# Analyzing HER catalytic sites of nickel sulphides, a DFT computational study

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Intermittent energy storage using hydrogen gas, produced by electrochemical water splitting, could prove to be invaluable as we move towards greener energy solutions. Conventional electrocatalysts are typically platinum-based but due to its scarcity this material is unsuitable to be deployed on a larger scale. The past decade much research has been done on finding other materials suitable for electrocatalysis that are cheaper and more efficient than platinum. Materials like transition metal oxides, metal sulphides, and phosphides have amassed a significant amount of interest. Among the metal sulphides, nickel sulphides have been shown to have a relatively low overpotential, making them excellent candidates as electrocatalysts. Nickel sulphides have been studied for their catalytic efficiency in the Hydrogen Evolution Reaction (HER), both theoretically and experimentally, but few studies have analysed the individual catalytic sites involved and their efficiency. In this study Density Functional theorem (DFT) modelling is used to analyse  $\alpha$ -NiS,  $\beta$ -NiS, NiS<sub>2</sub>, and Ni<sub>3</sub>S<sub>2</sub>. The electronic structure, adsorption energies, dissociative adsorption energies, hybridization, charge density difference, and electronic charge of all surfaces, sites, and adsorbents involved are determined and analysed. With  $\Delta G_{H}^*$  values of 0.10 and 0.05 eV the Ni<sub>3</sub>S<sub>2</sub> surface of miller index (101), Ni/Sterminated, presents the most promising sites for performing the Volmer step in HER of the nickel sulphides studied.



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### Ch 1. Introduction and general background

#### Ch 1.1 Introduction

As the amount of conventional fossil-fuel in the world is readily decreasing and become more knowledgeable about the hazards associated with producing energy from carbon-emitting fuels, the search for more sustainable energy sources is becoming more prevalent with each passing year. One major problem with most modern widely applied energy solutions is the unreliable production. Fig. 1 below shows the power production of wind and solar energy sources in October for Denmark. Throughout October there were four nights where the wind-turbine energy production exceeded the net consumption, even though the power produced from wind contributes to just 40% of the total amount of energy consumption for this month.



*Fig. 1: Electricity grid data from Denmark from October 2014. Denmark, at the time, had 4.8 GW of wind power and 0.5 GW of photovoltaic power installed, the base load of consumption is roughly 2.5 GW with peaks of 5 GW during the daytime, from Vesborg et al. (2015).* 

So, even when the green energy production methods contribute not even half of the total consumption there are already times when its production exceeds the consumption. As we are striving to increase our energy production via these more sustainable methods, the occurrences when the productions exceed the consumption will become more frequent. It would be very favourable to be able to store energy during peak hours, when the production exceeds the consumption, in order to use it at another time when the production is insufficient to meet the consumption. One such way of energy storage is by producing hydrogen gas (H<sub>2</sub>). Hydrogen can be produced by splitting water electrochemically  $(2H_2O (I) \rightleftharpoons 2H_2 (g) + O_2 (g))$ , it's a clean and renewable energy carrier and it could be used as an intermittent energy storage and in turn reduce the global greenhouse effect<sup>1</sup>.

#### Ch 1.1.1 Electrochemical water splitting

Water electrolysis occurs by way of two reactions which combine to create eq. 1. The reduction of H<sup>+</sup> ions happens at the cathode (2H<sup>+</sup> (aq) + 2e<sup>-</sup>  $\rightarrow$  H<sub>2</sub> (g)), this is called the Hydrogen Evolution Reaction (HER). At the anode its counterpart, the Oxygen Evolution Reaction (OER), oxidizes water (2H<sub>2</sub>O (I)  $\rightarrow$  O<sub>2</sub> (g) + 4H<sup>+</sup> (aq) + 4e<sup>-</sup>). Fig. 2<sup>2</sup> shows a schematic of the water electrolysis in an alkaline medium.

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$
 (1)

Both the HER and the OER are multistep reactions and they follow a different reaction path depending on whether the medium is acidic or alkaline<sup>3</sup>. In acidic media the HER and OER are as follows:

$$4e^{-} + 4H^{+}(aq) \to 2H_{2}(g)$$
 (2)

$$2H_2O(l) \to 4H^+(aq) + 4e^- + O_2(g) \quad (3)$$

In alkaline media the HER and OER will follow these paths:



Fig. 2: Schematic of water catalysis in alkaline electrolyte, Adapted from Santos et al. (2013).

$$4e^{-} + 4H_2O(l) \to 40H^{-}(aq) + 2H_2(g) \tag{4}$$

$$4 \, 0H^{-}(aq) \to 2H_2O(l) + 4e^{-} + O_2(g) \tag{5}$$

The HER is a multistep reaction taking place by way of two mechanisms. The first step is the Volmer reaction which discharges protons on the electrode surface in order to adsorb them onto the surface:

$$H^+(aq) + e^- \to H_{ads} \tag{6}$$

After the Volmer reaction two different mechanisms are possible, depending on the  $H_{ads}$  coverage on the surface. If the coverage of  $H_{ads}$  on the surface is low the final step will continue by the Heyrovsky reaction:

$$H_{ads} + H^+(aq) + e^- \to H_2(g) \tag{7}$$

With a high H<sub>ads</sub> coverage the final step occurs via the Tafel reaction:

$$H_{ads} + H_{ads} \to H_2(g) \tag{8}$$

#### Ch 1.2 Catalyst material

Classical electrocatalysts applied to the electrolysis of water are typically platinum-based. Platinum is relatively scarce which means it's very expensive to use this material as an electrocatalyst on a large scale. Much time has been invested in finding suitable materials to serve as electrocatalysts that are cheaper, easy to produce, and as efficient or more efficient than platinum. HER catalysts are generally more efficient under acidic conditions than under alkaline conditions. This means that there are plenty of materials with high HER catalytic efficiency under acidic conditions. However, there is a lack in non-precious materials that can perform the OER under acidic conditions. The existence of non-precious OER catalyst materials for alkaline conditions has increased the interest in materials that are HER catalytic efficient under alkaline conditions<sup>4</sup>.

Most of the interest lies with transition metal oxides, metal sulphides and phosphides. Among the metal sulphides, nickel sulphides have been shown to have a relatively low overpotential, which makes them attractive as catalysts and nickel has also been found to play an important role in hydrogenases (enzymes producing hydrogen) (NiFe)<sup>5</sup>. A considerable amount of work has already been done on nickel sulphides, both practical and theoretical studies, and they have shown promising results<sup>6,7</sup>. However, information is lacking regarding the active sites of the nickel sulphides. This study applies a theoretical approach using Density Functional Theorem (DFT) computation to analyse the active sites of four nickel sulphides during the Volmer step of the HER.

An ideal HER catalyst should be simultaneously efficient, durable and cost-effective. Efficiency of a catalysts is most often measured in the exchange current density ( $i_o$ ) and the Tafel slope. The exchange current density is proportional to the reaction rate between H<sup>+</sup> and H<sub>2</sub> at equilibrium and it refers to the current density flowing through either the anode or cathode under conditions of dynamic equilibrium. The exchange current density can be defined by the Butler-Volmer equation<sup>8</sup>, eq. 9. Here the reaction current density *j* is related to the overpotential  $\eta$ . *a* is the symmetry factor (usually equal to 0.5), *F* is the faraday constant, and R and T are the gas constant and temperature, respectively.

$$j = j_0 \left[ \exp\left(\frac{aF\eta}{RT}\right) - \exp\left(\frac{-(1-a)F\eta}{RT}\right) \right]$$
(9)

The Tafel slope is the voltage increase required to raise the current by an order of magnitude. An efficient HER catalysts should have a high exchange current density and a low Tafel slope.

A commonly used method to compare electrocatalysts is a volcano plot. On a volcano plot the  $\log(j_0/A \ cm^{-2})$  is measured on the y-axis and the  $\Delta G_{H^*}/eV$  or the M-H bond strength is given on the x-axis. Examples of both types of volcano plots can be found below (fig. 3). For both volcano plots types applies; the closer the material is located to the top of the volcano, the more efficient the material is for electrochemical water splitting. Both volcano plots indicate that precious metals like iridium and platinum should be among the most efficient catalysts.



Fig. 3: Left: Experimentally measure exchange current (log ( $i_0$ )) for hydrogen evolution on different metal surfaces plotted against the hydrogen adsorption energy ( $\Delta G_{H^*}$ ) from Nørskov et al. (2005). Right: Exchange currents for electric hydrogen evolution reaction plotted against the strength of the metal-hydrogen bond, from Conway & Jerkiewicz (2000)

#### Ch 1.3 Literature review

The start of modern day HER catalyst research originates from 1958 when Parsons established the theoretical basis for defining an optimal HER catalyst. Parsons related the catalytic efficiency directly to the heat of formation of the adsorption of hydrogen onto the surface. Hinnemann et al.<sup>9</sup> then followed up on this by realizing that computational chemistry could be used to predict this binding energy, which in turn could be used to predict the catalytic efficiency of a material. During this study it was discovered that not the heat of formation, but the Gibbs free energy of formation was the more accurate descriptor for the HER catalytic efficiency. The material that was studied was MoS<sub>2</sub> and this study is the foundation of computational chemistry studies regarding H<sub>2</sub> evolution.

#### MoS<sub>2</sub>

One of the first modern computational chemistry studies using DFT calculations to identify efficient HER catalysis materials was performed on MoS<sub>2</sub>. They chose MoS<sub>2</sub> because its edge structure bears close resemblance to the active site of nitrogenase (fig. 4). Nitrogenase is an enzyme involved in biogenic hydrogen evolution. The most important conclusion of the study was not the information gathered on MoS<sub>2</sub> itself, but it was the conclusion that the Gibbs free energy of hydrogen adsorption could be used as an effective signifier for the catalytic activity. Nevertheless, the results for MoS<sub>2</sub> are worth noting. The study identified that the  $(10\overline{1}0)$  Mo-edge contained the most efficient catalytic sites. The Gibbs free energy of adsorption onto the sites 0.1 eV, this is already quite close to the desirable 0.0 eV.



Fig. 4: Left: Nitrogenase with three hydrogen atoms bound at sulphur atoms. Middle: Hydrogenase active site with one bound hydrogen atom. Right:  $MoS_2$  slab with sulphur present at the Mo-edge. From Hinneman et al.

#### **Nickel sulphides**

Several studies have been done on nickel sulphides and their efficiency as a HER catalyst, in this section a couple of studies will be highlighted.

An experimental study by Kong et al.<sup>10</sup> from 2013 analysed first-row transition metal dichalcogenide catalysts for HER, one of which was NiS<sub>2</sub>. The study found Tafel slopes of 40 mV for several materials; CoS<sub>2</sub>, CoSe<sub>2</sub>, and NiS<sub>2</sub>. This low Tafel slope found for NiS<sub>2</sub> would make it a promising catalyst material. However, when a stability analysis was performed on all the materials, "by taking continuous cyclic

voltammograms at an accelerated scanning rate of 50 mV s<sup>-1</sup> for 1000 cycles", it was found that a loss in the cathodic current density was found for several of the materials, including NiS<sub>2</sub>. A decrease in the cathodic current density would be detrimental to the material's catalytic efficiency.

A more recent study by Yan et al.<sup>6</sup> 2017 used a NiS<sub>2</sub> nanosheet doped with Fe(III). There a Tafel slope of 37 mV was found and an overpotential of 121 mV at 10 mA/cm<sup>2</sup>. These values are very positive and very promising for this material. In this study the Tafel reaction is simulated using DFT calculations and they determine an activation energy of 0.63 eV for the NiS<sub>2</sub> nanosheet itself and an activation energy of 0.41 eV for the NiS<sub>2</sub> doped with Fe (III). The study concludes by performing a stability analysis, consisting of a reaction of 1100 min. They find a negligible loss in HER activity for Fe-NiS<sub>2</sub> which gives confidence about its stability.

