

Doped 2D Transition Metal Dichalcogenides MoSe_2 and MoTe_2 as gas sensors

BY

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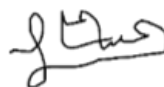
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **GHAITH NADHREEN** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN MATERIAL SCIENCE AND ENGINEERING**.

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2020

Dedication

To my parents who taught me to be curious and always encouraged me to learn.

To my family and friends...

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LIST OF ABBREVIATIONS

PPM	:	Part per million
QM	:	Quantum Mechanics
DFT	:	Density Functional Theory
TMDs	:	Transition Metal Dichalcogenides
QE	:	Quantum Espresso
PDOS	:	Partial Density of States
SCF	:	Self Consistent Function
HF	:	Hartree Fock
KS	:	Khon Sham
LDA	:	Linear Density Approximation
GGA	:	Generalized Gradient Approximation

LIST OF SYMBOLS

∇	:	Electron kinetic energy
v_{ne}	:	Nucleus-electron potential
Ψ	:	Wavefunction
$\hat{H}$	:	Hamiltonian operator
$\hat{T}$	:	Electron kinetic energy operator
$\widehat{V}_{ee}$	:	Electron-electron repulsion operator
$\widehat{V}_{ne}$	:	Nucleus-electron operator
Z	:	Charge on each nucleus
R	:	Internuclear separation
$\hat{z}$	:	Unit vector along the bond axis
n	:	Probability density
v_s	:	Mimicking potential
ϕ	:	One-electron wavefunction (orbital)
Φ	:	Product wavefunction of two orbitals. Φ_0 for ground state
v_s^{HF}	:	Hartree-Fock potential

ABSTRACT

Full Name : Ghaith Jamal Nadhreen
Thesis Title : Doped 2D Transition Metal Dichalcogenides MoSe₂ and MoTe₂ as gas sensors
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Gas sensing plays a vital role in the fields of agriculture, medicine, emission control, factories and safety. Many toxic gases cannot be detected with normal human senses because either they are odorless and colorless, or they can affect people with very small concentrations. As such, detection in PPM levels is of utmost importance. Graphene is a 2D material with many impressive properties. However, it lacks a bandgap making it unsuitable for gas sensing. One class of materials that is analogous to graphene but is a semiconductor is 2D transition metal dichalcogenides (TMDs). This thesis aims to study the viability of 2D MoSe₂ and MoTe₂ TMDs doped with Ge and Sb respectively as electrochemical gas sensors of NO, NO₂ and NH₃ using DFT. This is achieved by studying the adsorption influence on the electronic properties namely adsorption energies, charge transfer, PDOS and molecule-substrate atomic distances. Results indicate physisorption (chemisorption) on pristine (doped) MoSe₂ and MoTe₂. An exception is for NH₃-MoTe₂Sb where it exhibited stronger physisorption than MoTe₂. Pristine materials were found to be suitable for sensing NO₂ because of the impurity states that reduced the bandgaps. Other gases, despite having good physisorption, did not have a notable influence on the conductivity. On the other hand, doped materials showed strong chemisorption. This presents doped materials as potential gas scavengers instead of gas sensors.

ملخص الرسالة

الاسم الكامل : غيث جمال ناضرين
عنوان الرسالة : الفلزات الانتقالية MoSe_2 و MoTe_2 ثنائية الأبعاد المشابة كمستشعرات للغاز
التخصص : علم وهندسة المواد
تاريخ الدرجة العلمية : ابريل 2020

يلعب استشعار الغاز دوراً مهماً في مجالات الزراعة والطب ومراقبة الانبعاثات والمصانع والسلامة. ولا يمكن اكتشاف العديد من الغازات السامة بحواس الإنسان العادية لأنها إما عديمة الرائحة وعديمة اللون، أو أنها تؤثر على الأشخاص بتركيزات صغيرة جداً. وبالتالي من المهم الكشف عن الغازات بتركيزات جزء من المليون (PPM). الجرافين هي مادة ثنائية الأبعاد لديها العديد من الخصائص المبهرة. ومع ذلك، فهي تقتصر إلى فجوة النطاق (Bandgap) مما يجعلها غير مناسبة لاستشعار الغازات. واحدة من فئات المواد التي تشبه الجرافين ولكنها أشباه موصلات هي الفلوات الانتقالية ثنائية الأبعاد (TMDs). تهدف هذه الرسالة إلى دراسة جدوى MoSe_2 و MoTe_2 المشوبة بـ Ge و Sb على التوالي كمستشعرات كهروكيميائية للغازات NO و NO_2 و NH_3 باستخدام DFT. ويتحقق ذلك من خلال دراسة تأثير الإدمصاص على الخصائص الإلكترونية وهي طاقات الإدمصاص والشحنة المنقولة وكثافة المدارات (PDOS) والمسافات الذرية بين الغاز والمادة. تشير النتائج إلى إدمصاص فيزيائي (physisorption) على MoSe_2 و MoTe_2 النقي وإدمصاصاً كيميائياً (chemisorption) على المواد المشابة. الاستثناء هو $\text{NH}_3\text{-MoTe}_2\text{Sb}$ حيث أظهرت إدمصاصاً فيزيائياً أقوى بقليل من MoTe_2 . ولقد جدنا أن المواد النقية مناسبة لاستشعار NO_2 بسبب مدارات NO_2 الشائبة والتي أنقصت فجوات النطاق. أما الغازات الأخرى، فعلى الرغم من إدمصاصها الجيد، لم يكن لها تأثير ملحوظ على التوصيل الكهربائي. من ناحية أخرى، أظهرت المواد المشابة إدمصاصاً كيميائياً قوياً جداً مما يقترح إستعمالها كمادة جامعة لهذه الغازات من الجو بدلاً من مواد مستشعرة لها.

CHAPTER 1. INTRODUCTION

Gas sensors are important in many fields and they are mainly used in process controls, safety, environmental control and amenities. Due to the need to detect a variety of gases, many types of gas sensors were developed and many of them have become essential in civil life. With increasing industrialization and air pollution and advancing technology, demand for more sophisticated gas sensors is on the rise for emission monitoring and control. Detection with PPM levels of accuracy and good selectivity with a wide range of working temperatures are examples of properties desired in a modern sensor. Two-dimensional Transition Metal Dichalcogenides (TMDs) are one class of materials that have the potential to fill this role.

1.1 Transition Metal Dichalcogenides:

Since the discovery of graphene, interest in 2D materials is ever increasing due to their attractive and potent properties. But since graphene lacks an electronic bandgap and a semiconducting nature, it is obvious that the need for a 2D semiconducting material is of interest as many applications including but not limited to electronics could benefit from it [1].

TMDs are semiconductors that follow MX_2 formula where M is a transition metal like Mo and W and X is a Chalcogen like S, Se and Te. TMDs have direct band gaps, thickness of only a few atoms, strong spin-orbit coupling and generally good electronic and mechanical properties. This makes them interesting in many applications like applications in high-end electronics, spintronics, optoelectronics, energy harvesting, flexible electronics, DNA sequencing and personalized medicine [1].

2D TMDs can have several structural phases depending on the coordination number of the transition metal used. The two most common phases are the trigonal prismatic (2H) and octahedral

(1T). A simpler way to understand the difference between 2H and 1T is to look at the stacking order. The 2H phase has an ABA stacking order while 1T has ABC (Figure 6). Even though TMDs usually have 2H or 1T as the thermodynamically stable phase, the other phase can also occur as a metastable phase [1].

TMDs with 2H phase structures are semiconductors with an indirect bandgap. However, as the thickness decreases from bulk to monolayer, the positions of the valence and conduction bands also change the indirect bandgap to a direct one (Figure 7). Also, some TMDs were observed to have superconductive behavior [1].

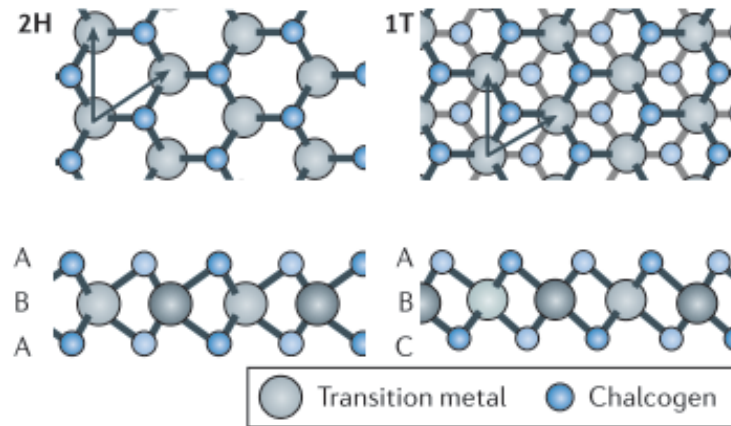


Figure 1. Top and side views of the stacking orders of 2H and 1T phases common in 2D TMDs [1].

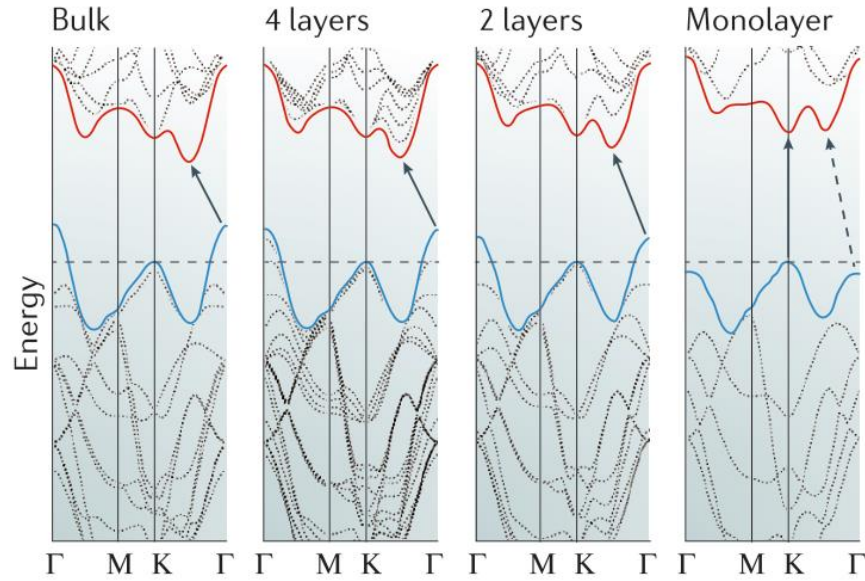


Figure 2. Band structure of 2H-MoSe₂ and evolution of the indirect bandgap into a direct one as the thickness of the material decrease [1].

1.2 Project Goals and Objectives:

Main Objective: To evaluate the potential of 2D MoSe₂ and MoTe₂ as electrochemical gas sensors of NO, NO₂ and NH₃ gas molecules using first-principle calculations.

In order to give a better understanding, some background concepts and literature will be covered first. For the main study, the following parameters will be evaluated that will give information about the adsorption nature like adsorption mode and strength:

- Adsorption energy
- Charge transfer
- Molecule-substrate atomic distance
- Partial density of states (PDOS)
- Work-function

The thesis project is a collaboration between KAUST and KFUPM under supervision from Prof. Udo Schwingenschlogl and Dr. AbdulJabar AlSayoud respectively. This document will cover the literature on gas sensors, TMDs as electrochemical gas sensors with a focus on first-principle calculations, computational parameters for the software used and results and discussion.

CHAPTER 2. BACKGROUND

2.1 Quantum Mechanics:

In order to understand the density functional theory (DFT), a basic understanding of the quantum mechanics (QM) and the Schrodinger equation is needed. QM is a theory that describes the nature of a system and the interaction between its constituents at the atomic scale. QM differs from macroscale classical physics theory in that the energies, momentums and angular momentums are quantized meaning they have discrete values. Objects at this level have both particle and wave natures at the same time and precision in measurements are limited by the uncertainty principle, which states that either position or momentum can be precisely obtained at one time but not both.

Any QM system can be described using the Schrodinger equation. This equation contains the different terms that describe the interaction between the particles at the atomic level. The following equation describes the interaction between two hydrogen atoms which is the simplest expression of the equation [2] [3]:

$$\left\{ -\frac{1}{2} \sum_{i=1,2} \nabla_i^2 + \frac{1}{|r_1 + r_2|} + \sum_{i=1,2} v_{ne}(r_i) \right\} \Psi(r_1, r_2) = E \Psi(r_1, r_2) \quad (1)$$

Where i is the number of the electrons in the system and v_{ne} is called the external potential or nucleus-electron potential. The expression between the curly brackets from equation (1) describes the Hamiltonian operator $\hat{H}$. This operator can be written as the sum of different operators:

$$\hat{H} = \hat{T} + \widehat{V}_{ee} + \widehat{V}_{ne} \quad (2)$$

Where $\hat{T}$ is the kinetic energy operator, $\widehat{V}_{ee}$ is the electron-electron repulsion energy operator and $\widehat{V}_{ne}$ is the nucleus-electron attraction energy operator and they correspond to the terms in equation (1) [2].

$$v_{ne}(r) = -\frac{Z}{r} - \frac{Z}{|r - R\hat{z}|} \quad (3)$$

From equation (3), $Z = 1$ is the charge on each nucleus, $\hat{z}$ is a unit vector along the bond axis and R is the internuclear separation [3].

Solving equation (1) to get the system's wavefunction is almost impossible for systems larger than Helium. The cause is the complicated electrostatic repulsion term V_{ee} where there are three coordinates needed for each electron to resolve it and all electrons in the system should be represented by this term. This means that for a simple two-electron system we need to solve a six coordinates system which is an arduous task. This problem becomes more complicated with each electron added because for a system with N electrons, we need $3N$ coordinates to solve it. This is where DFT is used in order to simplify the solution of the Schrödinger equation [3].

2.2 Density Functional Theory:

Density Functional Theory (DFT) proved very useful in quantum chemistry where approximated functionals were found to have a good balance between accuracy and computational cost. This enabled the calculation of larger systems with a reasonable cost while maintaining good accuracy

[3]. The basic idea of DFT is that instead of calculating interactions of each electron with every other particle in the system, we treat them as non-interacting electrons and apply a potential that simulates the interaction between them.

Figure (1) presents the exact solution of the Schrödinger equation as the total energy of the system versus atomic distance [3]. In general, we are interested in the minimum point. At this point, atomic spacing represents the equilibrium bond length while the energy value is the ground-state energy which defines the geometry or the lattice structure of a molecule or a solid respectively as well as all the vibrations and rotations.

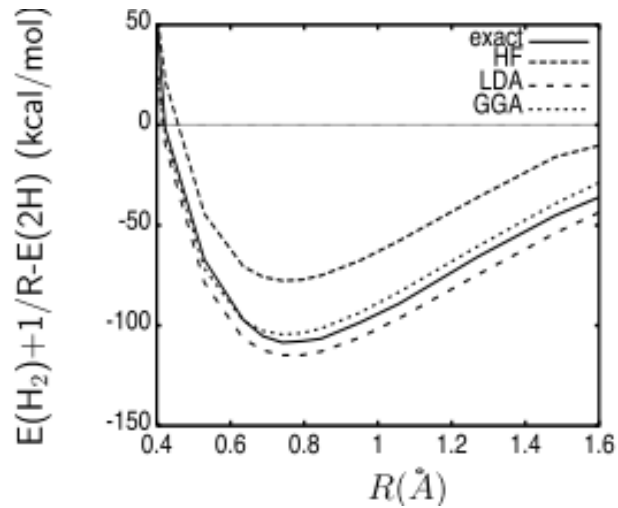


Figure 3. Total energy vs. atomic distance for H_2 system [3].

Most importantly however is that at the ground-state energy, it is easy to calculate the density probability of the system. This solution is:

$$n(r) = 2 \int d^3r' |\Psi(r, r')|^2 \quad (4)$$

This represents two decaying exponentials centered at nuclei and enhanced between them where the bond is formed [3].

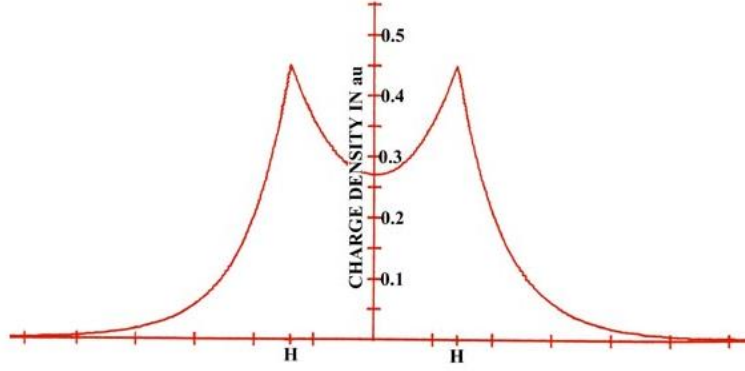


Figure 4. Probability density of H2 along the bond length [4].

