Effects of chlorine atoms doping on the electronic structure of
monolayer molybdenum disulfide

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Abstract. Two dimensional materials have special properties including small size effect, surface effect and quantum confinement effect caused by limited dimensionality, and their energy band can be tuned while doping by impurity elements. Recently, two dimensional transition metal dichalcogenides (TMDCs) are thought to be the most prospective material to fit Moore’s law. Among them, MoS$_2$ is the most common and important materials in research and it might have the best photoelectric property among all known two dimensional materials. In this article, we simulated n-doped monolayer MoS$_2$ with chlorine atoms with the method of density functional theory and studied the effect on its electronic structure like electronic density of states and energy band structures. The results showed that this chlorine doping can introduce a defect energy level in the band structure of the monolayer MoS$_2$ and make it become n-type semiconductor. Our work lays a foundation for further research on the doping of other two-dimensional materials besides MoS$_2$ together with the study on the materials’ electronic structure.

1. Introduction
Due to its special physical properties, two dimensional materials became one of the most intensively studied materials in physics recently [1-3]. After graphene has been first separated in 2004, it shows great performance in electricity, thermotics and other fields [2] and encourage scientists to find out more possibilities in this new field. As an important kind of two dimension materials, transition metal dichalcogenides are thought to be the most ideal materials to apply in electronic devices [4]. For example, there are more than 40 types of compound with stable structures and layer structures, including metals, semiconductors and superconductors [4]. Transition metal sulfide is a kind of layered material and van der Waals force bond different layers together, which means the electrostatic interaction and van der Waals force is very significant in this material [4]. With the help of physical peeling and chemical vapor deposition or other methods, monolayer transition metal sulfide can be got [5-7]. Due to its potential usage in the photoelectric field, MoS$_2$ is almost the most studied materials in two dimensional transition metal dichalcogenides [3].

Similar to graphene, monolayer MoS$_2$ possesses three layers of atoms, where Mo in the middle and covered by two layers of S in the top and bottom layers, and atoms in monolayer MoS$_2$ are connected by covalent bond [4]. Monolayer MoS$_2$ is a good semiconductor with direct band of 1.8eV, which has been used in many electronic devices [8]. In order to make MoS$_2$ useful in industry, scientists have tried to regulate and control electromagnetic property by means of altering the surface structure, adding stress, adding electric field and doping [3]. Among these methods, doping is a common way to change the performance of many kinds of semiconductors like enlarging the band gap or increasing
the conductivities [9-15]. So it is of great importance to study the electronic structure of MoS2 when doping. Recently, doping of MoS2 has been widely studied and found it can greatly change the properties of MoS2 by introducing impurities. For instance, the group of Izaak Williamson found doping of V and Ti enhances photosensitivity and photoresponsivity of MoS2 and the incidence is related to impurity concentration [4].

In this article, we study the effects of chlorine atoms doping on the electronic structure of a monolayer molybdenum disulfide. We aim to find out the influence of impurity atoms to the band structure as well as the density of electronic states, also figure out the semiconductor type of the material. The results show that this chlorine doping can indeed introduce a defect energy level in the band structure of the monolayer MoS2 and get it become n-type semiconductor. Besides, it seems that the spin state of the electrons might also have an influence on the electronic properties. Our work lays a foundation for further research on the doping of other two dimension materials besides MoS2 together with the study on the materials’ electronic structure.

2. Computational methods
Density functional theory (DFT) is a modified quantum mechanical method to study multi-electron system electronic structure, based on two mathematical theorems proposed by Kohn and Hohenberg and Kohn-Sham function [16]. This theory is chosen in our work to study the electrolyte structure of dopped MoS2. The work is done with Vienna Ab-initio Simulation Package (VASP) [17], a package used to perform ab initio quantum mechanical simulation through pseudopotential methods. VASP can be used to calculate energy and wave functions [17].