The paper that inspired this study, by Jiang et al. from 2016<sup>11</sup>, analyses multiple nickel sulphides, namely;  $\alpha$ -NiS, NiS<sub>2</sub>, and Ni<sub>3</sub>S<sub>2</sub>. One important thing to note is that this study performs its experiment under alkaline conditions, whilst the studies by Kong and Yan are done under acidic conditions. This study found an overpotential of 335 mV, 454 mV, and 474 mV for Ni<sub>3</sub>S<sub>2</sub>, NiS<sub>2</sub>, and NiS respectively (at current density of 10 mA/cm<sup>2</sup>). They also determined the Tafel slopes to be 97, 124, and 128 for Ni<sub>3</sub>S<sub>2</sub>, NiS, and NiS<sub>2</sub> respectively. These values are not as promising as the results from the previous studies under acidic conditions. However, we must keep in mind that a slightly efficient HER catalyst with a highly efficient OER catalyst under alkaline conditions is still better than a highly efficient HER catalyst with an inefficient (or very costly) OER catalyst under acidic conditions. The main conclusion of this study is that the catalytic efficiency of the nickel sulphides studied is Ni<sub>3</sub>S<sub>2</sub> > NiS<sub>2</sub> > NiS<sub>2</sub> >  $\alpha$ -NiS.

Lastly, Gong et al.<sup>4</sup> from 2016 provides us with a review study on nickel-based electrocatalysts under alkaline conditions. In this review it is argued that whilst promising catalytic efficiency has been observed under acidic conditions, the stability of these materials does not hold up under alkaline conditions. This review argues that materials like nickel phosphides and nickel sulphides are not chemically stable enough to perform under alkaline conditions and should only be used under acidic or neutral conditions.

#### Phosphides vs Sulphides vs Carbides

The review study of Vesborg et al.<sup>12</sup> provides a great overview of the development of HER catalysts of the ten years prior to its publication. The main parameter used here to quantify the catalytic efficiency is the overpotential required. The review paper provides an excellent comparison of catalysts based on phosphides, sulphides, and carbides. Fig. 5 shows one of the comparisons of the study. This figure shows a very clear decrease in overpotential as new catalysts are produced and tested, if this trend continues it will only be a matter of time until there are plenty of materials more suitable than platinum. One important thing to note with this figure is that this representation is purely based on the overpotential required, it does not consider the stability of the material.



*Fig. 5: Overpotential at 10 mA/cm<sup>2</sup> related to the time for different species of HER catalyst materials. Adapted from Vesborg et al.* 

#### Summary

Whilst many studies have been done on a plethora of materials, few studies have focussed on the actual adsorption that takes place on the surface. A very important factor that often omitted or disregarded is the chemical stability of the material. From the reviewed literature it becomes apparent that the chemical stability of nickel sulphides under alkaline conditions is questionable.

#### Ch 1.4 Key objectives

The key objectives of this study can be summarised by the following points:

- Evaluate the effects of nickel sulphide surfaces on water splitting
- Determine the electronic structure of nickel sulphides and how it is related to the HER
- Predict the stability of the surface structures
- Figure out both the molecular and the dissociative adsorption mechanisms on nickel sulphide surfaces
- Determine the Gibbs free energy of hydrogen adsorption on the surfaces

The natural progression of this study allows for each key objective to follow-up on the previous one. All these objectives have been achieved successfully and the results are presented in this report.

### Ch 2. Methodology and Computation details

As methodology for researching the topic at hand Density Functional Theory (DFT) calculations were used. DFT modelling is a well-established method to study systems where electron transfer plays the main role. Coincidently, this method has been awarded the Nobel prize in chemistry of 1998, it was awarded to Walter Kohn "for his development of density-functional theory" and to John A. Pople "for his development of computational methods in quantum chemistry". There is quite a list of software packages available that allow for DFT calculations to be performed, some of the more popular ones being Quantum Espresso, GAMESS and VASP. For this study the Vienna Ab initio Software Package (VASP) was used as this software is quite user friendly and offers an extensive library of pseudopotentials to be used for calculations. These DFT calculations cannot be performed on any old desktop, they require special High-Performance Computing (HPC) facilities in order to allow for the calculations to be performed. This due to the nature of the calculations itself and the fact that regular processor in a desktop do not have the correct architecture to perform these calculations efficiently.

#### Ch 2.1 DFT

DFT calculations all revolve on so-called 'energy minimisation'. In more simpler terms; DFT calculations look for the most stable configuration of the system that was given as an input. What constitutes the most stable configuration is referred to as the 'ground state' of the system. Electrons in atom can be at different levels of energy, fig. 6. If an electron absorbs energy it may jump from a ground state energy level to an excited state energy level (thus containing more energy). So, in DFT, the calculations are performed to find an electronic structure of the system where the electronic structure is in its ground state, the lowest energetic state of the system. We are interested in this ground state as we assume that this ground state is also the most stable state of the system and therefore representative of the what the system would look like in the physical world.



Fig. 6: Illustration of the energy levels of an electron in an atom. From Wikimedia Commons: https://commons.wikimedia.org/wiki/File:Energy\_levels.svg.

#### Ch 2.1.1 Theoretical background

The basis of DFT equations relies on solving the Many Body Schrödinger Equation (eq. 10) (MBSE). We try to find the ground state (most stable setup) for a collection of atoms by solving the MBSE.

$$\hat{H}\psi(\{r_i,\},\{R_I\}) = E\psi(\{r_i,\},\{R_I\})$$
(10)

For eq. 10  $\psi$  is the wave function and  $\hat{H}$  is the Hamiltonian, energy operator. The Hamiltonian consists of a kinetic energy operator ( $\hat{T}$ ) and a coulomb potential ( $\hat{V}_{coloumb}$ ), which consists of the coulomb interactions between charged particles.

$$\hat{H} = \hat{T} + \hat{V}_{coloumb} \tag{11}$$

We apply some approximations and theorems to the MBSE in order to simplify it and be able to use it for computational purposes. The first step is applying the Born Oppenheimer approximation with states that the mass of a nuclei is significantly larger than that of an electron ( $m_{nuclei} >> m_e$ ). This would indicate that they have separate dynamics which means we can decouple the wave functions as follows:

$$\psi(\{r_i,\},\{R_I\}) \to \psi_N(\{R_I\})\psi_e(\{r_i,\})$$
(12)

For solids (like in the case of this study) we solve the MBSE only for electrons:

$$\hat{H}\psi(r_1, r_2 \dots r_N) = E\psi(r_1, r_2 \dots r_N)$$
 (13)

The Hamiltonian now consists of three interactions:

- 1. Kinetic energy of electrons
- 2. Coulomb interactions between and electron and nuclei
- 3. Coulomb interactions between two electrons

We can define the electron density (n(r)) as the measure of the probability of an electron being present at a specific location and it can be determined using eq. 14.

$$n(r) = \psi^*(r_1, r_2 \dots r_N)\psi(r_1, r_2 \dots r_N)$$
(14)

Here  $\psi^*$  indicates the complex conjugate of the wave function.

Next, we can consider each electron as a point charge in the field of all other electrons. This would change the many-electron problem into many one-electron problems:

$$\psi(r_1, r_2 \dots r_N) = \psi_1(r_1) \times \psi_2(r_2) \times \dots \psi_N(r_n)$$
(15)

So, we can redefine the electron density as:

$$n(r) = 2\sum_{i} \psi_{i}^{*}(r) \psi_{i}(r)$$
(16)

where *i* are all the single electron wavefunctions. Next, we rely on two fundamental theorems:

- 1. We assume that the ground state energy is a unique functional of the electron density. Meaning that we can determine the ground state energy from just the electron density.
- 2. The electron density that minimizes the energy of the overall functional is the true ground state electron density.

Now using the simplifications applied to the MBSE and the two theorems we can begin calculations. The calculations begin by guessing some electron density and putting it in the Hamiltonian. The next step is applying a Kohn-Sham scheme with the guessed electron density to obtain the electron wavefunctions. Now using the single-electron wave functions a new electron density can be calculated using eq. 14. This new electron density is then compared with the originally guessed electron density. If they are the same the true ground state is found, if not the output electron density is put back in as the guessed electron density input.

#### Ch 2.1.1 DFT+U

A traditional DFT model does not correctly describe the electronic structure for materials which contain highly correlated electron systems<sup>13</sup>. The nickel sulphides studied do display prevalent correlated electron systems and so the standard DFT model needs to be corrected using a Hubbard U correction. The on-site Coulomb repulsion of the 3d orbitals of nickel was corrected for using the U correction<sup>14</sup>. In the literature this method is described as a DFT+U method where the '+U' part indicates a correction has been applied. In the INCAR file this correction is applied in the LDAU section. Do take note that even though the notation includes 'LDA' this does not necessarily mean that an LDA is used as XC functional. The value to be used for this correction of 4.5 eV is used throughout this study as this value has been used by previous studies of similar material with reliable results. For a highly detailed description of the Hubbard correction and its theoretical background the review article by Himmetoglu et al.<sup>15</sup> from 2014 is strongly recommended.

#### Ch 2.1.2 GGA-PBE

One of the fundamental steps in the theory behind DFT is changing a many electron problem to many single electron problems, see section 2.1.1. This adaptation makes it a fictious systems of many non-interacting particles. This then becomes a set of independent particle equations which can be solved numerically. The ground state energy is described in eq. 17 by Hohenberg and Kohn<sup>16</sup>, where the an approximation of G[n] is proposed by Kohn and Sham<sup>17</sup> as shown in eq. 18. Where  $T_s[n]$  is the kinetic energy of a system of non-interacting electrons and  $E_{xc}[n]$  is the exchange-correlation (xc) energy of an interacting system.

$$E = \int v(r)n(r)dr + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} dr dr' + G[n]$$
(17)

$$G[n] = T_s[n] + E_{xc}[n]$$
<sup>(18)</sup>

The study by Kohn and Sham then proceeds to provide an approximation for xc energy. Jones<sup>18</sup> defines the exchange correlation energy as "... the difference between the exact energy and other contributions that may evaluated numerically. In practice, is necessary to make approximations for this term...". Nowadays there are various ways of approximating the xc energy, each with its own strengths and weaknesses. Two of the more common xc functionals are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). The major difference between these two functionals is that the LDA only depends on the electron density and the GGA depends on both the electron density and its gradient. This leads to the logical conclusion that GGA is a more precise of an approximation for the xc energy than LDA but GGA has the downside that the amount of computational power required is higher. Besides LDA and GGA there are more precise approximations like meta-GGA, which incorporates the kinetic energy density, and different hybrid functionals. As the accuracy together with the complexity increases the computational time required of course increases so when deciding which one to use this must be balanced. The GGA has a multitude of different types which can be used in VASP<sup>1</sup> but the most commonly used include BLYP and PBE, for this study the PBE option was used. For further reading the review article by Jones<sup>18</sup> provides an extensive overview of the different functionals and the theory behind them.

<sup>&</sup>lt;sup>1</sup> https://cms.mpi.univie.ac.at/wiki/index.php/GGA

#### Ch 2.1.3 Van der Waals force & DFT-D3

Besides ionic and covalent bonding the van der Waals (vdW) force is also a force of attraction found in molecular physics. The strength of vdW force is substantially lower than that of both ionic and covalent bonding and its interaction results from a chemical electronic bond. The vdW force is named after the Dutch theoretical physicist and thermodynamicist Johannes Diderik van der Waals who postulated the existence of these forces for the first time back in 1873. VdW is often referred to as 'van der Waals interactions' or 'intermolecular interactions'. In an ideal world the vdW interactions would be included in the xc functional, as vdW interactions emanate from dynamic electron correlations. However, due the long-range nature of vdW interactions they are neglected in xc functionals and as such need to be approximated separately. As with the xc functional there are multiple ways to skin a cat and each method has its advantages/disadvantages and computational complexity. For this study the DFT-D3 method produced by Grimme et al.<sup>19</sup> is used, for more details on other vdW correction methods see Berland et al.<sup>20</sup>.

