Quantum-chemical calculations of 2H-MoS₂: modelling the structure and reactivity

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Quantum-chemical calculations of $2\text{H-MoS}_2$: modelling the structure and reactivity

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Abstract

Because of its particular structural and electronic properties, molybdenum disulfide (MoS$_2$) is technologically a very interesting material. It belongs to the family of layered transition-metal dichalcogenides with closed packed planes of molybdenum atoms sandwiched between two similar planes of sulfur atoms, which are stacked along the c-axis. The relative alignment of the sulfur layers can occur as two distinct two-dimensional arrangements of the sulfur atoms with respect to the molybdenum atoms, resulting in a trigonal-prismatic or octahedral coordination of the metal atoms. The thermodynamically most stable form is the semi-conducting 2H-MoS$_2$ with a trigonal prismatic coordination of molybdenum. The stoichiometrically balanced unit cell of this material contains two units of MoS$_2$, with one unit exposing molybdenum atoms and the other sulfur atoms (Mo and S edges, respectively).

The most important industrial application of MoS$_2$ is as a catalyst in the hydrodesulfurization (HDS) of crude oil fractions. HDS is the reaction of sulfur-containing molecules and hydrogen to form hydrocarbons and H$_2$S. Future specifications for diesel fuel will require a drastic reduction of their sulfur content. Hence, the aim of industry and academia is to improve the catalysts, the HDS process conditions and the reactor configurations. Despite intense efforts to understand the mechanism of the HDS reaction on transition-metal sulfide catalysts, there are still many unanswered questions. These include: What is the detailed structure of the catalyst particles? Which are the catalytically active sites and how are the promoter atoms linked to the MoS$_2$-type catalyst phase? What are the mechanisms of the reactions taking place at the catalyst surface? The study presented here attempts to answer these questions.

Chapter 4 presents a study of the geometric and electronic properties of bulk MoS$_2$ and its catalytically important (100) edge structure by means of Periodic Hartree-Fock and DFT methods. In these calculations the core electrons of molybdenum and sulfur are represented by the effective core pseudo-potentials developed by Hay and Wadt. The (100)-type surface structures of MoS$_2$, consisting of four, six or eight rows of molybdenum and sulfur atoms, were investigated. Surface relaxation results in an electronic charge distribution of the surface states different to that of the bulk states. Empty Mo $d$ states move into the band gap; the surface becomes a better electron acceptor, which furthers the interactions with sulfur-containing species.
Chapter 5 describes a theoretical study of the properties of different defects on the (100) MoS$_2$ surface investigated by the perturbed cluster method. The results provide an accurate description of the local defect properties, while the interactions between the defects and the surrounding crystal are taken into account. The type of cluster used in the calculations is medium-sized and has the stoichiometry of Mo$_2$S$_6$. The Mo edge was studied by means of four defects built by adding sulfur atoms to the Mo$_2$S$_6$ cluster. Defects obtained by removing up to three sulfur atoms from the Mo$_2$S$_6$ cluster representing the S edge were also studied. The chemistry of the defects differs from that of the perfect (100) “as-cleaved” surface. The enhanced reactivity of the specific sites is assigned to the anisotropy in the electrostatic potential. The presence of “nodes” (boundary regions between neighbouring positive and negative densities) in the surface electrostatic potential offers a possibility of adsorption of sulfur-containing molecules.

In Chapters 6, 7, 8 and 9, where the emphasis is on the reactivity of the surface, synchronous transit methods for localizing transition-state structures are used to study chemical reactions on the surface of MoS$_2$. The computational procedure is based on a combination of the linear and quadratic synchronous transit methods with a conjugate gradient refinement of the saddle point. The hydrogen dissociation on the (100) surface of MoS$_2$ is studied by starting with an H$_2$ molecule above the S- or Mo-terminated edges and ending with adsorbed hydrogen atoms on different surface sites. A notably higher energy barrier for the homolytic splitting of H$_2$ over the S-terminated edge than for the heterolytic splitting on the Mo-terminated edge led to the conclusion that the H$_2$ dissociation on the S-terminated edge requires high temperature, whereas on the Mo-terminated edge spontaneous H$_2$ dissociation is possible. This was the motivation for studying reactions preferentially on the Mo-terminated edge. The effect of Co and Ni promoter atoms on the H$_2$ dissociation has been investigated as well.

The hydrogenolysis reaction of CH$_3$SH to CH$_4$ on the catalytically active Mo edge of MoS$_2$ was studied by means of DFT. Thiol adsorption and CH$_4$ formation and desorption were investigated and compared for different sulfur coverage on the surface as were the effects of the Co and Ni promoters and of hydrogen adsorbed on the surface. The mechanism of the C-S bond breaking involves a direct reaction of the adsorbed thiolate with the molybdenum sulfide surface followed by a hydrogenolysis to form the desorbing methane. Calculations with C$_2$H$_5$SH were also performed to describe the difference between molecules containing one or two carbon atoms.
With emphasis on the structure and the reactivity of the MoS$_2$ catalyst, the contribution of the present thesis is two-fold:

1. With respect to the structure of the catalyst, a new point of view of the defects on the (100) catalytically active surface, treated locally by the perturbed cluster method, is presented.

2. With respect to the catalyst's reactivity, a novel approach to the reaction paths with emphasis on the location of the transition states by the linear/quadratic synchronous transit methods combined with a conjugate gradient refinement of the saddle point has been developed to study the reactions of sulfur-containing molecules with the (100) catalytically active surface.
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Zusammenfassung


Oberflächenrelaxation führt zu einer Ladungsverteilung auf der Oberfläche, die sich von der im Inneren der Festkörperstruktur unterscheidet. Unbesetzte Mo-\(d\)-Funktionen verschieben sich in den band gap hinein und die Oberfläche wird zu einem besseren Elektronenakzeptor, was die Wechselwirkungen zwischen der Oberfläche und der schwefelhaltigen Verbindung verstärkt.


wurden Reaktionen bevorzugt an der Mo-terminierten Oberfläche untersucht. Ebenfalls wurde der Einfluss von Co und Ni Promotoratomen auf die Dissoziation von H₂ untersucht.


Bezüglich Struktur und Reaktivität von MoS₂-Katalysatoren sind die folgenden zwei Punkte die zentralen Beiträge dieser Arbeit:

1. Es wird eine neue Betrachtung von Defektstellen auf der katalytisch aktiven (100) Oberfläche vorgestellt, deren Eigenschaften mit Hilfe der perturbed cluster Methode bestimmt wurden.

2. Im Hinblick auf die Reaktivität des Katalysators wird ein neuer Ansatz zur Untersuchung der Reaktionen von schwefelhaltigen Verbindungen auf der katalytisch aktiven (100) Oberfläche entwickelt. Darin liegt der Schwerpunkt auf der Bestimmung des Übergangszustandes, welcher mit der linear/quadratischen synchronous transit Methode mit anschliessender konjugierten Gradientenverfeinerung der Sattelpunkte berechnet wird.
Chapter 1

Introduction

1.1 The hydrodesulfurization process

Hydrotreating comprises a variety of processes of which the hydrodesulfurization (HDS) reaction is one of the most important. The removal of sulfur from feedstocks is one of the first steps in oil refining [1]. Feedstocks are highly complex mixtures of paraffins, naphthenes and polycyclic aromatics, that also contain organometallic Ni and V compounds, as well as organo-sulfur and nitrogen compounds. Due to new environmental legislation requiring further reduction of the amount of sulfur in oil products, the field has attracted increased attention. Currently the fuel specifications in the USA, Japan and Western Europe limit the sulfur content of diesel fuels to less than 500 ppm. Starting from January 1, 2005, new sulfur limits of 30-50 ppm for gasoline and diesel marketed in the European Community and the USA will be introduced [2,3]. To achieve this reduction in the sulfur content, more active catalysts are required. The more stringent environmental limits and the higher levels of sulfur in the feedstocks make sulfur removal very demanding. To optimize a large-scale industrial process such as desulfurization, economic as well as environmental aspects have to be taken into account. Therefore, improvements in refineries should be done with an emphasis to catalysts, process conditions and reactor configurations.

In the hydrodesulfurization (HDS) process, sulfur is removed from sulfur-containing compounds present in crude oil such as thiophene, dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT). The basic hydrodesulfurization process consists in treating oil fractions that contain sulfur-containing molecules with hydrogen at elevated temperature and pressure in the presence of a transition-metal sulfide catalyst [4]:

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Introduction

\[ C_xH_yS + nH_2 \rightarrow \text{Hydrocarbons} + H_2S \] (1.1)

The two desulfurization steps in HDS are the direct desulfurization (DDS) and the hydrogenation (HYD) as shown in Fig. 1.1. In the desulfurization of dibenzothiophene direct desulfurization yields biphenyl, while hydrogenation involves the hydrogenation of one of the benzene rings of dibenzothiophene followed by desulfurization of the resulting hexahydrodibenzothiophene to yield cyclohexylbenzene.

\[ \text{DDS} \quad \text{HYD} \]

\[ \text{DBT} \quad \times \quad \text{Cyclohexylbenzene} \]

Fig. 1.1. Hydrodesulfurization reaction paths for DBT and its derivatives.

The HDS reaction takes typically place in a common trickle bed reactor [5] where the oil mixes with gaseous hydrogen over the catalyst. The catalyst particles are usually supported on a high surface area support material, such as alumina. The structure and the active sites will be described in Chapters 4 and 5. The HDS reactions follow the overall scheme shown in Fig. 1.1. After passing through the reactor, the desulfurized oil and the \( H_2S \) containing gas are separated in a high-pressure phase separator [6]. The gas is scrubbed to remove hydrogen sulfide and other products and recycled to the reactor. When heavier feeds are treated, large amount of hydrogen is consumed and hydrogen has to be added to the recycle. The desulfurization reaction is exothermic and the reaction enthalpy in real feed HDS is typically \( \Delta H \equiv -54 \text{ kJ/mol} \) at 425°C [1]. The reactor has built-in interstage cooling of the reactants.
1.1.1 Reaction conditions

In oil refineries, the typical reaction conditions for the HDS process are high temperatures (about 300 - 400°C) and high pressures (about 50-100 bar), depending on the feedstock [7]. High temperatures are needed to lower the viscosity of the oil, which also assists in the removal of the sulfur atom, known to be strongly bound in polycyclic sulfur-containing organic compounds [8]. A high pressure of hydrogen is required to prevent a saturation of the surface with sulfur. Upper limits for pressures and temperatures during the operation are set by economy. Very high temperatures lead to deactivation of the catalyst due to sintering and reduction. Very high hydrogen pressure leads to hydrogenation of non-sulfur containing aromatics and thus, to an unwanted consumption of the hydrogen [9].

1.1.2 Sulfur-containing molecules

The organosulfur compounds present in petroleum fractions differ in molecular size, structure and reactivity. Classes of compounds include thiols, sulfides and disulfides and heterocyclic thiophene-derivatives with one to several aromatic rings and alkyl or aryl cycle substituent. In typical catalytic studies, dibenzothiophene (DBT) and dimethyldibenzothiophene (DMDBT) (shown in Fig. 1.2) are often used as probe molecules. These compounds are less reactive than thiols.

![Different organosulfur compounds: Thiophene, benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).](image)
1.2 Catalyst definition and structure

A *catalyst* is defined as a material that increases the rate of approach to equilibrium of a chemical reaction, without being substantially consumed in the reaction. A catalyst can change the kinetics of the reaction, but not the thermodynamics [10]. The fact that catalysts accelerate chemical reactions and can be used over and over again makes them tremendously applicable and important in industrial chemical processes.

Particularly three properties of a catalyst are desirable: activity, selectivity and stability. The activity of a catalyst is a quantitative measure and is usually defined as the reaction rate for conversion of the reactants into products. The selectivity is the catalyst's ability to direct the conversion of the reactants into the desired products. The stability is a measure of the rate of loss of catalytic activity and/or selectivity. These three properties as well as the cost are important factors in the choice of the catalyst.

There are three major reasons for deactivation of hydrotreating catalysts: 1) Sintering: the active phases grow together under loss of active surface area, 2) Coking: deposition of carbonaceous material at the catalysts surface and 3) Deposition of metal and metal-sulfides. The material deposition can block the active sites. To prolong the lifetime of the catalyst, a regeneration procedure is sometimes applied to recover the original activity. Typical lifetimes of the commercial hydrotreating catalysts range between a half and two years.

Catalysts used in HDS are molybdenum-based sulfides supported on alumina and promoted with Co or Ni (Fig. 1.3) [11].

MoS$_2$ crystallites consist of two layers of sulfur with one layer of molybdenum in between. Such units are stacked with only weak (van der Waals) interactions between the sulfur layers of neighbouring MoS$_2$ units. Crystals grow as platelets with relatively large dimensions parallel to the sulfur planes and small dimension perpendicular to the basal plane.

*Extended X-ray absorption fine structure* (EXAFS) measurements indicate that the diameter of MoS$_2$ catalyst particles is 10-20 Å at 300 - 400°C depending on the preparation conditions. The particle size increases with increasing sulfiding temperature [12,13,14]. Hydrodesulfurization takes place on the surface of these catalyst particles. Thus, a high degree of dispersion of the MoS$_2$ particles is favourable, so that they are prepared on a high area support, usually γ-Al$_2$O$_3$. The exact orientation of the crystallites is not known for certain. There are two main problems that hinder characterization with techniques such as *transmission electron microscopy* (TEM) or *X-ray diffraction* (XRD). First, the γ-Al$_2$O$_3$
structure is amorphous and has a non-planar surface. Second, the size of the crystallites is often so small that the crystallites cannot be observed with TEM or do not show sharp reflections in XRD experiments.

Fig. 1.3. Structure of the 2H-MoS₂. The white big balls are the sulfur atoms, the small black ball are the Mo atoms.

Investigations of model catalysts, consisting of MoS₂ grown on γ-Al₂O₃ films on the surfaces of MgAl₂O₄ supports have shown that MoS₂ grows with its basal plane parallel to the (111) surface of γ-Al₂O₃ and perpendicular to the (100) γ-Al₂O₃ surface [15]. This observation suggests that the edges of the MoS₂ particles are bonded to the (100) surface of γ-Al₂O₃ by Mo-O-Al bonds (Fig. 1.4). It has been proposed that besides a structural effect, the support has also an electronic influence on the performance of the HDS catalyst [16,17].
1.2.1 Active sites

Many experimental structure-activity studies have determined that the active sites in unpromoted HDS catalyst are located at the edges and corners of the crystallites, while the basal plane is inactive. The catalytically active surface of MoS$_2$ is the (100) surface. It exhibits two types of edges: one, exposing unsaturated molybdenum atoms (hereafter called the Mo terminated (1010) edge), the other one, exposing sulfur atoms (called the S terminated (1010) edge). Schematically, they are shown in Fig. 1.5.

Fig. 1.5. Stoichiometric, hexagonally shaped MoS$_2$ particle with 25 Å diameter and 40 % molybdenum edge atoms. The (1010) edges are terminated by sulfur atoms and the (1010) edges by molybdenum atoms [18].
Chapter 1

Catalysis therefore occurs at MoS$_2$ edges and corners rather than on basal planes, as verified in a surface science study in which a MoS$_2$ single crystal, with high ratio of basal plane to edge surface had a low HDS activity. Its activity increased after sputtering, during which sulfur atoms were removed from the basal plane and molybdenum atoms became exposed [19]. Chemisorption studies with probe molecules like O$_2$, CO, NO, have provided information about the location of the active sites [1]. Tauster et al. found that the HDS activity can be correlated with the oxygen uptake and not with the total (BET) surface area, so that all sites at the surface appear to be active in the HDS reaction [20]. Electron spin resonance (ESR) and NO chemisorption experiments by Derouane et al. verified that the active sites are located at the edges [21,22]. Salmeron et al. investigated the adsorption and binding of thiophene, butene and H$_2$S to the basal planes of MoS$_2$ single crystals [23]. The conclusion was that hydrodesulfurization catalysis takes place at the edges and the corners of the MoS$_2$ particles.

Scanning tunneling microscopy was used recently to image the MoS$_2$ nanoparticles on a gold substrate [24]. Most MoS$_2$ nanoparticles had triangular shapes rather than hexagonal shapes observed by electron microscopy for MoS$_2$ crystallites on Al$_2$O$_3$. In a subsequent study it was shown that the Co promoter atoms changed the shape of the MoS$_2$ nanoclusters to truncated trigonal [25]. Scanning tunneling microscopy of single layer MoS$_2$ nanoparticles grown on a gold substrate have shown one-dimensional metallic states on the edges, which were interpreted as conducting wires (Fig. 1.6). The study was combined with density functional theory calculations, which showed that the one-dimensional metallic edge states
could be the result of a Peierls distortion, leading to an opening of an energy gap at the Fermi level [26].

Fully coordinated metal atoms of the catalysts are unable to adsorb sulfur-containing molecules. Sites at the edges where the Mo atoms are exposed are usually called coordinatively unsaturated sites (CUS), or sulfur vacancies [27,28]. In contrast to the bulk Mo atoms, where the Mo coordination number is six, metal centers at the edges have a lower coordination number. Therefore, there should be at least one sulfur vacancy at a site to allow the reacting molecule to bind chemically to the molybdenum atom [18,29]. Voorhoeve and Stuiver proposed that the vacancies are in equilibrium with the hydrogen and hydrogen sulfide pressure via [28]:

$$H_2(g) + S^* \leftrightarrow H_2S(g) + *$$  

where $S^*$ denotes the adsorbed sulfur atom and * is the sulfur vacancy. The produced hydrogen sulfide competes with the organosulfur compound to be adsorbed on the CUS, and therefore, H$_2$S is an inhibitor in HDS. Furthermore, it is controversial whether different hydrotreating reactions like HDS and HYD occur on similar sites or if they require different sites.

Hydrogen is a reactant in the HDS reaction and is supplied in the form of H$_2$. The activation of dihydrogen and different dissociation pathways for H$_2$ on the catalytically active (100) surface of 2H-MoS$_2$ will be discussed in Chapter 6 and Chapter 7.

1.2.2 Promoters

It is a general observation that cobalt and also nickel enhance the hydrodesulfurization activity of a MoS$_2$ catalyst. Therefore, Co and Ni are referred to as promoters. Other transition metals, like Fe or Cu, do not have the same promotional effect. Ni may be present in three forms after sulfidation: as Ni$_3$S$_2$ crystallites on the support, as nickel atoms adsorbed at the edges of the MoS$_2$ crystallites (Ni-Mo-S phase) and as a nickel cations at tetrahedral or octahedral sites in the $\gamma$-Al$_2$O$_3$ support lattice (Fig. 1.7). Analogously, cobalt can be present as segregated Co$_9$S$_8$, as Co-Mo-S and as cobalt cations in the support.
Infrared spectroscopy (IR) and electron microscopy (EM) measurements, showed that Co atoms are located at the edges of the MoS$_2$ particles in the plane of the Mo atoms, forming the so-called Co-Mo-S structure [30]. IR measurements also showed that the Co or Ni promoted MoS$_2$ configurations are similar, concerning the structural environment. The maximum activity of the CoMo or NiMo catalysts are obtained at a Co(Ni)/(Co(Ni) + Mo) ratio of approximately 0.3.

![Diagram of Co-Mo-S structure](image)

Fig. 1.7. Three forms of Ni present in a sulfided NiMo/Al$_2$O$_3$ catalyst: as active sites on the MoS$_2$ edges (the so-called Ni-Mo-S phase), as segregated Ni$_3$S$_2$ and as Ni$^{2+}$ ions in the lattice support [18].

Although there are many proposals in literature to explain the promotional effect, its nature is not yet completely understood. It is well accepted that MoS$_2$ exists as hexagonally shaped particles and that the active sites are located at the edges or corners. Delmon proposed the existence of two phases, i.e. a cobalt-sulfide phase that activates dihydrogen to hydrogen atoms, which then spill-over to the molybdenum-sulfide phase [31,32]. Even a mechanical mixture of Co$_9$S$_8$ and MoS$_2$, when in close contact, can be rather active [33,34]. Another explanation of the promotional effect is in the concept of the CoMoS phase, proposed by Topsoe et al. [35]. This concept is based on the detection of a signal in Mössbauer emission spectra, which could not be assigned to any known Co phase at that time. Topsoe et al. attributed it to a mixed CoMoS phase, in which cobalt is located at the edges of the MoS$_2$ crystallites [35,36]. Duchet et al. [37] questioned the assumption of cobalt being a promoter in the CoMo catalyst based on the higher intrinsic activity of a carbon-supported cobalt catalyst when compared to a carbon-supported molybdenum catalyst. Thus, the cobalt itself could be considered to be the active phase. This observation was supported by the fact that
carbon-supported cobalt catalysts and carbon-supported CoMo catalysts had similar activities [38]. Therefore, the MoS$_2$ lattice could act as a secondary support for the cobalt sulfide particles, which would be more active than the pure molybdenum-sulfide phase. Although attempts to show direct proof of nickel or cobalt as the actual catalytically active sites gave both positive and negative results by EXAFS data of catalysts adsorbed with selenophene (an analogue of thiophene) [39,40,41,42], it seems clear that the first reaction takes place on the cobalt, but not on the molybdenum. Infrared [43] and EXAFS [44] data showed that molybdenum in CoMo and NiMo catalysts is fully coordinated and therefore not accessible to reactant molecules.

1.3 Scope of the thesis

The present thesis deals with an investigation of MoS$_2$ catalysts by applying *ab initio* calculations based on Hartree-Fock and Density Functional Theory, that are described in more detail in Chapter 2. During the last few years this type of calculations was used to study realistic catalytic systems and to explain their physical and chemical behaviour. Progress in computer resources, algorithms and theoretical methods also made a contribution to the fast development of the field. Furthermore, surface physics plays an important role in catalysis and the interplay between physics and chemistry has proven to be successful.

The outline of this thesis is as follows: Chapter 2 gives a brief summary of the theoretical methods and the details of the calculations. Chapter 3 is an overview of the recent progress of the theoretical investigations of the structure and reactivity of the MoS$_2$ catalyst. Chapter 4 deals with the structure of the bulk and the (100) surface of MoS$_2$ by means of periodic HF and DFT calculations using pseudopotentials. Chapter 5 describes the energetics and electronic properties of different defects on the (100) MoS$_2$ surface as studied by the perturbed cluster method. Chapter 6 and Chapter 7 present a study of hydrogen activation on the catalytically active surface as obtained with transition state search tools. Chapter 8 and Chapter 9 present a study of the reactivity of the catalyst surface towards adsorption of CH$_3$SH and C$_2$H$_5$SH. Comparison of the mechanisms in the presence of promoter atoms and hydrogen on the surface is given as well. Finally, a short conclusion and outlook are assembled in Chapter 10.
1.4 References

Introduction

Chapter 2

Computational Details

2.1 Introduction

Computational science involves the study of chemical or biological systems on computers with the aim to predict and describe their structures and properties. The large increase in computer power and the development of more and more powerful algorithms, determined the enormous progress that the computational science has experienced. Moreover, computational science attracts increasing interest from experimental chemists because of its potential to treat many complex chemical reactions on an accurate and realistic level.

The significance of the recently developed computational tools in describing the properties of the molecular systems has been widely acknowledged by the Nobel Prize to Walter Kohn and John Pople in 1998. Despite the success of modern computational tools, their application in transition-metal based chemistry is very challenging. Transition-metal centers require a specific treatment to describe their physical properties and chemical behaviour by means of quantum-chemical methods.

In materials science, the systems of interest typically consist of many particles (electrons, nuclei, atoms, molecules, etc.), of the order of Avogadro's constant $N_A = 6.023 \times 10^{23}$ mol$^{-1}$. The $N$-particle quantum-mechanical system is generally described by complex-valued functions of the particles' spatial and spin coordinates [1]. Solving the Schrödinger equation for a wave function that describes a number of particles in the order of the Avogadro's constant is neither useful, nor possible. Therefore, we use approximate methods in conjunction with powerful computers that allow the principles of quantum mechanics, which we usually call first principles, or ab initio, to be applied to real poly-atomic systems.
2.2 Born-Oppenheimer approximation

Consider a system consisting of $N_e$ electrons with coordinates $r = \{r_i\}$ and $N_i$ ions at points $R = \{R_j\}$, in the absence of external fields. When relativistic effects are negligible, its Hamiltonian has the well-known structure

$$H = \sum_{i=1}^{N_e} \frac{p_i^2}{2m} + \sum_{i=1}^{N_i} \frac{p_i^2}{2M_i} + V_{ee}(r) + V_{ei}(r, R) + V_{ii}(R),$$  \hspace{2cm} (2.1)$$

where the first two terms are the kinetic energies of the electronic ($T_e$) and the ionic ($T_i$) subsystem and $V_{ee}$, $V_{ei}$ and $V_{ii}$ are the contributions from the electron-electron, electron-ion and ion-ion Coulomb interaction.

Born and Oppenheimer realized in 1927 that the Hamiltonian of Eq. (2.1) can be treated perturbatively [2], because $T_i$ is usually small, due to the large masses of the atomic nuclei; $(m_{\text{nucleon}} \approx 10^3 \times m_{\text{electron}})$. Within perturbation theory [3], $H$ is denoted in the form

$$H = T_e + V_{ee} + V_{ei} + V_{ii} + T_i = H_0 + \lambda^4 H_i$$  \hspace{2cm} (2.2)$$

where $\lambda = (m/M_0)^{1/4}$. $\lambda$ is a parameter introduced by Born and Oppenheimer, and $M_0$ is the sum of the nuclear masses. Suppose that we have found the spectrum and the eigenstates of the zero order approximation $H_0$ for $R = R_0$, which is nothing else than the Hamiltonian of the system with fixed nuclei. The complete neglect of the $T_i$ term, i.e. $\lambda = 0$ in (2.2), yields the Born-Oppenheimer (BO) approximation. The total energy of the many particle system in this case is simply $U_0(R_0) = E_0(R_0) + V_{ii}(R)$, where $E_0(R_0)$ is the spectrum of the many-electron Hamiltonian $H_e = T_e + V_{ee} + V_{ei}$, depending parametrically on the nuclear coordinates. However, in the BO approximation the assumption is usually made that the electronic component stays in its ground state, $n = 0$, thus in the following the term (ground state) total energy of a particular configuration $R$ of the nuclei will refer to the quantity

$$E(R) = U_0(R) = E_0(R) + V_{ii}(R).$$  \hspace{2cm} (2.3)$$
Beyond the zero-order approximation the solution to the exact Hamiltonian, for some $R$, close to $R_0$, $R-R_0 = \lambda u$, is sought in the form

$$
\xi = U^{(0)}_n + \lambda U^{(1)}_n + \lambda^2 U^{(2)}_n + \ldots \ldots, \\
\Psi(r,u) = \Psi^{(0)}_n + \lambda \Psi^{(1)}_n + \lambda^2 \Psi^{(2)}_n + \ldots \ldots
$$

(2.4)

Born and Oppenheimer have shown that the zero-order approximation to the wave function simply factors into a product of the zero-order electronic $\psi^{(0)}_n(r)$ and the nuclear wave functions $\Phi^{(0)}(u)$, i.e. $\Psi^{(0)}_n(r,u) = \Phi^{(0)}(u)\psi^{(0)}_n(r)$, and the nuclear wave function satisfies the Schrödinger equation,

$$
\mathcal{A}^2 \left[ -\sum_{i} \frac{M_i}{M} \frac{\hbar^2}{2m} \nabla^2_{u_i} + U^{(2)}_n + \xi^{(2)}_n \right] \Phi^{(0)}(u) = 0
$$

(2.5)

where the second-order term $\lambda^2 U^{(2)}_n - \lambda^2 u^2$ in the expansion of $U_n(R_0 + \lambda u)$ plays the role of an effective potential for the nuclear motion. It is apparent that Eq. (2.5) describes harmonic nuclear oscillations of the electron around $R_0$, which is the fixed position of the nuclei. Thus, if the wave function in Eq. (2.4) is truncated to first order one obtains the harmonic approximation. If the perturbative expansion is made up to terms $O(\lambda^2)$, the wave function can be written as

$$
\Psi_n(r,u) = \left[ \Phi_n^{(0)}(u) + \lambda \Phi_n^{(1)}(u) + \lambda^2 \Phi_n^{(2)}(u) \right] \psi_n(r,R).
$$

(2.6)

The physical picture that emerges in the interpretation of (2.6) is the adiabatic approximation: the motion of the nuclei is described by the first factor and the electronic component adiabaticity follows the nuclear motion by adapting to the instantaneous nuclear configuration, as it follows from the presence of $R$ in the argument of the electronic wavefunction $\psi_n$.

The next level in the hierarchy of approximation appears when treating the many-electron problem. A significant reduction in the degrees of freedom can be achieved if the many-electron problem is reformulated in terms of a one-electron picture. The classic
example described in all textbooks of quantum mechanics is the *Hartree-Fock approximation* (HF), where one employs a Slater determinant of one-electron orbitals as a trial wavefunction and the ground state of the electronic Hamiltonian is determined by a variational approach.

Another approach to the quantum many-body problem is the *Density Functional Theory* (DFT) that allows for a maximum reduction in the degrees of freedom by reformulating the many-body problem in terms of the single particle density. This chapter gives an outline of the main framework of the HF and the DFT formalisms and discusses issues of the particular implementation used in the present work.

### 2.3 Hartree-Fock method

The most common type of *ab initio* calculation is called the Hartree-Fock method (HF), in which the primary approximation is the central field approximation [4]. This means that the Coulomb electron-electron interaction is taken into account by integrating the repulsion term. This gives an average effect of the repulsion, but not the explicit repulsion interaction. This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy, due to the variational principle.

One of the advantages of this method is that it breaks the many-body Schrödinger equation into many simpler one-electron equations. Each one-electron equation is solved to yield a single-electron wave function, called an orbital, and an energy, called an orbital energy. The orbital describes the behaviour of an electron in the net field of all the other electrons.

The second approximation in the HF method is due to the fact that the wave function must be described by some mathematical function, which is known exactly for only a few one-electron systems. The functions that are most often used are *linear combinations of Gaussian-type orbitals* \( \text{exp}(-ar^2) \), abbreviated GTO. The Gaussian functions are multiplied by an angular function in order to give the symmetry of \text{s, p, d, f} orbitals. These orbitals are then combined into a determinant, i.e. the *Slater determinant*.
This is done to satisfy two requirements of quantum mechanics. One is that the electrons must be indistinguishable. By having a linear combination of orbitals in which each electron appears in each orbital, it is only possible to say that an electron was put in a particular orbital but not which electron is. The second requirement is that the wave function for fermions must be antisymmetric with respect to the interchanging of two particles. Thus, if electron 1 and electron 2 are interchanged, the sign of the total wave function must change. This is satisfied by the determinant, because interchanging two electrons is equivalent to interchanging two columns of the determinant, which changes its sign. The functions put into the determinant do not need to be individual GTO functions, called Gaussian primitives. They can be a weighted sum of basis functions on the same or on different atoms. This makes the calculation faster.

The HF approximation is the method in which one tries to find the orthonormal orbitals ψ that minimize

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

for this determinantal form of $\Psi$. The normalization integral in the denominator is equal to 1, and the energy expectation value is given by the formula

$$E_{HF} = \langle \Psi_{HF} | H | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i<j}^{N} (J_{ij} - K_{ij})$$

These integrals are all real, and $J_{ij} \geq K_{ij} \geq 0$. The $J_{ij}$ integrals are called Coulomb integrals, the $K_{ij}$ integrals are called exchange integrals. Minimization of (2.9) subject of the orthonormalization conditions

$$\int \psi_{i}^{*}(x) \psi_{j}(x) dx = \delta_{ij}$$

gives the HF differential equations
The steps in the Hartree-Fock calculation start with an initial guess for the orbital coefficients, usually using a semiempirical method. This function is used to calculate an energy and a new set of orbital coefficients, which then can be used to obtain a new set and so on. This procedure continues iteratively until the energies and orbital coefficients remain constant from one iteration to the next. The calculation then has converged and the iterative procedure is called a self-consistent field procedure (SCF).

The HF method can be adapted to reflect the presence of paired or unpaired electrons. If a molecule has a singlet spin, then the same spatial orbital function can be used for the electrons with \( \alpha \) and \( \beta \) spin. This is called the Restricted HF method. There are two techniques to construct HF wave functions for molecules with unpaired electrons: first, to use two completely separate sets of orbitals for \( \alpha \) and \( \beta \) electrons (unrestricted HF method) or second, to let the paired electrons share the same spatial orbital (restricted open shell HF method).

One of the limitations of the HF method is that the average effect of the electron repulsion is considered (there is no electron correlation). Within this method, the distance of an electron to the nucleus but not the distance to the other electrons determines the probability of finding an electron at the same location around an atom. This is a consequence of the central field approximation and might be corrected \textit{a-posteriori} with methods such as the Møller-Plesset perturbation theory [5], the configuration interaction method, coupled cluster theory, or other methods.

### 2.4 Density Functional Theory

Density Functional Theory [6,7,8] allows us to use the electron density \( \rho(r) \) as a basic variable, instead of a complex \( N \)-electron wave function, as in the Hartree-Fock method. DFT started in the late twenties with the work of Thomas and Fermi [9,10]. Their contribution is the basis of the modern DFT, namely the statistical theory, in which the electronic structure of
atoms and molecules is described in terms of electron density. Today the DFT is based on two theorems introduced by Hohenberg, Kohn and Sham [11,12].

The first theorem states that the electron density, \( \rho(r) \) is determined by an external potential, \( V_{\text{ext}} \). Since \( \rho(r) \) determines also the number of electrons, it follows that \( \rho(r) \) determines the ground state wavefunction and all the properties of the investigated system in the ground state. The first theorem allows us to write the total energy as a function of the electron density in the following way:

\[
E(\rho) = T(\rho) + V_{\text{xc}}(\rho) + V_{\text{et}}(\rho)
\]

(2.12)

where \( V_{\text{xc}}(\rho) \) is the interaction energy between electrons and atomic nuclei:

\[
V_{\text{xc}}(\rho) = \int \rho(r) v(r) dr
\]

(2.13)

\( T(\rho) \) is the kinetic energy and \( V_{\text{et}}(\rho) = J(\rho) + E_{\text{et}}(\rho) \) is the electron-electron interaction energy that is given by the sum of the classical electrostatic repulsion \( J(\rho) \) and a non-classical term \( E_{\text{et}}(\rho) \).

The second theorem introduces the energy variational principle. For a given density, \( \tilde{\rho}(r) \) such as \( \tilde{\rho}(r) \geq 0 \) and \( \int \tilde{\rho}(r) dr = N \),

\[
E_0 \leq E[\tilde{\rho}]
\]

(2.14)

where the electron density is given by:

\[
\tilde{\rho}(r) = N \int [\psi^2] dx_1 dx_2 \ldots dx_n
\]

(2.15)

where \( \psi(x_1, x_2, \ldots, x_n) \) is the electronic wavefunction of a molecule with \( N \) electrons. This means that the minimum value of the total energy functional is the ground state energy of the system if the density \( \tilde{\rho}(r) \) is the exact ground state density \( \rho_0(r) \).

Therefore, for a given
the total ground state energy can be obtained as a minimum of the energy functional

\[ E[\rho] = \int \rho(r) v(r) dr + F_{\text{HK}}[\rho] \]  

Applying the variational theorem and using the Lagrange multipliers with the constraint that \( \int \rho(r) dr = N \) leads to

\[ \delta \left\{ E[\rho] - \mu \int \rho(r) dr - N \right\} = 0 \]  

and gives the Euler-Lagrange equation:

\[ \mu = \frac{\delta E}{\delta \rho(r)} = v(r) + \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(r)} \]  

where \( \mu \) represents the chemical potential, which measures the change of the total energy upon changes in the number of electrons.

Equation (2.19) is the basic equation with which the density functional theory operates. It can only be solved exactly if \( \delta F_{\text{HK}}[\rho] \) is known. However, the exact form of the terms describing the kinetic energy and the electrons interaction energy are not known. Therefore, approximations must be used.

Thomas and Fermi suggested to replace the term describing the inter-electronic interaction by the classical Coulomb potential and to take the term for the kinetic energy from the theory of the non-interacting electron gas. In addition to that, the model of Thomas-Fermi-Dirac adds to the electron interaction energy a term for the exchange and correlation corrections between electrons, but derived from the theory of the uniform electron gas. Since the atomic and the molecular clouds are clearly not a uniform electron gas, this approach experienced difficulties in reproducing the shell structure and chemical bonding.

In 1965, Kohn and Sham proposed a way to express the kinetic energy as the kinetic energy of an auxiliary system of non-interacting electrons.
Chapter 2

\[ T_i[\rho] = \sum_{i=1}^{N} \left( \rho_i \left| \frac{1}{2} \nabla^2 \right| \psi_i \right) \]  
(2.20)

with

\[ \rho(r) = \sum_{i=1}^{N} \sum_{s} |\psi_i(r,s)|^2 \]  
(2.21)

This expression of the electron density and the kinetic energy is exact for a one determinant wave function of a system of non-interacting electrons. The energy functional is written in terms of the kinetic energy as

\[ F_{HK}[\rho] = T[\rho] + J[\rho] + E_{\text{ex}}[\rho] \]  
(2.22)

with

\[ E_{\text{ex}} = T[\rho] - T_i[\rho] + V_{\text{ee}}[\rho] - J[\rho] \]  
(2.23)

This quantity is called the exchange-correlation energy and represents the non-classical part of the electron-electron interaction energy.

The Kohn-Sham energy functional of a set of \( N \) interacting electrons can be written as:

\[ E[\rho] = \int \psi^{*}(r) \rho(r) \psi(r) dr + T[\rho] + J[\rho] + E_{\text{ex}}[\rho] \]  
(2.24)

with

\[ J[\rho] = \frac{1}{2} \int \frac{\rho(r) \rho(r')}{|r-r'|} dr dr' \]  
(2.25)

The Euler-Lagrange equation (2.19) results in

\[ \nu_{\text{eff}}(r) = \nu(r) + \int \frac{\rho(r)}{|r-r'|} + \nu_{\text{sc}} \]  
(2.26)
where the exchange-correlation potential is

$$v_{sc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$ \hspace{1cm} (2.27)

Since the dependence of the introduced kinetic energy term on the electron density is not known, it is still not possible to solve equation (2.26) directly and the search for stationary points of the Kohn-Sham energy functional has to be affected in the space of the orbitals $\psi_i$ with the constraint that the latter are orthonormal. This leads to the $N$ one-particle equations:

$$\left( -\frac{1}{2} \nabla^2 + v(r) + \int \frac{\rho(r')}{|r-r'|} + v_{sc} \right) \psi_i = \varepsilon_i \psi_i$$ \hspace{1cm} (2.28)

where

$$v_{eff}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|} + v_{sc}$$ \hspace{1cm} (2.29)

and the effective one electron potential is generated by all the other electrons.

The one-particle equations (2.28) are the so-called Kohn-Sham equations, which can be solved exactly only if the exact form of the exchange-correlation potential is known. The exact form of the exchange-correlation potential is not yet known, so once again we are working with approximations.

