

Progress in First-Principles Studies of MoS₂

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Abstract. First-principles is a quantum mechanical calculation method that does not require any empirical parameters or experimental data input to predict material properties and calculate the electronic structure of materials. MoS₂ has extensive applications in nanoelectronics, optoelectronics, and other fields. To expand the application range of MoS₂ in nanodevices, its photoelectric properties need to be adjusted through methods such as changing the number of layers, doping, adsorption, applying external electric fields, or strain. This work reviews the research progress of first-principles calculations in MoS₂ in recent years, mainly summarizing the progress of first-principles calculations in two aspects: applying strain and doping MoS₂.

1 Introduction

With the continuous development of technology and theoretical improvement, there is a series of methods for simulating different scales of materials, among which first-principles calculation refers to the calculation of material atomic and electronic structure information using known physical parameters such as electron mass, speed of light, proton mass, neutron mass, and quantum mechanics principle, without using experimentally determined parameters. Through a series of approximate calculations, the state and properties of the microsystem can be reasonably predicted. With the continuous development of computer hardware and theoretical improvement, the accuracy and efficiency of first-principles calculations are becoming higher and higher. First-principles calculation only relies on the atomic configuration. The first-principles calculation method has been widely used in condensed matter physics and nanomaterials, and is an important foundation for computational materials science.

Nanomaterials have become the frontiers of current scientific research due to their unique structure and physical properties. Among them, graphene is currently the thinnest and strongest material in nature, with high conductivity and carrier transport properties. MoS₂ has a layered structure similar to graphene. As a lithium storage electrode material, it has a higher theoretical lithium storage capacity than graphite. When the thickness is thin to multiple layers or single layer, MoS₂ exhibits unique photoelectric semiconductor properties, so it and graphene have the potential for broad application in nanoelectronics, optoelectronics, and other fields. MoS₂ is a transition metal sulfide formed by covalent bonds between sulfur and molybdenum atoms. Due to the different relative positions of the molybdenum and sulfur atoms forming the bonding, it has three different crystal phase structures. Among them,

1T-MoS₂ and 3R-MoS₂ are easily subject to phase transitions under external conditions and are in a metastable state. 2H-MoS₂ exhibits semiconductor properties and is the most stable compared to the other two. This is the focus of this chapter's research. In order to expand the application range of two-dimensional materials in nanodevices, it is necessary to adjust the photoelectric properties of MoS₂ through some methods, such as changing the number of layers, doping adsorption, external electric field, or applying strain. The first-principles method has been widely used in nanomaterials, and this article briefly reviews the recent applications of first-principles calculations in MoS₂, focusing on the effect of strain on MoS₂, the influence of different element doping on MoS₂'s gas adsorption performance, electronic structure, and magnetic properties of single-layer and bulk MoS₂. It summarizes and analyzes representative literature.

2 Influence of strain on MoS₂

Strain is a common method to change the crystal structure and physical properties of materials by stretching or compressing them. The types of strain include uniaxial strain and biaxial strain. First-principles calculation is a method based on quantum mechanics that predicts the behavior and properties of materials without any input of empirical parameters or experimental data. It calculates the electronic structure of materials and studies the effect of strain on the electronic structure of MoS₂ to understand its electrical properties. Strain can change the electronic structure and behavior of charge carriers (electrons or holes) in MoS₂. In 2012, Wu Musheng et al. found that when a 0.5% strain was applied to single-layer MoS₂, the band structure changed from a direct gap to an indirect gap, and the bandgap width decreased linearly with stress. As strain increased,

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the band structure still exhibited an indirect bandgap. The reduction of the bandgap width in MoS₂ can improve its electrical transport properties, increase its conductivity, enhance the electron mobility and carrier density, and promote electron transport, thereby improving its application performance in electronic devices. Strain can also change the optical properties of MoS₂. In 2022, ChengYue Wang² utilized first-principles calculations based on density functional theory to investigate how uniaxial strain affects the binding energy, band structure, and optical characteristics of single-layer

MoS₂. The study found that the main effect of strain on the material was observed in the lower energy region, as indicated by the real part of the dielectric constant under tensile strain in Figure 1(a) and under compressive strain in Figure 1(b). The differences between the two systems become smaller at higher energy levels. The study observed that tensile strain boosts MoS₂'s peak value within the visible light spectrum of 1.63eV~3.10eV, whereas compressive strain diminishes it, indicating contrasting trends.