In order to simplify the solution, a system of two non-interacting electrons in a potential $v_s(r)$ is assumed making sure that the potential mimics the real one. Because both electrons are non-interacting, their coordinate systems are decoupled, and we are left with a simple 3-coordinate system. The one-electron wavefunction is called Orbitals and its equation is:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(r) \right\} \phi_i(r) = \epsilon_i \phi_i(r) \quad (5)$$

The resultant wavefunction is a simple product between the two one-electron Orbitals:

$$\Phi(r_1, r_2) = \Phi_0(r_1)\Phi_0(r_2) \quad (6)$$

The only thing left is to find a potential $v_s(r)$ that mimics the real system. There are many approximations for this potential like Hartree-Fock (HF) and Kohn-Sham (KS). HF potential essentially mimics the true wavefunction as the product of two non-interacting orbitals then minimizing the energy, we get the HF correction:

$$v_s^{HF}(r) = v_{ext}(r) + \frac{1}{2} \int d^3r' \frac{n(r')}{|r - r'|} \quad (7)$$

This type of approximation, along with similar ones, follows an iterative process. An initial value of the potential $v_s(r)$ is guessed and inserted into equation (5). Then the wavefunction is found

and the electronic density can then be calculated from equation (4). This density is inserted into the HF approximation equation (7) and new potential is found. This means we have a set of self-consistent equations (SCF). If the new value is the same as the previous one, then we reached self-consistency [3].

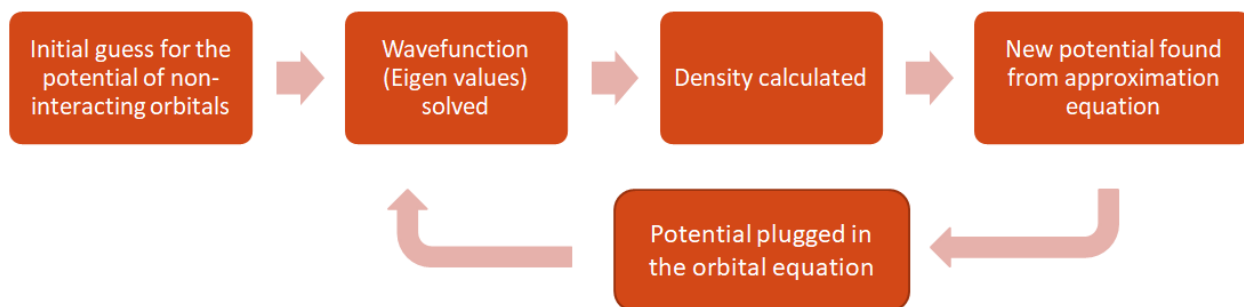


Figure 5. *Self-consistency loop.*

As can be seen from Figure (1), using the HF equation correctly gives an accurate position but it significantly under-binds the molecules compared with the true wavefunction. The reason for this was found to be the lack of the correlation energy, the interaction between electrons [3].

Kohn-Sham (KS) approximation is the most widely used nowadays. KS uses a pair of non-interacting electrons that have the exact density $n(r)$ as the physical system. By knowing how the energy depends on the density and using DFT, the potential can be derived. This can be applied to any electronic system. It is important to note that the resultant KS wavefunction is exact, not an approximation. This is because the wavefunction depends on the density and the KS density is exact to that of the physical system. Figure 4 shows how the physical and KS potential result with the same density. This means that good approximation of the KS potential leads to simpler equations and very accurate results [3].

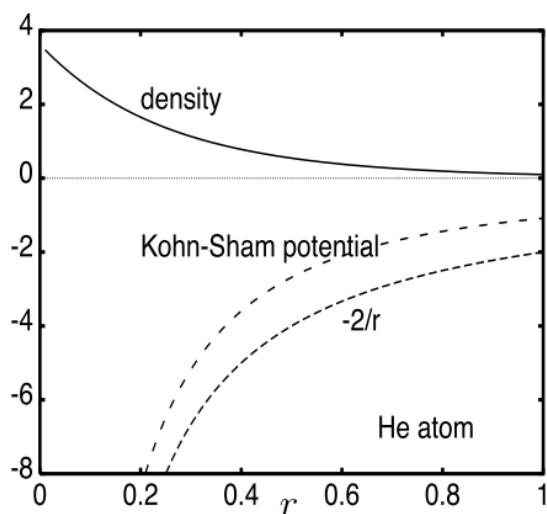


Figure 6. Physical and KS potentials with very accurate density [3].

Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) are some of the more common approximations used to improve the KS potential. LDA is the simplest functional that is much more accurate than HF approximation. As can be seen from Figure 1, LDA over-binds the molecules by around 1 eV. This is adequate for many solid-state calculations but falls short for quantum chemistry. GGA is a more sophisticated approximation and improves on LDA by a factor of five. More accurate approximations exist but, of course, the more accurate the functional is, the more expensive the calculations will be. Therefore, GGA is more widely used as it has adequate accuracy while keeping calculation cost reasonable [3].

2.3 Gas Sensing

There are many types of gas sensors like semiconductor metal oxides which are used to detect various types of gases. Inflammable gases like CH_4 and H_2 are detected using metal oxide sensors which can be found in leakage alarms in houses. Another example is stabilized zirconia which is used as oxygen sensors in monitoring car emissions and metallurgical control. Ceramics and polymer electrolytes are used to sense humidity which is used in air conditioning and food

processing. The increase in air pollutants like NO_x , SO_x and CO_2 calls for sensors to detect such gases in industrial facilities and automobiles. Another situation is the need to sense the same gas in a different environment which normal sensors are not able to do like sensing the oxygen dissolved in blood or water or the humidity sensors in environments with high working temperatures like industrial dryers. In order to come up with sensors suitable to detect different gases with various concentrations in different environments, it is important to know how to design a gas sensor [5].

The most basic gas sensor must perform two main functions: a receptor function and a transducer function. The receptor function is the ability of the sensor to detect a certain gas while the transducer function is concerned with converting this detection into a signal that can be interpreted into the type and concentration of the gas. This signal can be in the form of electrical resistance change, which is the most commonly used, or it can take other types like electromotive force, resonant frequency, optical absorption or emission. In most cases, gas identification is made by a solid-gas interaction like adsorption and chemical and electrochemical reactions while transduction depends on the type of material used in the sensor. Enhancing the receptor function increases selectivity while enhancing the transduction function increases sensitivity. In general, both functions should be improved in order to obtain good sensing characteristics. Practically, the receptor function can be enhanced by surface modifications of the sensor like doping and inducing defects like vacancies while the transducer function mainly depends on external factors like structure of the sensor device or the microstructure of material used [5].

There are different ways of classifying gas sensors according to the sensing material (like electrochemical and metal oxide semiconductor sensors), sensing method (mainly sensors based on the variation of electrical properties and ones based on the variation of other properties) and

measurement method (like DC conductometric gas sensors and Field-Effect-Transistor based gas sensors) [5]. There are many types of gas sensors that can be used for detecting a variety of gases and used in different situations. Here we briefly mention the common ones:

2.3.1. Catalytic:

Catalytic sensors are used to detect combustible gases in an environment. This type of sensors utilizes the catalytic principle which describes the ignition of the gas even below its normal ignition temperature due to specific chemical processes. The most common configuration in this type is the catalytic bead sensor where the sensing material is usually a Platinum wire which is covered by a bead shaped metal oxide coating. The bead sensor is then treated with a catalyst like Platinum or Palladium [6].

2.3.2. Optical:

This sensor type utilizes the absorption or emission scattering of gas species at certain wavelengths. The sensor consists of light emitting, photo-detecting and gas sensing elements. Usually, these sensors are employed to detect flammable gases like Hydrogen. A common sensor for this type is made of coated chemo-chromic oxides or thin films of Palladium [6].

2.3.3. Infrared:

Infrared sensors are usually considered a subtype of optical sensors. As the name implies, these sensors generate electrical signals by conversion of infrared rays or electromagnetic radiation. These sensors are usually used for CO₂ detection [6].

2.3.4. Acoustic:

This type of sensors works by detecting changes in velocities and amplitudes of the surface acoustic waves (SAW). These SAWs are generated from electrical signals by using the

piezoelectric effect, sent propagating through the sensor surface then reconverted back to electrical signals. The difference between the input and output signals can then be correlated to measure the physical quantity needed. This type of sensors is very versatile and can be used in a variety of different environments in many applications [6].

2.3.5. *Electrochemical:*

Electrochemical sensors work on the principle of the gas reacting with the sensor, generating or influencing the electronic signal passing through it which can then be correlated to detect the gas. There are wide varieties of gas sensors working on this principle notably sensors that reduce or oxidize the toxic gas like metal oxide sensors and semiconductor sensors like TMDs.

The basic working principle in electrochemical gas sensors is a measurable resistance change in the sensor material due to physisorption or chemisorption of the target gas molecule on it. This change can then be transduced into an electrical signal which can be correlated to the concentration of the target gas [7].

Compared with other types of sensors, electrochemical sensors are the most common sensors used for ambient toxic gas monitoring. This is due to their attractive qualities like low energy linear output with high resolution, good selectivity and repeatability, high accuracy, PPM level detection and being cheaper than other types of sensors [8].

However, electrochemical sensors are sensitive to temperature fluctuations, and have a minimal shelf life. That is why the environment's temperature should be stable in order to get the best performance [8].

Oxide semiconductor gas sensors are used to detect inflammable and oxidative gases by a change in the electrical resistivity. Identification (receptor function) of the gas molecules is done by the

adsorption reaction between the gas and the surface of the oxide. Transduction into a change in resistance is governed by the material's microstructure like grain size, nick size and relative depth of the surface space charge layer as shown in Figure 5 [5].

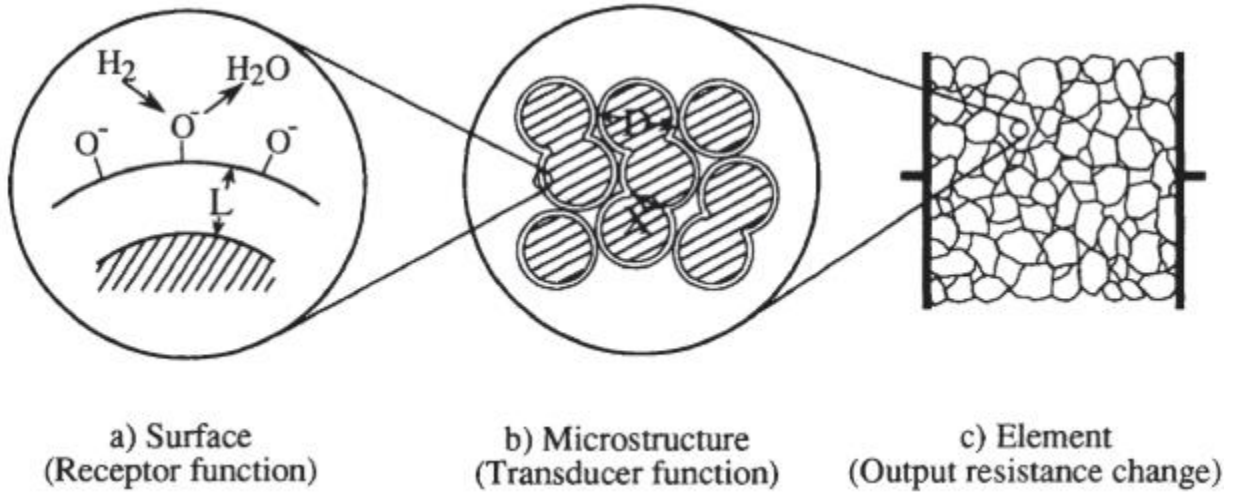


Figure 7. Receptor and transducer functions of the semiconductor gas sensor. D : particle size, X : neck size, L : thickness of space charge layer [5].

2.4 Literature Review:

Ingale et al. [9] studied C_2H_4Li as a potential gas sensor for oxide gases using DFT where they covered CO, CO₂, NO, NO₂, SO and SO₂. The study found that all molecules adsorbed chemically with varying adsorption energies. Their criteria for determining this was that all E_{ad} were larger than 0.2 eV and the minimum atomic distance between the molecule and substrate is less than 3 Å [9] which is the general criteria for chemisorption [10]. Chen et al. [11] studied the adsorption properties of arsenene as potential sensors for SO₂ and NO₂ using first principle calculations with different configurations. Evaluation was made with pristine, Boron- and Nitrogen-doped Arsenenes. They found that both molecules chemically adsorbed on Boron-doped Arsenenes and exhibited physically adsorbed on both pristine and Nitrogen-doped Arsenenes with moderate adsorption energies for both [11]. Mao et al. [12] studied the effects of point defects on the

capabilities of GeSe to sense NH_3 , SO_2 . The point defects types were a mono vacancy, anti-site and Phosphorus atom substitution defects. DFT first principles calculations were performed to study the structure, PDOS and work function of the gas molecules adsorption on GeSe. The bonding of gas molecules showed chemisorption characteristics in all cases except for P atom defect substituting Ge with NH_3 adsorbed [12]. Cui et al. [13] investigated the potential of C_3N as a potential gas sensor using first-principles calculations. Gases tested in this study were divided into atmospheric gases (N_2 , O_2 , CO_2 , and H_2O) and polluted gases (CO , NO , NO_2 , H_2S , NH_3 , and SO_2). found that only NO_2 and SO_2 showed good adsorption on the surface of C_3N . The adsorption appears to have a strong physisorption nature with no chemical bonds. From the adsorption energies and ELF, Cui et al. [13] found that only NO_2 and SO_2 showed good adsorption on the surface of C_3N . The adsorption appears to have a strong physisorption nature with no chemical bonds forming. From the PDOS, NO_2 has a sharp peak near the band gap that contributes its electronic levels to the material at the valence band maximum (VBM) enhancing the conductivity and leading to asymmetry in electrons and holes transport [13].

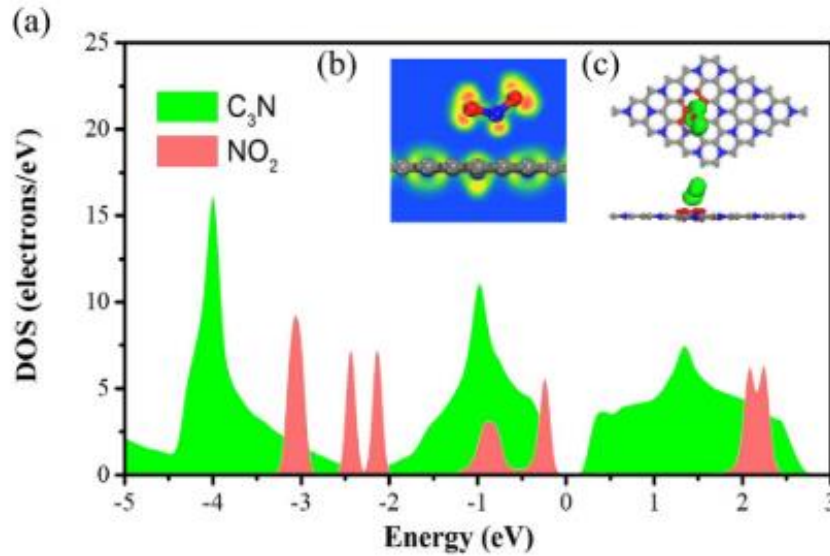


Figure 8. PDOS (a) of C_3N and NO_2 with inset images of ELF (b) and CDD (c) of NO_2 adsorbed on C_3N [13].

Cho et al. [14] combined experimental and DFT methods in order to synthesize 2D MoS₂ as a sensor for NO₂ and NH₃. The study was successfully able to synthesize highly uniform 2D MoS₂ using chemical vapor deposition (CVD). They found that NO₂ was an electron acceptor and NH₃ was a donor. The material sensitivity was found to increase for NO₂ but decrease for NH₃. This was explained by the smaller charge transfer of NH₃. From DFT calculations, both molecules were found to favorably adsorb on MoS₂ with moderate adsorption energies. The different adsorption behavior of NO₂ and NH₃ suggests great selectivity for MoS₂ with high sensitivity for NO₂ [14].

2.5 DFT software used:

There are many different applications that perform DFT calculations like VASP, Siesta and Quantum-Espresso (QE). Some of them are commercial and some are free and open source. QE is a reputable free software with many users and an active team still developing and maintaining it. However, one should be aware of possible sources of errors that can give results that are inaccurate and not representative of the real materials. There are two types of errors in the field of computational physics, modeling errors and computational errors. The computational errors can occur due to limitations in the software and the machines running the calculations. These errors include discretization, numerical and algorithmic errors. This type of errors is mostly concerned with developers and IT departments.