### 2.4.1. Local Density Approximation (LDA)

The simplest approximation to the exchange-correlation potential is the local density approximation (LDA). Kohn and Sham proposed it in 1965, considering the limiting case of a slowly varying electron density. If the model of the uniform electron gas is chosen as the reference system, the exchange correlation functional can be written in the following way:

$$E_{xc}^{LDA}[\rho] = \int \rho(r) \varepsilon_{xc}(\rho) dr$$ \hspace{1cm} (2.30)
where $\epsilon_{xc}(\rho)$ is the exchange-correlation energy of a uniform electron gas with density $\rho(r)$. $E_{xc}^{LDA} [\rho]$ is approximated in such a way that at every point in space with a given density $\rho(r)$ the exchange-correlation energy per particle is equal to that of a uniform electron gas of the same density. The function $\epsilon_{xc}(\rho)$ can be divided into an exchange and a correlation part:

$$\epsilon_{xc}(\rho) = \epsilon_x(\rho) + \epsilon_c(\rho)$$  \hspace{1cm} (2.31)

The exchange energy density of the uniform electron gas is known analytically:

$$\epsilon_x = - \frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \rho(r)^{\frac{1}{3}}$$  \hspace{1cm} (2.32)

For the correlation part no analytic expression is available, but more recently one makes use of different parametrizations of the quantum Monte Carlo results of Ceperley and Alder [13]. The use of this kind of functional for different density regimes is often referred to as the Local Density Approximation, because the approximation of $\epsilon_{xc}(\rho)$ depends on the electron density at a given point only. The LDA assumes that the exchange-correlation energy of the electron density in a volume element of an inhomogeneous system is the same as the exchange-correlation energy of the electron density in a volume element of an homogeneous system. The LDA is exact for a perfect metal (which has a constant electron density) and becomes less accurate for systems with varying electron density (highly inhomogeneous systems such as atoms and molecules).

It is well known that for many systems, including metals, transition-metal compounds, and also organic and inorganic molecules, the LDA gives surprisingly good results, especially for the prediction of structural properties. An improvement of the LDA is given by its spin generalization in which the energy functional is expressed as a function of $\alpha$-electron and $\beta$-electron spin densities (the local spin density approximation LSDA) [14]. It uses a fit to accurate numerical results (by Ceperley and Alder) of a uniform electron gas at low- and high-spin limits for several electron densities. Obviously, the LSDA is a better description of
the real system than the approximate \( \varepsilon_{xc} (\rho) \) for a homogeneous, spin compensated electron gas.

One of the drawbacks of the LDA/LSDA is the poor description of the atomic energies, which influences the results of the binding energies and may produce an error of 10-20%. In some cases the LDA performs well, even if the HF method fails completely (e.g. F\(_2\), Li\(_2\)). Inter-atomic distances and vibrational frequencies are calculated within a few percent, while dissociation energies are usually overestimated [15].

### 2.4.2. Generalized Gradient Approximation (GGA)

A number of methods have been developed to overcome the limits of the LDA by including not only the \( \rho(r) \) but also its local gradients \( \nabla \rho(r) \) in the exchange-correlation potential, in order to account for the inhomogeneity of the electron density distribution (the generalized gradient approximation):

\[
E_{xc}^{GGA} = \int e_{xc} \{ \rho(r) \nabla \rho(r) \} dr
\]  

(2.33)

There are several proposals for different Generalized Gradient Approximations and implemented in quantum chemical codes, such as the one of Becke [16] for the exchange part of Perdew, [17,18] Lee-Yang-Parr [19] and Perdew-Wang [20] for the correlation part. These functionals must obey a number of conditions such as the sum rules, boundary conditions etc. Some of them are based on empirical data, but some are deduced by fitting atomic data.

### 2.5  Practical aspects of the calculations

#### 2.5.1. Periodic supercells

In the preceding sections it was demonstrated that a given many-body problem can be simplified into equivalent effective single particle problems. But there still remains the formidable task of handling an infinite number of non-interacting electrons moving in the
static potential of an infinite number of nuclei or ions. Two difficulties must be overcome: a wave function must be calculated for each of the infinite number of electrons in the system, and, since each electronic wave function extends over the entire solid, the required basis set to expand each wave function is infinite. Performing calculations on periodic systems and applying Bloch's theorem to the electronic wave functions can overcome both problems.

2.5.1.1. Bloch's theorem

Bloch's theorem states that in a solid with a periodic structure each electronic wave function can be written as a product of a cell-periodic and a wavelike part [21,22]:

$$\psi_i(r) = \exp[ik \cdot r] f_i(r)$$  \hspace{1cm} (2.34).

The cell-periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal:

$$f_i(r) = \sum_G c_{iG} \exp[iG \cdot r]$$  \hspace{1cm} (2.35)

where the reciprocal lattice vectors $G$ are defined by $G \cdot l = 2\pi m$ for all $l$, where $l$ is a lattice vector of the crystal and $m$ is an integer. Therefore, each electronic wave function can be written as a sum of plane waves,

$$\psi_i(r) = \sum_G c_{iG} \exp[i(k + G) \cdot r]$$  \hspace{1cm} (2.36)

2.5.1.2. K-point sampling

Electronic states are allowed only at a set of $k$ points determined by the boundary conditions that apply to the bulk solid. The density of the allowed $k$ points is proportional to the volume of the solid. The infinite number of electrons in the solid is accounted for by an infinite number of $k$ points, and only a finite number of electronic states are occupied at each
**Computational details**

$k$ point. Bloch's theorem changes the problem of calculating an infinite number of electronic wave functions to one of calculating a finite number of electronic wave functions at a infinite number of $k$ points. The occupied states at each $k$ point contribute to the electronic potential in the bulk solid, so that, an infinite number of calculations is needed to compute this potential. The electronic wave functions at $k$ points that are very close together will be almost identical. Therefore, it is possible to represent the electronic wave functions over a region of $k$ space by the wave functions at a single $k$ point. In this case, the electronic states at only a finite number of $k$ points are required to calculate the electronic potential and hence to determine the total energy of the solid.

Several methods for $k$ point sampling have been proposed in the literature. In our simulations we use the scheme proposed by Monkhorst and Pack [23] for calculating the electronic states at a set of $k$ points in the Brillouin zone. Other methods for the $k$ points sampling were developed by Chadi and Cohen [24], Joannopoulos and Cohen [25] and Evarestov and Smirnov [26]. Using these methods one can obtain an accurate approximation for the electronic potential and the total energy of an insulator or a semi-conductor by calculating the electronic states at a very small number of $k$ points. The electronic potential and the total energy are more difficult to calculate if the system is metallic because in that case a dense set of $k$ points is required in order to define the Fermi surface precisely.

### 2.5.2. Nonperiodic systems

The Bloch theorem can neither be applied to a system that contains a single defect nor in the direction perpendicular to the crystal surface. A surface may have a periodicity in the plane of the surface, but it cannot have periodicity perpendicular to the surface. The supercell for a surface calculation is illustrated schematically in Fig. 2.1.
The supercell contains a crystal slab and a vacuum region. The supercell is repeated over all space and the total energy of an array of crystal slabs is calculated. To ensure that the results of the calculation accurately represent an isolated surface, the vacuum region must be wide enough so that faces of adjacent crystal slabs do not interact across the vacuum region and the crystal slab must be thick enough so that the two surfaces of each crystal slab do not interact through the bulk crystal. In the same manner defects can be treated and also molecules can be studied. Again, the supercell needs to be large enough so that the interactions are negligible.

### 2.5.3. The Gaussian basis set

Gaussian-type functions were introduced in the molecular orbital calculations by Boys [27,28]. In a Cartesian coordinate system they have the following form:

\[ \chi_{i}^{\text{GTF}} = \exp\left(-\alpha r^2\right) x^l y^m z^n \]  

(2.37)

where \( \alpha \) is the exponent, and \( l, m, n \) are not quantum numbers but simply integral exponents of Cartesian coordinates. In this form (called Gaussian primitives) they can be factorized into their Cartesian components:
where each Cartesian component has the form (introducing an origin such that the Gaussian is located at position \( x_a \)):

\[
\chi_{x_i}^{GTP} = (x - x_a)^i \exp\left(-\alpha (x - x_a)^2\right) \tag{2.39}
\]

This simplifies the calculation of integrals considerably.

In most applications, including the CRYSTAL98 code that we used in our work, the Gaussian-type basis functions are expanded as a linear combination (or "contraction") of individually normalized Gaussian primitives, \( g_f(r) \) characterized by the same center and angular quantum numbers, but with different exponents [29],

\[
\chi_i(r) = \sum_{j=1}^{L} d_j g_j(r) \tag{2.40}
\]

where

\[
g_j(r) = g(r; \alpha, l, m) = N_{lm}(\alpha) r^l Y_{lm}(\theta, \phi) \exp\left(-\alpha r^2\right) \tag{2.41}
\]

where \( L \) is the length of the contraction, \( \alpha_j \) is a contraction exponent, \( d_j \) is a contraction coefficient. The Gaussian primitives are written in terms of real spherical harmonics including a normalization constant. The exponents and the contraction coefficients are normally chosen on the basis of relative cheap atomic SCF calculations so as to give basis functions suitable for describing the exact Hartree-Fock atomic orbitals (CRYSTAL98 code). An approximate atomic basis function, whose shape is suitable for physical and chemical reasons, is thus expanded in a set of primitive Gaussians, whose mathematical properties are attractive from a computational point of view.

In comparison with plane waves (the simplest alternative to Gaussians in solid state calculations), the use of all electron Gaussian calculations allows us to accurately describe electronic distributions in the valence and the core region with a limited number of basis
functions. The local nature of the basis allows a treatment of finite systems and systems with periodic boundary condition, in one, two or three dimensions. This has advantages over plane wave conditions of molecules, polymers or surfaces, which work by imposing artificial periodicity: the calculations must be done on e.g. a three-dimensional array of molecules with a sufficiently large distance between them. Gaussian total energies can be calculated very precisely since all integrals are solved analytically (HF solution with CRYSTAL98 code, the DFT solution with the CRYSTAL98 code requires an additional numerical integration of the exchange-correlation potential).

The cost for using Gaussians is the loss of orthogonality, of universality (qualities which the plane waves basis set posess), the need for more sophisticated algorithms for the calculations of the integrals and difficulties in computing forces.

2.5.4. Pseudopotential approximation

It is well known that most physical properties of solids depend to a much greater extent on the valence electrons than on the core electrons. The pseudopotential approximation exploits this by replacing the core electrons and the strong ionic potential by a weaker pseudopotential that acts on a set of pseudowave functions rather than the true valence wave functions. The pseudopotential approximation allows the electronic wave function to be expanded using a much smaller number of basis functions [30,31]. Therefore, pseudopotentials are not orbitals but modifications to the Hamiltonian and are used because they can introduce significant computational efficiencies.

An ionic potential, valence wave function and the corresponding pseudopotential and pseudo wave function are illustrated schematically in Fig. 2.2.
It is shown that the valence wave function oscillates rapidly in the region occupied by the core electrons due to the strong ionic potential in this region. Therefore, the pseudopotentials should correctly represent the long range interactions of the core electrons and produce the pseudo wave function solutions that approach the full wave function outside a core radius \( r_c \). Inside this radius the pseudopotential and the pseudo wave function should be as smooth as possible, in order to be representable with a small plane wave kinetic energy cutoff. The “norm-conserving” pseudopotentials satisfy these requirements [32]. A pseudopotential that uses the same potential for all the angular momentum components of the wave function is called a local pseudopotential. A local pseudopotential is a function of the distance from the nuclei only. It can describe the electron nucleus interaction at a long range, but cannot perform well for the short-range electron nucleus interaction. Therefore, a “non-local” potential to account for the short-range interactions is needed, which uses different potentials for each angular momentum component of the wave function. The most general form of the “non-local” pseudopotential is:
where \( Y_{lm}(r) \) are spherical harmonics and \( V_l(r) \) is the pseudopotential for an angular momentum component \( l \). Acting on the electronic wave function, this "non-local" operator decomposes the wave function into spherical harmonics, each of which is multiplied by the relevant pseudopotential \( V_l(r) \). Separable norm-conserving pseudopotentials in which the semi-local part of the pseudopotential can be transformed into a non-local part [33] using the scheme developed by Kleinman and Bylander [34] have also been developed recently.

In plane wave calculations, pseudopotentials are essentially mandatory, since the core orbitals have very sharp features in the region close to the nucleus.

Pseudopotentials in the Gaussian basis set calculations are not mandatory and have slightly different characteristics to those designed for plane waves. The use of pseudopotentials with the CRYSTAL98 code decreases the number of coefficients in the wave function and gives significant savings in the SCF part of the calculation.

In the calculations with the CRYSTAL98 code, the core electrons of molybdenum and sulfur were represented by the effective core pseudopotentials, developed by Hay and Wadt [35,36]. The core electrons are described by using a large core pseudopotential in which the S (1s\(^2\), 2s\(^2\)p\(^6\)) and Mo (1s\(^2\),2s\(^2\)p\(^6\),3s\(^2\)p\(^6\)d\(^{10}\),4s\(^2\)p\(^6\)) orbitals are replaced by the effective core potential. The basis sets of Mo and S were formed from the corresponding valence basis sets by re-optimizing valence exponents with respect to the total energy of bulk 2H-MoS\(_2\) at the experimental geometry. Results from large core (LC) and all electron (AE) calculations are in good agreement, indicating that the treatment of the inner core electrons with the pseudopotential is a minor approximation. The significant saving of CPU time for using the LC basis set rather than AE basis set led to adopt this approximation for optimizing geometry and surface structure.
2.6 The CRYSTAL98 code

The CRYSTAL package performs *ab initio* calculations of the ground state energy, electronic wave function and properties of periodic systems. Hartree-Fock and Kohn-Sham Hamiltonians can be used. Systems that are periodic in zero (molecules, 0D), one (polymers, 1D), two (slabs, 2D) and three dimensions (crystals, 3D) can be treated [37]. In each case, the fundamental approximation made is the expansion of the single particle wave functions \( \psi(r; k) \) ("Crystalline orbital", CO) as a linear combination of Bloch functions \( \phi_{\mu}(r; k) \) (BF), defined in terms of local functions \( \varphi_{\mu}(r) \) (hereafter called as "Atomic orbitals", AOs) [38,39].

\[
\psi_{\mu}(r; k) = \sum_{\mu} a_{\mu}(k) \phi_{\mu}(r; k) \tag{2.43}
\]

\[
\phi_{\mu}(r; k) = \sum_{T} \varphi_{\mu}(r - A_{\mu} - T)e^{i\mathbf{k}\cdot\mathbf{T}} \tag{2.44}
\]

where \( A_{\mu} \) denotes the coordinate of the nucleus in the zero reference cell on which the \( \varphi_{\mu} \) is centered, and the sum \( \sum_{T} \) is extended to the set of all lattice vectors, \( T \) [40,41].

The local functions are expressed as linear combinations of a certain number, \( n_{G} \), of individually normalized Gaussian-type functions, characterized by the same centre, with fixed coefficients \( d_{j} \) and exponents \( \alpha_{j} \) defined in the input:

\[
\varphi_{\mu}(r - A_{\mu} - T) = \sum_{j} d_{j} G(\alpha_{j}; r - A_{\mu} - T) \tag{2.45}
\]

The AOs, belonging to a given atom, are grouped into shells, \( \lambda \). The shell can contain all AOs with the same quantum numbers \( n \) and \( l \) (for instance, 3s, 2p, 3d shells), or all the AOs with the same principal quantum number \( n \) if the number of the GTOs, and the corresponding exponents are the same for all of them (mainly \( sp \) shells, this is known as an \( sp \) constraint). These groupings permit a reduction in the number of auxiliary functions that need to be calculated in the evaluation of the electron integrals and, therefore, increase the speed of the calculation.
A single, normalized s-type GTO, $G_{\lambda}$, is associated with each shell (the adjoined Gaussian of shell $\lambda$). The $\alpha$ exponent is the smallest of the $\alpha_i$ exponents of the Gaussians in the contraction. The adjoined Gaussian is used to estimate the AO overlap and select the level of approximation to be adopted for the evaluation of the integrals [42].

The expansion coefficients of the Bloch functions, $\alpha_{\mu}(k)$, are calculated by solving the matrix equation for each reciprocal lattice vector, $k$:

$$F(k)A(k) = S(k)A(k)E(k)$$  \hspace{1cm} (2.46)

in which $S(k)$ is the overlap matrix over the Bloch functions, $E(k)$ is the diagonal energy matrix and $F(k)$ is the Fock matrix in the reciprocal space [43]:

$$F(k) = \sum_{T} F_{T} e^{i\mathbf{k} \cdot \mathbf{r}}$$  \hspace{1cm} (2.47)

The matrix elements of $F_{T}$, the Fock matrix in the direct space, can be written as a sum of one-electron and two-electron contributions in the basis set of the AO:

$$F_{12}^{T} = H_{12}^{T} + B_{12}^{T}$$  \hspace{1cm} (2.48)

The one-electron contribution is a sum of the kinetic and the nuclear attraction terms:

$$H_{12}^{T} = T_{12}^{T} + Z_{12}^{T} = \langle \phi_{1}^{\alpha} | T_{12}^{T} | \phi_{2}^{\alpha} \rangle + \langle \phi_{1}^{\alpha} | \widehat{Z}_{12}^{T} | \phi_{2}^{\alpha} \rangle$$  \hspace{1cm} (2.49)

In core pseudopotential calculations, $\widehat{Z}$ includes the sum of the atomic pseudopotentials.

The two-electron term is the sum of the Coulomb and the exchange contributions [44]:

$$B_{12}^{T} = C_{12}^{T} + X_{12}^{T} =$$

$$\sum_{3,4} \sum_{i} \sum_{\alpha i} \sum_{s} \left[ \langle \phi_{3}^{\alpha} \phi_{4}^{s \alpha} | \phi_{1}^{\alpha} \phi_{5}^{s \alpha} \rangle - \frac{1}{2} \langle \phi_{1}^{\alpha} \phi_{5}^{s \alpha} | \phi_{3}^{T} \phi_{4}^{s \alpha} \rangle \right]$$  \hspace{1cm} (2.51)
Computational details

The Coulomb interaction of the type electron-nucleus, electron-electron and nucleus-nucleus, are individually divergent, due to the infinite size of the system. The grouping of the corresponding terms is necessary in order to eliminate this divergence.

The $P^Q$ density matrix elements in the AOs basis set are computed by integration over the volume of the Brillouin zone (BZ) [45],

$$P_{\alpha}^Q = 2 \int_{BZ} dke^{\alpha \cdot Q} \sum_n a_n^*(k) a_n(k) \theta(\varepsilon_F - \varepsilon_n(k))$$  \hspace{1cm} (2.52)

where $a_n$ denotes the $i$-th component of the $n$-th eigenvector, $\theta$ is the step function, $\varepsilon_F$ is the Fermi energy and the $\varepsilon_n$ is the $n$-th eigenvalue [46].

The total electronic energy per unit cell is given by:

$$E^{\text{ele}} = \frac{1}{2} \sum_{1,2} \sum_T P_{12}^T (H_{12}^T + B_{12}^T)$$  \hspace{1cm} (2.53)

The total electronic energy is the fundamental observable. The CRYSTAL code can compute also the following quantities: band structure, density of states, electronic charge density, charge density gradient, Mulliken population analysis, electron momentum distribution, Compton profile and many others.

The CRYSTAL code consists of three parts: Integrals, SCF and Properties, shown in Fig. 2.3.
Chapter 2

Definition of geometry
Definition of translational symmetry
Calculation of symmetry information

→ Molecular graphics

Specification of basis set

→ Molecular programs

Classification and selection
Computation of one- and two-electron integrals
Coulomb and exchange series
Symmetry transformation of block of integrals

α) Reconstruction of $F^{-1}$ and Calculation of total energy

δ) Calculation of Fermi energy

β) Fourier transform of $F^{-1}$

γ) Diagonalization of $F(k)$

Properties

Fig. 2.3. Flow chart of the CRYSTAL code.
2.7 The DMol$^3$ code

DMol$^3$ is a DFT quantum-mechanical code for a simulation of processes in the gas phase, in a solvent, on surfaces and in solid environments with high accuracy and reliability [47,48]. The DMol$^3$ code could be applied to a variety of problems in homogeneous and heterogeneous catalysis, to molecular reactivity, etc. Applications include the study of complexation of heavy metals, automotive catalysts and the mechanism of a polymerization reaction.

The computational performance of the DMol$^3$ code is based on the use of numerical functions on an atom-centered grid (its atomic basis):

$$\chi^{AO} = R_n(r)Y_m(\theta, \phi)$$  \hspace{1cm} (2.54)

where $R_n(r)$ represents the radial part and the $Y_m(\theta, \phi)$ stands for the angular dependence of the wave function [49,50].

The atomic basis functions are obtained from the solution of the DFT equations for individual atoms and are stored as sets of cubic splines and their exact shape depends on the nuclear and atomic charges. Such basis sets are known to be very accurate; the high quality of these basis sets minimizes superposition effects, and e.g. the dissociation of molecules is accurately described. The long-range tail of the basis set exhibits a correct charge distribution and allows an improved description of molecular polarizabilities [51].

The electron density in DMol$^3$ is expanded in terms of multipolar partial densities. This procedure provides compact and highly accurate representation of the density. The multipolar representation of the electron density is used to evaluate the Coulomb potential via the solution of Poisson's equation:

$$\nabla^2 V_a(r, \theta, \phi) = -4\pi \rho_a(r, \theta, \phi)$$  \hspace{1cm} (2.55)

where $V_a(r, \theta, \phi)$ represents the electrostatic potential expansion and $\rho_a(r, \theta, \phi)$ is the density decomposition.
The calculation of the Coulomb potential is a costly step and is therefore replaced by a fast evaluation of the potential on each center. This is an operation which scales as $N^{3/2}$, $N$ being the number of the basis functions.

The Hamiltonian matrix elements are calculated by using numerical integration algorithms that scale close to the order of $N$, when sparsity is taken into account. The ability to incorporate the periodic boundary conditions into a calculation makes DMol$^3$ especially powerful for studying heterogeneous catalysis and transition-metal complexes [52]. Among the variety of possibilities of the code we were interested particularly in its ability to study transition states in chemical reactions.

2.7.1. Transition-state search methods

Transition-state structures and equilibrium geometries are key elements in every effort to understand chemical reactivity. Quantum-chemical methods based on a computational approach capable of localizing transition states with a reasonable accuracy on the associated potential energy surface have advanced very rapidly during the last decade [53,54]. Over the last several years a number of methods were developed to localize transition state structures, which can be divided mainly into two groups: walking algorithms and interpolation algorithms. Surface walking methods require only the reactant configuration and can predict the products, which will be formed by exploring the potential energy surface using the local gradient and the Hessian matrix. Surface walking algorithms often do not perform accurately for bimolecular reactions and unimolecular systems with several low frequency vibrational modes.

A very promising approach for localizing transition states is the first derivative based nudged elastic band (NEB) method, which belongs to the second type of algorithms: the interpolation algorithms [55]. This method finds the entire minimum energy path between two minima by creating a string of images connecting a reactant and a product. This algorithm requires Hooke constants for springs that keep the images uniformly spaced along the path. Problems may arise when the spring constants are chosen either too small or too big. These problems might be avoided by using the recently proposed string method, in which the parametrization density evolves so that the string grows from each end of the pathway
Towards the transition state as each of the growing sections of the string converge [56,57]. The growing string method thus finds the minimum energy path without requiring an initial guess for the pathway and obtains a saddle point faster than the NEB. However, the main focus using the NEB or string method is on the optimization of the geometries of several points along the reaction path, while the transition state is determined by moving the highest energy image on the band right to the saddle point (NEB) or the discretized string moves in the direction of the normal force at each image on the string (the string method).

Because of the significant role of the transition state structures in chemical reactions, a reasonable task is to formulate an approach with an emphasis on the accurate location of a transition state along a guessed reaction path. Halgren and Lipscomb proposed such a method based on the idea that the transition states might be located via linear (LST) and quadratic (QST) synchronous transit calculations [58]. In addition to the traditional LST/QST method, conjugate gradient (CG) minimization schemes were proposed by Bell and Crighton [59], and by Fischer and Karplus [60] in order to refine the intermediates found by the LST/QST method. Originally, the LST method was applied to model the two-dimensional energy surface and the electrocyclic interconversions of cyclopropyl and allyl cations and of cyclobutadiene and cis-butadiene. Later, the generalized synchronous transit method was extended to periodic systems and implemented in the DMol³ program from Accelrys (Material Studio 2.1). Govind et al. extended the synchronous transit method to periodic systems and applied it to study the ZrCl₄ dissociation on the Si (100) surface [61]. The LST/QST method as implemented in the DMol³ code was also applied to study the methanol conversion to hydrocarbons in a zeolite catalyst and to the oxidative dehydrogenation of ethane [62,63].

Fig. 2.4 shows the approach, which the DMol³ code follows, while performing the transition state search. First, the energies of the reactant and the product structures are computed. Using these two energy points, the maximum along the LST path is searched. Once the maximum is found, a CG optimization of the structure is performed. If the residual forces fall below a specified tolerance, the calculation is considered converged and is further analyzed. If not, a new maximum is searched along the QST path connecting the reactant, the product and current best transition intermediate. A new CG optimization cycle is then initiated until convergence is achieved. The calculated energy of the barrier (ΔE_barrier) is given as the highest maximum on the minimum energy path and is taken relative to the initial state.
Chapter 2

Compute energy of reactants and products

Determine LST maximum energy structure

Conjugate gradient refinement at saddlepoint

Converged?

Yes

Analysis

No

Determine QST maximum energy structure

Fig. 2.4. Flow chart of the DMol³ transition state search algorithm.

2.8 References


39
Computational details


Chapter 3

Structure and reactivity of MoS$_2$-type catalyst particles: current state of computational results

3.1 Introduction

*Ab initio* modelling has made an important contribution towards a better understanding of the structure and reactivity of transition-metal compounds. Quantum-chemical calculations of molybdenum-based sulfide catalysts have been performed in order to predict the equilibrium sulfur coverage on the edge structure of unpromoted and promoted MoS$_2$-type catalyst, to identify the energetically preferable promoter (Co, Ni) location, to investigate hydrogen activation on the catalytically active surface, as well as to study reactions of sulfur-containing molecules on active sites of the catalyst surface. Thus, theoretical simulations have brought insights into the structure and the properties of Mo-based sulfide catalysts that cannot be obtained by experiments. This chapter summarizes the published results, concerning the structure and reactivity of MoS$_2$ catalyst particle, the models used in the calculations and the different computational approaches.

3.2 Bulk structure of 2H-MoS$_2$

The first attempt to interpret the properties of transition metal dichalcogenides on the basis of theory was done by means of energy band schemes [1,2]. The ligand field splitting of metal $d$ levels in a trigonal-prismatic coordination as found in the MoS$_2$ structure was discussed based on crystal-field and simple molecular-orbital calculations. In other semi-empirical calculations employing linear combinations of atomic orbitals, a two-dimensional
approximation and nearest-neighbour interactions were used to present the structural and the physical properties of transition-metal dichalcogenides [3]. Subsequently, a lot of more sophisticated band structure methods were developed and applied to calculate properties of dichalcogenides. The augmented plane wave method was used to calculate the electronic band structure of several layered transition-metal dichalcogenides, including compounds with the 2H-MoS$_2$ structure [4]. The calculations were based on crystal potentials derived from the charge densities of the respective atoms. The results showed that the dichalcogenides of group 16 elements, such as 2H-MoS$_2$, are semiconductors with an indirect band gap of 1.2 eV, and that there is a hybridization gap of 1 eV in the $d_z^2$ and $d_{z^2-r^2}$ manifolds of the metal $d$ states. Methods to calculate the band structures of layered compounds that combine the transmission and reflection matrices from individual atomic layers have also been used [5]. These methods are based on the layer-scattering method, which was developed for low-energy electron diffraction. Another attempt to investigate the electrical properties and the magnitude of the indirect gap of the semiconducting layered transition-metal dichalcogenide crystals combined high temperature conductivity measurements and photoemission studies with band structure calculations [6]. Molecular orbital methods were also used to calculate the electronic band structure and bonding in layered transition-metal dichalcogenides [7]. It was concluded that the electronic structure of transition-metal dichalcogenides could be described in an ab initio atomic orbital basis with reasonable accuracy and thus reduce the crystal field integrals. The Korringa-Kohn-Rostoker method, including an ionic contribution to the lattice potential, was also used to obtain results of the energy bands in layer compounds [8]. Another approach combined the analysis of molecular and crystal orbitals for molybdenum chalcogenides: cluster, chains and extended solids were used to explain the bonding in three dimensions and to discuss the relationship between cluster frontier orbitals and surface states [9]. A comparison of octahedral and trigonal-prismatic coordination of Mo centers and clustering in transition-metal dichalcogenides was also done [10,11]. A combination of experimental studies of the promoting effect of the first row transition metals on the hydrodesulfurization (HDS) activity of MoS$_2$ and a theoretical investigation of the electronic structure of simplified models is presented in reference [12]. The band structures of layered compounds calculated with the augmented-spherical-wave method are presented in [13,14]. The authors compared the results of band structure calculations and photoemission spectroscopy and pointed out that at about 1 eV below the top
of the valence band a dispersionless state is present that is almost completely of Mo 4d character, which was not predicted by band structure calculations. An investigation of the electronic properties of intercalation compounds of transition metal dichalcogenides including phase transition and conductivity properties was presented in [15].

3.3 MoS2 edge structure

3.3.1 Model of the MoS2 edge structure

Crystallography, solid-state physics, quantum chemistry and catalysis use different terminology and semantics in describing the surface structure of MoS2. The terminology that is consistently used in this thesis and the model of the (100) surface of MoS2 is illustrated in Fig. 3.1. It considers two sheets in the z direction, where each sheet consists of n rows of MoS6 prisms stacked in the y direction plus a row of terminating Mo atoms on one side of the sheet. n = 1, 2 and 3 represent the “4-row”, “6-row” and “8-row” model, respectively. These models are periodically repeated in the x and z directions in our calculations. The surface is parallel to one of the square faces of the MoS6 prisms, which make up the hexagonal MoS2 structure. The (100) surface of MoS2 exhibits two types of edges: one, exposing unsaturated molybdenum atoms (hereafter called the Mo-terminated (1010) edge), the other one, exposing sulfur atoms (called the S-terminated (1010) edge).

Different atomic models have been used to describe the edge structure of the MoS2 particle based on previous experimental characterization [16,17]. Byskov et al. [18,19,20] used a model containing a single S-Mo-S sheet constructed from two MoS6 prisms (4-row model). To correct for the difference in the dipole moments of the S and the Mo edges, a dipole layer is added in their calculations. Raybaud et al. proposed a model with a non-polar surface, since the two sheets have opposite orientations [21,22,23], similar to that of Fig. 3.1. Clusters that include a finite number of atoms have also been used as models of MoS2 catalysts [24,25,26,27,28].
3.3.2 Electronic properties

In contrast to the semiconducting bulk, the (100) surface shows a finite density of states at the Fermi level, i.e. it has conducting properties. It was shown that the static relaxation of the surface causes the Mo atoms to move inwards and the sulfur atoms from the neighbouring edge to move outwards and reduce the distance between them. The surface relaxation and its ability to take up hydrogen atoms were predicted years ago by Farragher [29,30]. Molecular dynamic simulations show that this relaxed surface is thermodynamically stable up to 700 K [21].

States of coordinatively unsaturated Mo surface sites fill the band gap. These states are mainly $a_{1g}$ states, which moved up and $e_g$ states, which moved down into the band gap. The electron density protrudes from the surface, mainly from the $d_{yz}$ and the $d_{x^2-y^2}$ states. These states determine the reactivity of the surface with molecular species (electron donors). The density of states on the saturated Mo atoms resembled the bulk density of states.

On the unsaturated S surface states the local electrostatic field was changed as a consequence of the reduced coordination. This resulted in very intense dangling bond states at
the Fermi level that are inclined ± 45° relative to the surface normal. These states led to the formation of S-S couples on the surface (Fig. 3.2). On the other hand, some S 3p states from the saturated S surface states moved into the bulk gap. Electronic structure calculations and reactivity of defect MoS₂, relative stabilities of the clusters, edges and the electronic surface states were also published in reference [31].

Fig. 3.2. Relaxation of the surface atoms leading to the formation of S-S couples.

3.3.3 Thermodynamic properties

A step forward in the investigation of the MoS₂ structure was the investigation of its surface structure, chemical composition and electronic properties under HDS working conditions, i.e. taking into account the chemical potential of the reaction environment [22,23]. Under reactive conditions, various sulfur-containing molecules (such as H₂S, thiophene, DBT, DMDBT as well as H₂) are present. The surface sulfur coverage depends mainly on the chemical potential of these compounds in the gas phase. The sulfur coverage at equilibrium will correspond to the minimum free energy of the following reaction:

\[ H_2 (g) + (MoS_2 + S) \rightleftharpoons H_2S (g) + (MoS_2) \]  (3.1)

Reaction (3.1) describes the desorption of a sulfur atom from the surface and the formation of gas phase H₂S, while the reverse reaction describes the splitting of H₂S, adsorption of a sulfur atom on the MoS₂ surface and formation of molecular hydrogen. Reaction (3.1) gives an
overall picture and does not take mechanistical aspects into account, such as the formation of Mo-SH and Mo-S groups on the catalyst surface.

Up to a sulfur coverage of 50% the addition of sulfur atoms to the Mo edge (Fig. 3.3) is an exothermic process. Between 50 and 83% the process is endothermic and becomes exothermic again at higher sulfur coverage [22]. The endothermicity might be due to the fact that there is reconstruction of the surface and the sulfur atoms change from bridging positions (up to 50%) to positions that sulfur atoms would have in the MoS$_2$ crystal. When this reconstruction happens for the first time it costs additional energy and the result is the endothermicity observed from 50% to 83%.

![Fig. 3.3. Models of sulfur-covered (100) surface of MoS$_2$: dark grey balls are the Mo atoms, light grey balls, the S atoms; a) 50% sulfur-covered Mo edge; b) 100% sulfur-covered Mo edge.](image)

The removal of sulfur atoms from the sulfur edge is always endothermic. At low sulfur coverage the process is highly endothermic and the structure exhibits strong reconstruction during structural optimization.

Sulfur exchange at fixed stoichiometry showed that starting from an “as-cleaved” surface, the transfer of up to 50% of the sulfur atoms from the S to the Mo edge is an exothermic process. The energy gain was maximal if 50% of the sulfur atoms were transferred. This calculation was based on the assumption that the sulfur removal from the S edge and the sulfur addition to the Mo edge are two independent processes.
Varying the chemical potential of the species above the MoS$_2$ surface and taking the temperature into account, Raybaud et al. showed that the Mo edge is the most stable at 50% sulfur coverage and the S edge is the most stable at 100% sulfur coverage [22].

The effect of promoters on the surface sulfur coverage in a sulfiding environment was studied as well [23]. Calculations showed that the removal of up to 50% of the S atoms from the S terminated edge of Co promoted MoS$_2$ is exothermic, while is endothermic in the case of unpromoted MoS$_2$. Sulfur addition to a Co promoted Mo edge followed the energetic tendency obtained for unpromoted MoS$_2$ but the reaction enthalpies decreased strongly with the increase of the Co content at the edge.

### 3.4 Location and effect of Co and Ni promoter atoms

In the search for the position of the promoter atoms (Co or Ni) two models have been considered: the intercalation and the substitution model [23].

In the intercalation model the promoter atoms are located in the van der Waals gap, between two sheets in a surface intercalation position, or in a tetrahedral, octahedral or “bulk” intercalation position (Fig. 3.4). Among the intercalation models, the tetrahedral and the “bulk” intercalation models were found to be energetically preferred. In the substitution model the promoter atom decorates the edges, on crystallographic Mo positions. It was found that the most favourable localization of the promoter atom (Co or Ni) is on the Mo-terminated edge. The calculations were performed with the two sheet periodic structure of MoS$_2$. According to Byskov et al. Co promoter atoms replace Mo atoms on the S-terminated edge [19]. The calculations were done with a single sheet model.
In recent studies, Schweiger et al. combined DFT and thermodynamic calculations to simulate triangularly shaped Co(Ni)MoS particles. In such particles, Co shows an affinity for the S-terminated edge under intermediate sulfiding conditions, while the location of Ni was found to be critically dependent on the reaction conditions, i.e. on the chemical potential of sulfur [32,33]. In case of a high chemical potential of sulfur, the promoter was found to be stable on both particle edges. Intermediate sulfiding conditions enhance the selective affinity of Co for the S edge, whereas Ni remains stable on both edges. A destabilization of the mixed phases is found under highly reductive conditions ($\mu_S \leq -1.1$ eV). Fig. 3.5. shows the morphology and phase stability diagrams of the nanosized particles as a function of chemical potential of sulfur in case of MoS$_2$, Co promoted MoS$_2$ and Ni promoted MoS$_2$ [33]. Morphologies deduced from Fig. 3.5 show that promoted MoS$_2$ tends to adopt a hexagonal shape, while unpromoted MoS$_2$ is more likely to adopt a triangular shape. For high chemical potential of sulfur ($\mu_S \geq -0.25$ eV), Co was found to be 100% covered by sulfur with six-fold coordination on both edges (similar to that of Mo in the unpromoted case), while Ni preferred four- or five-fold coordination environments on the S-terminated edge. Under intermediate
sulfiding conditions (-1.1 eV ≤ μ_S ≤ -0.25 eV), Co showed an affinity for the S edge, while Ni preferred the Mo-terminated edge. Under highly reductive conditions (μ_S ≤ -1.1 eV) a complete destabilization of the mixed phase occurred.

Fig. 3.5. Morphology and phase stability diagrams of nanosized particles as a function of the chemical potential of sulfur: a) MoS_2, b) Co promoted MoS_2, c) Ni promoted MoS_2 [33]. The thick black line indicates the equilibrium morphology.

3.5 Hydrogen activation on the (100) MoS_2 edge structure

Reaction mechanisms on transition-metal sulfide catalysts have proposed that hydrogen atoms are present on the surface of MoS_2 [34,35,36]. Hydrogen atoms activate the MoS_2 edge surface by reaction with surface sulfur under creation of vacancies. Hydrogen molecules adsorb on the MoS_2 edge and are present in different forms of surface species. Neutron diffraction data of MoS_2 based catalysts suggested that hydrogen is bonded to sulfur atoms rather than to metal atoms [37]. However, there is also experimental evidence for the presence of Mo-H groups [38]. Hydrogen dissociation is an important factor in hydrotreating reactions. A recent review of Breysse et al. summarized results from experimental and theoretical studies about the activation of hydrogen on transition-metal sulfide catalysts [39].
Diatomic hydrogen can dissociate on the catalyst surface in two ways [40]:

1) heterolytically on an unsaturated metal site and a sulfur atom:

$$H_2 + \text{Mo-S} \rightarrow \text{Mo-H} + \text{SH} \quad (3.2)$$

2) homolytically on sulfur couples (Fig. 3.2) resulting in equivalent S-H groups:

$$H_2 + 2 \text{S} \rightarrow 2 \text{SH} \quad (3.3)$$

Some questions concerning the adsorption of hydrogen on the (100) surface of 2H-MoS$_2$ are still unanswered: Where and how does the dissociation of H$_2$ occur? Which surface structures form after the adsorption of hydrogen, and how do they act when sulfur-containing molecules approach the surface?