#### Ch 2.2 Surface characterization

2

Using the converged structure files obtained from the previous step the materials were 'cut' using METADISE<sup>2</sup>. METADISE tries to cut a material in a given miller index and verifies whether the cut is viable by checking if the sum of the surface is a neutral charge. Tasker<sup>21</sup> describes three types of surfaces for any ionic crystal: the first being a neutral surface with stoichiometric proportions of both anions and cations in each plane, the second type having charged surfaces but with no dipole moment in the repeat unit perpendicular to the surface (meaning that the charge of the surfaces cancel each other out) and lastly the third type described contains charged surfaces which do have a dipole moment in the repeat unit perpendicular to the surface. Tasker described that the last type has an infinite surface energy and an electric field due to the presence of the charged surfaces, for these reasons these kinds of surfaces cannot exist.

The surface energy for each of the surfaces created was calculated using eq. 19. Where  $\gamma$  is the surface energy in J/m<sup>2</sup>.  $E_{slab}$  is the total energy of the surface slab, n is the number of atoms in the surface slab.  $E_{bulk}$  is the bulk energy per atom, and A is the surface area of the slab. A surface closer to 0 means that the surface is more stable, it requires less energy to create that surface.

$$\gamma = \frac{E_{slab} - nE_{bulk}}{2A} \tag{19}$$

For all the materials the following miller indices were checked via METADISE (100, 010, 001, 110, 101, 011 and 111). By looking at Transmission Electron Microscopy (TEM) data of the materials and the results produced by METADISE surfaces with their accompanying terminations were chosen for further study. METADISE produces multiple terminations for each miller index cut, keeping in mind the charge of the surface. For every surface two terminations were used.

Now the material is cut and terminated a surface needed to be build. This was done by multiplying the unit cell in the z-direction until it reached a thickness of at least 10 Å. The next step was introducing a vacuum of 15 Å on top of this surface (fig. 7). The thickness of 10 Å was used in order to make sure that adsorbents would experience a similar electronic structure as if it were a bulk material the entire way through.

https://intranet.birmingham.ac.uk/it/teams/infrastructure/research/bear/bluebear/apps/METADISE/metadise -5.65.aspx



Fig. 7: Demonstration of what a surface model consists of; 10+ Å of bulk material cut a certain miller index and 15 Å of vacuum located above it.

After creating the position files for the surfaces, they were submitted to VASP. After finishing the calculations, the bottom half of each of the converged structures were fixed in the position files. Meaning that only the top half of the atoms of the surfaces were given freedom to change positions, this was done in order to decrease computational time later in the process and any adsorbent should have little to no effect on the position of the atoms so deep into the surface. These naked surfaces, with fixed bottom halves, were again submitted for a single point calculation in order to obtain PDOS plots and perform a Bader charge analysis.

#### Ch 2.3 Surface adsorption

#### Ch 2.3.1 Molecular adsorption

The first step after creating the stable surfaces was introducing a water molecule to said surfaces and allowing it to adsorb onto it. The surfaces were manually examined using XCrySDen<sup>3</sup> and all possible adsorption sites at the surface were identified. In the case of this study the nickel atoms located at the surface are the adsorption sites used. All of the surfaces were closely examined in order identify all likely sites for water adsorption, 'likely' is this case meaning nickel atoms that are located close to the surface which should be easy to reach for a water molecule without it interacting with other parts of the surface first. This means that for some of the surfaces multiple possible active sites were identified and each was made into separate model. All the unique catalytic sites identified and used in this study can be found in fig. 8.

<sup>&</sup>lt;sup>3</sup> http://www.xcrysden.org/

Using the surfaces from the previous step water molecules were adsorbed onto all the possible adsorption sites, each adsorbed water molecule making their own model. The water molecule was introduced to the surface by placing the oxygen atom centrally 2 Å above a nickel atom of the surface, allowing them to form an ionic bond. The hydrogen atoms where rotated to orientate them towards nearby sulphur atoms. It was decided to adsorb the water molecule onto the surface by bonding between an oxygen and a nickel atom because that bond would stronger than the bond between two hydrogen atoms and two sulphur atoms of the surface.

The adsorption energy of the water molecule onto the surface can be calculated using eq. 20.

$$E_{adsorption} = E_{total} - \left(E_{surf} + E_{mol}\right) \tag{20}$$

where  $E_{total}$  is the free energy of the total system, meaning the model with both the slab and the absorbent combined.  $E_{surf}$  is the free energy of the naked slab and  $E_{mol}$  is the free energy of the adsorbent (in this case the water molecule). In order to obtain  $E_{mol}$  a separate model was submitted where a water molecule was optimized in a cubic box of 15 Å size. By this definition, a negative value of  $E_{adsorption}$  corresponds to an exothermic and favourable adsorption process, whereas a positive value denotes an endothermic and unfavourable adsorption process.

#### Ch 2.3.2 Dissociative adsorption

The next step was taking the molecular water adsorption models and dissociating one of the hydrogen atoms, this is also referred to as an active water model. This step simulates the Volmer step (eq. 6) where a hydrogen atom that is dissociated from a water molecule gets adsorbed onto the surface, bonding with either a nickel or sulphur atom. The dissociation of the hydrogen atom can occur because the bonding of the water molecule onto the surface (the nickel-oxygen bond) weakens the remaining oxygen-hydrogen bonds of the water molecule.

For each model the most likely catalytic sites involved in the dissociating process were identified. In order to decide which of the two hydrogen atoms of the water molecule was to be dissociated the distance to the nearest site was used as the determining factor. This also means that it is possible for the sulphur dissociation models to have a different atom ID number of the dissociating hydrogen atom than its nickel dissociation counterpart, even though both were created from the same adsorption model. For most of the surfaces only a single nickel atom was located at the surface, as this nickel atom is occupied by the remaining hydroxyl group it was impossible to make a nickel dissociation model for those surfaces.

The adsorption energy of the dissociative water is calculated in a similar fashion as the one for molecular water adsorption, eq. 20.



#### Ch 2.3.3 Water dissociation products (OH & H)

Using the converged active water models, a closer examination was performed on the adsorbents themselves, instead of the system (fig. 9). The steps for producing these models were taking the converged active water models and removing either the adsorbed hydroxyl or adsorbed hydrogen component. These models were then submitted for calculation using VASP.



Fig. 9: Illustration of the dissociation products models. The converged dissociative model is split in two separate models, one for each adsorbent.

One of the most important results of this study are the adsorption energy values for the dissociated hydrogen. These values are an important indication for the catalytic potency of the material. The Gibbs free energy of hydrogen adsorption ( $\Delta G_H$ ), the best-known descriptor for the hydrogen evolution activity, was calculated by the free energy with respect to molecular hydrogen including zero-point energy and entropy terms via:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \tag{21}$$

where  $\Delta E_{\rm H}$  is the adsorption energy of hydrogen which is defined as:

$$\Delta E_H = E_{Ni_x S_y + H} - E_{Ni_x S_y} - \frac{1}{2} E_{H_2}$$
(22)

 $\Delta E_{ZPE}$  in equation 21 is the difference in zero-point energy between the adsorbed hydrogen and hydrogen in the gas phase, and  $\Delta S_H$  is the entropy difference between adsorbed state and gas phase. We can take the entropy of atomic hydrogen as  $\Delta S_H = -S_{H_2}/2$ , where  $S_{H_2}$  is the entropy of molecule hydrogen in gas phase. Under standard conditions,  $\Delta E_{ZPE} - T\Delta S_H$  is 0.24 eV, therefore  $\Delta G_H = E_H + 0.24 \ eV^{22,23}$ . A necessary but insufficient condition for a material to be an active HER catalyst is that  $\Delta G_H \approx 0,^{24,25}$  in that case it is energetically favourable for the hydrogen to adsorb to the surface but the adsorption is weak enough to be broken. The adsorption strength needs to be not to strong so the hydrogen can break free from the surface and form hydrogen gas, via either the Heyrovsky or Tafel reaction.

#### Ch 2.4 PDOS

One very important method of showing the electronic structure is by calculating a so-called Density of States (DOS) plot. This plot shows the number of energy states per energy interval. The most commonly found way of displaying the energy states distribution is by using a band structure diagram combined with a DOS plot (fig. 10A). In this study only the DOS plots are used to illustrate the electronic properties, fig. 10B shows an enlarged figure of the DOS plot of A. The x axis shows the energy level in electron volt (eV) and the y-axis shows the relative intensity. Fig. 11 below a DOS plot is shown similar to the ones used in this study, the black line indicates the total density of states, the distribution of all the electrons in the system as a whole, but for some cases we would like to single out particular electron orbitals to see how they behave and contribute to the electronic structure. When a DOS plot contains the distribution for an orbital of an atom this plot is called a Projected Density of States (PDOS) plot. In fig. 11 the blue line indicates the PDOS of the *d*-orbitals of the Nickel atoms in the system, the yellow line indicates the *p*-orbitals of the Sulphur atoms in the system.



Fig. 10: A: DOS and Band Structure of NiS<sub>2</sub>, red dotted lines indicate the band gap in both plots. B: Electronic Density of States plot of NiS<sub>2</sub>, red dotted lines indicate the band gap.



Fig. 11: Projected electronic Density of States plot for NiS<sub>2</sub>, the black lines indicate the total density of states and the blue and yellow line represent the density of states contribution of Ni-d orbitals and S-p orbitals, respectively.

Both the band diagram and the DOS plot can be used to determine the band gap of a material. The band gap is the difference in energy between the highest energy of the valence band (the fermi level) and the lowest energy of the conduction band. In the figures above below the band gap has a width of about 0.4 eV. The presence of a band gap, or lack thereof, indicates the conductive nature of the material. For a material to conduct electricity it needs to be able to transport electrons from the valence band into the conduction band (fig. 12). The width of the band gap indicates the amount of energy required for an electron to 'jump' from the valence band into the conduction band. Materials with a band gap of greater than 2 eV are called insulators as the band gap is too great of a width to allow electrons to jump across this gap. Materials with a band gap of larger than 0 eV but smaller than 2 eV are called semi-conductors as the gap is small enough to allow electrons to be transferred from the valence band into the conduction on the perquisite that some form of energy is provided to excite the electron. When there is no band gap to be found, meaning that the conduction band and the valence band are touching or overlapping, the material can conduct electricity freely and is called a metal. Metallic materials do not require an input of energy to transport electrons from the valence band into the conduction band.



Fig. 12: Diagram showing the valence and conduction bands of metals, semiconductors, and insulators. From Wikimedia Commons: https://commons.wikimedia.org/wiki/File:Isolator-metal.svg.

#### Ch 2.4.1 Hybridization

Hybridization is a term used to describe the interaction between two atomic orbitals that create a single new hybridized orbital. The method of hybridization influences the molecular geometry and the bonding properties. A good example to explain hybridization is by looking at the bonding in a methane (CH<sub>4</sub>) molecule. The central atom in the molecule, carbon, bonds with the surrounding hydrogen atoms by combining 3 p and 1 s orbitals to form hybrid orbitals. This type of hybridization is dubbed sp3 and it displays the characteristic geometry of methane, 109-degree angles between the hydrogen atoms. More detailed information on hybridization and its different shapes and effects can be found in 'Physical Chemistry'<sup>26</sup> by Chang or 'Comprehensive Materials Processing'<sup>27</sup> by Hashmi. For this study the term hybridization is used as an indication of bond formation between two atoms. Hybridization of two orbitals can be identified in a PDOS plot, overlapping of two orbitals here signifies hybridization of said orbitals<sup>28</sup> which in turn represents the formation of a bond between the orbitals' atoms. The PDOS plots used to verify the hybridization only show the density of states of the orbitals of the two species involved in the adsorption, whereas the standard PDOS plots contain the density of states of

the orbitals of all species in the system. This overlapping of two orbitals is used in this study as an argument for the formation of a bond between the two species to whom the orbitals belong.