In this research, all of the figures are calculated by VASP based on DFT. We choose MoS2 which belongs to space group p63/mmc with lattice constant a=b=3.16Å, c=12.3Å, and create a 4×4 supercell with Mo and S. Projector augmented-wave(PAW) is used to describe the interaction between ions and electrons, and Perdew-Burke-Ernzerhof(PBE) function to calculate exchange correlation energy in electron interaction. The cutoff energy is set to 600 eV and integral of energy and density in Brillouin zone are generated in Gamma ways using 9×9×3 k-points. All atoms are allowed to fully relax until any force is smaller than 0.01 eV/Å and the convergence criterion of energy in the selfconsistency process is set to 10−4 eV. Mo: [Kr]4d 55s1 and S:[Ne]3s23p4 are regarded as valence in PAW potentials. To avoid the interaction caused by periodic calculation, the vacuum is 15Å.

3. Result and discussion

![Figure 1](image1.png)

Figure 1. The structure of supercell used in calculation. Figure (a) shows a side view of 4×4 pristine monolayer MoS2 with vacuum of 15Å and a S atom is substituted by a Cl atom in (b). Purples spheres indicate Mo atoms, yellow spheres indicate S atoms and green sphere indicates Cl atom.
To calculate the energy band structure and electronic density of states (DOS) of monolayer MoS$_2$, we use VASP. Firstly we structurally optimize the 4×4 monolayer MoS$_2$ supercell (Figure 1(a)) then dope it with a Cl atom (Figure 1(b)) to calculate the energy band structure and DOS.

3.1. Electronic structure of pristine MoS$_2$

Figure 2. (a) is the band structure and (b) is the partial density of states (PDOS) and total density of states (TDOS) of 4×4 pristine monolayer MoS$_2$. Figures below the total DOS are PDOS of Mo and S. Dotted line presents Fermi energy ($E_F=0$).
In order to figure out what happens after doping Cl into MoS$_2$, we first calculate the band gap and electronic state density of the pristine MoS$_2$ as shown in Figure 2. The electronic band structure is presented in Figure 2(a), and the band gap is 1.658 eV at K point in pristine MoS$_2$ system when the minimum of conduction band and maximum of value band lie both in point K. A conclusion can be drawn that MoS$_2$ is a semiconductor with a direct band gap [1]. The value is slightly different from the theoretical value of 1.8eV [4]. Since we have not taken the spin of the electron into account and the calculating process is rough because of the computer performance, deviation exists. However, this will not influences the comparison between pristine and Cl-doped MoS$_2$ system, result with great reference can still be made. The value of DOS is 0 on Fermi surface, which meets the conclusion made in band structure that pristine MoS$_2$ is a type of semiconductor [3]. Meanwhile, most of the electron near the band gap in K point are provided by Mo. As the figure shows (Figure 2(b), Mo makes up more of the total DOS than S. The DOS is almost controlled by the d-state Mo and p-state S, and d-state Mo shows great locality in DOS. This conclusion is just the same with that of our reference “the occupied DOS is almost dominated by the S s state below − 12 eV that peaks at − 12.4 eV and by the Mo d state above 1.45 eV that peaks at 2.4 eV. Furthermore, there are antibonding states between − 5.9 eV and the Fermi level via hybridization interaction of Mo d state and S p state.”[3]

### 3.2. Electronic structure of Cl doped MoS$_2$

Then we introduce displacement doping by taking one Cl to replace one S in the supercell of monolayer MoS$_2$(Figure 1(b)). The change of electromagnetic property can be observed as shown in Figure 3. The electromagnetic property changes obviously in one Cl-doped system, the band gap of Cl-doped system (1.439 eV) is smaller than that of the pristine MoS$_2$ (1.658 eV), which also meet the conclusion made in reference [3]. This might because the doping of Cl makes pristine become n-type heavy doped degenerate semiconductor. In our calculation with VASP, temperature is set to 0 K and with no pressure. In practice, donor impurity is only partly ionized due to the carriers freeze-out effect. In this case, impurity has high concentration and the isolated impurity levels become bands and abate ionization energy of impurity. And these impurity levels formed new conduction bands and become its band tail, which causes the decrease of band gap. Meanwhile, the Fermi level goes up, which suggests more electrons are able to occupy the bands [8].