There have been several attempts to explain the adsorption and reaction of hydrogen on the (100) MoS$_2$ surface. Byskov et al. found that hydrogen adsorbs strongly on sulfur edge atoms, which suggests that the S-terminated edge is partially covered with SH groups during the catalytic process [41]. Their calculations were based on the assumption that the dissociation of the dihydrogen molecule has already occurred and hydrogen adsorption was described using the following reaction:

$$A + \frac{1}{2} zH_2 \rightarrow B \quad (3.4)$$

where $A$ and $B$ are the structures before and after the hydrogen adsorption and $z$ is the number of hydrogen molecules. Then the binding energy of the hydrogen atom was defined as:

$$\Delta E_H = \frac{1}{z} \left[ E(B) - E(A) - \frac{z}{2} E(H_2) \right] \quad (3.5)$$

where $E(A)$, $E(B)$ and $E(H_2)$ are the total energies of the initial and final structures and dihydrogen, respectively. A negative value of $\Delta E_H$ indicates hydrogen bonding to the surface. According to reaction (3.5), basal planes could not bind hydrogen, but the sulfur atoms on the edge structures could. Reactions of hydrogen with sulfur atoms from the sulfur couples were found to be exothermic, while the formation of Mo-H groups (or Mo-H and S-H groups) was found to be endothermic.
Travert et al. also performed periodic DFT calculations to investigate hydrogen adsorption on unpromoted and Co and Ni-promoted MoS₂ (100) surfaces under HDS conditions [42]. They concluded that hydrogen dissociation is endothermic and has a high activation barrier, under the conditions of HDS. According to their calculations, Co as a promoter lowers the energy barrier of the activation of molecular hydrogen and increases the ability of neighbouring sulfur atoms to bind hydrogen. On the Ni-Mo-S surfaces, Ni-S pairs were not stable and did not provide an efficient way for hydrogen activation.

DFT calculations by Cristol et al. showed that the dissociation of hydrogen on five- and six-coordinated Mo atoms on the MoS₂ catalyst surface is endothermic and leads to Mo-H and S-H groups [43,44]. The endothermicity of this process implies that hydrogen is only stable on the MoS₂ surface at high pressure and low temperature. Furthermore, the authors concluded that, considering the endothermicity of the hydrogen dissociation process, it would not lead to the formation of coordinatively unsaturated sites on the surface. Hydrogen adsorption on the Mo-terminated edge showed that the most stable configuration consists of one bridging Mo-H-Mo group and one S-H group. Again on the Mo-terminated edge, the H₂ dissociation was endothermic on bridging sulfur atoms (Fig. 3.3a) and exothermic on coordinatively unsaturated sites (Fig. 3.3a, minus one surface sulfur atom) or on the sulfur couples (Fig. 3.3b). On the S-terminated edge, the H₂ dissociation was exothermic on the sulfur couples of the surface (Fig. 3.3). Exothermic dissociation was also observed on a sulfur edge, with four surface sulfur atoms removed (two surface sulfur atoms are left on the edge), resulting in the formation of two bridging Mo-H groups (the most stable configuration). When three surface sulfur atoms were removed from the sulfur edge (three surface sulfur atoms are left), the process was slightly endothermic.

Bollinger et al. [45] investigated hydrogen activation on one-dimensional metallic states on the edges of MoS₂ and reported that the adsorption of the first hydrogen atom on a 50 % sulfur-covered Mo edge is exothermic (Fig. 3.3a). This finding differs from the results summarized above. An explanation could be that Cristol et al. added a hydrogen molecule to the (100) surface to simulate the dissociation of hydrogen on the surface using the Nudged Elastic Band method, while Bollinger et al. did this atom by atom. Moreover, Bollinger et al. used a single sheet model, while Cristol et al. used a two-sheet model for the calculations, which might have an influence on the results of the adsorption energies.

Paul and Payen investigated the mechanisms of vacancy formation on the thermodynamically stable surface by means of reactions of hydrogen dissociation and H₂S.
formation and removal from the catalytically active surface [46]. They reported a value of the activation energy for hydrogen dissociation on the Mo-terminated edge of less than 1 eV. Moreover, they claimed that the rate-determining step is the heterolytic dissociation of the H₂ molecule on the metallic edge leading to the formation of one Mo-H group and one S-H group. Therefore, the dynamic equilibrium took place on this edge. H₂ physisorption occurred on the Mo-terminated edge and the subsequent formation of two Mo-H species gave the most stable geometry. The mechanism of vacancy formation on the S-terminated edge could be decomposed into several elementary steps with activation energies less than 1.5 eV. In all cases, vacancy formation was endothermic. Release of one S atom from the S-terminated edge was found to be very unlikely, whereas release from the metallic edge in the form of H₂S was observed in agreement with sulfur exchange experiments.

3.6 Adsorption of sulfur-containing molecules on the (100) MoS₂ edge surface

Raybaud et al. compared different possible configurations of thiophene adsorption on the Mo-terminated edge using the model shown in Fig. 3.1 [47,48]. Adsorption of thiophene on the Mo-terminated edge was an exothermic process, while adsorption on the S-terminated edge was found to be endothermic. On the Mo edge, side-on adsorption (η₁) with the thiophene ring parallel to the surface was energetically preferred over the end-on adsorption (η₅) through the sulfur atom with the thiophene ring perpendicular to the edge surface. The effect of the adsorption on the aromatic ring was also discussed. It was found that in the η₁ adsorption mode thiophene remained planar, whereas in the η₅ adsorption mode it was tilted. Moreover, η₅ (π) adsorption destroyed the aromatic character of the thiophene ring. In order to explain this, an analysis of the charge density transfer based on the changes in the local density of states was performed. It indicated that electrons are donated from the highest occupied bonding orbital of thiophene to non-bonding Mo d surface states. The back donation was from occupied d Mo surface states to the antibonding C-S π states. This depletion of the π-bonding states and the filling of the antibonding states of the thiophene molecule weakened
the C-C and the C-S bonds. As a result it activated the saturation of the aromatic ring and the cleavage of the C-S bond.

Other DFT studies, using cluster models of MoS₂ catalyst to investigate thiophene adsorption, were performed by Ma and Shobert [49] and Orita et al. [50]. Lauritsen et al. combined scanning tunneling microscopy and DFT approaches to study thiophene adsorption on MoS₂ surface in the presence of hydrogen [51].

Various adsorption configurations of dibenzothiophene (DBT), one or two methyl-substituted DBT molecules and their hydrogenated derivatives on a MoS₂ nanocluster were studied by means of DFT [52]. Again the flat and perpendicular adsorption modes of the sulfur-containing molecules were calculated and compared.

Calculations of the desulfurization of benzothiophene and methylbenzothiophene on the MoS₂ catalyst surface, showed that the most endothermic step in the whole process is the site regeneration (creation of the vacancy) [53]. In a later study, Cristol et al. [54] investigated adsorption of DBT derivatives on MoS₂. The starting point of their calculations was not the "as-cleaved" surface but the thermodynamically most stable one, i.e. a Mo-terminated edge covered by S atoms in bridging position between surface Mo atoms (Fig. 3.3a). Three potentially interesting catalytically active sites, which are shown in Fig. 3.6, were investigated. The first structure exposes active sites that consist of two six-coordinated and one four-coordinated Mo atoms (site 1). The second exposes two five-coordinated and one four-coordinated Mo atoms (site 2), while the catalytically active surface in the third structure possesses one four-coordinated and two three-coordinated Mo atoms from the S-terminated edge (site 3). The adsorption of DBT was analyzed as a sum of the electronic and steric repulsion effects. Activation of DBT was stronger on site 3 than on site 1. The authors concluded that there is no straight correlation between the adsorption energies and the activation of the molecule, as far as sites 1 and 3 are concerned.
Adsorption of DBT on site 2 is more complicated. Adsorption via one of the benzene rings of DBT did not show any influence on the thiophene ring of the molecule. Adsorption through the thiophene ring yielded a high distortion of the benzene ring. The most favourable DBT adsorption modes were the $\eta^1 (S)$ and benzene adsorption modes. The influence of the defects on the adsorption of the molecules on the surface was studied as well. Comparing the two routes of the HDS reaction, i.e. hydrogenation and hydrogenolysis, it was concluded that there is no significant difference between DBT and DMDBT towards hydrogenation over unpromoted MoS$_2$, whereas hydrogenolysis of the methylated derivatives is more difficult than of the non-methylated ones. When only the $\eta^1$ adsorption mode was possible (site 1 and site 3), DMDBT could not adsorb on the surface, while adsorption of benzothiophene, methylbenzothiophene and DBT was possible. If vacancies allowed all possible adsorption modes, the most favourable one for benzothiophene and methylbenzothiophene involved the thiophene ring and strongly activated the C-S bond. Comparing both studies [53,54] Cristol et al. claimed that the adsorption properties of DBT and DMDBT (the real refractory molecules) are different than those of benzothiophene and methylbenzothiophene (the model
Structure and reactivity of MoS$_2$-type catalyst particles

compounds). Moreover, a direct correlation between the adsorption geometries and the reactivity of the molecules was not obvious. The general conclusion of their study was that the hydrogenation path proceeds on site 2 through adsorption of the benzene ring on the Mo edge, while the direct desulfurization proceeds through \( \eta \) (S) adsorption on site 3 on the S-terminated edge.

Possible modes of thiophene coordination to transition-metal centers in organo-metallic compounds, representing types of adsorption on metal sites in HDS catalysts, were summarized by Angelici [55]. Jubert et al. [56] performed calculations of thiophene adsorption on a MoS$_2$ cluster in the presence of hydrogen. Their calculations showed that thiophene adsorbs in the \( \eta \) mode, which was shown to be the active configuration for C-S bond cleavage.

Rodriguez published a molecular orbital study of the interaction of hydrogen and thiophene with Ni/MoS$_2$ and Zn/MoS$_2$ surfaces [57]. The observed charge-transfer was from the admetal (Ni or Zn) to MoS$_2$, which increased the negative charge on sulfur and reduced the positive charge on Mo. The electronic and chemical perturbations induced by Ni were larger than by Zn. On the Mo-terminated edge Ni facilitated the dissociation of hydrogen and the interaction with thiophene.

DFT studies of the chemisorption and diffusion properties of Ni and Ni-thiophene complexes on the MoS$_2$ basal plane [58] and the interaction of H, S, Ni-H complexes with the MoS$_2$ basal plane [59] were published as well. These studies referred to the work of Kushmerick and Weiss [60], claiming that adding metal promoters to the unreactive basal plane of MoS$_2$ increases the catalytic reactivity for binding and transporting sulfur-containing molecules. Spectroscopic imaging of Ni clusters adsorbed on the MoS$_2$ basal plane revealed that their electronic structure is well suited to bind nucleophilic reactant species [61]. The experiments were done with low-temperature ultrahigh vacuum scanning tunneling microscopy at 77 K.
3.7 Conclusion and overview

*Ab initio* calculations have made an extremely valuable contribution towards a better understanding of the structure and reactivity of molybdenum-based sulfide catalysts. However, some important questions concerning the physics and chemistry behind the formation of active sites and the performance during hydrodesulfurization still remain.

Almost all of the theoretical work summarized in this chapter employs plane waves as basis functions to characterize the changes in the geometrical structure and electronic properties of the surface. Super cell techniques have commonly been applied to periodic structures of MoS$_2$ that expose the (100) surface as well as different types of defects in simulating hydrodesulfurization reaction conditions. When adsorption of H$_2$ and sulfur-containing molecules was investigated, the only method used up to now was the nudged elastic band method (NEB), as implemented in the VASP code with a main focus on the optimization of the geometries of several states along the reaction path.

In the studies presented in this thesis *Gaussian-type basis sets* were used. The advantages of these basis sets were discussed in Chapter 2. The calculations of the geometrical and electronic structure of the bulk and the (100) surface of MoS$_2$ were done with CRYSTAL98 code using periodic boundary conditions. This thesis presents a new point of view on local defects on the catalytically active (100) surface, treated by the recently developed *perturbed cluster method* as implemented in the EMBED01 code. The advantages of this method are that the interactions between the defects in the neighbouring cells are avoided and that the long-range crystalline field and the short-range forces are automatically and correctly included in the calculations.

In the second part of the thesis (Chapters 6 - 9), the emphasis is on the reactivity of the surface. The interactions of hydrogen and sulfur-containing molecules with the active sites of the catalyst are discussed. The calculations were done with the DMol$^3$ code. Since the focus of interest lies on the accurate localization of transition states, the *linear/quadratic synchronous transit* method combined with a *conjugate gradient refinement* of the saddle point was the method of choice.
3.8 References


Chapter 4

Ab initio study of 2H-MoS₂ using Hay and Wadt effective core pseudo-potentials for modelling the (10\bar{1}0) surface structure

4.1 Abstract

Periodic Hartree-Fock and DFT methods were employed to calculate the geometric and electronic properties of bulk 2H-MoS₂ and of its catalytically important (10\bar{1}0) edge structure. The core electrons of molybdenum and sulfur were represented by the effective core pseudo-potentials, developed by Hay and Wadt. For the calculations (10\bar{1}0) type surface structures were generated by cutting sections from an 2H-MoS₂ crystal, which consists of four, six or eight rows of molybdenum and sulfur atoms. The calculated elastic constants follow the experimental constants and show that 2H-MoS₂ is an anisotropic covalent compound held together by weak dispersion interactions between neighbouring S-Mo-S units. The relaxation of the (10\bar{1}0) surface of 2H-MoS₂ leads to an inner relaxation of the Mo atoms and the formation of weakly coupled surface S-S species. As a result of the surface relaxation, the electronic charge of the surface states is different to that of the bulk states: empty Mo d states move into the band gap, and the surface becomes a better electron acceptor. In all calculations the model consisting of six rows of sulfur and molybdenum atoms is the most favourable one, because it provides an accurate description of the 2H-MoS₂ surface structure and enables calculations at reasonable computation time. The calculations based on pseudo-potentials are in good agreement with all-electron calculations and confirm that, in contrast to the semiconducting bulk, the (10\bar{1}0) 2H-MoS₂ surface has metallic properties.
Ab initio study of 2H-MoS₂

4.2 Introduction

The catalytic removal of heteroatoms such as sulfur, nitrogen and metals from crude oil is one of the most important processes in industry. Sulfides of molybdenum or tungsten supported on alumina are used as catalysts in these reactions, especially in the catalytic hydrodesulfurization (HDS) of oil fractions. The importance of these catalysts led to a significant amount of research aimed at characterization of the catalyst structure and the nature of the surface active sites. In the HDS process sulfur-containing molecules (e.g. thiophene, dibenzothiophene and their derivatives) react with hydrogen to hydrocarbons and H₂S. Knowledge of the structure and reactivity of the MoS₂-type catalyst is of fundamental importance for understanding the reactions that take place during HDS. Theoretical predictions, such as those obtained by Periodic LCAO calculations based on Hartree-Fock (HF) and Density Functional Theory (DFT) methods, are a significant contribution to our understanding of the reactions that take place on the catalyst surface.

There have been various attempts at interpreting the properties of transition-metal dichalcogenides. These include energy band schemes [1,2], semi-empirical LCAO calculations [3,4] as well as augmented plane wave [5] and augmented spherical wave [6, 7] methods. The results show that the dichalcogenides of group 16 elements, such as 2H-MoS₂, are semiconductors with an indirect band gap of 1.2 eV and a hybridization gap of 1 eV in the dₓε and dᵧ, dₓ₋ᵧ manifolds of the metal d states. Clusters, chains and extended solids were used to explain the three-dimensional bonding and to discuss the relationship between cluster frontier orbitals and surface states [8] as well as clustering in transition-metal dichalcogenides with octahedral and trigonal-prismatic coordination [9,10]. Electronic properties, including phase transitions and conductivity of intercalation compounds of transition-metal dichalcogenides, have also been studied [11]. An investigation of the electronic structure was combined with an experimental study of the promoting effect of the first-row transition metals on the HDS activity of MoS₂ [12].

Very little is known about the edge structure of MoS₂, even though remarkable advances have been made in scanning tunnelling microscopy [13]. This is mainly due to the difficulties in preparing samples suitable for surface studies. Accurate computer simulations are, therefore, of additional value in this area. Zonnevylle et al. used Extended Hückel tight binding calculations to model the reactive MoS₂ surface [14], while Pis Diez and Jubert used
a theoretical molecular-orbital approach [15]. Mitchell and Plant performed density functional calculations on small Mo-S and hydrogenated Mo-S clusters in order to model and investigate the active sites of an MoS$_2$ catalyst [16].

Fast computers combined with well-established theoretical methods, mainly based on DFT, have been employed recently for the simulation of the surface structure of MoS$_2$. Two models of the MoS$_2$ structures were used. The first model consists of single S-Mo-S arrangements [17] to study the effect of adsorbed hydrogen [18,19]. The second model was introduced by Raybaud et al. to calculate the bulk crystal and electronic structure [20,21], the (10\(\overline{1}0\)) surface [22], the catalytically active sites [23,24] and the thiophene adsorption on the Mo edge [25]. It was also used for HF and DFT investigations of the MoS$_2$ surface structure with the CRYSTAL98 simulation package [26,27]. An all-electron periodic HF method was used to calculate the geometric and electronic properties of 2H-MoS$_2$, IT-MoS$_2$ and the (10\(\overline{1}0\)) surface of MoS$_2$ and Li adsorbed on this surface [26]. DFT all-electron calculations were employed to investigate the properties of the catalytically important (10\(\overline{1}0\)) edge of MoS$_2$ and the hydrogen adsorption on this edge [27].

The goal of the present work is to evaluate the effective core pseudo-potentials proposed by Hay and Wadt (HWLCECP) [28,29] in the description of the properties of the bulk and the (10\(\overline{1}0\)) edge structure of 2H-MoS$_2$. The emphasis is on the geometrical and electronic properties of the (10\(\overline{1}0\)) surface, known to be catalytically active. It will be demonstrated that the HWLCECP works well in bulk and surface calculations, approaching the accuracy of all-electron calculations and giving a fast and accurate method for representing the properties of this surface. Bulk and surface calculations of 2H-MoS$_2$ by means of one periodic HF and two DFT pseudo-potential calculations employing the local density (LDA) and generalized gradient approximations (PWGGA) have been performed using the CRYSTAL98 program. On the basis of these results generated models of different sizes ("4-row", "6-row" and "8-row") (Fig. 4.1) of the surface of 2H-MoS$_2$ have been generated with the aim of elucidating the structural and electronic properties of the (10\(\overline{1}0\)) edge structure. The density of states, band structures and Mulliken population analysis of the examined models are reported.
4.3 Computational methods

The pseudo-potential calculations were performed with a DELL 530 workstation equipped with two 1.7 GHz Xeon processors and 1024 MB RDRAM using the CRYSTAL98 program [30]. The input parameters are taken from a previous study [27]. Calculations are based on HF or DF theory for periodic systems that expand the ground state wave function as a linear combination of atomic orbitals. Each atomic orbital is a linear combination of a certain number of Gaussian-type functions with fixed coefficients and exponents. The Kohn-Sham code works with Gaussian-type auxiliary functions in order to avoid the calculation of
four-centre integrals. The k-point sampling was performed on a Monkhorst-Pack grid [31] with a shrinking factor 8, which yields 50 and 41 symmetry inequivalent points in the irreducible Brillouin zones of the bulk crystal and (1\times1) (10\bar{1}0) surface cells, respectively.

The basis functions of the Mo and S atoms used in the present calculations differ from the previous studies [26,27] by the treatment of the valence and core electrons. The core electrons are described by using a large core pseudo-potential [28,29] in which the S (1s\(^2\), 2s\(^2\)p\(^6\)) and Mo (1s\(^2\), 2s\(^2\)p\(^6\), 3s\(^2\)p\(^6\)d\(^{10}\), 4s\(^2\)p\(^6\)) orbitals are replaced by effective core potential (S [28], Mo [29]). The basis sets of Mo and S were formed from the corresponding valence basis sets by re-optimizing valence exponents with respect to the total energy of bulk 2H-MoS\(_2\) at the experimental geometry. Results from large core (LC) and all electron (AE) calculations are in good agreement indicating that the treatment of the inner core electrons with the pseudo-potential is a minor approximation. The significant saving of CPU time for using the LC basis set rather than AE basis set led to adopt this approximation for optimizing geometry and surface structure.

Density functional calculations with two combinations of exchange and correlation corrections have been performed. For the first calculation (DFT-LDA/VWN), the local density approximation (LDA) [32] for the exchange term in combination with the Vosko, Wilk and Nusair (VWN) correction [33] to describe the correlation effect between electrons were used. For the second calculation (DFT-PWGGGA/PWGGGA) the Perdew-Wang generalized gradient approximation for the correlation (PWGGGA) [34] and the Perdew-Wang generalized gradient approximation for the exchange term (PWGGGA) [35] to take into account the non-local contribution to the exchange-correlation functional were used. The optimization of the unit cell parameters (a, c and z') of 2H-MoS\(_2\) in the pseudo-potential calculations was performed by computing the Kohn-Sham energy for the unit cell on a grid of a and c values in the range of 2.95 to 3.5 Å and 11.5 to 13.5 Å keeping the group symmetry fixed and fitting the values to a quadratic equation. Finally, the equilibrium lattice parameters of the 2H-MoS\(_2\) unit cell were computed by fitting series of total unit cell energies, obtained for different unit cell volumes (c/a = const), to the Murnaghan equation of state [36].
4.4 Results and discussion

4.4.1. Equilibrium unit cell parameters of 2H-MoS$_2$

First, the unit cell was optimized (Fig. 4.2) in order to determine the cell parameters that produce the lowest total energy. Table 4.1 lists the equilibrium values of the lattice parameters $a$ and $c$, the thickness of the S-Mo-S unit $2c'$, the interunit distance (the van der Waals gap) and the calculated values of the elastic constants $c_{ij}$. The HF and DFT methods overestimate the value of the $a$ lattice constant of the equilibrium geometry by 0.6% (HF), 0.3% (DFT-LDA/VWN) and 0.6% (DFT-PWGA/PWGA). Rydberg et al. [37] used a DFT-VdW approach and in their calculations the $a$ lattice constant is overestimated by 2.2% (Table 4.1).

![Unit cell of 2H-MoS$_2$](image)

Fig. 4.2. Unit cell of 2H-MoS$_2$. Table 4.1 lists the optimized values of the lattice parameters.
In an all-electron post-HF DF-type correlation corrected (PWGGA) calculation, the a lattice constant was underestimated by 3.2% [26]. When the full Kohn-Sham DFT method was applied, the cell parameters differed by 0.7% (a) and 0.4% (c) from the experimental values [27]. The thickness of the S-Mo-S unit 2cz' is overestimated by 0.8% (HF), 4.6% (DFT-LDA/VWN) and 5.8% (DFT-PWGGA/PWGGA) and the volume per atom by 6.3% (HF), 5.3% (DFT-LDA/VWN) and 7.2% (DFT-PWGGA/PWGGA). In a pseudo-potential calculation performed with the VASP code, LDA underestimated the atomic volume by 6%, while adding the non-local exchange-correlation corrections (GGA) led to an overestimation of 3% [20,22]. Compared to the experimental values, the calculated equilibrium Mo-S bond length is overestimated by 0.9% (HF), 2.5% (DFT-LDA/VWN) and 3% (DFT-PWGGA/PWGGA). The Mo-S bond length reported by Byskov et al. [18] is overestimated by 1.2%.

Table 4.1. Equilibrium geometry of 2H-MoS₂.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>HF</th>
<th>LDA/VWN</th>
<th>PWGGA/PWGGA</th>
<th>VdW-DF*</th>
<th>GGA**</th>
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<tr>
<td>a/Å</td>
<td>3.16</td>
<td>3.18</td>
<td>3.17</td>
<td>3.18</td>
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<td>c/Å</td>
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<td>12.39</td>
<td>12.87</td>
<td>13.015</td>
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<td>0.129</td>
<td>0.129</td>
<td>0.129</td>
<td></td>
</tr>
<tr>
<td>2cz'</td>
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<td>3.1940</td>
<td>3.32</td>
<td>3.36</td>
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<tr>
<td>VdW gap/Å</td>
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<td>3.0260</td>
<td>3.1150</td>
<td>3.1475</td>
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<tr>
<td>d(Mo-S)/Å</td>
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<td>2.43</td>
<td>2.47</td>
<td>2.48</td>
<td></td>
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</tr>
<tr>
<td>c_{11}/GPa</td>
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<td>218</td>
<td>240</td>
<td>211</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c_{12}/GPa</td>
<td>52</td>
<td>59</td>
<td>53</td>
<td>42</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>c_{13}/GPa</td>
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<td>-21</td>
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<td>-62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c_{23}/GPa</td>
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<td>39</td>
<td>32</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c_{44}/GPa</td>
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<td>30</td>
<td>26</td>
<td>19</td>
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<tr>
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<td>8.59</td>
<td>7.34</td>
<td>6.49</td>
<td>5.11</td>
<td></td>
</tr>
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</table>

*Ref. 37
**Refs. 20 and 22

4.4.2. Elastic properties and cohesive energies

The elastic constants are the second derivatives of the energy in a Taylor expansion series with respect to the strain components. Since MoS₂ has a hexagonal structure, there are five independent elastic constants (Table 4.1) obtained after an unconstrained optimization. The elastic constants, calculated with the HF and DFT methods, agree well with the
Ab initio study of 2H-MoS₂

experimental values [38] For instance, the HF and the DFT-PWGGAPWGGA methods underestimate \( c_{11} \) by 9 and 11%, while the DFT-LDA/VWN method overestimates it by 0.8%. The value of \( c_{33} \) is overestimated by the HF method by 13% and underestimated by the DFT-PWGGAPWGGA method by 19%. The best results for the bulk properties are obtained with the DFT-LDA/VWN method, where \( c_{33} \) was overestimated by 1.9%. The vdw-DF calculations of Rydberg et al. [37], however, underestimated \( c_{33} \) by 5.8% (Table 4.1). The largest discrepancies between the experimental and HF results are found for \( c_{12} \) and \( c_{44} \). The calculated values are 60% lower and 58% higher than the experimental values, respectively. All the methods predict a negative sign of \( c_{12} \) in agreement with the experimental results.

The trends and magnitudes of the elastic constants of 2H-MoS₂ are consistent with highly anisotropic bonding. For example, \( c_{11} \) is three to five times larger than \( c_{33} \), which reflects stronger intralayer than interlayer forces. Coupling between the layers is weak, as proven by the small magnitude of \( c_{13} \). The low value of \( c_{44} \) reflects the ease with which the layers can be sheared across each other.

On the basis of the calculated lattice and elastic constants, the DFT method, using the local density approximation (LDA) [32] as an exchange potential in combination with the Vosko, Wilk and Nusair (VWN) correlation correction produces reasonable results for bulk 2H-MoS₂. The HF and the DFT methods give comparable values for the elastic constants.

For the sake of completeness the structural and elastic properties from these calculations were compared with the results of a method in which a compensation for the van der Waals interactions is included [37]. Table 4.1 shows that the vdw-DF approach gives better results for the \( c \) lattice and the \( c_{33} \) elastic constants than the DFT-PWGGAPWGGA method, but not for the \( a \) lattice constant. Table 4.1 also shows that the DFT-LDA/VWN method gives better results for the \( c_{33} \) elastic and \( a \) lattice constants than the vdw-DF calculation. The LDA generally gives good molecular structures, vibrational frequencies and charge densities in strongly bound systems but it is not useful for thermochemistry; on the other hand GGAs yield good thermochemistry but at the level of the weakest chemical interactions GGAs apparently fail [39].

The cohesive energy is the difference between the total energy per atom in the compound and the weighted average of the total energies of the free atoms. It is defined as

\[
E_{coh} = (2E_{Mo} + 4E_s) - E_{tot}
\]
where $E_{\text{tot}}$ is the total energy calculated after optimization of the unit cell. Table 4.1 lists the results of cohesive energies, as obtained by means of the HF and DFT methods. The experimental cohesive energies were calculated from the heat of formation of the compounds and the heat of sublimation of the elements, using standard values. For the calculated crystal and atomic energies the same HWLCECP and the same auxiliary basis functions were used [27] (in the DFT calculations) to ensure the compatibility of the two types of energy (crystal and atomic energy). The cohesive energy is overestimated by all the methods in the calculations, in contrast to the all-electron HF calculations [26] where the calculated $E_{\text{coh}}$ is underestimated. The closest value to the experimental value was obtained by pseudo-potential plane wave GGA calculations [20]. The authors reported a value of 5.11 eV/atom (experimental value: 5.18 eV/atom).

Fig. 4.3. The first Brillouin zone of 2H-MoS$_2$. The $\Gamma$-M-K-$\Gamma$ symmetry points determine the direction in which the bulk band structure is calculated.
4.4.3. Electronic structure and Mulliken population analysis

Six sulfur atoms coordinate the Mo atoms in the 2H-MoS$_2$ structure in a trigonal-prismatic fashion with the overall crystal symmetry D$_{6h}^4$. Since the D$_{6h}^4$ symmetry group has a unique c axis the atomic S p functions divide into two groups, $p_x$, $p_y$ (1) and $p_z$ (2), and the Mo $d$ functions into three groups, $d_{z^2}$ ($t_{2g}^0$), $d_{xy}$, $d_{x^2-y^2}$ ($t_{2g}^+$, $t_{2g}^-$) and $d_{xt}$, $d_{yt}$ ($e_g$).

![Band structure of bulk 2H-MoS$_2$](image)

**Fig. 4.4.** Band structure of bulk 2H-MoS$_2$ as obtained from HF calculations (left), the total density of states (right) and the density of states projected onto the Mo atoms (dashed line) and onto the S atoms (dotted line).

The $d_{z^2}$ function is equivalent to a non-degenerate $a_{1g}$ state, while the $d_{xy}$ and $d_{x^2-y^2}$ functions correspond to $t_{2g}^+$ and $t_{2g}^-$ functions forming the doubly degenerate $e_g$ state, which splits off from the original $t_{2g}$ set.
Figs. 4.5, 4.6 and 4.7 show the band structures along Γ-M-K-Γ symmetry lines in the hexagonal Brillouin zone (Fig. 4.3) and the total DOS, calculated according to the effective core pseudopotentials HF, DFT-LDA/VWN and DFT-PWGA/PWGA methods. The band structures consist of four complex bands. With the HF method (Fig. 4.4) there is a low-lying band from −27.5 to −25.5 eV which is derived mainly from S 3s states, a valence band from −15.6 to −5.74 eV, at the top of which the Mo 4 d_{2} states are situated, and the lowest part of the conduction band from 0.06 to 2.55 eV. The band gap is estimated to be 4.5 eV according to the HF calculations and is overestimated compared to the experimental estimation. This is due the method, because the electron correlation energy is not taken into account. The same trends are found for the electronic structures, as revealed by the results of the DFT-LDA/VWN (Fig. 4.5) and DFT-PWGA/PWGA calculations (Fig. 4.6).

Fig. 4.5. Band structure of bulk 2H-MoS₂ as obtained from DFT-LDA/VWN calculations (left), the total density of states (right) and the density of states projected onto the Mo atoms (dashed line) and onto the S atoms (dotted line).
Fig. 4.6. Band structure of bulk 2H-MoS$_2$ as obtained from DFT-PWGGA/PWGGA calculations (left), the total density of states (right) and the density of states projected onto the Mo atoms (dashed line) and onto the S atoms (dotted line).

The main differences are that the low-lying S 3s states and the valence band are shifted upward and that the lowest part of the conduction band is shifted downward in the DFT calculations. This reduces the band gap considerably; in case of the DFT-LDA/VWN method it is estimated to be 0.9 eV, which is in very good agreement with the experimental value and shows that bulk 2H-MoS$_2$ is a semiconductor. The results of the DFT-PWGGA/PWGGA calculation are almost the same as those of the DFT-LDA/VWN calculation. The only difference is that, in the case of the DFT-PWGGA/PWGGA calculation, the lowest part of the conduction band is shifted downward even further. As a result, the band gap is reduced to 0.4 eV and is underestimated compared to the experimental value.
The Mulliken population analysis, used as an approximate indicator of the partitioning of charge between the atoms in the 2H-MoS$_2$ unit cell, shows that the electron transfer is from the Mo 5s/4d to the S 3s/3p states. The calculated net charges in 2H-MoS$_2$ are Mo$^{+0.7}$S$^{-0.35}$ in the HF calculation and Mo$^{+0.32}$S$^{-0.16}$ and Mo$^{+0.34}$S$^{-0.17}$ in the DFT calculations. Table 4.2 lists the results, which are in good agreement with all-electron calculations [26,27]. The degree of covalence of the bonds is confirmed by the bond population analysis (the last column of Table 4.2). The short Mo-S bond has a population of 0.27 to 0.25 electrons, which indicates the presence of a covalent bond.

Table 4.2. Equilibrium bond distances and Mulliken population analysis (bulk calculations).

<table>
<thead>
<tr>
<th>Method</th>
<th>Atom</th>
<th>Net charge</th>
<th>d(Mo-S)/Å</th>
<th>Mo-S bond population</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>Mo</td>
<td>+0.7</td>
<td>2.43</td>
<td>0.270</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDA/VWN</td>
<td>Mo</td>
<td>+0.32</td>
<td>2.47</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PWGGA/PWGGA</td>
<td>Mo</td>
<td>+0.34</td>
<td>2.48</td>
<td>0.248</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-0.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.4.4. Surface structure models and geometry optimization

Fig. 4.1 shows the models of the (1010) surface of MoS$_2$. The surface unit cell comprises two sheets in the z direction. Each sheet consists of n rows of MoS$_6$ prisms stacked in the y direction plus a row of terminating Mo atoms on one side of the sheet. For n = 1, 2 and 3 we have the “4-row”, “6-row” and “8-row” model respectively (Fig. 4.1). These models are periodically repeated in the x and z directions. The surface is parallel to one of the square faces of the MoS$_6$ prisms, which make up the hexagonal MoS$_2$ structure.

The surface studies are based on an optimized, not on the experimental structure of 2H-MoS$_2$ [41]. The optimized structure is a stress-free arrangement of the Mo and S atoms, so that the 2H-MoS$_2$ crystal is in equilibrium. Three structures were calculated by means of the HF, DFT-LDA/VWN and DFT-PWGGA/PWGGA methods. To determine the geometry of the stable surface, a static optimization of the surface structure was performed using the
Ab initio study of 2H-MoS₂

CRystal98 geometry optimizer. The surface atoms were allowed to relax, while the rest of the 2H-MoS₂ slab was kept at the equilibrium geometry of the bulk MoS₂ structure.

Fig. 4.7. Structure of the (1010) surface of MoS₂ (“6-row” model) and the DFT results of the Mulliken population analysis. The surface relaxations Δy (Mo), Δy (Si), Δz (Si) are given in Table 4.3 (“4-row” model), Table 4.4 (“6-row” model) and Table 4.5 (“8-row” model).

In the HF calculations with the “6-row” model, the metal atoms of the Mo-terminated edge relax inward by Δy (Mo) = -0.094 Å. Fig. 4.7 indicates the manner of relaxation. The atoms on the neighbouring sheet (S-terminated edge) relax outward by Δy (S) = 0.051 Å, while the relaxations Δz (S₁) = +0.022 Å and Δz (S₂) = -0.022 Å, perpendicular to the closely packed S planes, shorten the S-S distance across the sheet (Table 4.4). The DFT-PWGGa/PWGGa calculation also yielded an inward relaxation of the surface Mo atoms of Δy (Mo) = -0.082 Å and an outward relaxation of the surface S atoms of Δy (S) = 0.077 Å. The z relaxations were Δz (S₁) = +0.045 Å and Δz (S₂) = -0.045 Å. The DFT calculation with LDA/VWN exchange and correlation showed the same tendency: Δy (Mo) = -0.124 Å (more pronounced than in
the previous cases) and, for the S surface, $\Delta y (S) = 0.0424 \text{ Å}$ and $\Delta z (S) = +0.0252 \text{ Å}$, $\Delta z (S_2) = -0.0252 \text{ Å}$.

Table 4.3 Geometrical parameters and surface energy based on the “4-row” model of the (1010) surface of MoS$_2$.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>LDA/VWN</th>
<th>PWGGA/PWGGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta y (Mo)/\text{Å}$</td>
<td>-0.0878</td>
<td>-0.1347</td>
<td>-0.1194</td>
</tr>
<tr>
<td>$\Delta y (S)/\text{Å}$</td>
<td>0.0586</td>
<td>0.0424</td>
<td>0.075</td>
</tr>
<tr>
<td>$\Delta z (S)/\text{Å}$</td>
<td>0.0954</td>
<td>0.0679</td>
<td>0.041</td>
</tr>
<tr>
<td>$d(Mo-S)/\text{Å}$</td>
<td>2.4299</td>
<td>2.4444</td>
<td>2.4663</td>
</tr>
<tr>
<td>$d(Mo-S)/\text{Å}$</td>
<td>2.4710</td>
<td>2.4764</td>
<td>2.4863</td>
</tr>
<tr>
<td>$S/\text{Å}^2$</td>
<td>40.798</td>
<td>40.798</td>
<td>41.388</td>
</tr>
<tr>
<td>$E_{surf}/\text{eV}$</td>
<td>2.41</td>
<td>3.91</td>
<td>3.15</td>
</tr>
<tr>
<td>$\Delta V/\text{Å}^2$</td>
<td>0.059</td>
<td>0.096</td>
<td>0.076</td>
</tr>
</tbody>
</table>

$\Delta y (S) = \Delta y (S_2)$ and $\Delta z (S) = -\Delta z (S_2)$

Table 4.4 Geometrical parameters and surface energy based on the “6-row” model of the (1010) surface of MoS$_2$.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>LDA/VWN</th>
<th>PWGGA/PWGGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta y (Mo)/\text{Å}$</td>
<td>-0.094</td>
<td>-0.124</td>
<td>-0.082</td>
</tr>
<tr>
<td>$\Delta y (S)/\text{Å}$</td>
<td>0.051</td>
<td>0.0424</td>
<td>0.077</td>
</tr>
<tr>
<td>$\Delta z (S)/\text{Å}$</td>
<td>0.022</td>
<td>0.0252</td>
<td>0.045</td>
</tr>
<tr>
<td>$d(Mo-S)/\text{Å}$</td>
<td>2.4278</td>
<td>2.4379</td>
<td>2.4588</td>
</tr>
<tr>
<td>$d(Mo-S)/\text{Å}$</td>
<td>2.4745</td>
<td>2.4783</td>
<td>2.4882</td>
</tr>
<tr>
<td>$S/\text{Å}^2$</td>
<td>40.798</td>
<td>40.798</td>
<td>41.388</td>
</tr>
<tr>
<td>$E_{surf}/\text{eV}$</td>
<td>2.52</td>
<td>4.55</td>
<td>3.58</td>
</tr>
<tr>
<td>$\Delta V/\text{Å}^2$</td>
<td>0.062</td>
<td>0.112</td>
<td>0.087</td>
</tr>
</tbody>
</table>

$\Delta y (S) = \Delta y (S_2)$ and $\Delta z (S) = -\Delta z (S_2)$
### Table 4.5 Geometrical parameters and surface energy based on the “8-row” model of the (1010) surface of MoS₂

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>LDA/VWN</th>
<th>PWGA/PWGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δy (Mo₁)/Å</td>
<td>-0.111</td>
<td>-0.124</td>
<td>-0.1024</td>
</tr>
<tr>
<td>Δy (S₁)/Å</td>
<td>0.0477</td>
<td>0.0424</td>
<td>0.077</td>
</tr>
<tr>
<td>Δz (S₁)/Å</td>
<td>0.0677</td>
<td>0.0423</td>
<td>0.0425</td>
</tr>
<tr>
<td>d(Mo₁-S₃)/Å</td>
<td>2.4221</td>
<td>2.4278</td>
<td>2.4519</td>
</tr>
<tr>
<td>d(Mo₂-S₁)/Å</td>
<td>2.4744</td>
<td>2.4786</td>
<td>2.4891</td>
</tr>
<tr>
<td>S/Å²</td>
<td>40.798</td>
<td>40.798</td>
<td>41.388</td>
</tr>
<tr>
<td>Eₙₙₑrf/eV</td>
<td>2.67</td>
<td>4.39</td>
<td>4.40</td>
</tr>
<tr>
<td>Δ eV/Å²</td>
<td>0.066</td>
<td>0.108</td>
<td>0.106</td>
</tr>
</tbody>
</table>

Δy (S₁) = Δy (S₂) and Δz (S₁) = - Δz (S₂)

Δ = 0.102 eV/Å² in the GGA calculations of Ref. 22

Tables 4.3, 4.4 and 4.5 list the results of the surface relaxation obtained with the different computational techniques and models. The results of the surface displacements with the “8-row” and “6-row” models appear to be similar. However, the “8-row” model calculation takes more time. The geometry optimization of the “8-row” model took 96 hours, while it took only 48 hours for the “6-row” model. The surface relaxation affects the distance d(Mo₁-S₃) on the Mo-terminated edge and d(Mo₂-S₁) on the S-terminated edge (Fig. 4.7 and Tables 4.3, 4.4 and 4.5). The d(Mo₂-S₁) from the S-terminated edge is increased relative to the bulk d(Mo-S) value, as obtained with the HF and the DFT methods: the increase with the “6-row” and “8-row” models is greater than for the “4-row” model. All the methods show that the d(Mo₁-S₃) is shortened on the Mo-terminated edge, but the effect is more pronounced with the “6-row” and “8-row” models than with the “4-row” model.