Another type of errors is the modeling errors. These arise from uncertainty or simplifications in the approximate models used. That is why all approximations have varying degrees of precision. In practice, modeling errors can occur from choosing approximations that do not represent the real case because they have low precision, or they are not suitable for the system and the materials used. Examples of these errors are using unsuitable pseudopotentials or wrong exchange-correlation method. Lastly, there are general errors like using input parameters that do not result

in the least total energy. It is important to take all these types of errors into consideration in order to mitigate mistakes in the calculations. Finally, it is worth noting that QE and every DFT software are limited by the size of the system to only hundreds of atoms. This means that simulations at the macro level with thousands of atoms are almost impossible.

CHAPTER 3. COMPUTATIONAL METHOD

This work was performed using the Quantum-Espresso package [15][16] for main calculations and XCrySDen for structure visualization [17]. A (4 x 4 x 1) supercell was used with a 24 Å vacuum slab above it to prevent periodic interactions of the molecule with the substrate in the vertical axis. In order to find the preferential adsorption sites, six sites were tested on top of Mo (T1), on top of Se/Te (T2), on the Mo-Se/Te bridge (B1), on the hexagonal hollow center (H1), on the hollow centered between Se-Se/Te-Te (H2) and on the hollow centered between Se-Mo (H3) as shown in Figure 9. Each site was tested with the four rotations for all three molecules (NO, NO₂ and NH₃) adsorbed on (MoSe₂, MoSe₂/Ge, MoTe₂ and MoTe₂/Sb) making a total of 288 calculations. After finding favorable adsorption sites, the adsorption energy, charge transfer, PDOS, Charge Density Difference (CDD) and work function were evaluated. Adsorption energy was found using the following equation:

$$E_{adsorption} = E_{system} - E_{substrate} - E_{gas} \quad (5)$$

Charge transfer between the molecule and substrate was calculated using Lowdin method. CDD was obtained using the following equation:

$$\rho_{adsorption} = \rho_{system} - \rho_{substrate} - \rho_{gas} \quad (6)$$

Pseudopotentials with the generalized gradient approximation (Perdew–Burke–Ernzerhof parametrization) were used along with Grimme’s long-range third dispersion correction to account for the Wan der Waals interactions. A cutoff energy of 1088 eV was used and a Monkhorst-Pack grid of (2 x 2 x 1) was found to achieve proper convergence. Iterative calculations were performed until the energy difference was below 0.00001 eV and atomic forces were less than 0.0002 eV/ Å. PDOS was found using a denser k-mesh of (4 x 4 x 2).

Some calculations would not correctly finish due to many reasons. In such cases, a calculation is considered done when the system’s total energy passes the convergence criteria and the last SCF step difference is less than 5 meV. This value was chosen by adding the energy tolerances during optimization of k-mesh and energy cutoff.

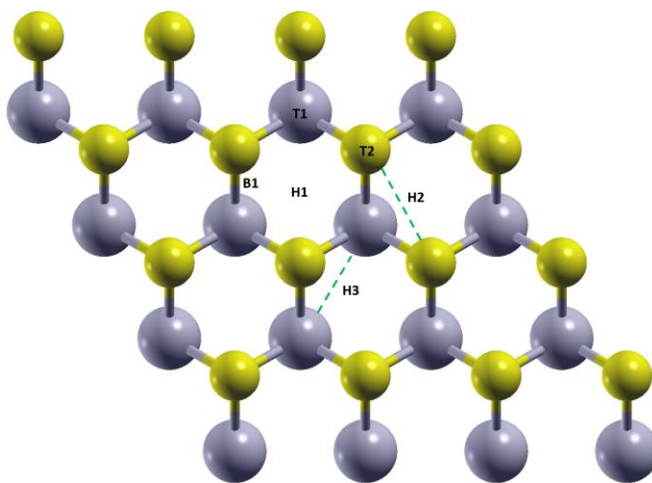


Figure 9. *MoSe₂ adsorption sites.*

CHAPTER 4. RESULTS AND DISCUSSION

In order to decide whether a material is a suitable gas sensor, we need to calculate its electronic properties which give us indications on how the behavior changes after gas adsorption. These are the adsorption energy, charge transfer, CDD, PDOS and work function. The discussion will cover reference data, groundwork, electronic properties and performance comparison.

4.1 Optimization, supercell and adsorption sites

Before covering the electronic properties, we need to tackle important three important steps: parameters optimization, building the supercell and testing the adsorption sites.

4.1.1. Parameters optimization:

In order to ensure accurate results within the used approximations, cutoff energies and k-mesh size need to be optimized. This was achieved by incrementally increasing the cutoff energies and mesh densities until the system's total energy converge. The optimized values were mentioned in the computational section.

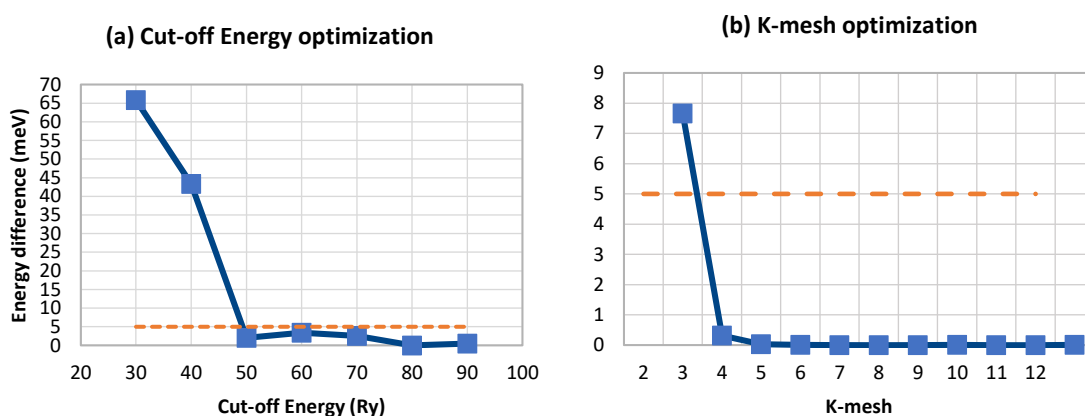


Figure 10. Convergence criteria for the cut-off energy (a) and K-mesh (b) of the unit cell.

4.1.2. Building the supercell:

Due to the periodic boundary conditions, building a supercell is important in order to prevent the gas molecule from interacting with itself in the x and y directions. In order to generate the supercells used in obtaining the electronic properties, we first started with a primitive cell extracted from the literature. Then the cell was copied four times in the horizontal directions and relaxed. Finally, a vacuum was introduced on top of the lattice to avoid gas interaction with the substrate from the top.

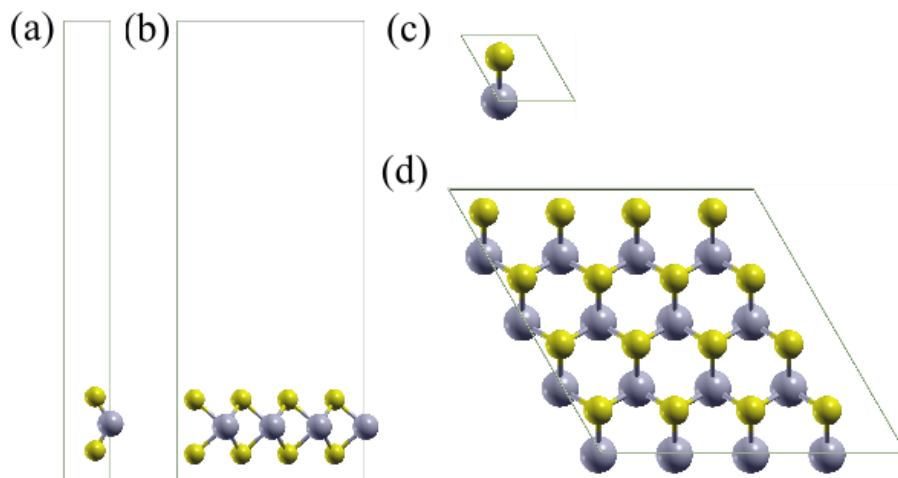


Figure 11. Steps of building the supercell starting with the primitive cell (a, c) then expanding the structure to get the 4x4 supercell (b, d). Also, the unit cell border was drawn to show the vacuum slab on top of the sheet.

4.1.3. Testing adsorption sites:

When gases adsorb in real life, they have a chemically favorable site to adsorb on. So, in order to ensure accurate results, all possible adsorption sites and orientations need to be tested. The site with the least energy is the most stable on and is the most likely to represent the real-life behavior. This is given that used approximations are good enough. The table below covers all adsorption sites in terms of energy difference from the least energy in eV. The most favorable site is boldened and highlighted in red. It is worth noting that in many cases the molecule moved to the optimum location hence the difference is found to be zero.

Table 1: Energy Difference from lowest energy (eV).

Positions (P) >	1	2	3	4	1	2	3	4	1	2	3	4
Sites (S) v	NO_N-down	NO_O-down	NO_hor_p	NO_hor_n	NH3_N-dn- HtoMo	NH3_N-dn- HtoSe	NH3_N- up-HtoMo	NH3_N- up-HtoSe	NO2_O- dn-p	NO2_O- dn-n	NO2_N- dn-p	NO2_N-dn-n
MoSe₂												
1	0.01769	0.06259	0.00272	0.00272	0.00653	0.00816	1.02043	0.02993	0.00000	0.00000	0.09116	0.09116
2	0.00136	0.00408	0.00000	0.00000	0.00544	0.00544	1.02043	1.01635	0.00000	0.00000	0.09116	0.09116
3	0.00000	0.00272	0.00272	0.00272	0.03401	0.03265	0.02993	0.02993	0.00136	0.00000	0.09252	0.09116
4	0.03946	0.06667	0.00136	0.00136	0.00000	0.00000	0.02585	0.02449	0.00000	0.00000	0.08980	0.09116
5	0.00000	0.00408	0.00272	0.00408	0.03674	0.00680	0.02993	0.05714	0.00000	0.00000	0.14014	0.09932
6	0.02585	0.01088	0.00272	0.00136	0.00000	0.00952	0.02721	0.02857	0.00272	0.01088	0.09252	0.09252
MoSe₂Ge												
1	0.00000	0.71974	0.35375	0.84219	0.00136	0.00136	0.00272	0.00680	0.02449	0.04490	0.17687	0.00000
2	0.00000	0.71974	0.00272	0.00272	0.00136	0.00000	0.00136	0.00136	0.02313	0.02449	0.17551	0.17551
3	0.00408	0.72246	0.00136	0.00136	0.00000	0.00000	0.00000	0.00000	0.04218	0.02041	0.17551	0.17415
4	0.00408	0.72246	0.00136	0.00136	0.00000	0.00000	0.00000	0.00000	0.02177	0.02449	0.00408	0.17551
5	0.01633	0.72382	0.00408	0.00408	0.00544	0.00136	0.00408	0.17960	0.04218	0.04354	0.00680	0.31837
6	0.01497	0.85852	0.01633	0.00272	0.00816	0.00272	0.00680	0.00136	0.08844	0.02177	0.17687	0.17687
MoTe₂												
1	0.00000	2.00276	1.92385	1.87078	0.00136	0.00952	0.03810	0.03129	0.00000	0.00408	0.12789	0.12789
2	0.00408	0.00408	0.00272	0.00000	0.07619	0.00272	0.07483	0.07456	0.00000	0.00272	1.13063	0.11973
3	0.00000	0.32109	0.02721	0.00136	0.02721	0.00000	0.03265	0.03265	0.00544	0.00272	0.12245	0.12245
4	0.32518	0.74287	1.97419	1.92112	0.00136	0.00680	0.03674	0.02993	0.00680	1.02043	1.16057	0.57688
5	0.00544	1.99868	0.45579	0.00272	0.00000	0.00680	0.03946	0.03810	1.89936	0.04490	0.13334	0.13198
6	1.93201	2.01364	1.90888	1.79187	1.94289	1.93881	2.02861	2.07623	1.80139	1.83949	1.91704	1.95650
MoTe₂Sb												
1	0.00000	0.70069	0.00259	0.35103	0.02449	0.00000	0.03674	0.04354	0.00136	0.04626	0.13198	0.04626
2	0.00136	0.70069	0.00272	0.00272	0.66396	0.66396	0.04354	0.17551	0.00136	0.00000	0.13061	0.13061
3	0.00136	0.69933	0.00000	0.00000	0.04490	0.04354	0.04354	0.04354	0.04626	0.00272	0.13742	0.13061
4	1.94970	2.31705	2.25174	2.24902	0.03129	0.02857	0.05578	0.04762	1.04220	0.00136	1.17961	1.18914
5	0.00816	0.70614	0.48844	0.00272	0.03129	0.04762	0.05442	0.05714	0.00136	0.06531	0.16055	0.13061
6	1.88983	2.30481	1.87350	2.38644	1.84901	1.90888	1.93745	1.97963	1.94425	1.83813	1.99596	1.99460

4.2 Electronic properties of pristine and doped materials

The main results are divided into eight groups. Properties covered are adsorption sites and energies, charge transfer, CDD, PDOS, the minimum distance and the work function. But before tackling the main results.

4.2.1. *MoSe₂ and MoSe₂Ge without gas:*

Structures of pristine and Ge-doped MoSe₂ are shown in Figure 12. From the side view of Ge-doped MoSe₂, we find that doping with Ge introduces slight compression in the lattice due to the size difference in the structure. Moreover, the bonding of Mo-Ge is clearly stronger than Mo-Se. This can be seen from the structure where the Mo-Ge bond length is comparable with that of Mo-Se which is around 2.5 Å. Doping with Ge also reduced the work function by 0.12 eV.

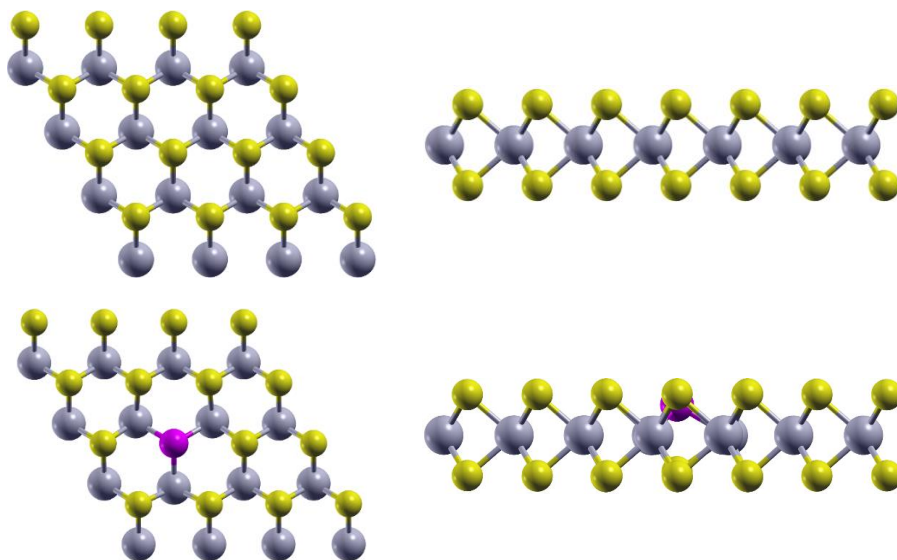


Figure 12. Structures of MoSe₂ and MoSe₂Ge. Grey: Mo, Yellow: Se, Pink: Ge.

Table 2: Properties of MoSe₂ and MoSe₂Ge

Property	MoSe ₂	MoSe ₂ Ge
Bandgap (eV)	1.50	1.3
Work Function (eV)	5.11	4.99
Atomic Distance (Å)	(Se-Mo) 2.55	(Ge-Mo) 2.46 (Se-Mo) 2.54

Studying PDOS for both pristine and doped MoSe₂ from Figure 13, we can note the following. We have the elemental contributions to the material's electronic structure. The energy scale is zeroed around the Fermi level. The left and right sides show the valance and conduction bands respectively separated by the bandgap. Finally, the positive and negative PDOS values representing the spin-up and spin-down directions respectively. From Figure 13 (a), we can see that around the Fermi level, Mo states are dominating. While going further inside the valance band, Se dominates. Moreover, different elements with matching patterns is an indication of hybridization suggesting chemical bonding. Finally, symmetry in PDOS peaks between the spin up and down directions suggest that the material is not spin polarized. Moving to Figure 13 (b), we can see that Ge introduces a new peak in the bandgap with Mo and Se contributing to it. The effect of this new band is a decreased bandgap and easier electron jump from the valance bands to the conduction bands. Finally, Ge states are hybridized with Mo and Se states despite the small Ge peaks which are explained by the number of Mo and Se atoms compared to just a single Ge atom.

