Controlling band gap of monolayer MnCl₂ with LDA+U

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Abstract. We performed the noncollinear first-principles calculations to control the band gap of 1T monolayer MnCl₂ using LDA+U. It was shown that the increase of the band gap is proportional to the increase of the effective Coulomb energy $U$, as long as the magnetic moments of the atoms do not reduce. The reduction of the magnetic moment leads to the so-called low spin state, in which the magnetic moment is almost half of the magnetic moment of the high spin state. It seems that the monolayer MnCl₂ can be a promising candidate for the spintronics applications.

1. Introduction
The properties of the two-dimensional materials, such as graphene (1-6), tungsten dichalcogenides (7-11), and metal dihalides (12-14) can be utilized for the spintronics devices. In this paper, we concern the metal dihalides, which have the chemical formulation AB₂ (A: metal cation, B: anion). These materials have promising characteristics, such as multiferroic properties (15,16), that can be utilized for the electronic devices.

Generally, a band gap of materials can be used to examine the quality of the spintronics devices. Indeed, this property is closely related to the insulator, in which the electron can transfer from the valence band to the conduction band. A usual exchange-correlation potential, such as the local density approximation (LDA) or the generalized gradient approximation (GGA), cannot describe the real band gap for some insulators, such as the oxide systems. Therefore, it is strongly recommended to extend the method, such as the LDA+U method (17,18) or GW method (19-21).

The purpose of the paper is to demonstrate that controlling the band gap of the monolayer MnCl₂, one of the metal dihalides, can be done by using the LDA+U method. We will show that there is a critical value of $U$ that can increase the band gap of the monolayer MnCl₂. Here, $U$ refers to the strength of the Coulomb repulsion between two electrons in the system. In Sec. 2 the model of the monolayer MnCl₂ will be given for our calculations. The change of the band gap with respect to $U$ will be discussed intensively in Sec. 3. We write our summary in Sec. 4.

2. Method and material
In our model, a structure of the monolayer MnCl₂ was built by one Mn atom and two Cl atoms in the unit cell, as shown in Fig. 1. The lattice constant and the vacuum area of the structure were set to 3.686 Å and 17.47 Å, which are taken from the bulk system (22). The calculation was performed using the OpenMX code (23) where the generalized gradient approximation (GGA) was chosen for the exchange functional (24). We sampled the unit cell with a $20 \times 20 \times 1$ k-point grid in the Brillouin zone.
Figure 1. Lattice structure of monolayer MnCl$_2$ from side view (a) and top view (b). The primitive unit cell is drawn by the black parallelogram, which connects Mn atoms (red color) and surrounds Cl atoms (yellow color).

For the basis sets, we used 41 orbitals including three $s$, three $p$, three $d$, and two $f$ orbitals for the Mn atom with the cutoff radius of 4.0 a.u. Meanwhile, 13 orbitals (two $s$, two $p$ and one $d$ orbitals) were set for the Cl atoms with the cutoff radius of 7.0 a.u. In addition, for producing the accurate result in the self-consistent calculation, we fixed the cutoff energy of 200 Ryd. This cutoff energy determines the convergence of the numerical integration to compute the total energy self-consistently. Therefore, the set value of the cutoff energy can increase the convergence with the chosen basis sets. Before carrying out the calculation, we made a structural optimization for fixing the atomic positions using the nonmagnetic structure. Moreover, we included the Coulomb energy $U$ since the Mn atom has the partially filled $d$-electron shell, which is similar to MnO, FeO, etc. Therefore, we hypothesized that the monolayer MnCl$_2$ has the same properties with the transition metal oxides, as mentioned before.

3. Results and discussions
Figures 2(a)-2(e) show the change of the band gap as $U$ increases up to 2 eV while the magnetic moment of the Mn atom decreases from $U > 3$ eV. The magnetic moments about 4 $\mu_B$ and 2 $\mu_B$ are related to the so-called the high spin state and the low spin state. As shown in Fig. 2(e) and table 1, we deduce that the decrease of the band gap is also influenced by the decrease of the magnetic moment of the Mn atom. This means that the sufficiently high $U$ will suppress both the band gap of the monolayer MnCl$_2$ and the magnetic moment of the Mn atom.
Figure 2. Band dispersions of monolayer MnCl$_2$ with $U = 0$ eV (a), $U = 1$ eV (b), $U = 2$ eV (c), $U = 3$ eV, and $U = 4$ eV (e), while the dependence of band gap on $U$ is given in (f).

Controlling the band gap in the insulator system is very important to check the possibility of spintronics application. Therefore, we justify that the monolayer MnCl$_2$ can be considered as a future material for the spintronics devices. At the same situation, since there is no reported band gap of the monolayer MnCl$_2$ until now, we will compare it with the similar system, the bulk MnO, to convince our results. According to Ref. (18), the calculated band gap was lied in the interval of 0.04 eV – 4.21 eV as $U$ increases. This means that the band gap of the similar system, such as the MnCl$_2$, should have the band gap in the same interval. Observing table 1, we claim that our results are consistent with the results of the MnO system.

It is also interesting to discuss the change of the magnetic moment in this system. Applying $U$ up to 2 eV the magnetic moment of each Cl atom is about 0.1 $\mu_B$ (not shown here). Indeed, this magnetic moment comes from the polarization of Mn atom as the magnetic atom. When $U \geq 3$ eV the magnetic moment of each Cl atom is about 0.01 $\mu_B$. If the value of the magnetic moment of each Cl atom at this situation can be neglected, we can obtain the local magnetic moment of the Mn atom. This means that the strength of $U$ can also be used to extract the local magnetic moment of the magnetic atom for the simplest system, such as one magnetic atom in the unit cell.
Table 1. Evaluated band gap and magnetic moment of Mn atom for the monolayer MnCl$_2$ with respect to $U$.

| $U$ (eV) | 0  | 1  | 2  | 3  | 4  |
|----------|----|----|----|----|----|
| Band gap (eV) | 1.49 | 2.17 | 2.86 | 1.2 | 1.81 |
| Mn moment (|$\mu_B$) | 4.63 | 4.67 | 4.86 | 2.96 | 2.97 |

4. Conclusions
We show that the strength of $U$ can control the band gap of the monolayer MnCl$_2$ and the magnetic moment of each Mn atom via the density functional theory. As long as the magnetic moment of the Mn atom is not suppressed by $U$, the band gap increases as $U$ increases. On the contrary, the band gap reduces as $U$ increases when the magnetic moment of Mn atom decreases. This means that the attempt to increase band gap can only be done if the high spin state is preserved. We also show that there is a linear dependence between the band gap and the magnetic moment of the Mn atom.

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