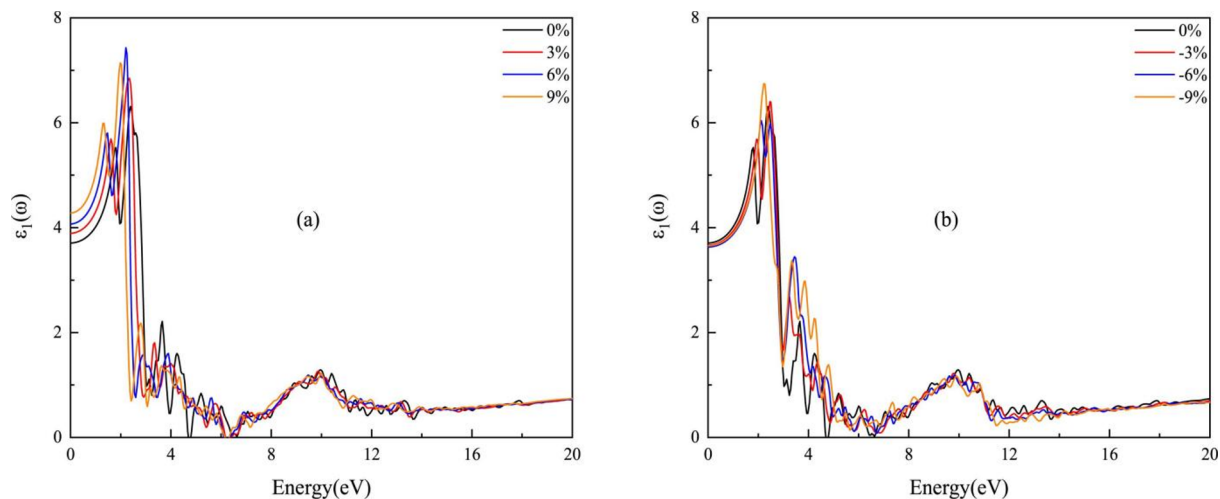


Figure 1. The dielectric constant of monolayer MoS₂ under uniaxial strain. (a, b) real part²

MoS₂ is a material with high catalytic activity, abundant reserves, and low cost, and it has a two-dimensional layer structure similar to graphene, with a large surface area that is conducive to light absorption. Therefore, in the field of photocatalytic hydrogen production, more and more people are paying attention to its application. In 2023, Zhang Yan et al.³ studied that the electron's carrier mobility is 10 times that of holes, so under light, electrons and holes can be effectively

separated. At the same time, strain can improve the electron carrier mobility, thereby improving the photocatalytic hydrogen production effect. Figure 2 shows the influence of strain on optical absorption coefficient. According to the factors of light absorption coefficient and photocatalytic hydrogen production conditions, strain can achieve the best photocatalytic hydrogen production effect in three cases of 2%, -2%, and -6%.

