due to a loss of the inversion symmetry in the ML case. Those results make the WS$_2$ and WSe$_2$ ML exhibits great potential for application, e.g. spin field-effect transistor. Applied electric field also appears direct semiconducting – indirect semiconducting – metallic transition of electronics structure. Controlling electronics structures by external electric field, makes WX$_2$($X$ = S, Se) ML potential candidates for future spintronic devices.

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