#### Ch 2.5 Charge density difference

Charge density difference is a relatively easy term to understand on a basic level; charge density is a unit (often symbolized using  $\rho$ ) that signifies the amount of electric charge per unit volume. By calculating the difference in the charge density between two states of singe system we can identify areas of charge accumulation and areas of charge depletion (fig. 13). The charge density difference can be calculated using eq. 23. These areas of accumulation and depletion provide information about the transfer of electrons (charge) throughout the system. In this study the charge density difference is used to analyze the change in the electronic structure of a material before and after a water molecule is adsorbed onto its surface.

$$\Delta \rho = \rho_{H_2 O@Ni_x S_y} - \left(\rho_{H_2 O} + \rho_{Ni_x S_y}\right) \tag{23}$$



Fig. 13: Charge density difference for molecular adsorption of water onto NiS<sub>2</sub> (100) sulphur terminated site a8. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

#### Ch 2.6 Bader charge analysis

The Bader charge analysis is a method of dividing a molecule in separate atoms as to approximate the electronic charge of a particular atom. The method was first described by Richard Bader and it was developed further by Henkelman et al.<sup>29</sup> The characterization of the atoms is based purely on the electronic charge density. The border between two atoms is defined by establishing a plane where the charge density perpendicular to the surface is at a minimum, the so-called 'zero flux' surface. The area enclosed by these zero flux surfaces is called the Bader volume and the total charge located in said Bader volume provides a good approximation of the total electronic charge of the atom. In this

study the Bader Charge Analysis is used to determine the total electronic charge of several atoms in the system to study the transfer of electrons.

#### Ch 2.7 Specifics

#### Ch 2.7.1 Bulk materials starting structures

The choice of materials was based on a paper by Jiang et al.<sup>11</sup> which describes a case study of crystalline NiS, NiS<sub>2</sub> Ni<sub>3</sub>S<sub>2</sub>. The study investigates just one of the polymorphs of NiS;  $\alpha$ -NiS, later during this study it was decided that another polymorph of NiS ( $\beta$ -NiS) would also be of interest and it was therefore also included in this study. Crystal structures (CIF data file-type) of Millerite (both  $\alpha$ -NiS and  $\beta$ -NiS), NiS<sub>2</sub> (Vaesite), and Ni<sub>3</sub>S<sub>2</sub> (Heazlewoodite) were obtained from the American Mineralogist Crystal Structure Database (AMCSD)<sup>4</sup>. The lattice parameters given by AMCSD were cross-checked with data from the Materials Project<sup>5</sup> in order to verify its accuracy. The CIF data files were converted to the POSCAR file-type using P4VASP<sup>6</sup>. For both the  $\alpha$ -NiS and the Vaesite the spin arrangements were taken into account<sup>30,31</sup>, the spin arrangements for the  $\beta$ -NiS and the Heazlewoodite were omitted.

#### Ch 2.7.2 KPOINTS

The KPOINTS used in VASP calculations define the mesh size for creating the k-point grid. Since the calculations performed are not based on an infinite system, but on a periodic system, we need to provide VASP with a mesh (a grid) that it can sample for the calculations. The k-point coordinate system is in reciprocal space, more precisely; they are sampling points in the first Brillouin zone of the material. The choice of size of k-point mesh depends on the size of the simulation cell, the mesh size has an inverse relation with the simulation cell size (because the k-points mesh is in reciprocal space). The ratio between the k-point coordinates of the mesh is dependent on the class of the lattice. The KPOINTS mesh chosen for each material is shown in table 1 below.

Material	KPOINTS mesh
α-NiS	11 x 13 x 7
β-NiS	3 x 3 x 9
NiS <sub>2</sub>	7 x 7 x 7
$Ni_3S_2$	7 x 7 x 7

Table 1: KPOINT mesh parameters used in bulk material calculations.

#### Ch 2.7.3 Pseudopotentials

Pseudopotentials are used as the starting input for DFT calculations and provide the model with some starting parameters. The valence electrons (outer shell) play an important role in material characteristics and during chemical bonding, the core electrons are of less importance. Pseudopotentials replace the electron density of a collection of core electrons with a smoothed density. This is called the Projector Augmented Wave (PAW) approximation. PAW potentials<sup>32</sup> supplied by VASP were used for the calculations.

#### Ch 2.7.4 INCAR

The INCAR file of VASP includes all the settings used for the calculation. An example of the typical INCAR file used in the modelling process can be found in fig. 14.

<sup>&</sup>lt;sup>4</sup> http://rruff.geo.arizona.edu/AMS/amcsd.php

<sup>&</sup>lt;sup>5</sup> https://materialsproject.org/

<sup>&</sup>lt;sup>6</sup> http://www.p4vasp.at/#/home

- 1. Precision for all the models was kept at medium. For the single point calculations used to obtain data for PDOS plots and charge density analysis an accurate precision was used.
- 2. For electronic exchange-correlation correction a generalized-gradient-approximation by Perdew Burke, and Ernzerhof was used<sup>33</sup>. This type of exchange-correlation correction was chosen as many other theoretical studies have used this method successfully when analysing adsorption on a nickel sulphide material<sup>14,34</sup> and this exchange-correlation offers a nice balance between accuracy and simplicity<sup>18</sup> (less computational time required).
- 3. As we are dealing with metallic surfaces the calculations performed are spin polarized.
- 4. Coulomb interaction energy was kept at 4.5 eV for nickel.
- 5. Van der Waals corrections were added using the DFT-D3 method<sup>19</sup>. A cut-off radius of 50.2 Å was used pair interactions and a cut-off radius of 20.0 Å for the calculation of the coordination numbers.
- 6. A cut-off energy of 600 eV was used for the planewave basis set.
- 7. The maximum number of electronic self-consistency (SC) steps was set at 200 and the global break condition for the electronic SC-loop was set at 10<sup>-6</sup> eV.
- 8. Conjugate gradient algorithm was used for the ionic relaxation. In the bulk material calculation, an ISIF=3 line was added in order to calculate the stress tensor and determine which degrees-of-freedom could change.

A tetrahedron method with Blöchl corrections was used to determine the partial occupancies for each orbital, with a smear width of 0.02 eV. For semiconductors it is recommended (by the official VASP wiki<sup>7</sup>) to use the tetrahedron method (ISMEAR = -5). As PAW pseudopotentials are used the LORBIT is set to 11, meaning no Wigner-Seitz radius needs to be specified and a DOSCAR and Im decomposed (azimuthal and magnetic quantum number) PROCAR file are written. For calculations aimed at producing PDOS plots an additional line was added setting the number of grid points to 1000.

<sup>&</sup>lt;sup>7</sup> https://cms.mpi.univie.ac.at/vasp/vasp/ISMEAR\_SIGMA\_FERWE\_FERDO\_SMEARINGS\_tag.html

```
Startparameter for this run
NWRITE
          =
             2
             MED 1
PE 2
2 3
PREC
GGA
ISPIN
          =
MAGMOM
          = 4*6 4*-6 11*0.6
LDAU
              .TRUE.
          =
LDAUL
             2 -1 -1 -1
          =
             4.5 0.0 0.0 0.0
LDAUU
LDAUJ
          =
             0.0 0.0 0.0 0.0
LMAXMIX
              4
IVDW
         = 11
VDW_RADIUS =
VDW_CNRADIUS
                             5
                  50.2
                 = 20.0
Electronic Relaxation
                             6
ENCUT
             600
          =
EDIFF
             1E-06
          =
LREAL
          =
             AUTO
                             7
NELM
             200
ALGO
          =
             FAST
Ionic relaxation
EDIFFG
             -0.001
          =
IBRION
          =
             2
                             8
NSW
             500
          =
POTIM
             0.10
DOS related values
ISMEAR
        =
            - 5
                             9
SIGMA
           0.02
LORBIT = 11
```

*Fig. 14: Example INCAR file used in VASP for the DFT calculations, the numbers correlate with clarifications in the text.* 

#### Ch 2.7.5 Supporting software

The program used to process the output and produce Projected Density of States (PDOS) plots was P4VASP. The PDOS plots were exported to a simple data file and further processed using Xmgrace. Visualization of the structures was done using Visualization for Electronic and Structural Analysis (VESTA)<sup>8</sup>, a 3D visualization program for structural models, volumetric data, and crystal morphologies. Fig. 4 shows a summary of the bulk data obtained.

#### Summary

DFT calculations try to simulate a real-world system and to they do this a plethora of approximations is used. The choice of approximation methods used relies on the nature of the system studied and what the focus of the research is.

<sup>&</sup>lt;sup>8</sup> http://jp-minerals.org/vesta/en/

#### Ch 3. Results

In the following section all the results will be presented, starting with the data gather on the bulk materials, followed by the surfaces created, the molecular and successive dissociative adsorption, and ending with the isolated dissociation products.

#### Ch 3.1 Bulk

All bulk materials were submitted for energy-minimization through DFT in order to obtain a bulk converged structure. From these calculations the PDOS of the materials could be determined, fig. 15 shows a unit cell of the materials with the spin arrangement if applicable, its lattice parameters and space group, and the PDOS plots for the materials where 0 eV is equal to the fermi level. The PDOS plots of the materials indicate that the  $\alpha$ -NiS and Nis<sub>2</sub> have semi-conductive properties, as they have a band gap at the fermi level of less than ~2 eV.  $\beta$ -NiS and Ni<sub>3</sub>S<sub>2</sub>, on the other hand, exhibit a metallic characteristic, in their PDOS plots no band gap is present at the fermi level. The conductivity of a material will have a significant influence on its catalytic efficiency as electrons need to be transported to the catalytic site for electrocatalysis.



Fig. 15: Basic structures of  $\alpha$ -Millerite,  $\beta$ -Millerite, Vaesite, and Heazlewoodite with their experimental lattice parameters and the lattice parameters obtained from DFT-D3 calculations. Blue: nickel, yellow: sulphur. For  $\alpha$ -Millerite and Vaesite the spin arrangement was taken into account, a '+' sign indicates a positive spin and a '-' sign indicates a negative spin. Located below each material is their respective PDOS plot, 0 eV is the Fermi level.

#### Ch 3.2 Surface

All the stable surfaces identified by METADISE were submitted to VASP in order to obtain their converged structures and all the accompanying data. For a detailed view of all the surfaces analysed inspect Appendix A.

#### Ch 3.2.1 NiS

The surface energies for both  $\alpha$ -NiS and  $\beta$ -NiS were calculated from the converged structure and their results are shown in table 2 below. All the values are in the range of 0.713 J/m<sup>2</sup> to 1.705 J/m<sup>2</sup>. Overall the Ni/S-terminated surfaces have a lower surface than their S-terminated counterpart in  $\alpha$ -Nis, the exact opposite applies to  $\beta$ -NiS.

Table 2: Surface energy data from the different terminations of NiS per miller index. A lower surface energy indicates a more stable surface.

Material	Surface	Termination	Surface energy (γ) [J/m2]
α-NiS	001	S-terminated	1.705
	101	Ni/S-terminated	1.305
		S-terminated	1.438
β-NiS 100	100	Ni/S-terminated	0.901
		S-terminated	1.390
	110	S-terminated	0.713
		Ni/S-terminated	1.001

PDOS plots were made for all surfaces and they can be found in Appendix B.. The PDOS plots (fig. 16) do not contain a band gap indicating the surfaces exhibit metallic or half-metallic characteristics.



Fig. 16: PDOS plot of α-NiS (101) Ni/S-terminated.

The last set of data gathered on the NiS naked surfaces was the net charge of various species in the surface. The species chosen played a role in the subsequent scenarios and thus the net charge in the naked surfaces were determined in order to have a baseline to compare to. The species in question and their associated net charge can be found in table 3.

Table 3: Net charge data from naked surface models of future water adsorption sites and dissociated hydrogen adsorption sites for  $\alpha$ -NiS. Missing dissociation sites indicate convergence to molecular water.

Material	Surface	Termination	Atom (ID)	Net charge (Q)
α-NiS	101	Ni/S-terminated	Ni (8)	0.7194
			S (16)	-0.6021
		S-terminated	Ni (4)	0.7459
			S (16)	-0.4627

#### Ch 3.2.2 NiS<sub>2</sub>

The surface energies for all surfaces of  $NiS_2$  analysed can be found in table 4. The values range from 0.865 J/m<sup>2</sup> to 1.835 J/m<sup>2</sup> and there seems to be no relation between the nature of the termination and the surface energy of the surface.