The energy necessary to form the surface is equal to

\[ E_{surf} = 0.5(E_{slab} - nE_{bulk}) \]

where \( E_{slab} \) and \( E_{bulk} \) are the total energy per unit cell for the slab and the bulk and \( n \) is the number of MoS₂ units included in the slab. For the “6-row” model the energy needed to form the surface (1x1) cell is 2.52 eV according to the HF calculation, while it is 3.58 eV according to the DFT-PWGA/PWGA calculation and 4.55 eV according to the DFT-LDA/VWN calculation. Compared to an ideal bulk-terminated non-relaxed surface, the relaxation of the “6-row” model lowers the total energy by only 10 meV (HF), 20 meV (DFT-LDA/VWN) and 2 meV (DFT-PWGA/PWGA). Lowering of the surface energy, as a result of the relaxation, occurs to a lesser extent with the present calculations than with other calculations [22,27]. This is due to the fact that only the first row of the surface atoms were allowed to relax. The calculated surface energy Δ in the “6-row” calculations has the following values:
0.087 eV/Å² (DFT-PWGa/PWGa), 0.112 eV/Å² (DFT-LDA/VWN) and 0.062 eV/Å² (HF). Raybaud et al. [22] reported a value of 0.102 eV/Å² considering a super cell with a surface area of 119.3 Å² (see Table 4.5).

4.4.5. Electronic structure of the (10\bar{1}0) surface of 2H-MoS\(_2\)

Figs. 4.8 to 4.10 give the electronic densities of the surface states (DOSS), calculated with the HF and DFT methods based on pseudo-potentials. Compared to the all-electron calculation, the ECP method reduces the computation time from eight to two hours for the "six-row" model. The DOSS of 2H-MoS\(_2\) shows a low-lying, filled S 3s band and an S 3p band, two thirds of which are filled, which overlaps with the Mo 4d states. The lowest part of the conduction band is formed by the rest of the Mo 4d states, and there is appreciable Mo e\(_g\) - S p mixing. In the bulk calculations band gaps of 4.5 eV (HF), 0.9 eV (DFT-LDA/VWN) and 0.4 eV (DFT-PWGa/PWGa) were obtained. In the surface DFT calculations the gap disappeared and a high DOSS were present at the Fermi level. This is due to the reduced ligand-field splitting and the breaking of two covalent Mo-Sp bonds per Mo surface site.

The effect of the unequal S\(_1\) (S\(_2\)) and S\(_3\) ligands can be qualitatively understood: The strongest electrostatic attraction will usually occur in the directions, in which the sulfur ligands have the lowest number of coordinated metal centres. On the surface, the charge on the sulfur ligand is not fully neutralized and, consequently its strength increases. The reduced coordination on the unsaturated S surface sites changes the local electrostatic field, causing a weak S-S coupling, the S 3s states move upward in comparison to the bulk S 3s states. The DOSS on the S-terminated edge is comprised of the 3s and 3p states of the two S surface atoms. For an unrelaxed surface the sulfur orbitals have sp\(^3\) hybridization and are oriented 45° relative to the surface normal. Relaxation leads to the re-hybridization of the 3s and 3p S surface orbitals from sp\(^3\) to an sp\(^2\) like hybridization state. There is 5% less electron density on the p\(_y\) orbital and 17% more on the p\(_z\) surface S orbital, compared to the respective orbitals in the bulk. There are two kinds of surface states on the unsaturated S atoms: a band of S 3s states, shifted upward relative to the bulk, and S 3p states concentrated around the Fermi level. As a consequence the DOSS at the Fermi level is increased on the S edge and the donor properties are better.
A bulk Mo centre is trigonally-prismatically coordinated and has $D_{3h}$ symmetry. As mentioned above the Mo $d$ orbitals split into three groups $d_{x^2}$ ($t_{2g}^0$), $d_{xy}$, $d_{z^2}$ ($t_{2g}^{-1}$, $t_{2g}^-$) and $d_{x^2}$, $d_{y^2}$ ($e_g$) in the bulk. The Mo atom on the surface has only $P_4$ symmetry, which leads to additional splitting of the Mo $d$ orbitals. In the DFT calculations the Mo $d_{x^2}$ states move up and the empty $e_g$ states move down and contribute to the gap states. The surface states of the unsaturated Mo atoms are concentrated in the bulk gap. Mainly the empty Mo states determine the acceptor properties of the surface. This result is in line with the findings reported in Refs. 22 and 25.

In the case of the DFT-LDA/VWN calculations with the “6-row” model, the surface $S$ 3$s$ states are between -13.15 and -12.19 eV and are derived from the bulk $S$ 3$s$ states (-18.51 to -16.29 eV) (see the projected density of states in Fig. 4.9). The part of the $S$ 3$p$ states, that is mixed with the Mo 4$d$ states, starts at -11.79 eV; the Fermi level is at -4.57 eV. In the case of the DFT-PWGA/PWGA calculations with the “6-row” model, the surface $S$ 3$s$ states, which shifted upward from the bulk, are between -17.09 and -15.84 eV (see the projected density of states in Fig. 4.9). The bulk $S$ 3$s$ states are between -18.45 and -16.13 eV. The $S$ 3$p$ states, which are mixed with the Mo $d$ states, are between -10.83 and 0.33 eV. There is no band gap due to the intense DOSS around the Fermi level.

In contrast to the semiconducting bulk, the MoS$_2$ (1010) surface has metallic properties according to the DFT calculations. Surface states at the Fermi level, which determine the reactivity of the surface, are derived from both the valence and the conduction bands. This tendency is not shown in the results of the HF calculations with the “6-row” model. The $S$ 3$s$ states are not shown in the graphs of the HF results (Fig. 4.9), because they are below -18.45 eV. (See too, the band structure for the bulk HF calculations.) The band gap is still present, because the electron correlation effects are not taken into account. On the other hand the DFT calculations tend to produce narrow gaps and bands, which is due to the approximations used.

The DOSS around the Fermi level in the electronic structure, obtained with the “4-row” model, is lower than that obtained with the “6-row” and “8-row” models in the DFT calculations (Figs. 4.8-4.10). The electronic structure obtained with the “8-row” model (Fig. 4.10) is similar to that of the “6-row” model as far as the projected DOSS is concerned but the bulk contribution is higher. Again the “6-row” model has an advantage over the “4-row” and
“8-row” models in the calculations of the electronic properties of the edge structure; it produces accurate data in a reasonable length of time.

4.4.5. Mulliken population analysis

The charges on the different atoms, starting with the surface row and calculated by means of the Mulliken population analysis, are as follow (see Fig. 4.7 for a definition of the Mo and S atoms):

HF calculations: Mo$_1$(+0.88) S$_3$(-0.41) Mo$_2$(+0.70)S$_1$(-0.44) Mo(+0.82)S(-0.35)
DFT calculations: Mo$_1$(+0.44) S$_3$(-0.18) Mo$_2$(+0.34)S$_1$(-0.22) Mo(+0.36)S(-0.17).

The Mulliken population analysis of the HF surface calculations shows that the S surface atoms are more negative by 0.10 electrons and Mo surface atoms more positive by 0.20 electrons compared to the respective atoms in the bulk. In the two DFT calculations (DFT-LDA/VWN and DFT-PWGGAPWGGA) the surface S is more negative by 0.05 electrons and the surface Mo more positive by 0.10 electrons than the bulk atoms.

This difference in the electronic charge, which is related to the relaxation of the surface, shows that the interaction of the (10$ar{1}$0) surface with molecular species is due to the existence of surface states around the Fermi level (from the valence as well as from the conduction band). The occupied sulfur 3s and 3p states move up (the energy of the HOMO increases) and empty Mo d states are lowered in the band gap. Accordingly the S edge of the MoS$_2$ surface becomes a better electron donor while the Mo atoms from the (10$ar{1}$0) edge will show better accepting properties. This different energy distribution of the surface states determines the donor-acceptor properties of the (10$ar{1}$0) edge structure.
Ab initio study of 2H-MoS$_2$

Fig. 4.8. Electronic density of surface states of the (1010) edge surface of MoS$_2$ ("4-row" model) as obtained from HF, DFT-LDA/VWN and DFT-PWGA/PWGA calculations. Dotted line: projected Mo density of surface states; dashed line: projected S density of surface states.
Fig. 4.9. Electronic density of surface states of the (1010) edge surface of MoS\(_2\) ("6-row" model) as obtained from HF, DFT-LDA/VWN and DFT-PWGGA/PWGA calculations. Dotted line: projected Mo density of surface states; dashed line: projected S density of surface states.
Ab initio study of 2H-MoS$_2$

Fig. 4.10. Electronic density of surface states of the (1010) edge surface of MoS$_2$ ("8-row" model) as obtained from HF, DFT-LDA/VWN and DFT-PWGA/PWGA calculations. Dotted line: projected Mo density of surface states; dashed line: projected S density of surface states.
4.5 Conclusion

The geometric and electronic properties of bulk 2H-MoS$_2$ and the (10\overline{1}0) surface structure were analyzed by means of HF and DFT calculations based on the ECP method. The \textit{ab initio} effective core pseudo-potentials facilitate valence electron calculations with an accuracy approaching that of all-electron calculations and reduce the computation time with a factor of four for the "six-row" model. The optimum geometry is in good agreement with the experimental data. The best results of the geometrical optimization of the bulk lattice parameters were achieved with the HF method. The calculated elastic constants follow the trends of the experiment and clearly show that 2H-MoS$_2$ is an anisotropic covalent compound held together by weak dispersion interactions between neighbouring S-Mo-S units. The best results of the electronic structure and the calculated band gap are obtained with the DFT-LDA/VWN method, while the HF method overestimates and the DFT-PWGGA/PWGGA method underestimates the band gap.

The relaxation of the (10\overline{1}0) surface shows that the S atoms relax outwards and form weak couples on the surface of an S-Mo-S sheet, while the surface Mo atoms relax inwards. The electronic structure of the surface is different from the bulk electronic structure, due to the reduced number of Mo-S bonds. The DFT methods predict conducting properties of the first surface layer of the relaxed (10\overline{1}0) surface in the calculations with the "6-row" and the "8-row" models, in contrast to the semi-conducting bulk. The electronic structure, obtained with the "4-row" model, has low DOSS around the Fermi level. The Mulliken population analysis shows that the surface S atoms are more negative by 0.05 electrons and the Mo surface atoms more positive by 0.10 electrons than the corresponding bulk atoms (DFT calculations). This is one of the consequences of the relaxation of the surface atoms. With HF calculations the surface remains semi-conducting and additional corrections to the exchange-correlation potential are necessary.

Finally, these theoretical results are in agreement with recent DFT studies, thus showing that the ECP method provides a realistic description of the (10\overline{1}0) 2H-MoS$_2$ surface. This approach can, thus, be used for investigating the adsorption process of sulfur-containing molecules on the "6-row" model of the surface, which will be the subject of the next chapters.
4.6 References

Chapter 5

Energetics and electronic properties of defects on the (100) MoS$_2$ surface studied by the perturbed cluster method

5.1 Abstract

The properties of defects on the (100) MoS$_2$ surface have been investigated by the perturbed cluster method. The perturbed cluster method provides an accurate description of the local defect properties while taking into account the interaction between the defect and the surrounding crystal. The surface energies, including correlation correction, of different defect structures of various sizes on the (100) MoS$_2$ surface are reported and compared with the energy of a reference surface cluster. The results, in conjunction with calculations of the electronic properties and electrostatic potential of the different defect sites, show that the chemistry of the defects differs from that of the perfect (100) "as-cleaved" surface. The enhanced reactivity of the defects is ascribed to the anisotropy in the electrostatic potential. The presence of "nodes" in the surface electrostatic potential suggests that the adsorption of small polarizable molecules will preferentially take place in the vicinity of these defects.
5.2 Introduction

Mineral surfaces often differ from the ideal crystallographic face that one would obtain by cleavage of the bulk material. This is a result of the different equilibrium conditions existing at the surface with respect to the bulk. The surface atoms typically undergo relaxation and reconstruction processes to adopt to the new equilibrium conditions. For catalysis, point defects, adatoms, dopants, vacancies or topological defects (dislocations) on the geometrical and electronic structure play an essential role in the structure of the active sites. Important changes in the surface properties, including surface energy, charge distribution, and reactivity, can be attributed to the presence of such defects.

The catalytically active (10\(\bar{1}0\)) surface of MoS\(_2\) is difficult to characterize experimentally and information about atomic processes on this surface is scarce. In part, this is due to the extensive reconstruction and to the creation of numerous defects on the (10\(\bar{1}0\)) and (\(\bar{1}01\bar{0}\)) edges. However, it is known that low coordination sites are commonly present at the surface of MoS\(_2\). Scanning tunneling microscopy of a single layer of MoS\(_2\) revealed coordinatively unsaturated sites as well as steps, produced by the sulfur atoms out of the normal sulfur layer positions [1,2].

Recently several theoretical studies have been carried out to unveil the properties of the perfect and restructured (10\(\bar{1}0\)) MoS\(_2\) surface [3-11]. Many of the studies employed pseudopotentials to describe the core electrons and plane waves to characterize the changes in the geometrical structure and electronic properties of this surface. Super cell techniques, commonly combined with density functional theory treatment (DFT) of the exchange and correlation, have been applied to periodic layered structures of MoS\(_2\) exposing the (10\(\bar{1}0\)) surface and different types of defects in the simulation of hydrodesulfurization reaction conditions. The basic hydrodesulfurization process consists of passing sulfur-containing molecules over a catalyst in the presence of hydrogen to yield hydrocarbons and hydrogen disulfide. These super cell methods exploit translational periodicity of the defects (reactants and active sites) and pay more attention to the nature of the catalyst. The advantage of this treatment is the use of translational symmetry and the use of properly defined boundary conditions (no need of saturating atoms). Also, such calculations are relatively cheap. The drawbacks are the approximate nature of the DF approximation, the need to use very large supercells if the interactions between neighboring defects are significant, and the constraints
imposed by the symmetry of the host crystal on the shape and type of the supercell (the translational periodicity must be a subgroup of the crystal group).

The complex defect structures (including Co and Ni substitutions) at the (10\(\bar{1}0\)) \(\text{MoS}_2\) face and dynamic reconstruction were first modeled on two-dimensional single-chain S-Mo-S layers [3]. This model of \(\text{MoS}_2\) can have two different edge terminations, the Mo (10\(\bar{1}0\)) edge and the S (\(\bar{1}010\)) edge. Based on DFT calculations, the coordinatively unsaturated sites along the edges were studied using a super cell with a width of two to three Mo atoms and a depth along the \(10\bar{1}0\) direction of four \(\text{MoS}_2\) layers (excluding the added atoms) [4]. The simulations of unpromoted, nonstoichiometric \(\text{MoS}_2\) reveal extensive reconstruction for both edges. The creation of the first vacancy on the S edge requires hardly any energy, while further removal of S atoms from that edge is energetically more demanding. A single vacancy is also easily created on the Mo edge filled with S atoms. These extra sulfur atoms on the edge do not occupy the normal lattice positions, but are situated in bridge positions between the Mo atoms [1]. The Co and Ni promoters were found to substitute for Mo atoms on the Mo as well as S edge. For these promoter structures, the sulfur-metal bond energy is reduced and S vacancies are more easily created [5]. Using periodic DF calculations the electronic properties of single-layered nanoparticles were shown to exhibit several metallic states. The edge states were interpreted as one-dimensional conducting wires, in agreement with the scanning tunnelling microscopy observations [6].

Applying DF simulations, Raybaud et al. have demonstrated that the (10\(\bar{1}0\)) \(\text{MoS}_2\) surface (the model incorporates the Mo edge and the S edge) is stable and undergoes modest reconstruction and relaxation even if the crystal is heated up to 700 K in a molecular dynamic simulation [7]. In addition, the influence of the working conditions on the equilibrium sulfur coverage of the active edge sites was studied by investigating the effect of varying the chemical potential of sulfur in the gas phase. Using the supercell technique, the authors showed that the chemical potential of sulfur may influence the local edge structure (sulfur coverage), as well as the shape of the \(\text{MoS}_2\) particles [8]. The local structure of cobalt and nickel-promoted \(\text{MoS}_2\) catalysts (represented by the (10\(\bar{1}0\)) face) and the location of the promoter were investigated in subsequent work [9]. The calculations illustrated that substitution of Mo atoms by Co and Ni promoter atoms on the edge gives the most stable state. The incorporation of the promoter atoms influences the sulfur-metal bond energy at the (10\(\bar{1}0\)) surface, leading to a reduction of the equilibrium S coverage of the active metal sites.
Finally, the morphology and shape of single layer MoS$_2$ nano-sized particles were simulated independently and the influence of the working conditions studied by modeling triangularly shaped MoS$_2$ clusters [10,11].

In this study we employ the embedded cluster technique [12,13], discussed in more detail in the following section. The aim of this work is two-fold. First, using the perturbative Møller-Plesset second order method (MP2) [14,15] we estimate the correlation correction to the energy of the surfaces with defects and the undefected reference surface and compare the electronic properties and characteristics with those obtained by the DF approximation. Second, we investigate the energetics and the electronic properties of several defects on the Mo and S edges of the (10\(\bar{1}0\)) MoS$_2$ surface and the factors that govern their relative stability. This will show which defect structures are energetically favoured and will provide valuable insight in the first steps of the mechanism of the hydrodesulfurization reaction. By identifying the most reactive sites and the electrostatic potential in their vicinity, we will attempt to predict how chemical species will react with the surface.

5.3 Computational details

5.3.1 Theoretical method

The periodic calculations for the bulk crystal and the surface cell were performed with the CRYSTAL 98 program [16,17]. The program solves the Schrödinger equation for the periodic structures in the HF approximation using a basis set of localized Gaussian functions centered on atoms. The basis set of Mo is best described as 6-3\(I\)\(G\) and those of the S atoms as 6-3\(I\)\(G^*\). Both basis sets were taken from a previous study of MoS$_2$ and have been optimized for minimizing the total energy of the unit cell at its experimental geometry [18]. To reduce the computational effort, the smaller Mo basis set (basis set 6-2\(I\)\(G\)) was used throughout, whose performance, in general, was found to be good for describing the MoS$_2$ structure.

The host crystal used for the bulk calculations is 2H-MoS$_2$. The optimized lattice constants $a$ and $c$ employed to describe the structure (corresponding to a Mo–S distance of 2.36 Å) are 3.15 and 12.35 Å respectively [19]. The model of the (10\(\bar{1}0\)) surface of MoS$_2$ adopted in the present periodic surface calculations is shown in Figure 5.1. It contains an
infinite number of sheets stacked along the Z (001) direction, each consisting of three MoS₂ units in the Y direction, and three MoS₂ units along the X (010) direction. The active surface is represented by the upper and lower layers parallel to the XZ plane and exhibits rows of molybdenum atoms (Mo edge) and couples of sulfur atoms (S edge). The fully relaxed geometries were taken from previous calculations [18,19].

**Fig. 5.1.** Model of the (10\overline{1}0) surface of MoS₂. The dark grey balls are the Mo atoms and the light grey balls are the S atoms.
In the present work we employ the perturbed cluster method in order to overcome the limits of the isolated cluster and the supercell technique. This method allows to correct the molecular solution of a cluster in the crystal field for the coupling with the infinite host lattice. In this way the long-range crystal field, as well as the short-range forces are automatically and correctly included in the calculations. The method has been implemented in the computer program EMBED01 [13] and was successfully applied to study oxygen vacancies on the surface of MgO and in bulk MgO [20,21]. The EMBED01 program receives the necessary information about the geometry, the basis sets, and the electronic structure of the host crystal (summarized in the projected density of states matrix $\rho_f(e)$, where the superscript $f$ refers to quantities related to the unperturbed crystal) from the periodic solution (CRYSTAL98 program). It solves the HF equations for local defects in the crystal self-consistently using the perturbed cluster technique. The type of the defect, the basis set associated with the added atoms or defects, and the shape and size of the perturbed cluster (PC) can be specified in the program input. The PC approach is based on a partitioning of all matrices into a local space, containing the defect (defined as the cluster submatrix), and all the nonvanishing matrix elements between the cluster orbital basis, the orbital basis of the indented crystal, and the complementary external space. The one-electron density matrix in the local space ($P_{\text{loc}}$) is expressed as a sum of the cluster molecular solution ($P_{\text{loc}}^{\text{clus}}$) and two corrective terms, $P_{\text{loc}}^{\text{cou}}$ and $P_{\text{loc}}^{\text{ext}}$, which represent the coupling and orthogonality corrections between the local and external space, respectively. The fundamental approximation which has to be made for solving the PC equations is the assumption that the projected density of states of the complete system in the external space is the same as for the unperturbed host crystal, so that the projected density of states matrix $\rho_f(e)$ can be used. The scheme can then be written as:

$$P_{\text{loc}} = P_{\text{loc}}^{\text{clus}}[\rho_f(e)] + P_{\text{loc}}^{\text{cou}}[\rho_f(e)] + P_{\text{loc}}^{\text{ext}}[\rho_f(e)]$$

$$P_{\text{ext}} = P_{\text{loc}}^{\text{ext}}$$

The defect formation energy is obtained by summing up all contributions to the exact HF total energy of the complete defect system and subtracting it from the corresponding quantity of the unperturbed system. In addition, the energy associated with the transfer of electronic charge between the local defect zone and the infinite host crystal is estimated with a variational-perturbative technique resulting in a quantity similar to the electrochemical potential. Finally, the correlation correction to the defect formation energy may be estimated a-posteriori by MP2 and DFT calculations. To summarize, the PC approach includes the following sequence of steps:
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1. Subdivide the entire defect system into a molecular cluster C containing the defect and an external region D, the indented crystal.

2. Calculate the wave function for the molecular cluster in the field of the indented crystal.

3. Correct the wave function in order to allow the propagation of the wave function into the indented crystal, while generating the density matrix of the defect system.

Following the conventions used within the PC method, we label the indented crystal as region D. Region A contains the added atoms and region B is the boundary region. In this way the cluster region C is made up by A + B. We define "defect energy" as the difference of the "local cluster energies":

\[ E_{\text{def}} = E(\text{B} + \text{A}) - E(\text{B}) - q\mu , \]

where \( q \) is the residual charge in the cluster and \( \mu \) is the "electrochemical potential" which is characteristic for a given cluster and material [22,23]. In this work, the energies \( E(\text{B} + \text{A}) \) and \( E(\text{B}) \) are obtained by two EMBED01 calculations utilizing exactly the same computational thresholds. The first evaluates the energy of a cluster composed by the adatoms (A) plus the boundary region (B) atoms, while the second is that of the (B) atoms only. The latter calculation corresponds to a case in which no defects are present. As a result, the electronic structure of B (Mulliken charges, electron charge density, etc) will coincide with the description yielded by the periodic calculations.

5.3.2 Defects

A medium sized cluster (Mo\textsubscript{2}S\textsubscript{6}) was used to model the isolated, charge-neutral, non-interacting defects on the (10\overline{1}0) MoS\textsubscript{2} surface. The Mo edge is studied using four defects built by the addition of S atoms to Mo\textsubscript{2}S\textsubscript{6} fragment representing a section of the Mo edge. The S adatoms were placed in certain positions above the Mo edge (the (10\overline{1}0) face of MoS\textsubscript{2}) and these were subsequently optimized.

The S edge was studied by removing one to three sulfur atoms from the Mo\textsubscript{2}S\textsubscript{6} cluster. The atom positions in the clusters used to calculate the bulk properties of the host crystal were not relaxed but were constrained to their optimized values obtained in the periodic
calculation. When surface S atoms from the S edge occupied positions within the S layers, their coordinates were also constrained to the optimized positions determined in the periodic calculations. They were, however, relaxed when placed in the Mo atom plane. The defects are shown in Figures 5.2 and 5.3.

Fig. 5.2. Clusters from the Mo edge. The two black balls are the Mo atoms, the dark grey balls are the cluster and the added atoms, the light grey balls are the atoms from the bottom layer. Sm: in the bridge position, and Sn in normal position of the adatom.
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Fig. 5.3. Clusters from the S edge. The two black balls are the Mo atoms, the dark grey balls are the S atoms of the cluster. The light grey balls are the atoms from the bottom layer.
The cluster region contains the adatoms and their first neighbours. In the present study we kept the Mo–S distances of the surface atoms to the values optimized for the (10\bar{1}0) MoS$_2$ surface (or to the values optimized in the bulk). The positions of the S and Mo atoms that were added to the surface were optimized and the correlation correction to fragments of the (10\bar{1}0) face and the defect surface energy were estimated using a second order method (MP2). This approach allows to obtain an independent assessment of the properties of this surface and different sites (defects) on this surface.

5.3.3 Defect and surface energy

For a non-defective surface, modeled by means of a slab consisting of two MoS$_2$ sheets, the surface energy ($E_{\text{surf}}$) is equal to half of the difference between the energy $E_{\text{slab}}$ per repeating unit cell of the slab and the energy $E_{\text{bulk}}$ for the same number of atoms in the bulk crystal. The factor two arises from the fact that the slab has two equivalent surfaces (cf. Fig. 5.1):

$$E_{\text{surf}} = \frac{1}{2}(E_{\text{slab}} - nE_{\text{bulk}})$$  \hspace{1cm} (5.1)

where $n$ is the number of MoS$_2$ units in the unit cell of the slab. This definition of surface energy sets a well-defined energy reference (the energy of the atoms in the bulk).

Similarly, the energy of a surface modeled by a cluster is expressed as:

$$E_{\text{surf}} = (E_{\text{surf}} - E_{\text{bulk}})$$  \hspace{1cm} (5.2)

where $E_{\text{surf}}$ and $E_{\text{bulk}}$ are the total energies of the Mo$_2$S$_6$ reference surface cluster and the energy of the reference Mo$_2$S$_6$ bulk cluster.

The surface energy, when $N$ atoms are added to the surface is expressed as:

$$\Delta E_{\text{ad}} = E_{\text{surf}} - (E_{\text{bulk}} + NE_{\text{ad}})$$  \hspace{1cm} (5.3)
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where $E_v$ is the energy of the added atom in vacuum and $E_{c-surf}$ is the total energy of the surface cluster containing the adatoms.

A similar equation is used to evaluate the surface energy when $N$ atoms are removed from the surface:

$$\Delta E_{def} = E_{c-surf} - (E_{cbulk} - NE_v)$$

(5.4)

where $\Delta E_{c-surf}$ is the energy of the surface cluster containing the defect.

In the present study, the Mo and S edges are treated separately.

5.4 Results

5.4.1 Properties of bulk MoS$_2$

Table 5.1 summarizes the results of the present calculations and compares them with the results of the periodic HF and DFT calculations discussed in Chapter 4. The Periodic HF calculation (electron correlation not included) of bulk MoS$_2$ predicted semi-conducting properties and a fundamental gap ($\Delta E$) of 4.7 eV. The optimized unit cell parameters and Mo-S distances were underestimated by 3%, compared to the experimental value of 2.41 Å, and the van der Waals interaction could only be accounted for when a post-theory DFT correction was included in the calculated energies. The periodic calculations using the DFT method (LDA-VWN approximations) and using the same basis sets for Mo and S as in the DFT method predicted better cell parameters ($a$ and $c$ differed only by 0.4% and 0.7% respectively), while the fundamental gap decreased to 0.8 eV [7,19]. The same value was obtained by the PC approach. For this reason it is particularly interesting to compare the properties of bulk MoS$_2$ and the (1010) MoS$_2$ surface obtained in the present EMBED01 calculations including the second order correlation correction with the results derived by the DF and PHF calculations.

The simple MoS$_2$ cluster conveniently models the bulk properties. The cluster energy corresponds to half of the unit cell energy obtained in the periodic calculations. The energy calculated for the unit cell within the PC method (including the MP2 correlation correction)
shows that the PC calculation yields values lower than the HF and DFT for the energy of the unit cell.

Table 5.1. Comparison of the results obtained for bulk MoS$_2$ by the *perturbed cluster* method and the Periodic HF and DFT calculations. Energies are given in eV. $\Delta E$ = gap energy.

<table>
<thead>
<tr>
<th></th>
<th>EMBED</th>
<th>EMBED+MP2</th>
<th>PHF</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>E unit cell</td>
<td>-258787.2</td>
<td>-258810.9</td>
<td>-258702.9</td>
<td>-258505.3</td>
</tr>
<tr>
<td>Fermi energy</td>
<td>-2.5</td>
<td>-2.5</td>
<td>-2.5</td>
<td>-2.5</td>
</tr>
<tr>
<td>E(Mo1s)</td>
<td>-19684.9</td>
<td>-19684.9</td>
<td>-19684.6</td>
<td>-19387.2</td>
</tr>
<tr>
<td>E(S1s)</td>
<td>-2501.3</td>
<td>-2501.3</td>
<td>-2501.2</td>
<td>-2396.0</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>1.1</td>
<td>0.8</td>
<td>4.7</td>
<td>0.8</td>
</tr>
<tr>
<td>Q(Mo)</td>
<td>0.87</td>
<td>2.36</td>
<td>0.59</td>
<td>0.38</td>
</tr>
<tr>
<td>Q(S)</td>
<td>-0.43</td>
<td>-1.18</td>
<td>-0.29</td>
<td>-0.19</td>
</tr>
<tr>
<td>Rs-s (Å)</td>
<td>2.36</td>
<td>2.36</td>
<td>2.36</td>
<td>2.36</td>
</tr>
<tr>
<td>RMo-Mo (Å)</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>Rs-s (Å)</td>
<td>3.01</td>
<td>3.01</td>
<td>3.01</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Table 5.1 shows also the Mulliken charges of the S and Mo atoms as well as the energy of the Mo and S 1s core levels calculated for bulk MoS$_2$ using the PHF, PC and DFT methods. The charges and 1s energies in the bulk will be used in the following as a reference to investigate the influence of the coordination and the crystalline potential on the defect sites formed on the surface.

### 5.4.2 The defect and surface energy

The crystallographic (1010) face of MoS$_2$ has been characterized in detail by means of periodic *ab-initio* calculations employing a slab model and multiple slab models [7,18]. It has been shown that six to eight layers along the (1010) direction reproduce the bulk properties at the center of the slab and give an accurate description of the surface [24]. The calculations revealed that Mo surface atoms relax inwards, while the exposed sulfur atoms relax outwards and toward each other across the S–Mo–S layer. The relaxation and minor reconstruction can be rationalized by considering that the electron density outside the crystal exposing the (1010) face of the MoS$_2$ is reduced as a result of the relaxation.

Previous periodic calculations found that, compared to the bulk, some properties of the (1010) MoS$_2$ surface change substantially although the relaxation/reconstruction of the
surface is small. The main features reported by several authors [3,4,5,7,18,19] are the formation of partially coupled S atoms and the conductivity of the first two layers. Under the experimental conditions of the hydrodesulfurization reaction, the most stable structure was calculated to have half of the S atoms removed from the S edge and the Mo atoms of the Mo edge covered with S atoms in bridging positions [4,5,8].

Tables 5.2a and 5.3a summarize the calculated surface energies for the models considered in this study (Figs. 5.2 and 5.3 respectively) and the values of $\Delta E_{ad}$ and $\Delta E_{def}$ for the different cases.

<table>
<thead>
<tr>
<th>N</th>
<th>Cluster</th>
<th>$\Delta E_{ad}$(HF)</th>
<th>$\Delta E_{ad}$(MP2)</th>
<th>E (HOCO)</th>
<th>E (LUCO)</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS$_2$ bulk</td>
<td>-</td>
<td>-</td>
<td>-2.4</td>
<td>-1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>Mo$_3$S$_6$ bulk</td>
<td>-</td>
<td>-</td>
<td>-8.0</td>
<td>-5.4</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>Mo$_2$S$_6$ surf</td>
<td>9.3</td>
<td>6.2</td>
<td>-4.2</td>
<td>-1.7</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>Mo$_2$S$_6$+1Sm</td>
<td>8.4</td>
<td>8.3</td>
<td>-3.8</td>
<td>-1.4</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>Mo$_2$S$_6$+2Sm</td>
<td>4.2</td>
<td>4.2</td>
<td>-2.8</td>
<td>-1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>Mo$_2$S$_6$+3Sm</td>
<td>2.5</td>
<td>2.2</td>
<td>-2.5</td>
<td>-1.9</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>Mo$_2$S$_6$+2Sn+1Sm</td>
<td>2.6</td>
<td>2.2</td>
<td>-2.0</td>
<td>-1.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

When sulfur atoms are added to the Mo edge, $\Delta E_{ad}$ decreases with increasing number of atoms added to the surface (Table 5.2a). However, the MP2 calculation shows that the addition of the first S atom increases the surface energy. The minimum energy is reached when three surface S atoms complete the coordination spheres of two Mo atoms modeled by the Mo$_2$S$_6$ surface fragment. It is also evident that adsorption of S atoms on sites located in the plane of the Mo atoms (Sm: middle) (structure 6), as well as adding the same number of atoms to surface sites in the S basal plane of MoS$_2$ (structure 7: with two normal sulfur atom positions (Sn) in MoS$_2$ crystal and one Sm), result in the most stable geometries. Experimental studies have shown that single S-Mo-S layers undergo extensive relaxation and reconstruction in the presence of H$_2$/H$_2$S and that up to four S atoms may be adsorbed as the number of the low coordinated sites at the Mo edge atoms are partially covered with sulfur [1]. Such reconstructions, correspond to structures 5, 6, and 7 created by addition of two and three S atoms to the Mo edge. The surface energies for the last two clusters are comparable and demonstrate that both structures 6 and 7 may serve as models of the sulfur-covered Mo edge. When adding S atoms to the Mo-terminated edge, the energy of the highest occupied
cluster orbital (HOCO) increases, i.e. the HOCO level moves up and the band gap decreases. This might be explained with a Peierls distortion effect [25].

Table 5.3a. S edge $- \Delta E_{\text{def}}$ energies of the highest occupied, the lowest unoccupied cluster orbitals (HOCO and LUCO) and the band gap $\Delta E$ in eV. The number $N$ refers to the model indicated in Fig.5.3. The reference energy of the Mo$_2$S$_6$ surface cluster is given in bold.

<table>
<thead>
<tr>
<th>N</th>
<th>cluster</th>
<th>$\Delta E_{\text{def}}$(HF)</th>
<th>$\Delta E_{\text{def}}$(MP2)</th>
<th>$E$(HOCO)</th>
<th>$E$(LUCO)</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS$_2$ bulk</td>
<td>-</td>
<td>-</td>
<td>-7.0</td>
<td>-6.2</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>Mo$_2$S$_6$ bulk</td>
<td>-</td>
<td>-</td>
<td>-5.9</td>
<td>-3.6</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>Mo$_2$S$_6$ surf</td>
<td>3.4</td>
<td>2.7</td>
<td>-6.0</td>
<td>-5.1</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>Mo$<em>2$S$</em>{7-1}$S</td>
<td>4.6</td>
<td>3.7</td>
<td>-2.8</td>
<td>-1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>Mo$<em>2$S$</em>{7-1}$S</td>
<td>3.2</td>
<td>2.4</td>
<td>-0.9</td>
<td>-0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>6</td>
<td>Mo$<em>2$S$</em>{7-2}$S</td>
<td>6.3</td>
<td>3.6</td>
<td>-2.4</td>
<td>-1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>Mo$<em>2$S$</em>{7-2}$S</td>
<td>1.2</td>
<td>1.1</td>
<td>-4.0</td>
<td>-4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>Mo$<em>2$S$</em>{7-2}$S</td>
<td>1.7</td>
<td>0.1</td>
<td>-2.5</td>
<td>-0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>9</td>
<td>Mo$<em>2$S$</em>{7-3}$S</td>
<td>-2.8</td>
<td>-1.9</td>
<td>-4.9</td>
<td>-4.1</td>
<td>0.8</td>
</tr>
<tr>
<td>10</td>
<td>Mo$<em>2$S$</em>{7-3}$S</td>
<td>8.6</td>
<td>7.8</td>
<td>-5.9</td>
<td>-5.6</td>
<td>0.3</td>
</tr>
<tr>
<td>11</td>
<td>Mo$<em>2$S$</em>{7-3}$S</td>
<td>3.6</td>
<td>3.3</td>
<td>-2.4</td>
<td>-2.2</td>
<td>0.2</td>
</tr>
<tr>
<td>12</td>
<td>Mo$<em>2$S$</em>{7-3}$S</td>
<td>8.1</td>
<td>8.6</td>
<td>-4.3</td>
<td>-2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>13</td>
<td>Mo$<em>2$S$</em>{7-3}$S</td>
<td>7.2</td>
<td>7.7</td>
<td>-2.6</td>
<td>-0.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>

A similar trend is observed for the vacancy creation on the perfect S edge of MoS$_2$ (cf. structures 1-13 in Table 5.3a). For the medium Mo$_2$S$_6$ cluster the energy minimum is reached when three S atoms are removed (structure 9, Table 5.3a). However, for a given structure with $n$ S atoms removed, the surface energy strongly depends on the geometry of the cluster. The geometry of the defects also affects the $E$(HOCO), $E$(LUCO), and the band gap. Structures 13, 12 and 10 have a high surface energy, due to the distorted tetrahedral coordination of the Mo atoms. If structure 13 is relaxed (13 $\rightarrow$ 12 $\rightarrow$ 10 $\rightarrow$ 9) the surface energy is reduced. For the Mo$_2$S$_6$ cluster the defect with geometry 8 also has a low energy (the corner atoms are removed). The minimum surface energy is achieved when three S atoms complete a tetrahedral configuration around each molybdenum atom with the sulfur edge surface atoms located in bridging positions. In this case, the S edge is reconstructed with respect to the reference S edge surface and the Mo atoms are coordinated to four sulfur atoms in a perfect tetrahedral configuration.