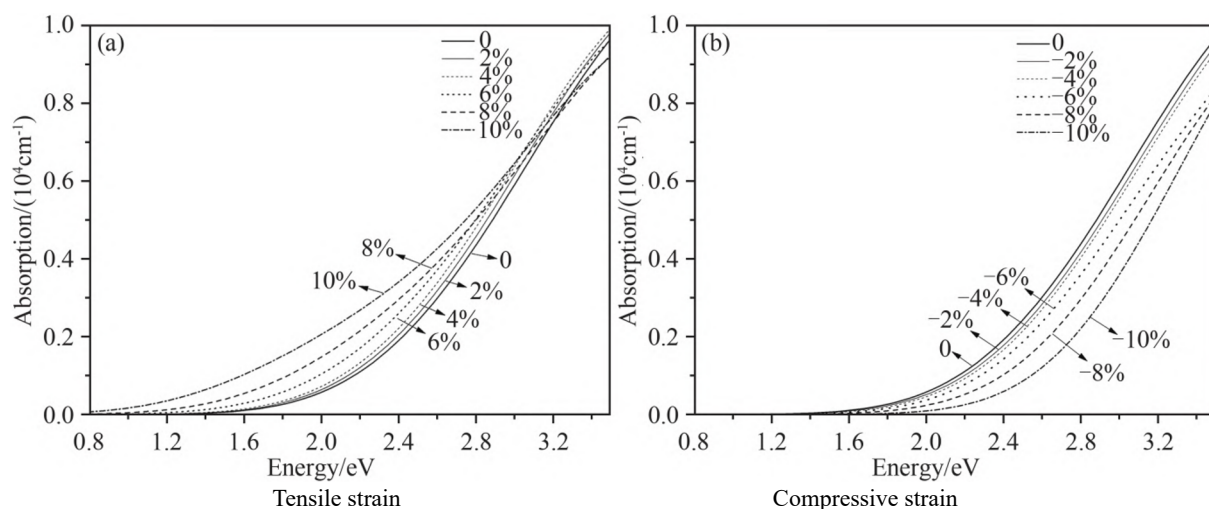


Figure 2. Absorption coefficients of monolayer 2H-MoS₂ with strains³

Strain affects its phonon properties and thermoelectric properties. In 2019, Junxiang Xiang⁴ et al. used first-principles calculations to explore the effect of strain on the thermoelectric properties of p-type single-layer MoS₂. Tensile strain decreases MoS₂'s

thermal conductivity and Seebeck coefficient, leading to inferior thermoelectric properties, as revealed by the study. In 2023, Saumen Chaudhuri⁵ carried out first-principles calculations on the geometric, electronic, and phonon properties of 2H and 1T phases of

single-layer MoS₂ under in-plane strain, and found that as the strain increases, the out-of-plane acoustic phonon (ZA) becomes imaginary, and compared to the 1T phase, The 2H phase has better stability under applied strain. The zigzag MoS₂ nanobelt is a nanomaterial formed by stacking monolayer MoS₂ atoms, and its shape is similar to a strip structure, but the edges present a serrated shape. In 2022, Suejeong⁶ You found that the effect of strain on the metal edge state energy of the metal nanobelt is asymmetrical, and the effect along the x-axis direction is greater than that along the y-axis direction. When the tensile strain along the x-direction is 5%, there will be a transition from the metal edge state to the insulator edge state, but this phenomenon was not observed under the 10% tensile strain along the y-direction.

3 Effect of doping on MoS₂

Doping refers to the process of introducing other elements or compounds into the MoS₂ structure, which can be achieved through methods such as chemical vapor deposition, solution method, and ion implantation. Its main effects include changing the electronic structure. For example, doping some impurities can introduce additional electrons or holes, thereby increasing conductivity, improving photoelectric properties, and suppressing catalytic toxicity. First-principles calculations can help predict the effects of different doping elements or doping concentrations on the electronic structure, gas sensitivity, photoelectric properties, etc. of MoS₂, thereby optimizing the material's properties. MoS₂ has a layered structure, large surface area, and natural bandgap, which has the potential to be applied in high-sensitivity gas sensing applications. Doping can affect the gas sensitivity of MoS₂. In 2021, Ehab Salih⁷ studied the electronic properties and adsorption parameter changes of Au and Ag co-doped MoS₂ as NO and NO₂ gas sensors using density functional theory calculations. Compared with original, Ag-doped, and Au-doped MoS₂, the adsorption gap of this system for NO and NO₂ gases has significantly changed, and Au-doped MoS₂ system has selectivity for NO, while co-doped MoS₂ system has selectivity for NO₂. In 2023, Zhang Ruien⁸ studied the sensing performance of Ru-MoS₂ as a gas sensing material for SO₂F₂ and H₂S in SF₆ decomposition products. First-principles calculations showed that Ru atoms filled the sulfur vacancies in MoS₂, which could hybridize with adjacent Mo atoms to form chemical adsorption. Ru-MoS₂ has stronger adsorption performance for H₂S gas. The sensing mechanism of Ru-MoS₂ as a resistive gas sensor during gas adsorption was explained, and the recovery time of desorption was calculated, proving its recovery at high temperature. As shown in Figure 3, it is quite difficult to desorb SO₂F₂ and H₂S from Ru-MoS₂ at room temperature, and the recovery time decreases with increasing temperature. In 2021, Liang Ting⁹ used first-principles calculations to study the mechanism of improvement in gas sensitivity of S atoms in single-layer 2D MoS₂ replaced by V atoms. The results showed that V atoms can be stably doped into

S vacancies, gradually improving the material's conductivity and increasing the material's adsorption capacity for gas molecules such as NO₂, NH₃, Salin, and mustard gas. Bader charge calculations showed that the V atoms gave a significant electron transfer to the surrounding Mo atoms, further proving that the doping of V atoms effectively improved the material's conductivity and gas sensing performance.