Table 4: Surface energy data from the different terminations of NiS <sub>2</sub> per miller index. A lower surface
energy indicates a more stable surface.

Material	Surface	Termination	Surface energy (γ) [J/m2]
NiS <sub>2</sub>	100	S-terminated	0.865
		Ni/S-terminated	1.835
	111	S-terminated	1.472
		Ni/S-terminated	1.310

The PDOS plots for the  $NiS_2$  surfaces all contain no band-gap and thus exhibit a metallic characteristic, apart from the (100) sulphur-terminated surface (fig. 17). The (100) S-terminated surface has a small band gap of 0.4 eV, like the bulk material.



Fig. 17: PDOS plot of NiS<sub>2</sub> (100) S-terminated.

Like the NiS, the net charge of certain species in the surface were identified in order to make a comparison after adsorption on the surface has taken place. The net charge values determined can be found in table 5 below.

Table 5: Net charge data from naked surface models of future water adsorption sites and dissociated hydrogen adsorption
sites for NiS <sub>2</sub> . Missing dissociation sites indicate convergence to molecular water.

Material	Surface	Termination	Atom (ID)	Net charge (Q)
NiS <sub>2</sub>	100	Ni/S-terminated	Ni (4)	0.6778
			S (23)	-0.4834
		S-terminated	Ni (8)	0.6794
	111	S-terminated	Ni (5)	0.7071
			S (34)	-0.5874
			Ni (6)	0.7874
			S (36)	-0.6175
			Ni (11)	0.7320
		Ni/S-terminated	Ni (5)	0.6080
			Ni (6)	0.5571

#### Ch 3.2.3 Ni<sub>3</sub>S<sub>2</sub>

Lastly, the two surfaces created for  $Ni_3S_2$  were submitted for energy minimization. The surface energy of the converged surfaces can be found in table 6.

Table 6: Surface energy data from the different terminations of  $Ni_3S_2$  per miller index. A lower surface energy indicates a more stable surface.

Material	Surface	Termination	Surface energy (γ) [J/m2]
Ni <sub>3</sub> S <sub>2</sub>	Ni <sub>3</sub> S <sub>2</sub> 101 S-terminated		1.128
		Ni/S-terminated	1.017

Both PDOS plots of  $Ni_3S_2$  exhibit metallic characteristics where the conduction band directly after the Fermi-level shows a strong preference for down-spin electrons, as can be seen in fig. 18.



Fig. 18: PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) S-terminated.

# Using the Bader Charge Analysis method, the net charge of species of interest contained in the surface were determined (table 7).

Table 7: Net charge data from naked surface models of future water adsorption sites and dissociated hydrogen adsorption sites for Ni<sub>3</sub>S<sub>2</sub>. Missing dissociation sites indicate convergence to molecular water.

Material	Surface	Termination	Atom (ID)	Net charge (Q)
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	Ni (12)	0.4862
			S (20)	-0.7256
		Ni/S-terminated	Ni (12)	0.5460
			S (19)	-0.6668
			S (20)	-0.7290

#### Ch 3.3 Molecular adsorption

The next step after producing the surfaces and analysing them was introducing the adsorbent to the surface: a single water molecule. For all the surfaces the bottom half of the slab was fixed in place, this was done in order to reduce the calculation time and should have little to no influence on the results as any adsorption induced relaxation permeates only the first few topmost atomic layers. For an overview of the structures of the molecular adsorption models, check Appendix C.

#### Ch 3.3.1 NiS

Starting again with  $\alpha$ -NiS and  $\beta$ -NiS a water molecule was introduced to the surface as an adsorbent. The water molecule could adsorb on all identified unique catalytic sites, as described in the method. Figures of the geometry of every adsorption model can be found in Appendix C. The adsorption energy for each molecular adsorption was calculated using eq. 20 and their values can be found in table 8, together with several relevant bond distances and angles. All the adsorption energies are negative indicating that all adsorption processes are exothermic of nature and favourable, apart from  $\alpha$ -NiS (001) S-terminated a4 where physisorption occurred.

Table 8: Adsorption energies for molecular water adsorption onto multiple sites of NiS. Bond length between the hydrogen atoms and its accompanying oxygen atom and the distance between the oxygen of the water molecule and its nickel adsorption site are given. \* Physisorption

Material	Surface	Termination	Site	Eads [eV]	O-H1 [Å]	O-H2 [Å]	Ө-НОН [°]	O-Ni [Å]
α-NiS	001	S-terminated	a4	*	0.9764	0.9761	103.457	4.3896
	101	Ni/S-terminated	a8	-1.37	0.9783	0.9821	104.208	2.2636
		S-terminated	a4	-0.88	0.9937	0.9751	109.967	2.1446
6-NiS	100	Ni/S-terminated	a17	-0.58	0.9788	0.9811	104.127	2.2506
			a18	-0.45	0.9814	0.9800	104.405	2.2096
		S-terminated	a17	-2.07	1.0510	0.9805	104.620	2.0356
	110	S-terminated	a25	-0.85	0.9913	0.9809	106.186	2.1658
		Ni/S-terminated	a26	-1.56	0.9988	0.9808	104.888	2.1984

A Bader charge analysis was performed on all significant (no physisorption)  $\alpha$ -NiS molecular adsorption systems and the net charge of all relevant species were calculated and can be found in table 9. The total sum of charge of the adsorbent was also determined and may be found in table 10. The charge sum of the adsorbent has become positive, indicating a donation of electrons from the adsorbent to the surface.

Table 9: Net charge data from water adsorption models of  $\alpha$ -NiS. Net charge value given of oxygen atom of the water molecule and its associated nickel atom adsorption site.

Material	Surface	Termination	Atom (ID)	Net charge (Q)
α-NiS	101	Ni/S-terminated	O (19)	-1.9600
			Ni (8)	0.7706
		S-terminated	O (19)	-1.9688
			Ni (4)	0.8578

Table 10: Charge sum data of the adsorbent of the water adsorption models for  $\alpha$ -NiS.

Material	Surface	Termination	Site	Charge sum H <sub>2</sub> O (Q)
α-NiS	101	Ni/S-terminated	a8	+0.0400
		S-terminated	a4	+0.0312

PDOS plots were created for the  $\alpha$ -NiS systems to analyse the electronic structure and in order to check for hybridization between the adsorbent and the adsorption site. All the PDOS plots can be found in Appendix D. The PDOS (fig. 19) plots all lack a band-gap, indicating metallic characteristics.



Fig. 19: PDOS plot of  $\alpha$ -NiS (101) Ni/S-terminated a8.

Hybridization was checked using the PDOS plots of the relevant species (fig. 20), in this case the oxygen of the molecular water and the nickel adsorption sites. All of the hybridization PDOS plots of molecular water adsorption can be found in Appendix E. The hybridization is most prevalent in the energy range of about -4 to -5.5 eV.



Fig. 20: Hybridization PDOS plot of  $\alpha$ -NiS (101) Ni/S-terminated a8.

The final data set gathered was the charge density difference. All the charge density difference structures for water adsorption models can be found in Appendix F, one of the charge density difference structures of  $\alpha$ -NiS is shown in fig. 21 below. The most notable features of the charge density difference structures are the areas of charge accumulation between the adsorbent and the adsorption site and in the case of  $\alpha$ -NiS (101) S-terminated a4 an area of charge accumulation is found between one of the hydrogen atoms of the adsorbent and a sulphur atom of the surface.



Fig. 21: Charge density difference structure of  $\alpha$ -NiS (101) Ni/S-terminated a8. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

#### Ch 3.3.2 NiS<sub>2</sub>

After the adsorbent was introduced to all identified catalytic sites of NiS<sub>2</sub>, and energy minimisation was performed by DFT calculation, the adsorption energy was calculated. All the calculated adsorption energies with relevant bond distances and angles can be found in table 11. Again, all the adsorption energies are negative indicating an exothermic process which means its energetically favourable.

Table 11: Adsorption energies for molecular water adsorption onto multiple sites of  $NiS_2$ . Bond length between the hydrogen atoms and its accompanying oxygen atom and the distance between the oxygen of the water molecule and its nickel adsorption site are given. \* Physisorption

Material	Surface	Termination	Site	E <sub>ads</sub> [eV]	O-H1 [Å]	О-Н2 [Å]	Ө-НОН [°]	O-Ni [Å]
NiS <sub>2</sub>	100	S-terminated	a8	-0.48	0.9763	0.9829	104.507	2.2509
		Ni/S-terminated	a4	-0.91	0.9771	1.0166	102.715	2.0676
	111	S-terminated	a5	-1.09	1.0212	0.9757	107.023	2.1185
			a6	-1.10	0.9976	0.9750	106.339	2.1959
			a11	-0.65	1.0154	0.9742	108.203	2.1492
		Ni/S-terminated	a5	-0.64	0.9783	0.9752	105.433	2.1368

The net charge of all relevant species and the charge sum of the adsorbent were determined using the Bader charge analysis method (tables 12 and 13). When looking at the charge sum of the adsorbent we see that it has increased in charge (in an isolated setting its charge would have been 0), this indicates a contribution of electrons from the adsorbent to the surface.

Material	Surface	Termination	Atom (ID)	Net charge (Q)
NiS <sub>2</sub>	100	Ni/S-terminated	O (27)	-1.9909
			Ni (4)	0.8276
		S-terminated	O (27)	-1.9703
			Ni (8)	0.7817
	111	S-terminated	O (39)	-1.9942
			Ni (5)	0.8543
			O (39)	-1.9894
			Ni (6)	0.8934
			O (39)	-1.9969
			Ni (11)	0.8577
		Ni/S-terminated	O (39)	-1.9443
			Ni (5)	0.7457

Table 12: Net charge data from water adsorption models of NiS<sub>2</sub>. Net charge value given of oxygen atom of the water molecule and its associated nickel atom adsorption site.
Material	Surface	Termination	Site	Charge sum H₂O (Q)
NiS <sub>2</sub>	100	Ni/S-terminated	a4	+0.0091
		S-terminated	a8	+0.0297
	111 S-terminated		a5	+0.0580
			a6	+0.0106
			a11	+0.0031
		Ni/S-terminated	a5	+0.0557

Table 13: Charge sum data of the adsorbent of the water adsorption models for NiS<sub>2</sub>.

The action was producing PDOS plots of the adsorbent systems and of the species which undergo hybridization. Fig. 22 below shows one of the PDOS plots for the  $NiS_2$  molecular adsorption systems, the rest of the PDOS plots can be found in Appendix D. Fig. 23 shows the hybridization PDOS plot of the same system. When examining the hybridization plots, Appendix E, it becomes evident that the hybridization takes place at electron in the energy range of -4 to -6 eV for the (100) surfaces and -4 to -7 eV for the (111) surfaces.



Fig. 22: PDOS plot of NiS<sub>2</sub> (100) S-terminated a8.



Fig. 23: Hybridization PDOS plot of  $NiS_2$  (100) S-terminated a8.

Lastly, the charge density difference structures were determined. All the structures can be found in Appendix F and one of the is shown in fig. 24. We can make out areas of charge accumulation between the adsorbent and its associated adsorption site. In the figure below it is also very clearly shown that an area of charge accumulation if located between one of the hydrogen atoms of the water molecule and a sulphur atom of the surface.



Fig. 24: Charge density difference structure of  $NiS_2$  (100) Ni/S-terminated a4. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

#### $Ch \; 3.3.3 \; Ni_3S_2$

The final set of molecular adsorption studies was done on  $Ni_3S_2$  and the resulting adsorption energies, together with various relevant bond lengths and angles, can be found in table 14. Just like we have seen for the previous materials all the adsorption energies are negative, except for (101) Ni/S-terminated a11 where the converged structure exhibited physisorption. This indicates that all molecular adsorptions on the chosen sites are exothermic and energetically favourable.