The surface energy calculated according to equation (5.2) reveals that the bare "as-cleaved" Mo edge is more destabilized ($E_{\text{ad}} = 6.2$ eV) than the S edge ($E_{\text{def}} = 2.7$ eV). Full relaxation of this Mo edge reduces the effect of the undercoordinated surface Mo atoms. A
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Step-like transfer of S atoms from the S edge to the naked Mo atoms of the Mo edge lowers the surface energy and is energetically beneficial, reaching its maximal effectiveness when three atoms are transferred. Similarly, when three S atoms are adsorbed on the Mo$_2$S$_6$ cluster modeling the Mo edge, the surface energy is lowered to 2.2 eV, which is close to the reference surface energy of the Mo$_2$S$_6$ cluster, in the S edge (2.7 eV). This structure, (3 S atoms on Mo edge plus fully covered S edge) was indicated as the most stable one also in periodic DFT calculations [8].

5.4.3 The (100) MoS$_2$ surface: electronic structure and properties

In the previous section we discussed the stability of different structures obtained by the removal of S atoms from the S edge and the addition of S atoms to the Mo edge. The electronic properties yield further insight into the chemistry related to the adsorption of S-containing species and hydrogen on the edges. We will examine the Mulliken charges and core level shifts dependence of the coordination of S and Mo atoms on the surface. These charges and shifts in the electronic core levels reflect the changes introduced by the adatoms and vacancies on the stability and reactivity of the corresponding edges. Moreover, we will examine the topology of the electrostatic potential generated by these structures, in order to reveal their reactivity towards different types of adsorption.

There is an essential discrepancy in the calculated electronic properties of the (1010) MoS$_2$ surface when modelled with multiple MoS$_2$ units (the surface unit cell contains Mo and S edges). The HF method predicts a reduction of the fundamental band gap but the surface preserves semi-conducting properties, while the DFT method predicts the first two layers to be conductive [7,24]. The present EMBED01 calculations (with correlation correction) demonstrate that the Mo and S edges remain semi-conducting, despite the fact that the HOCO - LU CO gap decreases considerably. However, the energy of the HOCO computed for the cluster model of the Mo edge (-4.2 eV) is higher than the energy of the LU CO of the cluster used to model the S edge (-5.1 eV) (cf. Tables 5.2a and 5.3a). Therefore, the surface unit cell simulated by multiple layers should be considered conductive with respect to the overlap of the bands derived from these levels, as long as the Mo and S edges in one sheet are far away enough (separated by at least three to four MoS$_2$ units) to suppress the interaction between the upper and lower surfaces.
Tables 5.2b and 5.3b show the Mulliken charges and the core level shifts of S and Mo for the bulk, the (10\text{1}0) surface, and for the various defects considered in this study. For the sulfur edge (Table 5.3b), the surface S atoms (-1.15) are more negative than in the bulk (-0.68), while the underlying S atoms from the third layer along the (10\text{1}0) direction are less negative than the bulk S atoms (-0.15). The Mo atoms constituting the second layer (just under the S atoms of the S edge) are less positive (2.45) than the Mo atoms in the bulk (3.47). For the Mo edge (Table 5.2b), the surface Mo atoms are more positive (3.72 versus 2.36), while the charge on the S atoms from the second layer is less negative (-0.80 versus -1.18) than that for the Mo and S atoms in bulk MoS$_2$, respectively.

The charge on the surface atoms becomes more negative by the removal of up to three S atoms from the S edge (-1.15 (4) → -1.20 (8) → -1.84 (9)). The reverse process of the addition of S atoms on the bare Mo edge increases the positive charge on the Mo atoms when one and two sulfur atoms are added (3.14 (4) → 3.22 (5)), and decreases when three sulfur atoms are added (2.21 (7) and 3.01 (7)). It reduces the charge on the underlying S atoms. The most pronounced changes are observed for the S atoms in optimized positions in the metal plane (cluster 9 on the S edge). These changes indicate that the surface sulfur in these defects might exhibit different properties with respect to the bulk-like coordinated S atoms. The coordination for these types of defects changes from trigonal prismatic to tetrahedral for the S edge, while for the Mo edge the added S atoms complete the trigonal prismatic environment of the exposed Mo atoms.

The energy shift of core levels belonging to an atom in a low coordination site relative to the same atom in the bulk is related to the crystal potential acting on that site. In the present case we take as reference the position of the 1s levels of sulfur and molybdenum located in the bulk (or in the center of the slab). The variations in the results (Tables 5.2b and 5.3b) are due to the effect of both the nature of these atoms (surface or bulk) and the atom coordination (number of neighboring atoms and the type, polarizability etc.). In general, the surface S atoms and the underlying Mo atoms experience a smaller crystal field than the bulk atoms. However, the defect creation changes the coordination and the local geometry and affects the 1s shifts for surface layers constituted by S and Mo atoms. Levels belonging to S and Mo atoms for clusters in which the type of coordination is changed are considerably more affected by the crystalline field.
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Table 5.2b. Mo edge – Mulliken charges and energies of the core levels for Mo and S in eV. The first value of Q(S) for a certain number N refers to the bottom sulfur layer, the second value to the top sulfur layer and further values to the added atoms.

<table>
<thead>
<tr>
<th>N</th>
<th>Cluster</th>
<th>Q (Mo)</th>
<th>Q (S)</th>
<th>Q (Mo) - MP2</th>
<th>Q (S) - MP2</th>
<th>E (Mo1s)</th>
<th>E (S1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS₂ bulk</td>
<td>0.87</td>
<td>-0.43</td>
<td>2.36</td>
<td>-1.18</td>
<td>-19677.5</td>
<td>-2497.3</td>
</tr>
<tr>
<td>2</td>
<td>Mo₂S₆ bulk</td>
<td>0.27</td>
<td>-1.43</td>
<td></td>
<td></td>
<td>-19683.5</td>
<td>-2501.3</td>
</tr>
<tr>
<td>3</td>
<td>Mo₂S₆ surf</td>
<td>0.54</td>
<td>-0.89</td>
<td>3.72</td>
<td>-0.80</td>
<td>-19677.5</td>
<td>-2501.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.03</td>
<td>-1.46</td>
<td>-19677.5</td>
<td>-2497.0</td>
</tr>
<tr>
<td>4</td>
<td>Mo₂S₆+1Sm</td>
<td>0.73</td>
<td>-0.23</td>
<td>3.14</td>
<td>-1.14</td>
<td>-19678.4</td>
<td>-2496.7</td>
</tr>
<tr>
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<td>-0.70</td>
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<td>-1.51</td>
<td>-19677.5</td>
<td>-2494.0</td>
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<td>5</td>
<td>Mo₂S₆+2Sm</td>
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<td>0.42</td>
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<td>-2496.7</td>
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<td></td>
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<td>-1.07</td>
<td>-0.85</td>
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<td>-2497.0</td>
</tr>
<tr>
<td>6</td>
<td>Mo₂S₆+3Sm</td>
<td>0.80</td>
<td>-1.52</td>
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<td></td>
<td>-19679.2</td>
<td>-2495.1</td>
</tr>
<tr>
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<td>-2496.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.97</td>
<td></td>
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<td>-2497.3</td>
</tr>
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<td></td>
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<td>-0.95</td>
<td></td>
<td>-19679.2</td>
<td>-2495.9</td>
</tr>
<tr>
<td>7</td>
<td>Mo₂S₆+2Sn+Sm</td>
<td>0.71</td>
<td>-1.48</td>
<td>2.21</td>
<td>0.33</td>
<td>-19678.6</td>
<td>-2497.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.80</td>
<td>-1.02</td>
<td>3.01</td>
<td>1.1</td>
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</tr>
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<td></td>
<td></td>
<td></td>
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<td>-0.84&lt;sub&gt;cluster&lt;/sub&gt;</td>
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<td>-2497.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.95&lt;sub&gt;(Sm)&lt;/sub&gt;</td>
<td>-1.39&lt;sub&gt;(Sm)&lt;/sub&gt;</td>
<td>-19678.6</td>
<td>-2497.3</td>
</tr>
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<td></td>
<td></td>
<td>-1.48&lt;sub&gt;(Sn)&lt;/sub&gt;</td>
<td>-1.51&lt;sub&gt;(Sn)&lt;/sub&gt;</td>
<td>-19678.6</td>
<td>-2496.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.50&lt;sub&gt;(Sn)&lt;/sub&gt;</td>
<td>-1.51&lt;sub&gt;(Sn)&lt;/sub&gt;</td>
<td>-19678.6</td>
<td>-2496.2</td>
</tr>
</tbody>
</table>

The charge of the Mo atom on the Mo edge is less affected by the coordination sphere (number of atoms and type of coordination) than that of Mo on the S edge. By adding S atoms to the Mo edge the E(Mo1s) of Mo moves down. For the S edge the number of the S atoms coordinated to Mo varies from six (perfect surface structure) to four (counting the sulfur atoms from the third layer below the surface) and removing S atoms moves the E(Mo1s) up. However, for the four-coordinated Mo, the coordination changes from trigonal prismatic through five-coordinated to distorted tetrahedral and concurrently the charge decreases. In addition, the charge of the Mo atoms of the S edge facing each other and not sharing a surface S atom is further reduced because of the repulsive interaction.
Table 5.3b. S edge – Mulliken charges and energies of the core levels for Mo and in eV. The first value of Q(S) for a certain structure N refers to the bottom sulfur layer, the second value to the top sulfur layer, and further values to the surface sulfur atoms.

<table>
<thead>
<tr>
<th>N</th>
<th>cluster</th>
<th>Q (Mo)</th>
<th>Q (S)</th>
<th>Q (Mo) - MP2</th>
<th>Q (S) - MP2</th>
<th>E (Mo1s)</th>
<th>E (S1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoS₂ bulk</td>
<td>0.87</td>
<td>-0.43</td>
<td>3.36</td>
<td>-1.18</td>
<td>-19684.9</td>
<td>-2481.7</td>
</tr>
<tr>
<td>2</td>
<td>MoS₂ bulk</td>
<td>0.88</td>
<td>-0.30</td>
<td>3.24</td>
<td>-1.08</td>
<td>-19688.4</td>
<td>-2498.6</td>
</tr>
<tr>
<td>3</td>
<td>MoS₆ surf</td>
<td>-1.20</td>
<td>-0.62</td>
<td>2.45</td>
<td>-0.29</td>
<td>-19658.6</td>
<td>-2497.8</td>
</tr>
<tr>
<td>4</td>
<td>MoS₆-1S</td>
<td>-0.96</td>
<td>-0.69</td>
<td>2.52</td>
<td>-0.29</td>
<td>-19681.1</td>
<td>-2500.2</td>
</tr>
<tr>
<td>5</td>
<td>MoS₆-1S</td>
<td>-0.52</td>
<td>-0.71</td>
<td>2.50</td>
<td>-0.03</td>
<td>-19680.8</td>
<td>-2500.2</td>
</tr>
<tr>
<td>6</td>
<td>MoS₆-2S</td>
<td>-0.93</td>
<td>-1.48</td>
<td>2.45</td>
<td>-1.22</td>
<td>-19680.5</td>
<td>-2500.2</td>
</tr>
<tr>
<td>7</td>
<td>MoS₆-2S</td>
<td>-2.28</td>
<td>-0.87</td>
<td>-1.96</td>
<td>-0.56</td>
<td>-19681.9</td>
<td>-2497.3</td>
</tr>
<tr>
<td>8</td>
<td>MoS₆-2S</td>
<td>-1.46</td>
<td>-0.56</td>
<td>1.25</td>
<td>-0.05</td>
<td>-19681.9</td>
<td>-2497.3</td>
</tr>
<tr>
<td>9</td>
<td>MoS₆-3S</td>
<td>2.85</td>
<td>-1.83</td>
<td>3.65</td>
<td>-1.93</td>
<td>-19674.0</td>
<td>-2497.8</td>
</tr>
<tr>
<td>10</td>
<td>MoS₆-3S</td>
<td>-1.78</td>
<td>-0.87</td>
<td>1.75</td>
<td>-1.80</td>
<td>-19680.3</td>
<td>-2498.9</td>
</tr>
<tr>
<td>11</td>
<td>MoS₆-3S</td>
<td>-0.67</td>
<td>-1.41</td>
<td>2.66</td>
<td>-1.19</td>
<td>-19681.4</td>
<td>-2497.3</td>
</tr>
<tr>
<td>12</td>
<td>MoS₆-3S</td>
<td>-2.44</td>
<td>-0.89</td>
<td>2.15</td>
<td>-1.89</td>
<td>-19680.8</td>
<td>-2500.2</td>
</tr>
<tr>
<td>13</td>
<td>MoS₆-3S</td>
<td>-1.56</td>
<td>-1.53</td>
<td>0.97</td>
<td>-0.07</td>
<td>-19681.1</td>
<td>-2497.0</td>
</tr>
<tr>
<td>14</td>
<td>MoS₆-3S</td>
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<td>-1.16</td>
<td>-1.22</td>
<td>-0.07</td>
<td>-19680.5</td>
<td>-2497.0</td>
</tr>
<tr>
<td>15</td>
<td>MoS₆-3S</td>
<td>-2.02</td>
<td>-0.87</td>
<td>1.32</td>
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<td>-19681.1</td>
<td>-2497.0</td>
</tr>
<tr>
<td>16</td>
<td>MoS₆-3S</td>
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<td>-1.22</td>
<td>-0.19</td>
<td>-19680.5</td>
<td>-2497.0</td>
</tr>
</tbody>
</table>

5.4.4 Electrostatic potential maps (EPM)

The topology of the electrostatic potential generated by the Mo edge surface, the S edge surface, and the different defects studied in this work is shown in the maps presented in Figures 5.4 (Mo edge) and 5.5 (S edge). They correspond to planes parallel to the (10\text{\textbar}0\text{\textbar}0) face positioned 0.6 Å above the surface and cutting a single slab (3x1 surface cell) from the edge (on the right hand side of the figures). Figures 5.4 and 5.5 refer also to planes parallel to the basal plane, perpendicular to the MoS₂ edge and containing the metal atoms (4x1 cell) (left hand side). Consecutive isopotential lines differ by 0.02 a.u. Positive densities are represented by continuous and negative densities by dashed lines. Furthermore we will focus on the EPM of the defects with low energy formation that could play an essential role in the restructuring.
of the (10\bar{1}0) edge and in the possible reactions of the MoS$_2$ edge with small molecules. The most important features of the defects are:

1. The potential generated by the defects on the S edge is spatially more extended than that of the corresponding relaxed (10\bar{1}0) surface (Mo and S edge respectively). This is most likely due to the destruction of the surface S–S pairs. The potential generated by the Mo edge and defects created on the Mo edge by addition of S atoms is more short-ranged (less extended) than that obtained for the defect sites on the S edge.

2. Addition of S atoms to the Mo edge changes the electrostatic potential of the surface. The lobes of the potential generated for clusters 5, 6, 7 on the Mo edge do not point perpendicular to the (10\bar{1}0) face as for the "as-cleaved" MoS$_2$ surface.

3. The defect creation by the removal of S atoms from the S edge leads to significant distortion of the electrostatic potential. The lobes of the potential generated for clusters 6, 7, 9, 10 and 12 representing defects on the S edge do not point perpendicular to the (10\bar{1}0) face. Moreover, for several sites (defects) on the S edge (8, 9 and 13) the generated potential exhibits nodes (boundary regions between neighbouring positive and negative densities), where most probably heterolytic dissociation of molecules such as H$_2$ might take place. This feature is not observed in the potential generated by the periodic solution of the (10\bar{1}0) MoS$_2$ surface.

These results demonstrate the importance of the defects in determining the reactivity of the (10\bar{1}0) edge surface. The directionality of the lobes and the presence of nodes of the electrostatic potential suggest that the physisorption of small, polarizable molecules could preferentially take place on certain defects and at different angles relative to the surface. The models for adsorption of small molecules should take into account the interaction of these molecules with the field generated by the defects. Even in the case of strongly chemisorbed molecules, the reaction path and the final geometry may be affected significantly by the electrostatic potential by the defect.
Fig. 5.4. Electrostatic potential maps of the defects on the Mo edge. The numbering refers to the numbering in Table 5.2a.
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3. Mo\textsubscript{2}S\textsubscript{6} surf

4. Mo\textsubscript{2}S\textsubscript{6-1S}

5. Mo\textsubscript{2}S\textsubscript{6-1S}

6. Mo\textsubscript{2}S\textsubscript{6-2S}
Fig. 5.5. Electrostatic potential maps of the defects on the S edge. The numbering refers to the numbering in Table 5.3a.
5.5 Conclusion

It was shown that the \textit{ab-initio perturbed cluster method} can be used to investigate the properties of the (10\overline{1}0) and (10\bar{1}0) edges of MoS$_2$ and the defects formed on the surface by removal or addition of S atoms. The energetics and the electronic properties of these defect structures as well as the low coordinated sites on the Mo edge modelled by S adatoms adsorbed on the (10\overline{1}0) face of MoS$_2$ were investigated.

The PC method predicts the properties of the bulk and the (10\overline{1}0) surface of MoS$_2$ correctly. Using second order perturbation corrections (MP2) to the calculated energy we find a fundamental gap of 0.8 eV for bulk MoS$_2$ and a metallic (10\overline{1}0) surface due to an overlap of the highest occupied orbitals from the Mo edge and lowest empty orbitals of the S edge. Comparing this result with the periodic DFT calculations it was concluded that the latter do not underestimate the fundamental gap.

The removal of S atoms from the MoS$_2$ S edge destabilizes the microcrystalline and electronic edge structure and generates a significant electrostatic potential. Lattice relaxation of the investigated Mo$_2$S$_6$ model clusters produced structures containing S atoms on the Mo plane and reduced the surface energy and the destabilizing effect of low-coordinated sites. These structures closely reproduce the properties of restructured (100) edges of the single-layer MoS$_2$ particles.

The bare Mo edge also destabilizes the microcrystalline structure and generates a significant electrostatic potential. For model clusters simulating the Mo edge and defects obtained by addition of S atoms to the edge surface the regular coordination (S atoms in normal positions) is energetically preferred. However, the surface energies for the cluster structures with relaxed S atoms occupying sites on the metal atoms plane may also exist on that surface.

The electrostatic potential generated by defects on the (100) MoS$_2$ edge is expected to affect the reactivity of the defective surface and to determine the adsorption of small molecules. The reactivity of these defective sites differs from that of the bare (100) MoS$_2$ surface. We attribute the enhanced reactivity of the defects to the anisotropy in the electrostatic potential. The presence of "nodes" in the surface electrostatic potential suggests that the adsorption of small polarizable molecules would preferentially take place in the vicinity of certain defects.
5.6 References


6.1 Abstract

Synchronous transit methods for localizing transition-state structures are used to study the adsorption of \( \text{H}_2 \) on the surface of MoS\(_2\). The computational procedure is based on a combination of the linear and quadratic synchronous transit methods with a conjugate gradient refinement of the saddle point. The hydrogen dissociation on the (100) surface of MoS\(_2\) is studied by starting with an \( \text{H}_2 \) molecule above the S- or Mo-terminated edge surface and ending with adsorbed hydrogen atoms on different surface sites. The calculations demonstrate that the energy barrier is significantly lower when the dissociation of \( \text{H}_2 \) takes place on the Mo-terminated edge of MoS\(_2\).

6.2 Introduction

Transition-state structures and equilibrium geometries are the key elements to understanding chemical reactivity. Quantum-chemical methods based on a computational approach, by which transition states can be localized on the respective potential energy surface with acceptable accuracy, have advanced rapidly during the last decade [1,2]. Two principle types of methods exist, namely walking and interpolation algorithms. Surface walking methods determine the products of a given reactant configuration by exploring the potential energy surface using the local gradient and the Hessian matrix. These algorithms are
often inaccurate in the case of bimolecular reactions and unimolecular systems with more than one low frequency-vibrational mode [3].

Very promising methods for localizing transition states are the first derivative-based nudged elastic band method and the growing string method, which belong to the interpolation algorithms [4]. Both methods detect the complete minimum energy path between two configurations, i.e. the reactant and the product of a chemical reaction. Both methods focus on the optimization of the geometries of several states along the reaction path, but the growing string method is more efficient [5,6]. The nudged elastic band method has been used to study the adsorption and activation of hydrogen on the catalytically active surface of MoS₂ [7,8].

Methods, which enable characterization of the transition state of a given chemical reaction, are important for understanding its mechanism. Halgren and Lipscomb proposed such a method, based on linear (LST) and quadratic synchronous transit (QST) calculations [9]. In order to refine the intermediates found by the LST/QST method conjugate gradient (CG), minimization schemes, as proposed by Bell and Crighton [10] and Fischer and Karplus [11], were added. The LST method was originally applied to model two-dimensional energy surfaces and electrocyclic interconversions of the cyclopropyl and allyl cations as well as of cyclobutadiene and cis-butadiene [9]. Later, the generalized synchronous transit method was extended to periodic systems, and Govind et al. applied it to study the ZrCl₄ dissociation on a Si (100) surface [12]. The LST/QST method, as implemented in the DMol³ code (Accelrys Material Studio 2.1), was used to study methanol conversion to hydrocarbons in zeolite catalysts and the oxidative dehydrogenation of ethanol [13,14].

The aim of this chapter is to describe the LST/QST method, combined with a CG refinement of the saddle point and to apply it to the activation of hydrogen on the (100) surface of MoS₂. Hydrogen activation on MoS₂ surfaces is crucial step for hydroprocessing of oil distillates, which is one of the most important industrial applications of heterogeneous catalysis. First, technical details of the computational procedure and the model of MoS₂ used in the calculations are present. Then follows a discussion on the energetics and structures along the reaction path of the H₂ dissociation.
6.3 Computational details

The DFT calculations were carried out using the DMol³ program of Accelrys (Material Studio 2.1) [15,16]. To localize the transition states, the traditional LST/QST methods proposed by Halgren and Lipscomb [9] in combination with the CG minimization algorithms of Bell and Crighton [10] and Fischer and Karplus [11] were used. First, the energies of the reactant and the product structures are computed. Using these two energy points, a search is made for the maximum along the LST path. Once the maximum is found, a CG optimization of the structure is performed. If the residual forces on the atoms fall below a specified tolerance (see below), the calculation is considered to have converged and is analyzed further. Otherwise a new maximum is looked for along the QST path. A new CG optimization cycle is then initiated until convergence is achieved. The calculated energy of the barrier ($\Delta E_{\text{barrier}}$) is the highest maximum on the minimum energy path and is taken relative to the initial state.

The investigated model of the (100) MoS₂ surface consists of two MoS₂ sheets in the z direction, six planes of alternating S and Mo atoms in the y direction and two Mo atoms in the x direction (thickness of 6 Å), separated by a vacuum layer of 9 Å (Figs. 6.1 and 6.2). Chapter 4 showed that this model correctly represents the properties of the catalytically active (100) surface of the MoS₂.

Effective core potential calculations were performed, in which the core electrons of S ($1s^2, 2s^2p^6$) and Mo ($1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6$) are represented by a weak pseudo-potential. A basis set, which is composed of two numerical functions per valence orbital, supplemented with a polarization function, was used. Each basis function was restricted to a volume with a cut-off radius of 5.5 Å, allowing efficient calculations without loss of accuracy. A combination of the local density approximation, to specify the exchange-correlation local potential [17] and corrected in the high- and low-density expansions, as proposed by Perdew and Wang [18] was used. The Brillouin zone integration was performed with a Monkhorst-Pack grid [19] at a k-point set of 3x2x1. The charge density mixing was 0.2. A thermal smearing of 3 kcal/mol was applied to the orbital occupation. Geometry optimization convergence thresholds of 0.01 kcal/mol, 2.5 kcal/mol, and 0.005 Å were used between the optimization cycles for the energy change, maximum force and maximum displacement, respectively.
6.4 Results and Discussion

The LST/QST method was applied to the dissociation of H₂ on the (100) surface of MoS₂, which is known to be the catalytically active. The (100) MoS₂ surface exhibits two types of edges, which expose either unsaturated molybdenum atoms or sulfur atoms, the so-called Mo-terminated and S-terminated edges (see Fig. 6.2, image a).

As mentioned above, the main effort of the nudged elastic band method is directed towards optimizing geometries of several points along the assumed reaction path. Since the aim is an accurate localization of transition states, the LST/QST method combined with a CG refinement of the saddle point is the method of choice. To determine the transition state the structures of the initial and the final states are necessary. In the calculations, the initial state is always an H₂ molecule located above the surface of MoS₂. For the final state two different structural situations were considered, namely one with two equivalent S-H bonds on the S edge (Fig. 6.1, image c) and another with one Mo-H bond on the Mo edge and one S-H bond on the S edge (Fig. 6.2, image d).

![Energy diagram](image)

**Fig. 6.1.** Energy versus a generalized reaction coordinate $\rho$ for H₂ dissociation with formation of two S-H bonds. Reaction path images: a-e. Image c represents the transition state. The MoS₂ structure is shown in the xy plane. The white spheres are the hydrogen atoms, the light grey spheres the sulfur atoms and the dark grey spheres the molybdenum atoms.
These final states represent the products of the homolytic and the heterolytic splitting of H₂ over MoS₂. Homolytic splitting occurs on two surface sulfur atoms of the S-terminated edge, while heterolytic splitting takes place on the Mo-terminated edge and is accompanied by the transfer of one of the hydrogen atoms to the S-terminated edge. To calculate the homolytic splitting, an H₂ molecule was located above the S-terminated edge of MoS₂ at a distance of z = 3 Å (the sum of the van der Waals radii of hydrogen and sulfur, r_H = 1.20 Å, r_S = 1.80 Å), which decreased to z = 2.807 Å after relaxation (Fig. 6.1, image a). The final state was as described above (Fig. 6.1, image e). Fig. 6.1 shows the reaction path images and energies during the search for the transition state between the selected initial and final states.

First, an LST + CG1 calculation was performed. Following a QST1 + CG2 calculation, a point with the lowest energy on the reaction path was found at ρ = 3. However, at that point the residual force is 4.5 kcal/mol.Å. This did not satisfy the convergence criteria of 2.5 kcal/mol.Å and, therefore, the computation was continued. The transition state with a reaction coordinate ρ = 5.5 was found after the QST2 path combined with the CG3 refinement of the saddle point. As required, the transition state was characterized by only one negative frequency (νTS = -1411 cm⁻¹). The transition state had the following geometry: d (H-H) = 1.805 Å and d (S₁-H₁) = 2.114 Å and d (S₂-H₂) = 2.155 Å (Fig. 6.1, image e). The energy of the barrier, which is the energy difference between the initial and the transition state, was ΔE_barrier = 67.5 kcal/mol and the reaction was endothermic with ΔH = 43.4 kcal/mol.

The energy barrier of 67.5 kcal/mol is rather high. Reactions with a barrier of about 20 kcal/mol or less usually proceed readily at room temperature, while reactions with activation energies higher than 50 kcal/mol are typically high-temperature gas phase reactions. Therefore, the calculations show that spontaneous dissociation does not occur on the S-terminated edge. In order to find a path with a lower energy barrier the metal edge was also taken into account by a closer look at the heterolytic splitting.

An H₂ molecule was placed at z = 3 Å above the Mo-terminated edge (about the sum of the van der Waals radii of hydrogen and molybdenum), which relaxed to z = 2.513 Å in the configuration of the initial state (Fig. 6.2, image a). The final state consisted of one Mo-H and one S-H species (Fig. 6.2, image d). Fig. 6.2 shows the reaction path images and energies during the transition state search between the selected initial and final states. Compared to the calculation shown in Fig. 6.1, the transition state search was more complicated. The transition state with a reaction coordinate ρ = 7 was found after a LST path and a QST path combined.
with a conjugate gradient refinement. After the LST + CGI calculation, a lowest energy point was found ($\rho = 2.5$). The residual force at this point was 5.5 kcal/molÅ, therefore, the calculation was continued until convergence. After a QST search a structure was found with higher energy than that obtained from the LST optimization (Fig. 6.2, image b). However, the subsequent CG2 refinement found the transition state (Fig. 6.2, image c), which was characterized by only one negative frequency ($v_{TS} = -480$ cm$^{-1}$). The images show that the maximum obtained with the LST (image b) represents the H$_2$ bond breaking and the formation of the Mo-H bond. Image c represents the transition state, where the S-H bond is formed. The reaction was exothermic with $\Delta H = -3.3$ kcal/mol, and the energy of the barrier was considerably reduced to 18.1 kcal/mol. The transition state had the following interatomic distances: $d$(H-H) = 3.168 Å, $d$(S-H) = 2.722 Å and $d$(Mo-H) = 1.992 Å. Therefore, considering the low energy of the barrier, H$_2$ dissociation is possible when the Mo-terminated edge is involved in the process of the H$_2$ dissociation.

Fig. 6.2. Energy versus a generalized reaction coordinate $\rho$ for H$_2$ dissociation with formation of a S-H and a Mo-H bonds. Reaction path images: a-d. Image c represents the transition state. The MoS$_2$ structure is shown in the yz plane. The white spheres are the hydrogen atoms, the light grey spheres the sulfur atoms and the dark grey spheres the molybdenum atoms.
6.5 Conclusion

These results show that the LST/QST method can be used successfully to investigate the dissociation of H₂ on the (100) MoS₂ edge structure. A significantly higher energy barrier for the homolytic splitting of H₂ over the S-terminated edge than for the heterolytic splitting on the Mo-terminated edge was calculated. Therefore, H₂ dissociation on the S-terminated edge requires high temperature, whereas on the Mo-terminated edge spontaneous H₂ dissociation is possible.

6.6 References

Chapter 7

Reactions of \( \text{H}_2 \) on unpromoted and Co- or Ni-promoted (100) 2H-MoS\(_2\) surfaces

7.1 Abstract

Hydrogen activation on the (100) surface of unpromoted and promoted MoS\(_2\) structures was investigated by means of periodic DFT calculations. Several reaction pathways starting with an \( \text{H}_2 \) molecule above the MoS\(_2\) surface and ending with hydrogen atoms adsorbed on different surface sites were calculated. The calculations include heterolytic and homolytic dissociation of hydrogen, i.e., an \( \text{H}_2 \) molecule dissociates on a MoS\(_2\) catalyst surface into two hydrogen atoms, which react further with the catalyst surface under formation of one Mo-H and one S-H (heterolytic) or of two S-H surface groups (homolytic). The results favour heterolytic hydrogen adsorption. The transition state of these processes can be determined by using the LST/QST method, if the \( \text{H}_2 \) molecule is at a distance above the surface that corresponds to the sum of the van der Waals radii of hydrogen and molybdenum or sulfur. For the Co and Ni promoter atoms several differences were observed. If an Mo atom of the metal edge is replaced by a Co or Ni atom, the heterolytic dissociation of \( \text{H}_2 \) becomes slightly endothermic and has a higher adsorption barrier than on the unpromoted MoS\(_2\) surface. Replacing an Mo atom of the S-terminated edge by a Co or Ni atom (Mo/Co(Ni) = 1/1) led to different effects. While Co enhanced the hydrogen splitting, Ni had no significant influence.
Chapter 7

7.2 Introduction

Hydrodesulfurization of oil fractions by transition-metal sulfides is one of the most important catalytic processes in industry [1]. The demand to reduce the sulfur content in feed stocks increases the need for more active catalysts and more efficient processes. This led to a significant amount of research aimed at characterizing the catalyst structure and the nature of the surface active sites. There is a great interest in reactions taking place on the (100) 2H-MoS₂ surface, which is known to be the catalytically active surface. The dissociation and adsorption of small sulfur-containing molecules on metal sulfides are poorly described compared to the dissociation and adsorption reactions on metal surfaces. Even for a process as simple as the adsorption of hydrogen on the (100) surface of 2H-MoS₂, important questions are still unanswered: Where and how does the dissociation of H₂ occur? Which surface structures form after the adsorption of hydrogen, and how do they act when sulfur-containing molecules approach the surface?

There have been several attempts to explain the adsorption and reaction of hydrogen on the (100) MoS₂ surface. Byskov et al. used a simple model (MoS₂ chains with and without promoter atoms at edge positions) to represent adsorption sites on the catalyst surface [2]. From density functional (DFT) calculations, they found that hydrogen adsorbs strongly on sulfur edge atoms, which suggests that the S-terminated edge is partially covered with SH groups during the catalytic process [3]. Travert et al. performed periodic DFT calculations to investigate the hydrogen adsorption process on unpromoted and Co and Ni-promoted MoS₂ (100) surfaces under HDS working conditions [4]. They concluded that hydrogen dissociation is always endothermic and has a high activation barrier. According to their calculations Co, as a promoter lowers the energy barrier of the activation of molecular hydrogen and increases the ability of neighbouring sulfur atoms to bind hydrogen. DFT calculations by Cristol et al. showed that the endothermic dissociation of hydrogen on the MoS₂ catalyst surface leads to Mo-H and S-H groups [5,6]. The finding that the dissociation of hydrogen is endothermic implies that hydrogen is not stable on the MoS₂ surface unless at very high pressure and very low temperature. Calculations by Anderson et al. [7] with the atom superposition and electron delocalization molecular orbital theory were in favour of heterolytic hydrogen dissociation. They concluded that heterolytic chemisorption at the edges of the crystal layers is the most stable type of chemisorption. According to their results H₂MoS₂ should be a conducting
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bronze. Hydrogen dissociation on a MoS$_2$ catalyst surface may thus occur by heterolytic dissociation, yielding Mo-H and S-H species, as well as homolytic dissociation, resulting in the formation of two SH groups. Neutron diffraction data of MoS$_2$ based catalysts supported the idea that hydrogen is bonded to one or more sulfur atoms rather than to metal atoms [8].

Up to now, only one investigation has used transition state theory to describe reactions occurring on the MoS$_2$ surface by using the nudge elastic band method as implemented in the VASP code. The calculations focused mainly on the activation energies of the adsorption and desorption of $H_2$ as well as on the formation and desorption of $H_2S$ in relation to a mechanism of vacancy formation [9].

The aim of this work is to study the process of hydrogen activation on the (100) surfaces of unpromoted and promoted MoS$_2$ structures, by periodic DFT calculations with the DMol$^3$ code [10,11]. The computational procedure and the linear/quadratic synchronous transit method that were used to determine the transition state were explained in Chapter 6. The energetical and structural properties of the surface models before and after $H_2$ dissociation are discussed and compared with recently published results. Several reaction pathways, starting with an $H_2$ molecule above the surface and ending with adsorbed hydrogen atoms on different surface sites are proposed. In the cases, where the transition state was found, the transition-state geometry is presented as well.

### 7.3 Computational Details

The DFT calculations were carried out using the DMol$^3$ program from Accelrys (Material Studio 2.1) [10,11]. The computational details and the model of the surface were given and discussed in Chapter 6.

Two types of distances between an $H_2$ molecule and the MoS$_2$ surface were considered: i) $z = 4.5 \text{ Å}$. This large distance gives an energy barrier of about 110 kcal/mol, which is close to the dissociation energy of the $H_2$ molecule (104 kcal/mol). At this large distance, the molecule is isolated and does not interact with the surface. ii) $z = 3 \text{ Å}$. This distance was used in addition to $z = 4.5 \text{ Å}$ to investigate the adsorption of $H_2$ on the S edge of promoted MoS$_2$, because it is close to the sum of the van der Waals radii of the surface atoms.
and the hydrogen. The calculated energy of the barrier ($\Delta E_{\text{barrier}}$) is taken relative to the initial state. This barrier energy differs from the experimental $E_{\text{act}}$ value, where the reference state is at infinity.

As mentioned before, the initial and final structures are needed to determine the transition state with the LST/QST method. Two final structures were chosen: the first with a Mo-H bond on the Mo edge and a S-H bond on the S edge and the second with two equivalent S-H bonds on the S edge. With these final structures one still has to determine the minimum energy pathway.

7.4 Results

7.4.1. Unpromoted MoS$_2$

Adsorption of H$_2$ involving the Mo and S edge of the (100) MoS$_2$ surface. The initial state of H$_2$ adsorption was selected with a distance of 4.5 Å between hydrogen and the Mo-terminated edge ($z = 4.306$ Å after relaxation). The $d$(H-H) value of the H$_2$ molecule after relaxation was 0.696 Å (Fig. 7.1a). The final state consisted of one Mo-H and one S-H bond with $d$(Mo-H) = 1.732 Å and $d$(S-H) = 1.325 Å, respectively (Fig. 7.1d). The surface structures were relaxed before we started calculating the adsorption. The adsorption of H$_2$ in the form of two hydrogen atoms was found to be exothermic with $\Delta H = -1.4$ kcal/mol. However, the dissociation required 110.9 kcal/mol ($\Delta E_{\text{barrier}} = E_{\text{dissociation}}$). The transition point of this reaction path is characterized by two negative frequencies. One of the vibrations represents the splitting of H$_2$ and the other the bonding of the hydrogen atoms to the surface. The high value of the activation energy and the presence of two negative frequencies indicate that the calculated reaction pathway does not correctly represent the experimental pathway. Therefore, another initial state was considered. The activation energy decreased when the H$_2$ molecule was brought close to the surface, from 3 Å to 2.513 Å (Fig. 7.1b), and was then dissociated into two hydrogen atoms with subsequent adsorption on two adjacent edges. The transition state and the activation energy barrier were found by interpolating the energies and forces between the reaction coordinates (LST/QST), followed by refining the estimate with the CG method, reducing the energy barrier to 18.1 kcal/mol, as shown in Chapter 6. The reaction stayed exothermic with $\Delta H = -3.3$ kcal/mol. A transition state with the interatomic
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distances $d(H-H) = 3.168 \text{ Å}$, $d(S-H) = 2.722 \text{ Å}$ and $d(Mo-H) = 1.992 \text{ Å}$ and with one negative frequency ($v_{TS} = -480 \text{ cm}^{-1}$) was found.

The energy barrier of the adsorption of $H_2$ on the Mo-terminated edge apparently depends on the reaction path. When the $H_2$ molecule was brought to $2 \text{ Å}$ above one of the undercoordinated Mo atoms of the Mo-terminated edge it relaxed to $z = 1.798 \text{ Å}$ above the surface (the sum of the covalent radii of hydrogen and molybdenum is $1.82 \text{ Å}$ [12]). In this state $d(H-H)$ increased to $2.255 \text{ Å}$ and the molecule dissociated (Fig. 7.1c). Further transfer of one of the hydrogen atoms to a sulfur atom of an adjacent S edge is endothermic with $\Delta H = 29.4 \text{ kcal/mol}$ and $\Delta E_{\text{barrier}} = 78.8 \text{ kcal/mol}$. The overall adsorption process of $H_2$ via this
pathway, i.e. dissociation of H$_2$ over the Mo edge and transfer of one hydrogen atom to an S atom of the S edge has $\Delta H = -1.3$ kcal/mol. These results demonstrate that the adsorption of H$_2$ on two (100) MoS$_2$ edges following the reaction path described initially should be energetically favoured over the reaction path, which passes through a state where hydrogen is adsorbed and split on Mo atoms of the Mo edge (a local minimum of the potential energy surface) and a hydrogen atom is transferred to a sulfur atom of the S edge. Details about the hydrogen dissociation on the Mo and S-terminated edges are given in Table 7.1.