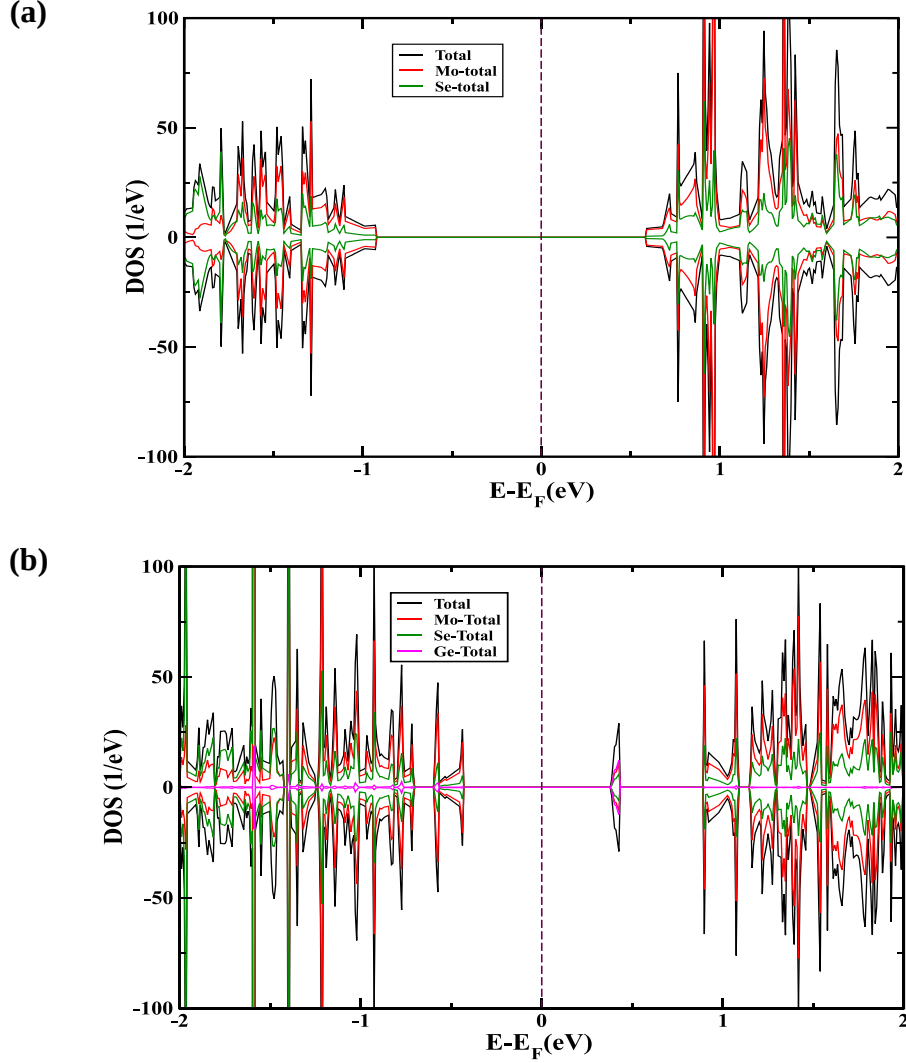


Figure 13. PDOS of (a) MoSe_2 and (b) MoSe_2Ge .

4.2.2. MoSe_2 and MoSe_2Ge with NO:

Testing adsorption of NO, we can see that bonding occurs between the Nitrogen atom and the substrate in both pristine and doped MoSe_2 instead of Oxygen. The adsorption energy for the pristine case was modest (around 0.4 eV) as shown in Figure 14 (a, b) and Table 3. The minimum atomic distance of NO with the sheet is around 3 Å. Moreover, the charge density difference is localized around the molecule itself. Charge transfer value also reflects these results with small

amounts of charge donated to the sheet. This suggests that NO is weakly physisorbed on MoSe₂. When doping with Ge, Figure 14 (c, d), the adsorption is stronger by a factor of three as shown in table 3. The adsorption site changed from the pristine sheet (top of Mo atom) to the top of the Ge atom. The closest atomic distance of the molecule to the sheet is much closer than the pristine case. In fact, the Ge-N distance is around 1.89Å which is shorter than the single bonded Ge-N distance and is equal to the double bonded Ge=N [18]. CDD map shows large interactions between the molecule and the substrate. Moreover, the molecule's influence seems to be strong enough to affect further Mo atoms around the adsorption site. Charge transfer is zero which may look contradictory at first when compared to the adsorption energy and CDD. However, charge transfer, as the name implies, is an indication of the ionic bond where the charge is transferred. In this case, this is a clear indication of a dominant covalent bond.

Table 3: Adsorption energy, charge transfer and minimum distance between NO and pristine and doped MoSe₂ sheets.

Property	MoSe ₂ NO	MoSe ₂ GeNO	Notes
Adsorption Energy (eV)	-0.36	-1.24	CDD: blue +, red -. Isovalue: 0.005 e/Å ³
Lowdin Charge Transfer (e)	+0.18	0.00	Positive sign (+) means Molecule donates to sheet and vice versa
Min. Distance between mol. and sub. (Å)	(Se-N) 3.24	(Ge-N) 1.89	

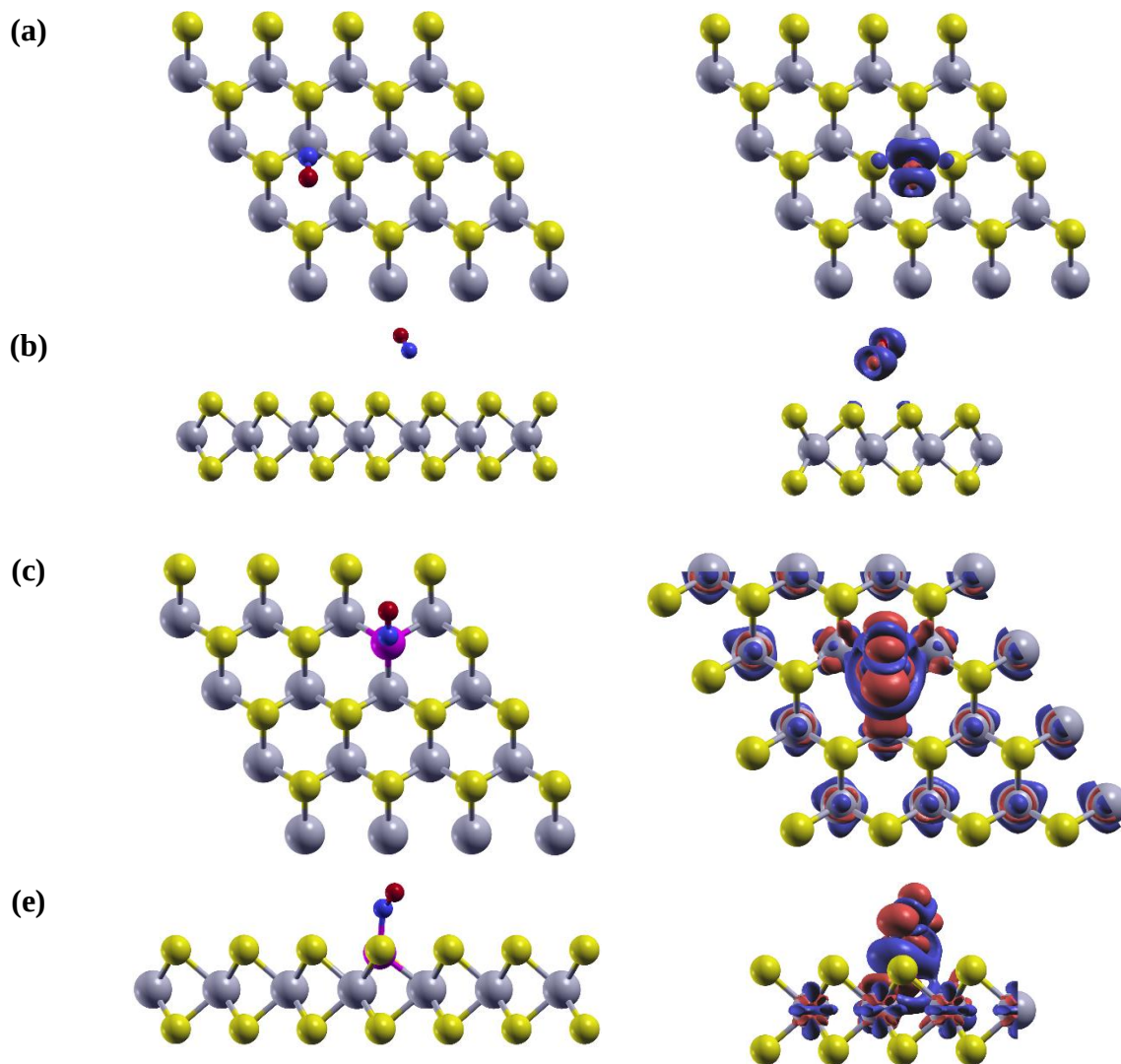


Figure 14. Top (a, c) and side (b, d) views of structure and CDD of pristine (a, b) and doped (c, d) MoSe₂ with NO. Blue is charge depletion (+) and red is charge accumulation (-). Isovalue = 0.005 e/A³.

Studying PDOS, the first thing to notice is that NO is a spin-polarized molecule. This, in turn, makes the whole material spin-polarized also which is reflected in the PDOS by the asymmetry in the PDOS axis. Comparing PDOS of undoped MoSe₂ alone and with NO adsorbed, Figure 13(a) and 15(a), we can see that NO introduces minor spin-polarization but does not have any major contribution to the electronic structure around the bandgap which agrees with the previous electronic properties. The only noticeable contribution of NO states is far in the conduction bands only in the spin-up direction.

Adsorption of NO on doped MoSe₂ on the other hand, Figure 13(b) and 15(b), introduces a total of three peaks in the bandgap that are dominated by NO states with some contributions of Mo, Se and Ge. These states ease the electronic jump and therefore can enhance conduction. Also, NO states hybridize with all other states, especially with Ge. This is well aligned with the previous results. Aside from the main contribution in the bandgap, small NO states can be found in the spin-up direction of the conduction bands. Spin-polarization is more pronounced than the pristine sample.

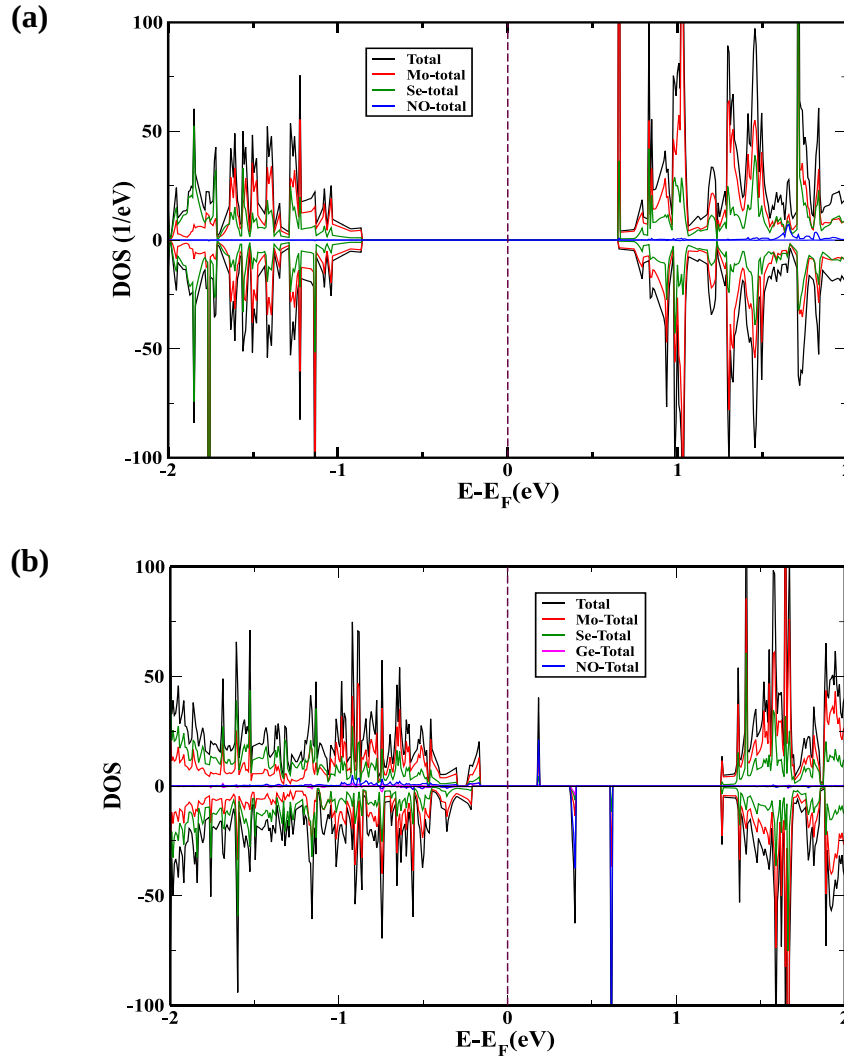


Figure 15. PDOS of (a) MoSe₂/NO and (b) MoSe₂Ge/NO.

4.2.3. *MoSe₂ and MoSe₂Ge with NO₂:*

Adsorption of NO₂ mostly shows a similar behavior to NO where doping enhances adsorption. For Pristine MoSe₂, NO₂ favored adsorption on the Mo-Se bridge with a rotation normal to Mo-Se bond. CDD shows a good interaction between the molecule and substrate. But ultimately, Adsorption energy and charge transfer are modest and the distance between the sheet and the molecule is large (~3 Å). This suggests moderate physisorption that is stronger than NO on pristine MoSe₂. Doping clearly shows some enhancement. First, adsorption site changed from Mo-Se bridge to be vertically standing on top of Ge with the O atom favored to bond with Ge. Second, adsorption energy is much larger; about 6.2 times larger than on pristine. Third, the bond length between atoms O and Ge is around 1.83 Å which is well within the typical lengths of chemically bonded Ge-O which is between 1.75 and 1.85 Å [19]. This is supported by the large interactions between NO₂ and MoSe₂Ge shown by CDD. Finally, charge transfer is slightly larger than the pristine case. This strongly suggests chemisorption similar to the NO case. However, NO₂ seems to have larger percentage of ionic bonding than NO that resulted in a higher charge transfer compared with NO on doped MoSe₂Ge.

Table 4: Adsorption energy, charge transfer and minimum distance between NO₂ and pristine and doped MoSe₂ sheets.

Property	MoSe ₂ NO ₂	MoSe ₂ GeNO ₂	Notes
Adsorption Energy (eV)	-0.33	-2.04	CDD: blue +, red -. Isovalue: 0.005 e/Å ³
Lowdin Charge Transfer (e)	-0.10	-0.16	Positive sign (+) means Molecule donates to sheet and vice versa
Min. Distance between mol. and sub. (Å)	(Se-O) 2.95	(Ge-O) 1.83	

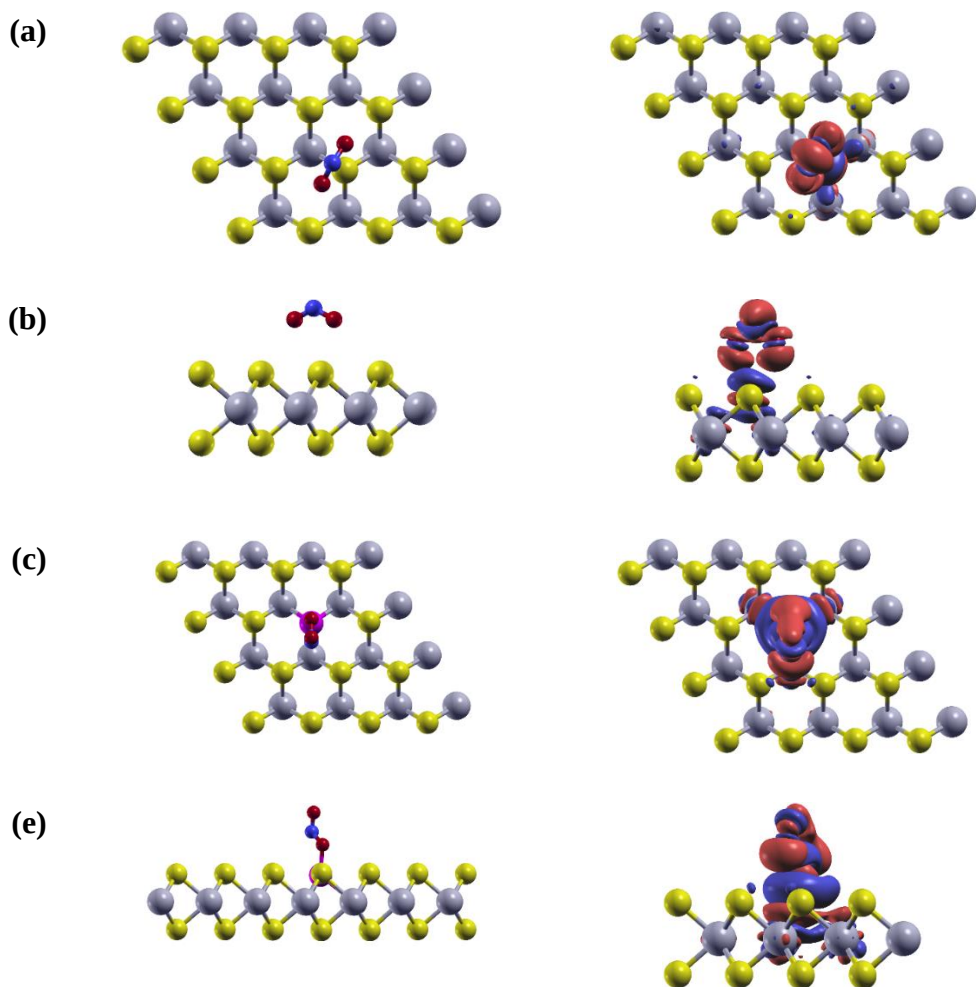


Figure 16. Top (a, c) and side (b, d) views of structure and CDD of pristine (a, b) and doped (c, d) MoSe₂ with NO₂. Blue is charge depletion (+) and red is charge accumulation (-). Isovalue = 0.005 e/Å³.