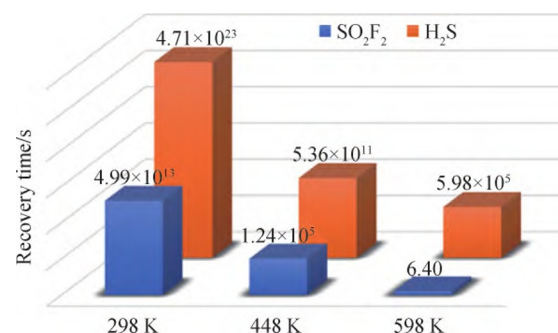


Figure 3. Recovery time of two gas adsorption systems at different temperatures⁸

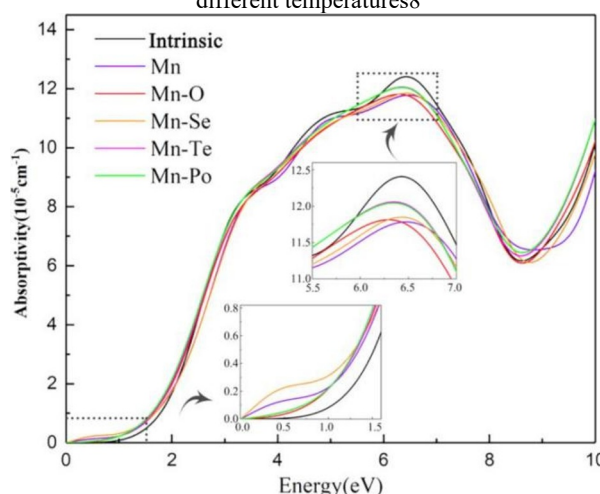


Figure 4. The absorption coefficient $\alpha(\omega)$ with intrinsic, Mn doped, Mn-X (X=O, Se, Te and Po) co-doped MoS₂ monolayers¹⁰

The enormous potential of two-dimensional materials in optoelectronic devices has received widespread attention. Due to the unsaturated d orbitals of Mo atoms, doping vacancies can adjust the magnetic moment of Mo atoms. In 2020, Qi-Zhi Lang¹⁰ used first-principles calculations to study the magnetic, optical, and electronic properties of Mn-X (X=O, Se, Te, Po) co-doped monolayer MoS₂. Mn and X co-doping in MoS₂ can significantly change the electronic and optical properties of the system. Mn-O co-doped MoS₂ system shows magnetic anisotropy, while Mn-Se and Mn-Te co-doped MoS₂ show ferromagnetic behavior. The analysis of the enlarged rectangular region in the energy range of 6.44~7.5 eV in Figure 4 shows that the native monolayer molybdenum disulfide system has better performance in manufacturing near ultraviolet (6.44~7.5eV) optoelectronic detectors. Precious metals, such as Pt, Ir, and Ru, are expensive and not ideal for electrocatalytic water splitting due to their low abundance. Transition metal dichalcogenide materials are a promising alternative due to their unique physical properties and large specific surface area. In 2022, P. Sundara Venkatesh¹¹ explored the effects of doping transition

metals (Ni, Fe, Co) on two-dimensional MoS₂ nanosheets for electrocatalytic hydrogen production. Ni-MoS₂ demonstrated exceptional HER performance, achieving an overpotential of -0.302 V on the reversible hydrogen electrode (RHE) and a current density of up to 10 mA cm⁻², as indicated in Table 1. Ni-MoS₂ outperformed other transition metal-doped MoS₂ (Co-MoS₂, Fe-MoS₂) in terms of performance.

Table 1. Onset, Over potential, and Tafel slope of bare and metal-doped MoS₂ nanosheets

Electrocatalyst	η_1 (V vs.RHE)	η_{10} (V vs.RHE)	Tafel slope (mV/dec)
MoS ₂	-0.27	-0.4066	95
Fe-MoS ₂	-0.31	-0.4900	93.67
Co-MoS ₂	-0.25	-0.3054	68.53
Ni-MoS ₂	-0.24	-0.3024	66.27

4 Conclusion

Through theoretical simulation calculations, valuable information can be provided for molybdenum disulfide nanomaterials, and molecular structures can be explained from the electronic microscopic level. These data can provide more accurate theoretical references for experiments. With the deepening of people's understanding of material crystal structures and the improvement of computer level, popular first-principles calculation software such as MaterialsStudio, VASP, WIEN, Gaussian, etc. can be used for various research, such as 3D modeling, quantum mechanical calculations, molecular dynamics calculations, material structure simulation, material synthesis process simulation, and material property prediction. These software provide researchers with more efficient and accurate calculation tools. First-principles calculation will have wider and deeper applications in molybdenum disulfide nanomaterials.

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