**Table 7.1. Heterolytic dissociation of H$_2$ on the Mo and S-terminated MoS$_2$ surface.**

<table>
<thead>
<tr>
<th>Fig. 7.1 a/d</th>
<th>Fig. 7.1 b/d</th>
<th>Fig. 7.1 c/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(H-H), Å</td>
<td>0.696</td>
<td>0.740</td>
</tr>
<tr>
<td>z(H$_2$- surface), Å</td>
<td>4.304</td>
<td>2.513</td>
</tr>
<tr>
<td>E$_{\text{reactant, Ha}}$</td>
<td>-10346.432</td>
<td>-10346.429</td>
</tr>
<tr>
<td>E$_{\text{product, Ha}}$</td>
<td>-10346.434</td>
<td>-10346.434</td>
</tr>
<tr>
<td>E$_{\text{trans. state, Ha}}$</td>
<td>-10346.255</td>
<td>-10346.401</td>
</tr>
<tr>
<td>$\Delta H$, kcal/mol</td>
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<td>-3.3</td>
</tr>
<tr>
<td>$\Delta E_{\text{barrier, kcal/mol}}$</td>
<td>110.9</td>
<td>18.1</td>
</tr>
</tbody>
</table>

* In this case this is d(Mo-H$_1$), since the H$_2$ molecule is split

Cristol et al. [5,6] and Travert et al. [4] calculated the heterolytic hydrogen dissociation with the VASP package. They only considered Mo atoms coordinated to six or five sulfur atoms. Cristol et al. [5,6] found that the dissociation of H$_2$ is always endothermic, with the heterolytic dissociation of hydrogen on a metal-sulfur pair as the most favourable configuration. Travert et al. [4] found two stable geometries, one with Mo-H and S-H bonds and one with two Mo atoms connected by one hydride, i.e., an Mo-H-Mo surface species. The latter geometry results from an exothermic hydrogen splitting ($\Delta H = -2.3$ kcal/mol). The present results reveal that on two four-coordinated metal centres and an S atom from the neighbouring S edge of the (100) MoS$_2$ surface, the heterolytic hydrogen dissociation and adsorption is also possible. Moreover, another reaction pathway is possible as well. It is energetically more demanding but still exothermic (gives 0.1 kcal/mol less) and involves dissociation of the H$_2$ molecule on the Mo edge and transfer of one of the hydrogen atoms to the S edge with the formation of an S-H bond.

**Homolytic dissociation of H$_2$ on the S-terminated edge.** The S-terminated edge of the (100) MoS$_2$ is characterized by the presence of S-S couples [2,3,13], which form upon...
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surface relaxation as a result of the local interaction of S atoms attached to surface Mo sites [14]. The formation of such weakly coupled $S_2$ species is also observed in the present calculations: $d(S^1-S^2) = 3.141 \, \text{Å}$, $d(S^1-S^3) = 3.177 \, \text{Å}$ (Fig. 7.2a). It was found that hydrogen atoms preferably bind to these S-S couples on the S edge of the MoS$_2$ structure [13]. The present study focuses on the mechanism of the splitting of the $H_2$ molecule, using the already known final configurations. The dissociative adsorption of hydrogen on one $S_2$ group should be homolytic since the resulting two S-H fragments are practically equivalent.

An $H_2$ molecule with $d(H-H) = 0.74 \, \text{Å}$ and $z = 4.5 \, \text{Å}$ with respect to the S-terminated edge as the initial state was chosen as an initial state. The geometries of the initial and final structures were optimized, giving $d(H-H) = 0.696 \, \text{Å}$ and $z = 4.021 \, \text{Å}$ in the initial state and two S-H species with $d(S-H) = 1.338 \, \text{Å}$ in the final state (Figs. 7.2a and d). The structure of the final state is similar to that calculated with the CRYSTAL98 and FHI98md codes, where the following structural parameters: $d(S-H) = 1.4 \, \text{Å}$, $\angle Mo-S-H = 77^\circ$ (all-electron) and $d(S-H) = 1.36 \, \text{Å}$, $\angle Mo-S-H = 71^\circ$ (pseudo-potential) were obtained, respectively [13].

It was found that $H_2$ dissociates homolytically with $\Delta H = 43.4 \, \text{kcal/mol}$. The energy barrier of the adsorption is 67.5 kcal/mol, the geometry of the calculated transition state is $d(H-H) = 1.805 \, \text{Å}$, $d(S-H) = 2.114$ and 2.155 Å, $\nu_{TS} = -1411 \, \text{cm}^{-1}$. In this case, variation of the distance $z$ between the surface and the molecule did not influence the energetic profile of the reaction.

So far a local minima of the potential energy surface, which might play an essential role in relation to the energy barriers and the final structures as in the case of the adsorption of $H_2$ on the Mo and S edges was not found. The dissociation of $H_2$ on the S edge is thus endothermic.

When two hydrogen atoms were adsorbed on two sulfur atoms of the S edge of MoS$_2$ the reaction was found to be exothermic by $\Delta H = -78.6 \, \text{kcal/mol}$. For calculating this reaction path two hydrogen atoms with an interatomic distance of 2.754 Å were placed above the surface at a distance of 4.20 Å (Fig. 7.2c). This reaction is energetically more favourable than the $H_2$ adsorption on the S edge, for which $\Delta H = -70.8 \, \text{kcal/mol}$ was calculated as the sum of the energy gain of the $H_2$ association (-110.9 kcal/mol) and the energy loss to bring the hydrogen molecule to the surface (40.1 kcal/mol). This difference of 7.8 kcal/mol can be ascribed to the different initial structures (Figs. 7.1a and 7.2c). Thus the adsorption of two
hydrogen atoms on two sulfur atoms of the S-terminated edge is less likely to occur, if the H₂ molecule is split on the S edge.

Fig. 7.2. Homolytic hydrogen adsorption on the S-terminated edge of unpromoted MoS₂: a-c) initial states; d) final state.
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Table 7.2. Homolytic dissociation of $H_2$ on the S-terminated MoS$_2$ surface.

<table>
<thead>
<tr>
<th></th>
<th>Fig. 7.2a/d</th>
<th>Fig. 7.2 b/d</th>
<th>Fig. 7.2c/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d(H-H)$, Å</td>
<td>0.696</td>
<td>0.697</td>
<td>2.754</td>
</tr>
<tr>
<td>$z(H_2$-surface), Å</td>
<td>4.021</td>
<td>2.807</td>
<td>4.200</td>
</tr>
<tr>
<td>$E_{\text{reactant}}$, Ha</td>
<td>-10346.435</td>
<td>-10346.440</td>
<td>-10346.246</td>
</tr>
<tr>
<td>$E_{\text{products}}$, Ha</td>
<td>-10346.371</td>
<td>-10346.371</td>
<td>-10346.371</td>
</tr>
<tr>
<td>$E_{\text{trans. state}}$, Ha</td>
<td>-10346.334</td>
<td>-10346.333</td>
<td></td>
</tr>
<tr>
<td>$\Delta H$, kcal/mol</td>
<td>40.1</td>
<td>43.5</td>
<td>-78.6</td>
</tr>
<tr>
<td>$\Delta E_{\text{barrier}}$, kcal/mol</td>
<td>63.2</td>
<td>67.5</td>
<td></td>
</tr>
</tbody>
</table>

From the calculated results of the homolytic dissociation of hydrogen on the S-terminated edge of MoS$_2$, it is obvious that the formation of S-H species is energetically favourable if the hydrogen molecule is already split, such as on a hot tungsten filament — as was experimentally done by Lauritsen et al. [15]. If the $H_2$ molecule is in the vicinity of the surface, at about 4 Å, the dissociation is still possible and a transition state with only one negative frequency is found. On the S-terminated edge the dissociation energy barriers are not strongly dependent on the molecule-surface distance, which, together with the energy barrier of the transition state implies that a spontaneous dissociation does not occur on the S-terminated edge. Details of the energies of the reactant, products, transition state and geometry parameters are given in Table 7.2.

**Hydrogen-transfer from the Mo to the S-terminated edge.** The present calculations show that the homolytic hydrogen adsorption on the S-terminated edge is endothermic, while the heterolytic hydrogen adsorption on the Mo and S-terminated edges is exothermic. Starting with a heterolytic adsorption of $H_2$ (yielding a Mo-H and an S-H surface fragment), followed by a hydrogen transfer of the second hydrogen atom from the Mo-terminated to the S-terminated edge, $\Delta H = 39.9$ kcal/mol was found (to be compared with the previous calculations by taking two independent processes into account $40.1 + 1.4 = 41.5$ kcal/mol) and $\Delta E_{\text{barrier}} = 69.3$ kcal/mol (Figs. 7.1d → 7.2d). Thus, a reaction path passing through a local minimum on the potential energy surface on the Mo-terminated edge (with hydrogen split and adsorbed on the metal edge) is energetically more demanding. However, a hydrogen transfer along one of the edges is energetically less demanding and will be shown in Chapter 8. Travert et al. examined several pathways for surface diffusion of dissociated species from metal to metal and from sulfur to metal [4]. They reported an activation energy of 0.54 eV.
(12.5 kcal/mol) for these displacement steps on a single edge and pointed out that S-H groups are always created.

**H$_2$ on the Mo-edge with 50% sulfur coverage.** Previous DFT studies have shown that the (100) MoS$_2$ surface is thermodynamically stable during the catalytic reaction and that its sulfur coverage is different from the crystallographic, as-cleaved surface [4-6,17,18]. Formally, it could be considered that for each Mo atom one S atom is transferred from the S edge to the Mo edge.

![Fig.7.3](image_url)

**Fig.7.3.** Hydrogen adsorption on a Mo edge with 50% sulfur coverage: a) initial state; b) final state.

To simulate the structures of the edge in this state, calculations with the Mo edge with S atoms in bridging positions in such a way that the Mo centres are coordinated by six sulfur atoms and hydrogen was adsorbed on the bridging S atoms were performed as well. The structures before and after adsorption were optimized and had the geometries shown in Figs. 7.3a and 7.3b.

The reaction was found to be endothermic with $\Delta H = 32.1$ kcal/mol and $\Delta E_{\text{barrier}} = 89$ kcal/mol. The endothermic properties of the hydrogen dissociation on this surface may be due to the fact that the Mo centres are fully coordinated and that there are no coordinatively unsaturated sites anymore. Compared to the S-terminated edge, H$_2$ dissociation on a sulfided
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metal edge is more favourable, but still energetically more demanding than the dissociation and adsorption on both neighbouring edges. Cristol et al. also investigated the dissociative adsorption of hydrogen on sulfur atoms bound to two molybdenum atoms in bridging positions on a Mo edge with 50% sulfur coverage [5,6]. Dissociative adsorption of hydrogen on this edge was found to be an endothermic process, while the heterolytic dissociation of hydrogen yielding Mo-H and S-H surface species required less energy. Bollinger et al. [16] reported that the adsorption of the first hydrogen atom on a 50% sulfur-covered Mo edge is exothermic ($\Delta H = -6.9$ kcal/mol). This result differs from the present results. A possible explanation is that in the present study two hydrogen atoms were added simultaneously to the (100) surface to simulate the dissociation of hydrogen on the surface, while Bollinger et al. did this one by one [16]. Moreover, they used a single-sheet model, while a two-sheet model was used in the present calculations, which might have an influence on the results of the adsorption energies.

7.4.2. Promoted MoS$_2$

It is well known that adding Co or Ni can significantly increase the catalytic activity of MoS$_2$-type catalysts. For this reason cobalt and nickel are referred to as promoter atoms. The origin of the promotional effect as well as the precise location of the promoter atoms is still not yet completely known. Among the possible locations of the promoter atoms the most accepted ones are certain positions at the MoS$_2$ edges. According to Byskov et al. [3], Co promoter atoms replace Mo atoms on the S-terminated edge. Based on DFT calculations with the edge substitution model of periodic slabs Raybaud et al. found that the preferred location of Co promoter atoms is the Mo-terminated edge [17,18]. In a later study, Schweiger et al. combined DFT and thermodynamic calculations to simulate triangularly shaped Co(Ni)MoS$_2$ particles. There, Co showed a selective affinity to the S-terminated edge under intermediate sulfiding conditions, while the location of Ni was found to be critically dependent on the reaction conditions [19,20]. In order to take the effect of the promoter atoms on the hydrogen dissociation process into account similar calculations as in the case of the unpromoted MoS$_2$ structure were performed, where every second surface Mo atom is replaced by a promoter atom (Co or Ni). For the (2×1) surface super cell, one Mo and one promoter atom are exposed on the first or on the second row of the metal or the sulfur edge, respectively.
Promoters on the Mo-terminated edge of 2H-MoS$_2$ and their influence on the heterolytic hydrogen dissociation

Substitution of Mo by Co. Geometry optimization of the initial state of the reaction path yielded $d$(H-H) = 0.74 Å and $z$ = 4.927 Å (4.5 Å before optimization). The Co atom on the surface relaxes inward and as a result the distance between the surface and the molecule increased (Fig. 7.4a). The calculated atomic distances in the surface are $d$(Mo-S) = 2.43 Å (2.41 Å in the experimental geometry of the unrelaxed structure) and $d$(Co-S) = 2.23 Å. The final state of the reaction path had one Mo-H and one S-H bond (Fig. 7.4c). After relaxation the distances of the final state were $d$(Mo-H) = 1.732 Å (1.68 Å before relaxation) and $d$(S-H) = 1.325 Å (1.410 Å before relaxation). The energy of the adsorption process was $\Delta H = 11.8$ kcal/mol and $\Delta E_{\text{barrier}} = 111.1$ kcal/mol (showing no interaction of the surface with the molecule at the reference state $z$). The high value of the dissociation energy suggests the
existence of another path with a lower energy of the barrier and, as in the case of the unpromoted surface, a search for an appropriate transition state was done, after a closer approach of the H₂ molecule to the surface in the initial state (Fig. 7.4b) and subsequent adsorption on the neighbouring edges. A transition state characterized by νₜₛ = -1844 cm⁻¹ was found with the following geometry: d(H-H) = 1.781 Å, d(Mo-H) = 1.854 Å and d(S-H) = 4.213 Å. The overall reaction was endothermic with ΔH = 4.0 kcal/mol and ΔE_barrier = 49.6 kcal/mol. The energy barrier was almost three times higher than that of the unpromoted surface, with states with the same geometry. The calculated distances of the optimized structure in the final state were d(Mo-S) = 2.38 Å and d(Co-S) = 2.23 (2.26) Å, while in the initial state the corresponding metal-sulfur distances were d(Mo-S) = 2.41 Å and d(Co-S) = 2.41 Å.

While the heterolytic dissociation on the unpromoted surface was slightly exothermic, the heterolytic dissociation of H₂ on the Co promoted surface was slightly endothermic. This difference might be explained by the metal-sulfur bond strength: a replacement of one Mo by one Co atom reduces the metal-sulfur bond energy, which in turn enhances the strength of neighbouring Mo-S bonds. As a consequence, the bonding of H to Mo weakens and hence the thermodynamics of the H₂ dissociation becomes less favourable.

**Substitution of Mo by Ni.** The influence of nickel as a promoter on the H₂ adsorption reaction was investigated as well (Fig. 7.4d and e) by using a similar reaction path: a H₂ molecule was allowed to approach the surface from 4.5 Å to 2.5 Å (about the sum of the van der Waals radii of H and Mo) and then to dissociate. The reaction was found to be slightly endothermic with ΔH = 4.0 kcal/mol and ΔE_barrier = 59.2 kcal/mol (10 kcal/mol more than for Co-promoted MoS₂). The calculated energy is different from that of the unpromoted surface, where the dissociation of hydrogen and subsequent adsorption on neighbouring edges is an exothermic process. The structural parameters of the transition state are d(H-H) = 1.784 Å, d(Mo-H) = 1.794 Å, d(S-H) = 4.385 Å and νₜₛ = -822 cm⁻¹.

Results concerning the location of Ni promoter atoms reported in the literature show that the location is strongly dependent on the reaction conditions [20]. The present results show that replacing Mo by Ni on the Mo-terminated edge does not enhance the splitting of hydrogen, but increases the adsorption barrier compared to the unpromoted or even to the Co-promoted MoS₂ surfaces. Details are listed in Table 7.3.
Table 7.3. Heterolytic dissociation of H₂ on the promoted MoS₂ catalyst surface.

<table>
<thead>
<tr>
<th></th>
<th>Fig. 7.4 a/c (Co)</th>
<th>Fig. 7.4 b/c (Co)</th>
<th>Fig. 7.4 b/c (Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(H-H), Å</td>
<td>0.740</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>z(H₂- surface), Å</td>
<td>4.927</td>
<td>2.513</td>
<td>2.513</td>
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<tr>
<td>E_{reactants}, Ha</td>
<td>-10424.103</td>
<td>-10424.044</td>
<td>-10449.091</td>
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<tr>
<td>E_{products}, Ha</td>
<td>-10424.037</td>
<td>-10424.037</td>
<td>-10449.085</td>
</tr>
<tr>
<td>E_{trans. state}, Ha</td>
<td>-10423.926</td>
<td>-10423.965</td>
<td>-10448.997</td>
</tr>
<tr>
<td>ΔH, kcal/mol</td>
<td>11.8</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>ΔE_{barrier}, kcal/mol</td>
<td>111.1</td>
<td>49.6</td>
<td>59.2</td>
</tr>
</tbody>
</table>

Promoters on the S-terminated edge of 2H-MoS₂ and their influence on the homolytic hydrogen dissociation

**Substitution of Mo by Co.** The distance of the molecule to the surface was set to 3 Å in the initial state, because variation of z between 4.5 and 3 Å changed neither d(H-H) nor the energy. For the final state we took 2 S-H bonds formed on the S atoms directly bonded to the Co promoter atom. The reaction was calculated to be endothermic with a transition state characterized by two negative vibration frequencies and therefore another pathway was considered. Further relaxation of the H₂ molecule to the surface to 2.191 Å, reduced the interatomic distance to 0.700 Å (Fig. 7.5a) and a transition state with v_{TS} = -1073 cm⁻¹, d(H-H) = 0.84 Å, d(S¹-H) = 1.760 Å and d(S²-H) = 1.696 Å was found. For this reaction path the homolytic hydrogen dissociation over the surface S atoms is exothermic with ΔH = -3.5 kcal/mol, and an energy barrier of 26.6 kcal/mol (Figs. 7.5a and b). In the final state the optimized Co-S distances at the surface increased to d_{surf}(Co-S¹) = 3.083 Å and d_{surf}(Co-S²) = 2.196 Å, while the bulk Co-S distances were as follow: d_{bulk}(Co-S¹) = 2.226 Å and d_{bulk}(Co-S²) = 2.229 Å.

**Substitution of Mo by Ni.** The calculations were repeated with Ni as a promoter, following the reaction path discussed above for Co: starting with an H₂ molecule at 3 Å above the surface and ending with two S-H species (Fig. 7.5c → 7.5d). The reaction is endothermic (ΔH = 21.2 kcal/mol) with an energy barrier of 32.4 kcal/mol and the following transition state was found: d(H-H) = 1.832 Å, d(S-H) = 2.457 Å, d(S-H) = 2.249 Å and v_{TS} = -2485 cm⁻¹; computational details are compiled in Table 7.4.
Fig. 7.5. Homolytic hydrogen adsorption on the Co and Ni-promoted S-terminated edge: a) initial state, Co; b) final state, Co; c) initial state, Ni; d) final state, Ni.

Table 7.4. Homolytic dissociation of H₂ on the promoted MoS₂ catalyst surface.

<table>
<thead>
<tr>
<th></th>
<th>Fig. 7.5 a/b (Co)</th>
<th>Fig. 7.5 c/d (Ni)</th>
</tr>
</thead>
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<tr>
<td>d(H-H), Å</td>
<td>0.700</td>
<td>0.740</td>
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<td>z(H₂ - surface), Å</td>
<td>2.191</td>
<td>2.896</td>
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<td>E_reactants, Ha</td>
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<td>-10448.949</td>
</tr>
<tr>
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<td>-10448.932</td>
</tr>
<tr>
<td>ΔH, kcal/mol</td>
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<td>21.2</td>
</tr>
<tr>
<td>ΔE_barrier, kcal/mol</td>
<td>26.6</td>
<td>32.4</td>
</tr>
</tbody>
</table>
7.5 Conclusion

The activation of hydrogen on (100) surfaces of unpromoted and promoted MoS$_2$ structures, as obtained from periodic DFT calculations have been reported. Several reaction pathways starting with an H$_2$ molecule above the surface and ending with adsorbed hydrogen atoms on different surface sites have been proposed. The formation of S-H species on the S-terminated edge of 2H-MoS$_2$ is only energetically favourable if the hydrogen molecule is already split. If the H$_2$ molecule is in the vicinity of the surface at about 4 Å, dissociation is possible and a transition state can be found. In the case of the S-terminated edge the energy barriers are not strongly dependent on the reaction path as well as the transition state, while there is a clear dependence in the case of the Mo-terminated edge. The results favour the heterolytic hydrogen adsorption and show that hydrogen species are present on the catalyst surface: the most stable configuration results from a heterolytic dissociation of hydrogen on a surface metal centre, which is coordinated to four sulfur atoms and a surface sulfur atom of an adjacent sulfur edge. Heterolytic splitting of H$_2$ on the Mo-terminated edge and subsequent transfer of a hydrogen atom to the S-terminated edge is slightly exothermic, but energetically less favourable. On Co or Ni promoted surfaces the heterolytic splitting of H$_2$ was found to be endothermic. This difference is explained by the different metal-sulfur bond strengths: replacing Mo by another metal reduces the metal-sulfur bond energy, which in turn enhances the bond energy of neighbouring Mo-S bonds. As a consequence the Mo-H bond weakens and hence H$_2$ dissociation becomes less favourable. When Co substitutes a Mo atom on the S-terminated edge (Mo/Co = 1/1) and the H$_2$ molecule was allowed to relax above the surface, the homolytic hydrogen dissociation was found to be exothermic. Co atoms on the S-terminated edge promote the dissociation of H$_2$ by lowering the energy barrier of the dissociation. From calculations of H$_2$ dissociation on a partially sulfided metal edge, which is different than the ideal "as-cleaved" surface, the adsorption process was energetically unfavourable, if the process excludes a diffusion of hydrogen.
7.6 References

A density functional theory study of the hydrogenolysis reaction of CH$_3$SH to CH$_4$ on the catalytically active (100) edge of 2H-MoS$_2$

8.1 Abstract

The breaking of the C-S bond is a crucial step in hydrodesulfurization, the removal of the sulfur atom from sulfur-containing molecules in crude oil. Therefore, the hydrogenolysis reaction of CH$_3$SH to CH$_4$ was studied by means of density functional theory on the catalytically active (100) edge of 2H-MoS$_2$, with and without Co and Ni promoter atoms. Thiol adsorption, C-S bond breaking, and the formation and desorption of CH$_4$ were investigated with different sulfur and hydrogen coverage of the surface. CH$_3$SH first adsorbs molecularly with its S atom in a bridging mode between two surface Mo atoms followed by S-H bond cleavage with moderate activation energy. The subsequent concerted C-S bond breaking and CH$_4$ formation occurs by means of a reaction of the adsorbed CH$_3$S group with the H atom of a neighbouring SH group at the molybdenum sulfide surface. Sulfur atoms, hydrogen atoms adsorbed on sulfur atoms, and promoter atoms (Co and Ni) at the catalyst surface weaken the bonding of adsorbed CH$_3$S and lower the energy barrier for CH$_4$ formation. Although the reactions of thiols on the metal sulfide surface are similar to reactions on metal surfaces, the chemistry is different. The reactions take place between intermediate alkyl and hydrogen fragments that are bonded to sulfur atoms and not to metal atoms, indicating that the metallic properties of small MoS$_2$ particles extend to the sulfur atoms at the edge.
8.2 Introduction

Crude oil contains organosulfur compounds such as thiophene and dibenzothiophene, and hydrodesulfurization (HDS) is one of the first steps in its processing. In HDS the sulfur-containing molecules react with hydrogen on the surface of metal sulfide catalysts to form hydrocarbons and $H_2S$ [1,2,3,4,5], after which the $H_2S$ is removed by absorption. HDS will become even more important as environmental regulations demand increasingly smaller amounts of sulfur in gasoline and gasoil fuels. Two basic HDS reactions have been identified as being responsible for the removal of sulfur from dibenzothiophene, one of the most difficult components to desulfurize: direct desulfurization and hydrogenation followed by sulfur removal. In the direct desulfurization reaction dibenzothiophene and $H_2$ react to biphenyl and $H_2S$. The hydrogenation reaction involves the hydrogenation of one of the benzene rings of dibenzothiophene, followed by desulfurization of the resulting hexahydrodibenzothiophene to yield cyclohexylbenzene. A large body of theoretical research has aimed at understanding the mechanisms of C-S bond breaking of thiophene and dibenzothiophene through their interaction with the metal sulfide catalyst surfaces [6,7,8,9,10,11,12,13,14,15,16]. Furthermore, organometallic chemistry has contributed to the understanding of C-S bond breaking. Various modes of thiophene coordination to transition metal complexes, representing different types of adsorption on metal sites in heterogeneous HDS catalysts, have been proposed [17,18,19,20,21,22,23].

Notwithstanding the intensive research into HDS, the reaction mechanism of the main route of the HDS of dibenzothiophene, direct desulfurization, is still being disputed. Some believe that the mechanism consists of an actual hydrogenolysis reaction, during which C-S bonds are broken and C-H and S-H bonds form simultaneously, so that biphenyl forms directly from dibenzothiophene and hydrogen on the catalyst surface [1,2,3,4]. A related mechanism may be the insertion of a metal atom in the C-S bond, as observed in organometallic complexes of thiophene and benzothiophene [20,21], followed by hydrogenation. Others argue that the mechanism consists of hydrogenation of dibenzothiophene to dihydrodibenzothiophene, followed by elimination to give biphenyl and $H_2S$ [24]. The much simpler hydrogenolysis reaction of alkanethiols to alkanes has not been studied in depth either; it is complicated by the occurrence of the parallel elimination reaction of the alkanethiols to alkenes. Over metal sulfide catalysts the HDS of alkanethiols is already
fast at 500 K [25]. Over pure metal surfaces the reaction is much faster [26]. Thus S-H bond breaking, giving a \( \text{C}_n\text{H}_{2n+1}\text{S} \) fragment and an H atom, occurs already at about 150 K on most metals and the C-S bond breaking of \( \text{C}_n\text{H}_{2n+1}\text{S} \) occurs at somewhat higher temperature but still below room temperature [27,28,29,30,31,32,33]. This demonstrates that metals are potentially much better HDS catalysts than metal sulfides. Nevertheless, industrially used HDS catalysts are based on the layered transition-metal sulfides of Mo or W, promoted by Co or Ni [1,2], because metals would quickly become metal sulfides during HDS.

While the experimental interaction of thiols with metal surfaces has been studied in depth, very little has been published about the interaction of alkanethiols with the surface of metal sulfides. The main reason for this is that it is much more difficult to perform surface science studies of metal sulfide surfaces than of clean metal surfaces. As a consequence, many fundamental aspects, such as the initial adsorption geometry, the nature of the catalytically active site, and the mechanism of the C-S bond breaking on metal sulfide surfaces, remain unclear. Organometallic studies have addressed mechanistic aspects of the desulfurization of thiols. Thus, Curtis and co-workers showed that the association of aromatic and aliphatic thiols with a \( \text{Cp'}^2\text{Mo}_2\text{Co}_2\text{S}_3(\text{CO})_4 \) cluster occurs by a rearrangement of the cluster and that the coordination of the thiol to the cluster results in a substantial weakening of its C-S bond energy [34,35]. They suggested that this association is the rate-determining step in the desulfurization reaction and that the subsequent cleavage of the C-S bond occurs rapidly.

We report the first ab initio computation of the reaction pathways for the dissociation of \( \text{CH}_3\text{SH} \) and for the geometry-optimized HS and \( \text{CH}_3\text{S} \) intermediates on the (100) catalytically active surface of \( 2\text{H-MoS}_2 \). The effect of Co and Ni promoter atoms and the presence of hydrogen on the surface have been taken considered as well. We chose the simplest alkanethiol, \( \text{CH}_3\text{SH} \), because for this molecule only hydrogenolysis to \( \text{CH}_4 \) can take place. Using density functional theory (DFT), we calculated the minimum energy path for the \( \text{CH}_3\text{SH} \) dissociation with the aim of determining the chronological order of the chemical reaction steps, the various energies of the reactions, and the activation barriers. In this way, we provide information about the chemisorption and reaction of thiols on the (100) catalytically active surface of \( 2\text{H-MoS}_2 \).
8.3 Computational details

In the DFT calculations we used the DMol$^3$ code [36,37] with a double-numeric polarized basis set, a medium level of integration grid amounting to approximately 1000 grid points per atom, and performed effective core potential calculations. Each basis function was restricted to within a cut-off radius of 5.5 Å. The local density approximation was used to specify the exchange-correlation local potential [38], and corrected in the high- and low-density expansions proposed by Perdew and Wang [39,40]. The Brillouin zone integration was performed with a set of 2x2x1 k-points. Direct inversion in an iterative subspace was used to accelerate the self-consistent field convergence, and a thermal smearing of 3 kcal/mol was applied to the orbital occupation. We selected a surface (4x1) super cell of the 2H-MoS$_2$ crystal structure with a vacuum slab of 9 Å and a slab thickness of 12 Å. The (4x1) model surface consists of two MoS$_2$ sheets in the y direction, six planes of atoms in the z direction (three MoS$_2$ units), and four surface Mo atoms in the x direction (Fig. 8.1).

![Fig. 8.1. Schematic representation of the 2H-MoS$_2$ (100) surface.](image)

The (100) MoS$_2$ surface exhibits two types of edges. On one edge, unsaturated molybdenum atoms are exposed (hereafter referred to as the Mo edge), whereas on the other edge sulfur atoms are exposed (the S edge). The geometry of all the atoms in the slabs were optimized. Geometry optimization convergence thresholds of 0.01 kcal/mol, 2.5 kcal/mol Å,
and 0.005 Å were used between the optimization cycles for the energy change, maximum force, and maximum displacement, respectively.

The CH$_3$SH molecule was thermally equilibrated with the surface in the initial state. The activation energy is determined by the highest maximum on the minimum energy path, obtained by the LST/QST method [41]. To calculate the minimum energy path between several reaction steps we used the linear/quadratic synchronous transit (LST/QST) method proposed by Halgren and Lipscomb [42] and implemented in the DMol$^3$ code. The reaction path connects the CH$_3$SH molecule above the surface with the products, the CH$_4$ molecule, desorbed to the gas phase, and the S atom, adsorbed on the catalyst surface. The path was divided into several steps between the reactant and products and the energies of these steps as well as the adsorption barriers were calculated. The success of the calculations by means of the LST/QST method is based on the close proximity of the end points for the transition state search. The selection of the end points for the transition state search was done by an interpolation along the path segments. This is most accurately done in a coordinate system, which naturally follows the adiabatic valley of the potential. Moreover, it reduces the number of intermediate path points to be refined.

8.4 Results

8.4.1 Dissociation of CH$_3$SH

Unpromoted Mo edge. DFT calculations have shown that the Mo edge of MoS$_2$ crystallites is fully covered with sulfur atoms under conditions that prevail in industrial HDS (0.01 < H$_2$S/H$_2$ < 0.1) [11,13,15]. Each Mo atom is surrounded by six sulfur atoms, four of which are linked to two other Mo atoms as well (as in bulk MoS$_2$) and two of which are at the surface in bridging positions between the Mo surface atoms. This prediction was confirmed by scanning tunnelling microscopy observations of MoS$_2$ particles on a gold substrate [43,44,45]. A recent DFT calculation on an enlarged Mo edge (with six instead of two or three MoS$_2$ units, as in former calculations) predicts, however, that the probability of one sulfur vacancy and five bridged sulfur atoms is at least a few % in the range 0.01 < H$_2$S/H$_2$ < 0.1 [46]. In the HDS literature authors generally assume that the reacting molecules are adsorbed on vacancies at the catalyst surface. Therefore, we studied the reaction of CH$_3$SH on the Mo
A density functional theory study of the hydrogenolysis reaction

edge covered with sulfur atoms in bridging positions between the surface Mo atoms and with at least one sulfur vacancy. Since our model surface contains four surface Mo atoms (Fig. 8.1), the number of bridging sulfur atoms \( N_{\text{br}} \) was varied from zero to three and, thus, the number of sulfur vacancies from four to one.

In a first series of calculations we started with a \( \text{CH}_3\text{SH} \) molecule located above the bare Mo-terminated edge surface, with the S atom of the \( \text{CH}_3\text{SH} \) molecule 4.5 Å from a surface metal atom (Fig. 8.2, a).

![Fig. 8.2. Reaction path of the reaction of CH3SH to CH4 by C-S bond breaking before S-H bond breaking on the bare unpromoted Mo edge of 2H-MoS2.](image)

The approach of \( \text{CH}_3\text{SH} \) to the surface and activation \( (a \rightarrow b \rightarrow c) \) were accompanied by energy changes of 12.6 kcal/mol (energy barrier) and -25.1 kcal/mol (reaction energy). The S atom of \( \text{CH}_3\text{SH} \) took a bridge position between two surface metal atoms with a Mo-S distance of 2.5 Å. The H atom from the \( \text{CH}_3\text{SH} \) molecule changed its orientation. In the initial state configuration the S-H bond was parallel to the row of metal atoms of the surface, while in the molecularly adsorbed state the S-H bond orientation was perpendicular to the metal.
row. The preference of the relaxed methanethiol for bonding in a bridge site can be
considered to be a compromise between the sulfur atom, which prefers a high coordination to
the Mo atoms and the hydrogen atom, which does not like to adsorb in the surface plane
because of repulsion, in agreement with the findings for other atomic adsorbates at metal
surfaces [47]. The C-S bond length increased from 1.8 Å (initial state, a) through 2.0 Å
(intermediate state, b) to 2.3 Å (molecularly adsorbed state, c).

C-S bond splitting of the activated CH$_3$SH molecule and migration of the S-H and CH$_3$
fragments to two adjacent Mo centres (c $\rightarrow$ d $\rightarrow$ e) have an energy barrier of only 4.5
kcal/mol. X-ray photoelectron and high-resolution electron energy-loss spectroscopy have
shown that surface C$_n$H$_{2n+1}$S intermediates are formed from thiols with an energy barrier
smaller than 7 kcal/mol when adsorbed on metallic Mo(110) [48]. The energy of state (e),
with adsorbed methyl and SH fragments, is 21.3 kcal/mol lower than that of the state with
molecularly adsorbed CH$_3$SH (c $\rightarrow$ e). The formation of CH$_4$ from the adsorbed CH$_3$ and S-H
fragments (e $\rightarrow$ g) has a high activation barrier of 68.6 kcal/mol due to the strong Mo-C and
MoS-H bonds that have to be broken. Since the metal atoms on the surface (a) have a
coordination number of only four, they try to increase the coordination number by adjusting
the adsorbed species via the Mo-S and Mo-C interactions. The removal of hydrogen from the
SH fragment changes the coordination mode of sulfur. The final state, with a CH$_4$ molecule
above the surface and two five-coordinated metal centres on the surface, is energetically the
most favourable situation, because in the final reaction step, too, the energy decreased by 19.9
kcal/mol. The remaining sulfur atom clearly prefers a high coordination, in a bridging mode
between two surface Mo atoms (Fig. 8.2, g), in agreement with the results of Hammer and
Nørskov for transition-metal surfaces [47].

In addition to the reaction path (Fig. 8.2), in which the C-S bond breaks first, we
investigated another hydrogenolysis reaction path, in which the S-H bond breaks first
(Fig. 8.3). In the latter case, the H atom and the CH$_3$S fragment in the intermediate state (e*)
are more strongly bound to the surface than the CH$_3$ and SH fragments in state (e) (Fig. 8.2).
In the intermediate state the S-C bond length increased to 2.2 Å. Because of the stronger
bonding of the intermediates to the surface, the energy barrier to form methane increased to
78.4 kcal/mol (e* $\rightarrow$ f*). Thus, this step is less likely than a step (e $\rightarrow$ f).

When one sulfur atom is already present on the Mo edge, it tends to take a bridging
position between two Mo atoms, the final surface state as shown in Fig. 8.2 (state g). In the
calculation of the interaction of CH₃SH with this surface, the CH₃SH molecule was initially positioned 4.5 Å above the surface and the C-S bond length was calculated to be 1.8 Å (Fig. 8.4, h).

Fig. 8.3. Reaction path of the reaction of CH₃SH to CH₄ by S-H bond breaking before C-S bond breaking on the bare unpromoted Mo edge of 2H-MoS₂.

In the intermediate state (j) the S-H bond is broken and the SCH₃ fragment is adsorbed in a bridging position between two metal atoms, adjacent to the bridging sulfur atom. In this state the C-S bond increased to 2.4 Å. The hydrogen atom went to the pre-adsorbed adjacent surface sulfur atom and the S-H bond orientation was perpendicular to the row of surface metal atoms. An energy barrier of 18.8 kcal/mol (h → i) and reaction energy of -38.9 kcal/mol (h → j) was calculated. Once again the coordination of the thiol to the surface is very favourable, as the high exothermicity of the reaction shows. The formation of CH₄ (j → k) requires a rather high activation energy (46.0 kcal/mol) but lower than in the corresponding step in Fig. 8.2 (68.6 kcal/mol) and Fig. 8.3 (78.4 kcal/mol). This is due to the presence of a sulfur atom already on the surface, which lowers the metal edge energy by making two of the surface metal centers five-coordinated. The last transition state (k) shows hydrogenation of
the CH$_3$ group with accompanying C-S bond breaking. The final state (l) consists of CH$_4$ in
the gas phase and a Mo-terminated surface with two sulfur atoms in bridging positions.

A third calculation of the hydrogenolysis of CH$_3$SH on the Mo edge of MoS$_2$ was
performed with two surface vacancies between two bridging S atoms (Fig. 8.5). Again, in the
initial state (m) the CH$_3$SH molecule was situated 4.5 Å above the surface, with d(S-C) = 1.8
Å. In the intermediate state (o), the CH$_3$S fragment was adsorbed on the sulfur vacancy and
the H atom on a neighbouring sulfur atom. The S-C distance was calculated as d(S-C) = 2.4
Å. The activation (m $\rightarrow$ n) and dissociation (n $\rightarrow$ o) of the molecule were accomplished with
an energy barrier of 16.6 kcal/mol and reaction energy of -22.9 kcal/mol. The final step was to
form CH$_4$ from the already adsorbed fragments and to remove it from the surface. This step
had a barrier of 30.0 kcal/mol (o $\rightarrow$ p) and the final state (q) was energetically preferred by
-55.2 kcal/mol. This activation energy was lower than that of the surface with one S atom (Fig. 8.4) and demonstrates the positive influence of pre-adsorbed S atoms.

A fourth calculation of the hydrogenolysis of CH₃SH on the Mo edge of MoS₂ was performed with one surface vacancy and three bridging S atoms (Fig. 8.6). The results were similar to those of the foregoing calculation. In the intermediate state the CH₃S fragment adsorbed on the sulfur vacancy and the H atom on a neighbouring sulfur atom. The activation energy barrier for adsorption and dissociation was 22.8 kcal/mol and the reaction energy -20.1 kcal/mol. The second step, to form CH₄ from the already adsorbed fragments and to remove it from the surface, had a barrier of 18.8 kcal/mol and reaction energy of -61.9 kcal/mol. This second activation energy was even lower than that for the surface with two S atoms (Fig. 8.5) and confirms the positive influence of pre-adsorbed S atoms. The results of all calculations with different numbers (Nbr) of bridging sulfur atoms on the Mo edge are given in Table 8.1.

Fig. 8.5. Reaction path of the reaction of CH₃SH to CH₄ on the unpromoted Mo edge of 2H-MoS₂ with two sulfur atoms in bridging position.
Fig. 8.6. Reaction path of the reaction of CH₃SH to CH₄ on the unpromoted Mo edge of 2H-MoS₂ with three sulfur atoms in bridging position.