Analysis of PDOS shows a small NO₂ level appeared in the bandgap in the spin-down direction. This peak is dominated by NO₂ but has small contributions from Mo and Se states. Combining previous results with the PDOS, is a clear evidence of strong physisorption. Also, the VBM shifted to higher energies to be closer to the Fermi level compared to MoSe₂ without NO₂. Aside from the main contribution of NO₂ states, minor some contributions are found in the spin-up direction of the valance and conduction bands with weak hybridization with Se states. For the doped case, adsorption of NO₂ made considerable changes. First, two new peaks dominated by NO₂ appended at CBM and lowered the conduction minima with contributions from Mo and Se states but no

contribution from the Ge states. Second, the Ge-dominated band that was present in the bandgap in the no-gas case disappeared and the largest contribution of Ge changed to another peak just above the Fermi level. Third, all energy levels shifted to higher energies, but the spin-down direction shifted more than the spin-up. Finally, although hard to notice, NO₂ states are strongly hybridized with Ge states. The new NO₂ peaks and strong hybridization with Ge along with previous results suggest chemisorption with some percentage of ionic bonding. Both pristine and doped cases are spin-polarized due to NO₂ adsorption.

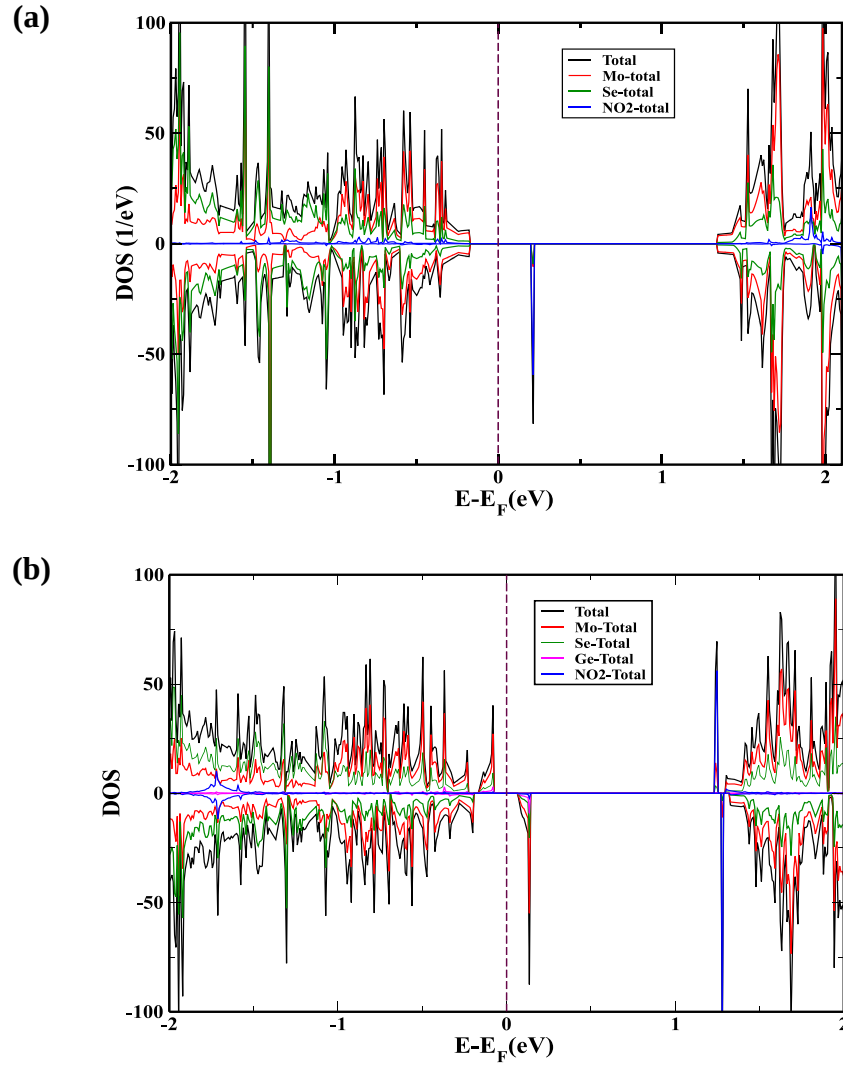


Figure 17. PDOS of (a) MoSe₂/NO₂ and (b) MoSe₂Ge/NO₂.

4.2.4. MoSe_2 and MoSe_2Ge with NH_3 :

Adsorption of NH_3 on pristine MoSe_2 favored the hexagon center with modest energy. CDD shows very little interaction between NH_3 and the sheet with little charge transfer. Doping clearly enhances the adsorption with a change in adsorption site to favor the top of Ge, an increase in adsorption energy of around 6 times larger, more charge transfer and more visual CDD interaction and closer distance to the sheet. Overall, this hints to weak (good) physisorption for pristine (doped) MoSe_2 .

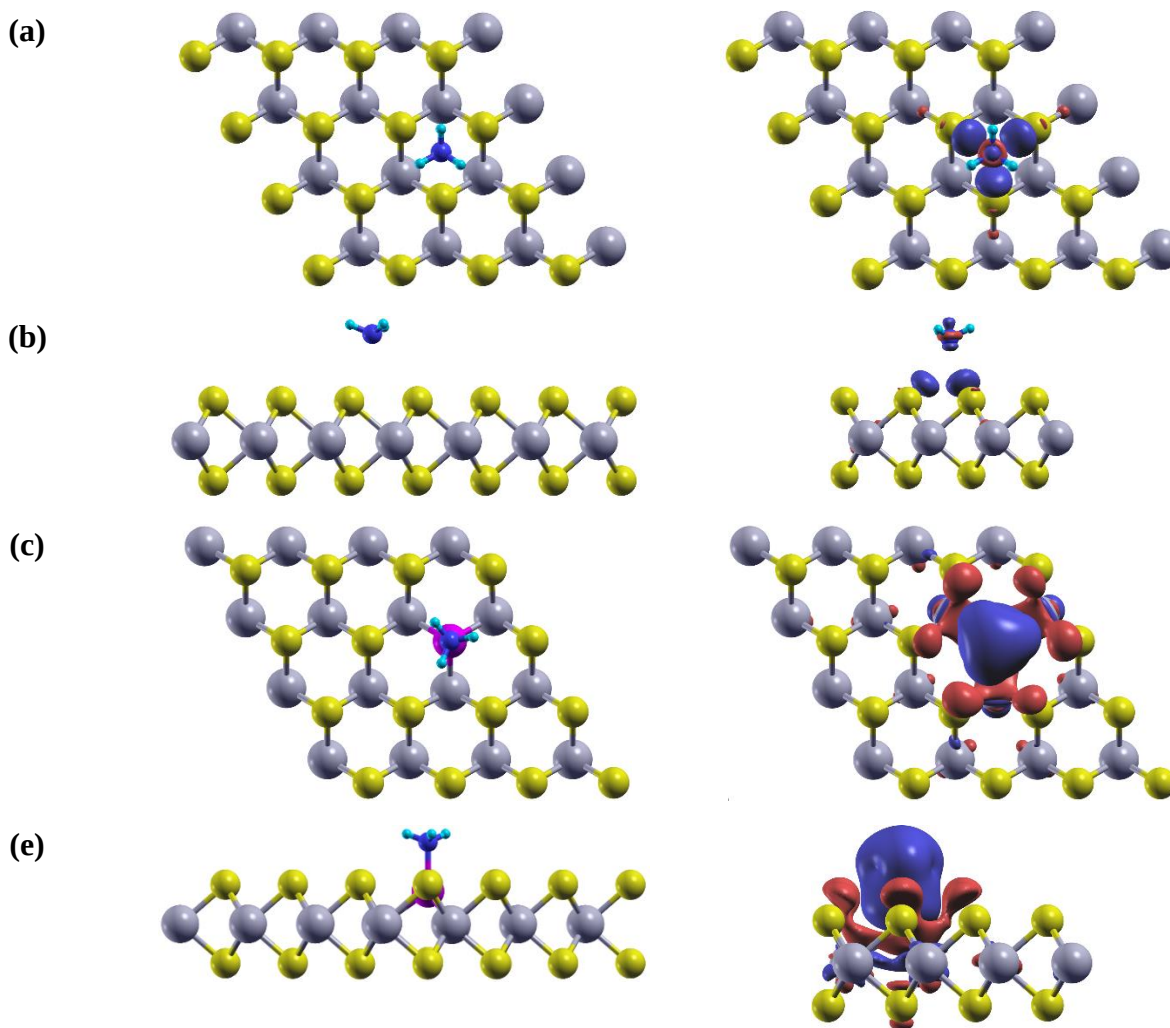


Figure 18. Top (a, c) and side (b, d) views of structure and CDD of pristine (a, b) and doped (c, d) MoSe_2 with NH_3 . Blue is charge depletion (+) and red is charge accumulation (-). Isovalue = 0.005 e/A³.

Table 5: Adsorption energy, charge transfer and minimum distance between NH₃ and pristine and doped MoSe₂ sheets

Property	MoSe ₂ NH ₃	MoSe ₂ GeNH ₃	Notes
Adsorption Energy (eV)	-0.26	-1.53	CDD: blue +, red -. Isovalue: 0.005 e/A ³
Lowdin Charge Transfer (e)	+0.17	+0.48	+ Molecule donates to sheet
Min. Distance between mol. and sub. (Å)	(Se-N) 3.42	(Ge-N) 2.08	

Looking at the PDOS we find for the pristine case that adsorption of NH₃ almost has no effects on the electronic structure of the material with no new states or even any contribution except very few states far in the valance band. For the doped case we see that adsorption of NH₃ removed the peak introduced in the bandgap by the Ge atom in the no-gas case. Also, all states shifted to lower energies. Again, NH₃ does not seem to have affected the electronic structure beside Ge peak removal which can make current conduction harder.

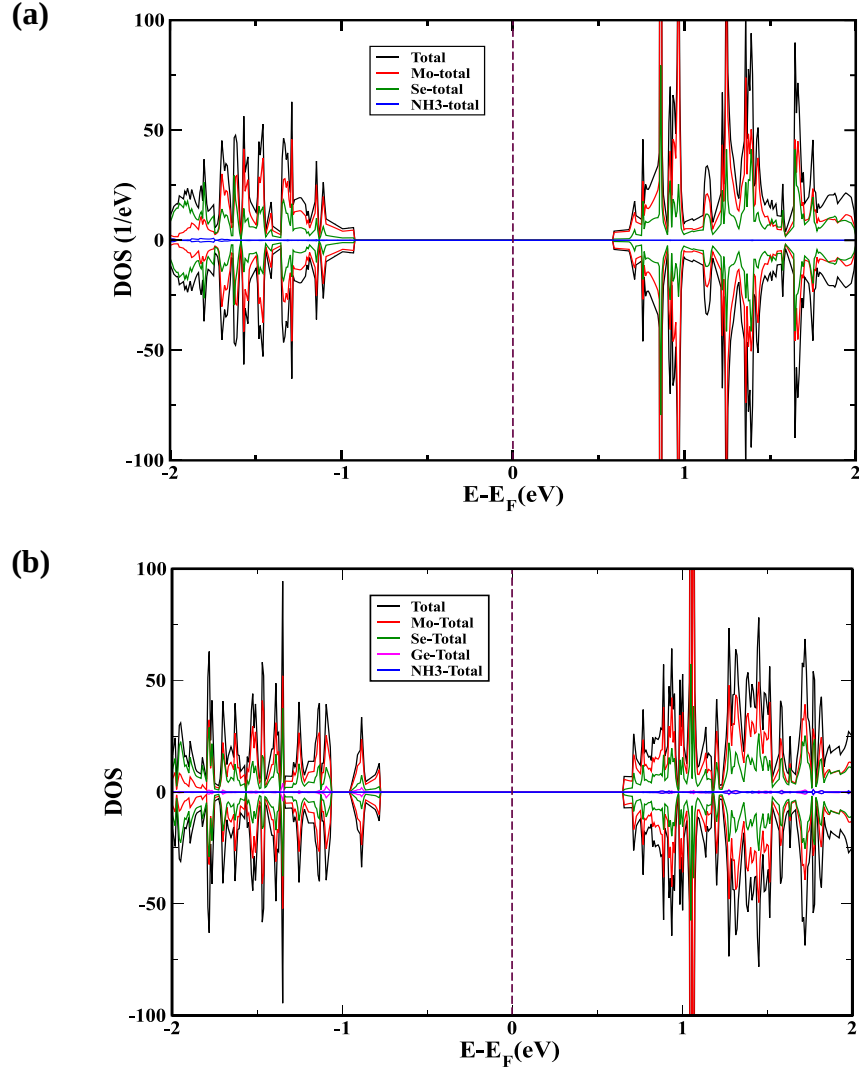


Figure 19. PDOS of (a) $\text{MoSe}_2/\text{NH}_3$ and (b) $\text{MoSe}_2\text{Ge}/\text{NH}_3$.

4.2.5. MoTe_2 and MoTe_2Sb without gases:

Structures of pristine and doped MoTe_2 is shown in Figure 9. Doping with Sb barely induced any structure distortion. In fact, Sb caused less distortion for MoTe_2 than Ge for MoSe_2 . Atomic distancing is almost the same between the pristine and the doped materials. Doping decreased the work function.

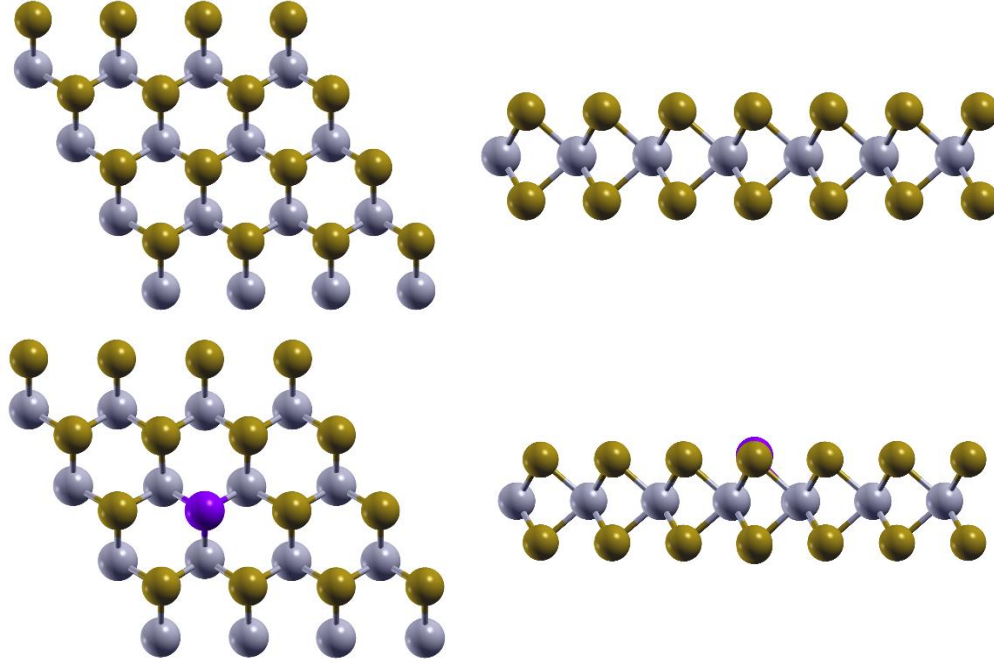


Figure 20. Structures of MoSe_2 and MoSe_2Ge . Grey: Mo, Brown: Te, Purple: Sb.

Table 6: Properties of MoTe_2 and MoTe_2Sb

Property	MoTe_2	MoTe_2Sb
Bandgap (eV)	1.14	Semi-metallic
Work Function (eV)	4.70	4.59
Atomic Distance (Å)	(Mo-Te) 2.74	(Mo-Sb) 2.80

PDOS charts give some insights about the effects of Sb. We can see that, as with MoSe_2 , pristine MoTe_2 is a semiconductor with a bandgap and is not spin-polarized. States near the bandgap are dominated by Mo and by Te further into the valance bands. Introducing Sb to MoTe_2 changes the behavior of MoTe_2 . Spin-polarization is introduced and causes a shift in the spin-down direction. As a result, all states shift to higher energies and in particular valance bands next to the bandgap shift past the Fermi level and the material becomes a semi-metal. Finally, Sb is hybridized with Mo and Te states which is an indication of chemical bonding.