Table 14: Adsorption energies for molecular water adsorption onto multiple sites of  $Ni_3S_2$ . Bond length between the hydrogen atoms and its accompanying oxygen atom and the distance between the oxygen of the water molecule and its nickel adsorption site are given. \* Physisorption

Material	Surface	Termination	Site	Eads [eV]	O-H1 [Å]	О-Н2 [Å]	<del>0</del> -нон [°]	O-Ni [Å]
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	a12	-0.83	0.9879	0.9777	104.717	2.0912
		Ni/S-terminated	a11	*	0.9743	0.9750	103.630	3.6134
			a12	-0.58	0.9821	0.9809	104.110	2.1862

The net charge of relevant species and the sum charge of the water molecule were determined using Bader charge analysis, the outcomes can be found in table 15 and 16. The sum charge of the water molecule tells a similar story here as with the previous materials; the water molecule has a positive charge meaning that a transfer of electrons from the water to the surface took place.

Table 15: Net charge data from water adsorption models of  $Ni_3S_2$ . Net charge value given of oxygen atom of the water molecule and its associated nickel atom adsorption site.

Material	Surface	Termination	Atom (ID)	Net charge (Q)
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	O (23)	-1.9999
			Ni (12)	0.6567
		Ni/S-terminated	O (23)	-1.9781
			Ni (12)	0.6860

Table 16: Charge sum data of the adsorbent of the water adsorption models for  $Ni_3S_2$ .

Material	Surface	Termination	Site	Charge sum H₂O (Q)
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	a12	+0.0001
		Ni/S-terminated	a12	+0.0219

Both the PDOS plots of the entire system and the PDOS plots for the species involved in hybridization can all be found in Appendix D and E. Figs. 25 and 26 below show representative plots of  $Ni_3S_2$ , as found in Appendix D and E. The hybridization is prevalent in the energy range of -4 to -6.5 eV.



Fig. 25: PDOS plot of  $Ni_3S_2$  (101) S-terminated a12.



Fig. 26: Hybridization PDOS plot of  $Ni_3S_2$  (101) S-terminated a12.

## Ch 3.4 Dissociative adsorption

The next step was taking the adsorption models and dissociating one of the hydrogen atoms. This step simulates the Volmer step (eq. 6) where a hydrogen atom that is dissociated from a water molecule get adsorbed onto the surface, bonding with either a nickel or sulphur atom. The dissociation of the hydrogen atom can occur because the bonding of the water molecule onto the surface (the nickel-oxygen bond) weakens the remaining oxygen-hydrogen bonds of the water molecule. Different dissociation scenarios were built for each of the water adsorption models (excluding the two models that expressed physisorption) and were optimized to obtain the lowest-energy structures. For a rundown of all dissociative adsorption structures modelled see Appendix G.

#### Ch 3.4.1 NiS

Starting with  $\alpha$ -NiS and  $\beta$ -NiS again, the adsorption energies of the dissociated adsorbent can be found in table 23. This time the adsorption energies are not of a single sign, we found both positive and negative values. Although there seems to be no very clear pattern, we do find that the adsorption energies of sulphur-dissociated systems are often lower their nickel-dissociated counterparts. The adsorption energies are in the range of -2.35 to 1.03 eV, which indicates that some of the systems are exothermic whilst other and endothermic. Three of the sulphur dissociative models and one of the nickel dissociative models reverted to molecular water.

The Bader charge analysis was performed on all relevant species. Which, in the case of the dissociative adsorption systems, means the original molecular adsorption nickel-site, the oxygen atom of the water molecule, the dissociated hydrogen, and its associated adsorption site (nickel or sulphur). Their net charges can be found in table 17. The charge sum of the adsorbents was also determined, and their outcomes can be found in table 18. The charge sum of the hydroxyl groups for both scenarios are very similar and both have decreased in charge (default charge would be -1) indicating a loss of electrons. Interestingly, the charge sum of the dissociated hydrogen particles of both scenarios are not as similar, the charge of the hydrogen in the  $\alpha$ -NiS (101) Ni/S-terminated a8 SH model has become significantly more negative (default is +1) whilst the charge of the hydrogen in the  $\alpha$ -NiS (101) S-terminated a4 SH model has also decreased but much less significantly. The decrease in charge sum for the dissociated hydrogen indicates that they accepted electrons from the surface as they adsorbed onto the surface, but the number of accepted electrons is different per scenario.

Table 17: Net charge data from active water models of  $\alpha$ -NiS. Net charge value given of oxygen atom of the water molecule and its associated nickel atom adsorption site, and the dissociated hydrogen and its associated sulphur or nickel adsorption site.\* Converged to S-dissociated dissimilar to its counterpart

Material	Surface	Termination	Dissociation	Atom (ID)	Net charge (Q)	Atom (ID)	Net charge (Q)
α-NiS	101	Ni/S-terminated	S-Dissociated	O (19)	-1.5099	H (18)	-1.2228
				Ni (8)	0.9391	S (16)	0.9445
		S-terminated	S-Dissociated	O (19)	-1.5758	H (17)	0.0584
				Ni (4)	1.0478	O (16)	-0.3889

Table 18: Charge sum data of the adsorbents of the active water models for  $\alpha$ -NiS.

Material	Surface	Termination	Site	Charge sum HO (Q)	Charge sum H (Q)
α-NiS	101	Ni/S-terminated	a8 SH	-0.5100	-1.2228
		S-terminated	a4 SH	-0.5758	+0.0584

Like the adsorption models, PDOS plots were created for the dissociative adsorption models as well. The hybridization plots for the dissociative models include the two cases of hybridization found in each scenario (two cases of adsorption per scenario). The PDOS plots for the active water models can found in Appendix H and the hybridization PDOS plots can be found in Appendix I. Looking at the PDOS plots (fig. 27) we see there is not band-gap indicating metallic characteristics. The hybridization (fig. 28) between the nickel-adsorption site and the oxygen of the hydroxyl group is induced by electrons in the energy ranges of 0 to -2 eV and -4.5 to -6.5 eV. The overlap in the hybridization plot of the dissociated hydrogen and its sulphur adsorption site is in the ranges of +4 to +8 eV and -6 to -7 eV.



Fig. 27: PDOS plot of  $\alpha$ -NiS (101) S-terminated a4 SH.



Fig. 28: Hybridization PDOS plot of  $\alpha$ -NiS (101) S-terminated a4 SH.

The charge density difference structures were obtained for each of the active water models and one of them is shown in fig. 29, the rest can be found in Appendix J. Just like with the molecular adsorption models we can identify an area of charge accumulation between the original nickel adsorption site and the oxygen of the hydroxyl group. The other noticeable feature is the area of charge accumulation between the dissociated hydrogen particle and its related sulphur adsorption site.



Fig. 29: Charge density difference structure of  $\alpha$ -NiS (101) Ni/S-terminated a8 SH. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

## Ch 3.4.2 NiS<sub>2</sub>

The adsorption energies for the active water models of  $NiS_2$  can be found in table 23, together with several important bond distances and angles. We can see that all the dissociative adsorption energies are negative, except for both  $NiS_2$  (111) Ni/S-terminated a5 NiH and SH. In total the adsorption energies range from -1.59 to 0.79 eV. As mentioned earlier only the  $NiS_2$  (111) Ni/S-terminated a5 NiH and SH scenarios displayed positive adsorption energies, meaning that these dissociative adsorptions are endotherm and thus energetically unfavourable. The rest of the  $NiS_2$  dissociative adsorption models produce negative adsorption energies meaning that they are exothermic and would be energetically favourable. All except one of the  $NiS_2$  (100) dissociative models reverted to molecular water.

The Bader charge analysis results (tables 19 and 20) reveal that the hydroxyl group donated electrons to the surface whilst the dissociated hydrogen accepted electrons from the surface. The NiS<sub>2</sub> (111) S-terminated a6 NiH (converged to SH) model stands out as the dissociated hydrogen particle in that model has accepted substantially more electrons than the dissociated hydrogen in the other models.

Table 19: Net charge data from active water models of NiS<sub>2</sub>. Net charge value given of oxygen atom of the water molecule and its associated nickel atom adsorption site, and the dissociated hydrogen and its associated sulphur or nickel adsorption site.\* Converged to S-dissociated dissimilar to its counterpart

Material	Surface	Termination	Dissociation	Atom (ID)	Valence	Atom (ID)	Valence
NiS <sub>2</sub>	100	Ni/S-terminated	S-Dissociated (2)	O (27)	-1.4654	H (25)	0.0409
				Ni (4)	0.8925	S (23)	-0.2130
	111	S-terminated	S-Dissociated	O (39)	-1.5044	H (37)	0.1749
				Ni (5)	0.8679	S (34)	-0.5325
			Ni-Dissociated*	O (39)	-1.5852	H (38)	-1.2895
				Ni (6)	0.9145	S (36)	0.8762
		Ni/S-terminated	Ni-Dissociated	O (39)	-1.5547	H (37)	-0.0749
				Ni (5)	0.9153	Ni (6)	0.6224

Table 20: Charge sum data of the adsorbents of the active water models for NiS<sub>2</sub>.

Material	Surface	Termination	Site	Charge sum HO (Q)	Charge sum H (Q)
NiS <sub>2</sub>	100	Ni/S-terminated	a4 SH(2)	-0.4654	+0.0409
	111	S-terminated	a5 SH	-0.5044	+0.1749
			a6 NiH*	-0.5852	-1.2895
		Ni/S-terminated	a5 NiH	-0.5547	-0.0749

All the PDOS plots and hybridization PDOS plots of NiS<sub>2</sub> can be found in Appendix H and I. Fig. 30 shows one of those PDOS plots and fig. 31 shows its accompanying hybridization plot. The hybridization between the p-orbitals of the oxygen atom from the hydroxyl group and the d-orbitals of the nickel adsorption site is most prevalent in the energy ranges of 0 to -2 eV and -4 to -7 eV. The hybridization between the s-orbital of the dissociated hydrogen the p-orbitals (or d-orbitals in the NiH systems) of its associated sulphur adsorption site is the strongest in the ranges of +4 to +8 eV and -5 to -7 eV, this varies quite substantially between the models. The NiS<sub>2</sub> 111 Ni/S-terminated a5 NiH displays more prominent hybridization in the ranges of +3.5 to +5 eV, 0 to +1 eV, and -6 to -7.5 eV. This energy levels for this hybridization is somewhat different than the other models since in this scenario the dissociated hydrogen is adsorbed onto a nickel adsorption site instead of a sulphur adsorption site (which is true for the other scenarios).



Fig. 30: PDOS plot of NiS<sub>2</sub> (111) S-terminated a5 SH.



Fig. 31: Hybridization PDOS plot of NiS<sub>2</sub> (111) S-terminated a5 SH.

The charge density difference structures can be found in Appendix J. Like what we saw in the results of NiS we can find an area of charge accumulation between the hydroxyl group and its adsorption site (fig. 32). We also notice an area of charge accumulation between the dissociated hydrogen and its adsorption site, in this case a nickel adsorption site.



Fig. 32: Charge density difference structure of NiS<sub>2</sub> (111) Ni/S-terminated a5 NiH. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

#### Ch 3.4.3 Ni<sub>3</sub>S<sub>2</sub>

Like with the previous materials, the adsorption energies for the dissociative adsorption models of  $Ni_3S_2$  can be found in table 23. The  $Ni_3S_2$  (101) S-terminated dissociation models show negative adsorption energies, indicating an exothermic adsorption process. The  $Ni_3S_2$  (101) Ni/S-terminated dissociation on the other hand show positive adsorption energies, which is indicative of an endothermic adsorption process.

The net charge of relevant species (table 21) and the charge sum of the adsorbents (table 22) show that the hydroxyl group donated electrons to the surface and the dissociated hydrogen in each scenario accepted a substantial number of electrons from the surface. The charge sum values of the adsorbents for all models are quite comparable.