Table 8.1. Activation energies and energy differences (in kcal/mol) in the reaction of CH₃SH to H₂S and CH₄ as a function of the number (Nₜ) of bridging S atoms on the Mo edge.

<table>
<thead>
<tr>
<th>Edge</th>
<th>Nₜ</th>
<th>Eₐ(1)</th>
<th>ΔE(1)</th>
<th>Eₐ(2)</th>
<th>ΔE(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0</td>
<td>12.6</td>
<td>46.4</td>
<td>68.6</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>12.6</td>
<td>50.9</td>
<td>78.4</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>18.8</td>
<td>38.9</td>
<td>46.0</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16.6</td>
<td>22.9</td>
<td>30.0</td>
<td>55.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>22.8</td>
<td>20.1</td>
<td>18.8</td>
<td>61.9</td>
</tr>
<tr>
<td></td>
<td>0 + SH</td>
<td>22.5</td>
<td>45.2</td>
<td>35.4</td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>2 + SH</td>
<td>26.8</td>
<td>44.7</td>
<td>34.6</td>
<td>58.4</td>
</tr>
<tr>
<td>Co-Mo</td>
<td>1</td>
<td>18.6</td>
<td>2.1</td>
<td>21.2</td>
<td>57.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.2</td>
<td>2.0</td>
<td>19.1</td>
<td>58.2</td>
</tr>
<tr>
<td>Ni-Mo</td>
<td>1</td>
<td>19.4</td>
<td>5.1</td>
<td>19.3</td>
<td>58.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.6</td>
<td>4.1</td>
<td>18.6</td>
<td>62.8</td>
</tr>
</tbody>
</table>
Mo edge in the presence of hydrogen. The influence of surface hydrogen was investigated by letting CH$_3$SH dissociate on a surface covered with a sulfur atom and a hydrogen atom. In the most stable initial state (Fig. 8.7, h**), the hydrogen atom is adsorbed on the sulfur atom, forming an SH group. In the intermediate state (j**) the hydrogen atom of methanethiol preferred to be adsorbed on the sulfur atom as well, forming adsorbed H$_2$S.

The energy barrier for CH$_3$SH adsorption and dissociation was 22.5 kcal/mol, which is 3.7 kcal/mol higher than the energy barrier in the absence of surface hydrogen (Fig. 8.4); the hydrogen atom, pre-adsorbed on the sulfur, creates steric repulsion for the adsorption of the second hydrogen atom on the same sulfur. On the other hand, the formation of CH$_4$ was easier (j** → k**) compared to the case of the hydrogen-free surface, as shown by the desorption
barrier of CH₄ which decreased from 46.0 kcal/mol for the hydrogen-free surface to 35.4 kcal/mol. On the hydrogenated surface, the intermediate and final products were more stable than on the surface without hydrogen atoms. The same calculation was performed starting with a surface covered with two S atoms and one SH group; the results are similar to those for the surface with an SH group only (Table 8.1).

Co- and Ni-promoted Mo edge. It is well known that the addition of Co or Ni significantly increases the catalytic activity of MoS₂-type catalysts [2]. For this reason cobalt and nickel are referred to as promoter atoms. While the origin of the promotional effect is still under study, the location of the promoter atoms has been clarified. Based on results of Mössbauer emission spectroscopy, Topsøe et al. proposed that the Co atoms are present on the Mo edges of the MoS₂ crystallites in Mo positions. They called the resulting structure the Co-Mo-S structure and used it to explain the promotional effect of cobalt on MoS₂ [49]. DFT calculations confirm that the promoter atoms are most probably located at the MoS₂ edges [50].

To study the effect of the promoter atoms on the CH₃SH dissociation process, we performed calculations similar to those for the unpromoted MoS₂ structure but with one surface Mo atom replaced by a promoter atom (Co or Ni). Since the calculations on the Mo edge showed that the presence of sulfur atoms is beneficial for the hydrogenolysis of CH₃SH, we put at least one sulfur atom at the Co or Ni-promoted surface in a bridging position between two Mo atoms. Furthermore, DFT calculations showed that the incorporation of promoter atoms leads to a reduction of the sulfur coverage of the metal edge [12,15,50]. Therefore, we considered only initial states with one or two sulfur atoms.

In the first calculations we put one sulfur atom on the edge (Fig. 8.8). A geometry optimization of the initial, intermediate, and final structures relaxed the Co atom inward and shortened its distance to the neighbouring sulfur atoms to 2.25 Å. The cobalt atom and one of the molybdenum atoms on the surface were four-coordinated, while the other two Mo atoms were five-coordinated (h*).
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Fig. 8.8. Reaction path of the reaction of CH$_3$SH to CH$_4$ on the Co- and Ni-promoted Mo edge of 2H-MoS$_2$ with one sulfur atom in bridging position. The values for the Ni-promoted surface are given in parentheses.

Due to the inward relaxation of the Co atom, the distance between the sulfur atom of the CH$_3$SH molecule and the surface Co atom increased from 4.5 Å for the unpromoted surface to 5 Å for the promoted surface, while the distance between the hydrogen atom of the CH$_3$SH molecule and the surface sulfur atom was 2.8 Å. The adsorption of CH$_3$SH on the surface had an energy barrier of 18.6 kcal/mol (h$^*$ → i$^*$), which was almost the same as for the unpromoted surface (Fig. 8.4). However, the CH$_3$S and H fragments were less strongly bound to the surface, i.e. favoured by only 2.1 kcal/mol (j$^*$), and consequently the energy barrier of the subsequent step, the breaking of the C-S bond, decreased from 46.0 kcal/mol for the unpromoted surface to 21.2 kcal/mol. The final state, with two sulfur atoms in bridging positions on the surface (i$^*$), was more stable by 57.9 kcal/mol than the intermediate state (j$^*$).

Similar calculations were performed with two sulfur atoms on the surface, between the Mo atoms. In this situation the cobalt atom is four-coordinated, while two Mo atoms are five-coordinated and one Mo atom is six coordinated. The results are similar to those when one sulfur atom is initially present on the surface (Table 8.1).
The Ni promoter also led to a less stable intermediate and to a lower energy barrier for CH₄ desorption. The energy barrier for dissociation and adsorption of the CH₃S and H fragments to the surface was 19.4 kcal/mol (Fig. 8.8, h* → i*). The intermediate state (j*) was favoured only by 5.1 kcal/mol compared to the initial state (h*), while the final state (l*) was energetically preferred by 58.9 kcal/mol compared to the intermediate state. In the final state, CH₄ was formed and desorbed from the surface. The corresponding barrier for desorption was 19.3 kcal/mol, lower than for the unpromoted and slightly lower than for the Co-promoted surface. Similar calculations were performed with two sulfur atoms on the surface (Table 8.1).

8.4.2 Dissociation of CH₃SCH₃

In addition to the hydrogenolysis of methanethiol we studied the hydrogenolysis of dimethylsulfide (CH₃SCH₃) on a surface with one and two sulfur vacancies as the starting position. The calculated reaction path for dimethylsulfide on the surface with two vacancies (Fig. 8.9) was similar to that of the hydrogenolysis of CH₃SH on the same surface (Fig. 8.5). Dimethylsulfide adsorbed with its S atom in the vacant position, bridging two Mo atoms. This adsorption had activation energy of 17.6 kcal/mol and was exothermic by 42.6 kcal/mol. The final step, combination of the methyl groups to ethane, had activation energy of 19.1 kcal/mol and was exothermic by 51.9 kcal/mol. For the surface covered with one vacancy the results are very similar (Table 8.2).

<table>
<thead>
<tr>
<th>Nᵥₑ</th>
<th>Eₐ(1) - ΔE(1)</th>
<th>Eₐ(2) - ΔE(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>17.6</td>
<td>42.6</td>
</tr>
<tr>
<td>3</td>
<td>20.6</td>
<td>36.8</td>
</tr>
</tbody>
</table>
We also calculated the alternative second reaction step, in which one of the methyl groups of the adsorbed dimethylsulfide is transferred to a neighboring adsorbed S atom, creating two CH₃S groups at the surface. This step had activation energy of 15.8 kcal/mol and was exothermic by ~24.1 kcal/mol. These CH₃S groups can form methane and adsorbed S.
atoms by reaction with adsorbed H atoms, as described above. The creation of these H atoms by dissociative chemisorption of H₂ on the catalyst surface will be discussed in the next section.

8.4.3 Hydrogen chemisorption and diffusion

Understanding the role of hydrogen is of great importance in the study of desulfurization reactions. Although some results have already been published [8,9,15], we performed additional calculations of the adsorption and diffusion of the surface hydrogen in order to learn more about the dynamics on the catalytically active (100) MoS₂ edge structure. Our calculations show that the homolytic hydrogen adsorption on the S edge is endothermic with a reaction energy of 43.5 kcal/mol and a barrier of 67.5 kcal/mol, while the heterolytic hydrogen adsorption on the bare Mo edge and the fully sulfided S edge is exothermic with a reaction energy of -3.3 kcal/mol and a barrier of 18.1 kcal/mol. This results in Mo-H and S-H surface fragments (Figs. 7.Id → 7.2d).

Starting with this situation and transferring the hydrogen from the Mo to the S edge, we find an energy barrier of 69.3 kcal/mol (Figs. 7.1d → 7.2d). Thus, a reaction path passing through a local minimum on the potential energy surface on the Mo edge (with hydrogen split and adsorbed on the metal edge) is energetically demanding as well.

The adsorption of H₂ on the Mo edge, fully covered with sulfur atoms in bridging positions and which is the most stable structure under hydrotreating conditions [13,14,15], was found to be endothermic with a reaction energy of 32.1 kcal/mol and an energy barrier of 89 kcal/mol (Fig. 7.3).

The strong endothermicity of the hydrogen dissociation on this surface might be due to the fact that the Mo atoms are fully coordinated and that there are no longer coordinatively unsaturated sites to bind the H atoms and thus compensate for the strong H-H bond. Dissociation of H₂ on the Mo edge covered by one sulfur atom led to one H atom bonded to the S atom bridging two Mo atoms and the other H atom bonded to one of these Mo atoms (Fig. 8.10). This reaction is endothermic (30.5 kcal/mol) and has an energy barrier of 33.5 kcal/mol. Transfer of the hydrogen atom from the Mo atom to the sulfur atom, giving adsorbed H₂S, is endothermic by 11.2 kcal/mol and has an energy barrier of 18.6 kcal/mol.
Hydrogen transfer along an edge is energetically less demanding than hydrogen transfer from the Mo to the S edge. Diffusion of a hydrogen atom on the sulfided Mo edge from one sulfur atom to the next (i.e. an exchange between a sulfur atom and an SH group) has an activation energy of only 5 kcal, while diffusion of a hydrogen atom from a sulfur atom to an adjacent SH group has an energy barrier of 25.8 kcal/mol and endothermic reaction energy of 12.8 kcal/mol (Fig. 8.11). As a result, adsorbed H$_2$S and a sulfur atom formed from two SH groups. Removal of the resulting H$_2$S from the surface during the formation of a sulfur vacancy has activation energy of 12.8 kcal/mol and an endothermic reaction energy of 8.6 kcal/mol. For a surface with one sulfur vacancy these activation energies and energy differences were similar ($E_a(1) = 18.6, \Delta E(1) = 11.6, E_a(2) = 10.8$, and $\Delta E(2) = 10.2$ kcal/mol).
8.5 Discussion

The calculations show that the hydrogenolysis of methanethiol with dihydrogen to methane and H$_2$S occurs in several steps. First, methanethiol adsorbs and dissociates in a CH$_3$S fragment and an H atom. This reaction occurs between the initial state I (methanethiol, H$_2$, and the surface with n sulfur vacancies) and the intermediate state II (CH$_3$S, H$_2$, and the surface with (n-1) vacancies). In the second step CH$_3$S reacts with an adsorbed H atom to methane, and the system moves from state II to state III (methane, H$_2$, and the surface with (n-1) vacancies). In the third step, the sulfur atom is removed from the surface by hydrogen atoms, which originate from the dissociative chemisorption of dihydrogen. The two-step reaction from state I to state III is strongly exothermic. As a consequence, the activation energies of the first (I→II) and second (II→III) reaction steps depend on the relative energy position of the intermediate state II. If state II is closer in energy to the final state III than to the initial state I, the activation energy of the first reaction step (I→II) will be lower and that of the second step (II→III) will be higher [51,52]. If state II is closer in energy to state I the reverse is true. As will be shown below, the energy of the intermediate state II relative to the energies of states I and III depends on the composition of the Mo edge. Adsorbed S and H
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atoms as well as promoter atoms influence the relative energies and thus the activation energies of the methanethiol dissociation and reaction to methane.

The calculated energy barriers for the dissociation of adsorbed CH$_3$SH to CH$_3$S and H and to CH$_3$ and SH fragments are low, while the energy barriers for the adsorption of the thiol on the surface and especially for methane formation are higher. For instance, dissociation of the adsorbed thiol on the bare surface is easy (4.5 kcal/mol) compared to thiol adsorption (12.6 kcal/mol) and the formation and removal of CH$_4$ from the surface (68.6 kcal/mol) (Fig. 8.2). The thermodynamic driving force for C-S bond scission in thiol desulfurization is the formation of a strong Mo-S bond [26]. The barrier $E_a(2)$ for the subsequent step, the reaction of CH$_3$ and hydrogen to CH$_4$, is reduced by the presence of S atoms on the metal edge (Table 8.1). As explained above, at the same time the barrier for the first step, the adsorption of the thiol, increases. On the bare surface (Fig. 8.2), the association of the thiol is a relatively easy step with an energy barrier of 12.6 kcal/mol, but the formation of CH$_4$ from adsorbed CH$_3$ and SH has a high barrier (68.6 kcal/mol). A pre-adsorbed sulfur atom makes the adsorption more difficult (18.8 kcal/mol) but substantially reduces the energy barrier for CH$_4$ formation to 46.0 kcal/mol (Fig. 8.4). Addition of a second S atom to the surface reduces the energy barrier further to 30.0 kcal/mol (Fig. 8.5) to form CH$_4$ and a third S atom reduces it even further to 18.8 kcal/mol. The adsorption and reaction of CH$_3$SH on the catalytically active (100) surface of MoS$_2$ thus clearly depend on the number of adsorbed sulfur atoms and thus on the nature of the exposed active surface sites.

The energy of the intermediate state of adsorbed CH$_3$S depends on the sulfur coverage of the Mo edge of MoS$_2$. The adsorption energy of CH$_3$SH (dissociating to CH$_3$S and H fragments) decreases with increasing S coverage of the Mo edge from 50.9 to 20.1 kcal/mol (Table 8.1). Similarly, the adsorption energy of atomic sulfur on transition-metal surfaces varies between 80 and 140 kcal/mol and decreases substantially with increasing S coverage [53]. This decrease can be explained with the Effective Medium Theory [54]. According to this theory, the adsorption energy of an adsorbate depends on the energy gain from embedding the atoms of the adsorbate in the surface electron gas and on the energy loss from the incomplete screening of the electrostatic interaction between the adsorbate and the surface ionic nuclei. The higher the metal coordination number, the broader the d band and, hence, the lower the energy of the d band centre will be. Adsorption on the Mo edge increases the metal coordination number and thus lowers the energy of the d band and the interaction with adsorbate molecules.
Dissociation of organosulfur molecules is much more difficult on MoS$_2$ than on metal surfaces. When MoS$_2$ is exposed to organosulfur molecules hydrocarbons and H$_2$S form and desorb to the gas phase. On metals, however, not only do H$_2$ and hydrocarbon species desorb to the gas phase but S and C atoms are also left on the surface. Clean W(211) [28], Ni(110) [31], Ni(100) [32], and Ni(111) [33] surfaces break many molecules completely to adsorbed atomic fragments at low coverage. Adsorbed oxygen, sulfur, and carbon atoms weaken the strong reducing power of the metallic surfaces and lead to adsorbed molecular fragments. The exact surface chemistry of organosulfur molecules depends on the metal and the complexity of the organosulfur molecule. In general, the S-H bond in H$_2$S and thiols breaks below 200 K, whereas the S-C bond in thiols and thiophene cleaves between 250 and 400 K [26,33]. These temperatures are much lower than the temperatures required for bond breakage over MoS$_2$. This demonstrates that the sulfur atoms below the surface Mo atoms on the Mo edge of MoS$_2$ weaken the ability of the Mo atoms from cleaving bonds, just as O, S, and C atoms do on the metal surface, to such an extent that C-C bonds cannot be broken; thus, no valuable fuel molecules are lost. However, bond breakage is sufficient to break C-S bonds and, thus, to remove sulfur atoms from organosulfur molecules in fuels.

Not only sulfur atoms, but also Co and Ni promoter atoms lead to a less strongly bound CH$_3$S intermediate and thus to a lower barrier for CH$_4$ formation and desorption from the surface. Activation energies of 19.1 and 18.6 kcal/mol were obtained for CH$_4$ formation over the Co-Mo and Ni-Mo edges with two bridging S atoms, respectively, whereas 18.8 kcal/mol was the lowest activation energy calculated for the unpromoted Mo edge (Table 8.1). A parallel can be drawn between this low activation energy for C-S bond breaking on the Co-Mo edge and the conclusion drawn by Curtis and co-workers that the association of the aliphatic thiols with a Cp$_2$Mo$_2$Co$_2$S$_3$(CO)$_4$ cluster is the rate-determining step in the reaction of the thiols [34,35]. The bridge bonding of the RS group between metal atoms of the Cp$_2$Mo$_2$Co$_2$S$_3$(CO)$_4$ cluster led to the activation of the C-S bond and eased the subsequent cleavage of the C-S bond (Fig. 8.12).
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Fig. 8.12. Adsorption of an alkane- or arenethiol on the Cp'$_2$Mo$_2$Co$_3$S$_3$(CO)$_4$ cluster followed by activation and cleavage of the C-S bond (Cp'=pentamethylcyclopentadienyl) and formation of a hydrocarbon (M=MoCp', N=Co(CO)$_2$).

After the adsorption and reaction of CH$_3$SH to methane and a sulfur atom adsorbed on the catalyst surface, the sulfur atom must be removed, so that the catalytic cycle of the reaction of methanethiol and H$_2$ to methane and H$_2$S is closed. The sulfur removal and the creation of a vacancy for subsequent adsorption of CH$_3$SH is achieved by dihydrogen. H$_2$ splits on the sulfided Mo-terminated edge and forms two SH groups with an energy barrier of 89 kcal/mol and an endothermic reaction energy of 32.1 kcal/mol. Cristol et al. [13,14] and Travert et al. [15] also found that the dissociation of H$_2$ on the fully covered Mo edge is endothermic, although less strong than in our case, while Sun et al. calculated H$_2$ adsorption to be slightly exothermic [46]. For Co-Mo-S surfaces, on the other hand, the H$_2$ dissociation was calculated to be exothermic and not strongly activated [15].
Diffusion of hydrogen over the fully sulfided Mo edge and formation of molecularly adsorbed H$_2$S costs 12.8 kcal/mol (Fig. 8.11). The desorption of H$_2$S from the surface leaves a surface with a sulfur vacancy and H$_2$S in the gas phase and is endothermic by 8.6 kcal/mol. Thus, the second step of the regeneration of the catalyst surface, the creation of the coordinatively unsaturated site on the Mo edge, is endothermic by 21.4 kcal/mol (Fig. 8.11). Therefore, the whole process of regeneration of the active site and closing of the catalytic cycle (H$_2$ dissociation, H diffusion on the sulfided surface, H$_2$S formation, and desorption) is endothermic by 53.5 kcal/mol. If only one S atom is left on the Mo-terminated edge, the process of regeneration of the active site takes place by first dissociating H$_2$ on the Mo and S atoms. This endothermic reaction costs 30.5 kcal/mol. Then H$_2$S forms by diffusion of the H atom from the Mo to the S atom (endothermic by 11.2 kcal/mol), and finally H$_2$S is desorbed (endothermic by 10.8 kcal/mol). The overall regeneration process of the active site thus costs 52.5 kcal/mol. With these regenerations of the active sites, energies of -14.4 and -13.8 kcal/mol are calculated for the overall hydrogenolysis reaction of CH$_3$SH + H$_2$ → CH$_4$ + H$_2$S on the surface with one S vacancy (Fig. 8.5) and the surface with three S vacancies (Fig. 8.3), respectively. These values are in good agreement with the experimental value of -17 kcal/mol and give confidence to the theoretical approach that we used.

A comparison of Figs. 8.5 and 8.6 shows that the energy of the final state, after dissociation of methanethiol and the formation of methane and an adsorbed sulfur atom, is not as low for the promoted surface as for the Mo-only surface. This is a result of the weaker Co-S and Ni-S bonds compared to the Mo-S bond. As a consequence, the energy required to remove the sulfur atom from the surface by hydrogenation to H$_2$S is 18 (Co-Mo surface) or 14 kcal/mol (Ni-Mo surface) lower than for the Mo surface. This indicates that the promoter also decreases the adsorption energy of the sulfur atom from methanethiol on the catalyst surface and thus decreases the sulfur-removal energy.

The calculated activation energies can be compared with the experimental activation energies of 22.9 and 22.0 kcal/mol for the hydrogenolysis of methanethiol and dimethylsulfide to methane and H$_2$S over unsupported MoS$_2$, respectively, while that for the formation of dimethylsulfide from methanethiol was 19.7 kcal/mol [25]. In case of zero order conditions, the experimental activation energy is equal to the activation energy of the rate-determining step, while in case of first order conditions it should be equal to the activation energy of that step minus the heats of adsorption of the reactants, respectively. Since the hydrogenolysis of methanethiol was studied under zero-order conditions, the observed
activation energy should be compared with the largest activation energy of the different reaction steps. In our case this is clearly the H₂ dissociation followed by the removal of the sulfur atom. Also the DFT calculation of the HDS of thiophene on the bare Mo edge of (100) MoS₂ indicated that the sulfur removal is the rate-determining step and that its energy cost depends on the sulfur coverage of the Mo edge [11]. On the other hand, on a metallic Ni(111) surface the rate determining step for methane formation from methanethiol was suggested to be C-S bond breaking [33], while a DFT calculation for small nickel sulfide clusters found S-C bond scission and sulfur removal to be about equally slow and rate determining for thiophene desulfurization [55]. A possible explanation for this difference is that the Ni-S bond is weaker than the Mo-S bond and that thus the stabilization of the sulfur-containing intermediates is lower on nickel sulfide. On the Mo edge of (100) MoS₂, the strong binding of CH₃S is a consequence of Mo-S interactions that involve the occupied sulfur lone pairs of the molecule and the empty 4d orbitals of molybdenum.

The calculations show that the hydrogenolysis reaction of methanethiol is not a concerted reaction of C-S bond breaking and C-H and S-H bond creation, but rather occurs in two steps. In the first step the S-H bond of methanethiol is broken and a CH₃S group is adsorbed on the surface. This adsorbed CH₃S and a neighbouring adsorbed SH group react to methane and two surface sulfur atoms. In the third step one of the sulfur atoms is removed from the surface by reacting with two adsorbed hydrogen atoms to H₂S that desorbs from the surface. The chemistry that is taking place is radical chemistry, as it were. The metal sulfide surface stabilizes the CH₃S, H, and SH radicals and allows them to react with each other. The chemistry is not the same as on the surface of a metal, however, where alkanethiols decompose to alkyl groups and sulfur and hydrogen atoms that all become attached to metal atoms. Instead, on the metal sulfide surface, the alkyl and hydrogen fragments are bonded to sulfur atoms and it is on these sulfur atoms that they react with each other to alkanes. It is as if the metallic properties extend from the metal atoms onto the sulfur atoms on the edges of the MoS₂ crystallites. This agrees with the STM investigation of Lauritsen et al. who observed that the metallic properties of small MoS₂ particles supported on gold extend to the edge sulfur atoms [43,44]. The results from this study show that in the presence of adsorbed sulfur atoms methanethiol and dimethylsulfide react as follows:

\[
\text{X-S-Y} + * + S* \rightarrow \text{X-S*} + \text{Y-S*} \rightarrow \text{X-Y} + 2S*,
\]

where \(X, Y = \text{CH}_3\) or H, and * indicates a site consisting of one or two Mo atoms.
Thus,
\[
\text{H}_2\text{S} + * + \text{S}^* \rightarrow 2 \text{H-S}^* \rightarrow \text{H}_2 + 2 \text{S}^* \quad \text{and}
\]
\[
\text{CH}_3\text{SH} + * + \text{S}^* \rightarrow \text{CH}_3\text{-S}^* + \text{H-S}^* \rightarrow \text{CH}_4 + 2 \text{S}^*.
\]

On the bare Mo edge, methanethiol adsorption and decomposition occur slightly differently:
\[
\text{CH}_3\text{SH} + 2 * \rightarrow \text{CH}_3^* + \text{HS}^* \rightarrow \text{CH}_4 + \text{S}^* + *.
\]

Since in reality the Mo edge is (almost) fully covered with S atoms, reactions (8.2) are not important for catalysis. Reaction (8.1) predicts that ethane may be formed from dimethylsulfide (X = Y = CH\(_3\)) and the calculations show that this reaction has a similar activation barrier as the reaction of methanethiol (X = CH\(_3\) and Y = H) to CH\(_4\). Nevertheless, experimentally no ethane has been observed in the HDS of dimethylsulfide. The reason is probably that the reaction of dimethylsulfide to two CH\(_3\)S groups is faster than the reaction to ethane, as suggested by the lower activation energy for the reaction of dimethylsulfide to two CH\(_3\)S groups.

The same chemistry that is responsible for the reaction of alkanethiols to alkanes might be responsible for the reaction of dibenzothiophene to biphenyl. Dibenzothiophene is exemplary for molecules present in gas oil and its sulfur atom is mainly removed by direct desulfurization, an apparent hydrogenolysis reaction. Surface science studies of the reaction of the related benzenethiol on metal surfaces have indeed shown a great similarity with the reactions of alkanethiols [56,57,58,59]. The S-H bond of benzenethiol is already broken at low temperature and the resulting C\(_6\)H\(_5\)S reacts to benzene below room temperature. This suggests that the hydrodesulfurization of arylthiols such as benzenethiol, benzothiophene, and dibenzothiophene on metal sulfides occurs in the same way as the hydrogenolysis of alkanethiols and dialkylsulfides. The alternative reaction, hydrogenation to a dihydro-arylthiol intermediate followed by elimination of H\(_2\)S [24], might then be of minor importance.
8.6 Conclusion

The present calculations show that the hydrogenolysis reaction of methanethiol is not a concerted reaction but takes place in consecutive steps. First, the S-H bond is broken and a CH$_3$S group is formed on the surface, which then reacts with a neighbouring adsorbed SH group to methane. Finally, a sulfur atom is removed from the surface by reacting with adsorbed hydrogen atoms to H$_2$S. Sulfur, promoter, and hydrogen atoms have a strong influence on the adsorption and reaction of methanethiol on the MoS$_2$ catalyst surface. At low sulfur coverage of the surface, the thiol adsorption has low activation energy, but the subsequent cleavage of the C-S bond and formation of methane is difficult. The C-S bond in adsorbed CH$_3$S is broken by reaction with the H atom on a neighbouring S atom, leaving the S atom on the surface and freeing CH$_4$ to the gas phase. Sulfur atoms adsorbed on the catalyst surface lower the activation energy for the reaction of CH$_3$S to methane. Also hydrogen atoms adsorbed on sulfur atoms at the catalyst surface and promoter atoms (Co and Ni) direct the hydrogenolysis to less strongly bound CH$_3$S and lower the energy barrier for a CH$_4$ desorption from the surface in the dissociation of the CH$_3$SH.

Although the reactions of methanethiol on the metal sulfide surface have many similarities with reactions on metal surfaces, the chemistry is not the same. On the metal sulfide surface, the alkyl and hydrogen fragments are bonded to sulfur atoms and not to metal atoms. This confirms the STM results of Lauritsen et al. that the metallic properties of small MoS$_2$ particles extend to the edge sulfur atoms. The results presented here suggest that also the hydrogenolysis of benzenethiol and dibenzothiophene occur by a similar mechanism.
8.7 References


A density functional theory study of the hydrogenolysis reaction


Chapter 9

A density functional theory study of the hydrogenolysis of \( \text{C}_2\text{H}_5\text{SH} \) to \( \text{C}_2\text{H}_6 \) and elimination to \( \text{C}_2\text{H}_4 \) on the catalytically active (100) edge of 2H-MoS\(_2\)

9.1 Abstract

The breaking of the C-S bond in \( \text{C}_2\text{H}_5\text{SH} \) on the catalytically active (100) edge of 2H-MoS\(_2\) was studied by means of density functional theory. Two reactions of \( \text{C}_2\text{H}_5\text{SH} \) were studied, hydrogenolysis to ethane and elimination to ethene and \( \text{H}_2\text{S} \). The adsorption geometry, involving a hydrogen atom from the methyl group of \( \text{C}_2\text{H}_5\text{SH} \) conducted reactions to more strongly bound surface intermediate states. In contrast, the Co promoter atom conducted the reactions to less strongly bound intermediate state and consequently lowered the energy barriers for products formation. The C-S bond breaking resulting in the ethane formation proceeds with a lower energy barrier than in the ethene formation when the energy of the barriers for desorption of the products from the surface are compared relative to the molecularly adsorbed \( \text{C}_2\text{H}_5\text{SH} \) state.
9.2 Introduction

In the hydrodesulfurization (HDS) process sulfur is removed from fuels such as naphtha and gasoil by passing them over a catalyst in the presence of hydrogen to decompose the sulfur-containing molecules to hydrocarbons and hydrogen sulfide. The most widely used catalysts contain MoS2 promoted with cobalt or nickel [1, 2]. Organosulfur compounds present in petroleum fractions differ in molecular size and structure and thus in their reactivities. Dibenzo thiophene and 4,6-dialkyldibenzo thiophene are difficult to desulfurize and therefore many experimental [1-5] and theoretical HDS investigations [6-10] have concentrated on these molecules. Two reactions are responsible for the sulfur removal from dibenzo thiophene and 4,6-dialkyldibenzo thiophene: direct desulfurization and hydrogenation followed by sulfur removal. In the direct desulfurization dibenzo thiophene reacts with H2 to biphenyl and H2S. In the hydrogenation reaction one of the benzene rings of dibenzo thiophene is hydrogenated, and the resulting hexahydrodibenzo thiophene reacts to cyclohexyl benzene and H2S.

Notwithstanding intensive research, the reaction that is responsible for the C-S bond breaking in direct desulfurization is still under discussion. It has been proposed that direct desulfurization occurs by a real hydrogenolysis reaction, in which C-S bonds are broken and C-H and S-H bonds are formed simultaneously, so that biphenyl is formed from dibenzo thiophene and hydrogen during one sojourn on the catalyst surface [1-4]. Thus, direct desulfurization would be similar to hydrogenolysis of hydrocarbons on metal catalysts. It has also been proposed that a metal atom might be inserted into the C-S bond, as observed in organometallic complexes of thiophene and benzo thiophene [11], followed by hydrogenation. Another possibility would be that dibenzo thiophene is hydrogenated to dihydro dibenzo thiophene, followed by elimination to give biphenyl and H2S [5]. Even the mechanism of the much simpler hydrogenolysis reaction of alkanethiols to alkanes has not very well been studied over metal sulfide catalysts [12, 13]. Much more work was done on investigations of the interaction of alkanethiols with metal surfaces [14-18], because such surfaces can be readily characterized by spectroscopic techniques. This makes them ideal for surface science model studies. Metal sulfides, on the other hand, are not very accessible to surface science studies and this has hampered progress in understanding of reactions of thiols on their surfaces.
Thiols that lack a β-carbon atom react by hydrogenolysis to an alkane and hydrogen sulfide. The simplest thiol, methanethiol, is therefore perfectly suited to study the S-H bond activation and, more importantly, the catalytic C-S bond scission. In the previous chapter the adsorption, dissociation, and reaction of methanethiol on the catalytically active Mo edge of MoS$_2$ as a function of the sulfur coverage and presence of H and promoter atoms by means of density functional theory (DFT) calculations were studied and also presented in [19]. The majority of thiols have a β-hydrogen atom, however, and they do not only undergo hydrogenolysis to alkanes but also H$_2$S elimination to alkenes. In the present chapter the study is extended to the mechanism of the C-S bond scission with DFT calculations of these two reaction pathways for the dissociation of ethanethiol on the (100) catalytically active surface of the 2H-MoS$_2$. This will provide a better understanding of HDS reactions, which occur in more complex reactions of larger sulfur-containing molecules.

9.3 Computational Details

The theoretical method that we used in the DFT calculations was the same as described before in Chapter 8 and in [19]. In short, the Dmol$^3$ code [20] with a double-numeric polarized basis set, a medium level of integration grid consisting of approximately 1000 grid points per atom was used, and effective core potential calculations were performed. The Dmol$^3$ code has shown an excellent performance for the hydrogenation reaction of C$_2$H$_4$ + H$_2$ to C$_2$H$_6$ by computing the reaction energy of 33.5 kcal/mol (the experimental value is 32.5 kcal/mol) [21]. A combination of the local density approximation to specify the exchange-correlation local potential [22] and corrected in the high- and low-density expansions as proposed by Perdew and Wang [23] was selected. The Brillouin zone integration was performed by using a set of 2x2x1 k-points. A (4x1) surface super cell of the 2H-MoS$_2$ crystal structure with a vacuum slab of 9 Å and a slab thickness of 12 Å was exploited. The (4x1) model surface consists of two MoS$_2$ sheets in the y direction, six planes of atoms in the z direction (three MoS$_2$ units), and four surface Mo atoms in the x direction (Fig. 8.1). The (100) MoS$_2$ surface exhibits two types of edges. On one edge, unsaturated molybdenum atoms are exposed (the so-called Mo edge), whereas on the other edge sulfur atoms are exposed (the S edge). The geometries of all atoms in the slabs were optimized.
To calculate the minimum energy path between several reaction steps the linear/quadratic synchronous transit (LST/QST) method [24] as implemented in the DMol\(^3\) code was used [20]. The activation energy is determined by the highest maximum on the minimum energy path, obtained by the LST/QST method. To calculate the energy of the reactions and the corresponding energy barriers the linear/quadratic synchronous transit (LST/QST) method proposed by Halgren and Lipscomb [25] have been selected for the calculations. The reaction path connects the C\(_2\)H\(_5\)SH molecule above the surface with the C\(_2\)H\(_4\) or C\(_2\)H\(_6\) molecule desorbed to the gas phase and the S atom adsorbed on the catalyst surface as final products. Following the adiabatic valley of the potential the path was divided into several steps between the reactant and products by an interpolation along its segments. The success of the calculations with the LST/QST method is based on the close proximity of the end points for the transition state search as shown in Chapter 6.

9.4. Results

The study of the hydrogenolysis of CH\(_3\)SH showed that starting from the "as-cleaved" Mo edge of the MoS\(_2\) surface, the formation of CH\(_4\) from the adsorbed CH\(_3\) fragment and the S-H group had a high activation barrier of 68.6 kcal/mol, due to the strong Mo-C and Mo-S-H bonds [19]. This high-energy barrier is due to the low coordination number of the surface molybdenum atoms, relative to the bulk coordination number, and the tendency of the surface molybdenum atoms to compensate for that by adjusting the adsorbed species, via the Mo-S and Mo-C interactions. The energy barrier decreased when sulfur atoms were put on the Mo edge in bridging positions between the Mo atoms and the lowest barrier was obtained for a surface that had the maximum number of sulfur atoms minus one, in other words a surface with one sulfur vacancy. Combined thermodynamic and DFT calculations have shown that the Mo edge of the MoS\(_2\) crystallites is strongly covered with sulfur atoms under industrial HDS conditions (0.01 < H\(_2\)S/H\(_2\) < 0.1) [6-10]. To allow adsorption of the thiol molecule, the (1010) Mo edge should not be completely sulfided. Therefore, three types of calculations on reactions of C\(_2\)H\(_5\)SH on the Mo edge were performed. In the first calculation, the Mo edge was covered by one sulfur atom on the (4x1) surface supercell (Fig. 8.1), while in the second and third calculations it was covered by two and three sulfur atoms, respectively. These states
correspond to three, two, and one sulfur vacancies, respectively. In agreement with others [7-9], the present calculations showed that the most stable positions for the sulfur atoms are in bridging positions between Mo atoms. Therefore, in the first calculation the Mo edge contains two four-coordinated and two five-coordinated Mo atoms, in the second calculation it contains four five-coordinated Mo atoms, and in the third calculation it contains two five-coordinated and two six-coordinated Mo atoms. The latter configuration resembles the (100) MoS₂ catalyst surface when a vacancy has been created, as observed by scanning tunneling microscopy [26, 27].

9.4.1 Three sulfur vacancies

In the first series of calculations, a C₂H₅SH molecule was positioned 4.5 Å above the Mo-terminated surface with one adsorbed sulfur atom. Subsequently C₂H₅SH was molecularly adsorbed on this sulfided surface and in the most stable state a hydrogen atom from the CH₃ group bridged the surface sulfur atom and the carbon atom, with an S-H distance of 2.1 Å. Fig. 9.1 shows the reaction path for C₂H₅SH adsorption, followed by H₂S elimination resulting in the formation of C₂H₄. The energy of the reaction from the initial state (with the C₂H₅SH molecule 4.5 Å above the surface, Fig. 9.1, a) to the intermediate state (molecularly adsorbed C₂H₅SH, Fig. 9.1, c) was -31.6 kcal/mol, while the energy barrier was 10.3 kcal/mol (a → b).

Fig. 9.1. Reaction path for C₂H₅SH adsorption, followed by H₂S elimination and the formation of C₂H₄.
Compared to CH$_3$SH, where dissociation and adsorption of the CH$_3$S and H fragments took place (ΔE = -38.9 kcal/mol), the molecular adsorption of C$_2$H$_5$SH led to a less stable intermediate state (Fig. 9.1, c: ΔE = -31.6 kcal/mol). In both cases there was a preference for bonding in a bridge site. This is a compromise between the preference of the sulfur atom for a high coordination to the Mo atoms and the preference of the hydrogen atom for adsorption out of the surface plane because of repulsion [28]. As a consequence of the lower heat of adsorption, the barrier for desorption of products in the form of C$_2$H$_4$ was reduced to 37.6 kcal/mol (Fig. 9.1, c → d). In the hydrogenolysis of CH$_3$SH the formation of CH$_4$ had an activation barrier of 46.0 kcal/mol [19]. The transition state (Fig. 9.1, d) involves a deformed, non-planar ethene weakly bonded to the surface sulfur atom by a weakly bonded hydrogen atom. The final state (Fig. 9.1, e) consists of two S-H groups in bridging positions between two Mo atoms and a C$_2$H$_4$ molecule in the gas phase. It is 31.3 kcal/mol lower in energy than the intermediate molecular adsorption state (Fig. 9.1, c).

In addition to elimination, ethanethiol can also undergo hydrogenolysis, resulting in ethane formation from the adsorbed C$_2$H$_5$S and H fragments. In the initial state the distance between the sulfur atom from the surface and the hydrogen atom of the C$_2$H$_5$SH molecule was 2.8 Å (Fig. 9.2, a).