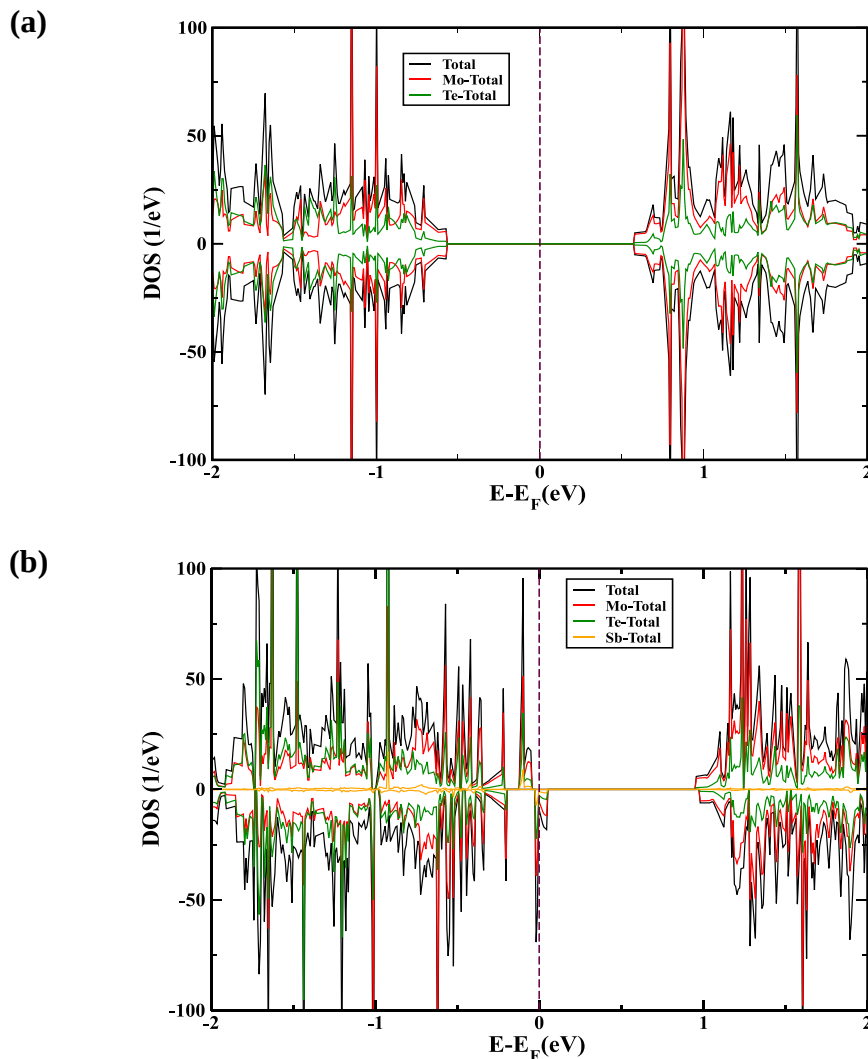


Figure 21. PDOS of (a) MoTe_2 and (b) MoTe_2Sb .

4.2.6. MoTe_2 and MoTe_2Sb with NO:

Adsorption of NO is favored on top of Mo with relatively low adsorption energy. CDD and charge transfer show modest interaction and transfer. This is coupled with a large distance between the molecule and substrate. All these observations suggest physical adsorption. Doping with Sb dramatically changes the outcome. Adsorption energy doubled with more interactions between the molecule and the substrate observed from CDD. Minimum atomic distance between molecule and

substrate is between Sb and N with the bond length well within the range of reported chemical bonding between them [20]. Even though N favored to adsorb on top of Mo, the typical Mo-N bond length is around 2.2 Å [21] but in our structure it is 3.72 Å which exclude the possibility of bonding between them. This suggests chemisorption.

In this optimized structure, O always leans towards the Sb atom which makes it worth investigating the bonding between them. Typical Sb-O bond length is 2.36 Å [22] while in our case it is 3.32 Å. However, the maximum reported bond length between Sb and O can reach up to 3.39 Å [22]. This can mean weak interaction in addition of Sb-N.

Table 7: Adsorption energy, charge transfer and minimum distance between NO and pristine and doped MoTe₂ sheets

Property	MoTe ₂ NO	MoTe ₂ SbNO	Notes
Adsorption Energy (eV)	-0.48	-0.95	CDD: blue +, red -. Isovalue: 0.005 e/Å ³
Lowdin Charge Transfer (e)	+0.05	+0.02	+ Molecule donates to sheet
Min. Distance between mol. and sub. (Å)	(Te-N) 3.04	(Sb-N) 2.48	

PDOS charts of NO with pristine MoTe₂ (Figure 23) show states shifting to higher energies. Also, adsorption of NO induced spin-polarization and a new peak appended to the end of CBM with Mo and Se states contributing to it. Adsorption of NO with doped MoTe₂ we can see four new peaks of NO in two positions: in the bandgap and appended to the CBM in both spin directions. It is also clear that there is some hybridization between Sb and NO states which support the previous findings. The peak in the CBM has Mo and Te states contributing to it along with Sb ones while the peak in the bandgap is lacking contribution of Sb states. Moreover, we can see that valance states shifted up to the Fermi level. Finally, it is worth noting that adsorption of NO cancelled the spin-polarization effect caused by doping.

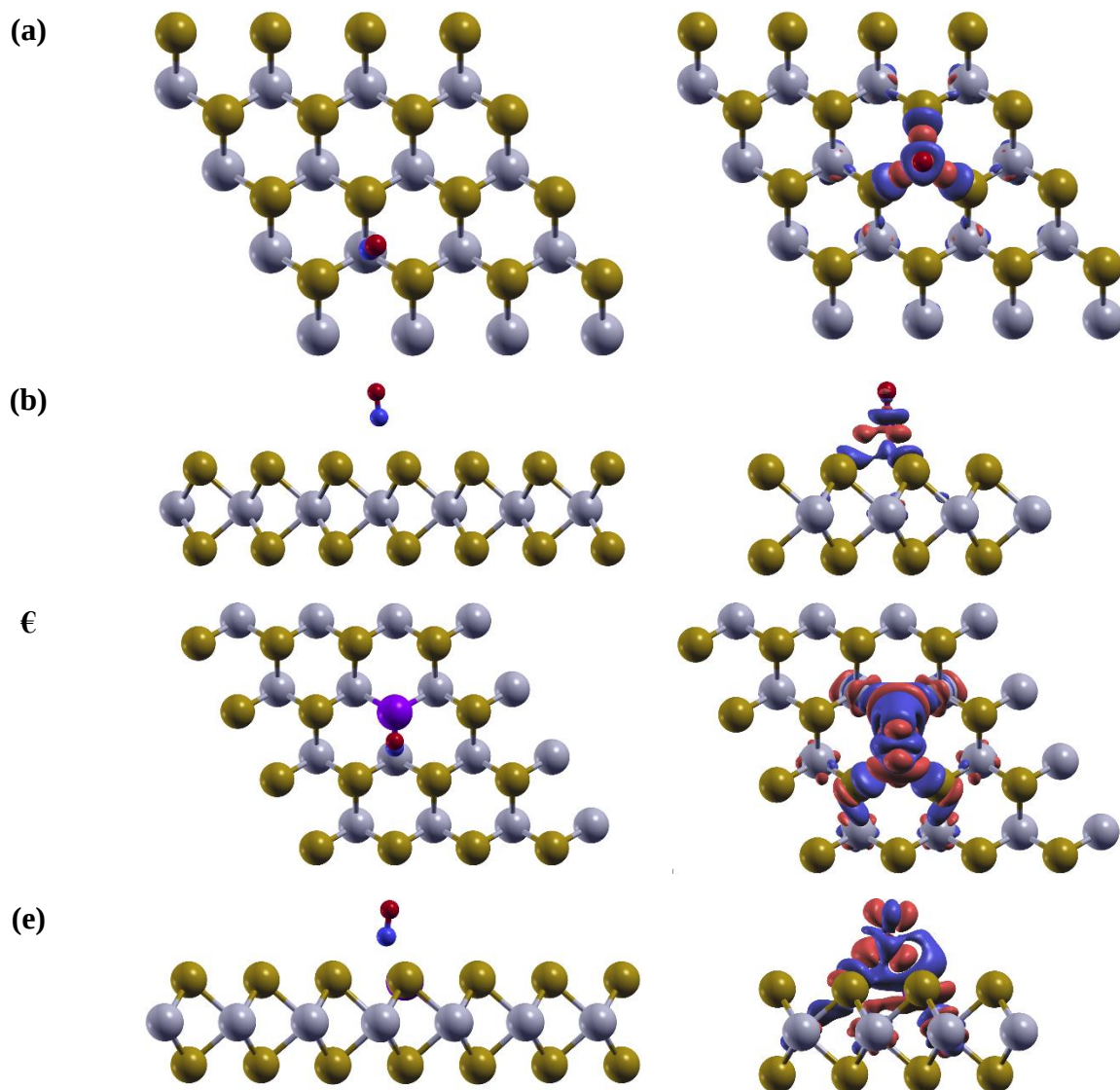


Figure 22. Top (a, c) and side (b, d) views of structure and CDD of pristine (a, b) and doped (c, d) MoTe₂ with NO. Blue is charge depletion (+) and red is charge accumulation (-). Isovalue = 0.005 e/A³.

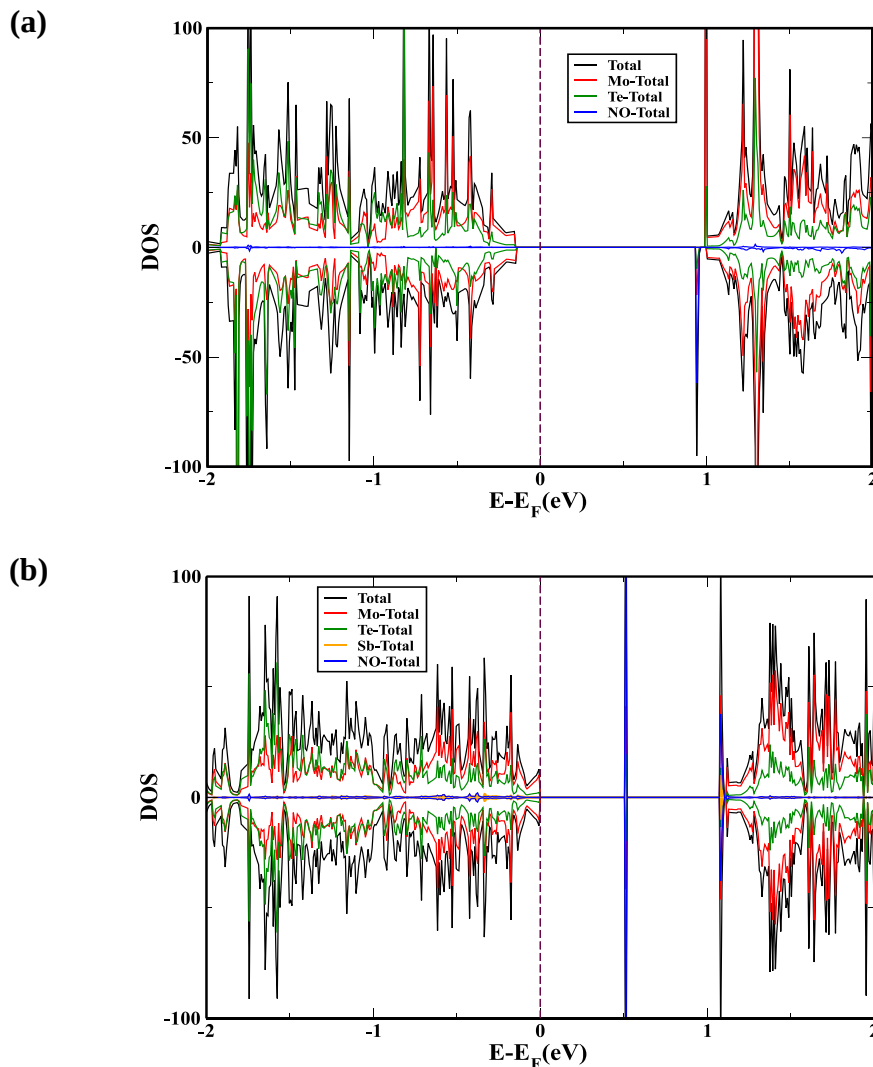


Figure 23. PDOS of (a) MoTe_2NO and (b) MoTe_2SbNO .

4.2.7. MoTe_2 and MoTe_2Sb with NO_2 :

NO_2 shows good adsorption on both pristine and doped MoTe_2 . Preferred adsorption site is the same which is on top of Te/Sb but with different rotation. In the pristine case, the molecule adsorbed on the Sb atom unlike the NO case. However, this can be because the molecule prefers this site anyway even in the pristine case. CDD figures show good interaction in both samples. That said, adsorption is stronger on doped MoTe_2 with higher energy, more charge transfer and a lower minimum distance between molecule and substrate as listed in Table 8.

Table 8: Adsorption energy, charge transfer and minimum distance between NO and pristine and doped MoTe₂ sheets

Property	MoTe ₂ NO ₂	MoTe ₂ SbNO ₂	Notes
Adsorption Energy (eV)	-0.51	-1.71	CDD: blue +, red -. Isovalue: 0.005 e/Å ³
Lowdin Charge Transfer (e)	-0.05	-0.20	+ Molecule donates to sheet
Min. Distance between mol. and sub. (Å)	(Te-O) 2.90	(Sb-O) 2.20	

Comparing cases with and without NO₂ (Figure 25a) we can see that for the pristine case, adsorption introduced slight spin-polarization and shifted all states to higher energies which made the VBM very close to the Fermi energy. Moreover, NO₂ introduced new states in the bandgap in the spin down direction with contributions from Mo and Te. Aside from the main effects, NO₂ has some contributions in the valence bands near the VBM and along with the valence band and some contributions in the conduction bands. NO₂ states seem to hybridize with Mo and Te states. Adding all trends along with the adsorption energy value, we can say that there is good physical adsorption.

For the doped case, adsorption of NO₂ changed the electronic structure. First, semi-metallic behavior is removed where both spin up and down directions moved to the Fermi level restoring semiconducting nature. Second, adsorption of NO₂ cancelled the spin-polarization effect introduced by the Sb atom. Third, there is some hybridization between Sb and NO₂ although not much. Finally, aside from the previous points, NO₂ has some contributions in the valence and conduction bands far from the bandgap with no new states introduced in the bandgap.