Table 21: Net charge data from active water models of  $Ni_3S_2$ . Net charge value given of oxygen atom of the water molecule and its associated nickel atom adsorption site, and the dissociated hydrogen and its associated sulphur or nickel adsorption site.\* Converged to S-dissociated dissimilar to its counterpart

Material	Surface	Termination	Dissociation	Atom (ID)	Valence	Atom (ID)	Valence
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	S-Dissociated	O (23)	-1.6015	H (21)	-1.27
				Ni (12)	0.6245	S (20)	0.856
		Ni/S-terminated	Ni-Dissociated*	O (23)	-1.5402	H (21)	-1.19
				Ni (12)	0.9266	S (20)	0.786
			S-Dissociated	O (23)	-1.5403	H (21)	-1.22
				Ni (12)	0.9455	S (19)	0.844

Material	Surface	Termination	Site	Charge sum HO (Q)	Charge sum H (Q)
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	a12 SH	-0.6016	-1.2678
		Ni/S-terminated	a12 NiH*	-0.5402	-1.1924
			a12 SH	-0.5407	-1.2169

Table 22: Charge sum data of the adsorbents of the active water models for Ni<sub>3</sub>S<sub>2</sub>.

The PDOS plots of  $Ni_3S_2$  dissociative models (fig. 33) can be found in Appendix H, they reveal that the surface with the dissociated adsorbent exhibit metallic characteristics with a strong preference for electrons with a down-spin.



Fig. 33: PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) Ni/S-terminated a12 SH.



Fig 34: Hybridization PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) Ni/S-terminated a12 SH.

The hybridization PDOS plots (fig. 34), Appendix I, bring to light the areas where the hybridization takes place. For the hybridization between the oxygen of the hydroxyl adsorbent and its associated nickel adsorption site we see it takes place in the range of 0 to -2.5 eV and -4 to -7 eV. The hybridization between the dissociated hydrogen and the sulphur adsorption site is most prevalent in the energy ranges of +4 to +8 eV and -3 to -7 eV for (111) models and -6 to -7 eV for (101) models.

The last data set obtained for the  $Ni_3S_2$  dissociative adsorption models are the charge density differences structures, which can be found in Appendix J. Fig. 35 shows of the structures and we can see some similarities with the dissociative models of the other materials; we can see an area of charge accumulation both between the hydroxyl group and the adsorption site and between the dissociated hydrogen and its associated adsorption site.



Fig. 35: Charge density difference structure of  $Ni_3S_2$  (101) Ni/S-terminated a12 NiH=SHn. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

Table 23: Dissociative adsorption energies, bond lengths of hydroxyl and dissociated hydrogen or water, and HOH angle is applicable. **a** Reverted back to molecular water; **b** Converged to S-dissociated, similar to its counterpart; **c** Converged to S-dissociated, dissimilar to its counterpart; **d** Converged to Ni-dissociated, similar to its counterpart; **\*** For systems where the dissociation reverted back to molecular water.

Material	Surface	Termination	Site	Dissociation	Ediss [eV]	O-H1 [Å]	O-H2 [Å]†	θ-НОН [°]*	0-Ni [Å]	H-S [Å]	H-Ni [Å]	Notes
<b>α</b> -NiS	101	Ni/S-terminated	a8	S-Dissociated	0.07	0.9789	-	-	1.8832	1.3521	-	
		S-terminated	a4	S-Dissociated	-0.93	0.9747	-	-	2.0250	1.3580	-	
$\beta$ -NiS	100	Ni/S-terminated	a17	Ni-Dissociated	1.03	0.9800	-	-	1.8116	-	1.4183	
			a17	S-Dissociated	0.43	0.9782	-	-	1.8091	1.4248	-	
			a18	Ni-Dissociated	0.79	0.9776	-	-	1.8336	1.3576	-	с
			a18	S-Dissociated	0.05	0.9783	-	-	1.8000	1.3614	-	
		S-terminated	a17	Ni-Dissociated	-0.31	0.9826	-	-	2.1269	-	1.4566	
			a17	S-Dissociated	-2.35	1.0535	0.9806	104.791	2.0174	-	-	а
	110	S-terminated	a25	Ni-Dissociated	0.38	0.9805	-	-	1.7993	1.3593	-	b
			a25	S-Dissociated	-0.79	0.9982	0.9803	105.910	2.1346	-	-	а
		Ni/S-terminated	a26	Ni-Dissociated	-1.58	1.0018	0.9803	105.795	2.1072	-	-	а
			a26	S-Dissociated	-1.32	1.0025	0.9804	105.027	2.1134	-	-	а
NiS <sub>2</sub>	100	S-terminated	a8	Ni-Dissociated	-0.97	0.9911	0.9810	104.935	2.1820	-	-	а
			a8	S-Dissociated	-0.66	0.9761	0.9827	104.714	2.2217	-	-	а
		Ni/S-terminated	a4	S-Dissociated	-1.49	0.9763	1.0117	103.832	2.0736	-	-	а
			a4	S-Dissociated (2)	-0.52	0.9820	-	-	1.7799	1.3634	-	
	111	S-terminated	a5	Ni-Dissociated	-0.85	0.9778	-	-	1.8515	1.3891	-	b
			a5	S-Dissociated	-0.91	0.9767	-	-	1.8526	1.3895	-	
			a6	Ni-Dissociated	-1.39	0.9770	-	-	2.0330	1.3644	-	с
			a6	S-Dissociated	-1.15	0.9968	0.9755	106.641	2.1201	-	-	а
			a11	Ni-Dissociated	-1.59	0.9852	0.9794	104.541	2.3414	-	-	а
			a11	S-Dissociated	-0.69	1.0203	0.9737	108.903	2.0870	-	-	а
		Ni/S-terminated	a5	Ni-Dissociated	0.62	0.9704	-	-	1.7972	-	1.4824	
			a5	S-Dissociated	0.79	0.9700	-	-	1.7974	-	1.6521	d
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	a12	Ni-Dissociated	-1.01	0.9881	0.9772	105.011	2.1057	-	-	а
			a12	S-Dissociated	-0.48	0.9739	-	-	1.9985	1.3839	-	
		Ni/S-terminated	a12	Ni-Dissociated	0.23	0.9741	-	-	1.8026	1.3549	-	
			a12	S-Dissociated	0.49	0.9745	-	-	1.8130	1.3635	-	

# Ch 3.5 Water dissociation products (OH & H)

Using the converged active water models a closer examination was performed on the adsorbents themselves, instead of the system. The most important of this examination was determining the adsorption energy of the adsorbed hydrogen, this value will give a good indication whether a site is a suitable location for catalysis. The adsorption energies for the individual adsorbents were calculated using eq. 20.

This adsorption energy can be converted to a Gibbs free energy value, as described in section 2.3.3, which makes it a more intuitive value. A Gibbs free energy as close to zero as possible would be ideal as it would mean that the adsorbed hydrogen can readily get adsorbed, but it can also get released without needing much energy input. The adsorption energy values for the hydroxyl and hydrogen atom are in table 24, the corrected Gibbs energy values for hydrogen adsorption are also included.

Material	Surface	Termination	Site	Dissociation	E <sub>ads</sub> [eV] NiOH	E <sub>ads</sub> [eV] SH/NiH	ΔG <sub>H*</sub> [eV] SH/NiH
α-NiS	101	Ni/S-terminated	a8	S-Dissociated	-4.72	-1.33	-1.09
		S-terminated	a4	S-Dissociated	-4.93	-0.61	-0.37
β-NiS	100	Ni/S-terminated	a17	Ni-Dissociated	-5.05	0.61	0.85
			a17	S-Dissociated	-5.05	-0.39	-0.15
			a18	Ni-Dissociated*	-4.58	0.34	0.58
			a18	S-Dissociated	-4.83	-0.07	0.17
		S-terminated	a17	Ni-Dissociated	-6.80	-1.75	-1.51
	110	S-terminated	a25	Ni-Dissociated*	-4.52	-0.30	-0.06
NiS <sub>2</sub>	100	Ni/S-terminated	a4	S-Dissociated (2)	-6.12	-1.23	-0.99
	111	S-terminated	a5	S-Dissociated	-5.02	-1.39	-1.15
			a6	Ni-Dissociated*	-5.86	-1.38	-1.14
		Ni/S-terminated	a5	Ni-Dissociated	-5.57	0.51	0.75
Ni <sub>3</sub> S <sub>2</sub>	101	S-terminated	a12	S-Dissociated	-6.14	0.17	0.41
		Ni/S-terminated	a12	Ni-Dissociated*	-4.87	-0.14	0.10
			a12	S-Dissociated	-4.87	-0.19	0.05

Table 24: Adsorption energy data of the hydroxyl group and the dissociated hydrogen. Gibbs free energy correction applied on the adsorption energy in order to obtain  $\Delta G_{H^*}$ . \* Converged to S-dissociated, dissimilar to its counterpart.

# Ch 4. Discussions

# Ch 4.1 Bulk

The bulk materials studied can be split into two groups; semi-conductors and metals. Both groups will be able to act as a catalyst for water electrolysis, but metals should theoretically have an edge as the conductivity of a material plays a major role in its catalytic efficiency. Although some studies may suggest that  $\alpha$ -NiS exhibits metallic properties and  $\beta$ -NiS exhibits insulating properties<sup>35</sup> this study has found information contradicting it. When examining the (P)DOS plot for bulk  $\alpha$ -NiS it becomes clear that a small band gap of roughly 1.0 eV is present above the Fermi level, indicating a semi-conductive material. The DOS plot of  $\beta$ -NiS contains no band gap directly above the Fermi level, indicating metallic properties. The metallic conductivity of the Ni<sub>3</sub>S<sub>2</sub> is expected as metal-metal bonds are present throughout the bulk material. However, for  $\beta$ -NiS the metal-metal bonds in the material are limited to isolated rings of three nickel atoms. In a study by Gibbs et al.<sup>36</sup> it is suggested that the conductive transport in  $\beta$ -NiS occurs by a cooperative hopping of the d-orbital electrons from the Ni<sub>3</sub> rings. In  $\alpha$ -NiS the transport of electrons across the band gap is enabled by *p*-orbitals of sulphur in the valence band and *d*-orbitals of nickel in the conduction bands, the same is true for NiS<sub>2</sub> but the density of electrons in the valence band close to the Fermi level is substantially lower.

# Ch 4.2 Surfaces

The PDOS plots for the naked surfaces indicate that all the surfaces exhibit metallic or half-metallic conductive properties, apart from  $NiS_2$  (100) S-terminated which has a small band gap of roughly 0.2 eV. For the materials that exhibit half-metal conductivity there seems to be a preference for conduction of electrons with a downward spin orientation.

# Ch 4.3 Molecular adsorption

When examining the adsorption energies of water onto the surface a pattern emerges. The surfaces with a higher surface energy (i.e. the less stable surfaces) show a stronger adsorption of the water molecule. The charge density difference figures confirm the suspicions derived from the structures and hybridization plots. In all the figures, where the water chemisorbed onto the surface, a clear area of charge accumulation can be seen between the water molecule and the slab surface. This charge



Fig. 36: Charge density difference of the adsorbed water model of  $NiS_2$  (111), S-terminated a5. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion. The red arrow points towards a n area of charge accumulation between a hydrogen atom of the water molecule and a sulphur atom of the slab surface. accumulation indicates an exchange of electrons between the water molecule and the nickel site of the surface, forming an ionic bond. Interestingly, there are multiple models (to be precise:  $\alpha$ -NiS (101) S-terminated a4, NiS<sub>2</sub> (100) Ni/S-terminated a4, S-terminated a5, a6, and a11) where the charge density difference figures indicate an area of charge accumulation between one of the hydrogen atoms of the water molecule and a sulphur atom of the surface. An example of the charge accumulation mentioned can be seen in Fig. 36, with the red arrow pointing at said charge accumulation area. This charge accumulation co-exists with the charge accumulation between the oxygen and nickel. This charge accumulation area would indicate an exchange of electrons between the hydrogen and sulphur atom, forming an ionic bond. The existence of this secondary ionic bond will weaken the primary ionic bond between the oxygen and nickel atoms.