![Fig. 9.2. Hydrogenolysis, resulting in an ethane formation from the adsorbed C$_2$H$_5$S and H fragments.](image)
The energy of the reaction from the C\textsubscript{2}H\textsubscript{5}SH molecule above the surface to dissociated C\textsubscript{2}H\textsubscript{5}S and H fragments was -26.2 kcal/mol (Fig. 9.2, a \rightarrow c). The energy barrier to split the C\textsubscript{2}H\textsubscript{5}SH to fragments was 16.5 kcal/mol (Fig. 9.2, a \rightarrow b). The experimental activation energy associated with the dissociation of ethanethiol on MoS\textsubscript{2} was reported to be 18 kcal/mol \cite{13}. This energy barrier is higher than that reported for dissociation on the metallic Mo (110) surface, which is less than 7 kcal/mol \cite{29}, because the M-S bonding on the surface of a transition-metal sulfide is weaker than on the surface of the metal. The energy barrier for the C\textsubscript{2}H\textsubscript{6} formation was 31.1 kcal/mol (Fig. 9.2, c \rightarrow d). The final state, consisting of a C\textsubscript{2}H\textsubscript{6} in the gas phase above the Mo surface terminated by two sulfur atoms in bridging positions (Fig. 9.2, e) was energetically 43.3 kcal/mol lower than the intermediate state (Fig. 9.2, c). Compared to the hydrogenolysis of CH\textsubscript{3}SH to CH\textsubscript{4}, the energy gain in the formation of ethane and an adsorbed sulfur atom from C\textsubscript{2}H\textsubscript{5}SH is 69.5 kcal/mol. That is 1 kcal/mol more than in the corresponding formation of methane and an adsorbed S atom from CH\textsubscript{4}SH and is in good agreement with the difference of 3.3 kcal/mol in the reactions of ethanethiol to ethane and of methanethiol to methane.

### 9.4.2 Two sulfur vacancies

In the second series of calculations a C\textsubscript{2}H\textsubscript{5}SH molecule was adsorbed on the Mo edge with two adsorbed sulfur atoms, exposing four five-coordinated molybdenum atoms. Also in this initial state, a hydrogen atom from the methyl group of ethanethiol bridged a surface sulfur atom and the carbon atom, with d(S-H) = 2.2 Å (Fig. 9.3, c). The energy barrier for this adsorption configuration is higher (23.5 kcal/mol, Fig. 9.3, a \rightarrow b) than for adsorption on a Mo edge covered with only one S atom (10.3 kcal/mol, Fig. 9.1, a \rightarrow b). Furthermore, the intermediate state is less stable, -27.3 kcal/mol (Fig. 9.3, c) relative to -31.6 kcal/mol (Fig. 9.1, c). The formation of C\textsubscript{2}H\textsubscript{4} had an activation energy of 38.8 kcal/mol (Fig. 9.3, c \rightarrow d). The final state has two S-H groups and one sulfur atom in a bridging mode between two molybdenum atoms on the surface (Fig. 9.3, e) and is 44.4 kcal/mol more stable than the intermediate state.

The C\textsubscript{2}H\textsubscript{5}SH molecule can also react by hydrogenolysis, i.e. ethane formation, starting from the intermediate indicated in Fig. 9.3 c. The energy barrier for ethane formation is 28.0 kcal/mol (Fig. 9.4, c \rightarrow d) and the C\textsubscript{2}H\textsubscript{6} molecule is stretched in the transition state (Fig. 9.4,
The final state (Fig. 9.4, e), with a sulfided surface and a C$_2$H$_6$ molecule in the gas phase, is 36.2 kcal/mol more stable than the intermediate state (Fig. 9.4, c), which represents the molecular adsorption of C$_2$H$_5$SH. Due to the larger size of the C$_2$H$_5$SH molecule compared to CH$_3$SH, the energy for adsorption on the surface is higher and state b (Fig. 9.4) is different from the equivalent transition state for the adsorption of CH$_3$SH [19]. While molecular dissociation and adsorption is easy for the smaller CH$_3$SH, this is not the case for C$_2$H$_5$SH. However, once on to the surface, the energy barriers for desorption of the hydrogenolysis products are similar, 30.0 kcal/mol for CH$_4$ formation and 28.0 kcal/mol for C$_2$H$_6$ formation.

Fig. 9.3. Reaction path for C$_2$H$_5$SH adsorption, followed by H$_2$S elimination resulting in the formation of a C$_2$H$_4$

Fig. 9.4. Hydrogenolysis, resulting in an ethane formation from the molecularly adsorbed C$_2$H$_5$SH.
9.4.3 One sulfur vacancy

In the third series of calculations a C$_2$H$_5$SH molecule was adsorbed on the Mo edge with three adsorbed sulfur atoms, exposing two five-coordinated and two six-coordinated molybdenum atoms (Fig. 9.5). The results were similar to those of the foregoing calculation. In the intermediate state (Fig. 9.5, c) the C$_2$H$_5$SH molecule adsorbed on the sulfur vacancy and the H atom took a position out of the Mo plane. The activation energy barrier (Fig. 9.5, a → b) was 24.6 kcal/mol and the reaction energy (Fig. 9.5, a → c) −25.9 kcal/mol. The formation of C$_2$H$_4$ had an activation energy of 36.7 kcal/mol (Fig. 9.5, c → d). The final state has two S-H groups and two sulfur atoms in a bridging mode between two molybdenum atoms on the surface (Fig. 9.5, e) and is 48.1 kcal/mol more stable than the intermediate state.

The second step of the hydrogenolysis reaction, i.e., to form C$_2$H$_6$ from the already adsorbed molecule and to remove it from the surface, had a barrier of 25.6 kcal/mol (Fig. 9.6, c → d) and a reaction energy of −46.4 kcal/mol (Fig. 9.6, c → e). This second activation energy was even lower than that for the surface with two S atoms (Fig. 9.4) and confirms the positive
influence of pre-adsorbed S atoms. The calculated activation energy $E_a(1)$ and energy difference $\Delta E(1)$ between initial and intermediate state and the activation energy $E_a(2)$ and energy difference $\Delta E(2)$ between intermediate and final state are collected in Table 9.1.

Fig. 9.6. Hydrogenolysis, resulting in an ethane formation from the molecularly adsorbed $\text{C}_2\text{H}_5\text{SH}$.

Table 9.1. Activation energies and energy differences (in kcal/mol) in the reactions of $\text{C}_2\text{H}_5\text{SH}$ to $\text{H}_2\text{S}$ and $\text{C}_2\text{H}_4$ or $\text{C}_2\text{H}_6$ as a function of the number (N) of bridging S atoms on the Mo edge

<table>
<thead>
<tr>
<th>Edge</th>
<th>N</th>
<th>$\text{C}_2\text{H}_4$</th>
<th>$\text{C}_2\text{H}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_a(1)$</td>
<td>$\Delta E(1)$</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>10.3</td>
<td>31.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>23.5</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>24.6</td>
<td>25.9</td>
</tr>
<tr>
<td>CoMo</td>
<td>2</td>
<td>18.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>
9.4.4 Co-promoted Mo edge

To study the effect of the promoter atoms on the reactions of hydrogenolysis to ethane and elimination to ethene and H$_2$S, calculations were performed similar to those for the unpromoted MoS$_2$ structure but with one surface Mo atom replaced by a Co promoter atom. Since the calculations on the Mo edge showed that the presence of sulfur atoms is beneficial for the hydrogenolysis reaction, two sulfur atoms were placed at the Co surface in a bridging position between three Mo atoms. Furthermore, DFT calculations showed that the incorporation of promoter atoms leads to a reduction of the sulfur coverage of the metal edge. Therefore, only initial state with two sulfur atoms was considered. A geometry optimization of the initial, intermediate, and final structures relaxed the Co atom inward and shortened its distance to the neighboring sulfur atoms to 2.25 Å. The cobalt atom was four-coordinated, while the other two Mo atoms were five-coordinated and one Mo atom was six-coordinated. The adsorption of C$_2$H$_5$SH on the surface had an energy barrier of 18.6 kcal/mol (Fig. 9.7, a $\rightarrow$ b).

![Fig. 9.7. Reaction path of the reaction of C$_2$H$_5$SH to C$_2$H$_4$ on the Co-promoted Mo edge of 2H-MoS$_2$ with two sulfur atoms in bridging positions.](image)
However, the molecular adsorption was favoured only by 4.5 kcal/mol (Fig. 9.7, c). Similar to CH$_3$SH, where dissociation and adsorption of the CH$_3$S and H fragments took place on the Co-promoted surface [19], the molecular adsorption of C$_2$H$_5$SH led to a less stable intermediate state (Fig. 9.7, c: $\Delta E = -4.5$ kcal/mol). In both cases there was a preference for bonding in a bridge site. This is a compromise between the preference of the sulfur atom for a high coordination to the Mo atoms and the preference of the hydrogen atom for adsorption out of the surface plane because of repulsion [28]. As a consequence of the weakly adsorbed state, the barrier for desorption of products in the form of C$_2$H$_4$ was reduced to 30.1 kcal/mol (Fig. 9.7, c $\rightarrow$ d). The transition state (Fig. 9.7, d) involves a deformed, non-planar ethene weakly bonded to the surface sulfur atom by a weakly bonded hydrogen atom resembling the one of the unpromoted surface. The final state (Fig. 9.7, e) consists of two S-H groups in bridging positions between two Mo atoms and a C$_2$H$_4$ molecule in the gas phase. It is 60.8 kcal/mol lower in energy than the intermediate molecular adsorption state (Fig. 9.7, c).

Fig. 9.7. Reaction path of the reaction of C$_2$H$_5$SH to C$_2$H$_6$ on the Co-promoted Mo edge of 2H-MoS$_2$ with two sulfur atoms in bridging positions.

Fig. 9.8. Reaction path of the reaction of C$_2$H$_5$SH to C$_2$H$_6$ on the Co-promoted Mo edge of 2H-MoS$_2$ with two sulfur atoms in bridging positions.
The energy barrier of the subsequent step of the hydrogenolysis reaction, the breaking of the C-S bond, decreased to 20.5 kcal/mol (Fig. 9.8, c → d). This shows that the hydrogenolysis is the easier reaction on the promoted surface and is in agreement with the results from the previous chapter, concerning the role of the promoter atoms to lower the energy barriers for the product formation. The final state, with three sulfur atoms in bridging positions on the surface was more stable by 59.1 kcal/mol than the intermediate state (Fig. 9.8, e).

9.5 Discussion

The measured activation energy for the reaction of C₂H₅SH on MoS₂ is slightly lower than for CH₃SH. The order in which the chemical bonds were activated was observed to be H-H > H-S > C-S ≈ C-H (C₂ compounds) > C-H (C₁ compounds) >> C-C [13]. The experimental activation energy associated with the disappearance of ethanethiol was reported to be 18 kcal/mol, while those for the ethene and ethane formation were 24 and 23 kcal/mol, respectively. Experiments showed that only three gaseous products were formed during the reaction of ethanethiol with the metallic Mo (110) surface: H₂, ethane, and ethene [30]. There was no evidence for the evolution of any other hydrocarbon, such as methane, acetylene, or benzene, or for the formation of gaseous sulfur-containing products. Ethanethiol did not desorb either. The temperature-programmed reaction spectroscopy results suggested that on Mo (110), the kinetics for desorption of ethane and ethene from the molecularly adsorbed ethanethiol proceeded by slow decomposition followed by fast hydrocarbon desorption.

Theoretical modelling suggested that the metal-sulfur bonding plays an essential role in the desulfurization process of sulfur-containing molecules on various metal-sulfide catalysts [31]. Our results show that the C-S bond in the adsorbed thiolate is slightly longer and consequently weaker than in the thiol and that the C-S bond scission and C-H bond formation occur nearly simultaneously.

Thiolates have been proposed as intermediates and understanding their reactivity is important in modelling product distribution. Methanethiol dissociates to methanethiolate on Ni(111) [32], Pt(111) [33], Mo(110) [34], W(211) [14], Cu(100) [35], and Fe(100) [36]. The C-S bond of the methanethiolate intermediate is subsequently cleaved, yielding methane and H₂ as gaseous products along with surface carbon and sulfur. DFT calculations of the
adsorption configurations of methanethiol on Au(111) were also in favour of the formation of strongly bound thiolates [37, 38]. Decomposition of ethanethiol over cadmium sulfide gave 24% ethene and 45% hydrogen sulfide at 900 K together with some free sulfur, hydrogen, and diethylsulfide [39]. Similar results were obtained with the sulfides of nickel, copper, cobalt, and iron. On reduced iron, however, the decomposition of ethanethiol at 500 K gave 63% ethane and 25% ethene [40].

Neither molybdenum nor tungsten sulfide catalysts showed any activity for the rupture of the C-C bond of ethanethiol below 600 K [13]. The conversion of adsorbed ethyl radicals to gaseous ethane was not particularly rapid but occurred more readily than the corresponding desorption of methyl radicals as methane from methanethiol. On the contrary, on metals, ethanethiol decomposes to atomic carbon, atomic sulfur and gaseous dihydrogen [30].

The molybdenum atoms on the (1010) Mo edge have a lower metal coordination number than the bulk atoms, a smaller $d$ bandwidth and hence a higher energy of the $d$ band centre [28]. The lower the coordination number of the surface metal atom is, the higher is its reactivity. Sulfur adsorption on the (1010) Mo edge increases the metal coordination number. Furthermore, the interaction between the occupied sulfur lone pairs of $C_2H_5SH$ and the empty $4d$ orbitals of the molybdenum atom lowers the energy of the $d$ band and stabilizes the thiolates on the surface.

The calculations indicate low energy barriers for dissociation when the molecule is positioned initially at the base of a step, resulting in a distance between the surface sulfur atom and the hydrogen atom of the ethanethiol of 2.8 Å (Fig. 9.2). Molecular adsorption (10.3 kcal/mol, Fig. 9.1) and dissociation (16.5 kcal/mol, Fig. 9.2) on a sulfur-deficient surface are easy steps, while the desorption of the final products ethene (37.6 kcal/mol, Fig. 9.1) and ethane (31.1 kcal/mol, Fig. 9.2) are less easy. Molecular adsorption in the sulfur vacancy has a higher adsorption barrier on the sulfided surface (23.5 and 24.6 kcal/mol). At the same time, the energy barrier for the ethane formation is reduced to 28.0 and 25.6 kcal/mol and the energy for the ethene formation (38.8 and 36.7 kcal/mol) differed only by 1.2 kcal/mol from that of the elimination on a surface with one sulfur atom. Therefore, the energy barriers for $C_2H_6$ formation and desorption from $C_2H_5SH$ are dependent on the surface sulfur coverage, as in the case of $CH_4$ formation and desorption from $CH_3SH$ [19]. Comparing the energy barriers for the $C_2H_4$ formation and desorption the present results do not show a clear dependence on the surface sulfur coverage.
The calculations show that the decomposition reactions of ethanethiol to ethane and ethene are easy reactions. The energy diagrams indicate that also the reverse reactions will be relatively easy. This means that the hydrogenation reaction of a double bond could very well occur on the fully sulfided Mo edge and does not need a vacancy. Namely, as we have seen in the foregoing, the forward decomposition reactions of ethanethiol are:

\[
\begin{align*}
C_2H_5SH + * + S^* & \rightarrow C_2H_5S^* + H-S^* \rightarrow C_2H_6 + 2S^* \\
& \rightarrow C_2H_4 + 2H-S^* 
\end{align*}
\]

(9.1) (9.2)

This leads to the following sequence of reverse reactions:

\[
C_2H_4 + 2H-S^* \rightarrow C_2H_5-S^* + H-S^* \rightarrow C_2H_6 + 2S^* 
\]

(9.3)

The hydrogen atoms needed in the hydrogenation come from neighbouring SH groups that can be formed by adsorption of H\(_2\) on the fully sulfided edge:

\[
H_2 + 2S^* \rightarrow 2H-S^* \rightarrow H_2S + * + S^* 
\]

(9.4)

Reactions (9.3) explain why Kieran and Kemball observed that the exchange rate of an H atom in the ethyl group of ethanethiol with deuterium is similar to that for the exchange of ethene with deuterium [13], because in both cases a surface ethanethiolate is formed. Reactions (9.3) would also explain the "bean-like" structures observed by Lauritsen et al. in the STM pictures of the edges of triangular MoS\(_2\) nanoclusters pre-exposed to hydrogen atoms and then exposed to thiophene at 500 K [41]. They suggested that the adsorbed H atoms hydrogenate the thiophene at the fully sulfided MoS\(_2\) edge to 2,5-dihydrothiophene and that this reacts further to but-2-ethiolate. The latter fragment would be the cause of the observed 'bean-like' structure. Their DFT calculation indicated that the final C-S bond cleavage would require modest activation energy of about 23 kcal/mol, but they did not calculate the barrier for the hydrogenation step. Of course, in the HDS of thiophene, not all reaction steps can occur on a fully sulfided Mo edge. In the final C-S bond-breaking step, the S atom needs a landing place at the catalyst surface. On the other hand, borrowing from
organometal chemistry, one could suggest that an associative, rather than a dissociative, mechanism at the catalyst surface might explain that no vacancy is needed at all:

\[ \text{RSH} + \text{H-S}^* \rightarrow \text{R-S}^* + \text{H}_2\text{S} \]

In this reaction the RSH molecule and the SH group would both be bridge bonded to the same two surface Mo atoms. Lauritsen et al. proposed another reaction that would not need a surface vacancy, namely that the but-2-enethiolate becomes bonded to a surface sulfur atom, apparently forming an alkyl disulfide fragment (R-S-S):

\[ \text{RSH} + 2\text{S}^* \rightarrow \text{R-S-S}^* + \text{H-S}^* \]

They assume that the final sulfur extrusion has to occur at a vacancy, however.

Not only the sulfur atoms, but also the Co promoter atom leads to a less strongly bound C\(_2\)H\(_5\)SH intermediate and thus to lower barriers for the hydrogenolysis and elimination reactions. Activation energies of 20.5 and 30.1 kcal/mol were obtained for C\(_2\)H\(_6\) and C\(_2\)H\(_4\) formation over the Co-Mo edge with two bridging S atoms, respectively, whereas 25.6 and 36.7 kcal/mol were the lowest activation energies calculated for the unpromoted Mo edge (Table 9.1).

### 9.6 Conclusion

After molecular adsorption or decomposition on the surface C\(_2\)H\(_5\)SH showed slightly lower energy barriers for desorption of the reaction products than CH\(_3\)SH. The C\(_2\)H\(_6\) formation and desorption from ethanethiolate proceeded with a lower energy barrier than the C\(_2\)H\(_4\) formation and desorption from the molecularly adsorbed C\(_2\)H\(_5\)SH state. The adsorption geometry, involving a hydrogen atom from the methyl group of C\(_2\)H\(_5\)SH, conducted reactions to more strongly bound intermediates. While the energy barriers for C\(_2\)H\(_6\) desorption from the surface are dependent on the surface sulfur coverage, as in the case of CH\(_4\) formation starting from CH\(_3\)SH, the investigated reaction paths for C\(_2\)H\(_4\) formation showed similar energy barriers for desorption from surfaces with one, two and three sulfur vacancies. The Co promoter atom
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conducted the reactions to a less strongly bound intermediate state and consequently lowered
the energy barriers for products formation.

The geometry of the adsorbed sulfur-containing molecule at the (1010) Mo edge is very
important for analyzing the product distribution. Molecules with one carbon atom split into H
and CH$_3$S fragments and adsorb on the surface. Larger molecules, like C$_2$H$_5$SH, also show a
tendency for molecular adsorption.

9.7 References

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A density functional theory study


Chapter 10

Concluding remarks

With the more stringent environmental legislation with respect to the amount of sulfur in oil products there is a need for catalysts with a better performance than those used today [1,2]. Hydrodesulfurization has been used in the refining of crude oil for over 60 years and has been accompanied by theoretical and applied research for many years. By combining surface science techniques, in-situ characterization and theoretical methods fundamental insight into the structure and reactivity has been gained. Quantum-chemical calculations provide knowledge that still cannot be obtained by experiments, assisting towards an improved understanding of the structure and reactivity of transition-metal compounds [3-16].

The present thesis offers an approach to the bulk and the catalytically active (100) surface structure of 2H-MoS₂. In addition to the structural characteristics, the investigation of the C-S and S-H bonds cleavage in thiols induces patterns in reactivity of sulfur-containing species and supply essential models for the related technologically important hydrodesulfurization reaction. This final chapter summarizes the results and presents perspectives for future research in this field.

10.1 Summary

The geometric and electronic properties of bulk 2H-MoS₂ and the (10\̅0) surface structure were analyzed by means of periodic HF and DFT calculations. The best results of the electronic structure and the calculated band gap are obtained with the DFT-LDA/VWN method, while the HF method overestimates and the DFT-PWGGA/PWGGA method underestimates the band gap. DFT methods predict conducting properties of the first surface layer of the relaxed (10\̅0) surface, different from the semi-conducting bulk. With HF calculations the surface remains semi-conducting and additional corrections to the exchange-correlation potential are necessary. Using second order perturbation corrections (MP2) to the
Concluding remarks

HF solution we find a reduction in the band gap for bulk MoS$_2$, when compared to the HF solution, and a metallic (1010) surface due to an overlap of the highest occupied orbitals of the Mo edge and lowest empty orbitals of the S edge.

The perturbed cluster method was used to investigate the properties of the defects formed on the (100) MoS$_2$ surface by the removal or addition of S atoms. A step-like transfer of S atoms from the S edge to the naked Mo atoms of the Mo edge lowers the surface energy of the metal edge and is energetically beneficial, reaching its maximal effectiveness when both edges have similar energy. The electrostatic potential generated by the defects on the (100) MoS$_2$ surface affects its reactivity.

LST/QST methods that were used to investigate the dissociation of H$_2$ on the (100) MoS$_2$ edge structure showed a significantly higher energy barrier for the homolytic splitting of H$_2$ over the S-terminated edge than for the heterolytic splitting on the Mo-terminated edge. The most stable configuration results from a heterolytic dissociation of hydrogen on a surface metal centre, which is coordinated to four sulfur atoms and a surface sulfur atom of an adjacent sulfur edge. On the S-terminated edge the energy barriers are not strongly dependent on the reaction path, while there is a clear dependence in the case of the Mo-terminated edge. H$_2$ dissociation on a partially sulfided metal edge, which is different from the ideal "as-cleaved" surface, is an energetically unfavourable process. On Co or Ni-promoted Mo-terminated edge surfaces the heterolytic splitting of H$_2$ was found to be endothermic. Substitution of an Mo atom of the S-terminated edge by a Co or Ni atom (Mo/Co(Ni) = 1/1) led to different effects. While Co enhanced the hydrogen splitting Ni had no significant influence.

The rate-determining step in the reaction of thiols over the Mo edge of the catalytically active (100) MoS$_2$ surface depends clearly on the number of the exposed active sites. At low sulfur surface coverage the rate-determining step is the initial association of the thiol to the surface. The C-S bond of the adsorbed CH$_3$S breaks under the formation and desorption of CH$_4$ into the gas phase, leaving an S atom on the surface. The latter step is easier at higher sulfur coverage. Co and Ni promoters lowered the energy barrier for CH$_4$ desorption from the surface. The presence of adsorbed hydrogen increased the activation energy for adsorption of CH$_3$S and H fragments, but led to a preferable formation of H$_2$S and a subsequent vacancy creation. Methyl mercaptan splits into H and CH$_3$S fragments which adsorb on the surface. Larger molecules, like C$_2$H$_5$SH, showed a tendency of molecular adsorption as well, and slightly lower energy barriers for desorption of the reaction products than CH$_3$SH.
10.2 Outlook

In heterogeneous catalysis, where the reaction mechanisms often involve a complicated network of reaction pathways including dissociative adsorption, surface reactions and desorption, the applied \textit{ab initio} methods must be able to reliably predict the relevant pathways associated with a given reactant state. The interpolation methods, such as the synchronous transit and nudged elastic band methods are based on transition path sampling, and have proven to be successful when applied to reactions on the MoS\textsubscript{2} catalyst surface. Since the reaction products must be assumed by using interpolation algorithms, unexpected chemical pathways and products cannot be revealed. Therefore, with respect to the methodology, the present study should be extended to exploit dynamic path sampling schemes, currently under development for use with \textit{ab initio} potential energy surfaces [17,18].

Another point of interest is the selection of the model of the MoS\textsubscript{2} catalyst particle. Recently, studies extending the two-sheet model to a three-sheet model or to triangularly shaped clusters have been performed [14,15,20]. Another issue is the location of the promoter atom. DFT studies showed a preferable location of the promoter atom on the S-terminated edge [4,15], while recent experimental characterizations favour the Mo-terminated edge. The calculations excluded a spin polarization correction.

With respect to the application, the present study can be extended to an investigation of reactions of aromatic thiols on the (100) MoS\textsubscript{2} edge structure. On MoS\textsubscript{2}, the hydrodesulfurization of derivatives of dibenzothiophene has been investigated: the so-called hydrogenation route proceeds via adsorption of the benzene ring on the Mo edge, whereas the so-called direct desulfurization proceeds by \sigma-adsorption via the S atom of dibenzothiophene [19,20]. The reactions of aromatic thiols were investigated on metals, but not on metal sulfides and showed that C-S bond breaking was followed by rapid hydrogenation of the adsorbed phenyl to form benzene, which desorbed from the sulfur-covered surface [21,22]. On MoS\textsubscript{2} the reactions of thiols have not been explained in the way done for metals [23]. Further research extending the approach from aliphatic to aromatic and cyclic thiols on the MoS\textsubscript{2} surface may clarify reaction mechanisms and supply models explaining steps in the hydrodesulfurization reaction.


10.3 References

Appendix
A. The perturbed cluster method in EMBED01 calculations

A1. Basis set, partitioned matrices

The partition of the basis set of the general representative matrix $X$ into blocks is done by a subdivision into a "local" ($X_1$) and an outer ($X_2$) matrix:

$$X = \begin{pmatrix} X_{cc} & X_{cd} \\ X_{dc} & X_{dd} \end{pmatrix} = \begin{pmatrix} 0_{cc} & 0_{cd} \\ 0_{dc} & X_{dd} \end{pmatrix} = X_1 + X_2 \quad (A.1)$$

where $C$ is the molecular cluster or the inner zone and $D$ is the outer zone. In the following, $S$, $F$ and $P$ will indicate the overlap, the Fock and the one-electron density matrix, the notation $Q(e) = eS - F$ will be also used.

The basic ingredient of the working formulae is the eigenvector, $|j\rangle$, and the eigenvalue, $e_j$, of the molecular-cluster problem:

$$\left(S^{-1/2}F^{-1/2}\right)|j\rangle = e_j|j\rangle \quad (A.2)$$

A2. The coupling matrices and the fundamental approximation

The most characteristic quantities of the perturbed cluster method (PC) are the energy dependent coupling matrices $M_{dd}(e;l)$, whose general element is defined as:

$$M_{\nu\mu}(e;l) = -\frac{g(A,e)}{pMV[A]} \frac{\partial^2}{\partial A^2} [A - e] \quad (A.3)$$

and its first and second derivative with respect to $e$, $M_{dd}(e;2)$, and $M_{dd}(e;3)$. They serve for correcting the molecular cluster solution for environmental effects. The cluster solution is corrected for coupling to the surroundings, following a quantum-mechanical embedding scheme based on the use of the host crystal Green function.

In equation (A.3) $pMV$ represents the $\nu\mu$ element of the projected density of states (PDOS) of the imperfect system, defined as $\rho_{\nu\mu}(\lambda) = \sum_i a_{\nu i} a_{\mu i} \delta(\epsilon_i - \lambda)$ in terms of corresponding eigenvalues $\epsilon_i$ and eigenvector coefficients $a_{\nu i}$. In the same equation $g(\lambda,e)$ is the 2D thermalized step function defined in terms of step occupancy $f(\lambda) = \frac{1}{1 + \exp(2\lambda/w)}$ as

$$g(\lambda,e) = f(\lambda) - f(e) \quad (A.4)$$

At zero temperature ($w = 0$), this simplifies to:

$$g(\lambda,e) = \theta(\lambda - e) - \theta(e - E) \quad (A.5)$$

where $\theta(x)$ is the Heaviside step function, and $E$ is the Fermi energy of the system. The evolution of the $M$ matrices requires the knowledge of the PDOS for the imperfect system in
the D region. The *fundamental approximation* of the PC method consists in assuming that this
is not very much changed with respect to the defect-free situation so that in eq. (A.3)
\[
\rho_{\mu\nu}(e) = \rho_{\mu\nu}(e)' \quad \text{(fundamental approximation)} \quad (A.6)
\]
The PDOS of the perfect host system $\rho_{\mu\nu}(e)'$ are calculated by CRYSTAL98 code as a sum of
the contributions from the different bands. EMBED01 utilizes the periodic solution for the
crystal in the form of its *Green function*, or PDOS. EMBED01 allows also going beyond the
fundamental approximation by introducing "band-bending" effects induced by charged
defects in the outer region.

**A3. Electron charge transfer between the cluster and its surrounding**

The charge balance when a defect is created is computed by perturbing the local zone with a
constant potential and looking for local energy changes associated with the charge transfer
between the cluster and the rest of the crystal. That is expressed by the equation:
\[
q[S'] + q[A] = q[S] + q[R] + q^{Mis} \quad (A.7)
\]
$q[A]$ and $q[R]$ are the net charges (nuclear minus electronic) of the impurities (added atoms)
or the removed species, respectively, while the two $q'$ terms are the net charges which are
found in the two local zones, corresponding to the sum of the nuclear charges in $C$, plus $Tr$
$[P_{CCSC} + P_{CDSC} + P_{CDSC}]$; the last term is the "missing charge" which is needed to
ensure the charge balance.

\[
q^{Mis} = (q[A] - q[R]) - (q[S] - q[S']) = q^{for} - q^{dif} \quad (A.8)
\]
where $q^{for}$ is the formal defect charge, and $q^{dif}$ is the difference between the two local charges.
The charge balance correction is:
\[
\Delta E^{corr} = \mu q^{Mis} \quad (A.9)
\]
$\mu$ is the "electro-chemical potential" and is determined by "$v$ - technique".
This technique superimposes a constant potential $v$ to the cluster. Four computations with $v = 
\pm 0.01$ and $\pm 0.02$ were performed.
For each calculation, the program provides the value of $q^{corr}[S' + v(Z)]$ and
\[
E^{corr}[S' + v(Z)] = E'[S' + v(Z)] - v Tr S_2 P[S' + v(Z)] \quad (A.10)
\]
$Z$ denotes the subspace in which the constant potential is superimposed.
Then a linear least-square fit of $E^{corr}[S' + v(Z)]$ versus $q^{corr}[S' + v(Z)]$ is computed; the
slope is the $\mu$ parameter.
A4. The PC expressions for the density matrix

In the following equations, the eigenvectors’ basis set $|j)$ is used in the cluster subspace; italic letters $(e_j)$ indicate the corresponding cluster eigenvalues; Greek indices refer to AO’s in the outer D zone. Two different expressions are used for the $P_{CD}$ and $P_{CC}$ blocks of the density matrix. For convenience, these expressions are written as a sum of “cluster” ($P^{\text{cl}}$), “coupling” ($P^{\text{cou}}$) and “constant” ($P^{\text{ct}}$) contributions. The first one is zero for the $P_{CD}$ block. The general element of the $P_{CD}$ block is expressed by the sum:

$$ P_{ji} = P_{ji}^{\text{cl}} + P_{ji}^{\text{ct}} \quad \text{(A.11)} $$

$$ P_{ji}^{\text{cl}} = -\sum_{\nu} Q_{\mu\nu}(e_j) M_{\nu\mu}(e_j;1) \quad \text{(A.12)} $$

$$ P_{ji}^{\text{ct}} = -\sum_{\nu} \{ 2S_{\mu\nu} P_{\nu\mu} \} \quad \text{(A.13)} $$

and for the general element of the $P_{CC}$ block:

$$ P_{jk} = P_{jk}^{\text{cl}} + P_{jk}^{\text{cou}} + P_{jk}^{\text{ct}} \quad \text{(A.14)} $$

$$ P_{jk}^{\text{cl}} = 2\delta_{jk} f(e_j) \quad \text{(A.15)} $$

$$ P_{jk}^{\text{cou}} = -\sum_{\mu} P_{ji}^{\text{cou}} S_{\mu k} \quad \text{(A.16)} $$

$$ P_{jk}^{\text{ct}} = N_{jk} + N_{ij} \quad \text{(A.17)} $$

In eq. (A.17) $P_{CC}^{\text{cou}}$ is expressed as the sum of the matrix $N_{CC}$ and its transpose. Two different expressions are used for $N_{ij}$ according to the separation $|e_j - e_k|$ between the two cluster eigenvalues. More precisely, if $d = \left| \frac{(e_j - e_k)}{E - \frac{1}{2} (e_j + e_k)} \right|^{{1/2}}$ is below a certain threshold $T$ (typically, $T = 10^{-3}$), then:

$$ N_{jk} = -\sum_{\mu} \frac{1}{2} P_{jk}^{\text{cou}} Q_{\mu k}(e_k) - \sum_{\mu} P_{ji}^{\text{cou}} S_{\mu k} , \quad P_{ji}^{\text{cou}} = -\sum_{\nu} Q_{\mu\nu}(e_j) M_{\nu\mu}(e_j;2) \quad \text{(A.18)} $$

else:

$$ N_{jk} = -\sum_{\mu} P_{ji}^{\text{cou}} \left[ Q_{\mu k}(e_k) \Delta (e_j - e_k) \right] \quad \text{(A.19)} $$

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The use of the symmetry-adapted eigenvectors allows restricting the sums over functions in the D zone in eq. (A.18) and (A.19) to the symmetry irreducible part; furthermore, the $P_{cc}$ matrix is block-diagonal by IRREP’s and respective rows. The resulting reduction of computer time and storage requirements is substantial in the case of high symmetry defects.

A5. The expression for the Fock matrix

The Fock matrix block $F_{cc}$ and $F_{cd}$ are calculated in AO basis set. The standard expression for the general Fock matrix element $F_{\gamma\mu}(\gamma \in C)$:

$$F_{\gamma\mu} = T_{\gamma\mu} + \sum_{\lambda} Z_{\gamma\lambda} + \sum_{\mu} P_{\lambda\mu} \left[ (\gamma\mu|\lambda\nu) - \frac{1}{2} (\gamma\lambda|\mu\nu) \right] = M_{\gamma\mu} + B_{\gamma\mu}$$ (A.20)

For simplicity, the same label $\lambda$ is used for nuclei and AOs. In the last passage the one-electron (kinetic plus nuclear, $M$) and the two-electron ($B$) part of the Hamiltonian are presented. The terms from the Fock matrix were described in more detail in Chapter 2.
B. Influence of the reaction environment on the surface structure and stoichiometry

Consider a surface that is in contact with a sulfur containing atmosphere (Fig. B.1). The surrounding H₂/H₂S atmosphere acts as a reservoir; it can give or take sulfur to (or from) the surface. Such a system can be described by the Gibbs free energy \( G(T, p, N_{Mo}, N_S) \) which depends on temperature, pressure and the number of molybdenum \( N_{Mo} \) and sulfur atoms \( N_S \) in the system.

![H₂/H₂S gas](image)

Fig. B.1: Schematic representation of the H₂/H₂S - surface and surface - bulk MoS₂ contacts.

The most stable surface structure is that with a minimal surface free energy:

\[
\gamma_{surf} = \frac{1}{A} \left( G_{MoS₂}^{surf} - N_S \mu_S - N_{Mo} \mu_{Mo} \right) \tag{B.1}
\]

where \( \mu_S \) and \( \mu_{Mo} \) are the chemical potentials of Mo and S and \( \gamma_{surf} \) is the surface energy normalized to the surface area \( A \).

If there is enough "bulk material", then it acts as a thermodynamic reservoir and the surface potential is related to the Gibbs free energy of the bulk sulfide:

\[
\mu_{Mo} + 2 \mu_S = g_{MoS₂}^{bulk} \tag{B.2}
\]

where \( g_{MoS₂}^{bulk} \) denotes the Gibbs free energy per formula unit.

By combining (B.1) and (B.2) the surface free energy can be expressed as a function of the sulfur chemical potential only:

\[
\gamma(T, p) = \frac{1}{A} \left[ G_{MoS₂}^{surf}(T, p) - N_{Mo} g_{MoS₂}^{bulk}(T, p) + (2N_{Mo} - N_S) \mu_S \right] \tag{B.3}
\]

or

\[
\gamma(T, p) = \frac{1}{A} \left[ (\Delta E_{surf} - \Delta E_{g_{MoS₂}}) + (2N_{Mo} - N_S) \mu_S \right] \tag{B.4}
\]

The next step is to determine the reasonable gas phase limits. At low concentration of sulfur in the containing atmosphere, the sulfur is released from the solid and pure molybdenum crystallites form. Therefore,

\[
\mu_{Mo} < g_{Mo}^{bulk}(T, p) \tag{B.5}
\]
\[ \mu_S = \frac{1}{2} \left( \delta_{\text{bulk}}^\text{Mo}(T,p) - \delta_{\text{Mo}}^\text{bulk}(T,p) \right) \] (B.6)

At low concentration of S:
\[ \mu_S = \frac{1}{2} \left( \delta_{\text{MoS}_2}^\text{bulk}(T,p) - \delta_{\text{Mo}}^\text{bulk}(T,p) \right) \] (B.7)

A reactive atmosphere that contains a lot of sulfur leads to condensation of sulfur on the surface, i.e.,

At high concentration of S:
\[ \mu_S = E_S^{\text{tot}} \] (B.8)

Therefore,
\[ \frac{1}{2} \Delta G_f(0,0) < \Delta \mu_S(T,p) < 0 \] (B.9)

\[ \Delta G_f(0,0) = -1.6 \text{ eV} \] calculated in the CRYSTAL98 calculations, which is in good agreement with the experimental value of \(-1.2 \text{ eV}\) [1]. The upper limit \(E_S^{\text{tot}}\) is calibrated to zero.

The next step is the calculation of the free energies of solids:
\[ G(T,p) = E^{\text{tot}} + F^{\text{trans}} + F^{\text{rot}} + F^{\text{vibr}} + F^{\text{config}} + pv \] (B.10)

which for solids at low temperature might be approximated as:
\[ G(T,p) = E^{\text{tot}} + F^{\text{config}} \] (B.11)

**Fig. B.2:** Surface energy as a function of the S chemical potential and the \(p(\text{H}_2\text{S})/p(\text{H}_2)\). The surface (6-0)/(0-6) is shown in Fig. 3.1 and the surface (6-3)/(3-6) is shown in Fig. 3.3 a. The dashed lines indicate the interval of \(p(\text{H}_2\text{S})/p(\text{H}_2)\) in real working conditions.

Furthermore, for the \(\text{H}_2/\text{H}_2\text{S} \) gas phase, \( \mu = \mu(T,p) \). Considering that \( \mu_S \) is in equilibrium with the gas-phase mixture, \( \mu_S = \mu(\text{H}_2\text{S}) - \mu(\text{H}_2) \) and

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\[ \mu(S) = [h(H_2S)_T - h(H_2)_T] - T[s(H_2S)_T - s(H_2)_T] + RT \ln\left(\frac{p(H_2S)}{p(H_2)}\right) \] (B.12)

where \( h \) and \( s \) are the enthalpies and the entropies, respectively, for the \( H_2 \) and \( H_2S \). The standard values are taken from [1]. At \( T = 600 \) K, and \( p(H_2S)/p(H_2) = 10^{-1}-10^{-1} \) the following surface termination shown in Fig. B.2 resulted.

Reference:

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