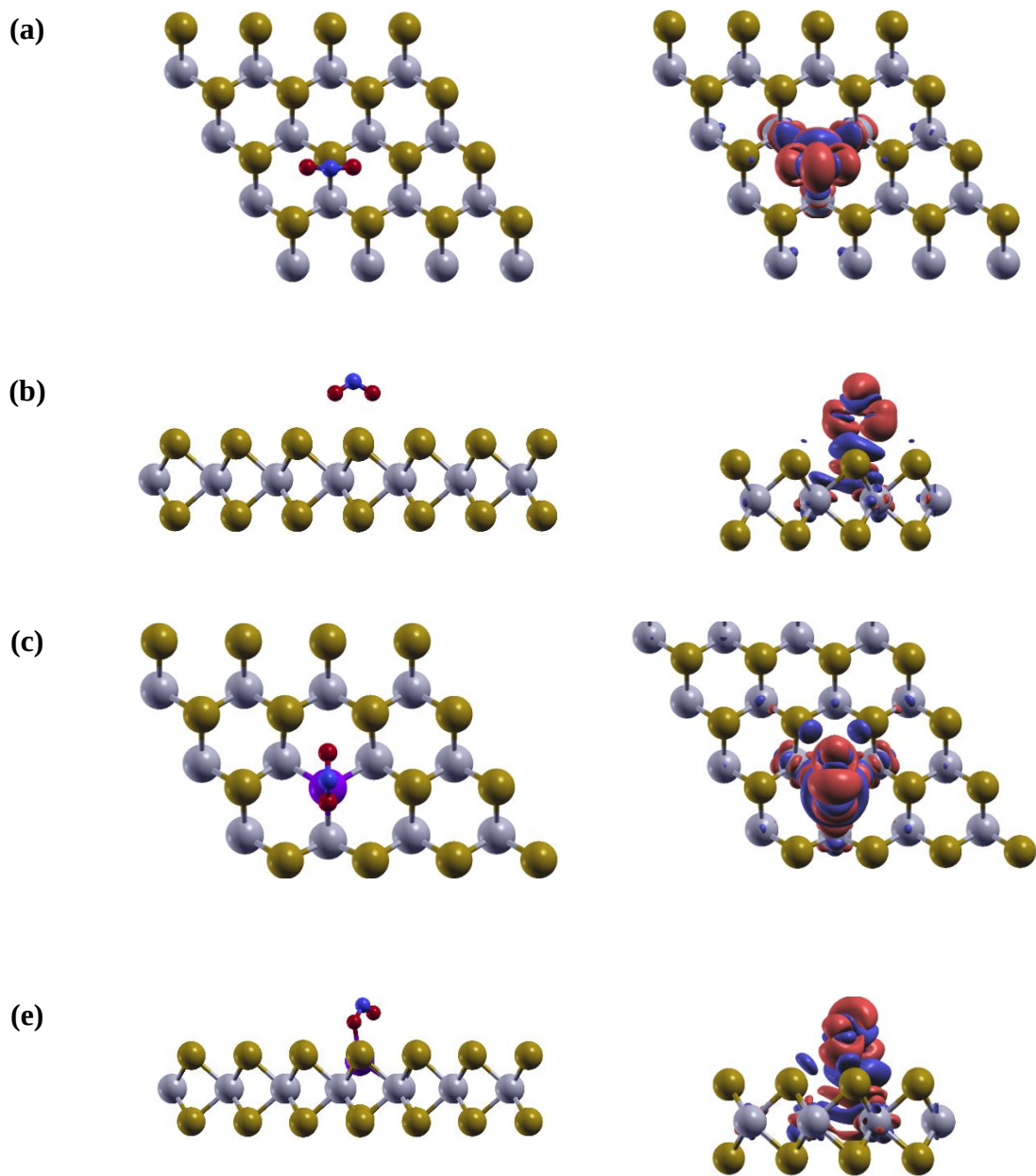


Figure 24. Top (a, c) and side (b, d) views of structure and CDD of pristine (a, b) and doped (c, d) MoTe_2 with NO_2 . Blue is charge depletion (+) and red is charge accumulation (-). Isovalue = $0.005 \text{ e/\text{\AA}^3}$.

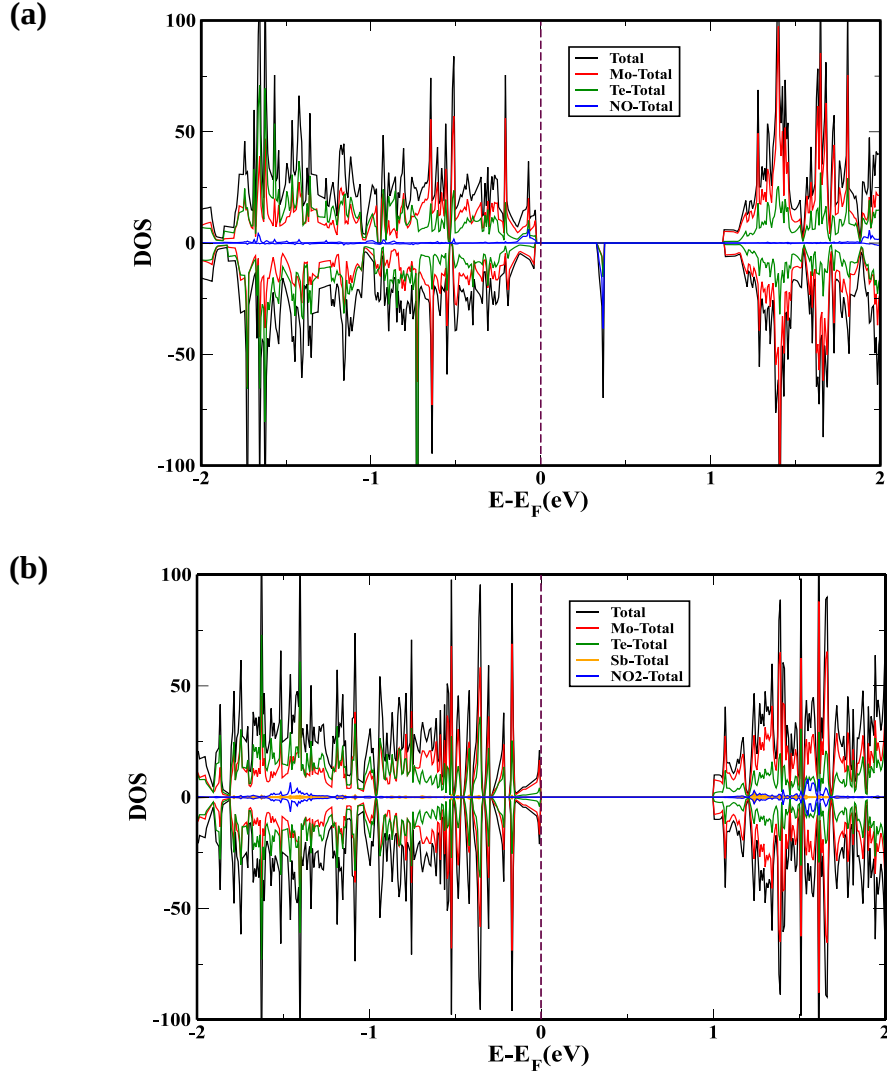


Figure 25. PDOS of (a) MoTe_2NO_2 and (b) $\text{MoTe}_2\text{SbNO}_2$.

4.2.8. MoTe_2 and MoTe_2Sb with NH_3 :

Studying adsorption of NH_3 on pristine and doped MoTe_2 we can see weak adsorption in both cases. In the pristine case, NH_3 preferred to adsorb on top of Mo with low adsorption energy and small charge transfer. CDD figures show little interaction between the substrate and the molecule. With these results and a large molecule-substrate distance, we can safely say that adsorption type is weak physisorption. Doping shows little difference from the pristine one with exception to the

adsorption site where NH_3 referred the hexagonal hollow. Adsorption value is still modest. And the molecule is a little closer to the substrate. The biggest difference is in the charge transfer where more charge transfer occurs compared to pristine. However, CDD figures still show little interaction. This suggests slightly better adsorption compared with the pristine case, but it is still weak physisorption.

Table 9: Adsorption energy, charge transfer and minimum distance between NO and pristine and doped MoTe_2 sheets.

Property	MoTe_2NH_3	$\text{MoTe}_2\text{SbNH}_3$	Notes
Adsorption Energy (eV)	-0.24	-0.33	CDD: blue +, red -. Isovalue: 0.005 e/Å ³
Lowdin Charge Transfer (e)	+0.17	+0.39	+ Molecule donates to sheet
Min. Distance between mol. and sub. (Å)	(Te-N) 3.65	(Te-N) 3.54	

Studying the PDOS profile for MoTe_2 and MoTe_2Sb (Figure 26) with NH_3 we note the following. For pure MoTe_2 , adsorption of NH_3 shifted all states to higher energies with VBM shifted to the Fermi level, but no real influence on the electronic structure happened. The material remains a semiconductor with a similar bandgap and no new states in the bandgap. Finally, there is no spin-polarization since neither MoTe_2 nor NH_3 have magnetic moments. For the doped case, states actually shifted to lower energies and CBM crossed the Fermi level changing the material behavior from semi-metallic to fully metallic. There is some hybridization between Sb and NH_3 . Finally, spin-polarization and shift caused by Sb doping is still present with the spin down direction offset from the spin direction to higher energies.

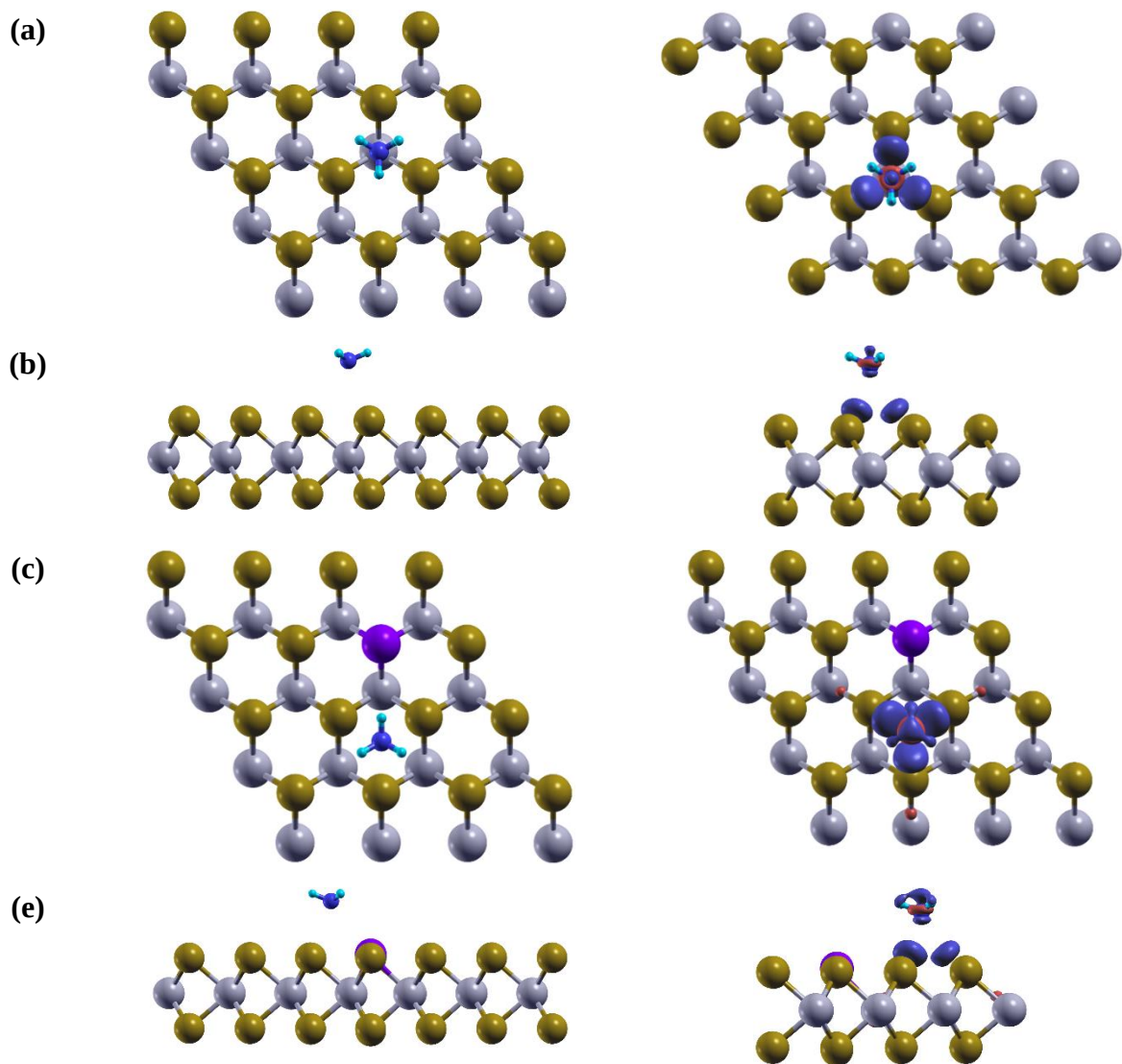


Figure 26. Top (a, c) and side (b, d) views of structure and CDD of pristine (a, b) and doped (c, d) MoTe_2 with NH_3 . Blue is charge depletion (+) and red is charge accumulation (-). Isovalue = 0.005 $e/\text{\AA}^3$.

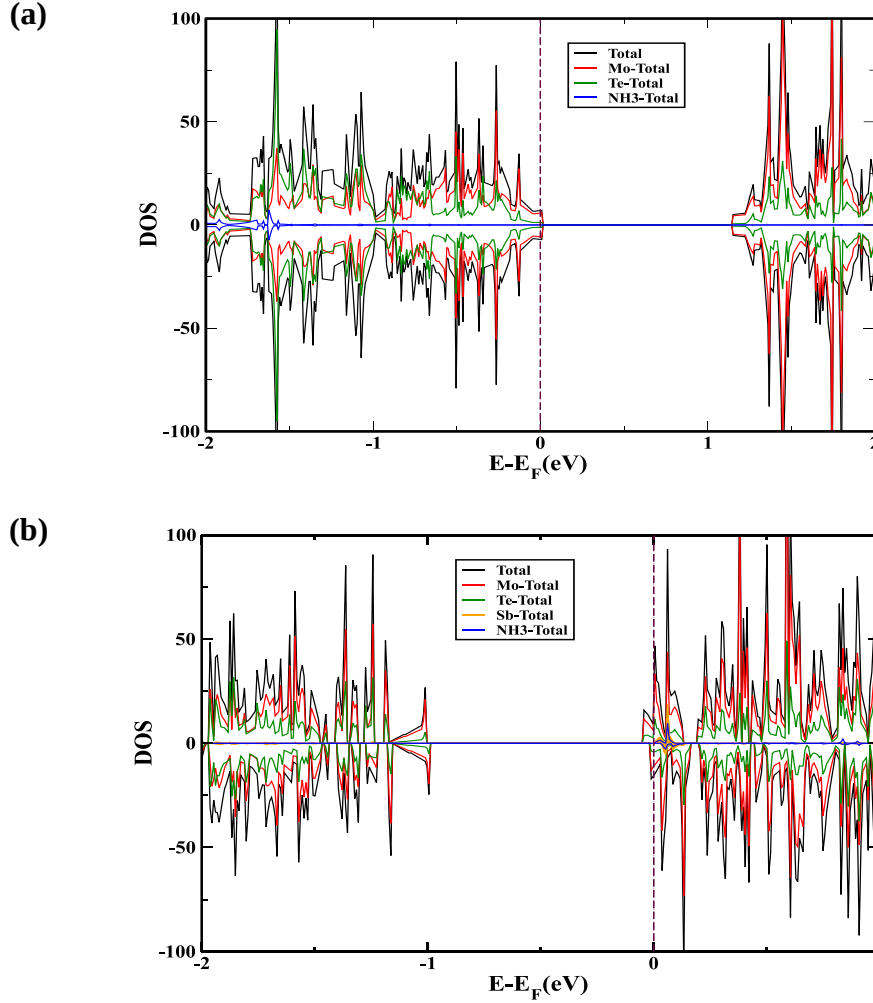


Figure 27. PDOS of (a) MoTe_2NH_3 and (b) $\text{MoTe}_2\text{SbNH}_3$.

4.2.9. Work functions:

PDOS gives us indications on the receptor properties of the material where it shows the changes in the electronic structure and for gas sensing applications, how easy it is for electrons to jump from valance bands, where it is bounded to the nucleus, to the conduction band where the electron is free to conduct electricity within the material. The work function is the measure from the Fermi level to the vacuum level on top of the conduction bands. If energy is larger than the vacuum level, the materials because the material starts to disintegrate. Hence, work function gives indications on the stability of the materials after doping and adsorption.

Looking at the work functions we can see the following trends when comparing no adsorption with the gases adsorbed. For MoSe_2 , adsorption of NH_3 and NO_2 slightly decreased the work functions. This is not the case for NO where work function was lowered by more than 1 eV. For MoSe_2Ge , the work function is almost the same with a very minor increase in all cases with gas molecules. MoTe_2 have a similar trend as MoSe_2 that is, adsorption of the gases slightly lowered the work function with NO having the lowest work function by 12 meV. For MoTe_2Sb , adsorption of NO and NO_2 raised the work function slightly but NH_3 lowered the work function by more than 1 eV. Overall, the work function was not impacted from doping hence we can say all materials are stable.

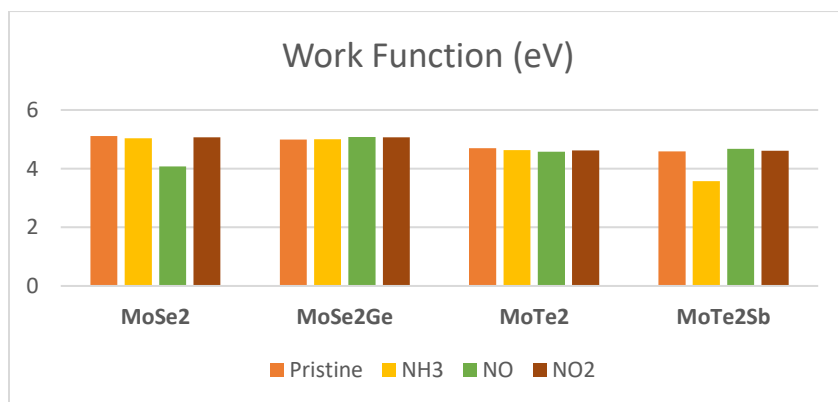


Figure 28. Summary of the work function values for all materials tested.

4.3 Performance comparison:

To summarize the general trends found from the results above. For MoSe_2 , Ge dopant directly influences the gas molecule to improve adsorption. This is apparent by the change of adsorption sites and the direct bonding of the molecule with the Ge atom. However, in MoTe_2 , Sb improves adsorption indirectly by influencing the substrate properties. This is evident by the enhanced adsorption, with the site remaining the same. Figure 29 clearly shows the effects of doping in both cases where adsorption energies are enhanced by doping though pristine materials show weak physical adsorption.