When comparing the PDOS plots of the naked surfaces with the ones from the water adsorption models it becomes clear that the adsorption of the water molecule had little to no influence on the overall electronic structure (and therefore the conductivity) of the slab. For comparison, in fig. 37 a PDOS plot of  $Ni_3S_2$  (101) S-terminated is shown next to a PDOS plot of an adsorbed water molecule onto atom 12 on the same surface. There is little to no difference between the two plots, indicating little change in the overall electronic structure.



Fig. 37: Left: PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) S-terminated. Right: PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) S-terminated with adsorbed water molecule on a12.

The Bader charge analysis of the water adsorption models reveals oxidization of the oxygen atom. The net charge of the nickel atom in the naked surfaces is more positive than the net charge of nickel atom in the water adsorption models.

#### Ch 4.4 Dissociative adsorption

#### Ch 4.4.1 NiS

Starting with the adsorption energies, comparing the adsorption energies of the dissociative water with the ones of molecular water we can see that the adsorption energy has increased (it becomes less negative), for some more drastic than others. When we disregard all of the models that converged back to molecular water only two models remain with a negative adsorption energy  $\alpha$ -NiS (101) S-terminated a4 SH and  $\beta$ -NiS (100) S-terminated NiH, meaning that of all the scenarios tested those two are the only exothermic adsorption processes and thus energetically favourable. When comparing the charge sum of the adsorbents before and after dissociation it becomes clear that the amount of electron transfer increases significantly as the active water is adsorbed. In all the dissociative adsorption cases the hydroxyl has increased in net charge when compared to its default, indicating that the hydroxyl group is oxidized. In contrast, the dissociated hydrogen has decreased in net charge

which indicates that this adsorbent has been reduced. Looking at the hybridization PDOS plots of Ni-O we can see a new area of hybridization has appeared in the range of 0 to -2 eV, this increase of overlap indicates that the hybridization (i.e. the bonding) between the oxygen atom of the hydroxyl group and its associated nickel site has increased. These findings also agree with the decrease in Ni-O bond distance that we observe.

### Ch 4.4.2 NiS<sub>2</sub>

Many of the active water models of NiS<sub>2</sub> reverted to molecular water meaning that either the dissociative state could not converge to a most stable state of the system or the choice of dissociation sites was inadequate. If we disregard all the models that reverted to molecular water, we can identify four scenarios where the dissociative adsorption energy is negative, meaning those adsorptions are energetically favourable exothermic processes. Those favourable sites are: NiS<sub>2</sub> (100) Ni/S-terminated a4 SH(2), NiS<sub>2</sub> (111) S-terminated a5 NiH, SH, and a6 NiH. But the NiS<sub>2</sub> (111) S-terminated a5 NiH converged to a sulphur dissociated model which made it the same as its SH counterpart, which also explains the similarity of the two adsorption energies. The NiS<sub>2</sub> (111) S-terminated a6 NiH also converged to a sulphur dissociated model but this was a different sulphur site than the one submitted for its SH counterpart. The charge sum of the adsorbents before and after dissociation tell a similar story as with NiS, the hydroxyl adsorbent is oxidized, and the dissociated hydrogen is reduced. However, one interesting thing to notice is that we see a very strong reduction of the dissociated hydrogen in the case of NiS<sub>2</sub> (111) S-terminated a6 NiH and this model also happens to be the one where we identify the strongest dissociative adsorption. When examining the hybridization PDOS plots we can make out an additional area of hybridization around 0 to -2 eV when compared to the original molecular adsorption models.

## Ch 4.4.3 Ni<sub>3</sub>S<sub>2</sub>

Just one of the Ni<sub>3</sub>S<sub>2</sub> dissociative adsorption models presented a negative, energetically favourable, adsorption energy. The overall charge sum of all adsorbents involved tells as similar story to what the previous materials have told us, the hydroxyl gets oxidized whilst the dissociated hydrogen gets reduced. In the case of Ni<sub>3</sub>S<sub>2</sub> there seems to be no relation between the charge sum of the adsorbed species and the dissociative adsorption energies. The hybridization of the Ni<sub>3</sub>S<sub>2</sub> (101) Ni/S-terminated a12 NiH and SH is much more evident than the hybridization for the Ni<sub>3</sub>S<sub>2</sub> (101) S-terminated a12 SH. The hybridization plots in the Ni/S-terminated models display a substantial overlap of the electrons in the range of 0 to -2 eV with a down-spin.

#### Ch 4.4.4 General

The PDOS plots for the active water models all tell a similar story to the ones produced for the molecular water adsorption models. When comparing the PDOS plots of the active water models with the ones from the naked surfaces (see fig. 38) no significant differences can be spotted, meaning that the adsorbents have little to no effect on the electronic structure of the slab.



Fig. 38: Left: PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) S-terminated. Right: PDOS plot of Ni<sub>3</sub>S<sub>2</sub> (101) S-terminated a12 S-dissociated.

Like the charge density difference figures for the water adsorption, the charge density difference figures for dissociated water configurations (fig. 39) show areas of charge accumulations in between the hydroxyl particle and its nickel adsorption site. Extra areas of charge accumulation are identified in between the dissociated hydrogen atom and its associated adsorption site. The bond length distance between the oxygen and nickel atom is shortened as a hydrogen atom is dissociated from the water molecule.



Fig. 39: Charge density difference structure of  $Ni_3S_2$  (101) Ni/S-terminated a12 SH. Green surfaces indicate charge accumulation and brown surfaces indicate charge depletion.

This shortening of the bond length is likely due to an increase in bond strength. The strengthening of the bond is also visible in the hybridization plots, the amount of overlap (hybridization) between the oxygen and nickel atom is much more significant in the active water models than in the water adsorption models. This strengthening of the bond is also evident when examining the net charge of both atoms. The net charge of the oxygen atom increases (gets less negative) by roughly +0.5, for comparison the change in net charge during water adsorption was only about +0.02. The dissociated hydrogen atom and its adsorption tell a similar story, but on a much more drastic scale. Overall the

hydrogen atom gets reduced, but this magnitude of reduction varies wildly per model, ranging from about -0.95 to -2.2. This reduction of hydrogen coincides time with an oxidization of its adsorption site, the net charge of sulphur in the naked surface was found to be -0.6 on average. The net charge of the sulphur in the active water models is in the range of -0.5 to +0.9, indicating a change of +0.1 to +1.5.

## Ch 4.5 Water dissociation products (OH & H)

Of all the adsorption energies the most favourable are the ones found in the Ni<sub>3</sub>S<sub>2</sub> (101) Ni/Sterminated. Both the Ni-dissociated model (which converged to a S-dissociated model) and the Sdissociated model appear to demonstrate very favourable hydrogen adsorption values of 0.10 and 0.05 eV respectively. Some of the scenarios studied for  $\beta$ -NiS also produced hydrogen adsorption values worthy of note. The  $\beta$ -NiS (100) Ni/S-terminated a17 SH, a18 SH and the (110) S-terminated a25 NiH produces Gibbs free energy of adsorption values of -0.15, 0.17 and -0.06, respectively.

# Ch 5. Summary, Conclusions and Future works

To summarize; the calculations and results from this study show that  $Ni_3S_2$  is the best performing catalyst for HER of all the nickel sulphides materials analysed here. These finding are consistent with the earlier predictions of Jian et al., whose conclusion was mostly based on the metallic characteristics of  $Ni_3S_2$ . These results show that  $Ni_3S_2$  could serve as very efficient HER catalyst under alkaline conditions and that more research is justified.

#### Concluding remarks

Water adsorption can occur on most of the surfaces studied. The dissociation of water is not as likely to occur, of the dissociation models tested roughly half of them reverted to molecular water. The exchange of electrons between the oxygen atom of the water and hydroxyl group and its nickel atom adsorption site increases significantly when going from molecular water to active water, in both cases the oxygen oxidizes. The hydrogen adsorption energies indicate that Ni<sub>3</sub>S<sub>2</sub> cut at miller index (101) with a Ni/S-termination contains the most favourable catalytic sites of the ones analysed in this study. Behind Ni<sub>3</sub>S<sub>2</sub> in catalytic favourability is  $\beta$ -NiS, trailed by  $\alpha$ -NiS with NiS<sub>2</sub> closely following it. This study should give some insight in how single catalytic sites of a material can be studied using DFT calculations, this knowledge of favourable catalytic sites may be applied in catalyst design.

#### Future works

For all the models only one molecular water was added onto the surface, meaning there was a single water molecule per unit cell. Most of the surfaces contained only one possible site for water adsorption, this meant that every site available was occupied for those surfaces. Depending on the size of the unit cell, this could give an unrealistic scenario as the distance between water molecules would be too short or too long. On the other hand, some of the surfaces had multiple water adsorption sites. For those models only one site was occupied every time and separate models were made for each site. In a real-world scenario it would be quite likely that multiple sites of the surface are occupied at the same time. This in turn would have an influence on the molecular adsorption, dissociative adsorption, and the hydrogen adsorption energies due to the presence of other water molecules its nearby vicinity. This influence could be negative or positive, depending on the orientation and location of the other water molecule. Further research could be focussed on making a larger unit cell for each model and creating a more realistic distribution of adsorbed water molecules on said unit cell.

Some terminations which are deemed unviable by METADISE could possibly become viable if they were built on a substrate. This would produce new surfaces with different terminations, which in turn means more new catalytic sites. The possibility of building hybrid electrocatalysts using nickel sulphides and, for example, carbon nanotubes provides exciting possibilities of building catalysts more efficient than any single material could ever be. The occurrence of defects in the material would also produce many new catalytic sites, some of which could be of interest. Fig. 40 by She et al. provides a nice overview of the two main possible ways of improving a material's catalytic efficiency; either by increasing the number of active sites or by increasing each site's intrinsic catalytic activity. As eluded to in the literature review section (1.3), the chemical stability of nickel sulphides is being questioned. More research in substrate or doping material to increase its chemical stability could help alleviate this problem.



Fig. 40: Different strategies of developing a catalytic material. From She et al.

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Appendices

# A (structure naked surfaces)

α-NiS



NiS<sub>2</sub>



Ni₃S₂



# B (PDOS plots naked surfaces)

# α-NiS

# (001) S-terminated



# (101) S-terminated





-8

-6

-4

-10



-2 0 2 Energy [eV]

65

8

6

4

10



# C (structures water adsorption models)

α-NiS



β-NiS (100)













(111)



Ni₃S₂



101 Ni/S-terminated atom12



101 S-terminated atom12



D (PDOS plots water adsorption models)

α-NiS





#### (101) S-terminated atom 4


(100) Ni/S-terminated atom 4



## (111) S-terminated atom 5



## (111) S-terminated atom 11



Ni₃S₂

(101) Ni/S-terminated atom 12



# (101) S-terminated atom 12



E (Hybridization plots water adsorption models)

## α-NiS











## (111) Ni/S-terminated atom 5



## (111) S-terminated atom 6









F (Charge density difference structure water adsorption models)  $\alpha$ -NiS (101)





NiS<sub>2</sub> (100)





(111)





Ni<sub>3</sub>S<sub>2</sub> (101)



# G (Structures active water models) $\alpha$ -NiS (101)



β-NiS (100)











(110)



# NiS<sub>2</sub> (100)



(111)





## H (PDOS plots active water models)

α-NiS











## (111) S-terminated atom 5 SH









# (101) S-terminated atom 12 SH



## I (Hybridization plots active water models)

## α-NiS





## (101) S-terminated atom 4 SH









(111) Ni/S-terminated atom 5 NiH



## (111) S-terminated atom 5 SH



## (111) S-terminated atom 6 NiH=SHn



## Ni<sub>3</sub>S<sub>2</sub>



## (101) Ni/S-terminated atom 12 NiH=SHn





# (101) S-terminated atom 12 SH



# J (Charge density difference structure active water models) $\alpha$ -NiS (101)



NiS<sub>2</sub> (100)









Ni<sub>3</sub>S<sub>2</sub> (101)