![Figure 3](image.png)

**Figure 3.** Band structure of 4×4 MoS$_2$ supercell doped by one Cl in Figure 1(b), whose band gap in K point is 1.493 eV.
Figure 4. Spin up and spin down band structure of one Cl-doped are shown in (a) and (b) respectively. The energies are adjusted according to the Fermi energy, and the Fermi energy is presented by the dotted line.

When considering there are two states of electrons including spin up and spin down, the band structure of the monolayer doped MoS$_2$ divided into two different types as shown in Figure 4. The results show that Cl-doped MoS$_2$ is a semiconductor with spin polarization [8]. There is something special that impurity energy levels in spin up band structure have lower energy that in spin down. After doping Cl, one extra electron is taken into the system and occupy conduction band with higher energy. Those energy levels used to be empty and now occupied partly. Since spin down has a lower energy level in the conduction band, this electron occupies the spin down energy level. So the top of value band goes up in spin up and band gap smaller, and the bottom of conduction band goes down in spin down and band gap bigger.

Figure 5. PDOS and TDOS for one-Cl doped MoS$_2$, curve up the horizontal axis indicates the spin up total DOS and curve down indicates the spin down. And figures below the total DOS are PDOS of Mo and S.
The DOS 1-Cl doped MoS$_2$ is shown in Figure 5, and it is almost the same with pictures of our reference [3]. Moreover, we enlarge the density of getting points in energy, so the DOS diagrams are more detailed than in references. In the total DOS of Cl doped MoS$_2$ system, DOS of spin up differs from spin down near the Fermi surface so we can also see the phenomena of spin polarization. In the calculation, we got the magnetic moment is 1.0005uB.

Figure 5 shows that in Cl doped MoS$_2$ system, nonzero density appeared in the band gap near the bottom of conduction band, which means there are some occupied states of the electrons. This occupied state is exactly an impurity energy level, which is close to the conduction band, meaning the Cl doped monolayer MoS$_2$ is n-type semiconductor and it might also be a heavily-doped semiconductor. Most of the electrons in impurity level come from Mo which fit the theory, but it is also reasonable for electrons from S to share the impurity level because of the interaction between atoms. In addition, the contribution of electrons in different shells might also vary [8].

![Figure 6. DOS of s, p and d-state of the Cl in the one Cl-doped MoS$_2$ supercell.](image)

As shown in Figure 6, the total DOS of the Cl-dopped monolayer MoS$_2$ is primarily controlled by the p-state Cl atom, and the s-state Cl shares a much smaller part and d-state Cl shares little. The DOS of Cl is very small compared with Mo and S and it peaks near the Fermi level which corresponds to the energy of impurity level [3]. So, it proved to be true that Cl is donor of MoS$_2$ and Cl doped MoS$_2$ is a n-type semiconductor.

4. Conclusions

Overall, after calculating the energy band structure and DOS of pristine monolayer MoS$_2$ and 1-Cl doped monolayer MoS$_2$ systems with the method of density functional theory with VASP packages. We make a conclusion that Cl acts as the donor in the semiconductor and caused spin polarization by generating impurity energy level. The band gap is smaller and the impurity level is near the bottom of valence band and occupied by electrons of Mo mainly, which meet its characters of n-type semiconductor [3].

Our calculation studied only 1-Cl displacement doped monolayer MoS$_2$ systems, the influence of types of impurity atoms and doping density still need to be addressed. However, our figure offers a method to analyze doping system and it is an example for further research to refer to. We are looking forward that there will be a breakthrough in the usage of doped MoS$_2$ theoretically or practically.
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Ruoxin Wang conceived the research, performed the calculations and data analysis, prepared the manuscript. All authors discussed the results, commented on the manuscript, and contributed to the writing of the paper.

Conflict of interest
The authors declare no conflict of interest.

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