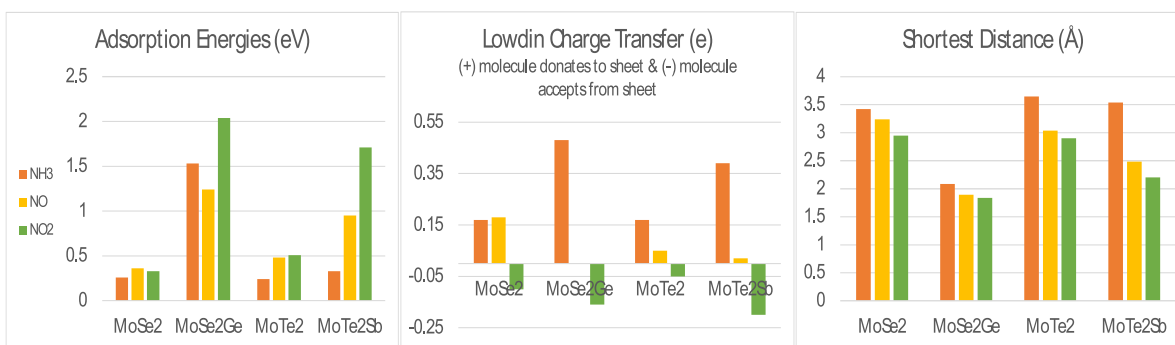


Figure 29. Adsorption energy, charge transfer and shortest atomic distance of the tested materials.

Moving to the doped cases it is clear that both materials favorably respond to NO_2 the most with the largest adsorption energies and the lowest atomic distances with good charge transfer resulting in chemisorption. This is also supported by the CDD and PDOS. It is safe to say that MoSe_2Ge and MoTe_2Sb are good materials for sensing NO_2 . Similar results are found for NO with good adsorption energies, although the weakest among other molecules, and relatively close atomic distances. The difference lies in the charge transfer where values are very low even with such strong interaction. This suggests that NO have a higher percentage of covalent bonding with the doped sheets whereas for NO_2 ionic bonding is dominant. Covalent bonding is an excellent indication of chemisorption and an evidence of MoSe_2Ge and MoTe_2Sb potential as good NO sensors. Again, CDD and PDOS figures support this claim. Adsorption of NH_3 ends the similarities between MoSe_2Ge and MoTe_2Sb . For MoSe_2Ge , NH_3 showed large values of adsorption energy and charge transfer with low atomic distance which is supported by CDD. These are good indications of chemisorption. However, PDOS did not show any meaningful changes. This means that although adsorption is favorable, NH_3 is not a suitable gas for sensing by the materials studies here. For MoTe_2Sb , all results point to physisorption with low adsorption energy and large atomic distance. CDD and PDOS also support this. Ultimately, both materials are not suited for NH_3 detection.

4.4 Validation and comparison with literature:

Since the bandgap is the most important property in the results because it indicates the influence of adsorption on conductivity, it is vital to make sure the values we get are representative of the real case. Looking at highly cited literature we find that monolayer MoSe₂ was found by DFT and experiment (CVD) to have a bandgap of around 1.57 eV [23]. This agrees with our results reported with 1.54 eV. For 2D MoTe₂, the bandgap was experimentally (mechanical exfoliation [24] and CVD [25]) found to be around 1.10 eV. This again agrees with our results of 1.14 eV. These indications support the precision of our calculations.

Observing adsorption behavior in other types of gas sensors to make sense of our results we see the following. Leenaerts et al. [26] found adsorption energies of NH₃, NO and NO₂ on graphene ranged from tens and to 100 meV with small charge transfer. Another study investigated MoO₃ metal oxide as a gas sensor for NO and NO₂ along with other gases [27]. The material was found useful in detecting NO₂ as adsorption energy was around -0.58 eV with moderate charge transfer. This is much smaller than the numbers reported in this thesis. These data strongly indicate that adsorption in this study is of the chemical type. This hints to the doped materials being suitable as scavengers rather than sensors because of the high adsorption energy.

CHAPTER 5. CONCLUSION

In the end, this thesis studied the potential of MoSe₂ and MoTe₂ as electrochemical gas sensors of NO_x and NH₃ gases. First, the report tackled the concepts of QM, DFT and gas sensing with the focus on 2D TMD's structures and properties, specifically MoSe₂ and MoTe₂. Next, some literature review was covered followed by the computational setup for the thesis. Finally, the results were discussed and are summarized below as follows:

- Pristine MoSe₂ and MoTe₂ showed good physical adsorption with all gases
- Pristine materials are good NO₂ sensors only
- This is because of the impurity bands in the bandgap for NO₂ while no noticeable effects for NO and NH₃ on conduction behavior.
- Substitutional doping dramatically enhanced adsorption in both materials for all gases except NH₃ on MoTe₂Sb
- Adsorption mode switched from physisorption to chemisorption when doped. This confirms the viability of doping MoSe₂ and MoTe₂ to increase their sensitivity for the gases covered
- Ge doping enhanced adsorption directly for MoSe₂ while Sb did so indirectly for MoTe₂. This was evident by the change in adsorption sites for MoSe₂ but not for MoTe₂
- Ultimately, adsorption energies for doped cases are too large to be useful as it becomes harder for molecules to desorb. This suggests using the doped materials as gas scavengers rather than sensors

CHAPTER 6. FUTURE WORK AND POSSIBLE TOPICS

With the findings and scope of this thesis, additional work can be done that can further our understanding of the properties of our materials and their adsorption behavior. Below are the possible future topics that can be covered in order to gain better insights about both materials but were outside the scope of this thesis:

- Studying the desorption behavior in order to confirm whether adsorption energies for the doped materials are too strong to be used as gas sensors
- Studying the effects of NO_x gases on spin polarization behavior of MoSe₂ and MoTe₂ and the potential of exploiting this as another method for detection of NO_x gases
- Effects of different types of doping like doping by adsorption instead of substitutional doping and its effects on adsorption
- Potential of MoSe₂ and MoTe₂ as sensors for Sulfur containing gases like SO₂ and H₂S

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APPENDIX

This section contains codes used during this work to be used if needed by the reader. These codes are primary input file for “pw.x” calculations, job scripts and some minor input file for post-processing. Here, ‘#’ means comments in shell scripts like the job script while in files related to the QE package like plane-wave file, it is ‘!’. Finally, files with codes copied from this report should be run through the ‘dos2unix’ command first (`dos2unix filename`). This is because windows formatting can include hidden characters that may cause QE to fail to read the file.

1. Plane-wave input:

To change calculation type, change the ‘calculation’ parameter to the desired one then add or remove relevant cards and parameters.

```
&control
  calculation = 'scf',
  verbosity = 'high'
!   restart_mode='restart'
  prefix = 'NO_MoTe2_CDD'
  outdir = './'
  etot_conv_thr = 1.0D-6
  forc_conv_thr = 1.0D-5
  nstep = 100
  max_seconds = 358200
  pseudo_dir = '/home/nadhrega/qe-course/pseudo/'
/
&system
 ibrav = 0,
A = 14.23484448,
nat = 50,
ntyp = 4,
ecutwfc = 80.0,
ecutrho = 280.0,
nspin=2
starting_magnetization(1) =0.5
```

```

    occupations = 'smearing',
    smearing = 'marzari-vanderbilt',
    degauss = 0.04
    vdw_corr = 'grimme-d3'
/
&electrons
    mixing_beta = 0.5
    conv_thr = 1.0D-9
/
&IONS
    ion_dynamics='bfgs'
/
CELL_PARAMETERS (alat)
  1          0.000000      0.000000
-0.499999849 0.866025388    0.000000
  0.00000    0.00000000    2.15620833
ATOMIC_SPECIES
Mo 95.95 Mo.pbe-spn-kjpaw_psl.0.2.UPF
Te 127.6 Te.pbe-dn-kjpaw_psl.0.2.2.UPF
N 14.01 N.pbe-n-kjpaw_psl.1.0.0.UPF
O 16.00 O.pbe-n-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (crystal)
Mo      -0.000027352  -0.000022942   0.125699693
Te       0.083183314   0.166365213   0.184820332
Te       0.083508194   0.166727868   0.066725189
Mo       0.249948263  -0.000103473   0.125664499
Te       0.333023281   0.166046561   0.184957299
Te       0.333321805   0.166643608   0.066641342
Mo       0.500004414  -0.000022940   0.125699693
Te       0.583181905   0.166365222   0.184820334
Te       0.583219678   0.166727877   0.066725187
Mo       0.749810775  -0.000378453   0.125781468
Te       0.833311108   0.166622215   0.184709118
Te       0.833315731   0.166631461   0.066883892
Mo       0.000318129   0.250127006   0.125784910
Te       0.083187103   0.416762402   0.184817106
Te       0.083502229   0.416715449   0.066726036
Mo      -0.000031260   0.499937482   0.125699380
Te       0.083357906   0.666715809   0.184668902
Te       0.083266635   0.666533266   0.066633590
Mo       0.000044743   0.749992959   0.125660409
Te       0.083355818   0.916580981   0.184671558
Te       0.083272567   0.916677198   0.066635185

```

Mo	0.249996036	0.249457724	0.125812841
Te	0.332086962	0.416021501	0.185026904
Te	0.334027005	0.416982530	0.067259936
Mo	0.499976927	0.499953850	0.126718020
Te	0.583927764	0.667855531	0.185015743
Te	0.582954055	0.665908112	0.067259319
Mo	0.750500537	0.749946446	0.125805173
Te	0.833575984	0.916755152	0.184814752
Te	0.833224064	0.916444738	0.066721416
Mo	0.250004164	0.500491364	0.125810464
Te	0.333022197	0.666923883	0.184955086
Te	0.333314631	0.666617745	0.066631584
Mo	0.249948214	0.749992962	0.125660409
Te	0.333225154	0.916580975	0.184671559
Te	0.333404625	0.916677193	0.066635184
Mo	0.499461690	0.249457726	0.125812841
Te	0.583934537	0.416021500	0.185026905
Te	0.582955525	0.416982528	0.067259935
Mo	0.499445917	0.749946449	0.125805173
Te	0.583179171	0.916755146	0.184814753
Te	0.583220678	0.916444733	0.066721415
Mo	0.749808876	0.250127007	0.125784910
Te	0.833575298	0.416762400	0.184817107
Te	0.833213220	0.416715447	0.066726035
Mo	0.750487201	0.500491368	0.125810464
Te	0.833901686	0.666923884	0.184955090
Te	0.833303115	0.666617746	0.066631580
N	0.500274968	0.500549864	0.258493257
O	0.500648638	0.501297207	0.296607290

K_POINTS (automatic)
2 2 1 0 0 0

2. IBEX job submission script:

```
#!/bin/bash
#SBATCH -N 1
#SBATCH --ntasks-per-node=16
#SBATCH --partition=batch
#SBATCH -J NO_MoSe2_CDD
#SBATCH -o NO_MoSe2_CDD.%J.out
#SBATCH -e NO_MoSe2_CDD.%J.err
#SBATCH --mail-user=your-email
#SBATCH --mail-type=ALL
```

```

#SBATCH --time=100:00:00
#SBATCH --mem=180G

#=====Load Modules=====#

module load quantumespresso/6.3/openmpi2.1.1-gnu6.4.0

#=====Define the scratch dir=====#

SCR_DIR=/yor-scratch-dir/

echo "This job run on $SLURM_NODELIST dated `date`";

mkdir -p $SCR_DIR
mkdir -p ./pdos

#=====Copy input files to scratch dir=====#

cp MoSe2.mono.lcell.scf.in $SCR_DIR

cp charge-system.pp.in $SCR_DIR

cp MoSe2.mono.lcell.nscf.in $SCR_DIR

cp pdos.in $SCR_DIR

#=====Go to scratch and run calculations=====#

cd $SCR_DIR

mpirun -np $SLURM_NPROCS pw.x -npool 2 < MoSe2.mono.lcell.scf.in
> MoSe2.mono.lcell.scf.out

mpirun -np $SLURM_NPROCS pw.x -npool 2 <
MoSe2.mono.lcell.nscf.in > MoSe2.mono.lcell.nscf.out

mpirun -np $SLURM_NPROCS pp.x < charge-system.pp.in > charge-
system.pp.out

mpirun -np $SLURM_NPROCS projwfc.x < pdos.in > pdos.out

#=====Copy outputs back to source dir=====#

cp MoSe2.mono.lcell.scf.out $SLURM_SUBMIT_DIR

```

```

cp MoSe2.mono.lcell.nscf.out $SLURM_SUBMIT_DIR

cp charge-system.pp.out $SLURM_SUBMIT_DIR

cp charge-system.dat $SLURM_SUBMIT_DIR

cp pdos.out $SLURM_SUBMIT_DIR

cp MoSe2NO* $SLURM_SUBMIT_DIR/pdos

cp *pdos_tot $SLURM_SUBMIT_DIR

cp *.lowdin $SLURM_SUBMIT_DIR

cp *.projwfc_down $SLURM_SUBMIT_DIR

cp *.projwfc_up $SLURM_SUBMIT_DIR

cp charge.plot.3d.dat $SLURM_SUBMIT_DIR

```

3. Post-processing files:

a. Charge density input:

```

&INPUTPP
  prefix = 'NO_MoSe2_CDD'
  outdir = './'
  filplot='charge-system.dat'
  plot_num=0
/

```

b. Charge density difference input:

```

&INPUTPP
/
&PLOT
  nfile=3
  filepp(1)='charge-system.dat'
  filepp(2)='charge-substrate.dat'
  filepp(3)='charge-gas.dat'
  weight(1)=1.0
  weight(2)=-1.0

```

```

weight(3)=-1.0
iflag=3
output_format=5
fileout='MoSe2NO-CDD.xsf'

```

c. PDOS input:

```

&PROJWFC
  outdir='./'
  prefix='NO_MoSe2_CDD'
  Emin=-20.0, Emax= 5.0, DeltaE=0.008
  degauss=0.002
  lsym=.true.
  filproj='MoSe2NO'
  filpdos = 'MoSe2NO'
/

```

d. Work function input:

```

&INPUTPP
  prefix = 'NH3_MoSe2_charge2'
  outdir = './'
  filplot='workfun-gas.dat'
  plot_num=11
/

```

4. Script for generating and running multiple calculations:

```

NAME="rho_ecut"

echo $NAME

for ECUT in 320 400 480 560 640 720 800 880 960
do
cat > ${NAME}_${ECUT}.in << EOF
! your input file
&control
  calculation = 'scf',
  verbosity = 'high'
.
.
.
.
.
.
.

```

```

K_POINTS (automatic)
  6 6 6 0 0 0

EOF

#cp MoSe2.bulk.scf.in $SCR_DIR

mpirun -np $SLURM_NPROCS pw.x < ${NAME}_${ECUT}.in >
${NAME}_${ECUT}.out

cp ${NAME}_${ECUT}.in $SLURM_SUBMIT_DIR

cp ${NAME}_${ECUT}.out $SLURM_SUBMIT_DIR

done

```

5. Order of calculations:

All the following calculations need an SCF calculation and thus only one is needed and all the following calculations can use that data from the SCF.

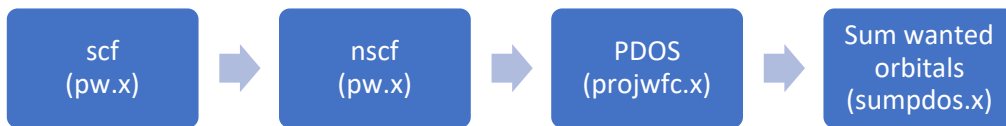


Figure 30. PDOS order of calculations by calculation type. Text in parentheses notes the program used.

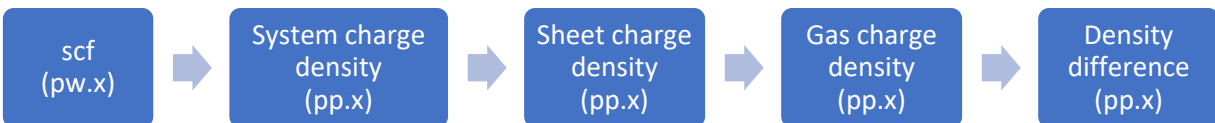


Figure 31. CDD order of calculations.



Figure 32. PDOS order of calculations.

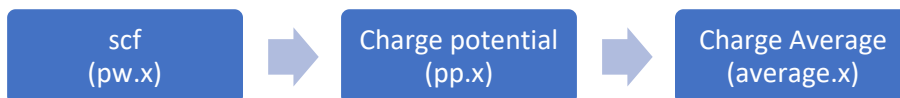


Figure 33. Work-function order of calculations.